CHM 364 PHYSICAL CHEMISTRY 2



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Chemistry 364 Physical Chemistry 2

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TABLE OF CONTENTS

Licensing

1: The Dawn of the Quantum Theory

1.1: Blackbody Radiation Cannot Be Explained Classically

1.2: Quantum Hypothesis Used for Blackbody Radiation Law

1.3: Photoelectric Effect Explained with Quantum Hypothesis

1.4: The Hydrogen Atomic Spectrum

1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum

1.6: Matter Has Wavelike Properties

1.7: de Broglie Waves can be Experimentally Observed

1.8: The Bohr Theory of the Hydrogen Atom

1.9: The Heisenberg Uncertainty Principle

1.E: The Dawn of the Quantum Theory (Exercises)

2: The Classical Wave Equation

2.1: The One-Dimensional Wave Equation

2.2: The Method of Separation of Variables

2.3: Oscillatory Solutions to Differential Equations

2.4: The General Solution is a Superposition of Normal Modes

2.5: A Vibrating Membrane

2.E: The Classical Wave Equation (Exercises)

3: The Schrödinger Equation and a Particle in a Box

3.1: The Schrödinger Equation

3.2: Linear Operators in Quantum Mechanics

3.3: The Schrödinger Equation is an Eigenvalue Problem

3.4: Wavefunctions Have a Probabilistic Interpretation

3.5: The Energy of a Particle in a Box is Quantized

3.6: Wavefunctions Must Be Normalized

3.7: The Average Momentum of a Particle in a Box is Zero

3.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

3.9: A Particle in a Three-Dimensional Box

3.E: The Schrödinger Equation and a Particle in a Box (Exercises)

4: Postulates and Principles of Quantum Mechanics

4.1: The Wavefunction Specifies the State of a System

4.2: Quantum Operators Represent Classical Variables

4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

4.4: The Time-Dependent Schrödinger Equation

4.5: Eigenfunctions of Operators are Orthogonal

4.6: Commuting Operators Allow Infinite Precision
4.E: Postulates and Principles of Quantum Mechanics (Exercises)

5: The Harmonic Oscillator and the Rigid Rotor

5.1: A Harmonic Oscillator Obeys Hooke's Law
5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule
5.3: The Harmonic Oscillator Approximates Molecular Vibrations
5.4: The Harmonic Oscillator Energy Levels
5.5: The Harmonic Oscillator and Infrared Spectra
5.6: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials
5.7: Hermite Polynomials are either Even or Odd Functions
5.8: The Energy Levels of a Rigid Rotor
5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
5.E: The Harmonic Oscillator and the Rigid Rotor (Exercises)

6: The Hydrogen Atom

6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly
6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics
6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision
6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers
6.5: s-orbitals are Spherically Symmetric
6.6: Orbital Angular Momentum and the p-Orbitals
6.7: The Schrödinger Wave Equation for the Hydrogen Atom
6.8: The Helium Atom Cannot Be Solved Exactly
6.E: The Hydrogen Atom (Exercises)

7: Approximation Methods

7.1: The Variational Method Approximation
7.2: Linear Variational Method and the Secular Determinant
7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters
7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems
7.E: Approximation Methods (Exercises)

8: Multielectron Atoms

8.1: Atomic and Molecular Calculations are Expressed in Atomic Units
8.2: Perturbation Theory and the Variational Method for Helium
8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method
8.4: An Electron has an Intrinsic Spin Angular Momentum
8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants
8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data
8.8: Term Symbols Gives a Detailed Description of an Electron Configuration
8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number

8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States
8.11: Using Atomic Term Symbols to Interpret Atomic Spectra
8.E: Multielectron Atoms (Exercises)

9: Computational Quantum Chemistry

9.1: Overview of Quantum Calculations
9.2: Gaussian Basis Sets
9.3: Extended Basis Sets
9.4: Orbital Polarization Terms in Basis Sets
9.E: Computational Quantum Chemistry (Exercises)

10: Chemical Bonding in Diatomic Molecules

10.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules
10.2: The $H_2^{\oplus}$ Prototypical Species
10.3: The Overlap Integral
10.4: Chemical Bond Stability
10.5: Bonding and Antibonding Orbitals
10.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital
10.7: Molecular Orbitals Can Be Ordered According to Their Energies
10.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule
10.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle
10.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic
10.11: Photoelectron Spectroscopy
10.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules
10.13: Molecular Term Symbols Describe Electronic States of Molecules
10.14: Molecular Term Symbols Designate Symmetry
10.E: Chemical Bond in Diatomic Molecules (Exercises)

11: Bonding in Polyatomic Molecules

11.1: Hybrid Orbitals Account for Molecular Shape
11.2: Hybrid Orbitals in Water
11.3: BeH_2 is Linear and H_2O is Bent
11.4: The pi-Electron Approximation of Conjugation
11.5: Butadiene is Stabilized by a Delocalization Energy
11.6: Benzene and Aromaticity
11.E: Bonding in Polyatomic Molecules (Exercises)

12: Molecular Spectroscopy

12.1: The Electromagnetic Spectrum
12.2: Rotations Accompany Vibrational Transitions
12.3: Unequal Spacings in Vibration-Rotation Spectra
12.4: Unequal Spacings in Pure Rotational Spectra
12.5: Vibrational Overtones

12.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
12.7: The Franck-Condon Principle
12.8: Rotational Spectra of Polyatomic Molecules
12.9: Normal Modes in Polyatomic Molecules
12.10: Time-Dependent Perturbation Theory
12.11: The Selection Rule for the Rigid Rotor
12.12: The Harmonic Oscillator Selection Rule
12.13: Group Theory Determines Infrared Activity
12.E: Molecular Spectroscopy (Exercises)

13: Lasers, Laser Spectroscopy, and Photochemistry

13.1: Electronically Excited Molecules can Relax by a Number of Processes
13.2: The Dynamics of Transitions can be Modeled by Rate Equations
13.3: A Two-Level System Cannot Achieve a Population Inversion
13.4: Population Inversion can be Achieved in a Three-Level System
13.5: What is Inside a Laser?
13.6: The Helium-Neon Laser
13.7: Modern Applications of Laser Spectroscopy
13.E: Lasers, Laser Spectroscopy, and Photochemistry (Exercises)

14: Math Chapters

14.1: Complex Numbers
14.2: Probability and Statistics
14.3: Determinants
14.3.1: The Solutions of Simultaneous Linear Equations
14.3.2: Calculation of a 3 × 3 determinant
14.3.3: The Determinant as a Volume
14.3.4: Properties of Determinants
14.3.5: Problems
14.4: Vectors
14.5: Spherical Coordinates
14.6: Matrices
14.7: Numerical Methods
14.8: Partial Differentiation
14.9: Series and Limits
14.10: Fourier Analysis
14.10.1: Fourier Analysis in Matlab
14.10.2: Fourier Synthesis of Periodic Waveforms
14.11: The Binomial Distribution and Stirling's Appromixation
14.12: Formula Sheets
14.12.1: Some Important Numbers

14.12.2: Quadratic Equation
14.12.3: Logarithms and Exponentials
14.12.4: Trigonometric Identities
14.12.5: Complex Numbers
14.12.6: Operators
14.12.7: Taylor Series
14.12.8: Fourier Series
14.12.9: Derivatives and Primitives (Indefinite Integrals)
14.12.10: Definite integrals
14.12.11: Differentiation Rules
14.12.12: Partial Derivatives
14.12.13: Coordinate Systems

Index

Glossary

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1: THE DAWN OF THE QUANTUM THEORY

"A profound change has taken place during the present century in the opinions physicists have held on the mathematical foundations of their subject. Previously they supposed that the principles of Newtonian mechanics would provide the basis for the description of the whole of physical phenomenon and that all the theoretical physicists had to do was suitably to develop and apply these principles. With the recognition that there is no logical reason why Newtonian and classical principles should be valid outside the domains in which they have been experimentally verified has come the realization that departures from these principles are indeed necessary. Such departures find their expression through the introduction of new mathematical formalisms, new schemes of axioms and rules of manipulation, into the methods of theoretical physics." **P. A. M. Dirac, "Quantum Mechanics" (1930).**

1.1: Blackbody Radiation Cannot Be Explained Classically

1.2: Quantum Hypothesis Used for Blackbody Radiation Law

1.3: Photoelectric Effect Explained with Quantum Hypothesis

1.4: The Hydrogen Atomic Spectrum

1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum

1.6: Matter Has Wavelike Properties

1.7: de Broglie Waves can be Experimentally Observed

1.8: The Bohr Theory of the Hydrogen Atom

1.9: The Heisenberg Uncertainty Principle

1.E: The Dawn of the Quantum Theory (Exercises)

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1.1: Blackbody Radiation Cannot Be Explained Classically

Learning Objectives

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation. Objectives for this section include

- Be familiar with black-body radiators
- Apply Stefan-Boltzmann's Law to estimate total light output from a radiator
- Apply Wien's Displacement Law to estimate the peak wavelength (or frequency) of the output from a black body radiator
- Understand the Rayleigh-Jeans Law and how it fails to properly model black-body radiation

All normal matter at temperatures above absolute zero emits electromagnetic radiation, which represents a conversion of a body's internal thermal energy into electromagnetic energy, and is therefore called *thermal radiation*. Conversely, all normal matter *absorbs* electromagnetic radiation to some degree. An object that absorbs ALL radiation falling on it, at all wavelengths, is called a blackbody. When a blackbody is at a uniform temperature, its emission has a characteristic frequency distribution that depends on the temperature. This emission is called *blackbody radiation*.

A room temperature blackbody appears black, as most of the energy it radiates is infra-red and cannot be perceived by the human eye. Because the human eye cannot perceive light waves at lower frequencies, a black body, viewed in the dark at the lowest just faintly visible temperature, subjectively appears grey, even though its objective physical spectrum peaks in the infrared range. When it becomes a little hotter, it appears dull red. As its temperature increases further it becomes yellow, white, and ultimately blue-white.



Figure 1.1.1 : Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

Blackbody radiation has a characteristic, continuous frequency spectrum that experimentally depends only on the body's temperature. In fact, we can be much more precise:

> A body emits radiation at a given temperature and frequency *exactly* as well as it absorbs the same radiation.

This statement was proved by Gustav Kirchhoff: the essential point is that if we *instead* suppose a particular body can absorb better than it emits, then in a room full of objects all at the same temperature, it will absorb radiation from the other bodies better than it radiates energy back to them. This means it will get hotter, and the rest of the room will grow colder, contradicting the second law of thermodynamics. *Thus, a body must emit radiation exactly as well as it absorbs the same radiation at a given temperature and frequency in order to not violate the second law of thermodynamics.*

Any body at any temperature above absolute zero **will** radiate to some extent, the intensity and frequency distribution of the radiation depending on the detailed structure of the body. To begin analyzing heat radiation, we need to be specific about the body doing the radiating: *the simplest possible case is an idealized body which is a perfect absorber, and therefore also (from the above argument) a perfect emitter*. So how do we construct a perfect absorber in the laboratory? In 1859 Kirchhoff had a good idea: a small hole in the side of a large box is an excellent absorber, since any radiation that goes through the hole bounces around inside, a lot getting absorbed on each bounce, and has little chance of ever getting out again. So, we can do this *in reverse*: have an oven with a tiny hole in the side, and presumably the radiation coming out the hole is as good a representation of a perfect emitter as we're going to find (Figure 1.1.2).

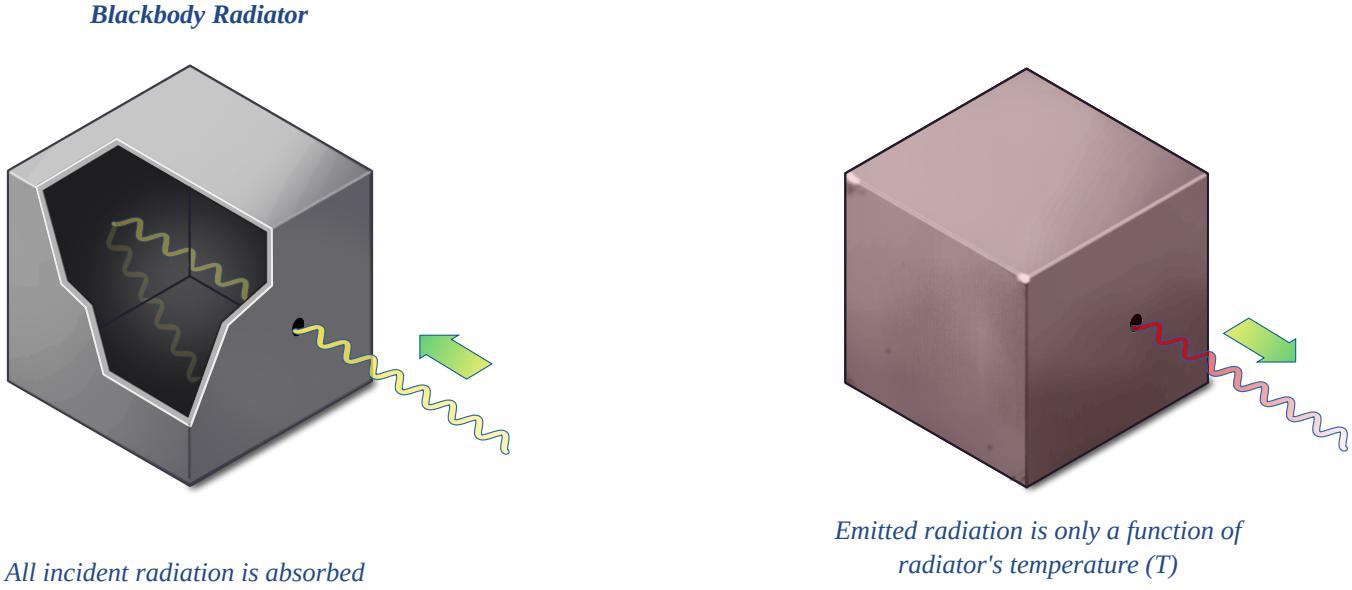


Figure 1.1.2 : Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation. (CC BY-NC; Ümit Kaya via LibreTexts)

By the 1890's, experimental techniques had improved sufficiently that it was possible to make fairly precise measurements of the energy distribution of blackbody radiation. In 1895, at the University of Berlin, Wien and Lummer punched a small hole in the side of an otherwise completely closed oven, and began to measure the radiation coming out. The beam coming out of the hole was passed through a diffraction grating, which sent the different wavelengths/frequencies in different directions, all towards a screen. A detector was moved up and down along the screen to find how much radiant energy was being emitted in each frequency range. They found a radiation intensity/frequency curve close to the distributions in Figure 1.1.3 .

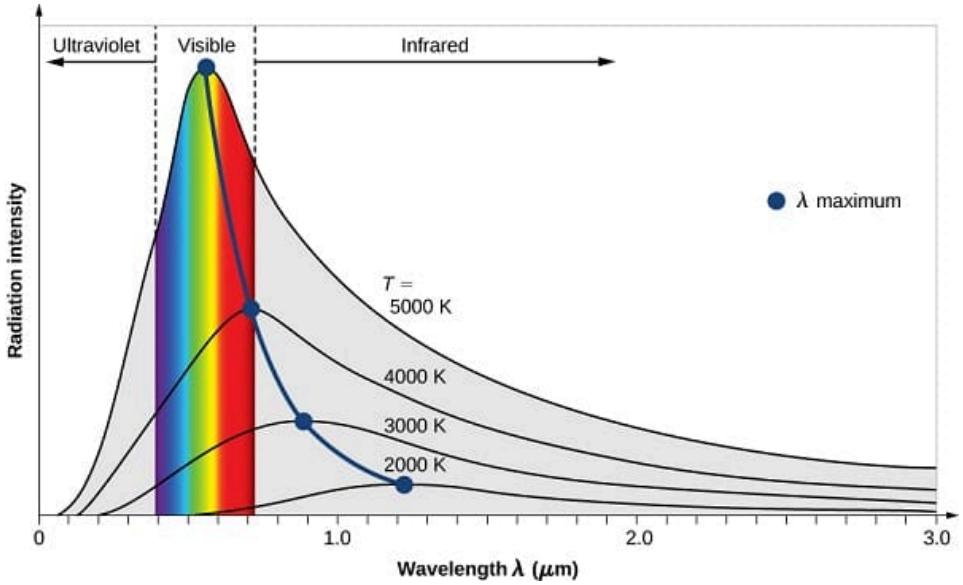
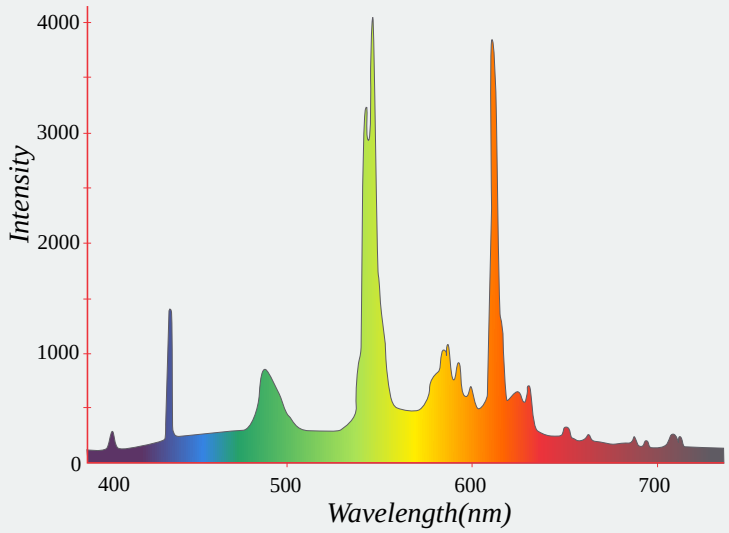


Figure 1.1.3 : Graphic representation of spectral distribution of blackbody radiation at different temperatures. The Stefan-Boltzmann's Law is observed as the increase in the emission amplitude with increasing temperature and the Wien's Displacement Law is observed as the shift to smaller wavelength with increasing temperature. (CC-BY 4.0; OpenStax)

By measuring the blackbody emission curves at different temperatures (Figure 1.1.3), they were also able to construct two important phenomenological Laws (i.e., formulated from experimental observations, not from basic principles of nature): **Stefan-Boltzmann's Law** and **Wien's Displacement Law**.

Not all radiators are blackbody radiators

The radiation of a blackbody radiator is produced by the thermal activity of the material, not the nature of the material, nor how it got thermally excited. Some examples of blackbodies include incandescent light bulbs, stars, and hot stove tops. The emission appears as a continuous spectrum (Figure 1.1.3) with multiple coexisting colors. However, not every radiator is a blackbody radiator. For example, the emission of a fluorescence bulb is not one. The following spectrum show the distribution of light from a fluoresce light tube and is a mixture of discrete bands at different wavelengths of light in contrast to the continuous spectra in Figure 1.1.3 for blackbody radiators.



Fluorescent lighting spectrum with emission peaks. Graph of Intensity (counts) vs. Wavelength (nm) in the visible spectrum. (CC BY-NC; Ümit Kaya via LibreTexts).

Fluorescent light bulbs contain a mixture of inert gases (usually argon and neon) together with a drop of mercury at low pressure. A different mix of visible colors blend to produce a light that appears to us white with different shadings.

The Stefan-Boltzmann Law

The first quantitative conjecture based on experimental observations was the **Stefan-Boltzmann Law** (1879) which states the total power (i.e., integrated over all emitting frequencies in Figure 1.1.3) radiated from one square meter of black surface goes as the *fourth power* of the absolute temperature (Figure 1.1.4):

$$P = \sigma T^4 \tag{1.1.1}$$

where

- P is the total amount of radiation emitted by an object per square meter ($Watts/m^2$)
- σ is a constant called the Stefan-Boltzman constant ($5.67 \times 10^{-8}\ Watts\ \ m^{-2}K^{-4}$)
- T is the absolute temperature of the object (in K)

The Stefan-Boltzmann Law is easily observed by comparing the integrated value (i.e., under the curves) of the experimental black-body radiation distribution in Figure 1.1.3 at different temperatures. In 1884, Boltzmann derived this T^4 behavior from theory by applying classical thermodynamic reasoning to a box filled with electromagnetic radiation, using Maxwell's equations to relate pressure to energy density. That is, the tiny amount of energy coming out of the hole (Figure 1.1.2) would of course have the same temperature dependence as the radiation intensity inside.

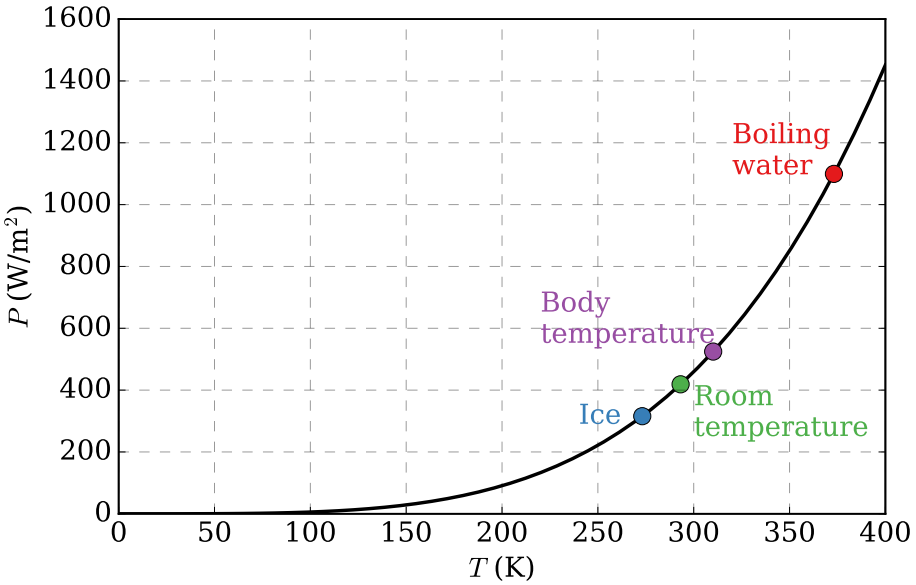


Figure 1.1.4 : Graph of a function of total emitted energy of a blackbody proportional to the fourth power of its thermodynamic temperature T according to the Stefan–Boltzmann law. (CC BY-SA 4.0; Nicoguaro)

Example 1.1.1

The sun's surface temperature is 5700 K.

a. How much power is radiated by the sun?
b. Given that the distance to earth is about 200 sun radii, what is the maximum power possible from a one square kilometer solar energy installation?

Solution A

First, we calculate the area of the sun followed by the flux (power). The sun has a radius of $6.96 \times 10^8 m$

The area of the sun is $A = 4\pi R^2$.

$$A = 4(3.1416)(6.96 \times 10^8 m)^2$$
$$= 6.08 \times 10^{18} m^2$$

The power radiated from the sun (via Stefan-Boltzmann Law) is $P = \sigma T^4$ (Equation 1.1.1).

$$P = (5.67 \times 10^{-8}\, Watts\, m^{-2} K^{-4})(5700K)^4$$
$$= 5.98 \times 10^7 Watts/m^2$$

This value is per square meter.

Solution B

To calculate the total power radiated by the sun is thus:

$$P_{total} = PA = (5.98 \times 10^7 Watts/m^2)(6.08 \times 10^{18} m^2)$$
$$= 3.6 \times 10^{26} Watts$$

Wien's Displacement Law

The second phenomenological observation from experiment was **Wien's Displacement Law**. Wien's law identifies the dominant (peak) wavelength, or color, of light coming from a body at a given temperature. As the oven temperature varies, so does the frequency at which the emitted radiation is most intense (Figure 1.1.3). In fact, that frequency is directly proportional to the absolute temperature:

$$\nu_{max} \propto T \tag{1.1.2}$$

where the proportionality constant is $5.879 \times 10^{10} Hz/K$.

Wien himself deduced this law theoretically in 1893, following Boltzmann's thermodynamic reasoning. It had previously been observed, at least semi-quantitatively, by an American astronomer, Langley. This upward shift in ν_{max} with T is familiar to everyone—when an iron is heated in a fire (Figure 1.1.1), the first visible radiation (at around 900 K) is deep red, the lowest frequency visible light. Further increase in T causes the color to change to orange then yellow, and finally blue at very high temperatures (10,000 K or more) for which the peak in radiation intensity has moved beyond the visible into the ultraviolet.

Another representation of Wien's Law (Equation 1.1.2) in terms of the peak wavelength of light is

$$\lambda_{max} = \frac{b}{T} \tag{1.1.3}$$

where T is the absolute temperature in kelvin and b is a constant of proportionality called **Wien's displacement constant**, equal to $2.89 \times 10^{-3} m\ K$, or more conveniently to obtain wavelength in micrometers, $b \approx 2900\ \mu m \cdot K$. This is an inverse relationship between wavelength and temperature. So the higher the temperature, the shorter or smaller the wavelength of the thermal radiation. The lower the temperature, the longer or larger the wavelength of the thermal radiation. For visible radiation, hot objects emit bluer light than cool objects.

Example 1.1.2

If surface body temperature is 90 °F.

a. How much radiant energy in $W\ m^{-2}$ would your body emit?
b. What is the peak wavelength of emitted radiation?
c. What is the total radiant energy emitted by your body in Watts? Note: The average adult human male has a body surface area of about 1.9 m^2 and the average body surface area for a woman is about 1.6 m^2.

Solution A

90 °F is 305 K. We use Stefan-Boltzmann Law (Equation 1.1.1). The total amount of radiation emitted will be $P = \sigma T^4$.

$$\begin{aligned} P &= (5.67 \times 10^{-8}\, Watts\, m^{-2} K^{-4})(305K)^4 \\ &= 491 W\, m^{-2} \end{aligned}$$

Solution B

The peak wavelength of emitted radiation is found using Wien's Law:

$$\begin{aligned} \lambda_{max} &= \frac{2.898 \times 10^{-3} m \cdot K}{T} \\ &= \frac{2.898 \times 10^{-3} m \cdot K}{305K} \\ &= 9.5 \times 10^{-6} m = 9.5 \mu m \end{aligned}$$

Solution C

The total radiant energy density in Watts is :

$$\begin{aligned} \text{Energy}_{\text{male}} &= (491 W\, m^{-2})(1.9 m^2) = 933 W \\ \text{Energy}_{\text{female}} &= (491 W\, m^{-2})(1.6 m^2) = 786 W \end{aligned}$$

Example 1.1.3 : The Temperature of the Sun

For example, if the Sun has a surface temperature of 5700 K, what is the wavelength of maximum intensity of solar radiation?

Solution

If we substitute 5700 K for T in Equation 1.1.3, we have

$$\begin{aligned} \lambda_{max} &= \frac{0.0029}{5700} \\ &= 5.1 \times 10^{-7}\, m \end{aligned}$$

Knowing that violet light has a wavelength of about 4.0×10^{-7} meters, yellow about 5.6×10^{-7} meters, and red about 6.6×10^{-7} meters, what can we say about the color of the Sun's peak radiation? The peak wavelength of the Sun's radiation is at a slightly shorter wavelength than the color yellow, so it is a slightly greenish yellow. To see this greenish tinge to the Sun, you would have to look at it from space. It turns out that the Earth's atmosphere scatters some of the shorter waves of sunlight, which shifts its peak wavelength to pure yellow.

Remember that thermal radiation always spans a wide range of wavelengths (Figure 1.1.2) and Equation 1.1.3 only specifies the single wavelength that is the **peak** of the spectrum. So although the Sun appears yellowish-white, when you disperse sunlight with a prism you see radiation with all the colors of the rainbow. Yellow just represents a characteristic wavelength of the emission.

Exercise 1.1.1

a. At what wavelength does the sun emit most of its radiation if it has a temperature of 5,778 K?
b. At what wavelength does the earth emit most of its radiation if it has a temperature of 288 K?

Answer a available at the end of this section.

The Rayleigh-Jeans Law

Lord Rayleigh and J. H. Jeans developed an equation which explained blackbody radiation at low frequencies. The equation which seemed to express blackbody radiation was built upon all the known assumptions of physics at the time. *The big assumption which Rayleigh and Jean implied was that infinitesimal amounts of energy were continuously added to the system when the frequency was increased*. Classical physics assumed that energy emitted by atomic oscillations could have any continuous value. This was true for anything that had been studied up until that point, including things like acceleration, position, or energy. Their resulting **Rayleigh-Jeans Law** was

$$d\rho\left(\nu,T\right)=\rho_{\nu}\left(T\right)d\nu \tag{1.1.4}$$

$$=\frac{8\pi k_{B}T}{c^{3}}\nu^{2}d\nu \tag{1.1.5}$$

Experimental data performed on the black box showed slightly different results than what was expected by the Rayleigh-Jeans law (Figure 1.1.5). The law had been studied and widely accepted by many physicists of the day, but the experimental results did not lie, something was different between what was theorized and what actually happens. The experimental results showed a bell type of curve, but according to the Rayleigh-Jeans law the frequency diverged as it neared the ultraviolet region (Equation 1.1.5). Ehrenfest later dubbed this the "ultraviolet catastrophe". It is important to emphasizing that Equation 1.1.5 is a **classical** result: the only inputs are classical dynamics and Maxwell's electromagnetic theory.

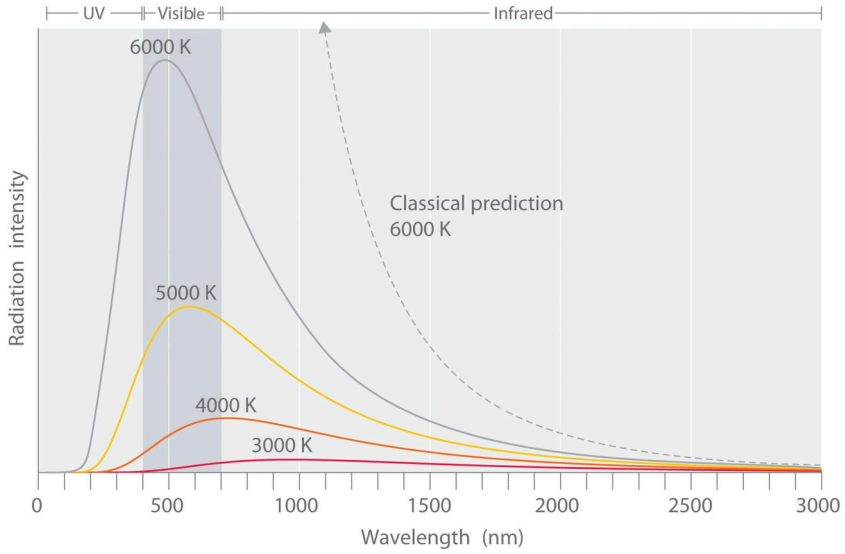


Figure 1.1.5 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the hot metalwork in Figure 1.1.5 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. (CC BY-SA-NC 3.0; anonymous)

Differential vs. Integral Representation of the Distribution

Radiation is understood as a continuous distribution of amplitude vs. wavelength or, equivalently, amplitude vs. frequency (Figure 1.1.5). According to Rayleigh-Jeans law, the intensity at a specific frequency ν and temperature is

$$\rho(\nu,T)=\frac{8\pi k_{b}T\nu^{2}}{c^{3}}.$$

However, in practice, we are more interested in frequency intervals. An exact frequency is the limit of a sequence of smaller and smaller intervals. If we make the assumption that, for a sufficiently small interval, $\rho(\nu,T)$ does not vary, we get your definition for the differential $d\rho(\nu,T)$ in Equation 1.1.5:

The assumption is fair due to the continuity of $\rho(\nu, T)$. This is the approximation of an integral on a very small interval $d\nu$ by the height of a point inside this interval ($\frac{8\pi k_b T\nu^2}{c^3}$) times its length ($d\nu$). So, if we sum an infinite amount of small intervals like the one above we get an integral. The total radiation between ν_1 and ν_2 will be:

$$\begin{aligned}\int_{\nu_1}^{\nu_2} \mathrm{d}\rho(\nu, T) &= \int_{\nu_1}^{\nu_2} \rho(\nu, T)\,\mathrm{d}\nu \\ &= \int_{\nu_1}^{\nu_2} \frac{8\pi k_b T\nu^2}{c^3}\mathrm{d}\nu \\ &= 8\pi k_b T\frac{v_2^3 - v_1^3}{3c^3}.\end{aligned}$$

Observe that $\rho(\nu, T)$ is quadratic in ν.

Example 1.1.4 : The Ultraviolet Catastrophe

What is the total spectral radiance of a radiator that follows the Rayleigh-Jeans law for its emission spectrum?

Solution

The total spectral radiance $\rho_{tot}(T)$ is the combined emission over all possible wavelengths (or equivalently, frequencies), which is an integral over the relevant distribution (Equation 1.1.5 for the Rayleigh-Jeans Law).

$$\begin{aligned}\rho_{tot}(T) &= \int_0^\infty d\rho\,(\nu, T) \\ &= \int_0^\infty \frac{8\pi k_B T}{c^3}\nu^2 d\nu\end{aligned}$$

but the integral

$$\int_0^\infty x^2 \mathrm{d}x$$

does not converge. Worse, it is infinite,

$$\lim_{k\to\infty}\int_0^k x^2 \mathrm{d}x = \infty$$

Hence, the classically derived Rayleigh-Jeans law predicts that the radiance of a blackbody is **infinite**. Since radiance is power per angle and unit area, this also implies that the total power and hence the energy a blackbody emitter gives off is infinite, which is patently absurd. This is called the ultraviolet catastrophe because the absurd prediction is caused by the classical law not predicting the behavior at high frequencies/small wavelengths correctly (Figure 1.1.5).

Contributors and Attributions

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- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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Answers

500 nm
10.0 microns

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1.2: Quantum Hypothesis Used for Blackbody Radiation Law

Learning Objectives

- To understand how energy is quantized in blackbody radiation

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could not be explained by the theories available at the time.

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation (Figure 1.2.1). Attempts to explain or calculate this spectral distribution from classical theory were complete failures. A theory developed by Rayleigh and Jeans predicted that the intensity should go to infinity at short wavelengths. Since the intensity actually drops to zero at short wavelengths, the Rayleigh-Jeans result was called the **ultraviolet catastrophe** (Figure 1.2.1 dashed line). There was no agreement between theory and experiment in the ultraviolet region of the blackbody spectrum.

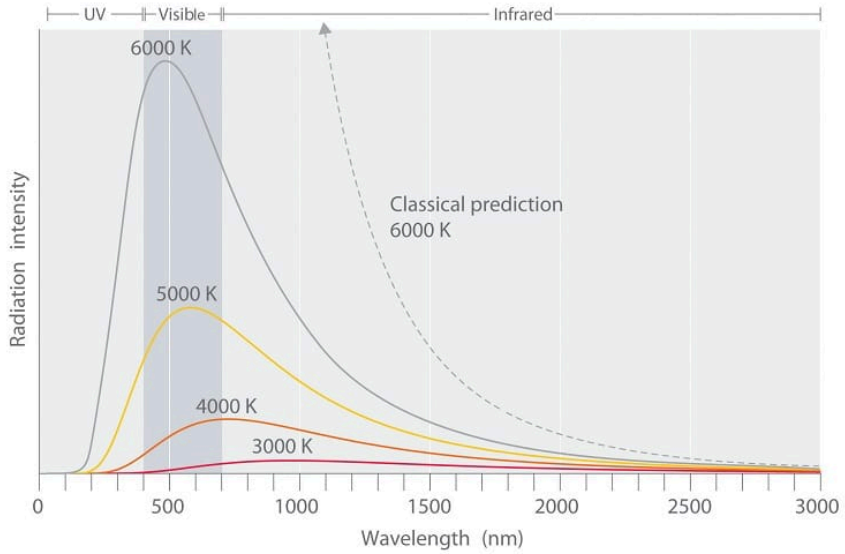


Figure 1.2.1 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun. Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity. (CC BY-SA-NC; anonymous).

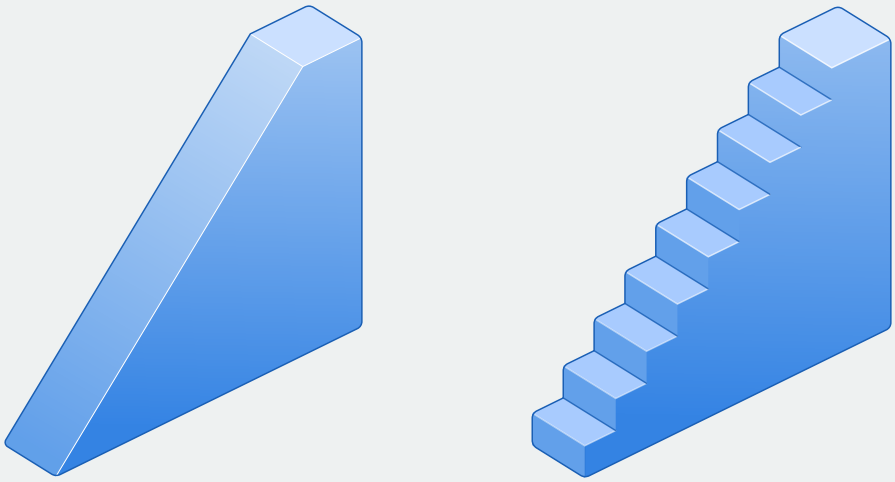
Quantizing Electrons in the Radiator

In 1900, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 1.2.1 , so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral

multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum.

Quantization

Although quantization may seem to be an unfamiliar concept, we encounter it frequently in quantum mechanics (hence the name). For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. It is also similar to going up and down a hill using discrete stair steps rather than being able to move up and down a continuous slope. Your potential energy takes on discrete values as you move from step to step. Even electrical charge is quantized: an ion may have a charge of –1 or –2, but *not* –1.33 electron charges.



A continuous vs. a quantized (gravitationaly) potential energy system. In the continuous case (left) a system can have any potential energy, but in the quantized case (right), a system can only have certain values (other values are not allowed). (CC BY-NC; Ümit Kaya via LibreTexts)

Planck's quantization of energy is described by the his famous equation:

$$E = h\nu \tag{1.2.1}$$

where the proportionality constant h is called **Planck's constant**, one of the most accurately known fundamental constants in science

$$h = 6.626070040(81) \times 10^{-34}\, J \cdot s$$

However, for our purposes, its value to four significant figures is sufficient:

$$h = 6.626 \times 10^{-34}\, J \cdot s$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\nu$, Planck devised an equation that fit the experimental data shown in Figure 1.2.1 . We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 1.2.1 , and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.

Max Planck explain the spectral distribution of blackbody radiation as result from oscillations of electrons. Similarly, oscillations of electrons in an antenna produce radio waves. Max Planck concentrated on modeling the oscillating charges that must exist in the oven walls, radiating heat inwards and—in thermodynamic equilibrium—themselves being driven by the radiation field. He found he could account for the observed curve if he required these oscillators not to radiate energy continuously, as the classical theory would demand, but they could **only** lose or gain energy in chunks, called **quanta**, of size $h\nu$, for an oscillator of frequency ν (Equation 1.2.1).

With that assumption, Planck calculated the following formula for the radiation energy density inside the oven:

$$d\rho(\nu,T) = \rho_\nu(T)d\nu \tag{1.2.2}$$

$$= \frac{8\pi h\nu^3}{c^3}\cdot\frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}d\nu \tag{1.2.3}$$

with

- $\pi = 3.14159$
- h = $6.626\times10^{-34}J\cdot s$
- c = $3.00\times10^{8}\ m/s$
- ν = $1/s$
- k_B = $1.38\times10^{-23}J/K$
- T is absolute temperature (in Kelvin)

Planck's radiation energy density (Equation 1.2.3) can also be expressed in terms of wavelength λ.

$$\rho(\lambda,T) = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda k_BT}-1}\right) \tag{1.2.4}$$

With a wavelength of maximum energy density at:

$$\lambda_{max} = \frac{hc}{4.965kT}$$

This can be used to calculate the radiance emitted from surface per unit frequency

$$dB_\nu(\nu,T) = \rho_\nu(T)d\nu$$

$$= \frac{2h\nu^3}{c^2}\cdot\frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}d\nu \tag{1.2.5}$$

or

$$B_\lambda(\lambda,T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/(\lambda k_BT)}-1} \tag{1.2.6}$$

Planck's equation (Equation 1.2.4) gave an excellent agreement with the experimental observations for all temperatures (Figure 1.2.2).

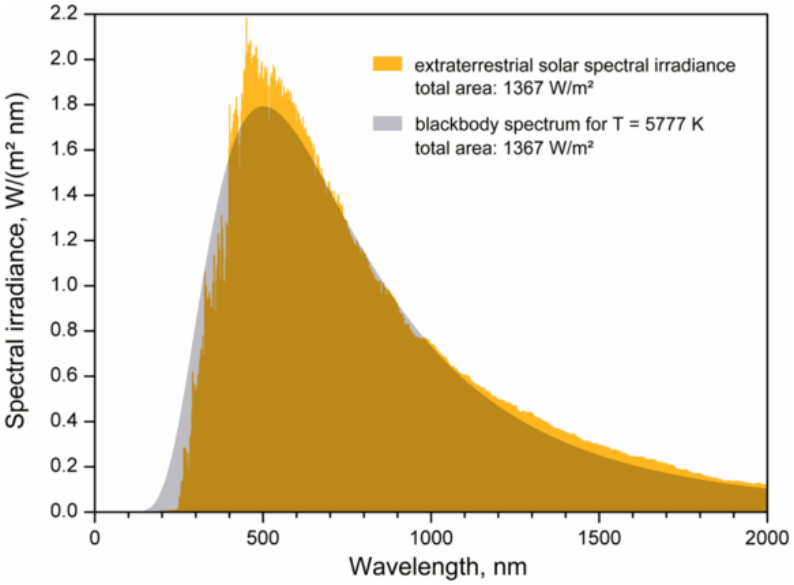
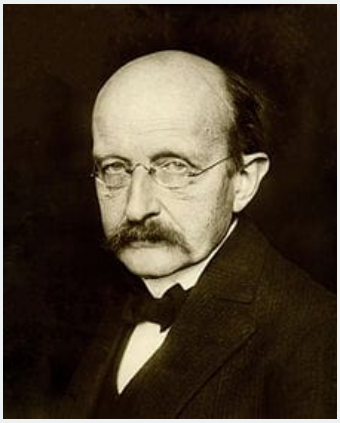


Figure 1.2.2 : The Sun is an excellent approximation of a blackbody. Its effective temperature is ~5777 K. (CC-SA-BY 3.0; Sch).

Max Planck (1858–1947)

Planck made many substantial contributions to theoretical physics, but his fame as a physicist rests primarily on his role as the originator of quantum theory. In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government.



MAX-PLANCK-GESELLSCHAFT

(left) The German physicist Max Planck had a major influence on the early development of quantum mechanics, being the first to recognize that energy is sometimes quantized. Planck also made important contributions to special relativity and classical physics. (Public Domain; Library of Congress via Wikimedia) (left) The society's logo features Minerva, the Roman goddess of wisdom. (Fair use)

One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler and bombing during the last weeks of World War II destroyed Planck's home. After WWII, the major German scientific research organization was renamed the Max Planck Society.

Exercise 1.2.1

Use Equation 1.2.4 to show that the units of $\rho(\lambda, T)\ d\lambda$ are J/m^3 as expected for an energy density.

The near perfect agreement of this formula with precise experiments (e.g., Figure 1.2.3), and the consequent necessity of energy

quantization, was the most important advance in physics in the century. His blackbody curve was completely accepted as the correct one: more and more accurate experiments confirmed it time and again, yet the radical nature of the quantum assumption did not sink in. Planck was not too upset—he didn't believe it either, he saw it as a technical fix that (he hoped) would eventually prove unnecessary.

> Part of the problem was that Planck's route to the formula was long, difficult and implausible—he even made contradictory assumptions at different stages, as Einstein pointed out later. However, the result was correct anyway!

The mathematics implied that the energy given off by a blackbody was not continuous, but given off at certain specific wavelengths, in regular increments. If Planck assumed that the energy of blackbody radiation was in the form

$$E = nh\nu$$

where n is an integer, then he could explain what the mathematics represented. This was indeed difficult for Planck to accept, because at the time, there was no reason to presume that the energy should only be radiated at specific frequencies. Nothing in Maxwell's laws suggested such a thing. It was as if the vibrations of a mass on the end of a spring could only occur at specific energies. Imagine the mass slowly coming to rest due to friction, but not in a continuous manner. Instead, the mass jumps from one fixed quantity of energy to another without passing through the intermediate energies.

> To use a different analogy, it is as if what we had always imagined as smooth inclined planes were, in fact, a series of closely spaced steps that only presented the illusion of continuity.

Summary

The agreement between Planck's theory and the experimental observation provided strong evidence that the energy of electron motion in matter is quantized. In the next two sections, we will see that the energy carried by light also is quantized in units of $h\bar{\nu}$. These packets of energy are called "photons."

Contributors and Attributions

- Michael Fowler (Beams Professor, Department of Physics, University of Virginia)
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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1.3: Photoelectric Effect Explained with Quantum Hypothesis

Learning Objectives

- To be familiar with the photoelectron effect for bulk materials
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light wavelength
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light intensity
- Describe what a workfunction is and relate it to ionization energy
- Describe the photoelectric effect with Einstein's quantized photon model of light

Nature, it seemed, was quantized (non-continuous, or discrete). If this was so, how could Maxwell's equations correctly predict the result of the blackbody radiator? Planck spent a good deal of time attempting to reconcile the behavior of electromagnetic waves with the discrete nature of the blackbody radiation, to no avail. It was not until 1905, with yet another paper published by Albert Einstein, that the wave nature of light was expanded to include the particle interpretation of light which adequately explained Planck's equation.

The photoelectric effect was first documented in 1887 by the German physicist Heinrich Hertz and is therefore sometimes referred to as the Hertz effect. While working with a spark-gap transmitter (a primitive radio-broadcasting device), Hertz discovered that upon absorption of certain frequencies of light, substances would give off a visible spark. In 1899, this spark was identified as light-excited electrons (called **photoelectrons**) leaving the metal's surface by J.J. Thomson (Figure 1.3.1).

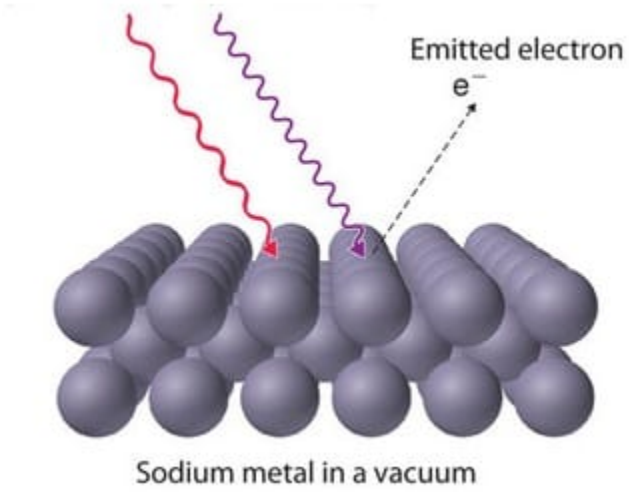


Figure 1.3.1 : The photoelectric effect involves irradiating a metal surface with photons of sufficiently high energy to cause the electrons to be ejected from the metal. (CC BY-SA-NC; anonymous)

The classical picture underlying the photoelectron effect was that the atoms in the metal contained electrons, that were shaken and caused to vibrate by the oscillating electric field of the incident radiation. Eventually some of them would be shaken loose, and would be ejected from the cathode. It is worthwhile considering carefully how the *number* and *speed* of electrons emitted would be expected to vary with the *intensity* and *color* of the incident radiation along with the time needed to observe the photoelectrons.

- Increasing the intensity of radiation would shake the electrons more violently, so one would expect more to be emitted, and they would shoot out at greater speed, on average.
- Increasing the frequency of the radiation would shake the electrons faster, so it might cause the electrons to come out faster. For very dim light, it would take some time for an electron to work up to a sufficient amplitude of vibration to shake loose.

Lenard's Experimental Results (Intensity Dependence)

In 1902, Hertz's student, Philipp Lenard, studied how the energy of the emitted photoelectrons varied with the intensity of the light. He used a carbon arc light and could increase the intensity a thousand-fold. The ejected electrons hit another metal plate, the collector, which was connected to the cathode by a wire with a sensitive ammeter, to measure the current produced by the illumination (Figure 1.3.2). To measure the energy of the ejected electrons, Lenard charged the collector plate negatively, to repel the electrons coming towards it. Thus, only electrons ejected with enough kinetic energy to get up this potential hill would contribute to the current.

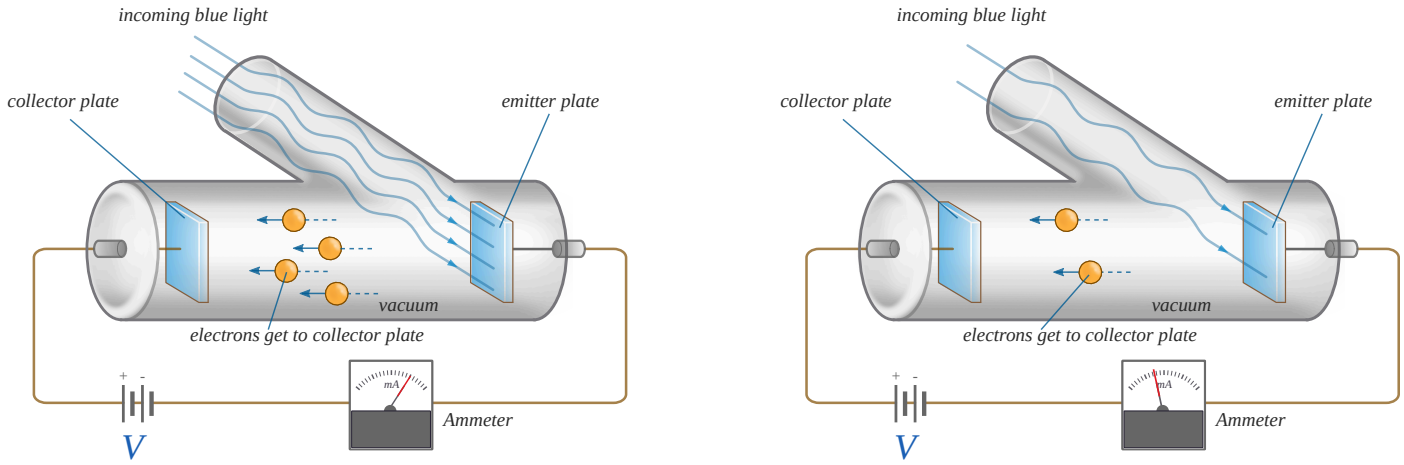


Figure 2: Lenard's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Lenard discovered that there was a well defined minimum voltage that stopped any electrons getting through (V_{stop}). To Lenard's surprise, he found that V_{stop} did not depend at all on the intensity of the light! Doubling the light intensity doubled the *number* of electrons emitted, but did not affect the *kinetic energies* of the emitted electrons. The more powerful oscillating field ejected more electrons, but the maximum individual energy of the ejected electrons was the same as for the weaker field (Figure 1.3.2).

Millikan's Experimental Results (Wavelength Dependence)

The American experimental physicist Robert Millikan followed up on Lenard's experiments and using a powerful arc lamp, he was able to generate sufficient light intensity to separate out the colors and check the photoelectric effect using light of different colors. He found that the maximum energy of the ejected electrons *did* depend on the color - the shorter wavelength, higher frequency light eject photoelectrons with greater kinetic energy (Figures 1.3.3).

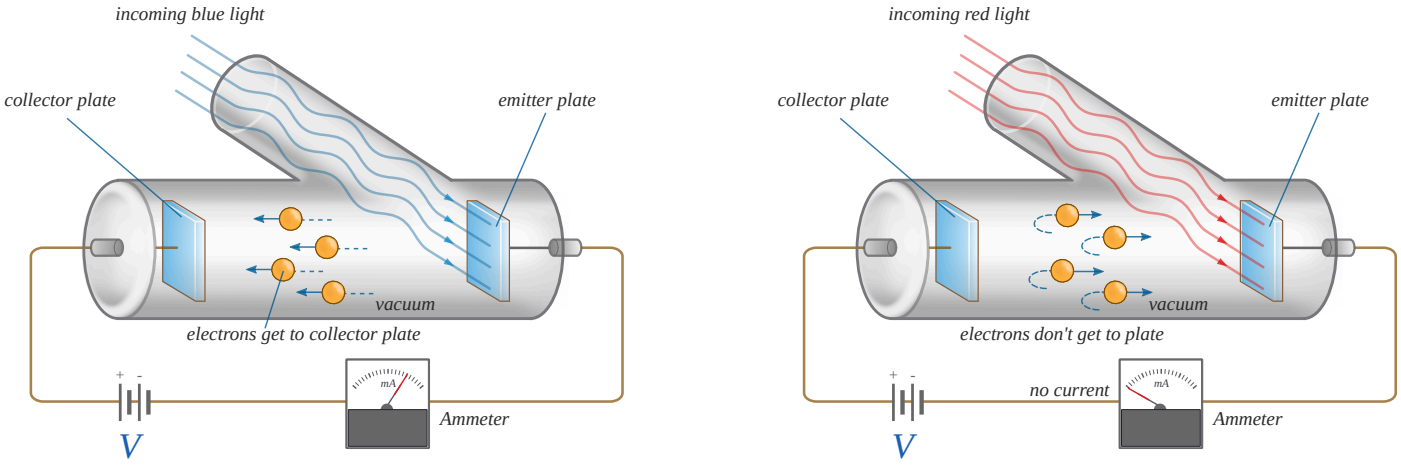


Figure 1.3.3 : Millikan's photoelectric experiment. (left) Incident high-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector plate, the potential supplied by the battery is less than V_{stop}, for blue light. (right) Indicent low-energy red light. Since the electrons ejected by the red light are not getting to the collector plate, the potential supplied by the battery exceeds V_{stop} for red light. (CC BY-NC; Ümit Kaya via LibreTexts)

As shown in Figure 1.3.4 , just the opposite behavior from classical is observed from Lenard's and Millikan's experiments. The intensity affects the number of electrons, and the frequency affects the kinetic energy of the emitted electrons. From these sketches, we see that

- the kinetic energy of the electrons is linearly proportional to the frequency of the incident radiation above a threshold value of ν_0 (no current is observed below ν_0), and the kinetic energy is independent of the intensity of the radiation, and
- the number of electrons (i.e. the electric current) is proportional to the intensity and independent of the frequency of the incident radiation above the threshold value of ν_0 (i.e., no current is observed below ν_0).

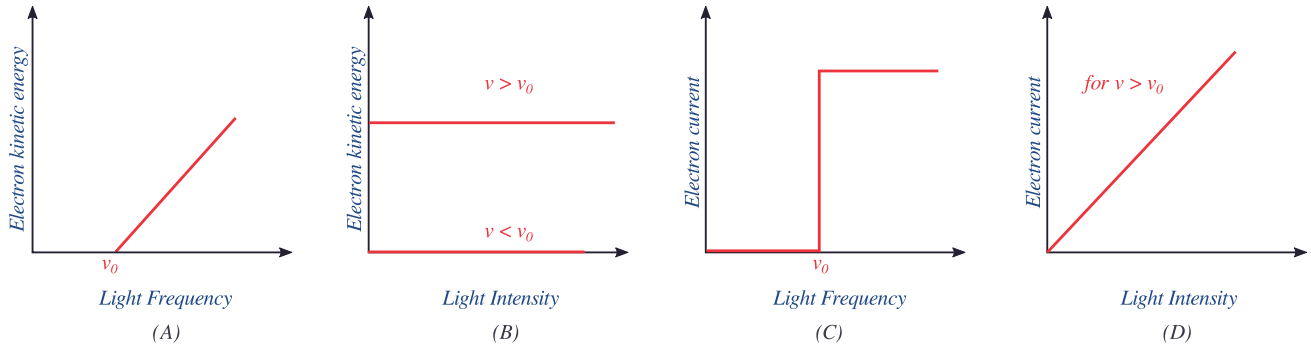


Figure 1.3.4 : Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the light intensity above the threshold frequency and zero below. (C) The number of electrons emitted per second (i.e. the electric current) is independent of light frequency above the threshhold frequency and zero below. (D) The number of electrons increases linearly with the light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Classical Theory does not Describe Experiment

Classical theory predicts that energy carried by light is proportional to its amplitude independent of its frequency, and this fails to correctly explain the observed wavelength dependence in Lenard's and Millikan's observations.

As with most of the experimental results we discuss in this text, the behavior described above is a simplification of the true experimental results observed in the laboratory. A more complex description involves a greater introduction of more complex

physics and instrumentation, which will be ignored for now.

Einstein's Quantum Picture

In 1905 Einstein gave a very simple interpretation of Lenard's results and borrowed Planck's hypothesis about the quantized energy from his blackbody research and assumed that the incoming radiation should be thought of as quanta of energy $h\nu$, with ν the frequency. In photoemission, one such quantum is absorbed by one electron. If the electron is some distance into the material of the cathode, some energy will be lost as it moves towards the surface. There will always be some electrostatic cost as the electron leaves the surface, which is the workfunction, Φ. The most energetic electrons emitted will be those very close to the surface, and they will leave the cathode with kinetic energy

$$KE = h\nu - \Phi \tag{1.3.1}$$

On cranking up the negative voltage on the collector plate until the current just stops, that is, to V_{stop}, the highest kinetic energy electrons (KE_e) must have had energy eV_{stop} upon leaving the cathode. Thus,

$$eV_{stop} = h\nu - \Phi \tag{1.3.2}$$

Thus, Einstein's theory makes a very definite quantitative prediction: if the frequency of the incident light is varied, and V_{stop} plotted as a function of frequency, the slope of the line should be $\frac{h}{e}$ (Figure $1.3.4A$). It is also clear that there is a minimum light frequency for a given metal ν_o, that for which the quantum of energy is equal to Φ (Equation 1.3.1). Light below that frequency, no matter how bright, will not eject electrons.

> According to both Planck and Einstein, the energy of light is proportional to its frequency rather than its amplitude, there will be a minimum *frequency* ν_0 needed to eject an electron with no residual energy.

Since every photon of sufficient energy excites only one electron, increasing the light's intensity (i.e. the number of photons/sec) only increases the *number* of released electrons and not their kinetic energy. In addition, no time is necessary for the atom to be heated to a critical temperature and therefore the release of the electron is nearly instantaneous upon absorption of the light. Finally, because the photons must be above a certain energy to satisfy the workfunction, a threshold frequency exists below which no photoelectrons are observed. This frequency is measured in units of Hertz (1/second) in honor of the discoverer of the photoelectric effect.

Einstein's Equation 1.3.1 explains the properties of the photoelectric effect quantitatively. A strange implication of this experiment is that light can behave as a kind of massless "particle" now known as a *photon* whose energy $E = h\nu$ can be transferred to an actual particle (an electron), imparting kinetic energy to it, just as in an elastic collision between to massive particles such as billiard balls.

> Robert Millikan initially did not accept Einstein's theory, which he saw as an attack on the wave theory of light, and worked for ten years until 1916, on the photoelectric effect. He even devised techniques for scraping clean the metal surfaces inside the vacuum tube. For all his efforts he found disappointing results: he confirmed Einstein's theory after ten years. In what he writes in his paper, Millikan is still desperately struggling to avoid this conclusion. However, by the time of his Nobel Prize acceptance speech, he has changed his mind rather drastically!

Einstein's simple explanation (Equation 1.3.1) completely accounted for the observed phenomena in Lenard's and Millikan's experiments (Figure 1.3.4) and began an investigation into the field we now call *quantum mechanics*. This new field seeks to provide a quantum explanation for classical mechanics and create a more unified theory of physics and thermodynamics. The study of the photoelectric effect has also lead to the creation of new field of photoelectron spectroscopy. Einstein's theory of the photoelectron presented a completely different way to measure Planck's constant than from black-body radiation.

The Workfunction (Φ)

The **workfunction** is an intrinsic property of the metal. While the workfunctions and ionization energies appear as similar concepts, they are independent. The workfunction of a metal is the minimum amount of energy (E) necessary to remove an electron from the surface of the bulk (*solid*) metal (sometimes referred to as **binding energy**).

$$\mathrm{M(s) + \Phi \rightarrow M^+(s) + e^-(free\ with\ no\ kinetic\ energy)}$$

The workfunction is qualitatively similar to ionization energy (IE), which is the amount of energy required to remove an electron from an atom or molecule in the *gaseous* state.

$$\mathrm{M(g) + IE\ \rightarrow M^+(g) + e^-(free\ with\ no\ kinetic\ energy)}$$

However, these two energies differ in magnitude (Table 1.3.1). For instance, copper has a workfunction of about 4.7 eV, but has a higher ionization energy of 7.7 eV. Generally, the ionization energies for metals are greater than the corresponding workfunctions (i.e., the electrons are less tightly bound in bulk metal).

Table 1.3.1 : Workfunctions and Ionization Energies of Select Elements

Element	Workfunction Φ (eV)	Ionization Energy (eV)
Lithium (Li)	2.93	5.39
Beryllium (Be)	4.98	9.32
Boron (B)	4.45	8.298
Carbon (C)	5.0	11.26
Sodium (Na)	2.36	5.13
Aluminum (Al)	4.20	5.98
Silicon (Si)	4.85	8.15
Potassium (K)	2.3	4.34
Iron (Fe)	4.67	7.87
Cobalt (Co)	4.89	7.88
Copper (Cu)	4.7	7.7
Gallium (Ga)	4.32	5.99
Germanium (Ge)	5.0	7.89
Arsenic (As)	3.75	9.81
Selenium (Se)	5.9	9.75
Silver (Ag)	4.72	7.57
Tin (Sn)	4.42	7.34
Cesium (Cs)	1.95	3.89
Gold (Au)	5.17	9.22
Mercury $(Hg)_{liquid}$	4.47	10.43
Bismuth (Bi)	4.34	7.29

Example 1.3.1 : Calcium

a. What is the energy in joules and electron volts of a photon of 420-nm violet light?
b. What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the workfunction for calcium metal is 2.71 eV?

Strategy

To solve part (a), note that the energy of a photon is given by $E = h\nu$. For part (b), once the energy of the photon is calculated, it is a straightforward application of Equation 1.3.1 to find the ejected electron's maximum kinetic energy, since Φ is given.

Solution for (a)

Photon energy is given by

$$E = h\nu$$

Since we are given the wavelength rather than the frequency, we solve the familiar relationship $c = \nu\lambda$ for the frequency, yielding

$$\nu = \frac{c}{\lambda}$$

Combining these two equations gives the useful relationship

$$E = \frac{hc}{\lambda}$$

Now substituting known values yields

$$\begin{aligned} E &= \frac{(6.63 \times 10^{-34}\ J \cdot s)(3.00 \times 10^{8} m/s)}{420 \times 10^{-9}\ m} \\ &= 4.74 \times 10^{-19}\ J \end{aligned}$$

Converting to eV, the energy of the photon is

$$\begin{aligned} E &= (4.74 \times 10^{-19}\ J)\left(\frac{1\ eV}{1.6 \times 10^{-19}\ J}\right) \\ &= 2.96\ eV. \end{aligned}$$

Solution for (b)

Finding the kinetic energy of the ejected electron is now a simple application of Equation 1.3.1. Substituting the photon energy and binding energy yields

$$\begin{aligned} KE_e &= h\nu – \Phi \\ &= 2.96\ eV – 2.71\ eV \\ &= 0.246\ eV. \end{aligned}$$

Discussion

The energy of this 420-nm photon of violet light is a tiny fraction of a joule, and so it is no wonder that a single photon would be difficult for us to sense directly—humans are more attuned to energies on the order of joules. But looking at the energy in electron volts, we can see that this photon has enough energy to affect atoms and molecules. A DNA molecule can be broken with about 1 eV of energy, for example, and typical atomic and molecular energies are on the order of eV, so that the UV photon in this example could have biological effects.

The ejected electron (called a photoelectron) has a rather low energy, and it would not travel far, except in a vacuum. The electron would be stopped by a retarding potential of 0.26 eV. In fact, if the photon wavelength were longer and its energy less than 2.71 eV, then the formula would give a negative kinetic energy, an impossibility. This simply means that the 420-nm photons with their 2.96-eV energy are not much above the frequency threshold. You can show for yourself that the threshold wavelength is 459 nm (blue light). This means that if calcium metal is used in a light meter, the meter will be insensitive to wavelengths longer than those of blue light. Such a light meter would be insensitive to red light, for example.

Exercise 1.3.1 : Silver

What is the longest-wavelength electromagnetic radiation that can eject a photoelectron from silver? Is this in the visible range?

Answer available at the end of this section.

Exercise 1.3.2

Why is the workfunction of an element generally lower than the ionization energy of that element?

Answer available at the end of this section.

Summary

Although Hertz discovered the photoelectron in 1887, it was not until 1905 that a theory was proposed that explained the effect completely. The theory was proposed by Einstein and it made the claim that electromagnetic radiation had to be thought of as a series of particles, called photons, which collide with the electrons on the surface and emit them. This theory ran contrary to the belief that electromagnetic radiation was a wave and thus it was not recognized as correct until 1916 when Robert Millikan experimentally confirmed the theory

The photoelectric effect is the process in which electromagnetic radiation ejects electrons from a material. Einstein proposed photons to be quanta of electromagnetic radiation having energy $E = h\nu$ is the frequency of the radiation. All electromagnetic radiation is composed of photons. As Einstein explained, all characteristics of the photoelectric effect are due to the interaction of individual photons with individual electrons. The maximum kinetic energy KE_e of ejected electrons (photoelectrons) is given by $KE_e = h\nu$–Φ, where $h\nu$ is the photon energy and Φ is the workfunction (or binding energy) of the electron to the particular material.

Conceptual Questions

1. Is visible light the only type of electromagnetic radiation that can cause the photoelectric effect?
2. Which aspects of the photoelectric effect cannot be explained without photons? Which can be explained without photons? Are the latter inconsistent with the existence of photons?
3. Is the photoelectric effect a direct consequence of the wave character of electromagnetic radiation or of the particle character of electromagnetic radiation? Explain briefly.
4. Insulators (nonmetals) have a higher Φ than metals, and it is more difficult for photons to eject electrons from insulators. Discuss how this relates to the free charges in metals that make them good conductors.
5. If you pick up and shake a piece of metal that has electrons in it free to move as a current, no electrons fall out. Yet if you heat the metal, electrons can be boiled off. Explain both of these facts as they relate to the amount and distribution of energy involved with shaking the object as compared with heating it.

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Answers

Given that the workfunction is 4.72 eV from Table 1.3.1 , then only photons with wavelengths lower than 263 nm will induce photoelectrons (calculated via $E = h\nu$). This is ultraviolet and not in the visible range.

The workfunction of a metal refers to the minimum energy required to extract an electron from the surface of a (**bulk**) metal by the absorption a photon of light. The workfunction will vary from metal to metal. In contrast, ionization energy is the energy needed to detach electrons from **atoms** and also varies with each particular atom, with the valence electrons require less energy to extract than core electrons (i.e., from lower shells) that are more closely bound to the nuclei. The electrons in the metal lattice there less bound (i.e., free to move within the metal) and removing one of these electrons is much easier than removing an electron from an atom because the metallic bonds of the bulk metal reduces their binding energy. As we will show in subsequent chapters, the more delocalized a particle is, the lower its energy.

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1.4: The Hydrogen Atomic Spectrum

Overview

- To introduce the concept of absorption and emission line spectra and describe the Balmer equation to describe the visible lines of atomic hydrogen.

The first person to realize that white light was made up of the colors of the rainbow was Isaac Newton, who in 1666 passed sunlight through a narrow slit, then a prism, to project the colored spectrum on to a wall. This effect had been noticed previously, of course, not least in the sky, but previous attempts to explain it, by Descartes and others, had suggested that the white light became colored when it was refracted, the color depending on the angle of refraction. Newton clarified the situation by using a second prism to reconstitute the white light, making much more plausible the idea that the white light was composed of the separate colors. He then took a monochromatic component from the spectrum generated by one prism and passed it through a second prism, establishing that no further colors were generated. That is, light of a single color did not change color on refraction. He concluded that white light was made up of all the colors of the rainbow, and that on passing through a prism, these different colors were refracted through slightly different angles, thus separating them into the observed spectrum.

Atomic Line Spectra

The spectrum of hydrogen *atoms*, which turned out to be crucial in providing the first insight into atomic structure over half a century later, was first observed by Anders Ångström in Uppsala, Sweden, in 1853. His communication was translated into English in 1855. Ångström, the son of a country minister, was a reserved person, not interested in the social life that centered around the court. Consequently, it was many years before his achievements were recognized, at home or abroad (most of his results were published in Swedish).

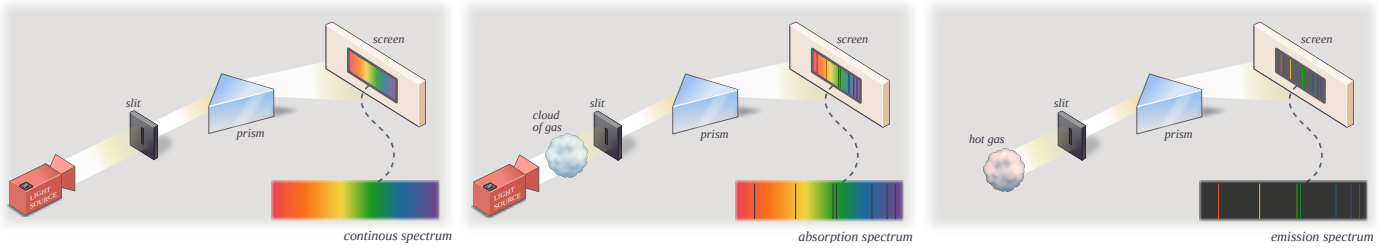


Figure 1.4.1 : Three Kinds of Spectra. When we see a lightbulb or other source of continuous radiation, all the colors are present. When the continuous spectrum is seen through a thinner gas cloud, the cloud's atoms produce absorption lines in the continuous spectrum. When the excited cloud is seen without the continuous source behind it, its atoms produce emission lines. We can learn which types of atoms are in the gas cloud from the pattern of absorption or emission lines. (CC BY-NC; Ümit Kaya via LibreTexts).

Most of what is known about atomic (and molecular) structure and mechanics has been deduced from spectroscopy. Figure 1.4.1 shows two different types of spectra. A continuous spectrum can be produced by an incandescent solid or gas at high pressure (e.g., blackbody radiation is a continuum). An emission spectrum can be produced by a gas at low pressure excited by heat or by collisions with electrons. An absorption spectrum results when light from a continuous source passes through a cooler gas, consisting of a series of dark lines characteristic of the composition of the gas.

Fraunhofer Lines

In 1802, William Wollaston in England had discovered that the solar spectrum had tiny gaps - there were many thin dark lines in the rainbow of colors. These were investigated much more systematically by Joseph von Fraunhofer, beginning in 1814. He increased the dispersion by using more than one prism. He found an "almost countless number" of lines. He labeled the strongest dark lines A, B, C, D, etc. Frauenhofer between 1814 and 1823 discovered nearly 600 dark lines in the solar

spectrum viewed at high resolution and designated the principal features with the letters A through K, and weaker lines with other letters (Table 1.4.1). Modern observations of sunlight can detect many thousands of lines. It is now understood that these lines are caused by absorption by the outer layers of the Sun.

Table 1.4.1 : Major Fraunhofer lines and the elements they are associated with.

Designation	Element	Wavelength (nm)
y	O_2	898.765
Z	O_2	822.696
A	O_2	759.370
B	O_2	686.719
C	H	656.281
a	O_2	627.661
D_1	Na	589.592
D_2	Na	588.995
D_3 or d	He	587.5618

The Fraunhofer lines are typical spectral absorption lines. These dark lines are produced whenever a cold gas is between a broad spectrum photon source and the detector. In this case, a decrease in the intensity of light in the frequency of the incident photon is seen as the photons are absorbed, then re-emitted in random directions, which are mostly in directions different from the original one. This results in an *absorption line*, since the narrow frequency band of light initially traveling toward the detector, has been turned into heat or re-emitted in other directions.

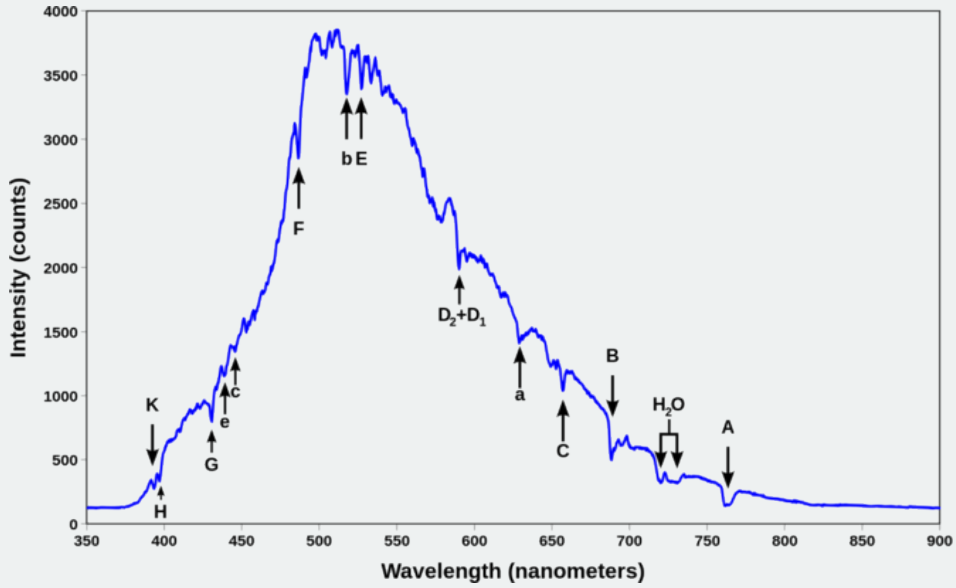


Figure 1.4.2 : Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. (CC BY-SA 4.0; Eric Bajart via Wikipedia).

By contrast, if the detector sees photons emitted directly from a glowing gas, then the detector often sees photons emitted in a narrow frequency range by quantum emission processes in atoms in the hot gas, resulting in an *emission line*. In the Sun, Fraunhofer lines are seen from gas in the outer regions of the Sun, which are too cold to directly produce emission lines of the elements they represent.

Gases heated to incandescence were found by Bunsen, Kirkhoff and others to emit light with a series of sharp wavelengths. The emitted light analyzed by a spectrometer (or even a simple prism) appears as a multitude of narrow bands of color. These so called *line spectra* are characteristic of the atomic composition of the gas. The line spectra of several elements are shown in Figure 1.4.3 .

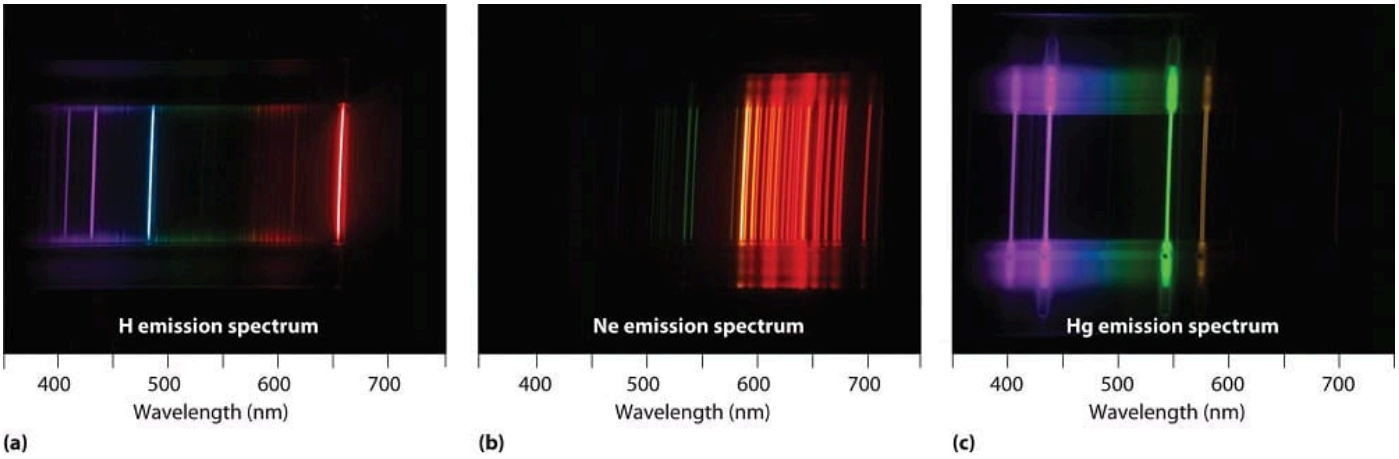


Figure 1.4.3 : The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV; these are not shown. (CC BY-SA-NC; Anonymous by request).

The Balmer Series of Hydrogen

Obviously, if any pattern could be discerned in the spectral lines for a specific atom (in contract to the mixture that Fraunhofer lines represent), that might be a clue as to the internal structure of the atom. One might be able to build a model. A great deal of effort went into analyzing the spectral data from the 1860's on. The big breakthrough was made by Johann Balmer, a math and Latin teacher at a girls' school in Basel, Switzerland. Balmer had done no physics before and made his great discovery when he was almost sixty.

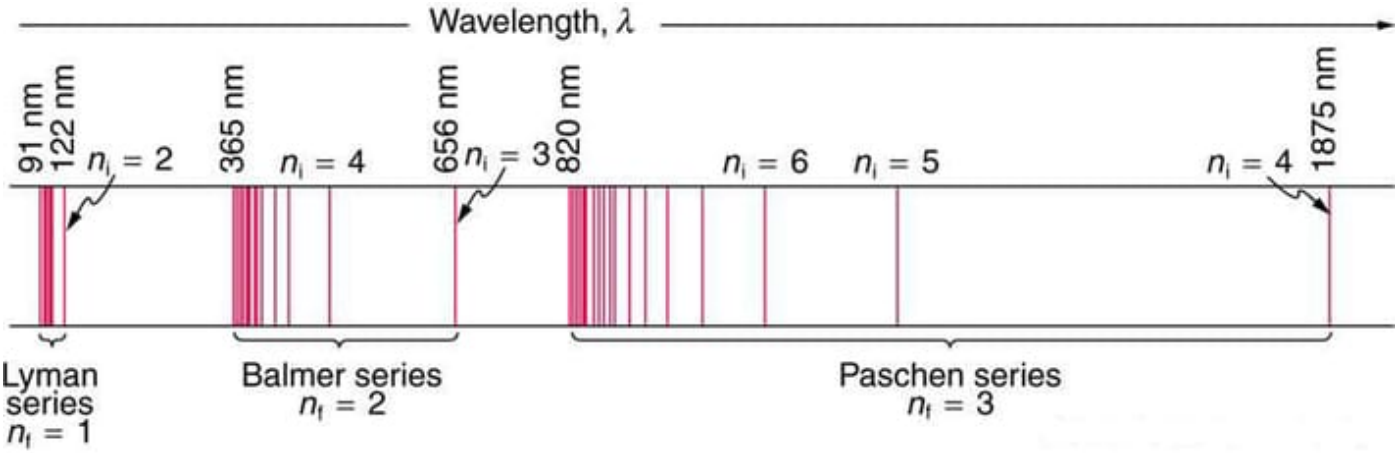


Figure 1.4.4 : A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of n_f and n_i are shown for some of the lines (CC BY-SA; OpenStax).

Balmer decided that the most likely atom to show simple spectral patterns was the lightest atom, hydrogen. Ångström had measured the four visible spectral lines to have wavelengths 656.21, 486.07, 434.01 and 410.12 nm (Figure 1.4.4). Balmer concentrated on just these four numbers, and found they were represented by the phenomenological formula:

$$\lambda = b\left(\frac{n_2^2}{n_2^2 - 4}\right) \tag{1.4.1}$$

where b = 364.56 nm and $n_2 = 3, 4, 5, 6$.

The first four wavelengths of Equation 1.4.1 (with n_2 = 3, 4, 5, 6) were in excellent agreement with the experimental lines from Ångström (Table 1.4.2). Balmer predicted that other lines exist in the ultraviolet that correspond to $n_2 \geq 7$ and in fact some of

them had already been observed, unbeknown to Balmer.

Table 1.4.2 : The Balmer Series of Hydrogen Emission Lines

n_2	3	4	5	6	7	8	9	10
λ	*656*	*486*	*434*	*410*	397	389	383	380
color	*red*	*teal*	*blue*	*indigo*	violet	not visible	not visible	not visible

The n_2 integer in the Balmer series extends theoretically to infinity and the series represents a monotonically increasing energy (and frequency) of the absorption lines with increasing n_2 values. Moreover, the energy difference between successive lines decreased as n_2 increases (1.4.4). This behavior converges to a highest possible energy as Example 1.4.1 demonstrates. If the lines are plot according to their λ on a linear scale, you will get the appearance of the spectrum in Figure 1.4.4 ; these lines are called the **Balmer series**.

Balmer's general formula (Equation 1.4.1) can be rewritten in terms of the inverse wavelength typically called the *wavenumber* ($\tilde{\nu}$).

$$\tilde{\nu} = \frac{1}{\lambda} \tag{1.4.2}$$

$$= R_H \left(\frac{1}{4} - \frac{1}{n_2^2} \right) \tag{1.4.3}$$

where $n_2 = 3, 4, 5, 6$ and R_H is the Rydberg constant (discussed in the next section) equal to 109,737 cm^{-1}.

He further conjectured that the 4 could be replaced by 9, 16, 25, ... and this also turned out to be true - but these lines, further into the infrared, were not detected until the early twentieth century, along with the ultraviolet lines.

The Wavenumber as a Unit of Frequency

The relation between wavelength and frequency for electromagnetic radiation is

$$\lambda\nu = c$$

In the SI system of units the wavelength, (λ) is measured in meters (m) and since wavelengths are usually very small one often uses the nanometer (nm) which is $10^{-9}\ m$. The frequency (ν) in the SI system is measured in reciprocal seconds 1/s – which is called a Hertz (after the discover of the photoelectron effect) and is represented by Hz.

It is common to use the reciprocal of the wavelength in centimeters as a measure of the frequency of radiation. This unit is called a wavenumber and is represented by ($\tilde{\nu}$) and is defined by

$$\tilde{\nu} = \frac{1}{\lambda}$$
$$= \frac{\nu}{c}$$

Wavenumbers is a convenient unit in spectroscopy because it is directly proportional to energy.

$$E = \frac{hc}{\lambda}$$
$$= hc \times \frac{1}{\lambda}$$
$$= hc\tilde{\nu}$$
$$\propto \tilde{\nu}$$

Example 1.4.1 : Balmer Series

Calculate the longest and shortest wavelengths (in nm) emitted in the Balmer series of the hydrogen atom emission spectrum.

Solution

From the behavior of the Balmer equation (Equation 1.4.1 and Table 1.4.2), the value of n_2 that gives the longest (i.e., greatest) wavelength (λ) is the smallest value possible of n_2, which is (n_2=3) for this series. This results in

$$\begin{aligned}\lambda_{longest} &= (364.56\ nm)\left(\frac{9}{9-4}\right)\\ &= (364.56\ nm)\,(1.8)\\ &= 656.2\ nm\end{aligned}$$

This is also known as the H_α line of atomic hydrogen and is bright red (Figure $1.4.3a$).

For the shortest wavelength, it should be recognized that the shortest wavelength (greatest energy) is obtained at the limit of greatest (n_2):

$$\lambda_{shortest} = \lim_{n_2\to\infty}(364.56\ nm)\left(\frac{n_2^2}{n_2^2-4}\right)$$

This can be solved via L'Hôpital's Rule, or alternatively the limit can be expressed via the equally useful energy expression (Equation 1.4.3) and simply solved:

$$\begin{aligned}\tilde{\nu}_{greatest} &= \lim_{n_2\to\infty} R_H\left(\frac{1}{4}-\frac{1}{n_2^2}\right)\\ &= \lim_{n_2\to\infty} R_H\left(\frac{1}{4}\right)\\ &= 27,434\ cm^{-1}\end{aligned}$$

Since $\frac{1}{\tilde{\nu}} = \lambda$ in units of cm, this converts to 364 nm as the shortest wavelength possible for the Balmer series.

The Balmer series is particularly useful in astronomy because the Balmer lines appear in numerous stellar objects due to the abundance of hydrogen in the universe, and therefore are commonly seen and relatively strong compared to lines from other elements.

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1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum

Learning Objectives

- Describe Rydberg's theory for the hydrogen spectra.
- Interpret the hydrogen spectrum in terms of the energy states of electrons.

In an amazing demonstration of mathematical insight, in 1885 Balmer came up with a simple formula for predicting the wavelength of any of the lines in atomic hydrogen in what we now know as the Balmer series. Three years later, Rydberg generalized this so that it was possible to determine the wavelengths of any of the lines in the hydrogen emission spectrum. Rydberg suggested that all atomic spectra formed families with this pattern (he was unaware of Balmer's work). It turns out that there are families of spectra following Rydberg's pattern, notably in the alkali metals, sodium, potassium, etc., but not with the precision the hydrogen atom lines fit the Balmer formula, and low values of n_2 predicted wavelengths that deviate considerably.

Rydberg's phenomenological equation is as follows:

$$\tilde{\nu} = \frac{1}{\lambda} \tag{1.5.1}$$

$$= R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.5.2}$$

where R_H is the **Rydberg constant** and is equal to 109,737 cm^{-1} ($2.18 \times 10^{-18}\ J$) and n_1 and n_2 are integers (whole numbers) with $n_2 > n_1$.

For the Balmer lines, $n_1 = 2$ and n_2 can be any whole number between 3 and infinity. The various combinations of numbers that can be substituted into this formula allow the calculation the wavelength of any of the lines in the hydrogen emission spectrum; there is close agreement between the wavelengths generated by this formula and those observed in a real spectrum.

Other Series

The results given by Balmer and Rydberg for the spectrum in the visible region of the electromagnetic radiation start with $n_2 = 3$, and $n_1 = 2$. Is there a different series with the following formula (e.g., $n_1 = 1$)?

$$\frac{1}{\lambda} = R_{\mathrm{H}} \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \tag{1.5.3}$$

The values for n_2 and wavenumber $\tilde{\nu}$ for this series would be:

Table 1.5.1 : The Lyman Series of Hydrogen Emission Lines ($n_1 = 1$)

n_2	2	3	4	5	...
λ (nm)	121	102	97	94	...
$\tilde{\nu}$ (cm^{-1})	82,2291	97,530	102,864	105,332	...

Do you know in what region of the electromagnetic radiation these lines are? Of course, these lines are in the UV region, and they are not visible, but they are detected by instruments; these lines form a **Lyman series**. The existences of the Lyman series and Balmer's series suggest the existence of more series. For example, the series with $n_1 = 3$ and $n_2 = 4, 5, 6, 7, \ldots$ is called **Paschen series**.

Other Series

The spectral lines are grouped into series according to n_1 values. Lines are named sequentially starting from the longest wavelength/lowest frequency of the series, using Greek letters within each series. For example, the ($n_1 = 1/n_2 = 2$) line is called "Lyman-alpha" (Ly-α), while the ($n_1 = 3/n_2 = 7$) line is called "Paschen-delta" (Pa-δ). The first six series have specific names:

- Lyman series with $n_1 = 1$
- Balmer series with $n_1 = 2$
- Paschen series (or Bohr series) with $n_1 = 3$
- Brackett series with $n_1 = 4$
- Pfund series with $n_1 = 5$
- Humphreys series with $n_1 = 6$

Example 1.5.1 : The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the *n* = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy

A. Substitute the appropriate values into Equation 1.5.2 (the Rydberg equation) and solve for λ.
B. Locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution

We can use the Rydberg equation (Equation 1.5.2) to calculate the wavelength:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Solution A

For the Lyman series, $n_1 = 1$.

$$\begin{aligned} \frac{1}{\lambda} &= R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ &= 1.097 \times 10^7 \, m^{-1} \left(\frac{1}{1} - \frac{1}{4} \right) \\ &= 8.228 \times 10^6 \, m^{-1} \end{aligned}$$

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit (wavenumbers) is particularly convenient. We can convert the answer in part A to cm^{-1}.

$$\tilde{\nu} = \frac{1}{\lambda}$$
$$= 8.228 \times 10^6 \cancel{m^{-1}} \left(\frac{\cancel{m}}{100\ cm} \right)$$
$$= 82,280\ cm^{-1}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm$$

This emission line is called Lyman alpha and is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone

Solution B

his wavelength is in the ultraviolet region of the spectrum.

Exercise 1.5.1 : The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the $n_1 = 5$. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer available at the end of this section.

The above discussion presents only a phenomenological description of hydrogen emission lines and fails to provide a probe of the nature of the atom itself. Clearly a continuum model based on classical mechanics is not applicable, and as the next Section demonstrates, a simple connection between spectra and atomic structure can be formulated.

Answers

$4.65 \times 10^3\ nm$; infrared

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1.6: Matter Has Wavelike Properties

Learning Objectives

- To introduce the wave-particle duality of light extends to matter
- To describe how matter (e.g., electrons and protons) can exhibit wavelike properties, e.g., interference and diffraction patterns
- To use algebra to find the de Broglie wavelength or momentum of a particle when either one of these quantities is given

The next real advance in understanding the atom came from an unlikely quarter - a student prince in Paris. Prince Louis de Broglie was a member of an illustrious family, prominent in politics and the military since the 1600's. Louis began his university studies with history, but his elder brother Maurice studied x-rays in his own laboratory, and Louis became interested in physics. After World War I, de Broglie focused his attention on Einstein's two major achievements, the theory of special relativity and the quantization of light waves. He wondered if there could be some connection between them. Perhaps the quantum of radiation really should be thought of as a particle. De Broglie suggested that if waves (photons) could behave as particles, as demonstrated by the photoelectric effect, then the converse, namely that particles could behave as waves, should be true. He associated a wavelength λ to a particle with momentum p using Planck's constant as the constant of proportionality:

$$\lambda = \frac{h}{p} \tag{1.6.1}$$

which is called the **de Broglie wavelength**. The fact that particles can behave as waves but also as particles, depending on which experiment you perform on them, is known as the **wave-particle duality**.

Deriving the de Broglie Wavelength

From the discussion of the photoelectric effect, we have the first part of the particle-wave duality, namely, that electromagnetic waves can behave like particles. These particles are known as *photons*, and they move at the speed of light. Any particle that moves at or near the speed of light has kinetic energy given by Einstein's special theory of relatively. In general, a particle of mass m and momentum p has an energy

$$E = \sqrt{p^2c^2 + m^2c^4} \tag{1.6.2}$$

Note that if $p = 0$, this reduces to the famous rest-energy expression $E = mc^2$. However, photons are massless particles (technically rest-massless) that always have a finite momentum p. In this case, Equation 1.6.2 becomes

$$E = pc.$$

From Planck's hypothesis, one quantum of electromagnetic radiation has energy $E = h\nu$. Thus, equating these two expressions for the kinetic energy of a photon, we have

$$h\nu = \frac{hc}{\lambda} = pc \tag{1.6.3}$$

Solving for the wavelength λ gives Equation 1.6.1:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

where v is the velocity of the particle. Hence, de Broglie argued that if particles can behave as waves, then a relationship like this, which pertains particularly to waves, should also apply to particles.

Equation 1.6.1 allows us to associate a wavelength λ to a particle with momentum p. As the momentum increases, the wavelength decreases. In both cases, this means the energy becomes larger. i.e., short wavelengths *and* high momenta correspond to high

energies.

> It is a common feature of quantum mechanics that particles and waves with short wavelengths correspond to high energies and vice versa.

Having decided that the photon might well be a particle with a rest mass, even if very small, it dawned on de Broglie that in other respects it might not be too different from other particles, especially the very light electron. In particular, maybe the electron also had an associated wave. The obvious objection was that if the electron was wavelike, why had no diffraction or interference effects been observed? But there was an answer. If de Broglie's relation between momentum and wavelength also held for electrons, the wavelength was sufficiently short that these effects would be easy to miss. As de Broglie himself pointed out, the wave nature of light is not very evident in everyday life. As the next section will demonstrate, the validity of de Broglie's proposal was confirmed by electron diffraction experiments of G.P. Thomson in 1926 and of C. Davisson and L. H. Germer in 1927. In these experiments it was found that electrons were scattered from atoms in a crystal and that these scattered electrons produced an interference pattern. These diffraction patterns are characteristic of wave-like behavior and are exhibited by both electrons (i.e., matter) and electromagnetic radiation (i.e., light).

Example 1.6.1 : Electron Waves

Calculate the de Broglie wavelength for an electron with a kinetic energy of 1000 eV.

Solution

To calculate the de Broglie wavelength (Equation 1.6.1), the momentum of the particle must be established and requires knowledge of both the mass and velocity of the particle. The mass of an electron is $9.109383 \times 10^{-28}\ g$ and the velocity is obtained from the given kinetic energy of 1000 eV:

$$\begin{aligned} KE &= \frac{mv^2}{2} \\ &= \frac{p^2}{2m} = 1000\ eV \end{aligned}$$

Solve for momentum

$$p = \sqrt{2mKE}$$

convert to SI units

$$p = \sqrt{(1000\ \cancel{eV})\left(\frac{1.6 \times 10^{-19}\ J}{1\ \cancel{eV}}\right)(2)(9.109383 \times 10^{-31}\ kg)}$$

expanding definition of joule into base SI units and cancel

$$\begin{aligned} p &= \sqrt{(3.1 \times 10^{-16}\ kg \cdot m^2/s^2)(9.109383 \times 10^{-31}\ kg)} \\ &= \sqrt{2.9 \times 10^{-40}\, kg^2\ m^2/s^2} \\ &= 1.7 \times 10^{-23} kg \cdot m/s \end{aligned}$$

Now substitute the momentum into the equation for de Broglie's wavelength (Equation 1.6.1) with Planck's constant ($h = 6.626069 \times 10^{-34}\ J \cdot s$). After expanding units in Plank's constant

$$\begin{aligned}\lambda &= \frac{h}{p} \\ &= \frac{6.626069 \times 10^{-34}\ kg \cdot m^2/s}{1.7 \times 10^{-23} kg \cdot m/s} \\ &= 3.87 \times 10^{-11}\ m \\ &= 38.9\ pm\end{aligned}$$

Exercise 1.6.1 : Baseball Waves

Calculate the de Broglie wavelength for a fast ball thrown at 100 miles per hour and weighing 4 ounces. Comment on whether the wave properties of baseballs could be experimentally observed.

Answer available at the end of this section.

Exercise 1.6.2 : Electrons vs. Protons

If an electron and a proton have the same velocity, which would have the longer de Broglie wavelength?

a. The electron
b. The proton
c. They would have the same wavelength

Answer available at the end of this section.

This was the prince's Ph.D. thesis, presented in 1924. His thesis advisor was somewhat taken aback, and was not sure if this was sound work. He asked de Broglie for an extra copy of the thesis, which he sent to Einstein. Einstein wrote shortly afterwards: "*I believe it is a first feeble ray of light on this worst of our physics enigmas*" and the prince got his Ph.D.

Answers

Following the unit conversions below, a 4 oz baseball has a mass of 0.11 kg. The velocity of a fast ball thrown at 100 miles per hour in m/s is 44.7 m/s.

$$m = (4\ \cancel{oz})\left(\frac{0.0283\ kg}{1\ \cancel{oz}}\right) = 0.11 kg$$

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{hr}}\right)\left(\frac{1609.34\ m}{\cancel{mi}}\right)\left(\frac{1\ \cancel{hr}}{3600\ s}\right) = 44.7\ m/s$$

The de Broglie wavelength of this fast ball is:

$$\lambda = \frac{h}{mv} = \frac{6.626069 \times 10^{-34}\ kg \cdot m^2/s}{(0.11\ kg)(44.7\ m/s)} = 1.3 \times 10^{-34} m$$

Equation 1.6.1 shows that the de Broglie wavelength of a particle's matter wave is inversely proportional to its momentum (mass times velocity). Therefore the smaller mass particle will have a smaller momentum and longer wavelength. The electron is the lightest and will have the longest wavelength.

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1.7: de Broglie Waves can be Experimentally Observed

Learning Objectives

- To present the experimental evidence behind the wave-particle duality of matter

The validity of de Broglie's proposal was confirmed by electron diffraction experiments of G.P. Thomson in 1926 and of C. Davisson and L. H. Germer in 1927. In these experiments it was found that electrons were scattered from atoms in a crystal and that these scattered electrons produced an interference pattern. The interference pattern was just like that produced when water waves pass through two holes in a barrier to generate separate wave fronts that combine and interfere with each other. These diffraction patterns are characteristic of wave-like behavior and are exhibited by both matter (e.g., electrons and neutrons) and electromagnetic radiation. Diffraction patterns are obtained if the wavelength is comparable to the spacing between scattering centers.

Diffraction occurs when waves encounter obstacles whose size is **comparable** with its wavelength.

Continuing with our analysis of experiments that lead to the new quantum theory, we now look at the phenomenon of electron diffraction.

Diffraction of Light (Light as a Wave)

It is well-known that *light* has the ability to diffract around objects in its path, leading to an interference pattern that is particular to the object. This is, in fact, how holography works (the interference pattern is created by allowing the diffracted light to interfere with the original beam so that the hologram can be viewed by shining the original beam on the image). A simple illustration of light diffraction is the Young double slit experiment (Figure 1.7.1). Here, light as waves (pictured as waves in a plane parallel to the double slit apparatus) impinge on the two slits. Each slit then becomes a point source for spherical waves that subsequently interfere with each other, giving rise to the light and dark fringes on the screen at the right.

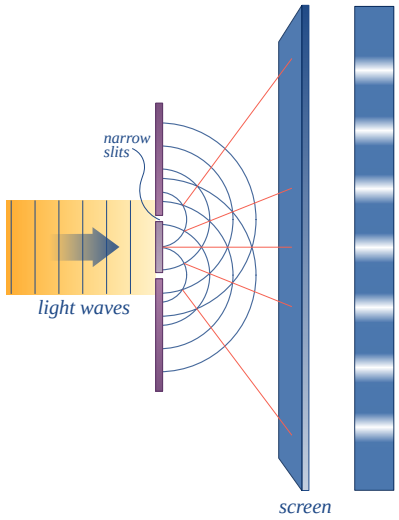


Figure 1.7.1 : Young double slit experiment. Two slits are illuminated by a plane light waves. (CC BY-NC; Ümit Kaya via LibreTexts)

The double-slit experiments are direct demonstration of wave phenomena via observed interference. These types of experiment were first performed by Thomas Young in 1801, as a demonstration of the wave behavior of light. In the basic version of this experiment, light is illuminated only a plate pierced by two parallel slits, and the light passing through the two slits is observed on a screen behind the plate (Figures 1.7.1 and 1.7.2).

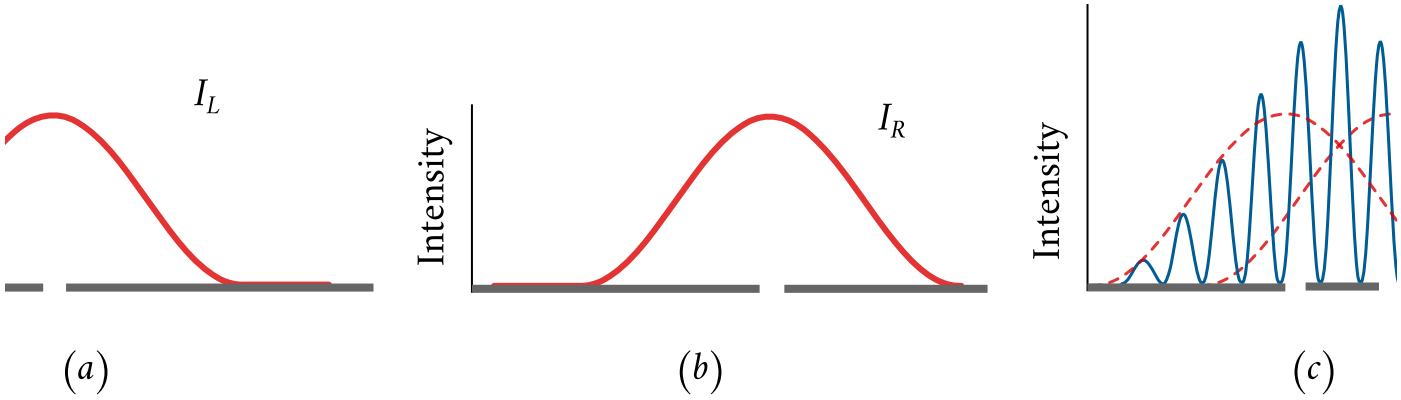


Figure 1.7.2 : Amplitude of particles through (a) left slit, (b) right slit, (c) through both slits. In absence of wavelength interference behavior, the intensity will be the sum of each single slit results (red) and when there is interference, pronounced oscillations in intensity is observed (blue curve). (CC BY; Ümit Kaya via LibreTexts)

The wave nature of light causes the light waves passing through the two slits to interfere, producing bright and dark bands on the screen – a result that would not be expected if light consisted of classical particles (Figure $1.7.0c$). However, the light is always found to be absorbed at the screen at discrete points, as individual particles (not waves); the interference pattern appears via the varying density of these particle hits on the screen. Furthermore, versions of the experiment that include detectors at the slits find that each detected photon passes through one slit (as would a classical particle), and not through both slits (as would a wave).

> Interference is a wave phenomenon in which two (or more) *waves* superimpose to form a resultant wave of greater or lower amplitude. It is the primary property used to identify wave behavior.

Diffraction of Electrons (Electrons as Waves)

According to classical physics, electrons should behave like particles - they travel in straight lines and do not curve in flight unless acted on by an external agent, like a magnetic field. In this model, if we fire a beam of electrons through a double slit onto a detector, we should get two bands of "hits", much as you would get if you fired a machine gun at the side of a house with two windows - you would get two areas of bullet-marked wall inside, and the rest would be intact (Figure 1.7.3 (left) and Figure 1.7.2).

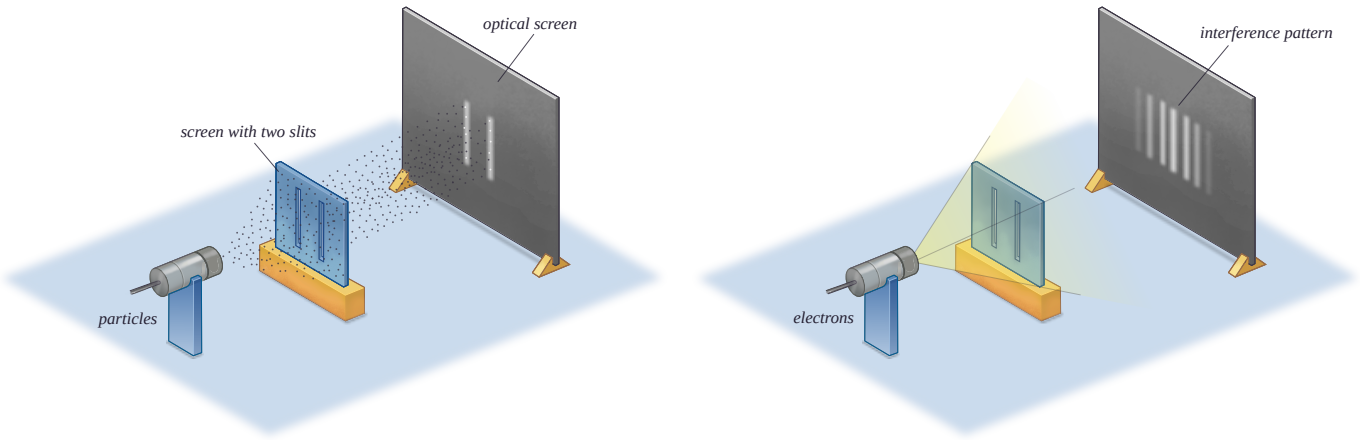


Figure 1.7.3 : (left) classical model of electrons. (right) wave property of electrons. (CC BY-NC; Ümit Kaya via LibreTexts)

However, if the slits are made small enough and close enough together, we actually observe the electrons are *diffracting* through the slits and *interfering* with each other just like waves (Figure 1.7.3 (right) and Figure 1.7.2 a,b). This means that the electrons have **wave-particle duality**, just like photons, in agreement with de Broglie's hypothesis discussed previously. In this case, they must have properties like wavelength and frequency. We can deduce the properties from the behavior of the electrons as they pass through our diffraction grating.

This was a pivotal result in the development of quantum mechanics. Just as the photoelectric effect demonstrated the particle nature of light, the Davisson–Germer experiment showed the wave-nature of matter, and completed the theory of wave-particle duality. For physicists this idea was important because it meant that not only could any particle exhibit wave characteristics, but that one could use wave equations to describe phenomena in matter if one used the de Broglie wavelength.



Figure 1.7.4 : An image of an ant in a scanning electron microscope based on the wave properties of electrons. (Public Domain; United States Geological Survey, an agency of the United States Department of the Interior)

An electron microscope use a beam of accelerated electrons as a source of illumination. Since the wavelength of electrons can be up to 100,000 times shorter than that of visible light photons, electron microscopes have a higher resolving power than light microscopes and can reveal the structure of smaller objects. A transmission electron microscope can achieve better than 50 pm resolution and magnifications of up to about 10,000,000x whereas most light microscopes are limited by diffraction to about 200 nm resolution and useful magnifications below 2000x (Figure 1.7.4).

Is Matter a Particle or a Wave?

An electron, indeed any particle, is neither a *particle* nor a *wave*. Describing the electron as a particle is a mathematical model that works well in some circumstances while describing it as a wave is a different mathematical model that works well in other circumstances. When you choose to do some calculation of the electron's behavior that treats it either as a particle or as a wave, you're not saying the electron **is** a particle or **is** a wave: you're just choosing the mathematical model that makes it easiest to do the calculation.

Neutron Diffraction (Neutrons as Waves)

Like all quantum particles, neutrons can also exhibit wave phenomena and if that wavelength is short enough, atoms or their nuclei can serve as diffraction obstacles. When a beam of neutrons emanating from a reactor is slowed down and selected properly by their speed, their wavelength lies near one angstrom (0.1 nanometer), the typical separation between atoms in a solid material. Such a beam can then be used to perform a diffraction experiment. Neutrons interact directly with the nucleus of the atom, and the contribution to the diffracted intensity depends on each isotope; for example, regular hydrogen and deuterium contribute differently. It is also often the case that light (low Z) atoms contribute strongly to the diffracted intensity even in the presence of large Z atoms.

Example 1.7.1 : Neutron Diffraction

Neutrons have no electric charge, so they do not interact with the atomic electrons. Hence, they are very penetrating (e.g., typically 10 cm in lead). Neutron diffraction was proposed in 1934, to exploit de Broglie's hypothesis about the wave nature of matter. Calculate the momentum and kinetic energy of a neutron whose wavelength is comparable to atomic spacing ($1.8 \times 10^{-10}\ m$).

Solution

This is a simple use of de Broglie's equation

$$\lambda = \frac{h}{p}$$

where we recognize that the wavelength of the neutron must be comparable to atomic spacing (let's assumed equal for convenience, so $\lambda = 1.8 \times 10^{-10}\ m$). Rearranging the de Broglie wavelength relationship above to solve for momentum (p):

$$\begin{aligned} p &= \frac{h}{\lambda} \\ &= \frac{6.6 \times 10^{-34} Js}{1.8 \times 10^{-10} m} \\ &= 3.7 \times 10^{-24}\, kg\ m\ s^{-1} \end{aligned}$$

The relationship for kinetic energy is

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

where v is the velocity of the particle. From the reference table of physical constants, the mass of a neutron is $1.6749273 \times 10^{-27}\ kg$, so

$$\begin{aligned} KE &= \frac{(3.7 \times 10^{-24}\, kg\ m\ s^{-1})^2}{2(1.6749273 \times 10^{-27}\, kg)} \\ &= 4.0 \times 10^{-21} J \end{aligned}$$

The neutrons released in nuclear fission are 'fast' neutrons, i.e. much more energetic than this. Their wavelengths be much smaller than atomic dimensions and will not be useful for neutron diffraction. We slow down these fast neutrons by introducing a "moderator", which is a material (e.g., graphite) that neutrons can penetrate, but will slow down appreciably.

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1.8: The Bohr Theory of the Hydrogen Atom

Learning Objectives

- Introduce the fundamentals behind the Bohr Atom and demonstrate it can predict the Rydberg's equation for the atomic spectrum of hydrogen

Rutherford's Failed Planetary Atom

Ernest Rutherford had proposed a model of atoms based on the α-particle scattering experiments of Hans Geiger and Ernest Marsden. In these experiments helium nuclei (α-particles) were shot at thin gold metal foils. Most of the particles were not scattered; they passed unchanged through the thin metal foil. Some of the few that were scattered were scattered in the backward direction; i.e. they recoiled. This backward scattering requires that the foil contain heavy particles. When an α-particle hits one of these heavy particles it simply recoils backward, just like a ball thrown at a brick wall. Since most of the α-particles don't get scattered, the heavy particles (the nuclei of the atoms) must occupy only a very small region of the total space of the atom. Most of the space must be empty or occupied by very low-mass particles. These low-mass particles are the electrons that surround the nucleus.

There are some basic problems with the Rutherford model. The Coulomb force that exists between oppositely charge particles means that a positive nucleus and negative electrons should attract each other, and the atom should collapse. To prevent the collapse, the electron was postulated to be orbiting the positive nucleus. The Coulomb force (discussed below) is used to change the direction of the velocity, just as a string pulls a ball in a circular orbit around your head or the gravitational force holds the moon in orbit around the Earth. The origin for this hypothesis that suggests this perspective is plausible is the similarity of gravity and Coulombic interactions. The expression for the force of gravity between two masses (Newton's Law of gravity) is

$$F_{gravity} \propto \frac{m_1 m_2}{r^2} \tag{1.8.1}$$

with m_1 and m_2 representing the **mass** of object 1 and 2, respectively and r representing the distance between the objects centers

The expression for the Coulomb force between two charged species is

$$F_{Coulomb} \propto \frac{Q_1 Q_2}{r^2} \tag{1.8.2}$$

with Q_1 and Q_2 representing the **charge** of object 1 and 2, respectively and r representing the distance between the objects centers.

However, this analogy has a problem too. An electron going around in a circle is constantly being accelerated because its velocity vector is changing. A charged particle that is being accelerated emits radiation. This property is essentially how a radio transmitter works. A power supply drives electrons up and down a wire and thus transmits energy (electromagnetic radiation) that your radio receiver picks up. The radio then plays the music for you that is encoded in the waveform of the radiated energy.

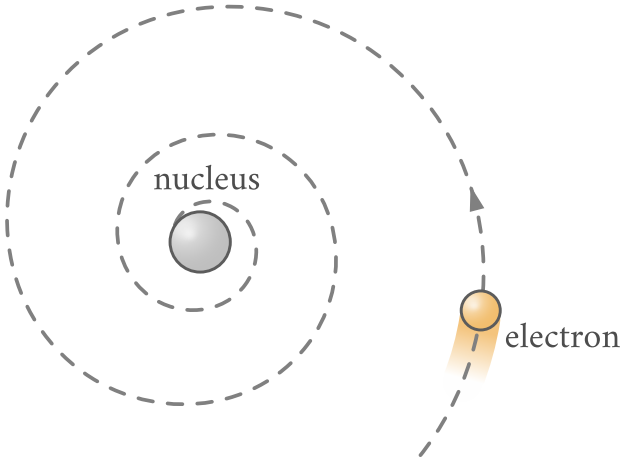


Figure 1.8.1 : The classical death spiral of an electron around a nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

If the orbiting electron is generating radiation, it is losing energy. If an orbiting particle loses energy, the radius of the orbit decreases. To conserve angular momentum, the frequency of the orbiting electron increases. The frequency increases continuously as the electron collapses toward the nucleus. Since the frequency of the rotating electron and the frequency of the radiation that is emitted are the same, both change continuously to produce a continuous spectrum and not the observed discrete lines. Furthermore, if one calculates how long it takes for this collapse to occur, one finds that it takes about 10^{-11} seconds. This means that nothing in the world based on the structure of atoms could exist for longer than about 10^{-11} seconds. Clearly something is terribly wrong with this classical picture, which means that something was missing at that time from the known laws of physics.

Conservative Forces can be explained with Potentials

A conservative force is dependent only on the position of the object. If a force is conservative, it is possible to assign a numerical value for the potential at any point. When an object moves from one location to another, the force changes the potential energy of the object by an amount that does not depend on the path taken. The potential can be constructed as simple derivatives for 1-D forces:

$$F = -\frac{dV}{dx}$$

or as gradients in 3-D forces

$$F = -\nabla V$$

where ∇ is the vector of partial derivatives

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

The most familiar conservative forces are gravity and Coulombic forces.

The Coulomb force law (Equation 1.8.2) comes from the corresponding Coulomb potential (sometimes call electrostatic potential)

$$V(r) = \frac{kQ_1Q_2}{r} \tag{1.8.3}$$

and it can be easily verified that the Coulombic force from this interaction ($F(r)$) is

$$F(r) = -\frac{dV}{dr} \tag{1.8.4}$$

As r is varied, the energy will change, so that we have an example of a potential energy curve $V(r)$ (Figure $1.8.2; left$). If Q_1 and Q_2 are the same sign, then the curve which is a purely **repulsive potential**, i.e., the energy increases monotonically as the charges are brought together and decreases monotonically as they are separated. From this, it is easy to see that like charges (charges of the same sign) repel each other.

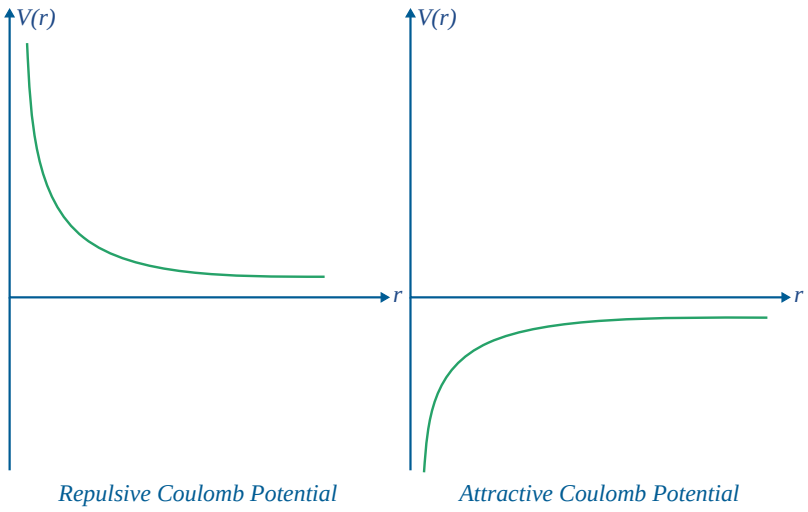


Figure 1.8.2 : Potential energy curve for the Coulomb interactions between two charges of same sign (left) and opposite signs (right). (CC BY-NC; Ümit Kaya via LibreTexts)

If the charges are of opposite sign, then the curve appears roughly Figure $1.8.2; right$ and this is a purely **attractive potential**. Thus, the energy decreases as the charges are brought together, implying that opposite charges attract

The Bohr Model

It is observed that line spectra discussed in the previous sections show that hydrogen atoms absorb and emit light at only discrete wavelengths. This observation is connected to the discrete nature of the allowed energies of a quantum mechanical system. Quantum mechanics postulates that, in contrast to classical mechanics, the energy of a system can only take on certain discrete values. This leaves us with the question: How do we determine what these allowed discrete energy values are? After all, it seems that Planck's formula for the allowed energies came out of nowhere.

The model we will describe here, due to Niels Bohr in 1913, is an early attempt to predict the allowed energies for single-electron atoms such as H, He^{+}, Li^{2+}, Be^{3+}, etc. Although Bohr's reasoning relies on classical concepts and hence, is not a correct explanation, the reasoning is interesting, and so we examine this model for its historical significance.

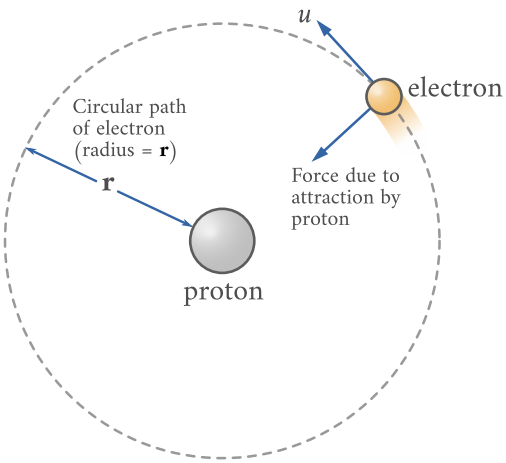


Figure 1.8.3 : Bohr atom with an electron revolving around a fixed nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

Consider a nucleus with charge $+Ze$ and one electron orbiting the nucleus. In this analysis, we will use another representation of the constant k in Coulomb's law (Equation 1.8.3), which is more commonly represented in the form:

$$k = \frac{1}{4\pi\epsilon_0} \tag{1.8.5}$$

where ϵ_0 is known as the **permittivity of free space** with the numerical value $\epsilon_0 = 8.8541878 \times 10^{-12}\ C^2 J^{-1} m^{-1}$.

The total energy of the electron (the nucleus is assumed to be fixed in space at the origin) is the sum of kinetic and potential energies:

$$E_{total} = \underbrace{\frac{p^2}{2m_e}}_{\text{kinetic energy}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r}}_{\text{potential energy}}$$

The force on the electron is

$$\vec{F} = -\frac{Ze^2}{4\pi\epsilon_0 r^3} r$$

and its magnitude is

$$F = |\vec{F}| = \frac{Ze^2}{4\pi\epsilon_0 r^3}|r| = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

since $\vec{F} = m_e\vec{a}$, the magnitude, it follows that $|\vec{F}| = m_e|\vec{a}|$. If we assume that the orbit is circular, then the acceleration is *purely centripetal*, so

$$|a| = \frac{v^2}{r}$$

where v is the velocity of the electron. Equating force $|F|$ to $m_e|a|$, we obtain

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = m_e\frac{v^2}{r}$$

or

$$\frac{Ze^2}{4\pi\epsilon_0} = m_e v^2 r$$

or

$$\frac{Ze^2m_er}{4\pi\epsilon_0} = (m_evr)^2 \tag{1.8.6}$$

The reason for writing the equation this way is that the quantity m_evr is the classical orbital angular momentum of the electron. Bohr was familiar with Maxwell's theory of classical electromagnetism and knew that in a classical theory, the orbiting electron should radiate energy away and eventually collapse into the nucleus (Figure 1.8.1). He circumvented this problem by following Planck's idea underlying blackbody radiation and positing that the orbital angular momentum m_evr of the electron could only take on specific values

$$m_evr = n\hbar \tag{1.8.7}$$

with $n = 1, 2, 3, ...$

Note that the electron must be in motion, so $n = 0$ is not allowed.

Substituting Equation 1.8.7 into the Equation 1.8.6, we find

$$\frac{Ze^2m_er}{4\pi\epsilon_0} = n^2(\hbar)^2 \tag{1.8.8}$$

Equation 1.8.8 implies that orbits could only have certain allowed radii

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{Ze^2m_e}n^2 \tag{1.8.9}$$

$$= \frac{a_0}{Z}n^2 \tag{1.8.10}$$

with $n = 1, 2, 3, ...$ The collection of constants has been defined to be a_0

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2m_e}$$

a quantity that is known as the **Bohr radius**.

We can also calculate the allowed momenta since $m_evr = n\hbar$, and $p = m_ev$. Thus,

$$p_nr_n = n\hbar$$

$$p_n = \frac{n\hbar}{r_n}$$

$$= \frac{\hbar Z}{a_0n}$$

$$= \frac{Ze^2m_e}{4\pi\epsilon_0\hbar n}$$

From p_n and r_n, we can calculate the allowed energies from

$$E_n = \frac{p_n^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0r_n}$$

Substituting in the expressions for p_n and r_n and simplifying gives

$$E_n = -\frac{Z^2e^4m_e}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} = -\frac{e^4m_e}{8\epsilon_0^2h^2}\frac{Z^2}{n^2} \tag{1.8.11}$$

We can redefine a new energy scale by defining **the Rydberg** as

$$1\ Ry = \frac{e^4m_e}{8\epsilon_0^2h^2} = 2.18 \times 10^{-18}\ J.$$

and this simplifies the allowed energies predicted by the Bohr model (Equation 1.8.11) as

$$E_n = -(2.18 \times 10^{-18})\frac{Z^2}{n^2}\ J = -\frac{Z^2}{n^2}\ R_y \tag{1.8.12}$$

Hence, the energy of the electron in an atom also is quantized. Equation 1.8.12 gives the energies of the electronic states of the hydrogen atom. It is very useful in analyzing spectra to represent these energies graphically in an energy-level diagram. An energy-level diagram has energy plotted on the vertical axis with a horizontal line drawn to locate each energy level (Figure 1.8.4).

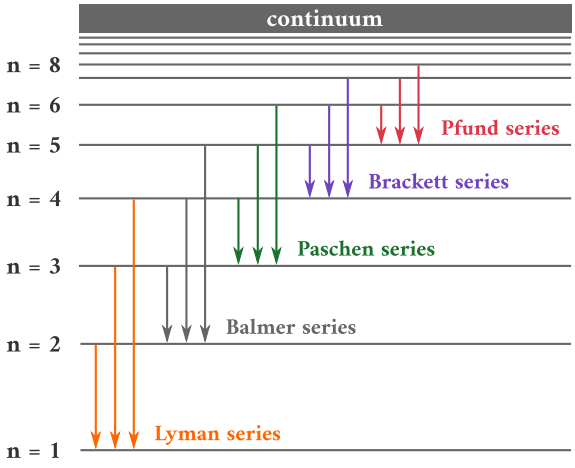


Figure 1.8.4 : Energy levels predicted by the Bohr model of hydrogen ($Z = 1$). (CC BY-NC; Ümit Kaya via LibreTexts)

These turn out to be the correct energy levels, apart from small corrections that cannot be accounted for in this pseudo-classical treatment. Despite the fact that the energies are essentially correct, the Bohr model masks the true quantum nature of the electron, which only emerges from a fully quantum mechanical analysis.

Exercise 1.8.1

Calculate a value for the Bohr radius using Equation 1.8.8 to check that this equation is consistent with the value 52.9 pm. What would the radius be for $n = 1$ in the Li^{2+} ion?

Answer available at the end of this section.

Exercise 1.8.2 : Rydberg states

How do the radii of the hydrogen orbits vary with n? Prepare a graph showing r as a function of n. States of hydrogen atoms with $n = 200$ have been prepared (called Rydberg states). What is the diameter of the atoms in these states?

Answer available at the end of this section.

The Wave Argument for Quantization

The above discussion is based off of a classical picture of an orbiting electron with the quantization from the angular momentum (Equation 1.8.7) requirement lifted from Planck's quantization arguments. Hence, only allows certain trajectories are stable (with differing radii). However, as discussed previously, the electron will have a wavelike property also with a de Broglie wavelength λ

$$\lambda = \frac{h}{p}$$

Hence, a larger momentum p implies a shorter wavelength. That means as n increases (Equation 1.8.12), the wavelength must also increase; this is a common feature in quantum mechanics and will be often observed. In the Bohr atom, the circular symmetry and the wave property of the electron requires that the electron waves have an integer number of wavelengths (Figure $1.8.1A$). If not, then the waves will overlap imperfectly and cancel out (i.e., the electron will cease to exist) as demonstrated in Figure $1.8.1B$.

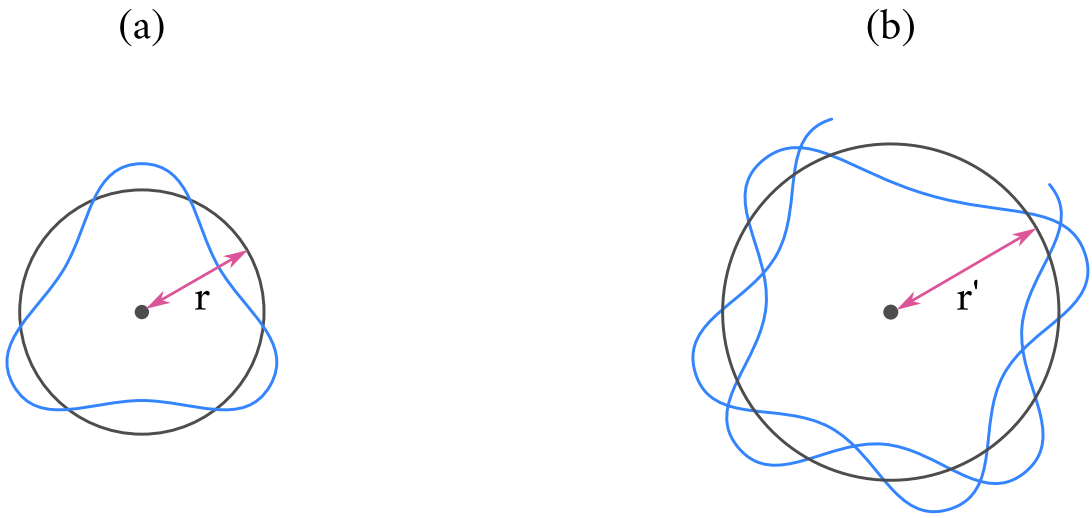


Figure 1.8.5 : Waves on a string have a wavelength related to the length of the string, allowing them to interfere constructively. (A) If we imagine the string bent into a closed circle, we get a rough idea of how electrons in circular orbits can interfere constructively. (B) If the wavelength does not fit into the circumference, the electron interferes destructively; it cannot exist in such an orbit. (CC BY-NC; Ümit Kaya via LibreTexts)

A more detailed discussion of the effect of electron waves in atoms will be discuss in the following chapters.

Derivation of the Rydberg Equation from Bohr Model

Given a prediction of the allowed energies of a system, how could we go about verifying them? The general experimental technique known as *spectroscopy* permits us to probe the various differences between the allowed energies. Thus, if the prediction of the actual energies, themselves, is correct, we should also be able to predict these differences. Let us assume that we are able to place the electron in Bohr's hydrogen atom into an energy state E_n for $n > 1$, i.e. one of its so-called *excited states*. The electron will rapidly return to its lowest energy state, known as the *ground state* and, in doing so, emit light. The energy carried away by the light is determined by the condition that the total energy is conserved (Figure 1.8.6).

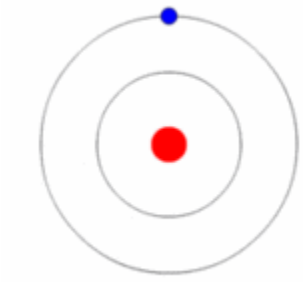


Figure 1.8.6 : A simple illustration of Bohr's model of the atom, with an electron making quantum leaps. (CC BY-SA 3.0 unported; Kurzon via Wikipedia)

Thus, if n_i is the integer that characterizes the initial (excited) state of the electron, and n_f is the final state (here we imagine that

$n_f = 1$, but is applicable in cases that $n_f < n_i$, i.e., emission)

$$E_{nf} = E_{ni} - h\nu$$

or

$$\nu = \frac{E_{ni} - E_{nf}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{1.8.13}$$

We can now identify the Rydberg constant R_H with the ratio of constants on the right hand side of Equation 1.8.13

$$R_H = \frac{m_e e^4}{8\epsilon_0^2 h^3}$$

Evaluating R_H from the fundamental constants in this formula gives a value within 0.5% of that obtained experimentally from the hydrogen atom spectrum.

Thus, by observing the emitted light, we can determine the energy difference between the initial and final energy levels, which results in the emission spectra discussed in Sections 1.4 and 1.5. Different values of n_f determine which emission spectrum is observed, and the examples shown in the figure are named after the individuals who first observed them. The figure below shows some of the transitions possible for different n_f and n_i values discussed previously.

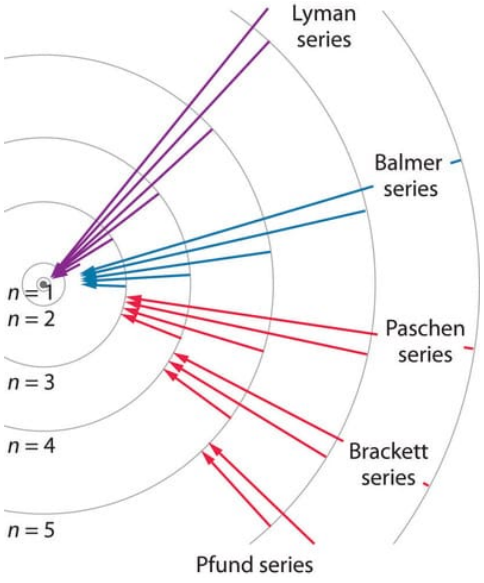


Figure 1.8.7 : Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. Orbits are not drawn to scale. (CC BY-NC-SA 3.0; anonymous)

If the atom absorbs light it ends up in an excited state as a result of the absorption. The absorption is only possible for light of certain frequencies, and again, conservation of energy determines what these frequencies are. If light is absorbed, then the final energy E_{nf} will be related to the initial energy E_{ni} with $n_f > n_i$ by

$$E_{nf} = E_{ni} + h\nu$$

or

$$\nu = \frac{E_{nf} - E_{ni}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

Exercise 1.8.3

a. Calculate the energy of a photon that is produced when an electron in a hydrogen atom goes from an orbit with $n = 4$ to an orbit with $n = 1$.
b. What happens to the energy of the photon as the initial value of n approaches infinity?

Answer available at the end of this section.

Bohr's proposal explained the hydrogen atom spectrum, the origin of the Rydberg formula, and the value of the Rydberg constant. Specifically it demonstrated that the integers in the Rydberg formula are a manifestation of quantization. The energy, the angular momentum, and the radius of the orbiting electron all are quantized. This quantization also parallels the concept of stable orbits in the Bohr model. Only certain values of E, M, and r are possible, and therefore the electron cannot collapse onto the nucleus by continuously radiating energy because it can only have certain energies, and it cannot be in certain regions of space. The electron can only jump from one orbit (quantum state) to another. The quantization means that the orbits are stable, and the electron cannot spiral into the nucleus in spite of the attractive Coulomb force.

Although Bohr's ideas successfully explained the hydrogen spectrum, they failed when applied to the spectra of other atoms. In addition a profound question remained. Why is angular momentum quantized in units of $\hbar$? As we shall see, de Broglie had an answer to this question, and this answer led Schrödinger to a general postulate that produces the quantization of angular momentum as a consequence. This quantization is not quite as simple as proposed by Bohr, and we will see that it is not possible to determine the distance of the electron from the nucleus as precisely as Bohr thought. In fact, since the position of the electron in the hydrogen atom is not at all as well defined as a classical orbit (such as the moon orbiting the earth) it is called an orbital. An electron orbital represents or describes the position of the electron around the nucleus in terms of a mathematical function called a wavefunction that yields the **probability** of positions of the electron.

Contributors and Attributions

- Mark Tuckerman (New York University)
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Template:Contriboundless

Answers

Starting from Equation 1.8.8 and solving for r:

$$\frac{Ze^2m_e r}{4\pi\epsilon_0} = n^2\hbar^2$$
$$r = \frac{4n^2\hbar^2\pi\epsilon_0}{Ze^2m_e}$$

with

- e is the fundamental charge: $e = 1.60217662 \times 10^{-19}C^2$
- m_e is the mass of an electron: $m_e = 9.10938356 \times 10^{-31}kg$
- ϵ_o is the permittivity of free space: $\epsilon_o = 8.854 \times 10^{-12}C^2N^{-1}m^{-2}$
- $\hbar$ is the reduced planks constant: $\hbar = 1.0546 \times 10^{-34}m^2kg/s$

For the ground-state of the hydrogen atom: $Z = 1$ and $n = 1$.

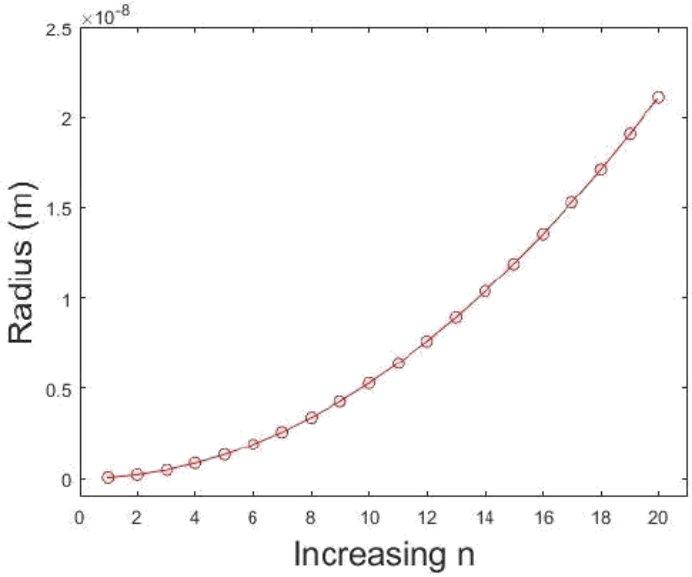
$$\begin{aligned} r &= \frac{4\hbar^2\pi\epsilon_0}{e^2m_e} \\ &= \frac{4(1.0546 \times 10^{-34}m^2kg/s)^2 \times \pi \times 8.854 \times 10^{-12}C^2N^{-1}m^{-2}}{(1.60217662 \times 10^{-19}C)^2(9.10938356 \times 10^{-31}kg)} \\ &= 5.29 \times 10^{-11}m = 52.9\,pm \end{aligned}$$

For the ground-state of the lithium +2 ion: $Z = 3$ and $n = 1$

$$\begin{aligned} r &= \frac{4\hbar^2\pi\epsilon_0}{3e^2m_e} \\ &= \frac{4(1.0546 \times 10^{-34}m^2kg/s)^2 \times \pi \times 8.854 \times 10^{-12}C^2N^{-1}m^{-2}}{3(1.60217662 \times 10^{-19}C)^2(9.10938356 \times 10^{-31}kg)} \\ &= 1.76 \times 10^{-11}m = 17.6\,pm \end{aligned}$$

As expected, the Li^{2+} has a smaller radius than the H atoms because of the increased nuclear charge.

This is a straightforward application of Equation of 1.8.10. The hydrogen atom has only certain allowable radii and these radii can be predicted from the equation that relates them with each n. Note that the electron must be in motion so $n = 0$ is not allowed.



This plot shows the relationship of radius as a function of n. Note that at $n = 1$ the radius is not zero. (CC BY-NC; Ümit Kaya via LibreTexts)

$4\pi\epsilon_0 = 1.113 \times 10^{-10}\mathrm{C}^2\mathrm{J}^{-1}\mathrm{m}^{-1}$ and $\hbar = 1.054 \times 10^{-34}\mathrm{Js}$, also knowing

$$e = 1.602 \times 10^{-19}\mathrm{C} \text{ with}$$
$$m_e = 9.109 \times 10^{-31}\mathrm{kg}$$

and Z is the nuclear charge, we use this equation directly. A simplification can be made by taking advantage of the fact that

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e}$$

resulting in

$$r_n = \frac{a_0}{Z}n^2$$

where $a_0 = 5.292 \times 10^{-11}\mathrm{m}$ which is the Bohr Radius.

Suppose we want to find the radius where $n = 200.n^2 = 40000$ so plugging in directly we have

$$r_n = \frac{(5.292 \times 10^{-11})}{(1)}(40000)$$
$$= 2.117 \times 10^{-6}m$$

for the radius of a hydrogen atom with an electron excited to the $\mathrm{n} = 200$ state. The diameter is then $4.234 \times 10^{-6}\mathrm{m}$.

a:

$$E_{\mathrm{nf}} = E_{ni} - h\nu$$
$$E_{photon} = h\nu = E_{nf} - E_{ni}$$
$$= \frac{Z^2 e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$
$$= \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{1^2} - \frac{1}{4^2}\right)$$
$$= 2.18 \times 10^{-18}\left(1 - \frac{1}{16}\right)$$
$$= 2.04 \times 10^{-18}J$$

b:

As $n_i \to \infty$

$$E_{photon} = \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$
$$\frac{1}{n_i^2} \to 0$$
$$E_{photon} \to \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2}\right)$$

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1.9: The Heisenberg Uncertainty Principle

Learning Objectives

- To understand that sometime you cannot know everything about a quantum system as demonstrated by the Heisenberg uncertainly principle.

In classical physics, studying the behavior of a physical system is often a simple task due to the fact that several physical qualities can be measured simultaneously. However, this possibility is absent in the quantum world. In 1927 the German physicist Werner Heisenberg described such limitations as the Heisenberg Uncertainty Principle, or simply the Uncertainty Principle, stating that it is not possible to measure both the momentum and position of a particle simultaneously.

The Heisenberg Uncertainty Principle is a fundamental theory in quantum mechanics that defines why a scientist cannot measure multiple quantum variables simultaneously. Until the dawn of quantum mechanics, it was held as a fact that all variables of an object could be known to exact precision simultaneously for a given moment. Newtonian physics placed no limits on how better procedures and techniques could reduce measurement uncertainty so that it was conceivable that with proper care and accuracy all information could be defined. Heisenberg made the bold proposition that there is a lower limit to this precision making our knowledge of a particle inherently uncertain.

Probability

Matter and photons are waves, implying they are spread out over some distance. What is the position of a particle, such as an electron? Is it at the center of the wave? The answer lies in how you measure the position of an electron. Experiments show that you will find the electron at some definite location, unlike a wave. But if you set up exactly the same situation and measure it again, you will find the electron in a different location, often far outside any experimental uncertainty in your measurement. Repeated measurements will display a statistical distribution of locations that appears wavelike (Figure 1.9.1).

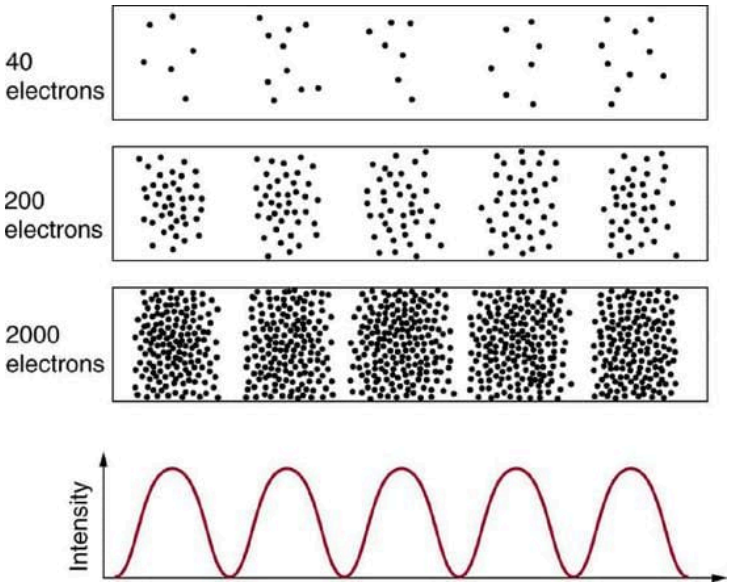


Figure 1.9.1 : The building up of the diffraction pattern of electrons scattered from a crystal surface. Each electron arrives at a definite location, which cannot be precisely predicted. The overall distribution shown at the bottom can be predicted as the diffraction of waves having the de Broglie wavelength of the electrons (CC BY 4.0; OpenStax).

After de Broglie proposed the wave nature of matter, many physicists, including Schrödinger and Heisenberg, explored the consequences. The idea quickly emerged that, *because of its wave character, a particle's trajectory and destination cannot be precisely predicted for each particle individually*. However, each particle goes to a definite place (Figure 1.9.1). After compiling

enough data, you get a distribution related to the particle's wavelength and diffraction pattern. There is a certain *probability* of finding the particle at a given location, and the overall pattern is called a **probability distribution**. Those who developed quantum mechanics devised equations that predicted the probability distribution in various circumstances.

It is somewhat disquieting to think that you cannot predict exactly where an individual particle will go, or even follow it to its destination. Let us explore what happens if we try to follow a particle. Consider the double-slit patterns obtained for electrons and photons in Figure 1.9.2 . The interferrence patterns build up statistically as individual particles fall on the detector. This can be observed for photons or electrons—for now, let us concentrate on electrons. You might imagine that the electrons are interfering with one another as any waves do. To test this, you can lower the intensity until there is never more than one electron between the slits and the screen. The same interference pattern builds up!

This implies that a particle's probability distribution spans both slits, and the particles actually interfere with themselves. Does this also mean that the electron goes through both slits? An electron is a basic unit of matter that is not divisible. But it is a fair question, and so we should look to see if the electron traverses one slit or the other, or both. One possibility is to have coils around the slits that detect charges moving through them. What is observed is that an electron always goes through one slit or the other; it does not split to go through both.

But there is a catch. If you determine that the electron went through one of the slits, you no longer get a double slit pattern—instead, you get single slit interference. There is no escape by using another method of determining which slit the electron went through. Knowing the particle went through one slit forces a single-slit pattern. If you do not observe which slit the electron goes through, you obtain a double-slit pattern. How does knowing which slit the electron passed through change the pattern? The answer is fundamentally important—*measurement affects the system being observed*. Information can be lost, and in some cases it is impossible to measure two physical quantities simultaneously to exact precision. For example, you can measure the position of a moving electron by scattering light or other electrons from it. Those probes have momentum themselves, and by scattering from the electron, they change its momentum *in a manner that loses information*. There is a limit to absolute knowledge, even in principle.

Heisenberg's Uncertainty Principle

It is mathematically possible to express the uncertainty that, Heisenberg concluded, always exists if one attempts to measure the momentum and position of particles. First, we must define the variable "x" as the position of the particle, and define "p" as the momentum of the particle. The momentum of a photon of light is known to simply be its frequency, expressed by the ratio h/λ, where h represents Planck's constant and λ represents the wavelength of the photon. The position of a photon of light is simply its wavelength (λ). To represent finite change in quantities, the Greek uppercase letter delta, or Δ, is placed in front of the quantity. Therefore,

$$\Delta p = \frac{h}{\lambda} \tag{1.9.1}$$

$$\Delta x = \lambda \tag{1.9.2}$$

By substituting Δx for λ into Equation 1.9.1, we derive

$$\Delta p = \frac{h}{\Delta x} \tag{1.9.3}$$

or,

$$\Delta p \Delta x = h \tag{1.9.4}$$

early form of uncertainty principle

A Common Trend in Quantum Systems

Equation 1.9.4 can be derived by assuming the particle of interest is behaving as a particle, and not as a wave. Simply let $\Delta p = mv$, and $\Delta x = h/(mv)$ (from De Broglie's expression for the wavelength of a particle). Substituting in Δp for mv in the second equation leads to Equation 1.9.4.

Equation 1.9.4 was further refined by Heisenberg and his colleague Niels Bohr, and was eventually rewritten as

$$\Delta p_x \Delta x \geq \frac{h}{4\pi} = \frac{\hbar}{2} \tag{1.9.5}$$

with $\hbar = \frac{h}{2\pi} = 1.0545718 \times 10^{-34}\ m^2 \cdot kg/s$.

Equation 1.9.5 reveals that the more accurately a particle's position is known (the smaller Δx is), the less accurately the momentum of the particle in the x direction (Δp_x) is known. Mathematically, this occurs because the smaller Δx becomes, the larger Δp_x must become in order to satisfy the inequality. However, the more accurately momentum is known the less accurately position is known (Figure 1.9.2).

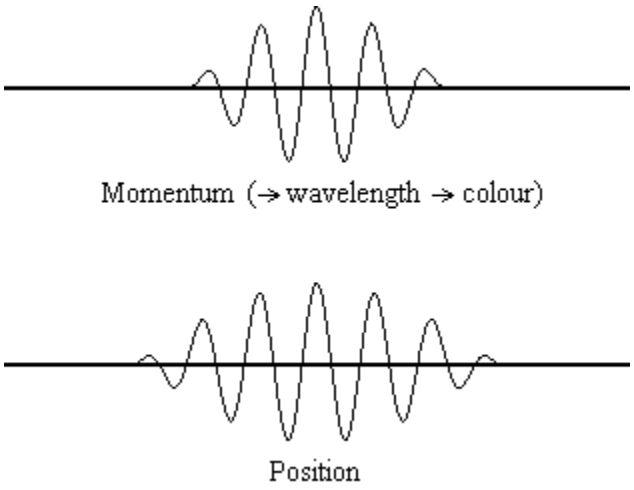


Figure 1.9.2 : The animation shows the relevant spreads in the uncertainty for position and momentum of light/photons (light wave's corresponding photon particle). From the result of de Broglie, we know that for a particle with known momentum, p will have a precise value for its de Broglie wavelength can be determined (and hence a specific color of the light).

What is the Proper Definition of Uncertainty?

Equation 1.9.5 relates the uncertainty of momentum and position. An immediate questions that arise is if Δx represents the full range of possible x values or if it is half (e.g., $\langle x \rangle \pm \Delta x$). Δx is the standard deviation and is a statistic measure of the spread of x values. The use of half the possible range is more accurate estimate of Δx. As we will demonstrated later, once we construct a wavefunction to describe the system, then both x and Δx can be explicitly derived. However for now, Equation 1.9.5 will work.

For example: If a problem argues a particle is trapped in a box of length, L, then the uncertainly of it position is $\pm L/2$. So the value of Δx used in Equation 1.9.5 should be $L/2$, not L.

Example 1.9.1

An electron is confined to the size of a magnesium atom with a 150 pm radius. What is the **minimum** uncertainty in its velocity?

Solution

The uncertainty principle (Equation 1.9.5):

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

can be written

$$\Delta p \geq \frac{\hbar}{2\Delta x}$$

and substituting $\Delta p = m\Delta v$ since the mass is not uncertain.

$$\Delta v \geq \frac{\hbar}{2\ m\ \Delta x}$$

the relevant parameters are

- mass of electron $m = m_e = 9.109383 \times 10^{-31}\ \ kg$
- uncertainty in position: $\Delta x = 150 \times 10^{-12} m$

$$\Delta v \geq \frac{1.0545718 \times 10^{-34}\ \cancel{kg}\ m^{\cancel{2}}/s}{(2)\ (9.109383 \times 10^{-31}\ \cancel{kg})\ (150 \times 10^{-12}\ \cancel{m})}$$
$$= 3.9 \times 10^{5}\ m/s$$

Exercise 1.9.1

What is the maximum uncertainty of velocity the electron described in Example 1.9.1 ?

Answer available at the end of this section.

Understanding the Uncertainty Principle through Wave Packets and the Slit Experiment

It is hard for most people to accept the uncertainty principle, because in classical physics the velocity and position of an object can be calculated with certainty and accuracy. However, in quantum mechanics, the wave-particle duality of electrons does not allow us to accurately calculate both the momentum and position because the wave is not in one exact location but is spread out over space. A "wave packet" can be used to demonstrate how either the momentum or position of a particle can be precisely calculated, but not both of them simultaneously. An accumulation of waves of varying wavelengths can be combined to create an average wavelength through an interference pattern: this average wavelength is called the "wave packet". The more waves that are combined in the "wave packet", the more precise the position of the particle becomes and the more uncertain the momentum becomes because more wavelengths of varying momenta are added. Conversely, if we want a more precise momentum, we would add less wavelengths to the "wave packet" and then the position would become more uncertain. Therefore, there is no way to find both the position and momentum of a particle simultaneously.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Several scientists have debated the Uncertainty Principle, including Einstein. Einstein created a slit experiment to try and disprove the Uncertainty Principle. He had light passing through a slit, which causes an uncertainty of momentum because the light behaves like a particle and a wave as it passes through the slit. Therefore, the momentum is unknown, but the initial position of the particle is known. Here is a video that demonstrates particles of light passing through a slit and as the slit becomes smaller, the final possible array of directions of the particles becomes wider. As the position of the particle becomes more precise when the slit is narrowed, the direction, or therefore the momentum, of the particle becomes less known as seen by a wider horizontal distribution of the light.

Example 1.9.2

The speed of a 1.0 g projectile is known to within $10^{-6}\ m/s$.

a. Calculate the *minimum* uncertainty in its position.
b. What is the *maximum* uncertainty of its position?

Solution a

From Equation 1.9.5, the $\Delta p_x = m\Delta v_x$ with $m = 1.0\ g$. Solving for Δx to get

$$\begin{aligned}\Delta x &= \frac{\hbar}{2m\Delta v} \\ &= \frac{1.0545718 \times 10^{-34}\ m^2 \cdot kg/s}{(2)(0.001\ kg)(10^{-6}\ m/s)} \\ &= 5.3 \times 10^{-26}\, m\end{aligned}$$

This negligible for all intents and purpose as expected for any macroscopic object.

Solution b

Unlimited (or the size of the universe). The Heisenberg uncertainty principles does not quantify the maximum uncertainty.

Exercise 1.9.2

Estimate the minimum uncertainty in the speed of an electron confined to a hydrogen atom within a diameter of $1 \times 10^{-10} m$?

Answer available at the end of this section.

Heisenberg's Uncertainty Principle not only helped shape the new school of thought known today as quantum mechanics, but it also helped discredit older theories. Most importantly, the Heisenberg Uncertainty Principle made it obvious that there was a fundamental error in the Bohr model of the atom. Since the position and momentum of a particle cannot be known simultaneously, Bohr's theory that the electron traveled in a circular path of a fixed radius orbiting the nucleus was obsolete. Furthermore, Heisenberg's uncertainty principle, when combined with other revolutionary theories in quantum mechanics, helped shape wave mechanics and the current scientific understanding of the atom.

Humor: Heisenberg and the Police

- Heisenberg get pulled over for speeding by the police. The officer asks him "Do you know how fast you were going?"
- Heisenberg replies, "No, but we know exactly where we are!"
- The officer looks at him confused and says "you were going 108 miles per hour!"
- Heisenberg throws his arms up and cries, "Great! Now we're lost!"

Answers

Infinity. There is no limit in the maximum uncertainty, just the minimum uncertainty.

We need to quantify the uncertainty of the electron in position. We can estimate that as $\pm 5 \times 10^{-10} m$. Hence, substituting the relavant numbers into Equation 1.9.5 and solving for Δv we get

$$\Delta v = 1.15 \times 10^{6}\, km/s$$

Notice that the uncertainty is significantly greater for the electron in a hydrogen atom than in the magnesium atom (Example 1.9.1) as expected since the magnesium atom is appreciably bigger.

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1.E: The Dawn of the Quantum Theory (Exercises)

Solutions to select questions can be found online.

1.1A

Sodium metal has a threshold frequency of 4.40×10^{14} Hz. What is the kinetic energy of a photoelectron ejected from the surface of a piece of sodium when the ejecting photon is 6.20×10^{14} Hz? What is the velocity of this photoelectron? From which region of the electromagnetic spectrum is this photon?

1.1B

What is the longest-wavelength electromagnetic radiation that can eject a photoelectron from silver, given that the work function is 4.73 eV? Is this in the visible range?

Solution

263 nm

1.1C

Find the longest-wavelength photon that can eject an electron from potassium, given that the work function is 2.24 eV. Is this visible electromagnetic radiation?

1.1C

What is the work function in eV of electrons in magnesium, if the longest-wavelength photon that can eject electrons is 337 nm?

Solution

3.69 eV

1.1D

Calculate the work function in eV of electrons in aluminum, if the longest-wavelength photon that can eject the electromagnetic is 304 nm.

1.1E

What is the maximum kinetic energy in eV of electrons ejected from sodium metal by 450-nm electromagnetic radiation, given that the work function is 2.28 eV?

Solution

0.483 eV

1.1F

UV radiation having a wavelength of 120 nm falls on gold metal, to which electrons are bound by 4.82 eV. What is the maximum kinetic energy of the ejected photoelectrons?

1.1G

Violet light of wavelength 400 nm ejects electrons with a maximum kinetic energy of 0.860 eV from sodium metal. What is the work function of electrons to sodium metal?

Solution

2.25 eV

1.1H

UV radiation having a 300-nm wavelength falls on uranium metal, ejecting 0.500-eV electrons. What is the work function of electrons to uranium metal?

1.1I

What is the wavelength of electromagnetic radiation that ejects 2.00-eV electrons from calcium metal, given that the work function is 2.71 eV? What type of electromagnetic radiation is this?

Solution

(a) 264 nm

(b) Ultraviolet

1.1J

Find the wavelength of photons that eject 0.100-eV electrons from potassium, given that the work function is 2.24 eV. Are these photons visible?

1.1K

What is the maximum velocity of electrons ejected from a material by 80-nm photons, if they are bound to the material by 4.73 eV?

Solution

1.95×10^{6} m/s

1.1L

Photoelectrons from a material with a work function of 2.71 eV are ejected by 420-nm photons. Once ejected, how long does it take these electrons to travel 2.50 cm to a detection device?

1.1M

A laser with a power output of 2.00 mW at a wavelength of 400 nm is projected onto calcium metal. (a) How many electrons per second are ejected? (b) What power is carried away by the electrons, given that the work function is 2.71 eV?

Solution

(a) $4.02 \times 10^{15}/s$

(b) 0.256 mW

1.1N

(a) Calculate the number of photoelectrons per second ejected from a 1.00-mm 2 area of sodium metal by 500-nm electromagnetic radiation having an intensity of $1.30\ kW/m^2$ (the intensity of sunlight above the Earth's atmosphere). (b) Given that the work function is 2.28 eV, what power is carried away by the electrons? (c) The electrons carry away less power than brought in by the photons. Where does the other power go? How can it be recovered?

1.1O

Red light having a wavelength of 700 nm is projected onto magnesium metal to which electrons are bound by 3.68 eV. (a) Use $KE_e = h\nu - \Phi$ to calculate the kinetic energy of the ejected electrons. (b) What is unreasonable about this result? (c) Which assumptions are unreasonable or inconsistent?

Solution

(a) –1.90 eV–1.90 eV

(b) Negative kinetic energy

(c) That the electrons would be knocked free.

Unreasonable Results

1.1P

(a) What is the work function of electrons to a material from which 4.00-eV electrons are ejected by 400-nm electromagnetic radiation? (b) What is unreasonable about this result? (c) Which assumptions are unreasonable or inconsistent?

1.2A

a. Suppose the electron in a hydrogen atom is in the circular Bohr orbit with n = 30. How many times per second does it go around?
b. Suppose now the electron drops to the n = 29 state, emitting a single photon. What is the frequency of this photon, in cycles per second?
c. Comment on the relation between your answers in (a), (b) above. What would you guess the relation to be for n = 300?

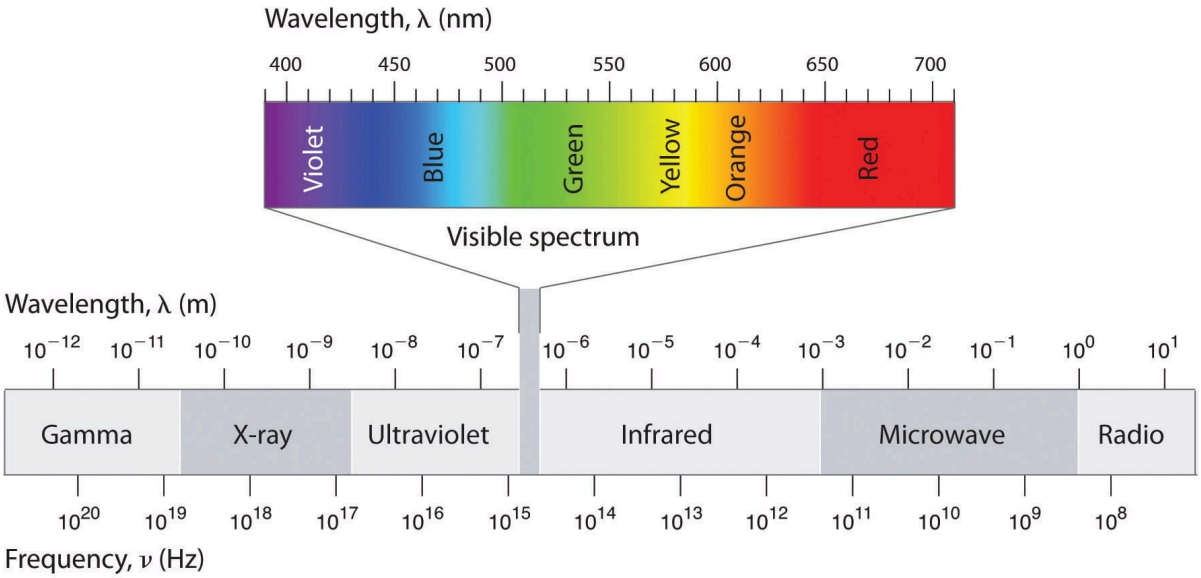
1.2B

The μ (muon) is a cousin of the electron, the only difference being its mass is 207 times greater. The μ has a lifetime of about 2 ms. If a beam of muons is directed at a solid, the muons will go into orbit around nuclei. The Bohr atom, with a muon replacing the electron, is a useful model for picturing this.

1. For a nucleus of charge Ze, how large is the n = 1 μ orbit compared with the electron orbit?
2. What is the frequency of the photon emitted by the μ in the n = 2 to n = 1 transition?
3. For the gold nucleus, the $n = 1$ μ orbit is inside the nucleus. Find the frequency of the emitted photon for $n = 2$ to $n = 1$ in this case. (Hint: you'll need the radius of the gold nucleus. Assume here that the positive charge is uniformly spread throughout the nucleus.)

1.3

Past Infrared region, in direction of the lower energies, the microwave region is located. In this region, radiation usually is characterized by frequency (ν) which is expressed in units of MHz, where Hz is a cycle per second. Given a microwave frequency of $2.0 \times 10^4\ \mathrm{MHz}$, calculate v, λ, and energy per photon for this radiation and then compare the results with figure below.



Solution

The frequency(v) of the microwave radiation is given and once convert to Hz get the following

$$v=2.0e^{4}MHz(1e^{6}Hz/1MHz)= 2.0e^{10}s^{-1}\ Hz$$

now we find the wavelength using formula and get

$$\lambda = \frac{c}{v} = \frac{2.998 \times 10^8 m\, s^{-1}}{2.0 \times 10^{10}\, s^{-1}} = 1.5 \times 10^{-2}\, m$$

finally we use E=hv to calculate the energy

$$E=hv=(6.626e^{-34}J*s)(2.0e^{10}s^{-1})= 1.3e^{-23}J$$

1.4

Compare the Planck Distribution and the Rayleigh-Jean Distributions. For large values of ν, which one would be greater?

Solution

The Planck Distribution is

$$d\rho = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\frac{h\nu}{k_B T}} - 1} d\nu$$

And the Rayleigh Jean Distribution is

$$d\rho = \frac{8\pi \rho^2 k_B T}{c^3} d\nu$$

For larger ν, the Rayleigh Jean Distribution increases, while the Planck Distribution decreases because of the exponential term in the denominator outweighing the ν^3 term.

1.4

Plancks principal assumption was that energies of electronic oscillator can only have values $E = nh\nu$ and $\Delta E = h\nu$. In fact, as v → 0 then ΔE → 0 and E becomes continuous. It should be expected that the nonclassical Plank distribution to go over to the classical Rayleigh-Jeans distribution at low frequencies, where ΔE → 0. Prove that Equation 1.2 reduces to Equation 1.1 as v → 0.

Note: The Taylor expansion of an exponential

$$e^x \approx 1 + x + \left(\frac{x^2}{2!}\right) + ...$$

can truncated to $e^x \approx 1 + x$ when x is small.

Solution

Important to know Planks equation and put it into use:

$$dp(v,T)=P_v(T)dv=(8\pi h/c^3)(v^3 dv/e^{hv/k_bT}-1)$$

Note: $P_v(T)dv \Rightarrow$ is the radiant energy density between frequencies v and v+dv

Now for small x we have $e^x \approx 1+x$

and as v → 0, $hv/k_bT \rightarrow 0$ once we have this we get the following

$$dp(v,T)=(8\pi h/c^3)*((v^3 dv)/(1+(hv/k_bT)-1))= 8\pi hv^3 k_B T dv/c^3 hv = 8\pi v^2 k_B T dv/c^3$$

and this is the classical Rayleigh-Jeans distribution.

1.5

The visible spectrum is in the 400-700 nm range, and contains about 40% of the sun's radiation intensity. Using the Planck Distribution, write an integral expression that can be evaluated to give this result (do not evaluate the integral).

Solution

The Planck Blackbody distribution in terms of wavelength is

$$\rho_\lambda(\lambda,T)d\lambda = \frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}}-1}d\lambda$$

And so the intensity contained in the visible spectrum (from 400 nm and 700 nm) is

$$\int_{400}^{700}\rho_\lambda(\lambda,T)d\lambda = \int_{400\,nm}^{700\,nm}\frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}}-1}d\lambda$$

The intensity contained in the whole spectrum can be given by

$$\int_0^\infty \rho_\lambda(\lambda,T)d\lambda = \int_0^\infty \frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}}-1}d\lambda$$

And thus

$$40\% = 100\% \times \frac{\rho_{visible}}{\rho_{total}} = 100\% \times \frac{\int_{400}^{700}\frac{8phc}{\lambda^5\left(e^{\frac{hc}{\lambda k_b T}}-1\right)}d\lambda}{\int_0^\infty \frac{8phc}{\lambda^5\left(e^{\frac{hc}{\lambda k_b T}}-1\right)}d\lambda}$$

1.13

What is the frequency and energy of a single 310 nm photon?

Solution

Given: λ = 310 nm.

To find the frequency:

$$\nu = \frac{c}{\lambda}$$

]

$$\nu = \frac{2.99\times10^8\frac{m}{s}}{310\ nm}$$

$$\nu = 9.67\times10^{14}s^{-1}$$

To find the energy:

$$E = h\nu$$

$$E = (6.626\times10^{-34})\times\nu$$

$$E = 6.41\times10^{-19}J$$

1.14

A laser emits 3.3×10^{17}photons per second. If the energy per photon is $6.4 \times 10^{-20} J$ per photon, find the a) wattage and b) wavelength of the laser. in what electromagnetic spectra is the laser in?

Solution

a)

$$W = (6.4 \times 10^{-20} J)(3.3 \times 10^{17} \frac{1}{s})$$

$$W = 0.02112 \frac{J}{s}$$

b)

$$E = h\frac{c}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{(3 \times 10^{8} \frac{m}{s})(6.626 \times 10^{-34} Js)}{6.4 \times 10^{-20} J}$$

$$\lambda = 3.106 \times 10^{-6} m$$

c)

infrared spectrum

1.15

What is the max wavelength with a given temperature of 7500K?

Solution

For a given temperature, the maximum wavelength allowed is given by:

$$T = \frac{2.9 \times 10^{-3} \text{mK}}{\lambda_{\text{max}}}$$

Given: T = 7500K

$$7500 = \frac{2.9 \times 10^{-3} \text{mK}}{\lambda_{\text{max}}}$$

$$\lambda_{\text{max}} = \frac{2.9 \times 10^{-3} \text{mK}}{7500 \text{K}}$$

$$\lambda_{\text{max}} = 3.8 \times 10^{-7} \text{m}$$

Q1.15

A light bulb is a blackbody radiator. What temperature is required such that $\lambda_{max} = \ 400nm$?

Solution

$$T = \frac{(2.90 \times 10^{-3} \ m \cdot K)}{400 \times 10^{-9} \ m} = 7250 \ K.$$

1.16

An unknown elemental metal has work function of $\Phi = 8.01 \times 10^{-19} J$. Upon illumination with UV light of wavelength 162 nm, electrons are ejected with velocity of at $2.95 \times 10^3 \frac{m}{s}$. What is the threshold wavelength? What is the work function in units of eV? What metal does this correspond to (you will need to consult Table B1)?

Solution

This question involves a bit of a trick in that neither the wavelength of radiation nor the velocity of electrons are necessary to solve for the threshold wavelength or material as requested. To solve for the threshold wavelength, we employ the concept that kinetic energy is 0 at threshold frequency and then use a relation equation to solve for threshold wavelength.

$$\frac{1}{2}mv^2 = h\nu - \Phi$$

So,

$$\nu_{threshold} = \frac{\Phi}{h} = 1.21 \times 10^{15} s^{-1}$$

and

$$\lambda_{threshold} = \frac{c}{\nu_{threshold}} = 248nm$$

With a basic conversion of

$$1\ J = 6.242 \times 10^{18} eV$$

we see that the work function is 5 eV. Using Table B1, we see that this value corresponds to Cobalt (discovered by Georg Brandt).

1.16

Given the work function of sodium is 1.87 eV, find the kinetic energy of the ejected electrons when light of frequency 2.3 times greater than the threshold frequency is used to excite the electrons.

Solution

step 1: convert work function from electron volts to joules

$$\phi = 1.87\ eV$$

1 eV = $1.602 \times 10^{-19} J$

$$\phi = 1.87 eV \times \frac{1.602 \times 10^{-19} J}{1\ eV} = 2.995 \times 10^{-19} J$$

Step 2: Solve for the threshold frequency

$$\phi = hf$$

$$\frac{\phi}{h} = f$$

$$\frac{2.995 \times 10^{-19} J}{6.626 \times 10^{-34} Js} = f$$

$$4.5 \times 10^{14} Hz = f$$

Step 3: Use threshold frequency to solve for kinetic energy at desired conditions

$$KE = h(2.3f - f)$$

$$KE = h(1.3f)$$

$$KE = (6.626 \times 10^{-34} Js)(1.3(4.5 \times 10^{14} Hz))$$

$$KE = 3.87 \times 10^{-19} J$$

Q1.17

Find kinetic energy emitted off surface of tungsten that is radiated with radiation of 250 nm. Work function of tungsten 4.50 eV.

Solution

Kinetic energy is represented by

$$E = h\nu$$

we then use $c = \nu\lambda$ for the frequency to find

$$E = \frac{hc}{\lambda}$$

Then substitute values to get

$$E = \frac{(6.626 \times 10^{-34}\ J \cdot s)(3.00 \times 10^{8} m/s)}{250 \times 10^{-9}\ m} = 7.95 \times 10^{-19}\ J$$

Convert to eV, to get

$$E = (7.95 \times 10^{-19}\ J)\frac{1\ eV}{1.6 \times 10^{-19}\ J} = 4.97\ eV.$$

Use $KE_e = h\nu – \Phi$ to finally get

$$KE_e = h\nu – \Phi = 4.97\ eV – 4.50\ eV = 0.47\ eV.$$

1.18

A smooth silver Thanksgiving platter and serving spoon (the pilgrims had knives and spoons but no forks) are irradiated with light of wavelength 317 nm. The work function is $\Phi = 6.825 \times 10^{-19} J$. What is the kinetic energy of the ejected electrons [eV]? The threshold frequency?

Solution

We first solve for the threshold frequency.

$$\frac{hc}{\lambda} = \Phi \ = h\nu$$

Rearrange to solve for ν

$$\nu = \frac{\Phi}{h}$$
$$= 1.03 \times 10^{15} s^{-1}$$

Now we solve for kinetic energy.

$$\frac{1}{2}mv^2 = h\nu - \Phi$$

where

$$\nu = \nu_{radiation}$$

and we recall that

$$\nu = \frac{c}{\lambda_{radiation}}$$

Using the right hand side of that kinetic energy equation, we find the result to be

$$KE = 2.55 \times 10^{-19}$$

Q1.18

When a clean surface of silver is irradiated with light of wavelength 255 nm, the work function of ejected electrons is 4.18 eV. Calculate the kinetic energy in eV of the silver and the threshold frequency.

Solution

Kinetic Energy of the electrons can be represented with the formula

$$KE = h\nu - \Phi$$

We have to solve for the Kinetic energy in eV

$$KE = h\nu - \Phi$$

substituting known values gives

$$KE = (6.626 \times 10^{-}34 Js)(\frac{3 \times 10^{8} m/s}{255 \times 10^{-}9 m}) - 6.69 * 10^{-}19 J$$

$$KE = 1.105 \times 10^{-}19 J \approx .690 eV$$

The second part of the question asks us to solve for the threshold frequency

$$\nu_o = \frac{\Phi}{h}$$

$$\nu_o = \frac{6.69 \times 10^{-}19J}{6.626 \times 10^{-}34J * s}$$

$$= 1.01 \times 10^{15} Hz$$

Q1.21

A line in the Paschen series of hydrogen has a wavelength of 1.01 x 10^{-6} m. Find the original energy of the electron.

Solution

For the Paschen series n_1= 3. To find n_2 we have to use the Rhydberg formula:

$$\frac{1}{\lambda} = R_H \times \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

substituting our known values will give us

$$\frac{1}{1.01 \times 10^{-6} m} = 109677 cm^{-1} \left(\frac{1}{3^2} + \frac{1}{n_2^2} \right)$$

converting our units and using algebra gives us

$$0.0903 = \left(\frac{1}{9} - \frac{1}{n_2^2} \right)$$

where

$$n_2 = 6.93 \approx 7$$

We approximate to 7 since n is an integer.

1.22

How does the energy change when a particle absorbs and releases a photon? Show the effects on the state that the particle is in and the energy itself.

Solution

The energy would increase when a photon is absorbed and decrease when a photon is released. We have two equations

$$E = \frac{hc}{\lambda}$$

$$\frac{1}{\lambda} = 109680 \left(\frac{1}{n_1} - \frac{1}{n_2} \right)$$

When a photon is absorbed, λ is positive and when a photon is released λ is negative. From the first equation, we can see that E only depends on the sign of λ. So when a photon is absorbed, energy is positive (increases) and when it is released, energy is negative (decreases).

The second equation shows that when λ is negative, n_1 must be greater than n_2 so the final state is at a lower quantum number than the initial and vice versa for when a photon is absorbed.

1.23

Show that the (a) wavelength of 100 nm occurs within the Lyman series, that (b) wavelength of 500 nm occurs within the Balmer series, and that (c) wavelength of 1000 nm occurs within the Paschen series. Identify the spectral regions to which these wavelengths correspond.

Solution

We can show the where the wavelengths occurs by calculate the maximum and minimum wavelengths of each series using the Rydberg formula.

a) Lyman Series:

$$Max: \frac{1}{\lambda} = 109680\left(1 - \frac{1}{2^2}\right) cm^{-1}$$

$$\lambda = 121.6nm$$

$$Min: \frac{1}{\lambda} = 109680\left(1 - \frac{1}{\infty}\right) cm^{-1}$$

$$\lambda = 91.2nm$$

The range for the Lyman series from 91.2 nm to 121.6 nm, therefore a wavelength of 100 nm occurs within the Lyman series. This corresponds to the ultraviolent region of the spectrum.

b) Balmer Series:

$$Max: \frac{1}{\lambda} = 109680\left(\frac{1}{2^2} - \frac{1}{3^2}\right) cm^{-1}$$

$$\lambda = 656.5nm$$

$$Min: \frac{1}{\lambda} = 109680\left(\frac{1}{2^2} - \frac{1}{\infty}\right) cm^{-1}$$

$$\lambda = 364.7nm$$

The range for the Balmer series from 364.7 nm to 656.5 nm, therefore a wavelength of 500 nm occurs within the Balmer series. This corresponds to the near ultraviolent region of the spectrum.

c) Paschen Series:

$$Max: \frac{1}{\lambda} = 109680\left(\frac{1}{3^2} - \frac{1}{4^2}\right) cm^{-1}$$

$$\lambda = 1875.6nm$$

$$Min: \frac{1}{\lambda} = 109680\left(\frac{1}{3^2} - \frac{1}{\infty}\right) cm^{-1}$$

$$\lambda = 820.6nm$$

The range for the Paschen series from 820.6 nm to 1875.6 nm, therefore a wavelength of 1000 nm occurs within the Paschen series. This corresponds to the near infrared region of the spectrum.

1.24

Calculate the wavelength and the energy of a photon associated with the series limit of the Balmer series.

Solution

First find the minimum wavelength for the Balmer series.

$$\frac{1}{\lambda} = 109,680 cm^{-1} \left(\frac{1}{2^2} - \frac{1}{\infty} \right)$$
$$\lambda = 364.7\, nm$$

Now we can use the wavelength to find the energy.

$$E = \frac{hc}{\lambda}$$
$$= \frac{(6.626 \times 10^{-34})(3 \times 10^{8})}{364.7 \times 10^{-9}}$$
$$= 5.45 \times 10^{-19}\, J$$

1.25

For the following particles (a) an electron with a kinetic energy of 50eV, (b) a proton with a kinetic energy of 50eV , and (c) an electron in the second Bohr orbit of a hydrogen atom, calculate the de Broglie wavelength of each.

Solution

We use $\lambda = \frac{h}{p}$ in all cases to find λ.

a.

$$KE = \frac{mv^2}{2}$$

$$50eV\left(\frac{1.602\times10^{-19}J}{1eV}\right) = \frac{(v^2)(9.109\times10^{-31}kg)}{2}$$

$$v = 4.19\times10^{6}\,m\cdot s^{-1}$$

So

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$
$$= \frac{6.626\times10^{-34}J\cdot s}{(9.109\times10^{-31}kg)(4.19\times10^{6}m\cdot s^{-1})}$$
$$= 1.23\times10^{-10}m = 0.123\,nm$$

b. Replace m_e with m_p in (a) to find $\lambda = 2.86\times10^{-3}nm$.

c. We must first determine the velocity of an electron in the second Bohr orbit of a hydrogen atom. The velocity of an electron is given by the following equation:

$$v = \frac{nh}{2(\pi)m_e r}$$

and we know

$$r = \frac{\epsilon_0 h^2 n^2}{(\pi)m_e e^2}$$

substituting the two equations we find that

$$v = \frac{e^2}{2nh\epsilon_0}$$

For $n = 2$, because we are talking about the second orbit

$$v = \frac{(1.602\times10^{-19}C)^2}{2(2)(6.626\times10^{-34}J\cdot s)(8.854\times10^{-12}C^2J^{-1}m^{-1})}$$
$$= 1.09\times10^{6}m\cdot s^{-1}$$

So

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$
$$= \frac{6.626\times10^{-34}J\cdot s}{(9.109\times10^{-31}kg)(1.09\times10^{6}m\cdot s^{-1}}$$
$$= 6.64\times10^{-10}m = 0.664\,nm$$

Q1.26

a. What is the velocity and wavelength of an electron with a voltage increase of 75 V?

b. What is the momentum of an electron with a de Broglie wavelength of 20 nm?(mass of an electron is $9.109 \times 10^{-31}\ kg$)

Solution

a.

$$\begin{aligned} KE &= (\text{electron charge}) \times (\text{potential}) \\ &= (1.602 \times 10^{-19}\, C)(75\, V) \\ &= 1.2 \times 10^{-17}\, J \\ &= (1/2)mv^2 \end{aligned}$$

$$v = \sqrt{\frac{2(KE)}{m}} = \sqrt{\frac{2(1.2 \times 10^{-17} J)}{(9.109 \times 10^{-31} kg)}} = 5.133 \times 10^{6} m * s^{-1}$$

$$\begin{aligned} \lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34} J * S}{(9.109 \times 10^{-31} kg)(5.133 \times 10^{6} m * s^{-1})} \\ &= 1.2267\, m \end{aligned}$$

b.

$$\lambda = \frac{h}{p}$$

$$\begin{aligned} p &= \frac{h}{\lambda} \\ &= \frac{6.626 \times 10^{-34} J * S}{20 \times 10^{-6} m} \\ &= 3.313 \times 10^{-29} kg * m * s^{-1} \end{aligned}$$

1.27

Through what potential a proton must initially at rest fall so its de Broglie wavelength is $1.83 \times 10^{-10}\ m$?

Q1.28

Calculate the energy and wavelength associated with a β particle that has fallen through a potential difference of 3.2 V. Take the mass of a β particle to be $9.1 \times 10^{-31}\text{kg}$.

Solution

A beta particle is an electron, so it has a -1 charge.

$$KE = (\beta\,\text{particle charge}) \times \text{ Potential} = |-1.602 \times 10^{-19}\text{C}| \ \times \ 3.2\text{V}$$

$$KE = 5.126 \times 10^{-19}\text{J per } \beta \text{ particle}$$

$$\lambda = \frac{h}{p}$$

$$KE = \frac{mv^2}{2} = \frac{p^2}{2m}$$

$$p = \sqrt{2\ KE\ m} = \sqrt{2\ \times\ 5.126 \times 10^{-19}\text{J}\ \times\ 9.1 \times 10^{-31}\text{kg}}$$

$$p = 5.66 \times 10^{-25}\text{kg m } s^{-1}$$

$$\lambda = \frac{6.626 \times 10^{-34}\text{J s}}{5.66 \times 10^{-25}\text{kg m s}^{-1}} = 6.86 \times 10^{-10}\text{m}$$

Q1.28

If a proton is going through a potential difference of 3.0V, what is the momentum and wavelength associated with this proton? (mass of a proton is equal to $1.6726 \times 10^{-27}\ kg$)

Solution

$$(charge) * (potential) = KE$$

$$charge = 1.602 \times 10^{-19} C$$

$$(1.602 \times 10^{-19} C) * (3.0V) = KE$$

$$KE = 4.806 \times 10^{-19} J$$

$$KE = \frac{p^2}{2m}$$

$$p = \sqrt{2(KE)m} = \sqrt{2(4.806 \times 10^{-19} J)(1.6726 \times 10^{-27} kg)} = 4.01 \times 10^{-23} kg * m * s^{-1}$$

$$\lambda = h/p = \frac{6.626 \times 10^{-34} J * S}{4.01 \times 10^{-23} kg * m * s^{-1}} = 1.65 \times 10^{-11} m = 0.165\, pm$$

1.29

Neutron diffraction is a modern technique to study structure. In the neutron diffraction, a collimated beam of neutrons was generated at some temperature from high-energy neutron source. This is achieved at several accelerator facilities around the world. If the speed of neutron is $v_n = (3k_BT/m)^{1/2}$ with m as the mass of neutron. What is the required temperature so that neutrons have a de Broglie wavelength of 200 pm? The mass of a neutron to be $1.67 \times 10^{-27}\ kg$.

1.29

While studying quantum mechanics one day, you wondered what temperature would be required for the Jumbo Jawbreaker you were about to eat to have a de Broglie wavelength of 1.9×10^{-24} meters? Assuming that the speed of a Jumbo Jawbreaker can be calculated from the equation $\nu_n = (\frac{3k_BT}{m})\frac{1}{2}$. You quickly measure the mass of your Jumbo Jawbreaker and found it to be $0.1kg$.

Solution

Knowing that the de Broglie wavelength has the form,

$$\lambda = \frac{h}{m\nu_n}$$

we can substitute the given equation for speed into the de Broglie wavelength equation

$$\lambda = \frac{h}{\sqrt{3mk_BT}}$$

rearrange to solve for temperature

$$T = \frac{h^2}{3mk_B\lambda^2}$$

Substituting in constants we can solve for temperature in Kelvin. Using $h = 6.626 \times 10^{-34} J*s$, $m = 0.1kg$, $k_B = 1.381 \times 10^{-21} J*K^{-1}$, and $\lambda = 1.9 \times 10^{-24}$ meters.

We find that

$$T = \frac{(6.626 \times 10^{-34} J*s)^2}{3(0.1kg)(1.381 \times 10^{-21} J*K^{-1})(1.9 \times 10^{-24})^2}$$

Therefore

$$\begin{aligned} T &= 293.5K \\ &= 20.35^{\circ}C \end{aligned}$$

1.30

For linear motion, show that a small change in the momentum, $\Delta \mathrm{p}$, changes a change in kinetic energy, $\Delta \mathrm{KE}$, of

$$\Delta \mathrm{KE} = \frac{p_0}{m}\Delta \mathrm{p}$$

where p_0 is initial momentum.

Solution

Since $\Delta \mathrm{p} = dp$ and $\Delta \mathrm{KE} = dKE$,

$$KE = \frac{p^2}{2m}$$

$$dKE = \frac{p_0}{m}dp$$

$$\Delta \mathrm{KE} = \frac{p_0}{m}\Delta \mathrm{p}$$

1.31

Derive the Bohr formula for $\frac{1}{\lambda_{vac}}$ for a multi-proton and single electron atom such as He^{+} or Li^{2+}.

Solution

The number of protons (Z) in the nucleus interact with the single electron with the same coulomb force (f). The total force of a nucleus with charge Z can be written as the sum of each proton individually interacting with the electron.

$$f_{Total} = \sum_{i=0}^{Z} \frac{e^2}{4r^2\pi\epsilon_\circ}$$

Simplifying this expression we find that

$$f_{Total} = \frac{Ze^2}{4r^2\pi\epsilon_\circ}$$

To prevent the electron from spiraling into or away from the nucleus, the centrifugal force $f = \frac{m_e v^2}{r}$ is equal to the Coulombic force. Therefore

$$\frac{Ze^2}{4r^2\pi\epsilon_\circ} = \frac{m_e\nu^2}{r}$$

For stability purposes a condition requires electrons to have a set number of complete wavelengths around the circumference of the orbit or

$$2\pi r = n\lambda \ , \ where \ n = 1, 2, 3...$$

using the de Broglie wavelength formula $\lambda = \frac{h}{p} = \frac{h}{m\nu}$ we find that

$$m_e\nu r = \frac{nh}{2\pi}$$

Solving for ν and substituting into our force relationship $\frac{Ze^2}{4r^2\pi\epsilon_\circ} = \frac{m_e\nu^2}{r}$ We find that

$$r = \frac{n^2h^2\epsilon_\circ}{m_e e^2 Z\pi}$$

Now solving for the total energy of the system

$$E = KE + V(r)$$
$$= \frac{1}{2}m_e\nu^2 - \frac{Ze^2}{4r\pi\epsilon_\circ}$$

Substituting in $m_e\nu^2$ found above into the kinetic energy portion we find

$$E = \frac{Ze^2}{8r\pi\epsilon_\circ} - \frac{Ze^2}{4r\pi\epsilon_\circ} = -\frac{Ze^2}{8r\pi\epsilon_\circ}$$

Substituting r from above we quantize the energy such that

$$E_n = \frac{-Z^2 m_e e^4}{8n^2h^2\epsilon_\circ^2}$$

Since this energy is quantized, the change in energy states will occur where electrons are excited by light or $h\nu$ into higher quantum states. Therefore

$$\Delta E = \frac{-Z^2 m_e e^4}{8h^2\epsilon_\circ^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu$$

Finally solve for $\frac{1}{\lambda_{vac}}$ remembering that $h\nu = \frac{hc}{\lambda_{vac}}$ where c is the speed of light. We obtain our final solution

$$\boxed{\frac{1}{\lambda_{vac}} = \frac{-Z^2 m_e e^4}{8h^3 c\epsilon_\circ^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

1.32

The series in the He^+ spectrum that corresponds to the set of transitions where the electron falls from a higher level into the n = 4 state is called the Pickering series, an important series in solar astronomy. Derive the formula for the wavelengths of the observed lines in this series. In what region of the spectrum does it occur?

Solution

If we derive the Bohr formula for $\tilde{v} = Z^2 R_H \left(\frac{1}{(n^2)_1} - \frac{1}{(n^2)_2}\right)$

In the Pickering series, the helium spectrum is in $Z = 2$ and $n_2 = 4$

$$\tilde{v} = 4(109,680 cm^-1)\left(\frac{1}{4^2} - \frac{1}{n_1^2}\right) \tag{1.E.1}$$

where \(n_1 = 5, 6, 7, 8.... \]).

$$n_1 = 5, \tilde{v}\ = 9871\,\mathrm{cm}^-1$$

or

$$\lambda = 1.013 * 10^{-6} meters$$

1.33A

Using the Bohr model, find the third ionization energy for the Lithium atom in eV and in J.

Solution

Energy transitions for a hydrogen like atom are given by $\Delta E = Z^2 R_y(1/n_i^2 - 1/n_f^2)$

where Z is the atomic number and R_y is 13.6 eV

When a hydrogen like atom is ionized, the electron transitions to its highest bound state, at n = infinity,so its quantum number nf goes to infinity, making $1/n_f^2 = 0$.

So $E_{ionization} = (3)^2(13.6)(1/(1)^2 - 0) = 122.9$ eV.

$122.9 \text{ eV} * 1.6 * 10^{-19} = 1.96 * 10^{-17}$ J

1.33B

Find the ionization energy in eV and $kJ \cdot mol^{-1}$ of singly ionized helium in the $n = 3$ state using Bohr theory

Solution

To find the ionization energy of helium, consider the case where we move an electron from the $n = 3$ state to an infinite distance from the nucleus.

Using the Bohr formula for $\tilde{v}$.

$$\tilde{v} = Z^2 R_H (\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

$$\tilde{v} = 2^2 (109680\, cm^{-1}) \left(\frac{1}{3^2} - \frac{1}{\infty^2} \right)$$

$$\tilde{v} = 4.87467 \times 10^4 cm^{-1}$$

Then plugging into $E = hc\tilde{v}$

$$E = (6.626 \times 10^{-34} J \cdot s)(2.998 \times 10^8 m \cdot s^{-1})(4.87467 \times 10^6 m^{-1})$$

$$E = 9.68 \times 10^{-19} J = 583 kJ \cdot mol^{-1} = 6eV$$

1.34A

The speed of electron in an *n*th Bohr orbit is given by the equation:

$$v = \frac{e^2}{2\epsilon_0 nh}$$

The force acting between an electron and proton a distance r from one another is given by Coulomb's law:

$$f = \frac{e^2}{4\pi\epsilon_0 r^2}$$

The centrifugal force acts in opposition to the Coulombic force and is given by the equation:

$$f = \frac{mv^2}{r}$$

Find the values of v for the Bohr orbits of n = 4, n = 5, and n = 6, and find the total force in an atom between a proton and electron a distance of 5 x 10^{-11} m away from one another, with the electron moving at a speed of 2 x 10^{6} m/s.

Solution

To find v simply substitute the values for n into the equation:

$$v = \frac{e^2}{2\epsilon_0 nh}$$

For the values of v at n = 4, n = 5, n = 6, we get

n = 1

$$v_1 = 546,923\ m \cdot s^{-1}$$

n = 2

$$v_2 = 437,538\ m \cdot s^{-1}$$

n = 3

$$v_3 = 364,615\ m \cdot s^{-1}$$

To find the force between a proton and electron, simply subtract the Coulombic force from the Centrifugal force and substitute appropriate values for the constants:

$$f = \frac{mv^2}{r} - \frac{e^2}{4\pi\epsilon_0 r^2}$$

For which we attain:

$$f = 7.2875 \times 10^{-8} N$$

1.34B

Prove that the speed of electron in an *n*th Bohr orbit is $v = \frac{e^2}{2\epsilon_0 nh}$

Then find the first few values of v the Bohr orbit.

Solution

First we have to know that the angular moment of the electron revolving in the nth Bohr orbit is quantized then

$$mvr = \frac{nh}{2\pi}$$

where r is the radius of the nth Bohr orbit.

Kinetic energy of the electron is given as $\frac{mv^2}{2} = \frac{e^2}{2(4\pi\epsilon_0)r}$

So the radius, r must equal $r = \frac{e^2}{(4\pi\epsilon_0)mv^2}$

Now after substituting the value above into the first equation, we get

$mv(\frac{e^2}{(4\pi\epsilon_0)mv^2} = \frac{nh}{2\pi}$

Thus the speed of the electron in the n Bohr orbit is

$v = \frac{e^2}{2\epsilon_0 nh}$

For the first few values of v in the nth Bohr orbit, we get

n = 1

$v = 2.188 \times 10^6 m * s^-1$

n = 2

$v_2 = 1.094 \times 10^6 m * s^-1$

n = 3

$v_3 = 7.292 \times 10^5 m * s^-1$

1.35

What is the uncertainty in an electron's position if the uncertainty in measuring its velocity is 5 $m \cdot s^{-1}$.

Solution

According to the Heisenburg Uncertainty Principle

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

$$\Delta x \geq \frac{\hbar}{2\Delta p}$$

Then by definition $\Delta p = m\Delta v$

$$\Delta x \geq \frac{\hbar}{2m\Delta v}$$

$$\Delta x \geq \frac{6.626 \times 10^{-34} J \cdot s}{4\pi(9.109 \times 10^{-31} kg)(5m \cdot s^{-1})}$$

$$\Delta x \geq 1.16 \times 10^{-5} m$$

1.35

What is the *uncertainty* in the speed of an electron if we locate it to within 50 pm?

Solution

It is known that the uncertainty of momentum is given by the expression

$$\Delta p = m\Delta v$$

and Heisenberg's Uncertainty Principle states that

$$\Delta x \Delta p \geq h$$

Then

$$\begin{aligned} \Delta x(m\Delta v) &\geq h \\ \Delta v &\geq \frac{h}{m\Delta x} \\ &\geq \frac{6.626 \cdot 10^{-34} J \cdot s}{(9.109 \cdot 10^{-31} kg)(50 \cdot 10^{-12} m)} \\ &\geq 1.45 \cdot 10^{7} m \cdot s \end{aligned}$$

1.35

If we know the velocity of an electron to within $3.5 \times 10^{7} \frac{m}{s}$, then what is the uncertainty in its position?

Solution

Using the Heisenberg Uncertainty Principle,

$$\Delta x \Delta p \geq h = \Delta x \times m\Delta v \geq h$$

and rearranging to solve for uncertainty in velocity,

$$\Delta x \geq \frac{h}{m\Delta v}$$

we can use $h = 6.626 \times 10^{-34} J \cdot s$, $m = 9.109 \times 10^{-31} kg$, and $\Delta v = 3.5 \times 10^{7} \frac{m}{s}$ and find that

$$\Delta x \geq \frac{(6.626 \times 10^{-34} J \cdot s)}{(9.109 \times 10^{-31} kg)(3.5 \times 10^{7} \frac{m}{s})}$$

and thus

$$\Delta x \geq 2.078 \times 10^{-11} meters$$

1.35

If a proton is located to within 1 angstrom, what is its uncertainty in velocity?

Solution

The Heisenberg uncertainty principle states

$\Delta x \Delta p = h/4\pi$

$\Delta x m \Delta v = h/4\pi$

$\Delta v = h/(4m_p\pi\Delta x)$ where m_p is the mass of a proton

$x \sim \Delta x$ the uncertainty in position is on the same order as the location it is confined to, here 1 angstrom

$\Delta v = h/(4m_p\pi x) = (6.626*10^{-34})/(4*(1.67*10^{-27})*3.14*10^{-10})$

= 315.7 m/s

1.36

If the position of an electron is within the 10 pm interval, what is the uncertainty of the momentum? Is this value similar to that of an electron in the first Bohr orbit?

Solution

According to the uncertainty principle for position and momentum,

$$\Delta x \Delta p \geq h$$
$$\Delta p \geq \frac{h}{\Delta x}$$

by substituting the respective values we get,

$$\Delta p \geq \frac{6.626 \times 10^{-34} J.s}{10.0 \times 10^{-12} m}$$
$$\geq 2.9 \times 10^{-23} kg.m.s^{-}1$$

Therefore, uncertainty in the momentum of an electron will be $2.9 \times 10^{-23} kg.m.s^{-}1$.

We can calculate the momentum of an electron in the first Bohr radius by using v since we know that,

$$p = m_e v$$
$$= (9.109 \times 10^{-31} kg)(2.188 \times 10^{6} m \cdot s^{-1})$$
$$= (1.992 \times 10^{-24} kg \cdot m \cdot s^{-1})$$

The uncertainty of the momentum of an electron somewhere in a 10 pm interval is greater that the momentum of an electron in the first Bohr radius.

1.37

The Heisenberg Uncertainty Principle

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

Show both sides have the same units

Solution

$$\Delta x = meters$$

$$\Delta p = m\Delta v$$

Planck's Constant has units of

$$J \cdot s$$

and

$$J = \frac{kg \cdot m^2}{s^2}$$

so apply these equations we get

$$m\frac{kg \cdot m}{s} \geq \frac{kg \cdot m^2 \cdot s}{s^2}$$

and simplify

$$\frac{kg \cdot m^2}{s} \geq \frac{kg \cdot m^2}{s}$$

Therefore Both sides have same units

1.38

The relationship between energy and time can be seen through the following uncertainty principle: $\Delta E \Delta t \geq h$. Through this relationship, it can be interpreted that a particle of mass m, the energy (E=mc^2) can come from nothing and return to nothing within a time Δt ≤ h/(mc^2). A real particle is one that lasts for time (Δt) or more; likewise, a particle that lasts for less than time (Δt) are called virtual particles. For a charged subatomic particle, a pion, the mass is $2.5 \times 10^{-28} kg$. For a pion to be considered a real particle, what is its minimum lifetime?

Solution

Based on the uncertainty principle for energy and time:

$$\Delta E \Delta t \geq h$$

$$\Delta t \geq \frac{h}{mc^2}$$

therefore $E = mc^2$. By plugging in the values, you get

$$\Delta t \geq \frac{6.626 \times 10^{-34} Js}{(2.5 \times 10^{-28} kg)(2.998 \times 10^8 ms^{-1})^2}$$
$$\geq 2.9 \times 10^{-23} s$$

Therefore, the minimum lifetime if the pion is to be considered a real particle will be $2.9 \times 10^{-23} s$.

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2: THE CLASSICAL WAVE EQUATION

The aim of this section is to give a fairly brief review of waves in various shaped elastic media—beginning with a taut string, then going on to an elastic sheet, a drumhead, first of rectangular shape then circular, and finally considering elastic waves on a spherical surface, like a balloon. The reason we look at this material here is that these are “real waves”, hopefully not too difficult to think about, and yet mathematically they are the solutions of the same wave equation the Schrödinger wavefunction obeys in various contexts, so should be helpful in visualizing solutions to that equation, in particular for the hydrogen atom.

2.1: The One-Dimensional Wave Equation

2.2: The Method of Separation of Variables

2.3: Oscillatory Solutions to Differential Equations

2.4: The General Solution is a Superposition of Normal Modes

2.5: A Vibrating Membrane

2.E: The Classical Wave Equation (Exercises)

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2.1: The One-Dimensional Wave Equation

Learning Objectives

- To introduce the wave equation including time and position dependence

In the most general sense, waves are particles or other media with wavelike properties and structure (presence of crests and troughs).

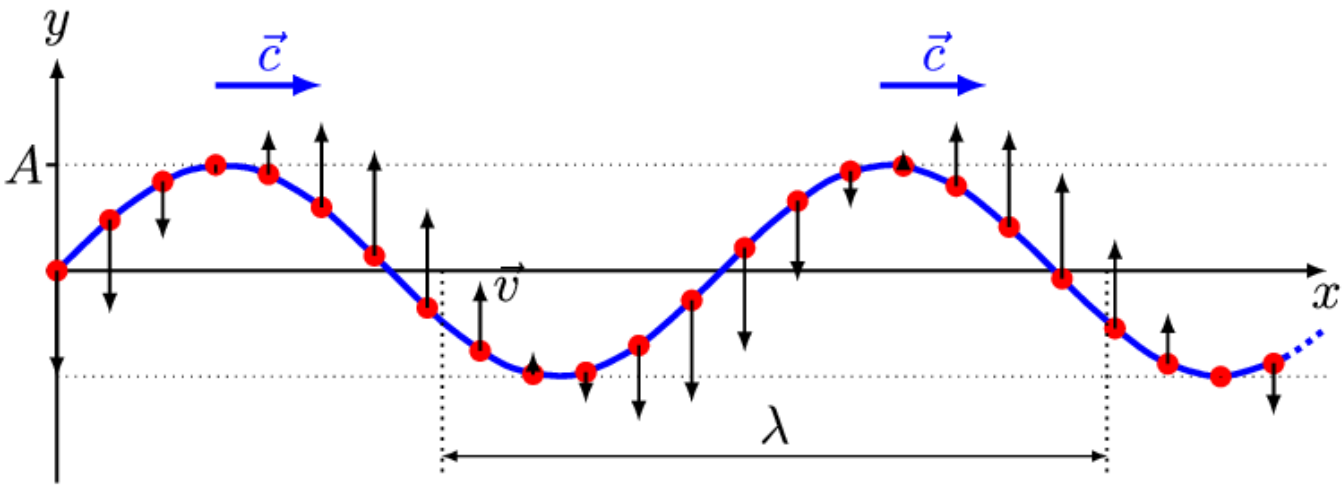


Figure 2.1.1 : A simple translational (transverse) wave. (CC BY-SA 4.0 International; And1mu via Wikimedia Commons)

The simplest wave is the (spatially) one-dimensional sine wave (Figure 2.1.1) with an varing amplitude A described by the equation:

$$A(x,t) = A_o \sin(kx - \omega t + \phi)$$

where

- A_o is the maximum amplitude of the wave, maximum distance from the highest point of the disturbance in the medium (the crest) to the equilibrium point during one wave cycle. In Figure 2.1.1 , this is the maximum vertical distance between the baseline and the wave.
- x is the space coordinate
- t is the time coordinate
- k is the wavenumber
- ω is the angular frequency
- ϕ is the phase constant.

One can categorize “waves” into two different groups: *traveling waves* and *stationary waves*.

Traveling Waves

Traveling waves, such as ocean waves or electromagnetic radiation, are waves that “move,” meaning that they have a frequency and are propagated through time and space. Another way of describing this property of “wave movement” is in terms of energy transmission – a wave travels, or transmits energy, over a set distance. The most important kinds of traveling waves in everyday life are electromagnetic waves, sound waves, and perhaps water waves, depending on where you live. It is difficult to analyze

waves spreading out in three dimensions, reflecting off objects, etc., so we begin with the simplest interesting examples of waves, those restricted to move along a line. Let's start with a rope, like a clothesline, stretched between two hooks. You take one end off the hook, holding the rope, and, keeping it stretched fairly tight, wave your hand up and back once. If you do it fast enough, you'll see a single bump travel along the rope:

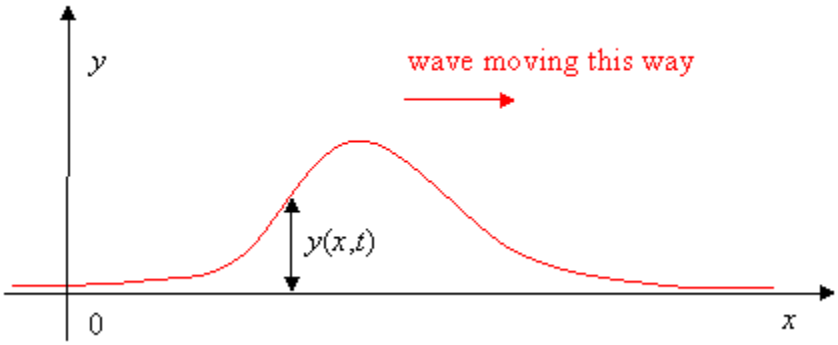


Figure 2.1.2 : A one-dimensional traveling wave at one instance of time t.

This is the simplest example of a *traveling wave*. You can make waves of different shapes by moving your hand up and down in different patterns, for example an upward bump followed by a dip, or two bumps. You'll find that the traveling wave *keeps the same shape* as it moves down the rope. Taking the rope to be stretched tightly enough that we can take it to be horizontal, we'll use its rest position as our *x*-axis (Figure 2.1.1). The y-axis is taken vertically upwards, and we only wave the rope in an up-and-down way, so actually $y(x,t)$ will be how far the rope is from its rest position at x at time t: that is, Figure 2.1.2 shows where the rope is at a single time t.

We can now express the observation that the wave "keeps the same shape" more precisely. Taking for convenience time $t = 0$ to be the moment when the peak of the wave passes $x = 0$, we graph here the rope's position at t = 0 and some later times t as a movie (Figure 2.1.3). Denoting the first function by $y(x,0) = f(x)$, then the second $y(x,t) = f(x - vt)$: it is the same function with the "same shape," but just moved over by vt, where v is the velocity of the wave.

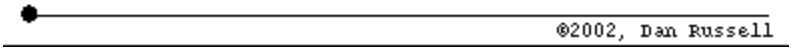


Figure 2.1.3 : A one-dimensional traveling wave at as a function of time. Traveling waves propagate energy from one spot to another with a fixed velocity v. (CC BY-NC-ND; Daniel A. Russell).

To summarize: on sending a traveling wave down a rope by jerking the end up and down, from observation the wave travels at constant speed and keeps its shape, so the displacement *y* of the rope at any horizontal position at x at time t has the form

$$y(x,t) = f(x - vt) \tag{2.1.1}$$

We are neglecting frictional effects—in a real rope, the bump gradually gets smaller as it moves along.

Standing Waves

In contrast to traveling waves, *standing waves,* or stationary waves, remain in a constant position with crests and troughs in fixed intervals. One way of producing a variety of standing waves is by plucking a melody on a set of guitar or violin strings. When placing one's finger on a part of the string and then plucking it with another, one has created a standing wave. The solutions to this problem involve the string oscillating in a sine-wave pattern (Figure 2.1.4) with no vibration at the ends. There is also no vibration at a series of equally-spaced points between the ends; these "quiet" places are *node*s. The places of maximum oscillation are *antinode*s.

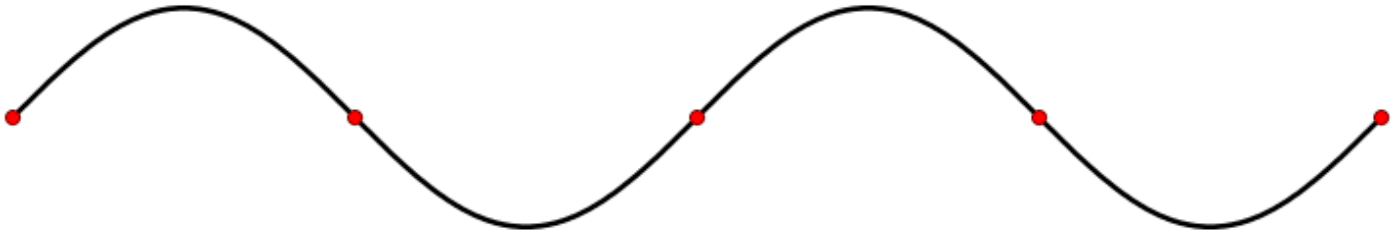


Figure 2.1.4 : Animation of standing wave in the stationary medium with marked wave nodes (red circles). (public domain; LucasVB).

Bound vs. Free particles and Traveling vs. Stationary Waves

Traveling waves exhibit movement and propagate through time and space and stationary wave have crests and troughs at fixed intervals separated by nodes. "Free" particles like the photoelectron discussed in the photoelectron effect, exhibit traveling wave like properties. In contrast, electrons that are "bound" waves will exhibit stationary wave like properties. The latter was invoked for the Bohr atom for quantizing angular moment of an electron bound within a hydrogen atom.

The Wave Equation

The mathematical description of the one-dimensional waves (both traveling and standing) can be expressed as

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2} \tag{2.1.2}$$

with u is the amplitude of the wave at position x and time t, and v is the velocity of the wave (Figure 2.1.2).

Equation 2.1.2 is called the classical wave equation in one dimension and is a *linear partial differential equation*. It tells us how the displacement u can change as a function of position and time and the function. The solutions to the wave equation ($u(x,t)$) are obtained by appropriate integration techniques. It may not be surprising that not all possible waves will satisfy Equation 2.1.2 and the waves that do must satisfy both **the initial conditions** and the **boundary conditions**, i.e. on how the wave is produced and what is happening on the ends of the string.

For example, for a standing wave of string with length L held taut at two ends (Figure 2.1.3), the boundary conditions are

$$u(0,t) = 0 \tag{2.1.3}$$

and

$$u(L,t) = 0 \tag{2.1.4}$$

for all values of t. As expected, different system will have different boundary conditions and hence different solutions.

Mathematical Origin of Quantization

The initial conditions and the boundary conditions used to solve the wave equation will result in restrictions of "allowed" waves to exist in a similar fashion that only certain solutions exist for the electrons in the Bohr atom.

The first six wave solutions $u(x,t)$ to Equation 2.1.2 subject to the boundary conditions in Equations 2.1.3 and 2.1.4 (discussed in detail later) results in the wave in Figure 2.1.5 . These are standing waves that exist with frequencies based on the number of *nodes* (0, 1, 2, 3,...) they exhibit (more discussed in the following Section).



Figure 2.1.5 : Standing waves in a string (both spatially and temporally). The first six solutions ($u(x,t)$. from Wikipedia.

Curvature of Wave Solutions

Since the acceleration of the wave amplitude (right side of Equation 2.1.2) is proportional to $\frac{\partial^2}{\partial x^2}$, the greater curvature in the material produces a greater acceleration, i.e., greater changing velocity of the wave (Figure 2.1.4) and greater frequency of oscillation. As discussed later, the higher frequency waves (i..e, more nodes) are higher energy solutions; this as expected from the experiments discussed in Chapter 1 including Plank's equation $E = h\nu$.

Summary

Waves which exhibit movement and are propagated through time and space. The two basic types of waves are traveling and stationary. Both exhibit wavelike properties and structure (presence of crests and troughs) which can be mathematically described by a wavefunction or amplitude function. Both wave types display movement (up and down displacement), but in different ways.Traveling waves have crests and troughs which are constantly moving from one point to another as they travel over a length or distance. In this way, energy is transmitted along the length of a traveling wave. In contrast, standing waves have nodes at fixed positions; this means that the wave's crests and troughs are also located at fixed intervals. Therefore, standing waves only experience vibrational movement (up and down displacement) on these set intervals - no movement or energy travels along the length of a standing wave.

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2.2: The Method of Separation of Variables

Learning Objectives

- To be introduced to the *Separation of Variables* technique as method to solved wave equations

Solving the wave equation involves identifying the functions $u(x,t)$ that solve the partial differential equation that represent the amplitude of the wave at any position x at any time t

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2} \tag{2.2.1}$$

This wave equation is a type of second-order partial differential equation (PDE) involving two variables - x and t. PDEs differ from ordinary differential equations (ODEs) that involve functions of only one variable. However, this difference makes PDEs appreciably more difficult to solve. In fact, the vast majority of PDE cannot be solved analytically and those classes of special PDEs that can be solved analytically invariably involve converting the PDE into one or more ODEs and then solving independently. One of these approaches is the the method of *separation of variables*.

Method of Separation of Variables

The general application of the *Method of Separation of Variables* for a wave equation involves three steps:

1. We find all solutions of the wave equation with the general form
$$u(x,t) = X(x)T(t)$$
for some function $X(x)$ that depends on x but not t and some function $T(t)$ that depends only on t, but not x. It is of course too much to expect that all solutions of Equation 2.2.1 are of this form, however, if we find a set of solutions $\{X_i(x)T_i(t)\}$ since the wave equation is a *linear equation*,
$$u(x,t) = \sum_i c_i X_i(x) T_i(t) \tag{2.2.2}$$
is also a solution for *any choice* of the constants c_i.
2. Impose constraints on the solutions based on the knowledge of the system. These are called the **boundary conditions**, which specify the values of $u(x,t)$ at the extremes ("boundaries"). This is a similar constraint to the solution as in initial value problems which the conditions $x(t_i)$ are specified at a specific time t_i. The goal is then to select the constants c_i in Equation 2.2.2 so that the boundary conditions are also satisfied.

Method of separation of variables is one of the most widely used techniques to solve partial differential equations and is based on the *assumption* that the solution of the equation is separable, that is, the final solution can be represented as a product of several functions, each of which is only dependent upon a single independent variable. If this assumption is incorrect, then clear violations of mathematical principles will be obvious from the analysis.

A Vibrating Spring Held Fixed Between Two Points

As discussed in Section 2.1, the solutions to the string example $u(x,t)$ for all x and t would be assumed to be a product of two functions: $X(x)$ and $T(t)$, where $X(x)$ is a function of only x, not t and $T(t)$ is a function of t, but not x.

$$u(x,t) = X(x)T(t) \tag{2.2.3}$$

Substitute Equation 2.2.3 into the one-dimensional wave equation (Equation 2.2.1) gives

$$\frac{\partial^2 X(x)T(t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 X(x)T(t)}{\partial t^2} \tag{2.2.4}$$

Since X is not a function of t and T is not a function of x, Equation 2.2.4 can be simplified

$$T(t)\frac{\partial^2 X(x)}{\partial x^2} = \frac{1}{v^2}X(x)\frac{\partial^2 T(t)}{\partial t^2} \tag{2.2.5}$$

Collecting the expressions that depend on x on the left side of Equation 2.2.5 and of t on the right side results in

$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2} = \frac{1}{v^2}\frac{1}{T(t)}\frac{\partial^2 T(t)}{\partial t^2} \tag{2.2.6}$$

Equation 2.2.6 is an interesting equation since each side can be set to a fixed constant K as that is the only solution that works for all values of t and x. Therefore, the equation can be separated into two *ordinary differential equations:*

$$\frac{d^2 T(t)}{dt^2} - Kv^2 T(t) = 0 \tag{2.2.7}$$

$$\frac{d^2 X(x)}{dx^2} - KX(x) = 0 \tag{2.2.8}$$

Hence, by substituting the new product solution form (Equation 2.2.3) into the original wave equation (Equation 2.2.1), we converted a partial differential equation of two variables (x and t) into two *ordinary differential equations* (differential equation containing a function or functions of one independent variable and its derivatives). Each differential equation involves only one of the independent variables (x or t).

- If $K = 0$, then the solution is the trivial $u(x, y,) = 0$ solution (i.e., no wave exists).
- If $K > 0$, then the general solution of Equation 2.2.8 is

$$X(x) = Ae^{\sqrt{K}x} + Be^{-\sqrt{K}x} \tag{2.2.9}$$

At this stage, Equation 2.2.9 implies that the solution to the two ordinary differential wave equations will be an infinite number of waves with no quantization to limit those that are allowed (i.e., any values of A and B are possible). Narrowing down the general solution to a specific solution occurs when taking the boundary conditions into account.

The boundary conditions for this problem is that the wave amplitude equal to zero at the ends of the string

$$u(0, t) = X(x)T(t) = 0 \tag{2.2.10}$$

$$u(L, t) = X(x)T(t) = 0 \tag{2.2.11}$$

for all times t.

Applying the two boundary conditions in Equations 2.2.10 and 2.2.11 into the general solution in Equation 2.2.9 results into relationships between A and B:

$$X(x = 0) = A + B = 0 \tag{2.2.12}$$

and

$$X(x = L) = Ae^{\sqrt{K}L} + Be^{-\sqrt{K}L} = 0 \tag{2.2.13}$$

Ignore the Trivial Solution

One solution to this is that $A = B = 0$, but this is the trivial solution from $K = 0$ and one we ignore since it provides no physical solution to the problem other than the knowledge that $0 = 0$, which is not that inspiring of a result.

Both Equations 2.2.7 and 2.2.8 can be generalized into the following equations

$$\frac{d^2 y(x)}{dx^2} - k^2 y(x) = 0 \tag{2.2.14}$$

where k is a real constant (i.e., not complex). Equation 2.2.14 is a *homogeneous* second order linear differential equation. The general solution to these types of differential equations has the form

$$y(x) = e^{\alpha x} \tag{2.2.15}$$

where α is a constant to be determined by the constraints of system. Substituting Equation 2.2.15 into Equation 2.2.14 results in

$$\left(\alpha^2 - k^2\right) y(x) = 0 \tag{2.2.16}$$

For this equation to be satisfied, either

- $\alpha^2 - k^2 = 0$ or
- $y(x) = 0$.

The later is the trivial solution and is ignored and therefore

$$\alpha^2 - k^2 = 0 \tag{2.2.17}$$

so

$$\alpha = \pm k \tag{2.2.18}$$

Hence, there are two solutions to the general Equation 2.2.14, as expected for a second order differential equation (first order differential equations have one solution), which are a result from substituting the α values from Equation 2.2.18 into Equation 2.2.15

$$y(x) = e^{k\,x}$$

$$y(x) = e^{-k\,x}$$

The general solution can then be any linear combination of these two equations

$$y(x) = c_1 e^{k\,x} + c_2 e^{-k\,x} \tag{2.2.19}$$

Example 2.2.1 : General Solution

Solve

$$y'' + 3y' - 4y = 0$$

Solution

The strategy is to search for a solution of the form

$$y = e^{\alpha t}$$

The reason for this is that long ago some geniuses figured this stuff out and it works. Now calculate derivatives

$$y' = \alpha e^{\alpha t}$$

$$y'' = \alpha^2 e^{\alpha t}$$

Substituting into the differential equation gives

$$\alpha^2 e^{\alpha t} + 3(\alpha e^{\alpha t}) - 4(e^{\alpha t}) = 0$$
$$(\alpha^2 + 3\alpha - 4)e^{\alpha t} = 0$$

Now divide by $e^{\alpha t}$ to get

$$\alpha^2 + 3\alpha - 4 = 0$$
$$(\alpha - 1)(\alpha + 4) = 0$$
$$\alpha = 1$$

and

$$\alpha = -4$$

We can conclude that two solutions are

$$y_1 = e^t$$

and

$$y_2 = e^{-4t}$$

Now let

$$L(y) = y'' + 3y' - 4y$$

It is easy to verify that if y_1 and y_2 are solutions to

$$L(y) = 0$$

then

$$y = c_1 y_1 + c_2 y_2$$

is also a solution. More specifically we can conclude that

$$y = c_1 e^t + c_2 e^{-4t}$$

Represents a two dimensional family (vector space) of solutions. Later we will prove that this is the most general description of the solution space.

Example 2.2.2 : Boundary Conditions

Solve

$$y'' - y' - 6y = 0$$

with $y(0) = 1$ and $y'(0) = 2$.

Solution

As before we seek solutions of the form

$$y = e^{rt}$$

Now calculate derivatives

$$y' = re^{rt}$$
$$y'' = r^2 e^{rt}$$

Substituting into the differential equation gives

$$r^2 e^{rt} + (re^{rt}) - 6(e^{rt}) = 0$$
$$(r^2 - r - 6)e^{rt} = 0$$

Now divide by e^{rt} to get

$$r^2 - r - 6 = 0$$
$$(r-3)(r+2) = 0$$

We can conclude that two solutions are

$$y_1 = e^{3t}$$

and

$$y_2 = e^{-2t}$$

We can conclude that

$$y = c_1 e^{3t} + C_2 e^{-2t}$$

Represents a two dimensional family (a "vector space") of solutions. Now use the initial conditions to find that

$$1 = c_1 + c_2$$

We have that

$$y' = 3C_1 e^{3t} - 2C_2 e^{-2t}$$

Plugging in the initial condition with y', gives

$$2 = 3c_1 - 2c_2$$

This is a system of two equations and two unknowns. We can use linear algebra to arrive at

$$c_1 = \frac{4}{5}$$

and

$$C_2 = \frac{1}{5}$$

The final solution is

$$y = \frac{4}{5} e^{3t} + \frac{1}{5} e^{-2t}$$

When $K > 0$, the general solutions of Equations 2.2.7 and 2.2.8 are oscillatory in time and space, respectively, as discussed in the following section.

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2.3: Oscillatory Solutions to Differential Equations

Learning Objectives

- Explore the basis of the oscillatory solutions to the wave equation
- Understand the consequences of boundary conditions on the possible solutions
- Rationalize how satisfying boundary conditions forces quantization (i.e., only solutions with specific wavelengths exist)

The boundary conditions for the string held to zero at both ends argue that $u(x,t)$ collapses to zero at the extremes of the string (Figure 2.3.1).



Figure 2.3.1 : Standing waves in a string (both spatially and temporally). from Wikipedia.

Unfortunately, when $K > 0$, the general solution (Equation 2.2.7) results in a sum of exponential decays and growths that cannot achieve the boundary conditions (except for the trivial solution); hence $K < 0$. This means we must introduce complex numbers due to the $\sqrt{K}$ terms in Equation 2.2.5. So we can rewrite K:

$$K = -p^2 \tag{2.3.1}$$

and Equation 2.2.4b can be

$$\frac{d^2X(x)}{dx^2} + p^2X(x) = 0 \tag{2.3.2}$$

The general solution to differential equations of the form of Equation 2.3.2 is

$$X(x) = Ae^{ipx} + Be^{-ipx} \tag{2.3.3}$$

Example 2.3.1

Verify that Equation 2.3.3 is the general form for differential equations of the form of Equation 2.3.2, which when substituted with Equation 2.3.1 give

$$X(x) = Ae^{ipx} + Be^{-ipx}$$

Solution

Expand the complex exponentials into trigonometric functions via Euler formula ($e^{i\theta} = \cos\theta + i\sin\theta$)

$$X(x) = A\left[\cos(px) + i\sin(px)\right] + B\left[\cos(px) - i\sin(px)\right]$$

collecting like terms

$$X(x) = (A+B)\cos(px) + i(A-B)\sin(px) \tag{2.3.4}$$

Introduce new *complex* constants $c_1 = A + B$ and $c_2 = i(A - B)$ so that the general solution in Equation 2.3.4 can be expressed as oscillatory functions

$$X(x) = c_1\cos(px) + c_2\sin(px) \tag{2.3.5}$$

Now let's apply the boundary conditions from Equation 2.2.7 to determine the constants c_1 and c_2. Substituting the first boundary condition ($X(x=0) = 0$) into the general solutions of Equation 2.3.5 results in

$$\begin{aligned} X(x=0) = c_1\cos(0) + c_2\sin(0) &= 0 \\ c_1 + 0 &= 0 \\ c_1 &= 0 \end{aligned} \tag{2.3.6}$$

and substituting the second boundary condition ($X(x=L) = 0$) into the general solutions of Equation 2.3.5 results in

$$X(x=L) = c_1\cos(pL) + c_2\sin(pL) = 0 \tag{2.3.7}$$

we already know that $c_1 = 0$ from the first boundary condition so Equation 2.3.7 simplifies to

$$c_2\sin(pL) = 0 \tag{2.3.8}$$

Given the properties of sines, Equation 2.3.7 simplifies to

$$pL = n\pi \tag{2.3.9}$$

with $n = 0$ is the *trivial solution* that we ignore so $n = 1, 2, 3....$

$$p = \frac{n\pi}{L} \tag{2.3.10}$$

Substituting Equations 2.3.10 and 2.3.6 into Equation 2.3.5 results in

$$X(x) = c_2\sin\left(\frac{n\pi x}{L}\right)$$

which can simplify to

$$X(x) = c_2\sin(\omega x)$$

with

$$\omega = \frac{n\pi}{L}$$

A similar argument applies to the other half of the *ansatz* ($T(t)$).

Exercise 2.3.1

Given two traveling waves:

$$\psi_1 = \sin(c_1x + c_2t) \quad \text{and} \quad \psi_2 = \sin(c_1x - c_2t)$$

a. Find the wavelength and the wave velocity of ψ_1 and ψ_2
b. Find the following and identify nodes:

$$\psi_+ = \psi_1 + \psi_2 \quad \text{and} \quad \psi_- = \psi_1 - \psi_2$$

Solution a

ψ_1 is a sin function. At every integer $n\pi$ where $n = 0, \pm 1, \pm 2, ...$, a sin function will be zero. Thus, $\psi_1 = 0$ when $c_1 x + c_2 t = \pi n$. Solving for the x, while ignoring trivial solutions:

$$x = \frac{n\pi - c_2 t}{c_1}$$

The velocity of this wave is:

$$\frac{dx}{dt} = -\frac{c_2}{c_1}$$

Similarly for ψ_2. At every integer $n\pi$ where $n = 0, \pm 1, \pm 2, ...$, a sin function will be zero. Thus, $\psi_2 = 0$ when $c_1 x - c_2 t = \pi n$. Solving for x, for ψ_2:

$$x = \frac{n\pi + c_2 t}{c_1}$$

The velocity of this wave is:

$$\frac{dx}{dt} = \frac{c_2}{c_1}$$

The wavelength for each wave is twice the distance between two successive nodes. In other words,

$$\lambda = 2(x_n - x_{n-1}) = \frac{2\pi}{c_1}$$

Solution b

Find $\psi_+ = \psi_1 + \psi_2 \quad \text{and} \quad \psi_- = \psi_1 - \psi_2$.

$$\begin{aligned}
\psi_+ &= \sin(c_1 x + c_2 t) + \sin(c_1 x - c_2 t) \\
&= \sin(c_1 x)\cos(c_2 t) + \cancel{\cos(c_1 x)\sin(c_1 t)} + \sin(c_1 x)\cos(c_2 t) - \cancel{\cos(c_1 x)\sin(c_1 t)} \\
&= 2\sin(c_1 x)\cos(c_2 t)
\end{aligned}$$

This should have a node at every $x = n\pi / c_1$ and

$$\begin{aligned}
\psi_- &= \sin(c_1 x + c_2 t) - \sin(c_1 x - c_2 t) \\
&= \cancel{\sin(c_1 x)\cos(c_2 t)} + \cos(c_1 x)\sin(c_1 t) - \cancel{\sin(c_1 x)\cos(c_2 t)} + \cos(c_1 x)\sin(c_1 t) \\
&= 2\cos(c_1 x)\sin(c_2 t)
\end{aligned}$$

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2.4: The General Solution is a Superposition of Normal Modes

Learning Objectives

- Separate the wave equation into individual spatial and temporal problems and solve them.
- Demonstrate that the general solution can be a superposition of solutions (normal modes)

As discussed previously, the solutions to the string example $u(x,t)$ for all x and t would be assumed to be a product of two functions: $X(x)$ and $T(t)$, where $X(x)$ is a function of only x, not t and $T(t)$ is a function of t, but not x.

$$u(x,t) = X(x)T(t)$$

By substituting the new product solution form into the original wave equation, one can obtain two *ordinary differential equations* (differential equation containing a function or functions of one independent variable and its derivatives). Each differential equation would involve only one of the independent variables (x or t).

Spatial Dependence of the Solution: $X(x)$

The boundary conditions for the string held to zero at both ends argue that $u(x,t)$ collapses to zero at the extremes of the string. Unfortunately, when $K > 0$, the general solution to the wave equation results in a sum of exponential decays and growths that cannot achieve the boundary conditions (except for the trivial solution that $u(x,t) = 0$); hence $K < 0$. This means we must introduce complex numbers due to the $\sqrt{K}$ terms in Equation 2.4.5. So we can rewrite K:

$$K = -p^2 \tag{2.4.1}$$

and Equation 2.4.4b can be

$$\frac{d^2X(x)}{dx^2} + p^2X(x) = 0 \tag{2.4.2}$$

The general solution to differential equations of the form of Equation 2.4.2 is

$$X(x) = Ae^{\sqrt{K}x} + Be^{-\sqrt{K}x} \tag{2.4.3}$$

that when substituted with Equation 2.4.1 give

$$X(x) = Ae^{ipx} + Be^{-ipx}$$

The complex exponentials in Equation 2.4.1 can be expressed as trigonometric functions via Euler formula ($e^{i\theta} = \cos\theta + i\sin\theta$)

$$X(x) = A\left[\cos(px) + i\sin(px)\right] + B\left[\cos(px) - i\sin(px)\right]$$

collecting like terms

$$X(x) = (A+B)\cos(px) + i(A-B)\sin(px) \tag{2.4.4}$$

The general solution in Equation 2.4.4 can be expressed as oscillatory functions by introducing new *complex* constants $C = A + B$ and $D = i(A - B)$:

$$X(x) = C\cos(px) + D\sin(px) \tag{2.4.5}$$

Exercise 2.4.1

Verify that Equation 2.4.3 is the general form for differential equations of the form of Equation 2.4.2.

Answer available at the end of this section.

Now let's apply the boundary conditions from Equation 2.4.5 to determine the constants C and D. Substituting the first boundary condition ($X(x=0)=0$) into the general solutions of Equation 2.4.5 results in

$$\begin{aligned} X(x=0) &= 0 \\ C\cos(0) + D\sin(0) &= 0 \\ C + 0 &= 0 \\ C &= 0 \end{aligned} \tag{2.4.6}$$

and substituting the second boundary condition ($X(x=L)=0$) into the general solutions of Equation 2.4.5 results in

$$X(x=L) = C\cos(pL) + D\sin(pL) = 0 \tag{2.4.7}$$

we already know that $C=0$ from the first boundary condition so Equation 2.4.7 simplifies to

$$D\sin(pL) = 0$$

Given the properties of sines, Equations 2.4.7 simplifies to

$$pL = n\pi$$

with $n=0$ is the *trivial solution* that we ignore so $n=1,2,3....$

$$p = \frac{n\pi}{L} \tag{2.4.8}$$

Substituting Equations 2.4.8 and 2.4.6 into Equation 2.4.5 results in

$$X(x) = D\sin\left(\frac{n\pi x}{L}\right) \tag{2.4.9}$$

Equation 2.4.9 presents a set of solutions to the spatial part of the solution to the wave equation subject to the boundary conditions (Figure 2.4.1). This set of solutions is infinitely large with individual solutions that are distinguished from each other by the n parameter introduced to account for the boundary conditions. This number is an example of a "quantum number" that are ubiquitously in quantum mechanics and are uniquely defined for each system.

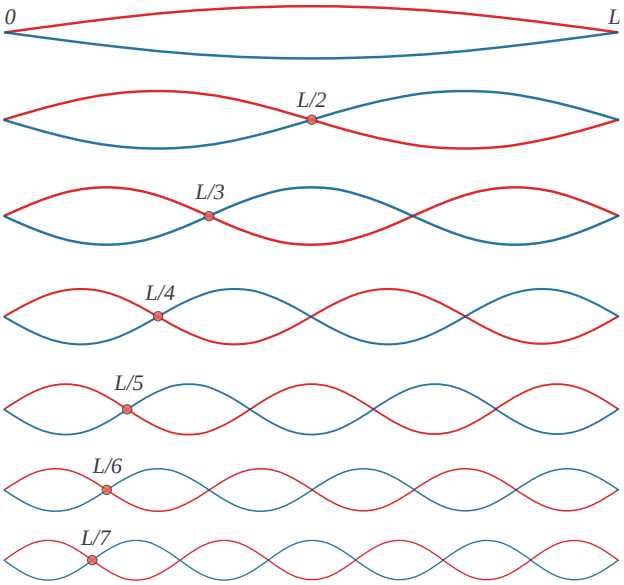


Figure 2.4.1: The first seven $X(x)$ solutions of a vibrating string of length L at the two times of maximum displacement (red and blue). (CC BY-NC; Ümit Kaya via LibreTexts).

Time Dependence of the Solution: $T(t)$

A similar argument applies to the other half of the *ansatz* ($T(t)$) originally proposed for the classical wave equation was obtain from solving Equation 2.4.4a, which qualitatively resembles the original spatial differential equation solved above (Equation 2.4.4b).

$$\frac{d^2T(t)}{dt^2} - Kv^2T(t) = 0$$

However, the constraints extracted from solving spatial dependence apply to the time dependence. When Equations 2.4.1 and 2.4.8 are substituted into Equation 2.4.4a, a more simplified expression is obtained

$$\frac{d^2T(t)}{dt^2} + p^2v^2T(t) = \frac{d^2T(t)}{dt^2} + \left(\frac{nv\pi}{L}\right)^2 T(t) = 0 \tag{2.4.10}$$

Define a new constant: ω_n

$$\omega_n = \left(\frac{nv\pi}{L}\right)$$

and substitute into Equation 2.4.10

$$\frac{d^2T(t)}{dt^2} + \omega_n^2T(t) = 0$$

This is the same functional form of Equation 2.4.2

$$T(t) = E\cos(\omega_n t) + F\sin(\omega_n t) \tag{2.4.11}$$

In contrast to the spatial dependence solution, we have no boundary conditions to use to identify the constants E and F.

The Principle of Superposition

Now let's revisit the original *ansatz* solution to the classical wave equation (Equation 2.4.1), which can be substituted with Equations 2.4.9 and 2.4.11

$$\begin{aligned} u(x,t) &= X(x)T(t) \\ &= \left[D\sin\left(\frac{n\pi x}{L}\right)\right](E\cos(\omega_n t) + F\sin(\omega_n t)) \end{aligned}$$

we can collect constants again with $G = DE$ and $H = DF$ and introduce a n dependence to each since E and F may be n dependence.

$$u_n(x,t) = \underbrace{[G_n\cos(\omega_n t) + H_n\sin(\omega_n t)]}_{\text{temporal solution}}\underbrace{\sin\left(\frac{n\pi x}{L}\right)}_{\text{spatial solution}} \tag{2.4.12}$$

The functions represented in Equation 2.4.12 are set of solutions including both spatial and temporal features that solve the wave equation of a string held tight on two ends.

Linearity of the Wave Equation

The wave equation has a very important property: if we have two solutions to the equation, then the sum of the two is *also* a solution to the equation. It's easy to check this:

$$\frac{\partial^2(f+g)}{\partial x^2} = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 g}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 f}{\partial t^2} + \frac{1}{v^2}\frac{\partial^2 g}{\partial t^2} = \frac{1}{v^2}\frac{\partial^2(f+g)}{\partial t^2}$$

Any differential equation for which this property holds is called *a linear differential equation*. Also note that $af(x,t) + bg(x,t)$ is also a solution to the equation if a, b are constants. So you can add together—superpose—multiples of any two solutions of the wave equation to find a new function satisfying the equation.

The linearity property is easy to interpret *visually*: if you can draw two wave solutions, then at each point on the string simply add the displacement $u_n(x,t)$ of one wave to the other $u_m(x,t)$—the sum of the two waves together is a solution. So, for example, as two traveling waves moving along the string in opposite directions meet each other, the displacement of the string at any point at any instant is just the sum of the displacements it would have had from the two waves singly.



Figure 2.4.2: Interference of Multiple Pulses. ("for non-profit educational purposes."; Tom Walsh via ophysics.com)

This simple addition of the displacements is interference, doubtless because if the waves meeting have displacements in opposite directions, the string will be displaced less than by a single wave. This is also called the ***Principle of Superposition***.

Principle of Superposition

The *Principle of Superposition* is the sum of two or more solutions is also a solution.

Since the wave equation is a linear homogeneous differential equation, the total solution can be expressed as a sum of all

possible solutions described by Equation 2.4.12.

$$u(x,t) = \sum_{n=1}^{\infty} u_n(x,t) \tag{2.4.13}$$

$$= \sum_{n=1}^{\infty} \left(G_n \cos(\omega_n t) + H_n \sin(\omega_n t)\right) \sin\left(\frac{n\pi x}{L}\right) \tag{2.4.14}$$

Each $u_n(x,t)$ solution is called a **normal mode** of the system and can be characterized via their corresponding frequencies $\frac{n\pi}{L}$ with $n = 1, 2, 3....$ The spatial dependence of the first seven normal modes are shown in Figure 2.4.1 and are standing waves. The first term with $n = 1$ is typically called the *fundamental* and each subsequent modes is called an *overtone* or *harmonic*. The temporal dependence of the normal modes is sinusoidal with angular frequencies ω_n that can be expanded to natural frequencies ν_n via

$$\nu_n = \frac{\omega_n}{2\pi} = \frac{nv}{2L} \tag{2.4.15}$$

Hence, as the spatial curvature of the normal mode increases, the temporal oscillation of that mode also increases. This is a common trait in quantum mechanical systems and is a direct consequence of the wave equation.

Answers

In order to show that

$$X(x) = Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x} \tag{2.4.16}$$

is a general solution to the differential equation

$$\frac{d^2X(x)}{dx^2} + p^2X(x) = 0.$$

We then have to take the second derivative of Equation 2.4.16 and substitute it and the original function into the appropriate locations in Equation 2.4.3 and verify that it does in fact equal 0.

First we have to take the first and then second derivative of Equation 2.4.16

$$\frac{d}{dx}\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) = \sqrt{k}Ae^{\sqrt{k}x} - \sqrt{k}Be^{-\sqrt{k}x}$$

$$\frac{d^2}{dx^2}\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) = kAe^{\sqrt{k}x} + kBe^{-\sqrt{k}x}$$

Now that we have the second derivative of Equation 2.4.16 we plug the relevant values into Equation 2.4.2

$$\frac{d^2X(x)}{dx^2} + p^2X(x) = 0$$

$$kAe^{\sqrt{k}x} + kBe^{-\sqrt{k}x} + p^2\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) \stackrel{?}{=} 0$$

We are given in Equation 2.4.2 that

$$k = -p^2$$

So

$$p^2 = -k$$

Now we can plug that into our differential equation to simplify

$$kAe^{\sqrt{k}x} + kBe^{-\sqrt{k}x} - k\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) \stackrel{?}{=} 0$$

$$\cancel{kAe^{\sqrt{k}x}} + \cancel{kBe^{-\sqrt{k}x}} - \cancel{kAe^{\sqrt{k}x}} - \cancel{kBe^{-\sqrt{k}x}} \stackrel{\checkmark}{=} 0$$

As all of these terms cancel to equal 0, we prove that the solution given is a general solution to the differential equation. It is important to remember though that it is not the only solution to the differential equation.

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2.5: A Vibrating Membrane

Learning Objectives

- To apply the wave equations to a two-dimensional membrane (rectangles and circles)
- To recognize the possible geometries of a nodes in two-dimensional systems

So far, we've looked at waves in one dimension, traveling along a string or sound waves going down a narrow tube. However, waves in higher dimensions than one are very familiar—water waves on the surface of a pond, or sound waves moving out from a source in three dimensions. It is pleasant to find that these waves in higher dimensions satisfy wave equations which are a very natural extension of the one we found for a string, and—very important—they also satisfy the *Principle of Superposition*, in other words, if waves meet, you just add the contribution from each wave. In the next two paragraphs, we go into more detail, but this Principle of Superposition is the crucial lesson.

The Wave Equation and Superposition in More Dimensions

What happens in higher dimensions? Let's consider two dimensions, for example waves in an elastic sheet like a drumhead. If the rest position for the elastic sheet is the (x, y) plane, so when it's vibrating it's moving up and down in the z-direction, its configuration at any instant of time is a function. $u(x, y, t)$

In fact, we could do the same thing we did for the string, looking at the total forces on a little bit and applying Newton's Second Law. In this case that would mean taking one little bit of the drumhead, and instead of a small stretch of string with tension pulling the two ends, we would have a small *square* of the elastic sheet, with tension pulling all around the edge. Remember that the net force on the bit of string came about because the string was curving around, so the tensions at the opposite ends tugged in slightly different directions, and did not cancel. The $\frac{\partial^2}{\partial x^2}$ term measured that curvature, the rate of change of slope. In two dimensions, thinking of a small square of the elastic sheet, things are more complicated. Visualize the bit of sheet to be momentarily like a tiny patch on a balloon, you'll see it curves in two directions, and tension forces must be tugging all around the edges. The total force on the little square comes about because the tension forces on opposite sides are out of line if the surface is curving around, now we have to add *two* sets of almost-opposite forces from the two pairs of sides. The math is now shown here, but it is at least plausible that the equation is:

$$\frac{\partial^2 u(x,y,t)}{\partial x^2} + \frac{\partial^2 u(x,y,t)}{\partial y^2} = \frac{1}{v^2}\frac{\partial^2 u(x,y,t)}{\partial t^2} \tag{2.5.1}$$

The physics of this equation is that the acceleration of a tiny bit of the sheet comes from out-of-balance tensions caused by the sheet curving around in *both* the *x*- and *y*-directions, this is why there are the two terms on the left hand side.

And, going to three dimensions is easy: add one more term to give

$$\frac{\partial^2 u(x,y,,z,t)}{\partial x^2} + \frac{\partial^2 u(x,y,z,t)}{\partial y^2} + \frac{\partial^2 u(x,y,z,t)}{\partial z^2} = \frac{1}{v^2}\frac{\partial^2 u(x,y,z,t)}{\partial t^2} \tag{2.5.2}$$

This sum of partial differentiations in space is so common in physics that there's a shorthand:

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2}, \frac{\partial^2}{\partial y^2}, \frac{\partial^2}{\partial z^2}\right)$$

so Equation 2.5.2 can be more easily written as

$$\nabla^2 u(x,y,z,t) = \frac{1}{v^2}\frac{\partial^2 u(x,y,z,t)}{\partial t^2}$$

Just as we found in one dimension traveling harmonic waves (no boundary conditions)

$$u(x,t) = A\sin(kx - \omega t)$$

with $\omega = \nu k$, you can verify that the *three*-dimensional equation has harmonic solutions

$$u(x, y, z, t) = A \sin(k_x x + k_x + k_z z - \omega t)$$

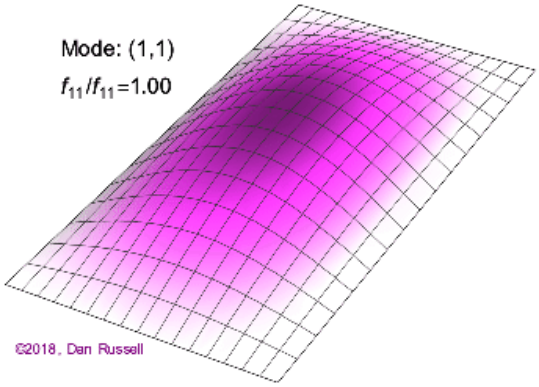
with $\omega = \nu|\vec{k}|$ where $|k| = \sqrt{k_x^2 + k_y^2 + k_z^2}$.

$\vec{k}$ is a vector in the direction the wave is moving. The electric and magnetic fields in a radio wave or light wave have just this form (or, closer to the source, a very similar equivalent expression for outgoing spheres of waves, rather than plane waves).

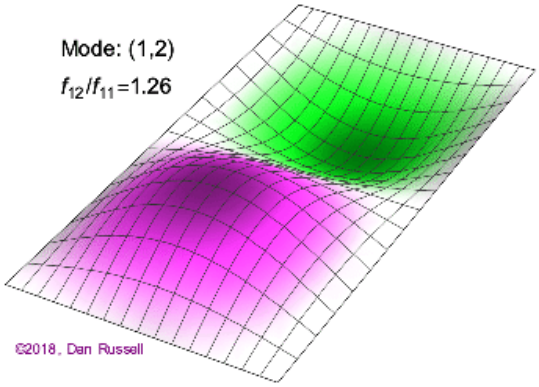
> It's important to realize that the 2D wave equation (Equation 2.5.1) is still a ***linear*** equation, so the Principle of Superposition still holds. If two waves on an elastic sheet, or the surface of a pond, meet each other, the result at any point is given by simply adding the displacements from the individual waves. We'll begin by thinking about waves propagating freely in two and three dimensions, than later consider waves in restricted areas, such as a drum head.

Vibrational Modes of a Rectangular Membrane

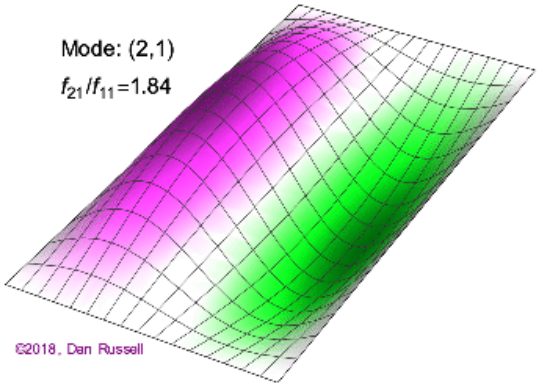
A one-dimensional wave does not have a choice in how it propagates: it just moves along the line (well, it could get partly reflected by some change in the line and part of it go backwards). However, when we go to higher dimensions, how a wave disturbance starting in some localized region spreads out is far from obvious. But we can begin by recalling some simple cases: dropping a pebble into still water causes an outward moving circle of ripples. If we grant that light is a wave, we notice a beam of light changes direction on going from air into glass. Of course, it is not immediately evident that light *is* a wave: we'll talk a lot more about that later. A few solutions (both temporal and spatials) are shown below together with their quantum numbers (n_x and n_y).



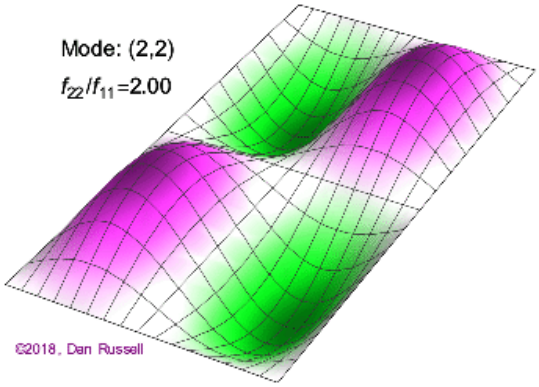
The ($n_x = 1$, $n_y = 1$) Solution



The ($n_x = 1$, $n_y = 2$) Solution



The ($n_x = 2$, $n_y = 1$) Solution



The ($n_x = 2$, $n_y = 2$) Solution

Figure 2.5.1: Select Vibrational Modes of a Rectangular Membrane. Animations courtesy of Dr. Dan Russell via Grad. Prog. Acoustics, Penn State).

Solving for the function $u(x, y, t)$ in a vibrating, rectangular membrane is done in a similar fashion by separation of variables, and setting boundary conditions. The solved function is very similar, where

$$u(x, y, t) = A_{nm} \cos(\omega_{nm} t + \phi_{nm}) \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \tag{2.5.3}$$

where

- a is the length of the rectangular membrane and b is the width, and
- n_x and n_y are two quantum numbers (one in each dimension).

As with the solutions to 1-D wave equations, a **node** is a point (or line) on a structure that does not move while the rest of the

structure is vibrating.

Example 2.5.1: Nodal Geometries in Rectangular Membranes

For the following 2-D solutions in Figure 2.5.1, how many nodes are there, what is the geometry and how would you characterize them?

a. $(n_x = 1, n_y = 1$
b. $(n_x = 2, n_y = 1$

Solution a

The $(n_x = 1, n_y = 1$ solution in Figure 2.5.1 has zero nodes. That is, no spot in the membrane (other than the boundaries) is not moving during the motion of the membrane.

Solution b

The $(n_x = 2, n_y = 1$ solution in Figure 2.5.1 has one node. It is a line at half the length of the x direction and extends over the entire length of the y direction.

Exercise 2.5.1

For the $(n_x = 2, n_y = 2$ solution to a rectangular membrane in Figure 2.5.1 : how many nodes are there, what is the geometry and how would you characterize them?

Answer available at the end of this section.

Vibrational Modes of a Circular Membrane

The basic principles of a vibrating rectangular membrane applies to other 2-D members including circular membranes. However, the mathematics and solutions are a bit more complicated. The solutions are best represented in polar notation (instead of rectangular like in Equation 2.5.3) and have the following functional form

$$u(r, \theta, t) = J_m(\lambda_{mn} r) \cos m\theta \cos c\lambda_{mn} t$$

where J_m are Bessel functions (these are oscillatory functions) and λ are constants. This system has two quantum numbers (m and n) that serve the same function as n_x and n_y do in the rectangular membranes. In the animations in Figure 2.5.2 , the nodal diameters and circles show up as white regions that do not oscillate, while the red and blue regions indicate positive and negative displacements.

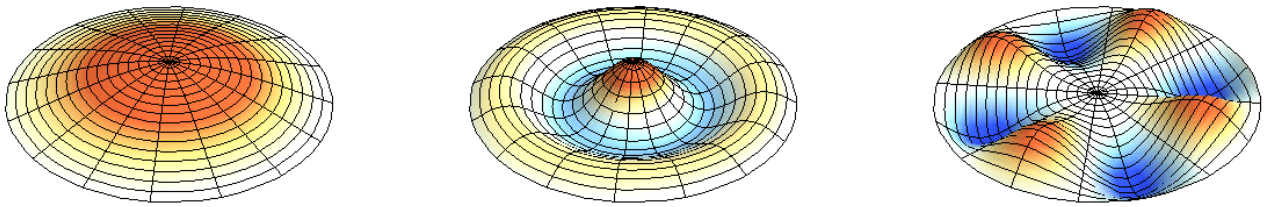


Figure 2.5.2: Select Vibrational Modes of a Circular Membrane. (CC BY-SA-ND 4.0; Dan Russell, via Grad. Prog. Acoustics, Penn State.

Figure 2.5.2 (left) shows the fundamental mode shape for a vibrating circular membrane, while the other two modes are excited

modes with more complex nodal character.

Exercise 2.5.2

How many nodes are there in the three solutions for a circular membrane in Figure 2.5.2, what are their geometries, and how would you characterize them?

Answer available at the end of this section.

Answers

Exercise 2.5.1

There are two nodes. They are lines and one is at half the length of the x direction and extends over the entire length of the y direction and one if and one is at half the length of the y direction and extends over the entire length of the x direction

Exercise 2.5.2

(left) zero nodes

(middle) two nodes. They are circular at approximately 1/3 and 2/3 the radius (these are radial nodes = at fixed radii)

(right) four nodes. They are lines at 45° angle from the center (these are angular nodes = at fixed angles).

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2.E: The Classical Wave Equation (Exercises)

Solutions to select questions can be found online.

2.1A

Find the general solutions to the following differential equations:

a. $\frac{d^2y}{dx^2} - 4y = 0$
b. $\frac{d^2y}{dx^2} - 3\frac{dy}{dx} - 54y = 0$
c. $\frac{d^2y}{dx^2} + 9y = 0$

2.1B

Find the general solutions to the following differential equations:

a. $\frac{d^2y}{dx^2} - 16y = 0$
b. $\frac{d^2y}{dx^2} - 6\frac{dy}{dx} + 27y = 0$
c. $\frac{d^2y}{dx^2} + 100y = 0$

2.1C

Find the general solutions to the following differential equations:

a. $\frac{dy}{dx} - 4\sin(x)y = 0$
b. $\frac{d^2y}{dx^2} - 5\frac{dy}{dx} + 6y = 0$
c. $\frac{d^2y}{dx^2} = 0$

2.2A

Practice solving these first and second order homogeneous differential equations with given boundary conditions:

a. $\frac{dy}{dx} = ay$ with $y(0) = 11$
b. $\frac{d^2y}{dt^2} = ay$ with $y(0) = 6$ and $y'(0) = 4$
c. $\frac{d^2y}{dt^2} + \frac{dy}{dt} - 42y = 0$ with $y(0) = 2$ and $y'(0) = 0$

2.3A

Prove that $x(t) = \cos(\theta)$ oscillates with a frequency

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

Prove that $x(t) = \cos(\theta)$ also has a period

$$T = 2\pi\sqrt{\frac{m}{k}}$$

where k is the force constant and m is mass of the body.

2.3B

Try to show that

$$x(t) = \sin(\omega t)$$

oscillates with a frequency

$$\nu = \omega/2\pi$$

Explain your reasoning. Can you give another function of x(t) that have the same frequency.

2.3C

Which two functions oscillate with the same frequency?

a. $x(t) = \cos(\omega t)$
b. $x(t) = \sin(2\omega t)$
c. $x(t) = A\cos(\omega t) + B\sin(\omega t)$

2.3D

Prove that $x(t) = \cos(\omega(t))$ oscillates with a frequency

$$\nu = \frac{\omega}{2\pi}.$$

Prove that $x(t) = A\cos(\omega(t) + B\sin(\omega(t))$ oscillates with the same frequency:

$$\nu = \frac{\omega}{2\pi}.$$

2.4

Show that the differential equation:

$$\frac{d^2y}{dx^2} + y(x) = 0$$

has a solution

$$y(x) = 2\sin x + \cos x$$

2.7

For a classical harmonic oscillator, the displacement is given by

$$\xi(t) = v_0\sqrt{\frac{m}{k}}\sin\sqrt{\frac{k}{m}}t$$

where $\xi = x - x_0$. Derive an expression for the velocity as a function of time, and determine the times at which the velocity of the oscillator is zero.

2.11

Verify that

$$Y(x,t) = A\sin\left(\frac{2\pi}{\lambda}(x - vt)\right)$$

has a frequency $\nu = v/\lambda$ and wavelength λ traveling right with a velocity v.

2.13A

Explain (in words) how to expand the Hamiltonian into two dimensions and use it solve for the energy

2.13B

Given that the Schrödinger equation for a two-dimensional box, with sides a and b, is

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{(8\pi^2 mE)}{h^2}\Psi(x,y) = 0$$

and it has the boundary conditions of

$$\Psi(0,y) = \Psi(a,y) = 0 \text{ and } \Psi(o,x) = \Psi(x,b) = 0$$

for all x and y values, show that

$$E_{2,2} = \left(\frac{h^2}{2ma^2}\right) + \left(\frac{h^2}{2mb^2}\right).$$

2.14

Explain, in words, how to expand the Schrödinger Equations into a three-dimensional box

2.18

Solving for the differential equation for a pendulum gives us the following equation,

$$\phi(x) = c_1 \cos\sqrt{\frac{g}{L}} + c_2 \sin\sqrt{\frac{g}{L}}$$

Assuming $c_1 = 2$, $c_3 = 5$, $g = 7$ and $L = 3$, what is the position of the pendulum initially? Does this make sense in the real world. Why or why not? (We can ignore units for this problem).

2.23

Consider a Particle of mass m in a one-dimensional box of length a. Its average energy is given by

$$\langle E\rangle = \frac{1}{2m}\langle p^2\rangle$$

Because

$$\langle p\rangle \ = 0$$

$$\langle p^2\rangle = \sigma_p^2$$

where σ_p can be called the uncertainty in p. Using the Uncertainty Principle, show that the energy must be at least as large as $\hbar/8ma^2$ because σ_x, the uncertainty in x, cannot be larger than a.

2.33

Prove $y(x,t) = A\cos[2\pi/\lambda(x - vt)]$ is a wave traveling to the right with velocity v, wavelength λ, and period λ/v.

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3: THE SCHRÖDINGER EQUATION AND A PARTICLE IN A BOX

The particle in a box model (also known as the infinite potential well or the infinite square well) describes a particle free to move in a small space surrounded by impenetrable barriers. The model is mainly used as a hypothetical example to illustrate the differences between classical and quantum systems. In classical systems, for example a ball trapped inside a large box, the particle can move at any speed within the box and it is no more likely to be found at one position than another. However, when the well becomes very narrow (on the scale of a few nanometers), quantum effects become important. The particle may only occupy certain positive energy levels. The particle in a box model provides one of the very few problems in quantum mechanics which can be solved analytically, without approximations. This means that the observable properties of the particle (such as its energy and position) are related to the mass of the particle and the width of the well by simple mathematical expressions. Due to its simplicity, the model allows insight into quantum effects without the need for complicated mathematics. It is one of the first quantum mechanics problems taught in undergraduate physics courses, and it is commonly used as an approximation for more complicated quantum systems.

3.1: The Schrödinger Equation

3.2: Linear Operators in Quantum Mechanics

3.3: The Schrödinger Equation is an Eigenvalue Problem

3.4: Wavefunctions Have a Probabilistic Interpretation

3.5: The Energy of a Particle in a Box is Quantized

3.6: Wavefunctions Must Be Normalized

3.7: The Average Momentum of a Particle in a Box is Zero

3.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

3.9: A Particle in a Three-Dimensional Box

3.E: The Schrödinger Equation and a Particle in a Box (Exercises)

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3.1: The Schrödinger Equation

Learning Objectives

- To be introduced to the general properties of the Schrödinger equation and its solutions.

De Broglie's doctoral thesis, defended at the end of 1924, created a lot of excitement in European physics circles. Shortly after it was published in the fall of 1925 Pieter Debye, Professor of Theoretical Physics at Zurich and Einstein's successor, suggested to Erwin Schrödinger that he give a seminar on de Broglie's work. Schrödinger gave a polished presentation, but at the end Debye remarked that he considered the whole theory rather childish: why should a wave confine itself to a circle in space? It wasn't as if the circle was a waving circular string, real waves in space diffracted and diffused, in fact they obeyed three-dimensional wave equations, and that was what was needed. This was a direct challenge to Schrödinger, who spent some weeks in the Swiss mountains working on the problem and constructing his equation. There is no rigorous derivation of Schrödinger's equation from previously established theory, but it can be made very plausible by thinking about the connection between light waves and photons, and construction an analogous structure for de Broglie's waves and electrons (and later, other particles).

The Schrödinger Equation: A Better Approach

While the Bohr model is able to predict the allowed energies of any single-electron atom or cation, it by no means, a general approach. Moreover, it relies heavily on classical ideas, clumsily grafting quantization onto an essentially classical picture, and therefore, provides no real insights into the true quantum nature of the atom. Any rule that might be capable of predicting the allowed energies of a quantum system must also account for the *wave-particle duality* and implicitly include a wave-like description for particles. Nonetheless, we will attempt a heuristic argument to make the result at least plausible. In classical electromagnetic theory, it follows from Maxwell's equations that each component of the electric and magnetic fields in vacuum is a solution of the 3-D wave equation for electromagnetic waves:

$$\nabla^2\Psi(x,y,z,t) - \frac{1}{c^2}\frac{\partial^2\Psi(x,y,z,t)}{\partial t^2} = 0 \tag{3.1.1}$$

The wave equation in Equation 3.1.1 is the three-dimensional analog to the wave equation presented earlier (Equation 2.1.1) with the velocity fixed to the known speed of light: c. Instead of a partial derivative $\dfrac{\partial^2}{\partial x^2}$ in one dimension, the Laplacian (or "del-squared") operator is introduced:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{3.1.2}$$

Corresponding, the solution to this 3D equation wave equation is a function of *four* independent variables: x, y, z, and t and is generally called the **wavefunction** ψ.

We will attempt now to create an analogous equation for de Broglie's matter waves. Accordingly, let us consider a only 1-dimensional wave motion propagating in the *x*-direction. At a given instant of time, the form of a wave might be represented by a function such as

$$\Psi(x) = f\left(\frac{2\pi x}{\lambda}\right) \tag{3.1.3}$$

where $f(\theta)$ represents a sinusoidal function such as $\sin\theta$, $\cos\theta$, $e^{i\theta}$, $e^{-i\theta}$ or some linear combination of these. The most suggestive form will turn out to be the complex exponential, which is related to the sine and cosine by Euler's formula

$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta \tag{3.1.4}$$

Each of the above is a periodic function, its value repeating every time its argument increases by 2π. This happens whenever x increases by one wavelength λ. At a fixed point in space, the time-dependence of the wave has an analogous structure:

$$T(t) = f(2\pi\nu t) \tag{3.1.5}$$

where ν gives the number of cycles of the wave per unit time. Taking into account both x and t dependence, we consider a wavefunction of the form

$$\Psi(x,t) = exp\left[2\pi i\left(\frac{x}{\lambda} - \nu t\right)\right] \tag{3.1.6}$$

representing waves traveling from left to right. Now we make use of the Planck formula ($E = h\nu$) and de Broglie formulas ($p = \frac{h}{\lambda}$) to replace ν and λ by their particle analogs. This gives

$$\Psi(x,t) = \exp\left[\frac{i(px - Et)}{\hbar}\right] \tag{3.1.7}$$

where

$$\hbar \equiv \frac{h}{2\pi} \tag{3.1.8}$$

Since Planck's constant occurs in most formulas with the denominator 2π, the $\hbar$ symbol was introduced by Paul Dirac. Equation 3.1.5 represents in some way the wavelike nature of a particle with energy E and momentum p. The time derivative of Equation 3.1.7 gives

$$\frac{\partial\Psi}{\partial t} = -\left(\frac{iE}{\hbar}\right)\exp\left[\frac{i(px - Et)}{\hbar}\right] \tag{3.1.9}$$

Thus from a simple comparison of Equations 3.1.7 and 3.1.9

$$i\hbar\frac{\partial\Psi}{\partial t} = E\Psi \tag{3.1.10}$$

or analogously differentiation of Equation 3.1.9 with respect to x

$$-i\hbar\frac{\partial\Psi}{\partial x} = p\Psi \tag{3.1.11}$$

and then the second derivative

$$-\hbar^2\frac{\partial^2\Psi}{\partial x^2} = p^2\Psi \tag{3.1.12}$$

The energy and momentum for a *nonrelativistic* free particle (i.e., all energy is kinetic with no potential energy involved) are related by

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{3.1.13}$$

Substituting Equations 3.1.12 and 3.1.10 into Equation 3.1.13 shows that $\Psi(x,t)$ satisfies the following partial differential equation

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} \tag{3.1.14}$$

Equation 3.1.14 is the applicable differential equation describing the wavefunction of a *free particle* that is not bound by any external forces or equivalently not in a region where its potential energy $V(x,t)$ varies.

For a particle with a non-zero potential energy $V(x)$, the total energy E is then a sum of kinetics and potential energies

$$E = \frac{p^2}{2m} + V(x) \tag{3.1.15}$$

we postulate that Equation 3.1.3 for matter waves can be generalized to

$$\underbrace{i\hbar\frac{\partial\Psi(x,t)}{\partial t}=\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\Psi(x,t)}_{\text{time-dependent Schrödinger equation in 1D}} \tag{3.1.16}$$

For matter waves in three dimensions, Equation 3.1.6 is then expanded

$$\underbrace{i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\Psi(\vec{r},t)}_{\text{time-dependent Schrödinger equation in 3D}} \tag{3.1.17}$$

Here the potential energy and the wavefunctions Ψ depend on the three space coordinates x, y, z, which we write for brevity as $\vec{r}$. Notice that the potential energy is assumed to depend on position only and not time (i.e., particle motion). This is applicable for conservative forces that a potential energy function $V(\vec{r})$ can be formulated.

The Laplacian Operator

The three second derivatives in parentheses together are called the Laplacian operator, or del-squared,

$$\begin{aligned}\nabla^2 &= \nabla\cdot\nabla \\ &= \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\end{aligned} \tag{3.1.18}$$

with the del operator,

$$\nabla=\left(\vec{x}\frac{\partial}{\partial x}+\vec{y}\frac{\partial}{\partial y}+\vec{z}\frac{\partial}{\partial z}\right) \tag{3.1.19}$$

Remember from basic calculus that when the del operator is direclty operates on a field (e.g, $\nabla f(x,y,x)$, it denotes the gradient (i.e, the locally steepest slope) of the field. The symbols with arrows in Equation 3.1.19 are unit vectors.

Equation 3.1.17 is the *time-dependent Schrödinger* equation describing the wavefunction amplitude $\Psi(\vec{r},t)$ of matter waves associated with the particle within a specified potential $V(\vec{r})$. Its formulation in 1926 represents the start of modern quantum mechanics (Heisenberg in 1925 proposed another version known as matrix mechanics).

For *conservative* systems, the energy is a constant, and the time-dependent factor from Equation 3.1.7 can be separated from the space-only factor (via the *Separation of Variables* technique discussed in Section 2.2)

$$\Psi(\vec{r},t)=\psi(\vec{r})e^{-iEt/\hbar} \tag{3.1.20}$$

where $\psi(\vec{r})$ is a wavefunction dependent (or time-independent) wavefuction that only depends on space coordinates. Putting Equation 3.1.20 into Equation 3.1.17 and cancelling the exponential factors, we obtain the time-independent Schrödinger equation:

$$\underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\psi(\vec{r})=E\psi(\vec{r})}_{\text{time-independent Schrödinger equation}} \tag{3.1.21}$$

The overall form of the Equation 3.1.21 is not unusual or unexpected as it uses the principle of the **conservation of energy**. Most of our applications of quantum mechanics to chemistry will be based on this equation (with the exception of spectroscopy). The terms of the time-independent Schrödinger equation can then be interpreted as total energy of the system, equal to the system kinetic energy plus the system potential energy. In this respect, it is just the same as in classical physics.

Time Dependence to the Wavefunctions

Notice that the wavefunctions used with the time-independent Schrödinger equation (i.e., $\psi(\vec{r})$) do not have explicit t dependences like the wavefunctions of time-dependent analog in Equation 3.1.17 (i.e., $\Psi(\vec{r},t)$). That does **not imply** that there is no time dependence to the wavefunction. Equation 3.1.20 argues that the time-dependent (i.e., full spatial and temporal) wavefunction ($\Psi(\vec{r},t)$) differs from from the time-independent (i.e., spatial only) wavefunction $\psi(\vec{r})$ by a "phase factor" of constant magnitude. Using the Euler relationship in Equation 3.1.4, the total wavefunction above can be expanded

$$\Psi(\vec{r},t) = \psi(\vec{r})\left(\cos\frac{Et}{\hbar} - i\,\sin\frac{Et}{\hbar}\right) \tag{3.1.22}$$

This means the total wavefunction has a **complex behavior** with a real part and an imaginary part. Moreover, using the trigonometry identity $\sin(\theta) = \cos(\theta - \pi/2)$ Equation 3.1.22 can further simplified to

$$\Psi(\vec{r},t) = \psi(\vec{r})\cos\left(\frac{Et}{\hbar}\right) - i\psi(\vec{r})\cos\left(\frac{Et}{\hbar} - \frac{\pi}{2}\right)$$

This shows that both the real and the imaginary components of the total wavefunction oscillate, the imaginary part of the total wavefunction oscillates **out of phase** by $\frac{\pi}{2}$ with respect to the real part.

Note that while all wavefunctions have a time-dependence, that dependence may not impact in simple quantum problems as the next sections discuss and can often be ignored.

Before we embark on this, however, let us pause to comment on the validity of quantum mechanics. Despite its weirdness, its abstractness, and its strange view of the universe as a place of randomness and unpredictability, quantum theory has been subject to intense experimental scrutiny. It has been found to agree with experiments to better than $10^{-10}\%$ for all cases studied so far. When the Schrödinger Equation is combined with a quantum description of the electromagnetic field, a theory known as *quantum electrodynamics*, the result is one of the most accurate theories of matter that has ever been put forth. Keeping this in mind, let us forge ahead in our discussion of the quantum universe and how to apply quantum theory to both model and real situations.

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3.2: Linear Operators in Quantum Mechanics

Learning Objectives

- Classical-Mechanical quantities are represented by linear operators in Quantum Mechanics
- Understand that "algebra" of scalars and functions do not always to operators (specifically the commutative property)

The bracketed object in the time-independent Schrödinger Equation (in 1D)

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{3.2.1}$$

is called an *operator*. An operator is a generalization of the concept of a function applied to a function. Whereas a function is a rule for turning one number into another, an operator is a rule for turning one function into another. For the time-independent Schrödinger Equation, the operator of relevance is the Hamiltonian operator (often just called the Hamiltonian) and is the most ubiquitous operator in quantum mechanics.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})$$

We often (but not always) indicate that an object is an operator by placing a 'hat' over it, eg, $\hat{H}$. So time-independent Schrödinger Equation can then be simplified from Equation 3.2.1 to

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \tag{3.2.2}$$

Equation 3.2.2 says that the Hamiltonian operator operates on the wavefunction to produce the energy, which is a scalar (i.e., a number, a quantity and observable) times the wavefunction. Such an equation, where the operator, operating on a function, produces a constant times the function, is called an **eigenvalue equation**. The function is called an eigenfunction, and the resulting numerical value is called the eigenvalue. Eigen here is the German word meaning self or own. We will discuss this in detail in later Sections.

Fundamental Properties of Operators

Most properties of operators are straightforward, but they are summarized below for completeness.

1. The sum and difference of two operators $\hat{A}$ and $\hat{B}$ are given by
$$(\hat{A} \pm \hat{B})f = \hat{A}f \pm \hat{B}f$$
2. The product of two operators is defined by
$$\hat{A}\hat{B}f \equiv \hat{A}[\hat{B}f]$$
3. Two operators are equal if
$$\hat{A}f = \hat{B}f$$
for **all** functions f.
4. The identity operator $\hat{1}$ does nothing (or multiplies by 1)
$$\hat{1}f = f$$
5. The n-th power of an operator $\hat{A}^n$ is defined as n successive applications of the operator, e.g.
$$\hat{A}^2 f = \hat{A}\hat{A}f$$
6. The *associative law* holds for operators
$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$$

7. The *commutative law* does **not** generally hold for operators. In general, but not always,

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}. \tag{3.2.3}$$

To help identify if the inequality in Equation 3.2.3 holds for any two specific operators, we define the commutator.

Definition: The Commutator

It is convenient to define the **commutator** of $\hat{A}$ and $\hat{B}$

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

If $\hat{A}$ and $\hat{B}$ commute, then

$$[\hat{A}, \hat{B}] = 0.$$

If the commutator is not zero, the order of operating matters and the operators are said to "not commute." Moreover, this property applies

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}].$$

Linear Operators

The action of an operator that turns the function $f(x)$ into the function $g(x)$ is represented by

$$\hat{A}f(x) = g(x) \tag{3.2.4}$$

The most common kind of operator encountered are *linear operators* which satisfies the following two conditions:

$$\underset{\text{Condition A}}{\hat{O}(f(x) + g(x)) = \hat{O}f(x) + \hat{O}g(x)} \tag{3.2.5}$$

and

$$\underset{\text{Condition B}}{\hat{O}cf(x) = c\hat{O}f(x)} \tag{3.2.6}$$

where

- $\hat{O}$ is a linear operator,
- c is a constant that can be a complex number ($c = a + ib$), and
- $f(x)$ and $g(x)$ are functions of x

If an operator fails to satisfy either Equations 3.2.5 or 3.2.6 then it is not a linear operator.

Example 3.2.1

Is this operator $\hat{O} = -i\hbar\dfrac{d}{dx}$ linear?

Solution

To confirm is an operator is linear, both conditions in Equation 3.2.6 must be demonstrated.

Condition A (Equation 3.2.5):

$$\hat{O}(f(x)+g(x)) = -i\hbar\frac{d}{dx}\left(f(x)+g(x)\right)$$

From basic calculus, we know that we can use the **sum rule for differentiation**

$$\begin{aligned}\hat{O}(f(x)+g(x)) &= -i\hbar\frac{d}{dx}f(x) - i\hbar\frac{d}{dx}g(x)\\ &= \hat{O}f(x)+\hat{O}g(x) \quad \checkmark\end{aligned}$$

Condition A is confirmed. Does Condition B (Equation 3.2.6) hold?

$$\hat{O}cf(x) = -i\hbar\frac{d}{dx}cf(x)$$

Also from basic calculus, this can be factored out of the derivative

$$\begin{aligned}\hat{O}cf(x) &= -ci\hbar\frac{d}{dx}f(x)\\ &= c\hat{O}f(x) \quad \checkmark\end{aligned}$$

Yes. This operator is a linear operator (this is the linear momentum operator).

Exercise 3.2.1

Confirm if the square root operator $\sqrt{f(x)}$ linear or not?

Answer available at the end of this section.

The most operators encountered in quantum mechanics are *linear operators*.

Hermitian Operators

An important property of operators is suggested by considering the Hamiltonian for the particle in a box:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Let $f(x)$ and $g(x)$ be arbitrary functions which obey the same boundary values as the eigenfunctions of $\hat{H}$ (e.g., they vanish at $x = 0$ and $x = a$). Consider the integral

$$\int_0^a f(x)\,\hat{H}\,g(x)\,\mathrm{d}x = -\frac{\hbar^2}{2m}\int_0^a f(x)\,g''(x)\,\mathrm{d}x$$

Now, using integration by parts,

$$\int_0^a f(x)\,g''(x)\,\mathrm{d}x = -\int_0^a f'(x)\,g'(x)\,\mathrm{d}x + \left.f(x)\,g'(x)\right|_0^a \tag{3.2.7}$$

The boundary terms vanish by the assumed conditions on f and g. A second integration by parts transforms Equation 3.2.7 to

$$\int_0^a f''(x)\,g(x)\,\mathrm{d}x - \left.f'(x)\,g(x)\right|_0^a$$

It follows therefore that

$$\int_0^a f(x)\,\hat{H}\,g(x)\,\mathrm{d}x = \int_0^a g(x)\,\hat{H}\,f(x)\,\mathrm{d}x$$

An obvious generalization for complex functions will read

$$\int_0^a f^*(x)\,\hat{H}\,g(x)\,\mathrm{d}x = \left(\int_0^a g^*(x)\,\hat{H}\,f(x)\,\mathrm{d}x\right)^*$$

In mathematical terminology, an operator $\hat{A}$ for which

$$\int f^*\,\hat{A}\,g\,\mathrm{d}\tau = \left(\int g^*\,\hat{A}\,f\,\mathrm{d}\tau\right)^*$$

for all functions f and g which obey specified boundary conditions is classified as *Hermitian* or *self-adjoint*. Evidently, the Hamiltonian is a **Hermitian operator**. It is postulated that *all* quantum-mechanical operators that represent dynamical variables are Hermitian. The term is also used for specific times of matrices in linear algebra courses.

> *All* quantum-mechanical operators that represent dynamical variables are Hermitian.

Answers

To confirm is an operator is linear, both conditions in Equations 3.2.5 and 3.2.6 must be demonstrated. Let's look first at Condition B.
Does Condition B (Equation 3.2.6) hold?

$$\hat{O}cf(x) = c\hat{O}f(x)$$
$$\sqrt{cf(x)} \neq c\sqrt{f(x)}$$

Condition B does not hold, therefore the square root operator is not linear.

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3.3: The Schrödinger Equation is an Eigenvalue Problem

Learning Objectives

- To recognize that each quantum mechanical observable is determined by solve by an eigenvalue problem with different operators for different observable
- Confirm if a specific wavefunction is an eigenfunction of a specific operation and extract the corresponding obserable (the eigenvalue)
- To recognize that the Schrödinger equation, just like all measurable, is also an eigenvalue problem with the eigenvalue ascribed to total energy
- Identity and manipulate several common quantum mechanical operators

As per the definition, an operator acting on a function gives another function, however a special case occurs when the generated function is proportional to the original

$$\hat{A}\psi \propto \psi \tag{3.3.1}$$

This case can be expressed in terms of a equality by introducing a proportionality constant k

$$\hat{A}\psi = k\psi \tag{3.3.2}$$

Not all functions will solve an equation like in Equation 3.3.2. If a function does, then ψ is known as an **eigenfunction** and the constant k is called its **eigenvalue** (these terms are hybrids with German, the purely English equivalents being "characteristic function" and "characteristic value", respectively). Solving eigenvalue problems are discussed in most linear algebra courses.

In quantum mechanics, every experimental measurable a is the eigenvalue of a specific operator ($\hat{A}$):

$$\hat{A}\psi = a\psi \tag{3.3.3}$$

The a eigenvalues represents the possible measured values of the $\hat{A}$ operator. Classically, a would be allowed to vary continuously, but in quantum mechanics, a typically has only a sub-set of allowed values (hence the quantum aspect). Both time-dependent and time-independent Schrödinger equations are the best known instances of an eigenvalue equations in quantum mechanics, with its eigenvalues corresponding to the allowed energy levels of the quantum system.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{3.3.4}$$

The object on the left that acts on $\psi(x)$ is an example of an **operator**.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right] \tag{3.3.5}$$

In effect, what is says to do is "take the second derivative of $\psi(x)$, multiply the result by $-(\hbar^2/2m)$ and then add $V(x)\psi(x)$ to the result of that." Quantum mechanics involves many different types of operators. This one, however, plays a special role because it appears on the left side of the Schrödinger equation. It is called the **Hamiltonian** *operator* and is denoted as

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{3.3.6}$$

Therefore, the time-dependent Schrödinger equation can be (and it more commonly) written as

$$\hat{H}\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \tag{3.3.7}$$

and the time-independent Schrödinger equation

$$\hat{H}\psi(x) = E\psi(x) \tag{3.3.8}$$

Note that the functional form of Equation 3.3.8 is the same as the general eigenvalue equation in Equation 3.3.2 where the eigenvalues are the (allowed) total energies (E).

The Hamiltonian, named after the Irish mathematician Hamilton, comes from the formulation of Classical Mechanics that is based on the total energy, $H = T + V$, rather than Newton's second law, $F = ma$. Equation 3.3.8 says that the Hamiltonian operator operates on the wavefunction to produce the energy E, which is a scalar (e.g., expressed in Joules) times the wavefunction.

Correspondence Principle

Note that $\hat{H}$ is derived from the classical energy $p^2/2m + V(x)$ simply by replacing $p \rightarrow -i\hbar(d/dx)$. This is an example of the **Correspondence Principle** initially proposed by Niels Bohr that states that the behavior of systems described by quantum theory reproduces classical physics in the limit of large quantum numbers.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is then the eigenvalue, and the system is said to be in an eigenstate. Equation 3.3.8 states this principle mathematically for the case of energy as the observable. If the wavefunction is not the eigenfunction of the operation, then the measurement will give an eigenvalue (by definition), but not necessarily the same one for each measurement (this will be discussed in more detail in later section).

Common Operators

Although we could theoretically come up with an infinite number of operators, in practice there are a few which are much more important than any others.

- **Linear Momentum:**

  The linear momentum operator of a particle moving in one dimension (the x-direction) is

  $$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.3.9}$$

  and can be generalized in three dimensions:

  $$\hat{\vec{p}} = -i\hbar\nabla \tag{3.3.10}$$

- **Position**

  The position operator of a particle moving in one dimension (the x-direction) is

  $$\hat{x} = x \tag{3.3.11}$$

  and can be generalized in three dimensions:

  $$\hat{\vec{r}} = \vec{r} \tag{3.3.12}$$

  where $\vec{r} = (x, y, z)$.

- **Kinetic Energy**

  Classically, the kinetic energy of a particle moving in one dimension (the x-direction), in terms of momentum, is

  $$KE_{classical} = \frac{p_x^2}{2m} \tag{3.3.13}$$

Quantum mechanically, the corresponding kinetic energy operator is

$$\hat{KE}_{quantum} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{3.3.14}$$

and can be generalized in three dimensions:

$$\hat{KE}_{quantum} = -\frac{\hbar^2}{2m}\nabla^2 \tag{3.3.15}$$

- **Angular Momentum:**

  Angular momentum requires a more complex discussion, but is the cross product of the position operator $\hat{\vec{r}}$ and the momentum operator $\hat{p}$

$$\hat{\vec{L}} = -i\hbar(\vec{r} \times \nabla) \tag{3.3.16}$$

- **Hamiltonian:**

  The Hamiltonian operator corresponds to the total energy of the system

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{3.3.17}$$

  and it represents the total energy of the particle of mass m in the potential $V(x)$. The Hamiltonian in three dimensions is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{3.3.18}$$

- **Total Energy:**

  The energy operator from the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t) \tag{3.3.19}$$

  The right hand side of Equation 3.3.6 is the Hamiltonian Operator. In addition determining system energies, the Hamiltonian operator dictates the time evolution of the wavefunction

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{3.3.20}$$

  This aspect will be discussed in more detail elsewhere.

Eigenstate, Eigenvalues, Wavefunctions, Measurables, and Observables

In general, the **wavefunction** gives the "state of the system" for the system under discussion. It stores all the information available to the observer about the system. Often in discussions of quantum mechanics, the terms *eigenstate* and *wavefunction* are used interchangeably. The term eigenvalue is used to designate the value of measurable quantity associated with the wavefunction.

- If you want to measure the energy of a particle, you have to operate on the wavefunction with the Hamiltonian operator (Equation 3.3.6).
- If you want to measure the momentum of a particle, you have to operate on wavefunction with the momentum operator (Equation 3.3.9).
- If you want to measure the position of a particle, you have to operate on wavefunction with the position operator (Equation 3.3.11).
- If you want to measure the kinetic energy of a particle, you have to operate on wavefunction with the kinetic energy operator (Equation 3.3.14).

When discussing the eigenstates of the Hamiltonian ($\hat{H}$), the associated eigenvalues represent energies and within the context

of the momentum operators, the associated eigenvalues refer to the momentum of the particle. However, not all wavefunctions (ψ) are eigenstates of an operator (ϕ) – and if they are not, they can be usually be written as superpositions of eigenstates.

$$\psi = \sum_i c_i \phi_i$$

This will be discussed in more detail in later sections.

While the wavefunction may not be the eigenstate of an observable, when that operator operates on that wavefunction, the wavefunction **becomes** an eigenstate of that observable and only eigenvalues can be observed. Another way to say this is that the wavefunction "collapses" into an eigenstate of the observable. Because quantum mechanical operators have different forms, their associated eigenstates are similarly often (i.e., most of the time) different. For example, when a wavefunction is an eigenstate of total energy, it will **not** be an eigenstate of momentum.

> If a wavefunction is an eigenstate of one operator, (e.g., momentum), that state is not necessarily an eigenstate of a different operator (e.g., energy), although not always.

The wavefunction immediately after a measurement is an eigenstate of the operator associated with this measurement. What happens to the wavefunction after the measurement is a different topic.

Example 3.3.1

Confirm that the following wavefunctions are eigenstates of linear momentum and kinetic energy (or neither or both):

a. $\psi = A\sin(ax)$
b. $\psi = Ne^{-ix/\hbar}$

Strategy

This question is asking if the eigenvalue equation holds for the operators and these wavefunctions. This is just asking if these wavefunctions are solutions to Equation 3.3.2 using the operators in Equations 3.3.9 and 3.3.14, i.e., are these equations true:

$$\hat{p}_x\psi = p_x\psi \tag{3.3.21}$$

$$\hat{KE}\psi = KE\psi \tag{3.3.22}$$

where p_x and KE are the measurables (eigenvalues) for these operators.

Solution a

Let's evaluate the left side of the linear momentum eigenvalue problem (Equation 3.3.21)

$$-i\hbar\frac{\partial}{\partial x}A\sin(ax) = -i\hbar Aa\cos(ax)$$

and compare to the the right side of Equation 3.3.21

$$p_x A\sin(ax)$$

These are **not** the same so this wavefunction is not an eigenstate of momentum.

Let's look at the left side of the kinetic energy eigenvalue problem (Equation 3.3.22)

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}A\sin(ax) &= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}Aa\cos(ax) \\ &= +\frac{\hbar^2}{2m}Aa^2\sin(ax) \end{aligned}$$

and compare to the right side

$$KEA\sin(ax)$$

These are same, so this specific wavefunction is an eigenstate of kinetic energy. Moreover, the measured kinetic energy will be

$$KE = +\frac{\hbar^2}{2m}a^2$$

Solution b

Let's look at the left side of Equation 3.3.21 for linear momentum

$$-i\hbar\frac{\partial}{\partial x}Ne^{-ix/\hbar} = -Ne^{-ix/\hbar}$$

and the right side of Equation 3.3.21

$$p_x Ne^{-ix/\hbar}$$

These are the same so this wavefunction is an eigenstate of momentum with momentum $p_x = -N$.

Let's look at the left side of Equation 3.3.22 for kinetic energy

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}Ne^{-ix/\hbar} &= +i\frac{\hbar}{2m}\frac{\partial}{\partial x}Ne^{-ix/\hbar} \\ &= +\frac{1}{2m}Ne^{-ix/\hbar} \end{aligned}$$

and the right side

$$KENe^{-ix/\hbar}$$

These are same so this wavefunction is an eigenstate of kinetic energy. And the measured kinetic energy will be

$$KE = \frac{1}{2m}$$

This wavefunction is an eigenstate of both momentum and kinetic energy.

Exercise 3.3.1

Are $\psi = Me^{-bx}$ functions eigenstates of linear momentum and kinetic energy (or neither or both)?

Answer available at the end of this section.

Answers

ψ is an eigenstate of linear momentum with a eigenvalue of $bi\hbar$ and also an eigenstate of kinetic energy with an eigenvalue of b^2.

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3.4: Wavefunctions Have a Probabilistic Interpretation

Learning Objectives

- To understand that wavefunctions can have probabilistic interpretations.
- To calculate the probabilities directly from a wavefunctions

For a single-particle system, the wavefunction $\Psi(\vec{r},t)$, or $\psi(\vec{r})$ for the time-independent case, represents the amplitude of the still vaguely defined matter waves. Since wavefunctions can in general be complex functions, the physical significance cannot be found from the function itself because the $\sqrt{-1}$ is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e. the absolute square of the wavefunction, which also is called the **square of the modulus** (also called absolute value).

$$P(\vec{r},t) = \Psi^*(\vec{r},t)\Psi(\vec{r},t) \tag{3.4.1}$$

$$= |\Psi(\vec{r},t)|^2 \tag{3.4.2}$$

where $\vec{r}$ is a vector (x,y,z) specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field.

Born proposed in 1926, the most commonly accepted interpretation of the wavefunction **that the square of the modulus** (Equation 3.4.2) is **proportional** to the **probability density** (probability per unit volume) that the electron is in the volume $d\tau$ located at r_i. Since the wavefunction represents the wave properties of matter, the probability amplitude $P(x,t)$ will also exhibit wave-like behavior. Probability density is the three-dimensional analog of the diffraction pattern that appears on the two-dimensional screen in the double-slit diffraction experiment for electrons. The idea that we can understand the world of atoms and molecules only in terms of probabilities is disturbing to some, who are seeking more satisfying descriptions through ongoing research.

> The Born interpretation therefore calls the wavefunction the probability amplitude, the absolute square of the wavefunction is called the probability density, and the probability density times a volume element in three-dimensional space ($d\tau$) is the probability P

The probability that a single quantum particle moving in one spatial dimension will be found in a region $x \in [a,b]$ if a measurement of its location is performed is

$$P(x \in [a,b]) = \int_a^b |\psi(x)|^2 dx \tag{3.4.3}$$

In three dimensions, Equation 3.4.3 is represented differently

$$P(x \in [a,b]) = \int_V |\psi(\vec{\tau})|^2 d\tau \tag{3.4.4}$$

This integration extends over a specified volume (V) with the symbol $d\tau$ designating the appropriate volume element (including a Jacobian) of the coordinate system adopted:

- Cartesian:

$$d\tau = dx\, dy\, dz$$

- Spherical:

$$d\tau = r^2 \sin\phi\, dr\, d\theta\, d\phi$$

- Cylindrical:

$$d\tau = r\, dr\, d\phi\, dz.$$

For rectilinear Cartesian space, Equation 3.4.4 can be is expanded with dimension explicitly indicated

$$P(x \in [a,b]) = \int_{a_x}^{b_x} \int_{a_y}^{b_y} \int_{a_z}^{b_z} |\psi(x,y,z)|^2 dx\, dy\, dz \tag{3.4.5}$$

where the limits of integration are selected to encompass the volume V of consideration.

The Born interpretation (Equation 3.4.2) of relating the wavefunction to probability forces certain demands on its mathematical behavior of wavefunctions and not any mathematical function can be a valid wavefunction.

Required Properties of Wavefunction

- The wavefunction must be a *single-valued function* of all its coordinates, since the probability density ought to be *uniquely determined* at each point in space.
- The wavefunction should be both *finite* as an infinite probability has no meaning.
- The wavefunction should be *continuous everywhere*, as expected for a physically-meaningful probability density.

The conditions that the wavefunction be single-valued, finite and continuous--in short, "well behaved"-- lead to restrictions on solutions of the Schrödinger equation such that only certain values of the energy and other dynamical variables are allowed. This is called *quantization* and is in the feature that gives *quantum* mechanics its name.

It is important to note that this interpretation implies the wavefunction does **not** mean the particle is distributed over a large region as a sort of "charge cloud". The wavefunction is used to describe the electron motion that behaves like waves and satisfies a wave equation. This is akin to how a grade distribution in a large class does not represent a smearing of grades for a single student, but only makes sense when taking into account that the distribution is the result of many measurables (e.g., student performances).

Example 3.4.1

Show that the square of the modulus of $\Psi(\vec{r},t) = \psi(\vec{r})e^{-i\omega t}$ is time independent. What insight regarding stationary states do you gain from this proof?

Example 3.4.2

According to the Born interpretation, what is the physical significance of $e\psi^*(r_0)(r_0)d\tau$?

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3.5: The Energy of a Particle in a Box is Quantized

Learning Objectives

- Solve the particle-in-a-box model used to describing a trapped particle in 1 D well
- Characterize the particle-in-a-box eigenstates (i.e., wavefunctions) and the eigenenergies as a function of the quantum number
- Demonstrate that the eigenstates are orthogonal

The *particle in the box* model system is the simplest non-trivial application of the Schrödinger equation, but one which illustrates many of the fundamental concepts of quantum mechanics. For a particle moving in one dimension (again along the x- axis), the Schrödinger equation can be written

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x)$$

Assume that the particle can move freely between two endpoints $x = 0$ and $x = L$, but cannot penetrate past either end. This is equivalent to a potential energy dependent on x with

$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & x < 0 \; and \; x > L \end{cases}$$

This potential is represented in Figure 3.5.1 . The infinite potential energy constitutes an impenetrable barrier since the particle would have an infinite potential energy if found there, which is clearly impossible.

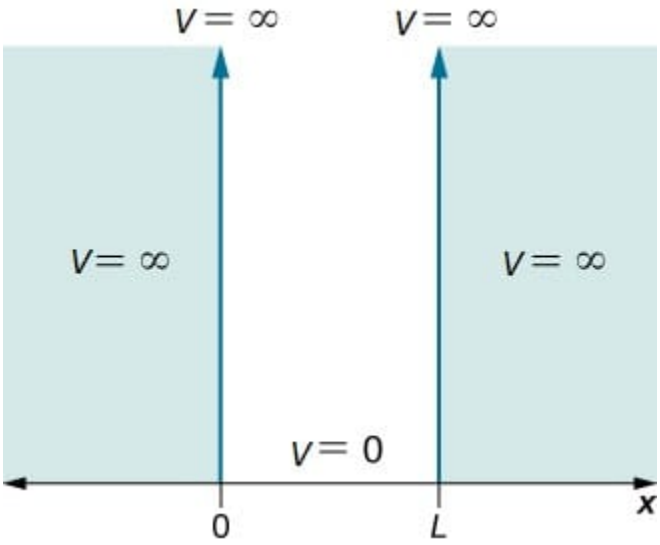


Figure 3.5.1 : The barriers outside a one-dimensional box have infinitely large potential, while the interior of the box has a constant, zero potential. (CC-BY 4.0; OpenStax).

The particle is thus bound to a "*potential well*" since the particle cannot penetrate beyond $x = 0$ or $x = L$

$$\psi(x) = 0 \quad for \;\; x < 0 \;\; and \;\; x > L \tag{3.5.1}$$

By the requirement that the wavefunction be continuous, it must be true as well that

$$\psi(0) = 0 \quad and \quad \psi(L) = 0 \tag{3.5.2}$$

which constitutes a pair of boundary conditions on the wavefunction within the box. Inside the box, $V(x) = 0$, so the Schrödinger

equation reduces to the free-particle form:

$$-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x) \tag{3.5.3}$$

with $0 \le x \le L$.

We again have the differential equation

$$\psi''(x) + k^2\psi(x) = 0 \tag{3.5.4}$$

with

$$k^2 = \frac{2mE}{\hbar^2} \tag{3.5.5}$$

The general solution can be written

$$\psi(x) = A\ \sin\ kx\ +\ B\ \cos\ kx \tag{3.5.6}$$

where A and B are constants to be determined by the boundary conditions in Equation 3.5.2. By the first condition, we find

$$\psi(0) = A\ \sin\ 0\ +\ B\ \cos\ 0\ =\ B\ = 0 \tag{3.5.7}$$

The second boundary condition at $x = L$ then implies

$$\psi(a) = A\ \sin\ kL\ =\ 0 \tag{3.5.8}$$

It is assumed that $A \neq 0$, for otherwise $\psi(x)$ would be zero everywhere and the particle would disappear (i.e., the trivial solution). The condition that $\sin kx = 0$ implies that

$$kL\ =\ n\pi \tag{3.5.9}$$

where n is a integer, positive, negative or zero. The case $n = 0$ must be excluded, for then $k = 0$ and again $\psi(x)$ would vanish everywhere. Eliminating k between Equation 3.5.4 and 3.5.9, we obtain

$$E_n = \frac{\hbar^2\pi^2}{2mL^2}\ n^2 = \frac{h^2}{8mL^2}n^2 \tag{3.5.10}$$

with $n = 1, 2, , 3....$

These are the only values of the energy which allows solutions of the Schrödinger Equation 3.5.3 consistent with the boundary conditions in Equation 3.5.2. The integer n, called a **quantum number**, is appended as a subscript on E to label the allowed energy levels. Negative values of n add nothing new because the energies in Equation 3.5.10 depends on n^2.

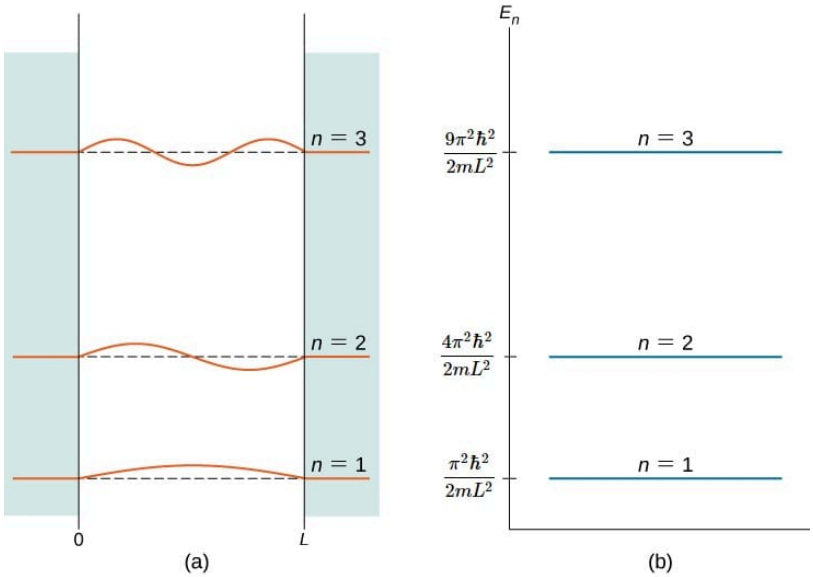


Figure 3.5.2 : A plot of $\psi_n(x)$ for the first four wavefunctions. (CC-BY 4.0; OpenStax).

Figure 3.5.2 shows part of the energy-level diagram for the particle in a box. The occurrence of discrete or quantized energy levels is characteristic of a bound system, that is, one confined to a finite region in space. For the free particle, the absence of confinement allowed an energy continuum. Note that, in both cases, the number of energy levels is infinite-denumerably infinite for the particle in a box, but nondenumerably infinite for the free particle.

The particle in a box assumes its lowest possible energy when $n = 1$, namely

$$E_1 = \frac{h^2}{8mL^2} \tag{3.5.11}$$

The state of lowest energy for a quantum system is termed its *ground state*.

Zero Point Energy

An interesting point is that $E_1 > 0$, whereas the corresponding classical system would have a minimum energy of zero. This is a recurrent phenomenon in quantum mechanics. The residual energy of the ground state, that is, the energy in excess of the classical minimum, is known as **zero point energy**. In effect, the kinetic energy, hence the momentum, of a bound particle cannot be reduced to zero. The minimum value of momentum is found by equating E_1 to $p^2/2m$, giving $p_{min} = \pm h/2L$. This can be expressed as an *uncertainty* in momentum given by $\Delta p \approx h/L$. Coupling this with the uncertainty in position, $\Delta x \approx L$, from the size of the box, we can write

$$\Delta x \Delta p \approx h \tag{3.5.12}$$

This is in accord with the *Heisenberg uncertainty principle*.

The particle-in-a-box eigenfunctions are given by Equation 3.5.13, with $B = 0$ and $k = n\pi/L = a$, in accordance with Equation 3.5.9

$$\psi_n(x) = A \sin \frac{n\pi x}{L} \tag{3.5.13}$$

with $n = 1, 2, 3....$

These, like the energies, can be labeled by the quantum number n. The constant A, thus far arbitrary, can be adjusted so that $\psi_n(x)$ is normalized. The normalization condition is, in this case,

$$\int_0^a [\psi_n(x)]^2 \, dx = 1 \tag{3.5.14}$$

the integration running over the domain of the particle $0 \leq x \leq L$. Substituting Equation 3.5.13 into Equation 3.5.14,

$$A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = A^2 \frac{L}{n\pi} \int_0^{n\pi} \sin^2 \theta \, d\theta \tag{3.5.15}$$

$$= A^2 \frac{L}{2} = 1 \tag{3.5.16}$$

We have made the substitution $\theta = n\pi x/L$ and used the fact that the average value of $\sin^2 \theta$ over an integral number of half wavelengths equals 1/2 (alternatively, one could refer to standard integral tables). From Equation 3.5.16, we can identify the general normalization constant

$$A = \sqrt{\frac{2}{L}}$$

for all values of n. Finally we can write the normalized eigenfunctions:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \tag{3.5.17}$$

with $n = 1, 2, 3....$

The first few eigenfunctions and the corresponding probability distributions are plotted in Figure 3.5.3 . There is a close analogy between the states of this quantum system and the modes of vibration of a violin string. The patterns of standing waves on the string are, in fact, identical in form with the wavefunctions in Equation 3.5.17.

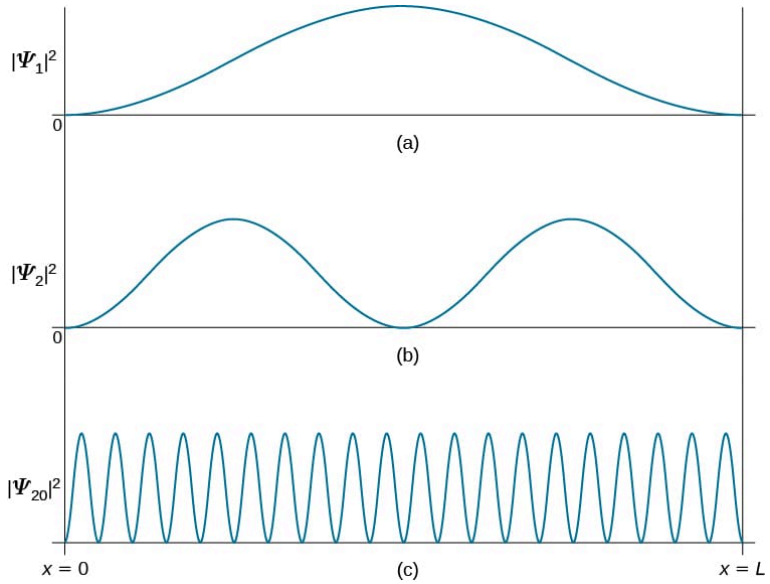


Figure 3.5.3 : The probability density distribution $|\psi_n(x)|^2$ for a quantum particle in a box for: (a) the ground state, $n = 1$; (b) the first excited state, $n = 2$; and, (c) the nineteenth excited state, $n = 20$. (CC-BY 4.0; OpenStax).

Nodes and Curvature

A significant feature of the particle-in-a-box quantum states is the occurrence of *node*s. These are points, other than the two end points (which are fixed by the boundary conditions), at which the wavefunction vanishes. At a node there is exactly zero probability of finding the particle. The *n*th quantum state has, in fact, $n - 1$ nodes. It is generally true that the number of nodes increases with the energy of the quantum state, which can be rationalized by the following qualitative argument. As the number of nodes increases, so does the number and the steepness of the 'wiggles' in the wavefunction. It's like skiing down a slalom course. Accordingly, the average curvature, given by the second derivative, must increase. But the second derivative is proportional to the kinetic energy operator. Therefore, the more nodes, the higher the energy. This will prove to be an invaluable guide in more complex quantum systems.

Example 3.5.1 : Excited State Probabilities

For a particle in a one-dimensional box of length L, the second excited state wavefunction ($n = 3$) is

$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

a. What is the probability that the particle is in the left half of the box?
b. What is the probability that the particle is in the middle third of the box?

Strategy

Probability that the particle will be found between a and b is

$$P(a,b) = \int_a^b \psi^2 \, dx$$

For this problem,

$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

therefore,

$$\begin{aligned} P(a,b) &= \frac{2}{L} \int_a^b \sin^2 \frac{3\pi x}{L} \, dx \\ &= \frac{2}{L} \left(\frac{x}{2} - \frac{L \sin\left(\frac{6\pi x}{L}\right)}{12\pi} \right) \Bigg|_a^b \\ &= \frac{b-a}{L} - \frac{1}{6\pi} \left[\sin\left(\frac{6\pi b}{L}\right) - \sin\left(\frac{6\pi a}{L}\right) \right] \end{aligned}$$

Solution a

The probability that the particle is in the left half of the box is

$$\begin{aligned} P\left(0, \frac{L}{2}\right) &= \frac{\frac{L}{2} - 0}{L} - \frac{1}{6\pi} \left[\sin\left(\frac{6\pi\left(\frac{L}{2}\right)}{L} \right) - \sin\left(\frac{6\pi(0)}{L}\right) \right] \\ &= \frac{1}{2} \end{aligned}$$

Solution b

The probability that the particle is in the middle third of the box

$$\begin{aligned} P\left(\frac{L}{3}, \frac{2L}{3}\right) &= \frac{\frac{2L}{3} - \frac{L}{3}}{L} - \frac{1}{6\pi} \left[\sin \frac{6\pi\left(\frac{2L}{3}\right)}{L} - \sin \frac{6\pi\left(\frac{L}{3}\right)}{L} \right] \\ &= \frac{1}{3} \end{aligned}$$

Exercise 3.5.1 : Ground State Probability

For a particle in a one-dimensional box, the ground state wavefunction is

$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{x\pi}{L}$$

What is the probability that the particle is in the left half of the box in the ground state?

Answer available at the end of this section.

Time Dependence and Complex Nature of Wavefunctions

Recall that the time-dependence of the wavefunction with time-independent potential was discussed in Section 3.1 and is expressed as

$$\Psi(x,t) = \psi(x) e^{-iEt/\hbar}$$

so for the particle in a box, these are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} e^{-iE_n t/\hbar} \tag{3.5.18}$$

with E_n given by Equation 3.5.10.

The phase part of Equation 3.5.18 can be expanded into a real part and a complex components. So the total wavefunction for a particle in a box is

$$\Psi(x,t) = \underbrace{\left(\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}\right)\left(\cos \frac{E_n t}{\hbar}\right)}_{\text{real part}} - i \underbrace{\left(\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}\right)\left(\sin \frac{E_n t}{\hbar}\right)}_{\text{imaginary part}}$$

which can be simplified (slightly) to

$$\Psi(x,t) = \underbrace{\left(\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}\right)\left(\cos \frac{E_n t}{\hbar}\right)}_{\text{real part}} - i \underbrace{\left(\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}\right)\left(\cos \frac{E_n t}{\hbar} - \frac{\pi}{2}\right)}_{\text{imaginary part}}$$

As discussed previously, the imaginary part of the total wavefunction oscillates out of phase by $\pi/2$ with respect to the real part (we call this "out of phase"). This is demonstrated in the time-dependent behavior of the first three eigenfunctions in Figure 3.5.4 .

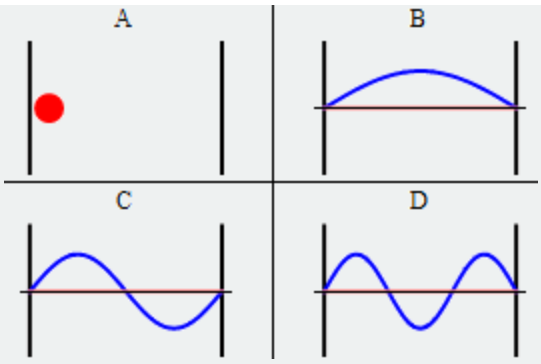


Figure 3.5.4 : Some trajectories of a particle in a box according to Newton's laws of classical mechanics (A), and according to the Schrödinger equation of quantum mechanics (B-D). In (B-D), the horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the wavefunction. The states (B, C, D) are energy eigenstates. (Public Domain; Sbyrnes321 via Wikipedia).

Note that as n increased, the energy of the wavefunction increases (Equation 3.5.10) and both the number of nodes and antinodes increase and the frequency of oscillation of the wavefunction increases.

It is generally true in quantum systems (not just for particles in boxes) that the number of nodes in a wavefunction increases with the energy of the quantum state.

Orthonormality of the Eigenstates

Another important property of the eigenfunctions in Equation 3.5.17 applies to the integral over a product of two *different* eigenfunctions (Equation 3.5.17). It is easy to see from Figure 3.5.5 that the integral

$$\int_0^L \psi_2(x)\psi_1(x)dx = 0 \tag{3.5.19}$$

The integral in Equation 3.5.19 is zero when the two eignestates differ and when integrated over the entire range of the system (from $-\infty$ to ∞ for a 1-D particle in the box, but this can be a narrow region of 0 to L since the eigenstates are zero outside of the box).

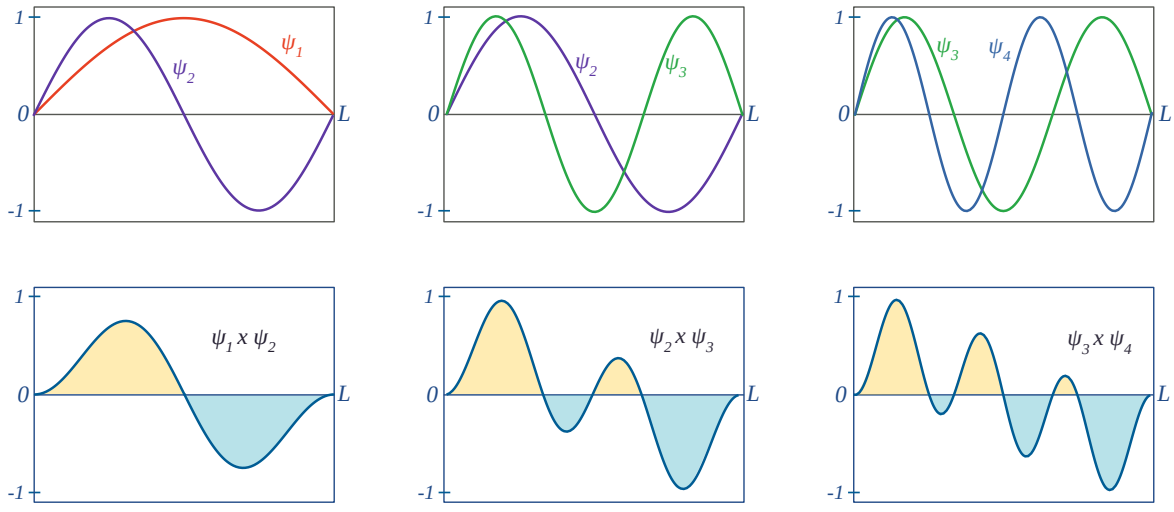


Figure 3.5.5 : (Top Row): Select plots of the $n = 1$ (red curves), $n = 2$ (purple curves), $n = 3$ (green curves), and $n = 4$ (blue curves) eigenfunctions. (Bottom Row): Product of different eigenstates with positive (tan) and negative (cyan) areas emphasized. Note that the negative and positive areas perfectly cancel when added together. Created via fooplot (CC BY-NC; Ümit Kaya via LibreTexts)

To prove Equation 3.5.19 for a particle in a box model, we can use the trigonometric identity

$$\sin\,\alpha\,\sin\,\beta = \frac{1}{2}\left[\cos(\alpha-\beta)-\cos(\alpha+\beta)\right] \tag{3.5.20}$$

to show that

$$\int_0^L \psi_m(x)\psi_n(x)dx = 0 \quad if \quad m \neq n \tag{3.5.21}$$

This property is called **orthogonality**. We will show in the next chapter, that this is a general result from quantum-mechanical eigenfunctions. The normalization (Equation 3.5.19) together with the orthogonality (Equation 3.5.21) can be combined into a single relationship

$$\int_0^L \psi_m(x)\psi_n(x)dx = \delta_{mn} \tag{3.5.22}$$

In terms of the *Kronecker delta*

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \tag{3.5.23}$$

A set of functions $\{\psi_n\}$ which obeys Equation 3.5.22 is called *orthonormal*.

Example 3.5.2

Evaluate

a. $\langle\psi_3|\psi_3\rangle$
b. $\langle\psi_4|\psi_4\rangle$
c. $\langle\psi_3|\psi_4\rangle$
d. $\langle\psi_4|\psi_3\rangle$

for the normalized wavefunctions:

$$|\psi_3\rangle = \sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}$$

and

$$|\psi_4\rangle = \sqrt{\frac{2}{L}}\sin\frac{4\pi x}{L}$$

Strategy

These are four different integrals and we can solve them directly or use orthonormality (Equation 3.5.23) to evaluate.

Solution a

$$\begin{aligned}\langle\psi_3|\psi_3\rangle &= \int_{-\infty}^{+\infty}\left(\sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}\right)\left(\sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}\right)dx \\ &= \frac{2}{L}\int_{-\infty}^{+\infty}\sin^2\frac{3\pi x}{L}\,dx\end{aligned}$$

This is an integration over an even function, so it cannot be tossed out via symmetry. We can use the Trigonometry relationship in Equation 3.5.20 to get

$$\frac{2}{L}\int_{-\infty}^{+\infty}\sin^2\frac{3\pi x}{L}\,dx = \frac{2}{L}\int_{-\infty}^{+\infty}\frac{1}{2}\left(1-\cos\frac{6\pi x}{L}\right)dx$$

and we can continue the fun. However, there is no need. Since the we can recognize that $\langle\psi_3|\psi_3\rangle$ is 1 by the normalization criteria which is folded into the orthonormal criteria (Equation 3.5.23).

Therefore $\langle\psi_3|\psi_3\rangle = 1$.

Solution b

$$\begin{aligned}\langle\psi_4|\psi_4\rangle &= \int_{-\infty}^{+\infty}\left(\sqrt{\frac{2}{L}}\sin\frac{4\pi x}{L}\right)\left(\sqrt{\frac{2}{L}}\sin\frac{4\pi x}{L}\right)dx \\ &= \frac{2}{L}\int_{-\infty}^{+\infty}\sin^2\frac{4\pi x}{L}\,dx\end{aligned}$$

We can expand and solve, but again there is no need. The wavefunctions are normalized therefore $\langle\psi_4|\psi_4\rangle = 1$.

Solution c

$$\begin{aligned}\langle\psi_3|\psi_4\rangle &= \int_{-\infty}^{+\infty}\left(\sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}\right)\left(\sqrt{\frac{2}{L}}\sin\frac{4\pi x}{L}\right)dx \\ &= \frac{2}{L}\int_{-\infty}^{+\infty}\sin\left(\frac{3\pi x}{L}\right)\sin\left(\frac{4\pi x}{L}\right)dx\end{aligned}$$

We can expand this integral and evaluate, but since the integrand is odd (and even function times an odd), this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.5.23).

Solution d

$$\begin{aligned}\langle\psi_4|\psi_3\rangle &= \int_{-\infty}^{+\infty}\left(\sqrt{\frac{2}{L}}\sin\frac{4\pi x}{L}\right)\left(\sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}\right)dx \\ &= \frac{2}{L}\int_{-\infty}^{+\infty}\sin\left(\frac{4\pi x}{L}\right)\sin\left(\frac{3\pi x}{L}\right)dx\end{aligned}$$

We can expand this integral and evaluate, but since the integrand is odd (and even function times an odd function), this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.5.23).

However, since the wavefunctions are real, then

$$\langle\psi_4|\psi_3\rangle = \langle\psi_3|\psi_4\rangle$$

which also means

$$\langle\psi_4|\psi_3\rangle = 0$$

from the results of section c.

Answers

$$\begin{aligned}P\left(0,\frac{L}{2}\right) &= \frac{2}{L}\int_0^{\frac{L}{2}}\sin^2\frac{x\pi}{L}dx \\ &= \frac{2}{L}\frac{\frac{L\pi}{L}+\sin 0+\sin\frac{L\pi}{L}}{\frac{4\pi}{L}} \\ &= \frac{1}{2}\end{aligned}$$

This is the same answer as for the ψ_3 state in Example 3.5.1 . This is because the eigenstate squared (.e., probability density) for the particle in a 1D box will always be symmetric around the center of the box. So there will be equal probability to be on either side (i.e., no side is favored).

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3.6: Wavefunctions Must Be Normalized

Learning Objectives

- Calculate the probability of an event from the wavefunction
- Understand the utility and importance of normalizing wavefunctions
- Demonstrate how to normalize an arbitrary wavefunction

Extracting Probabilities

Since wavefunctions can in general be complex functions, the physical significance of wavefunctions cannot be found from the functions themselves because the $\sqrt{-1}$ is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e. the absolute square of the wavefunction, which also is called the **square of the modulus**.

$$\Psi^*(r,t)\Psi(r,t) = |\Psi(r,t)|^2 \tag{3.6.1}$$

where r is a vector specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field. Remember that the Born interpretation is that $\psi^*(r_i)\psi(r_i)$ $d\tau$ is the **probability** that the electron is in the volume $d\tau$ located at r_i. The Born interpretation therefore calls the wavefunction the probability amplitude, the absolute square of the wavefunction is called the **probability density**, and the probability density times a volume element in three-dimensional space ($d\tau$) is the probability.

Since the squared magnitude $|\psi|^2$ of the wavefunction of a particle can be interpreted as the probability density, then the probability for a one-dimensional wavefunction between the points $x = a$ and $x = b$ can be calculated by

$$P_{1D} = \int_a^b |\psi(x)|^2 \mathrm{d}x \tag{3.6.2}$$

This is just the area under the under the $|\psi|^2$ curve (Figure 3.6.1).

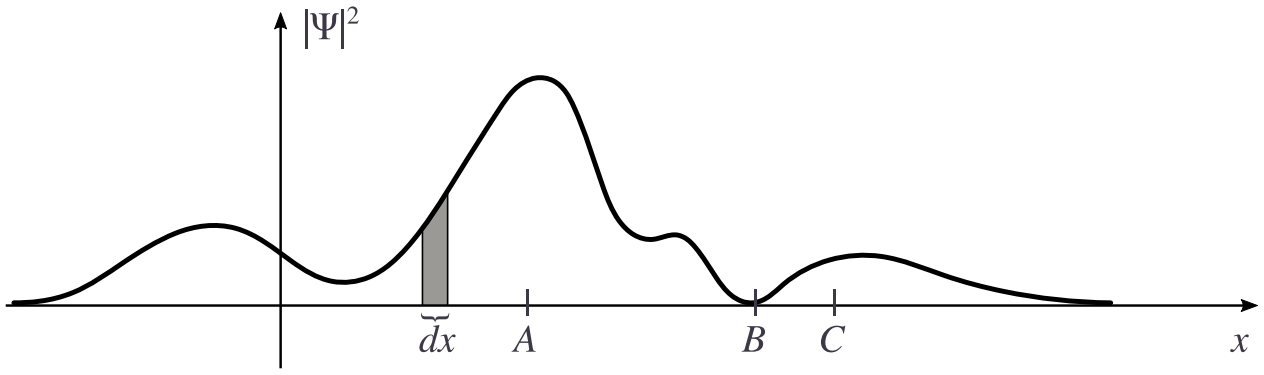


Figure 3.6.1 : The probability can be interpreted as an area under the probability density $|\psi|^2$. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

If the probability of a two-dimensional wavefunction is being evaluated, then Equation 3.6.2 will be amended to included a double integral:

$$P_{2D} = \iint_{a_1,a_2}^{b_1,b_2} |\psi(x,y)|^2 \mathrm{d}x\mathrm{d}y$$

and similarly a triple integral would be used for calculating probabilities of three-dimensional wavefunctions:

$$P_{3D} = \iiint_{a_1,a_2,a_3}^{b_1,b_2,b_3} |\psi(x,y,z)|^2 \mathrm{d}x\mathrm{d}y\mathrm{d}z$$

Example 3.6.1 : Probability of a Particle in a Box

Calculate the probability of finding an electron at $L/2$ in a box of infinite height within an interval ranging from $\frac{L}{2} - \frac{L}{200}$ to $\frac{L}{2} + \frac{L}{200}$ for the $n = 1$ and $n = 2$ states. Since the length of the interval, $L/100$, is small compared to L, you can get an approximate answer without explicitly integrating.

Solution

The wavefunction for the particle in a box is

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

and the wavefunction for the $n = 1$ state is

$$\psi_{n=1} = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

From the interpretation that the wavefunction modulus squared is the probability density, we can establish the following integral to solve the problem (note the limits of integration)

$$|\psi_{n=1}|^2 = \frac{2}{L} \int_{\frac{99L}{200}}^{\frac{101L}{200}} \sin^2\left(\frac{\pi x}{L}\right) dx \tag{3.6.3}$$

We can solve this, but we can also recognize that Equation 3.6.3 is just calculating an area that can be approximated as the area of a rectangle with a height ($\frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)$ at $x = L/2$) and width $\Delta x = L/100$ (Figure 3.6.2).

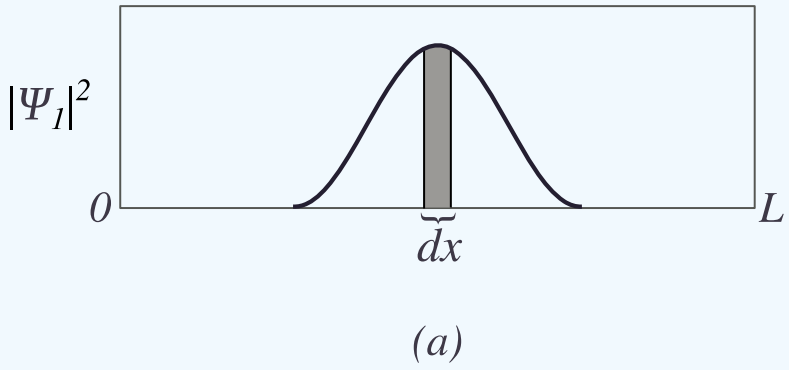


Figure 3.6.2 : The probability can be interpreted as an area under the probability density $|\psi_1|^2$. (CC BY-NC; Ümit Kaya via LibreTexts)

This area can be computed:

$$\begin{aligned} |\psi_{n=1}|^2 &\approx \frac{2}{L} \sin^2\left(\frac{\pi(L/2)}{L}\right)^{1} \Delta x \\ &\approx \left(\frac{2}{L}\right)(L/100) \\ &\approx 1/50 = 0.02 \end{aligned}$$

Given that the wavefunction is sinusoidal, the actual probability of finding an electron within the given interval at $\frac{L}{2}$ should be slightly less because of the behavior of the sinusoid at $\frac{L}{2}$ is at its peak of the wavefunction (Figure 3.6.2).

The wavefunction for the $n = 2$ state

$$\psi_{n=2} = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$$

so the integral that we need to construct and solve is

$$|\psi_{n=2}|^2 = \frac{2}{L} \int_{\frac{99L}{200}}^{\frac{101L}{200}} \sin^2\left(\frac{2\pi x}{L}\right) dx$$

We can use the same graphical interpretation as above, but using the probability density of the ψ_2 wavefunction (Figure 3.6.3).

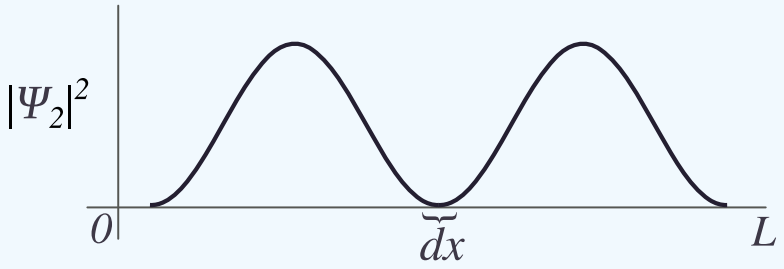


Figure 3.6.3 : The probability can be interpreted as an area under the probability density $|\psi_2|^2$. (CC BY-NC Copyright; Ümit Kaya via LibreTexts)

$$|\psi_{n=1}|^2 \approx \frac{2}{L} \sin^2\left(\frac{2\pi(L/2)}{L}\right)^{0} \Delta x$$
$$\approx 0$$

The probability of finding an electron in a box at $\frac{L}{2}$ for $n = 2$ is approximately zero.

Exercise 3.6.1

Show that the square of the modulus of $\Psi(r,t) = \psi(r)e^{-i\omega t}$ is time independent. What insight regarding stationary states do you gain from this proof?

Solution

The square of the modulus of a wavefunction is $\Psi(r,t)^*\Psi(r,t)$ so for wavefunctions of this form, the square of the modulus is

$$\Psi(r,t)^*\Psi(r,t) = \psi(r)\cancel{e^{+i\omega t}}\,\psi(r)\cancel{e^{-i\omega t}}$$
$$= \psi(r)^2$$

Hence, there is no time dependence to the modulus of wavefunctions of this work, which from the probability interpretation of the wavefunction means that the probability density is time-independent.

Normalizing of the Wavefunction

A probability is a real number between 0 and 1, inclusive. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. According to Equation 3.6.1, the probability of a measurement of x yielding a result between $-\infty$ and $+\infty$ is

$$P_{x\in-\infty:\infty}(t)=\int_{-\infty}^{\infty}|\psi(x,t)|^2dx. \tag{3.6.4}$$

However, a measurement of x *must* yield a value between $-\infty$ and $+\infty$, since the particle has to be located somewhere. It follows that $P_{x\in-\infty:\infty}(t)=1$, or

$$\int_{-\infty}^{\infty}|\psi(x,t)|^2dx=1, \tag{3.6.5}$$

which is generally known as the **normalization condition** for the wavefunction.

Example 3.6.2 : Normalizing a Gaussian Wavepacket

Normalize the wavefunction of a Gaussian wave packet, centered on $x=x_o$ with characteristic width σ:

$$\psi(x)=\psi_0\mathrm{e}^{-(x-x_0)^2/(4\sigma^2)}. \tag{3.6.6}$$

Solution

To determine the normalization constant ψ_0, we simply substitute Equation 3.6.6 into Equation 3.6.5, to obtain

$$|\psi_0|^2\int_{-\infty}^{\infty}\mathrm{e}^{-(x-x_0)^2/(2\sigma^2)}dx=1.$$

Changing the variable of integration to $y=(x-x_0)/(\sqrt{2}\sigma)$, we get

$$|\psi_0|^2\sqrt{2}\sigma\int_{-\infty}^{\infty}\mathrm{e}^{-y^2}dy=1.$$

However, from an integral table we know

$$\int_{-\infty}^{\infty}\mathrm{e}^{-y^2}dy=\sqrt{\pi},$$

which implies that

$$|\psi_0|^2=\frac{1}{(2\pi\sigma^2)^{1/2}}.$$

Hence, a general normalized Gaussian wavefunction takes the form

$$\psi(x)=\frac{e^{\mathrm{i}\phi}}{(2\pi\sigma^2)^{1/4}}e^{-(x-x_0)^2/(4\sigma^2)}$$

where ϕ is an arbitrary real phase-angle.

Exercise 3.6.2

Normalize this wavefunction for a particle in a harmonic well:

$$\psi=xe^{-x^2}$$

Answer available at the end of this section.

Time Dependence to the Wavefunction

Now, it is important to demonstrate that if a wavefunction is initially normalized then it stays normalized as it evolves in time according to the time-dependent Schrödinger's equation. If this is not the case then the probability interpretation of the wavefunction is untenable, since it does not make sense for the probability that a measurement of x yields *any* possible outcome (which is, manifestly, unity) to change in time. Hence, we require that

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi(x,t)|^2 dx = 0$$

for wavefunctions satisfying the time-dependent Schrödinger's equation (this results from the time-dependent Schrödinger's equation and Equation 3.6.5). The above equation gives

$$\frac{d}{dt}\int_{-\infty}^{\infty}\psi^*\psi\, dx = \int_{-\infty}^{\infty}\left(\frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t}\right)dx = 0. \tag{3.6.7}$$

Now, multiplying Schrödinger's equation by $\psi^*/(\mathrm{i}\hbar)$, we obtain

$$\psi^*\frac{\partial\psi}{\partial t} = \frac{\mathrm{i}}{2m}\psi^*\frac{\partial^2\psi}{\partial x^2} - \frac{\mathrm{i}}{\hbar}V|\psi|^2 \tag{3.6.8}$$

The complex conjugate of this expression yields

$$\psi\frac{\partial\psi^*}{\partial t} = -\frac{\mathrm{i}}{2m}\psi\frac{\partial^2\psi^*}{\partial x^2} + \frac{\mathrm{i}}{\hbar}V|\psi|^2 \tag{3.6.9}$$

since

- $(AB)^* = A^*B^*$,
- $A^{**} = A$, and
- $i^* = -i$.

Summing Equation 3.6.8 and 3.6.9 results in

$$\frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t} = \frac{\mathrm{i}}{2m}\left(\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2}\right) \tag{3.6.10}$$

$$= \frac{\mathrm{i}}{2m}\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right). \tag{3.6.11}$$

Equations 3.6.7 and 3.6.11 can be combined to produce

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2 dx = \frac{\mathrm{i}}{2m}\left[\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right]_{-\infty}^{\infty} = 0. \tag{3.6.12}$$

The above equation is satisfied provided the wavefunction converges

$$\lim_{|x|\to\infty}|\psi| = 0 \tag{3.6.13}$$

However, this is a necessary condition for the integral on the left-hand side of Equation 3.6.5 to converge. Hence, we conclude that all wavefunctions which are *square-integrable* [i.e., are such that the integral in Equation 3.6.5 converges] have the property that if the normalization condition Equation 3.6.5 is satisfied at one instant in time then it is satisfied at all subsequent times.

Not all Wavefunctions can be Normalized

Not all wavefunctions can be normalized according to the scheme set out in Equation 3.6.5. For instance, a planewave wavefunction for a quantum free particle

$$\Psi(x,t) = \psi_0 \mathrm{e}^{\mathrm{i}(kx-\omega t)}$$

is not square-integrable, and, thus, cannot be normalized. For such wavefunctions, the best we can say is that

$$P_{x\in a:b}(t) \propto \int_a^b |\Psi(x,t)|^2 dx.$$

In the following, all wavefunctions are assumed to be square-integrable and normalized, unless otherwise stated.

Answers

$$\psi = 2\left(\frac{2}{\pi}\right)^{1/4} x e^{-x^2}$$

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3.7: The Average Momentum of a Particle in a Box is Zero

Learning Objectives

- Calculate the expectation value for a measurement
- Apply the expectation value concept to calculate average properties of a participle in a box model
- Understand the origin of a zero-point energy/zero-point motion.
- Extend the concept of orthogonality from vectors to mathematical functions (and wavefunctions).

Now that we have mathematical expressions for the wavefunctions and energies for the particle-in-a-box, we can answer a number of interesting questions. The answers to these questions use quantum mechanics to predict some important and general properties for electrons, atoms, molecules, gases, liquids, and solids. Key to addressing these questions is the formulation and use of expectation values. This is demonstrated below and used in the context of evaluating average properties (momentum of the particle in a box for the case below).

Classical Expectation Values

The expectation value is the probabilistic expected value of the result (measurement) of an experiment. It is not the most probable value of a measurement; indeed the expectation value may even have zero probability of occurring. The expected value (or expectation, mathematical expectation, mean, or first moment) refers to the value of a variable one would "expect" to find if one could repeat the random variable process an infinite number of times and take the average of the values obtained. More formally, the expected value is a weighted average of all possible values.

Example 3.7.1 : Classical Expectation Value of Exam Scores (a discretized example)

A classical example is calculating the expectation value (i.e. average) of the exam grades in the class. For example if the class scores for an exam were

65	67	94	43	67	76	94	67

The discrete way is to sum up all scores and divide by the number of students:

$$\langle s \rangle = \frac{\sum_{i}^{N} s(i)}{N} \tag{3.7.1}$$

which of this example of scores is

$$\begin{aligned} \langle s \rangle &= \frac{65+67+94+43+67+76+94+76}{8} \\ &= 71.625 \end{aligned}$$

Notice that the average is not an allowable score on an individual exam. Equation 3.7.1 can be rewritten with "probability" or "probability weights"

$$\langle s \rangle = \sum_{i}^{N} s(i) P_s(i) \tag{3.7.2}$$

where $P_s(i)$ is the probability of observing a score of s. This is just the number of times it occurs in a dataset divided by the number of elements in that data set. Applying Equation 3.7.2 to the set of scores, we need to calculate these weights:

Score	65	67	94	43	76
P_s	1/8	3/8	2/8	1/8	1/8

As with all probabilities, the sum of all probabilities possible must be one. These confirm that for the weights here:

$$\frac{1}{8}+\frac{3}{8}+\frac{2}{8}+\frac{1}{8}+\frac{1}{8}=\frac{8}{8}=1$$

This is the discretized "normalization" criterion (the same as why we normalize wavefunctions).

So, now we can use Equation 3.7.2 properly

$$\begin{aligned}\langle s\rangle &= 65\times\frac{1}{8}+67\times\frac{3}{8}+94\times\frac{2}{8}+43\times\frac{1}{8}+76\times\frac{1}{8}\\ &= 71.625\end{aligned}$$

Hence, Equation 3.7.2 gives the same result, as expected, from Equation 3.7.1.

Quantum Expectation Values

The extension of the classical expectation (average) approach in Example 3.7.1 using Equation 3.7.2 to evaluating quantum mechanical expectation values requires three small changes:

1. Switch from descretized to continuous variables
2. Substitute the wavefunction squared for the probability weights (i.e., the probability distribution)
3. Use an operator instead of the scalar

Hence, the quantum mechanical expectation value $\langle o\rangle$ for an observable, o, associated with an operator, $\hat{O}$, is given by

$$\langle o\rangle=\int_{-\infty}^{+\infty}\psi^*\hat{O}\psi\,dx \tag{3.7.3}$$

where x is the range of space that is integrated over (i.e., an integration over all possible probabilities). The expectation value changes as the wavefunction changes and the operator used (i.e, which observable you are averaging over).

> In general, changing the wavefunction changes the expectation value for that operator for a state defined by that wavefunction.

Average Energy of a Particle in a Box

If we generalize this conclusion, such integrals give the average value for any physical quantity by using the operator corresponding to that physical observable in the integral in Equation 3.7.3. In the equation below, the symbol $\langle H\rangle$ is used to denote the average value for the total energy.

$$\langle H\rangle=\int_{-\infty}^{\infty}\psi^*(x)\hat{H}\psi(x)dx \tag{3.7.4}$$

$$=\int_{-\infty}^{\infty}\psi^*(x)\hat{KE}\psi(x)dx+\int_{-\infty}^{\infty}\psi^*(x)\hat{V}\psi(x)dx \tag{3.7.5}$$

$$=\underbrace{\int_{-\infty}^{\infty}\psi^*(x)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x)dx}_{\text{average kinetic energy}}+\underbrace{\int_{-\infty}^{\infty}\psi^*(x)\hat{V}(x)\psi(x)dx}_{\text{average potential energy}} \tag{3.7.6}$$

The Hamiltonian operator consists of a kinetic energy term and a potential energy term. The kinetic energy operator involves

differentiation of the wavefunction to the right of it. This step must be completed before multiplying by the complex conjugate of the wavefunction. The potential energy, however, usually depends only on position and not momentum (i.e., it involves conservative forces). The potential energy operator therefore only involves the coordinates of a particle and does not involve differentiation. For this reason we do not need to use a caret over V in Equation 3.7.6.

Equation 3.7.6 can be simplified

$$\langle H \rangle = \langle KE \rangle + \langle V \rangle \tag{3.7.7}$$

The potential energy integral then involves only products of functions, and the order of multiplication does not affect the result, e.g. 6×4 = 4×6 = 24. This property is called the **commutative property**. The average potential energy therefore can be written as

$$\langle V \rangle = \int_{-\infty}^{\infty} V(x)\psi^*(x)\psi(x)dx \tag{3.7.8}$$

This integral is telling us to take the probability that the particle is in the interval dx at x, which is $\psi^*(x)\psi(x)dx$, multiply this probability by the potential energy at x, and sum (i.e., integrate) over all possible values of x. This procedure is just the way to calculate the average potential energy $\langle V \rangle$ of the particle.

Exercise 3.7.2 : Particle in Box

Evaluate the two integrals in Equation 3.7.6 for the PIB wavefunction $\psi(x) = \sqrt{\frac{2}{L}}\sin(kx)$ with the potential function $V(x) = 0$ from 0 to the length of a box L with $k = \frac{\pi}{L}$.

Solution

The *average kinetic energy* is

$$\begin{aligned}
\langle KE \rangle &= \int_0^L \left(\sqrt{\frac{2}{L}}\right)\sin(kx)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\left(\sqrt{\frac{2}{L}}\right)\sin(kx)dx \\
&= \left(\frac{2}{L}\right)\int_0^L \sin(kx)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial}{\partial x}\cos(kx)(k)dx \\
&= \left(\frac{2}{L}\right)\int_0^L \sin(kx)\left(\frac{-\hbar^2}{2m}\right)\sin(kx)(k)(-k)dx \\
&= \left(\frac{2}{L}\right)\left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \sin^2(kx)dx
\end{aligned}$$

We can solve this intergral using the standard half-angle representation from an integral table. Or we can recognize that we already did this integral when we normalized the PIB wavefunction by rewriting this integral:

$$\langle KE \rangle = \left(\frac{2}{L}\right)\left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \sin^2(kx)dx$$

$$= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \left(\frac{2}{L}\right)\sin^2(kx)dx$$

$$= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \psi^*(x)\psi(x)dx \quad (= 1)$$

$$= \frac{k^2\hbar^2}{2m}$$

Thus, the average value for the total energy of this particular system is

$$\langle KE \rangle = \frac{k^2\hbar^2}{2m} = \frac{\pi^2\hbar^2}{2mL^2}$$

Hence, the average kinetic energy of the wavefunction is dependent on the n quantum number

The *average potential energy* is

$$\langle V \rangle = \int_{-\infty}^{\infty} \sin(kx)0\sin(kx)dx = 0$$

Thus, the average potential energy of the PIB is 0 irrespective of the wavefunction.

Hence via Equation 3.7.7 for this system and set of wavefunctions

$$\langle H \rangle = \frac{\pi^2\hbar^2}{2mL^2}$$

This is the same result obtained from solving the eigenvalue equation for the PIB. However, if the wavefunctions used were NOT eigenstates of energy, then we cannot use the eigenvalue approach and need to rely on the expectation values to describe the energy of the system.

What is the lowest energy for a particle in a box? The lowest energy level is E_1, and it is important to recognize that this lowest energy of a particle in a box is not zero. This finite energy is called the **zero-point energy**, and the motion associated with this energy is called the zero-point motion. Any system that is restricted to some region of space is said to be bound. The zero-point energy and motion are manifestations of the wave properties and the Heisenberg Uncertainty Principle, and are general properties of bound quantum mechanical systems.

Exercise 3.7.2 : Progressing to the Classical Limit

What happens to the energy level spacing for a particle-in-a-box when mL^2 becomes much larger than h^2? What does this result imply about the relevance of quantization of energy to baseballs in a box between the pitching mound and home plate? What implications does quantum mechanics have for the game of baseball in a world where h is so large that baseballs exhibit quantum effects?

Answer available at the end of this section.

The first derivative of a function is the rate of change of the function, and the second derivative is the rate of change in the rate of change, also known as the curvature. A function with a large second derivative is changing very rapidly. Since the second derivative of the wavefunction occurs in the Hamiltonian operator that is used to calculate the energy by using the Schrödinger equation, a wavefunction that has sharper curvatures than another, i.e. larger second derivatives, should correspond

to a state having a higher energy. A wavefunction with more nodes than another over the same region of space must have sharper curvatures and larger second derivatives, and therefore should correspond to a higher energy state.

Exercise 3.7.3 : Nodes and Energies

Identify a relationship between the number of nodes in a wavefunction and its energy by examining the graphs you made above. A node is the point where the amplitude passes through zero. What does the presence of many nodes mean about the shape of the wavefunction?

Average Position of a Particle in a Box

We can calculate the most probable position of the particle from knowledge of probability distribution, $\psi^*\psi$. For the ground-state particle in a box wavefunction with $n = 1$ (Figure $3.7.1a$)

$$\psi_{n=1} = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \tag{3.7.9}$$

This state has the following probability distribution (Figure $3.7.1b$):

$$\psi^*_{n=1}\psi_{n=1} = \frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)$$

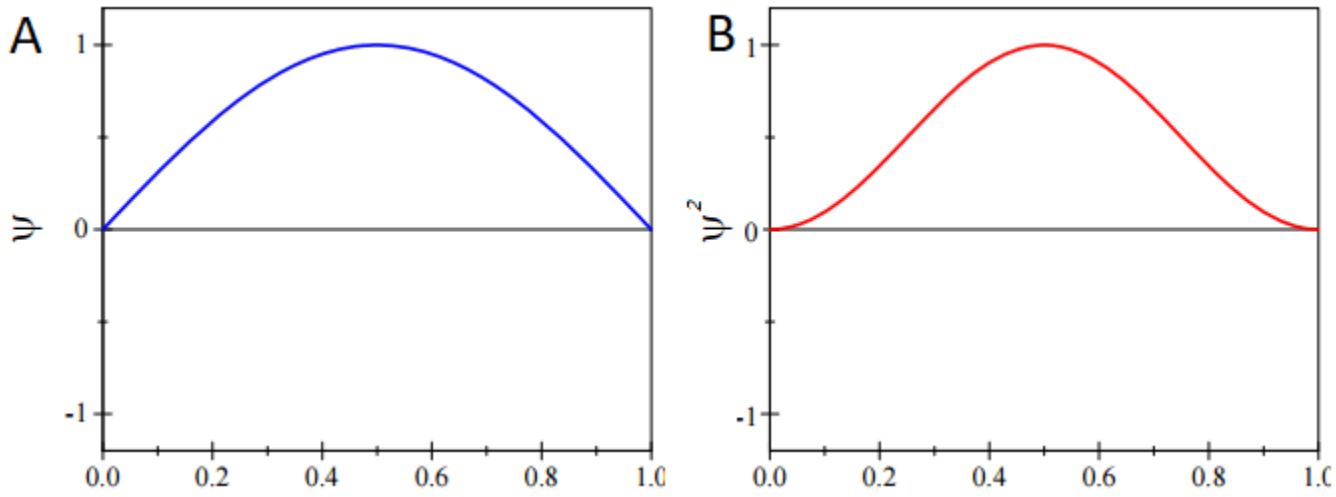


Figure 3.7.1 : (left) The ground-state ($n = 1$) wavefunction for a particle in a box. (right) The ground-state ($n = 1$) probability for a particle in a box.

The expectation value for position with the $\hat{x} = x$ operation for any wavefunction (Equation 3.7.3) is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^* x \psi \, dx$$

which for the ground-state wavefunction (Equation 3.7.9) shown in Figure 3.7.1 is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) x \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \tag{3.7.10}$$

$$= \frac{2}{L} \int_{-\infty}^{+\infty} x \sin^2\left(\frac{\pi x}{L}\right) \tag{3.7.11}$$

Solution by Inspection

Without even having to evaluate Equation 3.7.11, we can get the expectation value from simply inspecting $\psi^*_{n=1}\psi_{n=1}$ in (Figure $3.7.1; right$). This is a symmetric distribution around the center of the box ($L/2$) so it is just as likely to be found in the left half than the right half. Moreover, specifically at any point a fixed distance away from the mean, i.e.

$$\psi^*_{n=1}\psi_{n=1}(L/2+\Delta x) = \psi^*_{n=1}\psi_{n=1}(L/2-\Delta x)$$

Therefore, the particle is most likely to be found at the center of the box. So

$$\langle x\rangle = \frac{L}{2}$$

Exercise 3.7.4

Use the general form of the particle-in-a-box wavefunction for any n to find the mathematical expression for the position expectation value $\langle x\rangle$ for a box of length L. How does $\langle x\rangle$ depend on n?

Average Momentum of a Particle in a Box

What is the average momentum of a particle in the box? We start with Equation 3.7.3 and use the momentum operator

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.7.12}$$

We note that the particle-in-a-box wavefunctions are **not** eigenfunctions of the momentum operator (Exercise 3.7.4). However, this does not mean that Equation 3.7.3 is inapplicable as Example 3.7.2 demonstrates.

Example 3.7.3 : The Average Momentum of a Particle in a Box is Zero

Even though the wavefunctions are not momentum eigenfunctions, we can calculate the expectation value for the momentum. Show that the expectation or average value for the momentum of an electron in the box is zero in every state (i.e., arbitrary values of n).

Strategy

First write the expectation value integral (Equation 3.7.3) with the momentum operator. Then insert the expression for the wavefunction and evaluate the integral as shown here.

Solution

$$\begin{aligned}\langle p\rangle &= \int_0^L \psi_n^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi_n(x)dx \\ &= \int_0^L \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)\left(-i\hbar\frac{d}{dx}\right)\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)dx \\ &= -i\hbar\left(\frac{2}{L}\right)\int_0^L \sin\left(\frac{n\pi x}{L}\right)\left(\frac{d}{dx}\right)\sin\left(\frac{n\pi x}{L}\right)dx \\ &= -i\hbar\left(\frac{2}{L}\right)\left(\frac{n\pi}{L}\right)\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx \\ &= 0\end{aligned}$$

Note that this makes sense since the particles spends an equal amount of time traveling in the $+x$ and $-x$ direction.

Interpretation

It may seem that this means the particle in a box does not have any momentum, which is incorrect because we know the energy is never zero. In fact, the energy that we obtained for the particle-in-a-box is entirely kinetic energy because we set the potential energy at 0. Since the kinetic energy is the momentum squared divided by twice the mass, it is easy to understand how the average momentum can be zero and the kinetic energy finite

Exercise 3.7.5

Show that the particle-in-a-box wavefunctions are not eigenfunctions of the momentum operator (Equation 3.7.12).

Answer available at the end of this section.

Exercise 3.7.6

Write the particle-in-a-box wavefunction as a normalized linear combination of the momentum eigenfunctions e^{ikx} and e^{-ikx} by using Euler's formula. Show that the momentum eigenvalues for these two functions are $p = +\hbar k$ and $-\hbar k$.

The interpretation of the results of Exercise 3.7.6 is physically interesting. The exponential wavefunctions in the linear combination for the sine function represent the two opposite directions in which the electron can move. One exponential term represents movement to the left and the other term represents movement to the right (Figure 3.7.2).

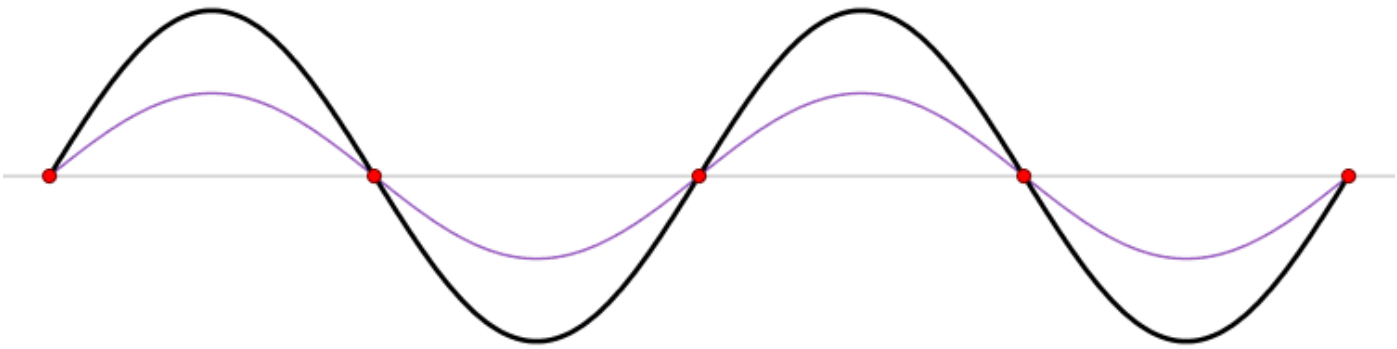


Figure 3.7.2 : Two waves traveling in opposite directions across the same medium combine linearly. In this animation, both waves have the same wavelength and the sum of amplitudes results in a standing wave. (Public Domain; LucasVB).

The electrons are moving, they have kinetic energy and momentum, yet the average momentum is zero.

Did we just Violate the Uncertainty Principle?

Does the fact that the average momentum of an electron is zero and the average position is $L/2$ violate the Heisenberg Uncertainty Principle? No, because the Heisenberg Uncertainty Principle pertains to the uncertainty in the momentum and in the position, not to the average values. Quantitative values for these uncertainties can be obtained to compare with the limit set by the Heisenberg Uncertainty Principle for the product of the uncertainties in the momentum and position. However, to do this we need a quantitative definition of uncertainty, which is discussed in the following Section.

Orthogonality

In vector calculus, *orthogonality* is the relation of two lines at right angles to one another (i.e., perpendicularity), but is generalized into n dimensions via zero amplitude "dot products" or "inner products." Hence, orthogonality is thought of as describing **non-overlapping**, **uncorrelated**, or **independent** objects of some kind. The concept of orthogonality extends to functions (wavefunctions or otherwise) too. Two functions ψ_A and ψ_B are said to be orthogonal if

$$\int_{allspace} \psi_A^* \psi_B d\tau = 0 \tag{3.7.13}$$

In general, eigenfunctions of a quantum mechanical operator with different eigenvalues are orthogonal. Are the eigenfunctions of the particle-in-a-box Hamiltonian orthogonal?

Exercise 3.7.7

Evaluate the integral $\int \psi_1^* \psi_3 dx$ for all possible pairs of particle-in-a-box eigenfunctions from $n = 1$ to $n = 3$ (use symmetry arguments whenever possible) and explain what the results say about orthogonality of the functions.

Answers

As mL^2 becomes much larger than h^2, as everyday objects are, the spacing between energy levels becomes much smaller. This shows how the quantizations of energy levels become irrelevant for an everyday object, as the quantizations of the energy of baseballs in a box between the pitching mound and home plate would appear particularly continuous for such a relatively large mass and box length. If h were so large that a baseball experiences quantum effects then a game of baseball would be far less predictable, in a classical world the position of a baseball can be easily predicted by the everyday understanding of projectile motion, however, in such a quantum world the baseball would not behave with expected projectile motion but instead behave wave-like with a probability of being in a certain position.

The easiest way to address this question is asking if the PIB wavefunction also satisfies the eigenvalue equation using the momentum operation instead of the Hamiltonian operator (3rd postulate of QM). That is

$$\hat{p}_x\psi(n) = p\psi(n)$$

with the following PIB wavefunctions

$$\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

and

$$\hat{p} = -i\hbar\frac{d}{dx}$$

and p is a real scalar (since it is a measurable).

$$\begin{aligned}\hat{p}_x\psi_n &= -i\hbar\frac{d}{dx}\left[\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\right]\\ &= -i\hbar\sqrt{\frac{2}{L}}\cos\left(\frac{n\pi x}{L}\right)\left(\frac{n\pi}{L}\right)\\ &\neq p\psi_n\end{aligned}$$

Hence, the PIB wavefunctions are NOT eigenfunctions of the momentum operator.

Alternative Solution

An alternative, albeit more complicated, approach is to recognize that the uncertainty of p must be zero if the wavefunction is an eigenstate of the momentum operator. Hence

$$\sqrt{\langle p^2\rangle - \langle p\rangle^2} = 0$$

This requires calculating the $\langle p^2\rangle$ and $\langle p\rangle$ expectation values:

$$\begin{aligned}\langle p\rangle &= \int_0^L \psi^*\left[-i\hbar\frac{d}{dx}\right]\psi dx\\ &= -i\hbar\int_0^L \frac{2}{L}\sin\left(\frac{n\pi x}{L}\right)\frac{d}{dx}x\sin\left(\frac{n\pi x}{L}\right)dx\\ &= -i\frac{\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx\\ &= 0\end{aligned}$$

This integral is zero via orthonormality of the sine and cosine functions (although you can expand the integrand and confirm this).

$$\begin{aligned}\langle p^2\rangle &= \int_0^L \psi^*\left[-i\hbar\frac{d}{dx}\right]^2\psi dx\\ &= \frac{\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\frac{d^2}{dx^2}\sin\left(\frac{n\pi x}{L}\right)dx\\ &= \frac{-\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx\\ &= -\frac{\mathrm{h}^2}{L}\end{aligned}$$

Now the integral above is 1 using orthonormality (although you can expand the integrand and confirm this). Now we calculate the uncertainty in momentum in the PIB wavefunctions:

$$\begin{aligned}\sqrt{\langle p^2\rangle - \langle p\rangle^2} &= \sqrt{\frac{-\mathrm{h}^2}{L} - 0^2}\\ &= \sqrt{\frac{-\mathrm{h}^2}{L}}\\ &\neq 0 \rightarrow\end{aligned}$$

Since the uncertainty is not 0, different measurements (experiments) will results in different values of momentum being quantified. Hence, the PIB wavefunctions are **not** eigenfunctions of the momentum operator.

It must be equally likely for the particle-in-a-box to have a momentum $-p$ as $+p$. The average of $+p$ and $-p$ is zero, yet p^2 and the average of p^2 are not zero. The information that the particle is equally likely to have a momentum of $+p$ or $-p$ is contained in the wavefunction. In fact, the sine function is a representation of the two momentum eigenfunctions e^{+ikx} and e^{-ikx} (Figure 3.7.2).

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3.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

Learning Objectives

- Expand on the introduction of Heisenberg's Uncertainty Principle by calculating the Δx or Δp directly from the wavefunction

As will be discussed in Section 4.6, the operators $\hat{x}$ and $\hat{p}$ are not compatible and there is **no** measurement that can precisely determine the coresponding observables (x and p) simultaneously. Hence, there must be an uncertainty relation between them that specifies how uncertain we are about one quantity given a definite precision in the measurement of the other. Presumably, if one can be determined with infinite precision, then there will be an infinite uncertainty in the other. The uncertainty in a general quantity A is

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} \tag{3.8.1}$$

where $\langle A^2 \rangle$ and $\langle A \rangle$ are the expectation values of $\hat{A}^2$ and $\hat{A}$ operators for a specific wavefunction. Extending Equation 3.8.1 to x and p results in the following uncertainties

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \tag{3.8.2}$$

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \tag{3.8.3}$$

These quantities can be expressed explicitly in terms of the (time-dependent) wavefunction $\Psi(x,t)$ using the fact that

$$\langle x \rangle = \langle \Psi(t) | \hat{x} | \Psi(t) \rangle \tag{3.8.4}$$

$$= \int \Psi^*(x,t) x \Psi(x,t)\, dx \tag{3.8.5}$$

and

$$\langle x^2 \rangle = \langle \Psi(t) | \hat{x}^2 | \Psi(t) \rangle \tag{3.8.6}$$

$$= \int \Psi^*(x,t) x^2 \Psi(x,t)\, dx \tag{3.8.7}$$

The middle terms in both Equations 3.8.4 and 3.8.6 are the integrals expressed in Dirac's Bra-ket notation. Similarly using the definition of the linear momentum operator:

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}.$$

So

$$\langle p \rangle = \langle \Psi(t) | \hat{p} | \Psi(t) \rangle \tag{3.8.8}$$

$$= \int \Psi^*(x,t) - i\hbar \frac{\partial}{\partial x} \Psi(x,t)\, dx \tag{3.8.9}$$

and

$$\langle p^2 \rangle = \langle \Psi(t) | \hat{p}^2 | \Psi(t) \rangle \tag{3.8.10}$$

$$= \int \Psi^*(x,t) \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) \Psi(x,t)\, dx \tag{3.8.11}$$

Time-dependent vs. time-independent wavefunction

The expectation values above are formulated with the total time-dependence wavefunction $\psi(x,t)$ that are functions of x and t. However, it is easy to show that the same expectation value would be obtained if the time-independent wavefunction $\psi(x)$ that are functions of only x are used. If $V(x)$ in $\hat{H}$ is time independent, then the wavefunctions are stationary and the expectation value are time-independent. You can easily confirm that by comparing the expectation values using the general formula for a stationary wavefunction

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

and for $\psi(x)$.

The Heisenberg uncertainty principle can be quantitatively connected to the properties of a wavefunction, i.e., calculated via the expectation values outlined above:

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{3.8.12}$$

This essentially states that the greater certainty that a measurement of x or p can be made, the greater will be the *uncertainty* in the other. Hence, as Δp approaches 0, Δx must approach ∞, which is the case of the free particle (e.g, with $V(x) = 0$) where the momentum of a particles can be determined precisely.

Example 3.8.1 : Uncertainty with a Gaussian wavefunction

A particle is in a state described by the wavefunction

$$\psi(x) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} \tag{3.8.13}$$

where a is a constant and $-\infty \leq x \leq \infty$. Verify that the value of the product $\Delta p \Delta x$ is consistent with the predictions from the uncertainty principle (Equation 3.8.12).

Solution

Let's calculate the average of x:

$$\begin{aligned}
\langle x \rangle &= \int_{-\infty}^{\infty} \psi^* x \psi \, dx \\
&= \int_{-\infty}^{\infty} (2a/\pi)^{\frac{1}{4}} e^{-ax^2} x (2a/\pi)^{\frac{1}{4}} e^{-ax^2} \, dx \\
&= \int_{-\infty}^{\infty} x (2a/\pi)^{\frac{1}{2}} e^{-2ax^2} \, dx \\
&= 0
\end{aligned}$$

since the integrand is an odd function (an even function times an odd function is an odd function). This makes sense given that the gaussian wavefunction is symmetric around $x = 0$.

Let's calculate the average of x^2:

$$\begin{aligned}\langle x^2\rangle &= \int_{-\infty}^{\infty} \psi^* x^2 \psi \, dx \\ &= \int_{-\infty}^{\infty} (2a/\pi)^{\frac{1}{4}} e^{-ax^2} (x^2) (2a/\pi)^{\frac{1}{4}} e^{-ax^2} \, dx \\ &= \int_{-\infty}^{\infty} x^2 (2a/\pi)^{\frac{1}{2}} e^{-2ax^2} \, dx \\ &= \frac{1}{4a}\end{aligned}$$

Let's calculate the average in p:

$$\begin{aligned}\langle p\rangle &= \int_{-\infty}^{\infty} \psi^* p \psi \, dx \\ &= \int_{-\infty}^{\infty} \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} - i\hbar \frac{d}{dx} \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} \, dx \\ &= \int_{-\infty}^{\infty} \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} (-i\hbar) \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} (-2ax) \, dx \\ &= 0\end{aligned}$$

since the integrand is an odd function.

Let's calculate the average of p^2:

$$\begin{aligned}\langle p^2\rangle &= \int_{-\infty}^{\infty} \psi^* p^2 \psi dx \\ &= -\hbar^2 \left(\frac{2a}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} 2a(ax^2 - 1) e^{-2ax^2} dx \\ &= -4\hbar^2 a^2 \left(\frac{2a}{\pi}\right)^{1/2} \int_0^{\infty} x^2 e^{-2ax^2} dx + 4\hbar^2 a \left(\frac{2a}{\pi}\right)^{1/2} \int_0^{\infty} e^{-2ax^2} dx \\ &= a\hbar^2\end{aligned}$$

We use Equation 3.8.1 to check on the uncertainty

$$\begin{aligned}\Delta x^2 &= \langle x^2\rangle - \langle x\rangle^2 = \frac{1}{4a} - 0 \\ \Delta x &= \sqrt{\Delta x^2} = \frac{1}{2\sqrt{a}} \\ \Delta p^2 &= \langle p^2\rangle - \langle p\rangle^2 = a\hbar^2 - 0 \\ \Delta p &= \sqrt{\Delta p^2} = \hbar\sqrt{a}\end{aligned}$$

Finally we have

$$\Delta p \Delta x = \left(\frac{1}{2\sqrt{a}}\right)(\hbar\sqrt{a}) = \frac{\hbar}{2}$$

Not only does the Heisenburg uncertainly principle hold (Equation 3.8.12), but the equality is established for this wavefunction. This is because the Gaussian wavefunction (Equation 3.8.13) is special as discussed later.

Exercise 3.8.1

A particle is in a state described by the ground state wavefunction of a particle in a box

$$\psi = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

where L is the length of the box and $0 \leq x \leq L$. Verify that the value of the product $\Delta p \Delta x$ is consistent with the predictions from the uncertainty principle (Equation 3.8.12).

The uncertainty principle is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space.

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3.9: A Particle in a Three-Dimensional Box

Learning Objectives

- To demonstrate how the particle in 1-D box problem can extend to a particle in a 3D box
- Introduction to nodal surfaces (e.g., nodal planes)

The quantum particle in the 1D box problem can be expanded to consider a particle within a higher dimensions as demonstrated elsewhere for a quantum particle in a 2D box. Here we continue the expansion into a particle trapped in a 3D box with three lengths L_x, L_y, and L_z. As with the other systems, there is NO FORCE (i.e., no potential) acting on the particles *inside* the box (Figure 3.9.1).

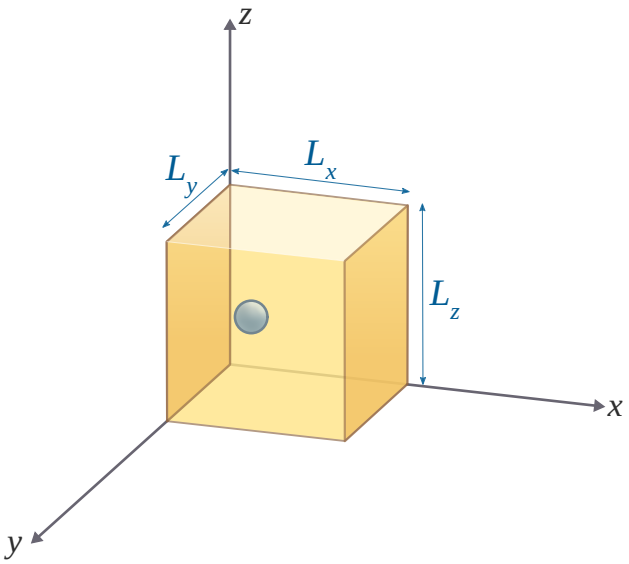


Figure 3.9.1 : A particle in 3D box with three lengths L_x, L_y, and L_z. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The potential for the particle inside the box

$$V(\vec{r}) = 0$$

- $0 \leq x \leq L_x$
- $0 \leq y \leq L_y$
- $0 \leq z \leq L_z$
- $L_x < x < 0$
- $L_y < y < 0$
- $L_z < z < 0$

$\vec{r}$ is the vector with all three components along the three axes of the 3-D box: $\vec{r} = L_x\hat{x} + L_y\hat{y} + L_z\hat{z}$. When the potential energy is infinite, then the wavefunction equals zero. When the potential energy is zero, then the wavefunction obeys the Time-Independent Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r) \tag{3.9.1}$$

Since we are dealing with a 3-dimensional figure, we need to add the 3 different axes into the Schrondinger equation:

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2}\right) = E\psi(r) \tag{3.9.2}$$

The easiest way in solving this partial differential equation is by having the wavefunction equal to a **product** of individual function for each independent variable (e.g., the Separation of Variables technique):

$$\psi(x,y,z) = X(x)Y(y)Z(z) \tag{3.9.3}$$

Now each function has its own variable:

- $X(x)$ is a function of variable x only
- $Y(y)$ is a function of variable y only
- $Z(z)$ is a function of variable z only

Now substitute Equation 3.9.3 into Equation 3.9.2 and divide it by the xyz product:

$$\frac{d^2\psi}{dx^2} = YZ\frac{d^2X}{dx^2} \Rightarrow \frac{1}{X}\frac{d^2X}{dx^2}$$

$$\frac{d^2\psi}{dy^2} = XZ\frac{d^2Y}{dy^2} \Rightarrow \frac{1}{Y}\frac{d^2Y}{dy^2}$$

$$\frac{d^2\psi}{dz^2} = XY\frac{d^2Z}{dz^2} \Rightarrow \frac{1}{Z}\frac{d^2Z}{dz^2}$$

$$\left(-\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2}\right) + \left(-\frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2}\right) + \left(-\frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2}\right) = E \tag{3.9.4}$$

E is an energy constant, and is the sum of x, y, and z. For this to work, each term must equal its own constant. For example,

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0$$

Now separate each term in Equation 3.9.4 to equal zero:

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0$$

$$\frac{d^2Y}{dy^2} + \frac{2m}{\hbar^2}\varepsilon_y Y = 0$$

$$\frac{d^2Z}{dz^2} + \frac{2m}{\hbar^2}\varepsilon_z Z = 0$$

Now we can add all the energies together to get the total energy:

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E \tag{3.9.5}$$

Do these equations look familiar? They should because we have now reduced the 3D box into three particle in a 1D box problems!

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}E_x X = 0 \approx \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \tag{3.9.6}$$

Now the equations are very similar to a 1-D box and the boundary conditions are identical, i.e.,

$$n = 1, 2, ..\infty$$

Use the normalization wavefunction equation for each variable:

$$\psi(x) = \begin{cases} \sqrt{\dfrac{2}{L_x}}\sin\dfrac{n\pi x}{L_x} & \text{if } 0 \le x \le L \\ 0 & \text{if } L < x < 0 \end{cases}$$

Normalization wavefunction equation for each variable (that substitute into Equation 3.9.3):

$$X(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi x}{L_x}\right) \tag{3.9.7}$$

$$Y(y) = \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y \pi y}{L_y}\right) \tag{3.9.8}$$

$$Z(z) = \sqrt{\frac{2}{L_z}} \sin\left(\frac{n_z \pi z}{L_z}\right) \tag{3.9.9}$$

The limits of the three quantum numbers

- $n_x = 1, 2, 3, ...\infty$
- $n_y = 1, 2, 3, ...\infty$
- $n_z = 1, 2, 3, ...\infty$

For each constant use the de Broglie Energy equation:

$$\varepsilon_x = \frac{n_x^2 h^2}{8mL_x^2} \tag{3.9.10}$$

with $n_x = 1...\infty$

Do the same for variables n_y and n_z. Combine Equation 3.9.3 with Equations 3.9.7-3.9.9 to find the wavefunctions inside a 3D box.

$$\psi(r) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \tag{3.9.11}$$

with

$$V = \underbrace{L_x \times L_y \times L_z}_{\text{volume of box}}$$

To find the Total Energy, add Equation 3.9.10 and Equation 3.9.5.

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{3.9.12}$$

Notice the similarity between the energies a particle in a 3D box (Equation 3.9.12) and a 1D box.

Degeneracy in a 3D Cube

The energy of the particle in a 3-D cube (i.e., $L_x = L_y = L$) in the *ground state* is given by Equation 3.9.12 with $n_x = 1$, $n_y = 1$, and $n_z = 1$. This energy ($E_{1,1,1}$) is hence

$$E_{1,1,1} = \frac{3h^2}{8mL^2}$$

The ground state has only one wavefunction and no other state has this specific energy; the ground state and the energy level are said to be **non-degenerate**. However, in the 3-D cubical box potential the energy of a state depends upon the sum of the squares of the quantum numbers (Equation 3.9.11). The particle having a particular value of energy in the excited state *MAY* has several different stationary states or wavefunctions. If so, these states and energy eigenvalues are said to be **degenerate**.

For the first excited state, three combinations of the quantum numbers $(n_x,\ n_y,\ n_z)$ are $(2,\ 1,\ 1)$, $(1, 2, 1)$, $(1, 1, 2)$. The sum of squares of the quantum numbers in each combination is same (equal to 6). Each wavefunction has same energy:

$$E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = \frac{6h^2}{8mL^2}$$

Corresponding to these combinations three different wavefunctions and **three** different states are possible. Hence, the first

excited state is said to be three-fold or triply degenerate. The number of independent wavefunctions for the stationary states of an energy level is called as the **degree of degeneracy** of the energy level. The value of energy levels with the corresponding combinations and sum of squares of the quantum numbers

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

as well as the degree of degeneracy are depicted in Table 3.9.1 .

Table 3.9.1 : Degeneracy properties of the particle in a 3-D cube with $L_x = L_y = L$.

$n_x^2 + n_y^2 + n_z^2$	Combinations of Degeneracy (n_x, n_y, n_z)						Total Energy (E_{n_x,n_y,n_z})	Degree of Degeneracy
3	(1,1,1)						$\frac{3h^2}{8mL^2}$	1
6	(2,1,1)	(1,2,1)	(1,1,2)				$\frac{6h^2}{8mL^2}$	3
9	(2,2,1)	(1,2,2)	(2,1,2)				$\frac{9h^2}{8mL^2}$	3
11	(3,1,1)	(1,3,1)	(1,1,3)				$\frac{11h^2}{8mL^2}$	3
12	(2,2,2)						$\frac{12h^2}{8mL^2}$	1
14	(3,2,1)	(3,1,2)	(2,3,1)	(2,1,3)	(1,3,2)	(1,2,3)	$\frac{14h^2}{8mL^2}$	6
17	(2,2,3)	(3,2,2)	(2,3,2)				$\frac{17h^2}{8mL^2}$	3
18	(1,1,4)	(1,4,1)	(4,1,1)				$\frac{18h^2}{8mL^2}$	3
19	(1,3,3)	(3,1,3)	(3,3,1)				$\frac{19h^2}{8mL^2}$	3
21	(1,2,4)	(1,4,2)	(2,1,4)	(2,4,1)	(4,1,2)	(4,2,1)	$\frac{21h^2}{8mL^2}$	6

Example 3.9.1 : Accidental Degeneracies

When is there degeneracy in a 3-D box when none of the sides are of equal length (i.e., $L_x \neq L_y \neq L_z$)?

Solution

From simple inspection of Equation 3.9.12 or Table 3.9.1 , it is clear that degeneracy originates from different combinations of n_x^2/L_x^2, n_y^2/L_y^2 and n_z^2/L_z^2 that give the same value. These will occur at common multiples of at least two of these quantities (the Least Common Multiple is one example). For example

if

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2}$$

there will be a degeneracy. Also degeneracies will exist if

$$\frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}$$

or if

$$\frac{n_x^2}{L_x^2} = \frac{n_z^2}{L_z^2}$$

and especially if

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}.$$

There are two general kinds of degeneracies in quantum mechanics: degeneracies due to a symmetry (i.e., $L_x = L_y$) and accidental degeneracies like those above.

Exercise 3.9.1

The 6th energy level of a particle in a 3D Cube box is 6-fold degenerate.

a. What is the energy of the 7th energy level?
b. What is the degeneracy of the 7th energy level?

Answer a available at the end of this section.

References

1. Atkins, Peter. Physical Chemistry 5th Ed. USA. 1994.
2. Fitts, Donald. Principles of Quantum Mechanics. United Kingdom, Cambridge. University Press. 1999
3. McQuarrie. Donald. Physical Chemistry A Molecular Approach. Sausalito, CA. University Science Books. 1997.
4. Riggs. N. V. Quantum Chemistry. Toronto, Ontario. The Macmillan Company. 1969
5. C. A. Hollingsworth, Accidental Degeneracies of the Particle in a Box, J. Chem. Educ., 1990, 67 (12), p 999

Answers

$\frac{17h^2}{8mL^2}$
three-fold (i.e., there are three wavefunctions that share the same energy.

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3.E: The Schrödinger Equation and a Particle in a Box (Exercises)

Solutions to select questions can be found online.

3.2

Determine from the following operators which are linear and nonlinear:

a. $\hat{A}f(x) = f(x)^2$ [square f(x)]
b. $\hat{A}f(x) = f^*(x)$ [form the complex conjugate of f(x)]
c. $\hat{A}f(x) = 0$ [multiply f(x) by zero]
d. $\hat{A}f(x) = [f(x)]^{-1}$ [take the reciprocal of f(x)]
e. $\hat{A}f(x) = f(0)$ [evaluate f(x) at x=0]
f. $\hat{A}f(x) = \ln f(x)$ [take the log of f(x)]

Solution

It is important to note that an operator $\hat{A}$ is *linear* if

$$\underbrace{\hat{A}[c_1 f(x) + c_2 f_2(x)]}_{\text{left side}} = \underbrace{c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)}_{\text{right side}}$$

and the operator is *nonlinear* if

$$\underbrace{\hat{A}[c_1 f_1(x) + c_2 f_2(x)]}_{\text{left side}} \neq \underbrace{c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)}_{\text{right side}}$$

a)

Evaluate the left side

$$\begin{aligned} \hat{A}[c_1 f(x) + c_2 f_2(x)] &= [c_1 f_1(x) + c_2 f_2(x)]^2 \\ &= c_1^2 f_1(x)^2 + 2 c_1 f_1(x) c_2 f_2(x) + c_2^2 f_2(x)^2 \end{aligned}$$

Evaluate the right side

$$c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) = c_1 [f_1(x)]^2 + c_2 [f_2(x)]^2 \neq \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is nonlinear

b)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1^* f_1^*(x) + c_2^* f_2^*(x)$$

Evaluate the right side

$$\begin{aligned} c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) &= c_1 f_1^*(x) + c_2 f_2^*(x) \\ &= \hat{A}[c_1 f_1(x) + c_2 f_2(x)] \end{aligned}$$

This operator is linear

c)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = 0$$

Evaluate the right side

$$c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) = c_1 f_1(x) + c_2 f_2(x) = 0$$

$$= \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is linear

d)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = \frac{1}{c_1 f_1(x) + c_2 f_2(x)}$$

Evaluate the right side

$$c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) = \frac{c_1}{f_1(x)} + \frac{c_2}{f_2(x)}$$

$$\neq \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is nonlinear

e)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 f_1(0) + c_2 f_2(0)$$

Evaluate the right side

$$= c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$$

This operator is linear

f)

Evaluate the left side

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = \ln[c_1 f_1(x) + c_2 f_2(x)]$$

Evaluate the right side

$$c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) = c1 \ln f_1(x) + c_2 \ln f_2(x)$$

$$\neq \hat{A}[c_1 f_1(x) + c_2 f_2(x)]$$

This operator is nonlinear

3.8

Show that for a particle in a box with length a with state $n = 3$ that there are 3 locations along the x axis where the probability density is at a maximum.

Solution

The probability density for a particle in a box for state $n = 3$ is

$$\psi^*\psi = \frac{2}{a}\sin^2\frac{3px}{a}$$

To maximize the probability density, take its derivative and set it equal to zero and solve for x .

$$\frac{d}{dx}\left[\frac{2}{a}\sin^2\frac{3\pi x}{a}\right] = \frac{2}{a}\cdot 2\cdot \sin\frac{3\pi x}{a}\cdot\cos\frac{3\pi x}{a}\cdot\frac{3\pi}{a} = 0$$

$$\sin\frac{3\pi x}{a}\cos\frac{3\pi x}{a} = 0$$

We want to not choose values of x that make $\sin\frac{3\pi x}{a} = 0$, as that means that the probability density will be zero. We will only choose the zeros of $\cos\frac{3\pi x}{a}$. So the possible values for x which make

$$\cos\frac{3\pi x}{a} = 0$$

are

$$\frac{3px}{a} = \frac{2m+1}{2}p \qquad m = 0, 1, 2, ...$$

$$x = \frac{(2m+1)\,a}{6}$$

We only choose $m = 0, 1, 2$ and not 3 because $m = 3$ would give $x = \frac{7a}{6}$ which is outside the box. So the locations are

$$x = \frac{a}{6}$$

$$x = \frac{a}{2}$$

$$x = \frac{5a}{6}$$

3.13

What range for L is possible for σ_x given:

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

where L is the length of the 1-D box? Hint: Remember that σ_x is the uncertainty in the position of a particle in a box.

Solution

For a particle in a box:

$$\langle x \rangle = \frac{\mathrm{L}}{2}$$

and

$$\langle x^2 \rangle = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$$

$$\sigma_x = \sqrt{\frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - (\frac{\mathrm{L}}{2})^2}$$

By inspection, only values of σ_x less than L will make this statement true.

3.14

Using the trigonometric identity

$$\cos(2x) = 2\cos^2 x - 1$$

show that

$$\int_0^a 2\cos^2 \frac{n\pi x}{a} - 1 dx = 0$$

$$\int_0^a \cos \frac{2n\pi x}{a} dx = 0$$

$$\frac{a}{2n\pi} \sin(2n\pi) = 0$$

3.18

Is the wavefunction $\phi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ orthonormal over $0 \leq x \leq L$. Explain your reasoning.

Solution

For a wavefunction to be orthonormal, it has to satisfy these conditions 1.) it has to be orthogonal and 2.) it has to be normalized.

To show that it is orthogonal:

$$\int_0^L \phi_m \phi *_n \, dx = 0$$

when $m \neq$ n

To show that that the wavefunction is normalized it must follow that

$$\int_0^L \phi_n \phi *_n \, dx = 1$$

when m=n

Because our wavefunction satisfies both conditions, it is an orthonormal function.

We find that

$$\langle \psi_3 | \psi_3 \rangle = \int_{-\infty}^{\infty} \frac{2}{L} (\sin \frac{3\pi x}{L})^2 dx = 1$$

and

$$\langle \psi_4 | \psi_4 \rangle = \int_{-\infty}^{\infty} \frac{2}{L} (\sin \frac{3\pi x}{L})(\sin \frac{4\pi x}{L}) dx = 0$$

From orthogonality, we can learn that if n is not equal to m, our dot product will always be zero. But if n = m our dot product will equal 1.

3.22

What is the Heisenberg Uncertainty Principle? Do position and momentum follow the uncertainty principle; why or why not? If they do, what is the minimum uncertainty in the velocity of an electron if it is known to be within 1.5nm of a nucleus?

Solution

The Heisenberg Uncertainty Principle states that two properties that follow cannot be **simultaneously** measured to **arbitrary** precision. Position and momentum follow the principle. If one were to try and commute these two operators, one would not get zero and therefore the properties do not commute. If they do not commute then they cannot be measured to arbitrary precision.

We know that

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

And that p = mv. This gives

$$m\Delta x \Delta v \geq \frac{\hbar}{2}$$

The mass of an electron is known is $m_e \approx 9.1 \times 10^{-31}\ kg$. The problem also gives Δx to be 1.5 nm. From here, it becomes a plug and chug to solve for Δv.

$$\Delta v = 3.86 \times 10^4$$

3.23

Describe the degeneracies of a two-dimensional box whose two sides have different lengths.

Solution

The energies of a two-dimensional box is given by,

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

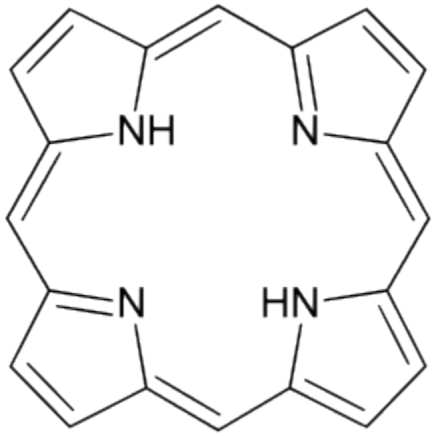
We can see that even if $a \neq b$, the energy levels will not necessarily be degenerate.

3.26

How many degenerate states do the first three energy levels for a three-dimensional particle in a box have if $a = b = c$?

3.27

Metal porphyrin molecules are commonly in many proteins and it has the general structure.



This molecule is planar, so we can approximate π electrons as being confined inside a square. What are energy levels and corresponding degeneracies of a particle in a square of side m? Porphyrin molecules have 18 π electrons. If the length of the molecule is 850 pm, what is the lowest energy absorption of the porphyrin molecules? (the experimental value ≈ 17,000 cm^{-1})

Solution

The first energy level is $E_{(1,1,1)}$ which has no degeneracy.

The second energy state is $E_{(2,1,1)}=E_{(1,2,1)}=E_{(1,1,2)}$, therefore it has three degenerate states.

The third energy state is $E_{(2,2,1)}=E_{(2,1,2)}=E_{(1,2,2)}$, therfeore it has three degenerate states.

3.26

For a two dimensional box of width w and height $h = \sqrt{a}w$, calculate all possible energy combinations between E_{11} and E_{33} note any degeneracy.

Solution

The energy of a two dimensional particle in the box has the form,

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{w^2} + \frac{n_y^2}{h^2}\right)$$

In this specific case $h = \sqrt{a}w$ so we can simplify the problem to,

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{w^2} + \frac{2n_y^2}{w^2}\right)$$

Now we can tabulate the energy level indicating degeneracy.

E_{xy}	Degeneracy	$\frac{E8mw^2}{h^2}$
E_{11}	1	3
E_{12}. E_{31}	2	5
E_{21}	1	4
E_{22}	1	6
E_{13}. E_{32}	2	7
E_{23}	1	8
E_{33}	1	9

3.32

In this problem, we will explore the quantum-mechanical problem of a free particle that is not restricted to a finite region. Remember quantized energies of a particle in a box is a direct result from the boundary conditions set by the confines of the box.

When the potential energy $V(x)$ is equal to zero and the Schrodinger equation become

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

The two solutions to this Schrodinger equation are

$$\psi_1(x) = A_1 e^{ikx}$$

$$\psi_2(x) = A_2 e^{-ikx}$$

where

$$k = \frac{(2mE)^(1/2)}{\hbar}$$

Show that $\psi_1(x)$ and $\psi_2(x)$ are solution to the Schrodinger equation where the potential energy $V(x)$ is equal to zero

Solution

In order to prove that $\psi_1(x)$ and $\psi_2(x)$ are solutions we need to mention a few values

$$p = \hbar k \rightarrow k = p/\hbar \rightarrow k = \frac{(2mE)^{1/2}}{\hbar}$$

Now we have

$$\frac{d^2 Ae^{\pm ikx}}{dx^2} + \frac{2mE}{\hbar^2}Ae^{\pm ikx} = 0$$

$$A(\pm ik)^2 e^{\pm ikx} + \frac{2mE}{\hbar^2}Ae^{\pm ikx} = 0 \rightarrow -k^2 + \frac{2mE}{\hbar^2} = 0$$

Cancel the like terms

Thus, $k = \frac{(2mE)^{1/2}}{\hbar}$, which equals the original k value

3.32

Show that E had to be a positive value, since when E is negative the wave function become unbounded for large x values

Solution

If E < 0 then k becomes imaginary, $k = ik$

$\psi = Ae^{\pm ikx} = Ae^{\pm i(ik)x}Ae^{\pm kx}$

For $\psi_1(x) = A_1 e^{-kx}$ this will blow up for x → - ∞

For $\psi_2(x) = A_2 e^{kx}$ this will blow up for x → ∞

3.32

With $\hat{P}\ \psi_1(x)$ and $\hat{P}\ \psi_2(x)$ as eigenvalue equations, show that

$$\hat{P}\psi_1(x) = -i\hbar\frac{d\psi_1}{dx} = \hbar k\psi_1$$

and

$$\hat{P}\psi_2(x) = -i\hbar\frac{d\psi_2}{dx} = -\hbar k\psi_2$$

Solution

$$\hat{P}\psi_1(x) = -i\hbar\frac{d\psi_1}{dx} = -i\hbar\frac{d}{dx}A_1e^{+ikx} = -i\hbar A_1(ik)e^{ikx} = +\hbar kA_1e^{ikx} = +\hbar k\psi_1$$

$$\hat{P}\psi_2(x) = -i\hbar\frac{d\psi_2}{dx} = -i\hbar\frac{d}{dx}A_2e^{-ikx} = -i\hbar A_2(-ik)e^{ikx} = -\hbar kA_1e^{-ikx} = -\hbar k\psi_2$$

Now we can show that

$$E = \frac{p^2}{2m} = \frac{\pm(\hbar)^2}{2m} = \frac{\hbar^2k^2}{2m}$$

3.32

Show that $\psi_1^*\psi_1(x) = A_1^*A_1 = |A_1|^2$ and that $\psi_2^*\psi_2(x) = A_2^*A_2 = |A_2|^2$

Solution

$$\begin{aligned}\psi_1^*\psi_1(x) &= (A_1e^{ikx})^*A_1e^{ikx} \\ &= A_1^*A_1e^{-ikx}e^{ikx} \\ &= A_1^*A_1e^{-ikx+ikx} = A_1^*A_1e^0 \\ &= A_1^*A_1\end{aligned}$$

$$\begin{aligned}\psi_2^*\psi_2(x) &= (A_2e^{-ikx})^*A_2e^{-ikx} \\ &= A_2^*A_2e^{ikx-ikx} \\ &= A_2^*A_2e^0 = A_2^*A_2\end{aligned}$$

ψ has equal probability to be everywhere when $\Delta x = \infty$ and $\Delta p = 0$

3.33A

Assuming that a particle is characterized by a standing de Broglie wave, come up with an equation for the allowed energies of a particle in a one-dimensional box.

Solution

The de Broglie relationship is

$$\lambda = \frac{h}{p}$$

Because the waves are standing waves, an integral number of half wave-lengths will fit in the box or:

$$a = \frac{n\lambda}{2}$$

and

$$a = \frac{nh}{2p}$$

Solving for p yields

$$p = \frac{nh}{2a}$$

and the corresponding energy is

$$E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{1}{2m}\frac{n^2h^2}{4a^2} = \frac{n^2h^2}{8ma^2}$$

3.33B

Derive the lowest allowed velocity for a proton in a box of length 10^{-14} m (approximate size of nucleus), assuming the particle is described by a standing deBroglie wave.

Solution

The de Broglie wavelength is

$$\lambda = \frac{h}{p} = \frac{h}{m_p v}$$

For a one dimensional wave that has nodes on both ends of a box, an integer number of half wavelengths can fit, so

$$n\left(\frac{\lambda}{2}\right) = L$$

Substituting this wavelength in the de Broglie relationship, one gets

$$\nu = \frac{hn}{2m_L}$$

lowest allowed velocity will have $n = 1$

$$\begin{aligned}\nu &= \frac{(6.626 \times 10^{-34})(1)}{2 \times (1.67 \times 10^{-27})(10^{-14})} \\ &= 19.8 \times 10^{6} m/s\end{aligned}$$

3.33C

If a particle in a one-dimensional box is described by standing de Broglie waves within the box, derive an equation for the allowed energies. Then use that equation to find the transition energy from n=1 to n=2 given the length of the box is 350 pm and the mass of an electron is $9.109 \times 10^{-31} kg$.

Solution

The de Broglie formula is

$$\lambda = \frac{h}{p}$$

An integral number of half-wavelengths will fit in the box because the waves are standing waves so

$$\frac{n\lambda}{2} = a$$

$$\frac{nh}{2p} = a$$

Then solving for p

$$p = \frac{nh}{2a}$$

Therefore the energy equation is

$$E = \frac{mv^2}{2} = \frac{p^2}{2,m} = \frac{1}{2m}\frac{n^2h^2}{4a^2} = \frac{n^2h^2}{8ma^2}$$

Just plug into the equation to find the transition energy

$$\Delta E = \frac{h^2}{8m_e a^2}(2^2 - 1^2)$$

$$\Delta E = \frac{(6.626 \times 10^{-34} J \cdot s)^2(3)}{8(9.109 \times 10^{-31} kg)(350 \times 10^{-12} m)^2}$$

$$\Delta E = 1.47 \times 10^{-18} J$$

3.35A

Consider the two wavefunctions

$$\psi_n(x) = \sin \frac{n\pi x}{a}$$

with even n numbers and

$$\psi_n(x) = \cos \frac{n\pi x}{a}$$

with odd n numbers.

Prove that the wavefunctions can be symmetric and antisymmetric by using the operation x to -x, a is a constant.

Given that the Schrödinger equation has the expression:

$$\hat{H}(x)\psi_n(x) = E_n\psi_n(x)$$

Through the operation x to -x, the equation now becomes:

$$\hat{H}(-x)\psi_n(-x) = E_n\psi_n(-x)$$

Show that

$$\hat{H}(x) = \hat{H}(-x)$$

is true to prove the Schrödinger equation.

Solution

Substituting x by $-x$, for odd n numbers,

$$\hat{\psi}_n(-x) = \cos \frac{-n\pi x}{a} = \cos \frac{n\pi x}{a} = \hat{\psi}_n(x) \tag{3.E.1}$$

For even n numbers,

$$\hat{\psi}_n(-x) = sin\frac{-n\pi x}{a} = -sin\frac{n\pi x}{a} = -\hat{\psi}_n(x) \tag{3.E.2}$$

Thus, the wavefunction for odd n number is symmetric and even n numbers is antisymmetric.

And,

$$\hat{H}(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} = \hat{H}(x) \tag{3.E.3}$$

$$\hat{H}(-x) = -\frac{\hbar^2}{2m}\frac{d^2}{d(-x)^2} = \hat{H}(x) \tag{3.E.4}$$

Thus,

$$\hat{H}(x) = \hat{H}(-x)$$

and

$$\hat{H}(x)$$

is an even function of x.

3.35B

Show that the Hamiltonian for a Rigid Rotor Model is odd.

Solution

$$\hat{H}(x) = \hat{H}(-x)$$

so

$$\hat{H} = -\frac{h^2}{4\pi\mu}\nabla^2$$

$$\nabla^2 = \frac{d^2y}{dx^2}\frac{d^2y}{dy^2}\frac{d^2y}{dz^2}$$

so

$$\frac{d^2y}{dx^2}(x) = 0$$

and

$$\frac{d^2y}{dx^2}(-x) = 0$$

so

$$\hat{H}(x) = 0$$

and

$$\hat{H}(-x) = 0$$

so

$$\hat{H}(x) = \hat{H}(-x)$$

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4: POSTULATES AND PRINCIPLES OF QUANTUM MECHANICS

4.1: The Wavefunction Specifies the State of a System

4.2: Quantum Operators Represent Classical Variables

4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

4.4: The Time-Dependent Schrödinger Equation

4.5: Eigenfunctions of Operators are Orthogonal

4.6: Commuting Operators Allow Infinite Precision

4.E: Postulates and Principles of Quantum Mechanics (Exercises)

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4.1: The Wavefunction Specifies the State of a System

Learning Objectives

- Introduce the first postulate of quantum mechanics
- Recognize invalid wavefunction categories

In classical mechanics, the configuration or state of a system is given by a point (x, p) in the space of coordinates and momenta. This specifies everything else in the system in a fully deterministic way, in that any observable Q that can be expressed as $Q(x, p)$ can be found, and any that cannot is irrelevant. Yet, as we have seen with the diffraction of electrons, it is **impossible** to know both the position and momentum of the electron exactly at every point along the trajectory. This is mathematically expressed as the famous position-momentum uncertainty principle. Hence, specifying a state by (x, p) in classical mechanics clearly will not work in quantum mechanics. So what specifies the state of a quantum system? This is where the **first Postulate of quantum mechanics** comes in.

Postulate I

The state of the system is **completely** specified by ψ. All possible information about the system can be found in the wavefunction ψ.

The properties of a quantum mechanical system are determined by a wavefunction $\psi(r, t)$ that depends upon the spatial coordinates of the system and time, r and t. For a single particle system, r is the set of coordinates of that particle $r = (x_1, y_1, z_1)$. For more than one particle, r is used to represent the complete set of coordinates $r = (x_1, y_1, z_1, x_2, y_2, z_2, ... x_n, y_n, z_n)$. Since the state of a system is defined by its properties, ψ specifies or identifies the state and sometimes is called the state function rather than the wavefunction.

What does ψ mean? This is best answered in terms of the probability density $P(x)$ that determines the probability (density) that an object in the state $\psi(x)$ will be found at position x (the Born interpretation).

$$P(x) = \psi^*(x)\psi(x) \tag{4.1.1}$$

$$= |\psi(x)|^2 \tag{4.1.2}$$

Hence, for valid (e.g., well-behaved) wavefunctions, the normalized probability in Equation 4.1.2 holds true, such that the integral over all space is equal to 1.

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)\, dx = 1 \tag{4.1.3}$$

Equation 4.1.3 means that the chance to find a particle is 100% somewhere within all space (e.g. somewhere between $-\infty$ and $+\infty$). A wavefunction is said to be **square-integrable** if Equation 4.1.3 can be satisfied (so that the Born Interpretation to be applicable).

Definition: Square-Integrable Functions

A complex-valued function, $f(x)$, is a *square-integrable* function if the integral of the square of the absolute value is finite.

$$\int_{-\infty}^{\infty} f^*(x)f(x)\, dx < \infty$$

For this to be true, the integrals of the positive and negative portions of the real and imaginary parts of $f(x)$ must both be finite.

Let us examine this set of examples in further detail in Figure 4.1.1 . The first wavefunction ψ_1 is sharply peaked at a particular value of x, and the probability density, being its square, is likewise peaked there as well. This is the wavefunction for a particle well localized at a position given by the center of the peak, as the probability density is high there, and the width of the peak is small, so the uncertainty in the position is very small.

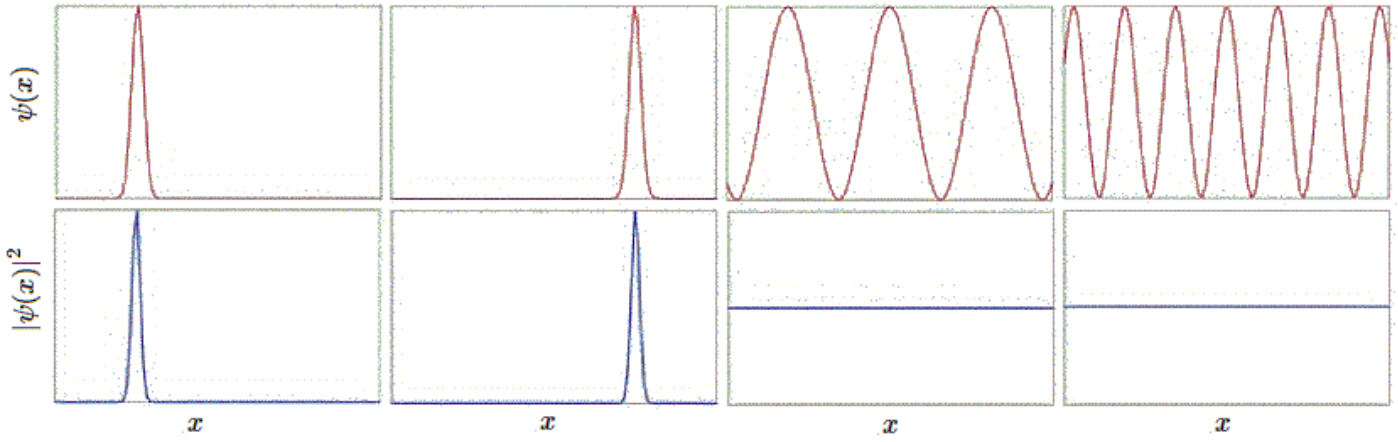


Figure 4.1.1 : Examples of good wavefunctions, $\psi(x)$, (red, top) and corresponding probability densities, $P(x)$, (blue, bottom).

The second wavefunction ψ_2 has the same peak profile, but shifted to a different position center. All of the properties of the first wavefunction hold here too, so this simply describes a particle that is well-localized at that different position. The third and fourth wavefunctions ψ_3 and ψ_4 respectively look like sinusoids of different spatial periods. The wavefunctions are actually complex of the form

$$\psi(x) = Ne^{ikx}$$

so only the real part is being plotted in Figure 4.1.1 . Note that even though the periods, k, of the oscillating wavefunctions are different,

$$\begin{aligned} P(x) &= \psi^*(x)\psi(x) \\ &= |e^{ikx}|^2 \\ &= N^2 \left(e^{-ikx}\right)\left(e^{ikx}\right) \\ &= N^2 \end{aligned}$$

for all k, so the corresponding probability densities, $P(x)$, are the same except for the normalization constant (Equation 4.1.2). We saw before that it does not make a whole lot of sense to think of a sinusoidal wave as being localized in some place. Indeed, the positions for these two wavefunctions are ill-defined, so they are not well-localized, and the uncertainty in the position is large in each case. This is Heisenberg Uncertainty Principle in action.

Ill-behaved (invalid) Wavefunctions

The Born interpretation in Equation 4.1.2 means that many wavefunctions which would be acceptable mathematical solutions of the Schrödinger equation are **not acceptable** because of their implications for the physical properties of the system. To satisfy this interpretation, wavefunctions must be:

- single valued,
- continuous, and
- finite.

These aspects mean that the valid wavefunction must be one-to-one, it cannot have an undefined slope, and cannot go to $-\infty$ or

$+\infty$. For example, the wavefunction must not be infinite over any finite region. If it is, then the integral in Equation 4.1.3 is equal to infinity. This implies that the particle described by such a wavefunction has a zero probability of being anywhere where the wavefunction is not infinite, but is certain to be found at all points where the wavefunction is infinite.

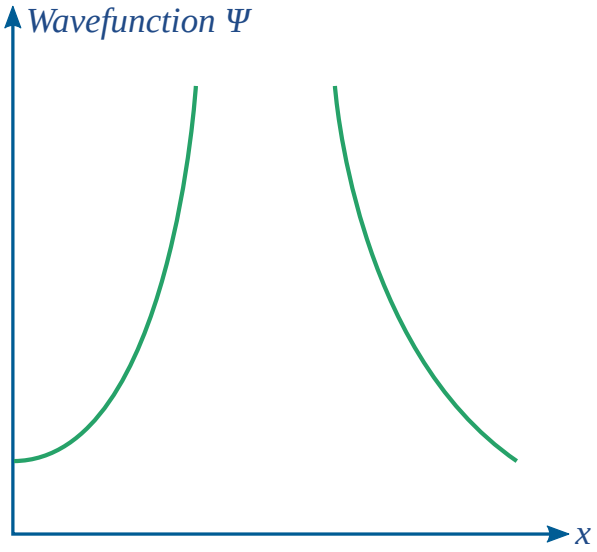


Figure 4.1.2 : This function is an invalid wavefunction since the amplitude is going to infinity over a region (the middle in this case). (CC BY-NC; Ümit Kaya via LibreTexts)

The Born interpretation also renders unacceptable solutions of the Schrödinger equation for which $|\psi(x)|^2$ has more than one value at any point. This would suggest that there were multiple different probabilities of finding the particle at that point, which is clearly absurd. The requirement that the square modulus of the wavefunction must be single-valued usually implies that the wavefunction itself must be single valued. The function in Figure 4.1.3 violates this requirement. The grey lines indicate the region where the wavefunction is multivalued.

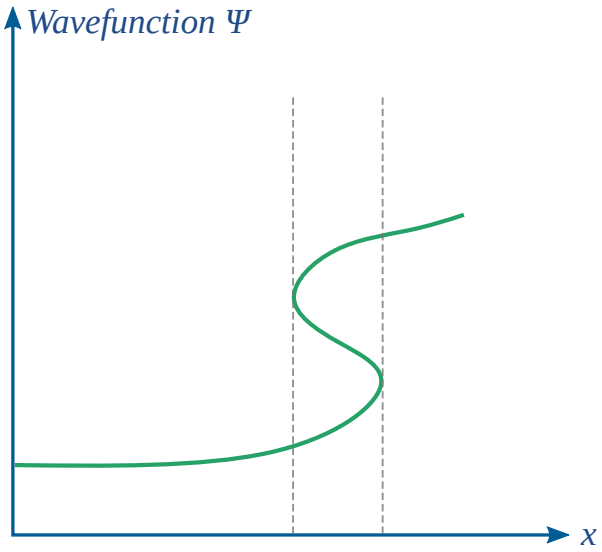


Figure 4.1.3 : This function is an invalid wavefunction since it is not a proper function (i. e., not one-to-one). (CC BY-NC; Ümit Kaya via LibreTexts)

Further restrictions arise because the wavefunction must satisfy the Schrödinger equation, which is a second-order differential equation. This implies that the second derivative of the function must exist, which implies that the first derivative of the wavefunction to exist (otherwise the second derivative is also undefined and the wavefunction cannot be a solution of the Schrödinger equation). The functions in Figure 4.1.4 are also not acceptable for these reasons.

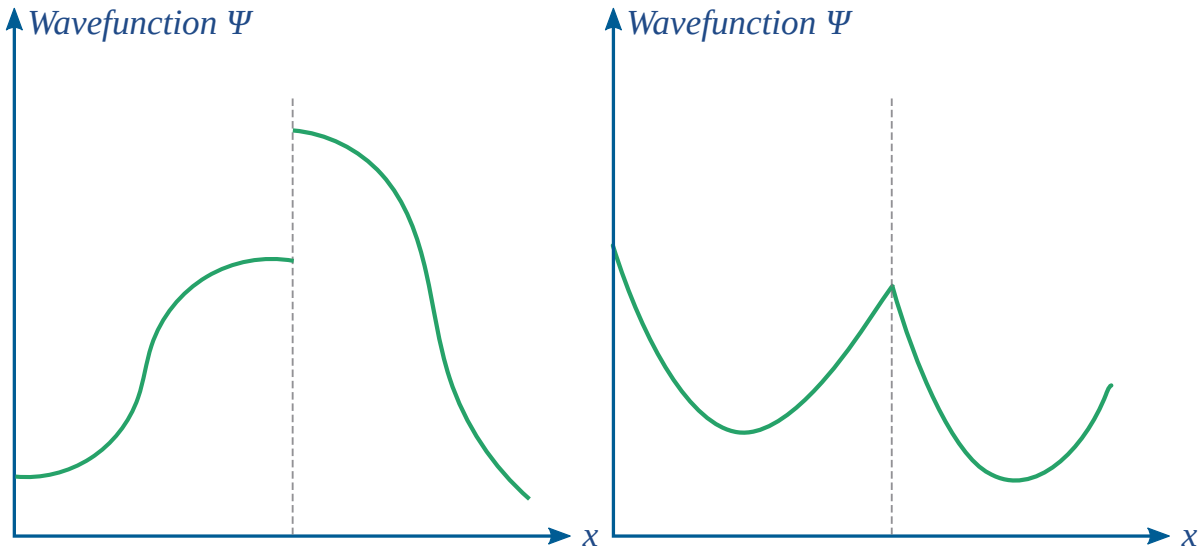


Figure 4.1.4 : These functions are invalid wavefunctions. (left) The first derivative of a function gives its gradient at a given point, and it thus exists as long as the function is continuous - only if there is a break in the function is there a point at which its first derivative does not exist. (right) The second derivative of this wavefunction is discontinuous at the point indicated, where the gradient of the line changes by more than 180°. In practice, this requirement may be somewhat flexible, particularly if the potential energy of the system shows rapid changes with distance. (CC BY-NC; Ümit Kaya via LibreTexts)

Exercise 4.1.1

Determine if each of the following functions is acceptable as a wavefunction over the indicated regions:

a. $\cos x$ over $(0, \infty)$
b. e^{x} over $(-\infty, \infty)$
c. e^{-x} over $[0, \infty)$
d. $\tan \theta$ over $[0, 2\theta]$

Solution a available at the end of this section.

Solution b available at the end of this section.

Solution c available at the end of this section.

Solution d available at the end of this section.

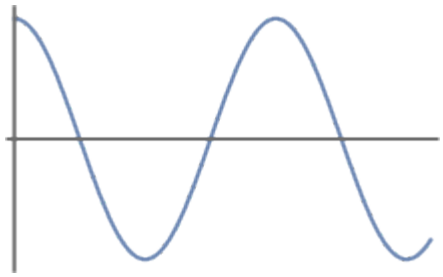
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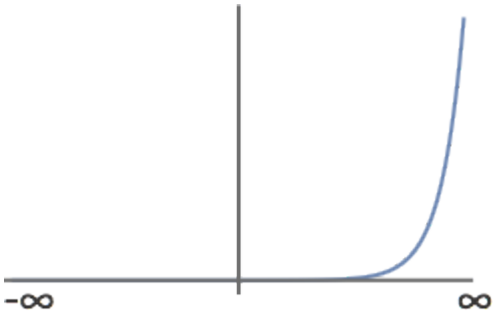
Answers

This is not an acceptable wavefunction. It is **single-valued** across the entire range. There is a single value for each value of x. It is **continuous** over the defined limits of integration, as we can see from a plot given below. However, it is not square-integrable.

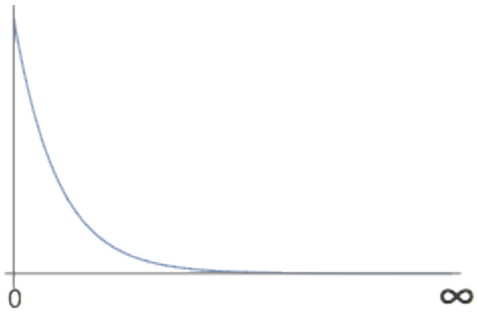
$$\int_{0}^{\infty} |\cos(x)|^{2} dx \not< \infty$$



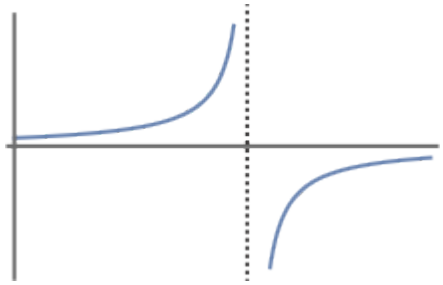
This is not an acceptable wavefunction. Over the limits of integration from $-\infty$ to ∞, this function is not square-integrable. Note in the plot below, how the function is indefinite approaching the limits of ∞.



This is an acceptable wavefunction over the given limits. It is **finite** over the given limits. It is **continuous** within given limits. It is **single-valued.** It is square-integrable with $\int_0^\infty |\Psi(x)|^2 dx = \frac{1}{2}$.



This is not an acceptable wavefunction. It is discontinuous over the limits of integration.



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4.2: Quantum Operators Represent Classical Variables

Learning Objectives

- Understand how the correspondence principle argues that a unique quantum operator exist for every classical observable.
- Recognize several of the commonly used quantum operators

An observable is a dynamic variable of a system that can be experimentally measured (e.g., position, momentum and kinetic energy). In systems governed by classical mechanics, it is a real-valued function (never complex), however, in quantum physics, every observable in quantum mechanics is represented by an independent operator that is used to obtain physical information about the observable from the wavefunction. It is a general principle of quantum mechanics that there is an operator for every physical observable. For an observable that is represented in classical physics by a function $Q(x,p)$, the corresponding operator is $Q(\hat{x},\hat{p})$.

Postulate II: The Correspondence Principle

For every observable property of a system there is a corresponding quantum mechanical operator. This is often referred to as the **Correspondence Principle**.

Classical dynamical variables, such as x and p, are represented in quantum mechanics by *linear operators* which act on the wavefunction. The operator for position of a particle in three dimensions is just the set of coordinates x, y, and z, which is written as a vector, r:

$$\vec{r} = (x,y,z) \tag{4.2.1}$$

$$= x\vec{i} + y\vec{j} + z\vec{k} \tag{4.2.2}$$

The operator for a component of linear momentum is

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{4.2.3}$$

and the operator for kinetic energy in one dimension is

$$\hat{T}_x = \left(-\frac{\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} \tag{4.2.4}$$

and in three dimensions

$$\hat{p} = -i\hbar\nabla \tag{4.2.5}$$

and

$$\hat{T} = \left(-\frac{\hbar^2}{2m}\right)\nabla^2 \tag{4.2.6}$$

The total energy operator is called the Hamiltonian operator, $\hat{H}$ and consists of the kinetic energy operator plus the potential energy operator.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{4.2.7}$$

The Hamiltonian Operator

The Hamiltonian operator is named after the Irish mathematician William Hamilton and comes from the his formulation of Classical Mechanics that is based on the total energy:

$$\hat{H} = \hat{T} + \hat{V}$$

rather than Newton's second law,

$$\vec{F} = m\vec{a}$$

In many cases only the kinetic energy of the particles and the electrostatic or Coulomb potential energy due to their charges are considered, but in general all terms that contribute to the energy appear in the Hamiltonian. These additional terms account for such things as external electric and magnetic fields and magnetic interactions due to magnetic moments of the particles and their motion.

Table 4.2.1 : Some common Operators in Quantum Mechanics

Name	Observable Symbol	Operator Symbol	Operation
Position (in 1D)	x	$\hat{X}$	Multiply by x
Position (in 3D)	$\vec{r}$	$\hat{R}$	Multiply by $\vec{r}$
Momentum (in 1D)	p_x	$\hat{P}_x$	$-\imath\hbar\frac{d}{dx}$
Momentum (in 3D)	$\vec{p}$	$\hat{P}$	$-\imath\hbar\left[\hat{i}\ \frac{d}{dx} + \hat{j}\frac{d}{dy} + \hat{k}\frac{d}{dz}\right]$
Kinetic Energy (in 1D)	T_x	$\hat{T}_x$	$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$
Kinetic Energy (in 3D)	T	$\hat{T}$	$\frac{-\hbar^2}{2m}\left[\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right]$ Which can be simplified to $\frac{-\hbar^2}{2m}\bigtriangledown^2$
Potential Energy (in 1D)	$V(x)$	$\hat{V}(x)$	Multiply by $V(x)$
Potential Energy (in 3D)	$V(x,y,z)$	$\hat{V}(x,y,z)$	Multiply by $V(x,y,z)$
Total Energy	E	$\hat{E}$	$\frac{-\hbar^2}{2m}\nabla^2 + V(x,y,z)$
Angular Momentum (x axis component)	L_x	$\hat{L_x}$	$-\imath\hbar\left[y\frac{d}{dz} - z\frac{d}{dy}\right]$
Angular Momentum (y axis component)	L_y	$\hat{L_y}$	$-\imath\hbar\left[z\frac{d}{dx} - x\frac{d}{dz}\right]$
Angular Momentum (z axis component)	L_z	$\hat{L_z}$	$-\imath\hbar\left[x\frac{d}{dy} - y\frac{d}{dx}\right]$

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4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

Learning Objectives

- To be introduced to the role of eigenvalue equations in obtaining observables from a system
- Understand how expectation values are calculated if the wavefunctions is not an eigenstate of the operator for the observable.

Recall, that we can identify the total energy operator, which is called the Hamiltonian operator, $\hat{H}$, as consisting of the kinetic energy operator plus the potential energy operator.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{4.3.1}$$

Using this notation, we write the Schrödinger Equation as

$$\hat{H}|\psi(x,y,z)\rangle = E|\psi(x,y,z)\rangle \tag{4.3.2}$$

Equation 4.3.2 says that the Hamiltonian operator operates on the wavefunction to produce the energy, which is a number, (a quantity of Joules), times the wavefunction. Such an equation, where the operator, operating on a function, produces a constant times the function, is called an **eigenvalue equation**. The function is called an **eigenfunction**, and the resulting numerical value is called the **eigenvalue**. Eigen here is the German word meaning self or own.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is the eigenvalue, and the system is said to be in an eigenstate. Equation 4.3.2 states this principle mathematically for the case of energy as the observable.

Postulate III: Obtaining Observables Requires Solving Eigenvalue Problems

If a system is described by the eigenfunction Ψ of an operator $\hat{A}$ then the value measured for the observable property corresponding to $\hat{A}$ will always be the eigenvalue a, which can be calculated from the eigenvalue equation.

$$\hat{A}|\Psi\rangle = a|\Psi\rangle \tag{4.3.3}$$

Consider a general real-space operator $A(x)$. When this operator acts on a general wavefunction $\psi(x)$ the result is usually a wavefunction with a completely different shape. However, there are certain special wavefunctions which are such that when A acts on them the result is just a multiple of the original wavefunction. These special wavefunctions are called *eigenstates*, and the multiples are called *eigenvalues*. Thus, if

$$A|\psi_a(x)\rangle = a|\psi_a(x)\rangle \tag{4.3.4}$$

where a is a complex number, then ψ_a is called an **eigenstate** of A corresponding to the eigenvalue a.

Suppose that A is an operator corresponding to some physical dynamical variable. Consider a particle whose wavefunction is ψ_a. The expectation of value A in this state is simply

$$\begin{aligned}\langle A\rangle &= \int_{-\infty}^{\infty} \psi_a^* A \psi_a dx \\ &= a\int_{-\infty}^{\infty} \psi_a^* \psi_a dx \\ &= a.\end{aligned}$$

where use has been made of Equation 4.3.4 and the normalization condition. Moreover,

$$\begin{aligned}\langle A^2\rangle &= \int_{-\infty}^{\infty} \psi_a^* A^2 \psi_a dx \\ &= a\int_{-\infty}^{\infty} \psi_a^* A \psi_a dx \\ &= a^2\int_{-\infty}^{\infty} \psi_a^* \psi_a dx \\ &= a^2.\end{aligned}$$

So the variance of A is

$$\begin{aligned}\sigma_A^2 &= \langle A^2\rangle - \langle A\rangle^2 = a^2 - a^2 \\ &= 0.\end{aligned}$$

The fact that the variance is *zero* implies that every measurement of A is bound to yield the same result: namely, a. Thus, the eigenstate ψ_a is a state which is associated with a *unique* value of the dynamical variable corresponding to A. This unique value is simply the associated eigenvalue determined by Equation 4.3.4.

Expectation Values

We have seen that $|\psi(x,t)|^2$ is the probability density of a measurement of a particle's displacement yielding the value x at time t. Suppose that we made a large number of independent measurements of the displacement on an equally large number of identical quantum systems. In general, measurements made on different systems will yield different results. However, from the definition of probability, the mean of all these results is simply

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi|^2 dx \tag{4.3.5}$$

Here, $\langle x\rangle$ is called the *expectation value* of x. Similarly the expectation value of any function of x is

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)|\psi|^2 dx. \tag{4.3.6}$$

Postulate IV

The average value of an observable measurement of a state in (*normalized*) wavefunction ψ with operator $\hat{A}$ is given by the expectation value $\langle a\rangle$:

$$\langle a\rangle = \langle\psi|a|\psi\rangle \tag{4.3.7}$$

$$= \int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx \tag{4.3.8}$$

If an unnormalized wavefunction where used, then Equation 4.3.8 changes to

$$\langle a \rangle = \frac{\langle \psi | a | \psi \rangle}{\langle \psi | \psi \rangle} \tag{4.3.9}$$

$$= \frac{\int_{-\infty}^{\infty} \psi^* \hat{A} \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx} \tag{4.3.10}$$

The denominator is just the normalization requirement discussed earlier. In general, the results of the various different measurements of x will be scattered around the expectation value $\langle x \rangle$. The degree of scatter is parameterized by the quantity

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 |\psi|^2 dx \tag{4.3.11}$$

$$\equiv \langle x^2 \rangle - \langle x \rangle^2, \tag{4.3.12}$$

which is known as the *variance* of x. The square-root of this quantity, σ_x, is called the *standard deviation* of x. We generally expect the results of measurements of x to lie within a few standard deviations of the expectation value (Figure 4.3.1).

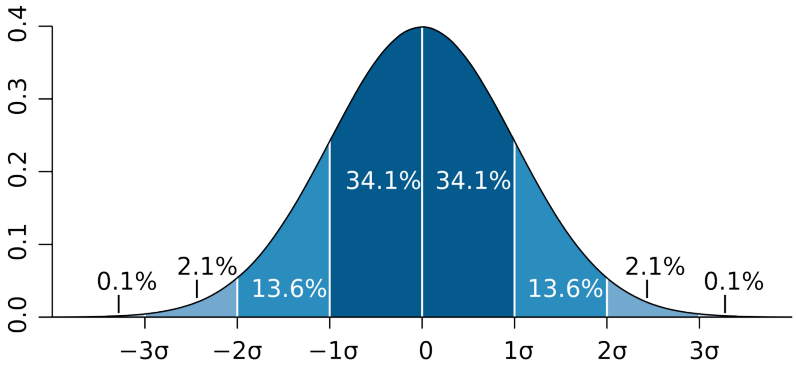


Figure 4.3.1 : A plot of a normal distribution (or bell-shaped curve) where each band has a width of 1 standard deviation. image usd with permission from Wikipedia.

Example 4.3.1

For a particle in a box in its ground state, calculate the expectation value of the

a. *position*,
b. the *linear momentum*,
c. the *kinetic energy*, and
d. the total energy

Solution

First the wavefunction needs to be defined. From the particle in the box solutions, the ground state wavefunction ($n = 1$) is

$$\psi = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

We can confirm that the wavefunction is normalized.

$$\int \psi^* \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx = 1$$

Hence, the Equation 4.3.8 is the relevant equation to use.

Solution a

The expectation value of the **position** is:

$$\begin{aligned}\langle x\rangle &= \int \psi^* x \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} x \sin\left(\frac{\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2}{L}\int_0^L x \sin^2\left(\frac{\pi x}{L}\right) dx \\ &= \frac{L}{2}\end{aligned}$$

Solution b

The expectation value of the **momentum** is:

$$\begin{aligned}\langle p\rangle &= \int \psi^* \hat{p} \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \left(-i\hbar\frac{d}{dx}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2i\hbar\pi}{L^2}\int_0^L \sin\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right) dx \\ &= 0\end{aligned}$$

Solution c

The expectation value of the **kinetic energy** is:

$$\begin{aligned}\langle T\rangle &= \int \psi^* \hat{K} \psi \, d\tau = \frac{2}{L}\int_0^L \sin\left(\frac{\pi x}{L}\right) \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right) \sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{\hbar^2\pi^2}{2mL^2}\frac{2}{L}\int_0^L \sin^2\left(\frac{\pi x}{L}\right) dx \\ &= \frac{\hbar^2\pi^2}{2mL^2}\end{aligned}$$

A position "on average" is in the middle of the box ($L/2$). It has equal probability of traveling towards the left or right, so the average momentum and velocity must be zero.

Solution d

The average kinetic energy must be equal to the total energy of the ground state of the particle in the box, as there is no other energy component (i.e, $V = 0$).

Expanding the Wavefunction

It is also possible to demonstrate that the eigenstates of an operator attributed to a observable form a **complete set** (*i.e.*, that any general wavefunction can be written as a linear combination of these eigenstates). However, the proof is quite difficult, and we shall not attempt it here.

In summary, given an operator $\hat{A}$, any general wavefunction, $\psi(x)$, can be written

$$\psi = \sum_i c_i \phi_i$$

where the c_i are complex weights, and the $\phi(x)$ are the properly normalized (and mutually orthogonal) eigenstates of $\hat{A}$: i.e.,

$$A\phi_i = a_i \phi_i$$

where a_i is the eigenvalue corresponding to the eigenstate ϕ_i, and

$$\int_{-\infty}^{\infty} \phi_i^* \phi_j dx = \delta_{ij}. \tag{4.3.13}$$

Here, δ_{ij} is called the **Kronecker delta-function**, and takes the value unity when its two indices are equal, and zero otherwise. It follows from Equations 4.3.10 and 4.3.13 that

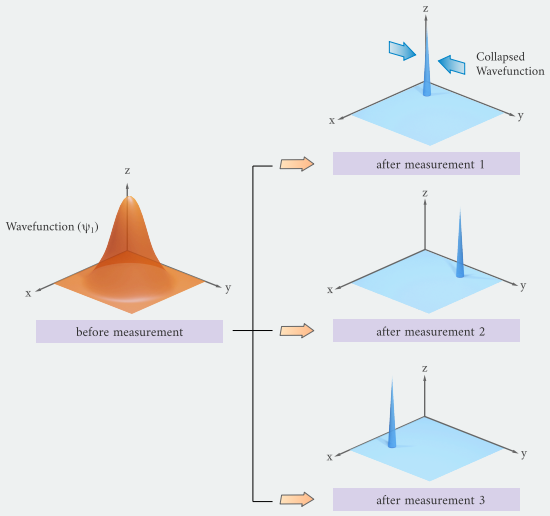
$$c_i = \int_{-\infty}^{\infty} \phi_i^* \psi dx. \tag{4.3.14}$$

Thus, the expansion coefficients in Equation 4.3.14 are easily determined, given the wavefunction ψ and the eigenstates ϕ_i. Moreover, if ψ is a properly normalized wavefunction then Equations 4.3.10 and 4.3.13 yield

$$\sum_i |c_i|^2 = 1.$$

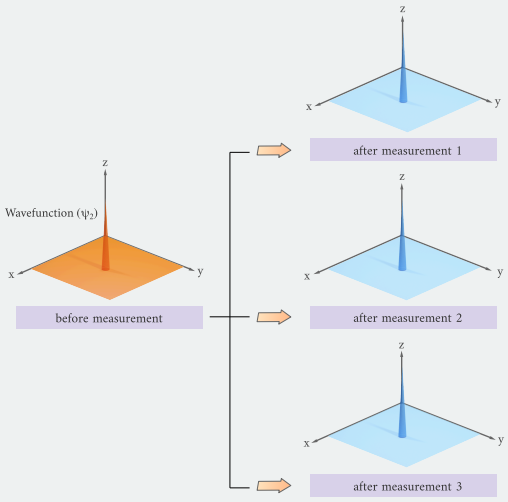
Collapsing the Wavefunction

Wavefunction collapse is said to occur when a wavefunction—initially in a superposition of several eigenstates—appears to reduce to a single eigenstate (by "observation"). A particle (or a system in general) can be found in a given state $\psi(x,t)$. Suppose now a measurement is performed on the wavefuction to characterize a specific property of the system.



The measurement of position (with the position operator) effectively collapses this wavefunction that is a superposition of position eigenstates, which are delta-functions and are continuous - i.e. not quantized. Using a different measurement operation may in quantized values (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Mathematically, an operator $\hat{A}$ is associated with this measurement process, which you suppose has a *complete orthonormal set* of eigenvalues: $\{\phi_i\}$ that is typically an infinite set of functionals that depend on quantum number n. The wavefunction Ψ can be expand and a set of basis functions can be selected to specifies the wavefunction is the coefficients $\{c_n\}$ of the expansion. Therefore, if the system is perturbed, then your wavefunction will have another set of coefficients $\{c_n'\}$.



The measurement of position (with the position operator) does not collapse this wavefunction since it is in a position eigenstate in contrast to the wavefunction above. Using a different measurement operation (e.g., kinetic energy) may "collapse" the wavefunction into a different eigenstate (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

If you wavefunction is in the eigenstate of the operator, then each measurement via that operator will give the same result.

Contributors and Attributions

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4.4: The Time-Dependent Schrödinger Equation

Learning Objectives

- Recognize the differences between the time-dependent and the time-independent Schrödinger equations
- To distinguish between stationary and non-stationary wavefunctions

There are two "flavors" of Schrödinger equations: the time-dependent and the time-independent versions. While the time-dependent Schrödinger equation predicts that wavefunctions can form standing waves (called stationary states), that if classified and understood, then it becomes easier to solve the time-dependent Schrödinger equation for any state. Stationary states can also be described by the time-independent Schrödinger equation (used only when the Hamiltonian is not explicitly time dependent). However, it should be noted that the solutions to the time-independent Schrödinger equation still have time dependencies.

Time-Dependent Wavefunctions

Recall that the time-independent Schrödinger equation

$$\hat{H}\psi(x) = E\psi(x) \tag{4.4.1}$$

yields the allowed energies and corresponding wavefunctions. However, it does not tell us how the system evolves in time. It would seem that something is missing, since, after all, classical mechanics tells us how the positions and velocities of a classical system evolve in time. The time dependence is given by solving Newton's second law

$$m\frac{d^2x}{dt^2} = F(x) \tag{4.4.2}$$

But where is t in quantum mechanics? First of all, what is it that must evolve in time? The answer is that the wavefunction (and associated probability density) must evolve. Suppose, therefore, that we prepare a system at $t = 0$ according to a particular probability density $p(x, 0)$ related to an amplitude $\Psi(x, 0)$ by

$$p(x, 0) = |\Psi(x, 0)|^2 \tag{4.4.3}$$

How will this initial amplitude $\Psi(x, 0)$ look at time t later? Note, by the way, that $\Psi(x, 0)$ does *not* necessarily need to be one of the eigenstates $\psi_n(x)$. To address this, we refer to the time-dependent Schrödinger equation that tells us how $\Psi(x, t)$ will evolve starting from the initial condition $\Psi(x, 0)$:

$$\hat{H}\Psi(x, t) = i\hbar\frac{\partial}{\partial t}\Psi(x, t) \tag{4.4.4}$$

It is important to know how it works physically and when it is sufficient to work with the time-independent version of the Schrödinger equation (Equation 4.4.1).

Postulate V

The time dependence of wavefunctions is governed by the Time-Dependent Schrödinger Equation (Equation 4.4.4).

Stationary States

Suppose that we are lucky enough to choose

$$\Psi(x, 0) = \psi_n(x)$$

with corresponding probability density

$$p(x,0) = |\psi_n(x)|^2 \tag{4.4.5}$$

We will show that

$$\Psi(x,t) = \psi_n(x)e^{-iE_nt/\hbar} \tag{4.4.6}$$

From the time-dependent Schrödinger equation

$$\frac{d\Psi}{dt} = \psi_n(x)\left(\frac{-iE_n}{\hbar}\right)e^{-iE_nt/\hbar}$$
$$i\hbar\frac{d\Psi}{dt} = E_n\psi_n(x)e^{-iE_nt/\hbar}$$

Similarly

$$\begin{aligned}\hat{H}\Psi(x,t) &= e^{-iE_nt/\hbar}\hat{H}\psi_n(x)\\ &= e^{-iE_nt/\hbar}E_n\psi_n(x)\end{aligned}$$

Hence $\psi_n(x)exp(-iE_nt/\hbar)$ satisfies the Time-Dependent Schrödinger Equation (Equation 4.4.4).

Consider the probability density for this wavefunction: $p(x,t) = |\Psi(x,t)|^2$

$$\begin{aligned}p(x,t) &= \left[\psi_n(x)e^{iE_nt/\hbar}\right]\left[\psi_n(x)e^{-iE_nt/\hbar}\right]\\ &= \psi_n^2(x)e^{iE_nt/\hbar}e^{-iE_nt/\hbar}\\ &= |\psi_n(x)|^2 = p(x,0)\end{aligned}$$

the probability does not change in time and for this reason, $\psi_n(x)$ is called a *stationary state*. In such a state, the energy remains **fixed** at the well-defined value E_n.

Nonstationary States

Suppose, however, that we had chosen $\Psi(x,0)$ to be some arbitrary linear combination of the two lowest energy states:

$$\Psi(x,0) = a\psi_1(x) + b\psi_2(x) \tag{4.4.7}$$

for example

$$\Psi(x,0) = \frac{1}{\sqrt{2}}[\psi_1(x) + \psi_2(x)] \tag{4.4.8}$$

as in the previous example. Then, the probability density at time t

$$p(x,t) = |\Psi(x,t)|^2 \neq p(x,0) \tag{4.4.9}$$

For such a mixture to be possible, there must be sufficient energy in the system that there is some probability of measuring the particle to be in its excited state.

Finally, suppose we start with a state

$$\Psi(x,0) = \frac{1}{\sqrt{2}}[\psi_1(x) + \psi_2(x)]$$

and we let this state evolve in time. At any point in time, the state $\Psi(x,t)$ will be some mixture of $\psi_1(x)$ and $\psi_2(x)$, and this mixture changes with time. Now, at some specific instance in time t, we measure the energy and obtain a value E_1. What is the state of the system *just after* the measurement is made? Once we make the measurement, then we know with 100% certainty that the energy is E_1. From the above discussion, there is only one possibility for the state of the system, and that has to be the wavefunction $\psi_1(x)$, since in this state we know with 100% certainty that the energy is E_1. Hence, just after the measurement, the state *must*

be $\psi_1(x)$, which means that because of the measurement, any further dependence on $\psi_2(x)$ drops out, and for all time thereafter, there is *no* dependence on $\psi_2(x)$. Consequently, any subsequent measurement of the energy would yield the value E_1 with 100% certainty. This discontinuous change in the quantum state of the system as a result of the measurement is known as the **collapse of the wavefunction**. The idea that the evolution of a system can change as a result of a measurement is one of the topics that is currently debated among quantum theorists.

The Quantum Observer Effect

The fact that measuring a quantum system changes its time evolution means that the experimenter is now coupled to the quantum system. This **observer effect** means that the act of observing will influence the phenomenon being observed. In classical mechanics, this coupling does not exist. A classical system will evolve according to Newton's laws of motion independent of whether or not we observe it. This is not true for quantum systems. The very act of observing the system changes how it evolves in time.

Put another way, by simply observing a system, we change it!

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4.5: Eigenfunctions of Operators are Orthogonal

Learning Objectives

- Understand the properties of a Hermitian operator and their associated eigenstates
- Recognize that all experimental obervables are obtained by Hermitian operators

Consideration of the quantum mechanical description of the particle-in-a-box exposed two important properties of quantum mechanical systems. We saw that the eigenfunctions of the Hamiltonian operator are orthogonal, and we also saw that the position and momentum of the particle could not be determined exactly. We now examine the generality of these insights by stating and proving some fundamental theorems. These theorems use the Hermitian property of quantum mechanical operators that correspond to observables, which is discuss first.

Hermitian Operators

Since the eigenvalues of a quantum mechanical operator correspond to measurable quantities, the eigenvalues must be real, and consequently a quantum mechanical operator must be Hermitian. To prove this, we start with the premises that ψ and φ are functions, $\int d\tau$ represents integration over all coordinates, and the operator $\hat{A}$ is **Hermitian** by definition if

$$\int \psi^* \hat{A} \psi \, d\tau = \int (\hat{A}^* \psi^*) \psi \, d\tau \tag{4.5.1}$$

This equation means that the complex conjugate of $\hat{A}$ can operate on ψ^* to produce the same result after integration as $\hat{A}$ operating on φ, followed by integration. To prove that a quantum mechanical operator $\hat{A}$ is Hermitian, consider the eigenvalue equation and its complex conjugate.

$$\hat{A}\psi = a\psi \tag{4.5.2}$$

$$\hat{A}^* \psi^* = a^* \psi^* = a\psi^* \tag{4.5.3}$$

Note that $a^* = a$ because the eigenvalue is real. Multiply Equation 4.5.2 and 4.5.3 from the left by ψ^* and ψ, respectively, and integrate over the full range of all the coordinates. Note that ψ is normalized. The results are

$$\int \psi^* \hat{A} \psi \, d\tau = a \int \psi^* \psi \, d\tau = a \tag{4.5.4}$$

$$\int \psi \hat{A}^* \psi^* \, d\tau = a \int \psi \psi^* \, d\tau = a \tag{4.5.5}$$

Since both integrals equal a, they must be equivalent.

$$\int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau \tag{4.5.6}$$

The operator acting on the function,

$$\hat{A}^* \int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau_*$$

produces a new function. Since functions commute, Equation 4.5.6 can be rewritten as

$$\int \psi^* \hat{A} \psi d\tau = \int (\hat{A}^* \psi^*) \psi d\tau \tag{4.5.7}$$

This equality means that $\hat{A}$ is Hermitian.

Orthogonality Theorem

Eigenfunctions of a Hermitian operator are orthogonal if they have different eigenvalues.

Because of this theorem, we can identify orthogonal functions easily without having to integrate or conduct an analysis based on symmetry or other considerations.

Proof

ψ and φ are two eigenfunctions of the operator Â with real eigenvalues a_1 and a_2, respectively. Since the eigenvalues are real, $a_1^* = a_1$ and $a_2^* = a_2$.

$$\hat{A}\psi = a_1\psi$$

$$\hat{A}^*\psi^* = a_2\psi^*$$

Multiply the first equation by φ^* and the second by ψ and integrate.

$$\int \psi^* \hat{A}\psi \, d\tau = a_1 \int \psi^*\psi \, d\tau$$

$$\int \psi \hat{A}^*\psi^* \, d\tau = a_2 \int \psi\psi^* \, d\tau \tag{4.5.8}$$

Subtract the two equations in Equation 4.5.8 to obtain

$$\int \psi^* \hat{A}\psi \, d\tau - \int \psi \hat{A}^*\psi^* \, d\tau = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{4.5.9}$$

The left-hand side of Equation 4.5.9 is zero because $\hat{A}$ is Hermitian yielding

$$0 = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{4.5.10}$$

If a_1 and a_2 in Equation 4.5.10 are not equal, then the integral **must** be zero. This result proves that **nondegenerate eigenfunctions** of the same operator are orthogonal.

□

Two wavefunctions, $\psi_1(x)$ and $\psi_2(x)$, are said to be *orthogonal* if

$$\int_{-\infty}^{\infty} \psi_1^*\psi_2 \, dx = 0. \tag{4.5.11}$$

Consider two eigenstates of $\hat{A}$, $\psi_a(x)$ and $\psi_{a'}(x)$, which correspond to the two *different* eigenvalues a and a', respectively. Thus,

$$A\psi_a = a\psi_a \tag{4.5.12}$$

$$A\psi_a' = a'\psi_a' \tag{4.5.13}$$

Multiplying the complex conjugate of the first equation by $\psi_{a'}(x)$, and the second equation by $\psi_{a'}^*(x)$, and then integrating over all x, we obtain

$$\int_{-\infty}^{\infty} (A\psi_a)^*\psi_{a'} dx = a \int_{-\infty}^{\infty} \psi_a^*\psi_{a'} dx, \tag{4.5.14}$$

$$\int_{-\infty}^{\infty} \psi_a^*(A\psi_{a'}) dx = a' \int_{-\infty}^{\infty} \psi_a^*\psi_{a'} dx. \tag{4.5.15}$$

However, from Equation 4.5.9, the left-hand sides of the above two equations are equal. Hence, we can write

$$(a - a') \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx = 0.$$

By assumption, $a \neq a'$, yielding

$$\int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx = 0.$$

In other words, eigenstates of an Hermitian operator corresponding to *different* eigenvalues are automatically *orthogonal*.

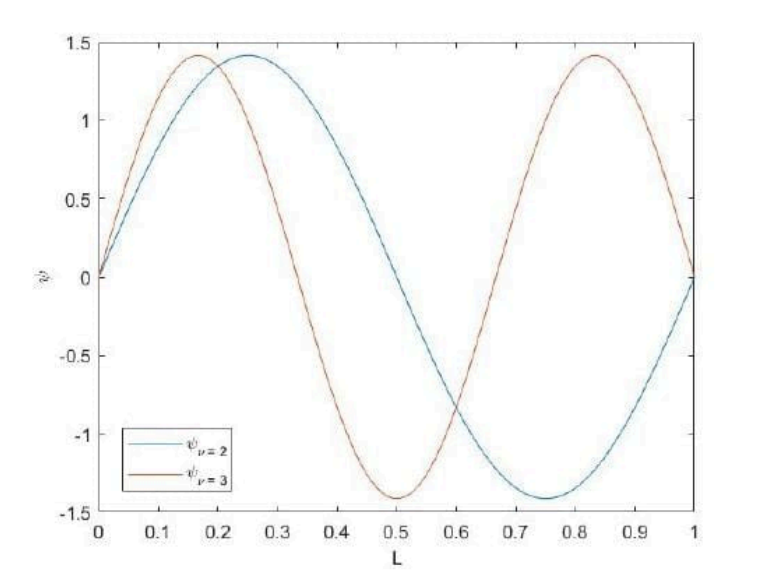
> The eigenvalues of operators associated with experimental measurements are all *real*.

Example4.5.1

Draw graphs and use them to show that the particle-in-a-box wavefunctions for $\psi(n = 2)$ and $\psi(n = 3)$ are orthogonal to each other.

Solution

The two PIB wavefunctions are qualitatively similar when plotted



These wavefunctions are orthogonal when

$$\int_{-\infty}^{\infty} \psi(n = 2)\psi(n = 3)dx = 0$$

and when the PIB wavefunctions are substituted this integral becomes

$$\int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{2n}{L}x\right) \sqrt{\frac{2}{L}} \sin\left(\frac{2n}{L}x\right) dx = ?$$

$$\frac{2}{L} \int_0^L \sin\left(\frac{2}{L}x\right) \sin\left(\frac{3}{L}x\right) = ?$$

We can expand the integrand using trigonometric identities to help solve the integral, but it is easier to take advantage of the symmetry of the integrand, specifically, the $\psi(n=2)$ wavefunction is even (blue curves in above figure) and the $\psi(n=3)$ is odd (purple curve). Their product (even times odd) is an odd function and the integral over an odd function is zero. Therefore $\psi(n=2)$ and $\psi(n=3)$ wavefunctions are orthogonal.

This can be repeated an infinite number of times to confirm the entire set of PIB wavefunctions are mutually orthogonal as the Orthogonality Theorem guarantees.

Orthogonality of Degenerate Eigenstates

Consider two eigenstates of $\hat{A}$, ψ_a and ψ'_a, which correspond to the *same* eigenvalue, a. Such eigenstates are termed **degenerate**. The above proof of the orthogonality of different eigenstates fails for degenerate eigenstates. Note, however, that *any* linear combination of ψ_a and ψ'_a is also an eigenstate of $\hat{A}$ corresponding to the eigenvalue a. Thus, even if ψ_a and ψ'_a are not orthogonal, we can always choose two linear combinations of these eigenstates which are orthogonal. For instance, if ψ_a and ψ'_a are properly normalized, we can define the **overlap integral**

$$S = \int_{-\infty}^{\infty} \psi_a^* \psi'_a dx, \tag{4.5.16}$$

It is easily demonstrated (but not here) that

$$\psi''_a = \frac{|S|}{\sqrt{1-|S|^2}} \left(\psi_a - S^{-1}\psi'_a\right) \tag{4.5.17}$$

is a properly normalized eigenstate of $\hat{A}$, corresponding to the eigenvalue a, which is orthogonal to ψ_a. It is straightforward to generalize the above argument to three or more degenerate eigenstates. Hence, we conclude that the eigenstates of a Hermitian operator are, or can be chosen to be, **mutually orthogonal.**

Theorem: Gram-Schmidt Orthogonalization

Degenerate eigenfunctions are **not** automatically orthogonal, but can be made so mathematically via the Gram-Schmidt Orthogonalization.

The above theorem argues that if the eigenvalues of two eigenfunctions are the same then the functions are said to be degenerate and linear combinations of the degenerate functions can be formed that will be orthogonal to each other. Since the two eigenfunctions have the same eigenvalues, the linear combination also will be an eigenfunction with the same eigenvalue. The proof of this theorem shows us one way to produce orthogonal degenerate functions.

Proof

If ψ_a and ψ'_a are degenerate, but not orthogonal, we can define a new composite wavefunction $\psi''_a = \psi'_a - S\psi_a$ where S is the overlap integral:

$$S = \langle \psi_a | \psi'_a \rangle$$

then ψ_a and ψ''_a will be orthogonal.

$$\begin{aligned} \langle \psi_a | \psi''_a \rangle &= \langle \psi_a | \psi'_a - S\psi_a \rangle \\ &= \cancelto{S}{\langle \psi_a | \psi'_a \rangle} - S \cancelto{1}{\langle \psi_a | \psi_a \rangle} \\ &= S - S = 0 \end{aligned}$$

$$\int \psi_a^* \psi_a d\tau$$

then ψ_a and Φ will be orthogonal.

$$\begin{aligned}\int \psi_A^* \Phi d\tau &= \int \psi_a^* (\psi_a' - S\psi_a) d\tau \\ &= \int \psi_a^* \psi_a' d\tau - S \int \psi_a^* \psi_a d\tau \\ &= S - S = 0\end{aligned}$$

□

Exercise 4.5.2

Find N that normalizes ψ if $\psi = N(\varphi_1 - S\varphi_2)$ where φ_1 and φ_2 are normalized wavefunctions and S is their overlap integral.

$$S = \langle \varphi_1 | \varphi_2 \rangle$$

Answer available at the end of this section.

We conclude that the eigenstates of operators are, or can be chosen to be, **mutually orthogonal**.

Contributors and Attributions

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Answers

Remember that to normalize an arbitrary wavefunction, we find a constant N such that $\langle \psi | \psi \rangle = 1$. This equates to the following procedure:

$$\begin{aligned}\langle \psi | \psi \rangle &= \langle N(\varphi_1 - S\varphi_2) | N(\varphi_1 - S\varphi_2) \rangle = 1 \\ N^2 \langle (\varphi_1 - S\varphi_2) | (\varphi_1 - S\varphi_2) \rangle &= 1 \\ N^2 \left[\cancelto{1}{\langle \varphi_1 | \varphi_1 \rangle} - S \cancelto{S}{\langle \varphi_2 | \varphi_1 \rangle} - S \cancelto{S}{\langle \varphi_1 | \varphi_2 \rangle} + S^2 \cancelto{1}{\langle \varphi_2 | \varphi_2 \rangle} \right] &= 1 \\ N^2(1 - S^2 \cancel{- S^2 + S^2}) &= 1 \\ N^2(1 - S^2) &= 1\end{aligned}$$

therefore

$$N = \frac{1}{\sqrt{1 - S^2}}$$

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4.6: Commuting Operators Allow Infinite Precision

Learning Objectives

- To connect the Heisenberg Uncertainty principle to the commutation relations.
- Develop proficiency in calculating the commutator of two operators.

If two operators commute then both quantities can be measured at the same time with infinite precision, if not then there is a tradeoff in the accuracy in the measurement for one quantity vs. the other. This is the mathematical representation of the Heisenberg Uncertainty principle.

Commuting Operators

One important property of operators is that the order of operation matters. Thus in general

$$\hat{A}\hat{E}f(x) \neq \hat{E}\hat{A}f(x)$$

unless the two operators **commute**. Two operators commute if the following equation is true:

$$\left[\hat{A},\hat{E}\right] = \hat{A}\hat{E} - \hat{E}\hat{A} = 0$$

To determine whether two operators commute first operate $\hat{A}\hat{E}$ on a function $f(x)$. Then operate$\hat{E}\hat{A}$ the same function $f(x)$. If the same answer is obtained subtracting the two functions will equal zero and the two operators will commute.on

If two operators commute, then they can have the same set of eigenfunctions. By definition, two operators $\hat{A}$ and $\hat{B}$ commute if the effect of applying $\hat{A}$ then $\hat{B}$ is the same as applying $\hat{B}$ then $\hat{A}$, i.e.

$$\hat{A}\hat{B} = \hat{B}\hat{A}.$$

For example, the operations brushing-your-teeth and combing-your-hair commute, while the operations getting-dressed and taking-a-shower do not. This theorem is very important. If two operators commute and consequently have the same set of eigenfunctions, then the corresponding physical quantities can be evaluated or measured exactly simultaneously with no limit on the uncertainty. As mentioned previously, the eigenvalues of the operators correspond to the measured values.

If $\hat{A}$ and $\hat{B}$ commute and ψ is an eigenfunction of $\hat{A}$ with eigenvalue b, then

$$\hat{B}\hat{A}\psi = \hat{A}\hat{B}\psi = \hat{A}b\psi = b\hat{A}\psi \tag{4.6.1}$$

Equation 4.6.1 says that $\hat{A}\psi$ is an eigenfunction of $\hat{B}$ with eigenvalue b, which means that when $\hat{A}$ operates on ψ, it cannot change ψ. At most, $\hat{A}$ operating on ψ can produce a constant times ψ.

$$\hat{A}\psi = a\psi \tag{4.6.2}$$

$$\hat{B}(\hat{A}\psi) = \hat{B}(a\psi) = a\hat{B}\psi = ab\psi = b(a\psi) \tag{4.6.3}$$

Equation 4.6.3 shows that Equation 4.6.2 is consistent with Equation 4.6.1. Consequently ψ also is an eigenfunction of $\hat{A}$ with eigenvalue a.

Example 4.6.1

Do the following pairs of operators commute?

a. $\hat{A} = \dfrac{d}{dx}$ and $\hat{E} = x^2$
b. $\hat{B} = \dfrac{\hbar}{x}$ and $\hat{C}\{f(x)\} = f(x) + 3$
c. $\hat{J} = 3x$ and $\hat{O} = x^{-1}$

Solution a available at the end of this section.

Solution b available at the end of this section.

Solution c available at the end of this section.

General Heisenberg Uncertainty Principle

Although it will not be proven here, there is a general statement of the uncertainty principle in terms of the commutation property of operators. If two operators $\hat{A}$ and $\hat{B}$ do not commute, then the uncertainties (standard deviations σ) in the physical quantities associated with these operators must satisfy

$$\sigma_A \sigma_B \geq \left| \int \psi^* [\hat{A}\hat{B} - \hat{B}\hat{A}] \psi \, d\tau \right| \tag{4.6.4}$$

where the integral inside the square brackets is called the **commutator**, and $\left|\ \right|$ signifies the modulus or absolute value. If $\hat{A}$ and $\hat{B}$ commute, then the right-hand-side of Equation 4.6.4 is zero, so either or both σ_A and σ_B could be zero, and there is no restriction on the uncertainties in the measurements of the eigenvalues a and b. If $\hat{A}$ and $\hat{B}$ do not commute, then the right-hand-side of Equation 4.6.4 will not be zero, and neither σ_A nor σ_B can be zero unless the other is infinite. Consequently, both a and b cannot be eigenvalues of the same wavefunctions and cannot be measured simultaneously to arbitrary precision.

Exercise4.6.1

Show that the commutator for position and momentum in one dimension equals $-i\hbar$ and that the right-hand-side of Equation 4.6.4 therefore equals $\hbar/2$ giving $\sigma_x \sigma_{px} \geq \frac{\hbar}{2}$.

Applications

Operators are very common with a variety of purposes. They are used to figure out the energy of a wavefunction using the Schrödinger Equation.

$$\hat{H}\psi = E\psi$$

They also help to explain observations made in the experimentally. An example of this is the relationship between the magnitude of the angular momentum and the components.

$$\left[\hat{L}^2, \hat{L}_x^2\right] = \left[\hat{L}^2, \hat{L}_y^2\right] = \left[\hat{L}^2, \hat{L}_z^2\right] = 0$$

However the components do not commute themselves. An additional property of commuters that commute is that both quantities can be measured simultaneously. Thus, the magnitude of the angular momentum and ONE of the components (usually z) can be known at the same time however, NOTHING is known about the other components.

The physical quantities corresponding to operators that commute can be measured simultaneously to any precision.

4.6.2AExa

Determine whether the following two operators commute:

$$\hat{K} = \alpha \int [1]^{[\infty]} d[x]$$

and

$$\hat{H} = d/dx$$

Solution available at the end of this section.

4.6.2B Exa

Determine whether the following two operators commute:

$$\hat{I} = 5$$

and

$$\hat{L} = \int_{[1]}^{[\infty]} d[x]$$

Solution available at the end of this section.

4.6.2C Exe

Show that the components of the angular momentum do not commute.

$$\hat{L}_x = -i\hbar \left[-\sin\left(\phi \frac{\delta}{\delta\theta}\right) - \cot(\Theta)\cos\left(\phi \frac{\delta}{\delta\phi}\right)\right]$$

$$\hat{L}_y = -i\hbar \left[\cos\left(\phi \frac{\delta}{\delta\theta}\right) - \cot(\Theta)\cos\left(\phi \frac{\delta}{\delta\phi}\right)\right]$$

$$\hat{L}_z = -i\hbar \frac{\delta}{\delta\theta}$$

Solution available at the end of this section.

References

1. Gohberg, I. Basic Operator Theory; Birkhäuser: Boston, 2001
2. McQuarrie, D.A. Quantum Chemistry, 2nd Edition; University Science Books:Sausalito, 2008
3. Schechter, M. Operator Methods in Quantum Mechanics; Dover Publications, 2003

Answers

This requires evaluating $\left[\hat{A}, \hat{E}\right]$, which requires solving for $\hat{A}\{\hat{E}f(x)\}$ and $\hat{E}\{\hat{A}f(x)\}$ for arbitrary wavefunction $f(x)$ and asking if they are equal.

$$\hat{A}\{\hat{E}f(x)\} = \hat{A}\{x^2 f(x)\} = \frac{d}{dx}\{x^2 f(x)\} = 2xf(x) + x^2 f'(x)$$

From the product rule of differentiation.

$$\hat{E}\{\hat{A}f(x)\} = \hat{E}\{f'(x)\} = x^2 f'(x)$$

Now ask if they are equal

$$\left[\hat{A}, \hat{E}\right] = 2xf(x) + x^2 f'(x) - x^2 f'(x) = 2xf(x) \neq 0$$

Therefore the two operators do not commute.

This requires evaluating $\left[\hat{B}, \hat{C}\right]$ like in Example 4.6.1 .

$$\hat{B}\{\hat{C}f(x)\} = \hat{B}\{f(x)+3\} = \frac{h}{x}(f(x)+3) = \frac{hf(x)}{x} + \frac{3h}{x}$$

$$\hat{C}\{\hat{B}f(x)\} = \hat{C}\{\frac{h}{x}f(x)\} = \frac{hf(x)}{x} + 3$$

Now ask if they are equal

$$\left[\hat{B},\hat{C}\right] = \frac{hf(x)}{x} + \frac{3h}{x} - \frac{hf(x)}{x} - 3 \neq 0$$

The two operators do **not** commute.

This requires evaluating $\left[\hat{J},\hat{O}\right]$

$$\hat{J}\{\hat{O}f(x)\} = \hat{J}\{f(x)3x\} = f(x)3x/x = 3f(x)$$

$$\hat{O}\{\hat{J}f(x)\} = \hat{O}\{\frac{f(x)}{x}\} = \frac{f(x)3x}{x} = 3f(x)$$

$$\left[\hat{J},\hat{O}\right] = 3f(x) - 3f(x) = 0$$

Because the difference is zero, the two operators commute.

Evaluate

$$\left[\hat{K},\hat{H}\right]$$

The identity operator, $\hat{I}$ is a real number and commutes with everything. Thus, these two operators commute. We can also directly evaluate the commutator:

$$\left[\hat{I},\hat{L}\right]$$

$$\left[\hat{I},\hat{L}\right]f(x) = 5\int_1^\infty f(x)d(x) - \int_1^\infty 5f(x)d(x) = 0$$

This requires evaluating the following commucators:

$$\left[\hat{L}_z,\hat{L}_x\right] = i\hbar\hat{L}_y$$

$$\left[\hat{L}_x,\hat{L}_y\right] = i\hbar\hat{L}_z$$

$$\left[\hat{L}_y,\hat{L}_z\right] = i\hbar\hat{L}_x$$

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4.E: Postulates and Principles of Quantum Mechanics (Exercises)

Solutions to select questions can be found online.

4.3

The function $\psi^*\psi$ has to be real, nonnegative, finite, and of definite value everywhere. Why?

Solution

If we follow the Born interpretation of wavefuntions, then $\psi^*\psi$ is a probability density and hence must follow standard probability properties including being non-negative, finite and of a definite value at any relevant point in the space of the wavefunction. Moreover, the integral of $\psi^*\psi$ over all this space must be equal to 1.

4.5

Why are the following functions not acceptable wave functions for a 1D particle in a box with length a ? N is a normalization constant.

a. $\psi = N\cos\dfrac{n\pi x}{L}$
b. $\psi = \dfrac{N}{\sin\dfrac{n\pi x}{a}}$
c. $\psi = N\tan\dfrac{n\pi x}{a}$

Solution

The boundary conditions that need to be met are $\psi(0) = \psi(a) = 0$. This does not meet them. The proposed wavefunction blows up to infinity at $x = 0$ and $x = a$ Tan is not defined for $x = \dfrac{a}{2}$

4.12

Show that the sets of functions: $\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ where n = 1,2,3... is orthonormal.

Solution

Let

$$\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

Because $\psi^* = \psi$ and is real, then

$$\int_0^L \psi^*\psi dx = \int_0^L \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{m\pi x}{L}\right)dx$$

Letting $n = m$

$$\begin{aligned}\int_0^L \psi^*\psi dx &= \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx \\ &= \frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx \\ \frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx &= 1\end{aligned}$$

Letting $n \neq m$

$$\begin{aligned}\int_0^L \psi^*\psi dx &= \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{m\pi x}{L}\right)dx \\ &= \frac{2}{L}\frac{1}{2}\int_0^L \left[\cos\left(\frac{(n-m)\pi x}{L}\right) - \cos\left(\frac{(n+m)\pi x}{L}\right)\right]dx \\ &= \frac{1}{L}\left[\frac{L}{(n-m)\pi}\left[\sin\left(\frac{(n-m)\pi L}{L}\right) - \sin\left(\frac{(n-m)\pi 0}{L}\right)\right] - \frac{L}{(n+m)\pi}\left[\sin\left(\frac{(n+m)\pi L}{L}\right) - \sin\left(\frac{(n+m)\pi 0}{L}\right)\right]\right] = 0\end{aligned}$$

and thus $\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ (n=1, 2, 3, ...) are orthonormal.

4.13

Show that $a \cdot b \cdot c = \sum_{ik} a_i b_i c_k e_k$

$$\sum_i a_i e_i \cdot \sum_j b_j e_j \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$\sum_i \sum_j a_i b_j (e_i \cdot e_j) \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$e_i \cdot e_j = \delta_{ij} = 1$$

when $i = j$

$$\sum_i a_i b_i \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$\sum_{ik} a_i b_i c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

4.14

Determine if the following operators commute

$$\hat{B} = \frac{d}{dx}$$

and

$$\hat{C} = x^5$$

Solution

We must solve $\left[\hat{B}, \hat{C}\right]$, by solving for $\hat{B}\{\hat{C}f(x)\}$ and $\hat{C}\{\hat{B}f(x)\}$ for a wavefunction $f(x)$ and see if they are equal.

$$\hat{B}\{\hat{C}f(x)\} = \hat{B}\{x^5 f(x)\} = \frac{d}{dx}\{x^5 f(x)\} = 5xf(x) + x^5 f'(x)$$

$$\hat{C}\{\hat{B}f(x)\} = \hat{C}\{f'(x)\} = x^5 f'(x)$$

since

$$\left[\hat{B}, \hat{C}\right] = 5xf(x) + x^5 f'(x) - x^2 f'(x) = 5xf(x) \neq 0$$

The two operators do not commute.

4.15

Do the following combinations of angular momentum operators commute? Show work to the justify the answer (do not just write "yes" or no").

a. $\mathbf{L}_x$ and $\mathbf{L}_y$
b. $\mathbf{L}_y$ and $\mathbf{L}_z$
c. $\mathbf{L}_z$ and $\mathbf{L}_x$

with

$$\mathbf{L}_x = -\mathrm{i}\,\hbar\left(y\,\frac{\partial}{\partial z} - z\,\frac{\partial}{\partial y}\right)$$

$$\mathbf{L}_y = -\mathrm{i}\,\hbar\left(z\,\frac{\partial}{\partial x} - x\,\frac{\partial}{\partial z}\right)$$

$$\mathbf{L}_z = -\mathrm{i}\,\hbar\left(x\,\frac{\partial}{\partial y} - y\,\frac{\partial}{\partial x}\right)$$

Estimate the answer to Part C based on the pattern gathered from parts A and B; no work necessary for Part C.

Solution

a.

$$[\mathbf{L}_x, \mathbf{L}_y] = (yp_z - zp_y)(zp_x - xp_z)\Psi - (zp_x - xp_z)(yp_z - zp_y)\Psi,$$

$$= (zp_xyp_z - z^2p_xp_y - xyp_zp_z - xzp_yp_z)\Psi - (yp_zzp_x - yxp_zp_z + z^2p_yp_x + zxp_zp_y)\Psi$$

$$[\mathbf{L}_x, \mathbf{L}_y] = i\hbar\mathbf{L}_z,$$

Does **not** commute, i.e., is not zero.

b.

$$[\mathbf{L}_y, \mathbf{L}_z] = (zp_x - xp_z)(xp_y - yp_x)\Psi - (xp_y - yp_x)(zp_x - xp_z)\Psi$$

$$= (xp_yzp_x - x^2p_yp_z - yzp_xp_x - yxp_zp_x)\Psi - (zp_xxp_y - zyp_xp_x + x^2p_zp_y + xyp_xp_z)\Psi$$

$$[\mathbf{L}_y, \mathbf{L}_z] = i\hbar\mathbf{L}_x,$$

Does **not** commute, i.e., is not zero.

c. This part only requires that we notice the rotation of variables and consistency of format/equations. In doing so, we better understand the relation between the parts of the angular momentum operator. The work below does not need to be shown for credit, but it may clarify things or make the solution clearer if you are still having trouble assessing and using the pattern.

$$[\mathbf{L}_z, \mathbf{L}_x] = (xp_y - yp_x)(yp_z - zp_y)\Psi - (yp_z - zp_y)(xp_y - yp_x)\Psi$$

$$= (yp_zxp_y - y^2p_zp_x - zxp_yp_y - zyp_xp_y)\Psi - (xp_yyp_z - xzp_yp_y + y^2p_xp_z + yzp_yp_x)\Psi$$

$$[\mathbf{L}_z, \mathbf{L}_x] = i\hbar\mathbf{L}_y,$$

Does not commute, i.e., is not zero.

These calculations show that you can have only one well-defined component of the angular momentum because of the uncertainty principle says the others will not be known (since they do not commute).

4.17

For two operators to commute, what property must hold? Use the operators $\hat{L}^2$ and $\hat{L}_z$ as an example to show that this property holds.

Solution

The commuters when applied to a wavefunction must equal the 0 eigenfunction.

$$\hat{L}^2\hat{L}_z\psi(x) - \hat{L}_z\hat{L}^2\psi(x) = 0$$

$$\hat{L}^2\hat{L}_z - \hat{L}_z\hat{L}^2\psi(x) = \hat{0}\psi(x)$$

$$\hat{L}^2\hat{L}_z - \hat{L}_z\hat{L}^2 = 0$$

4.21

Show that the angular momentum and kinetic energy operators commute and therefore can be measured simultaneously to arbitrary precision.

Solution

Show that

$$[\hat{K}, \hat{L}] \; = \; 0$$

where the operators can be broken up into 3 components

$$L_x = -\mathrm{i}\,\hbar\left(y\,\frac{\partial}{\partial z} - z\,\frac{\partial}{\partial y}\right)$$

$$L_y = -\mathrm{i}\,\hbar\left(z\,\frac{\partial}{\partial x} - x\,\frac{\partial}{\partial z}\right)$$

$$L_z = -\mathrm{i}\,\hbar\left(x\,\frac{\partial}{\partial y} - y\,\frac{\partial}{\partial x}\right)$$

and $\hat{K}_x \; = \; \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. The same can be written for $\hat{K}$ in the y and z directions.

$$[\hat{K}, \hat{L}] = [\hat{K}_x, \hat{L}_x] + [\hat{K}_y, \hat{L}_y] + [\hat{K}_z, \hat{L}_z]$$

For the x-direction

$$[\hat{K}_x, \hat{L}_x] = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, -i\hbar\Big(y\frac{d}{dz} - z\frac{d}{dy}\Big)\Big)\right]$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\Big(-i\hbar\Big(y\frac{d}{dz} - z\frac{d}{dy}\Big)\Big) - -i\hbar\Big(y\frac{d}{dz} - z\frac{d}{dy}\Big)\Big)\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\frac{i\hbar^3}{2m}\Big(y\frac{d^3}{dx^2dz} - z\frac{d^3}{dx^2dy}\Big) - \frac{i\hbar^3}{2m}\Big(y\frac{d^3}{dx^2dz} - z\frac{d^3}{dx^2dy}\Big) \; = \; 0$$

The process can be repeated for the y and z directions and following the same steps the commutations turn out to be 0. Therefore, kinetic energy and angular momentum commute.

4.22

Show that the position and angular momentum operator commutes. Can the position and angular momentum be measured simultaneously to a arbitrary precision?

Solution

First, we must prove that the position operator, $\hat{\mathbf{R}} = \mathbf{i}\hat{x} + \mathbf{j}\hat{y} + \mathbf{k}\hat{z}$, and the angular momentum operator $\hat{\mathbf{L}} = \mathbf{i}\hat{L_x} + \mathbf{j}\hat{L_y} + \mathbf{k}\hat{L_z}$, commute.

In order to prove the commutation,

$$[\hat{\mathbf{R}}, \hat{\mathbf{L}}] = [\mathbf{i}\hat{x} + \mathbf{j}\hat{y} + \mathbf{k}\hat{z}, \mathbf{i}\hat{L_x} + \mathbf{j}\hat{L_y} + \mathbf{k}\hat{L_z}]$$

$$= [\hat{x}, \hat{L_x}] + [\hat{y}, \hat{L_y}] + [\hat{z}, \hat{L_z}]$$

$$= 0$$

where we have used the fact that

$$\mathbf{i} \cdot \mathbf{i} = \mathbf{j} \cdot \mathbf{j} = \mathbf{k} \cdot \mathbf{k} = 1$$

and

$$\mathbf{i} \cdot \mathbf{j} = \mathbf{j} \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{i} = 0$$

Now that we have proved that the two operators commute, the relationship of commutation means that the position and total angular momentum of any electrons can be measured simultaneously to arbitrary precision.

4.25

If both $|\Psi_n\rangle$ and $|\Psi_m\rangle$ satisfy the **time-independent** Schrödinger Equation (these are called *stationary states*)

$$|\Psi_n(x,t)\rangle = \Psi_n(x)e^{-iE_nt/\hbar}$$

and

$$|\Psi_m(x,t)\rangle = \Psi_m(x)e^{-iE_mt/\hbar}$$

show that any linear superposition of the two wavefunctions

$$|\Psi(x,t)\rangle = c_n|\Psi_n(x,t)\rangle + c_m|\Psi_m(x,t)\rangle$$

also satisfies the **time-dependent** Schrödinger Equation.

Solution

The time-dependent Schrödinger Equation is

\[\hat{H}Ψ(x,t) =iħ ∂Ψ(x,y)/∂t\nonumber \]

Plug Ψ(x,t) into the time-dependent equation.

\[\hat{H}c_nΨ$_n$(x)e$^{-iE_nt/ ħ}$ + c_mΨ$_m$(x)e$^{-iE_mt/ ħ}$ = iħ ∂/∂tc_nΨ$_n$(x)e$^{-iE_nt/ ħ}$ + c_mΨ$_m$(x)e$^{-iE_mt/ ħ}$ \nonumber \]

\[\hat{H}c_nΨ$_n$(x)e$^{-iE_nt/ ħ}$ + c_mΨ$_m$(x)e$^{-iE_mt/ ħ}$ = E_nc_nΨ$_n$(x)e$^{-iE_nt/ ħ}$ + E_mc_mΨ$_m$(x)e$^{-iE_mt/ ħ}$\nonumber \]

\[∂/∂tc_nΨ$_n$(x)e$^{-iE_nt/ ħ}$ + c_mΨ$_m$(x)e$^{-iE_mt/ ħ}$ = -[(iE_mc_me$^{-iE_mt/ ħ}$Ψ$_m$(x))/ħ]-[(iE_nc_ne$^{-iE_nt/ ħ}$Ψ$_n$(x))/ħ]\nonumber \]

combine all the constants (except for E) into c_n and c_m

\[iħ [-[(ic_me$^{-iE_mt/ ħ}$Ψ$_m$(x))/ħ]-[(ic_ne$^{-iE_nt/ħ}$ Ψ$_n$(x))/ħ]]=E_nc_nΨ$_n$(x)e$^{-iE_nt/ ħ}$ + E_mc_mΨ$_m$(x)e$^{-iE_mt/ ħ}$\nonumber \]

\[Since \hat{H}Ψ(x,t) and iħ ∂Ψ(x,y)/∂t are equal, they satisfy the time-dependent equation. \nonumber \]

4.26

Starting with

$$\langle x\rangle = \int \psi^*(x,t)x\psi(x,t)dx$$

and the time-independent Schrödinger equation, demonstrate that

$$\frac{d\langle x\rangle}{dt} = \int \psi^* \frac{i}{\hbar}(\hat{H}x - x\hat{H})\psi dx$$

Given that

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

show that

$$\hat{H}x - x\hat{H} = -2\frac{\hbar^2}{2m}\frac{d}{dx} = -\frac{\hbar^2}{m}\frac{i}{\hbar}\hat{P}_x = -\frac{ih}{m}\hat{P}_x$$

4.28

Derive the condition on operators that arises from forcing eigenvalues to be real with complex conjugates.

Solution

Starting with an eigenvalue problem with a $\hat{G}$ as our operator we recognize

$$\hat{G}\psi = \lambda\psi$$

Solving for our eigenvalue we must multiply by our complex conjugate wavefunction and integrate both sides to see

$$\int \psi^* \hat{G}\psi d\tau = \int \psi^* \lambda\psi d\tau = \lambda \int \psi^*\psi d\tau = \lambda$$

We can repeat this calculation but with a complex conjugate of our initial eigenvalue problem

$$\hat{G}^*\psi^* = \lambda^*\psi^*$$

Solving for our eigenvalue we multiply ψ and integrate both sides to find that

$$\int \psi\hat{G}^*\psi^* d\tau = \int \psi\lambda^*\psi^* d\tau = \lambda^* \int \psi\psi^* d\tau = \lambda$$

Since we restricted λ to be real both eigenvalue problems return the same eigenvalue. We can then relate the operator side of both equations to know that

$$\boxed{\int \psi^* \hat{G}\psi d\tau = \int \psi\hat{G}^*\psi^* d\tau}$$

4.31

Prove that the position operator is Hermitian.

Solution

We must see if the operator satisfies the following requirement to be in Hermitian:

$$\int_{-\infty}^{\infty} (\hat{A}\psi^*)\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{A}\psi \, dx$$

Substitute $\hat{X}$ for $\hat{A}$ into the above equation:

$$\int_{-\infty}^{\infty} (\hat{A}\psi^*)\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{A}\psi \, dx$$

$$\int_{-\infty}^{\infty} (\hat{X}\psi^*)\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi \, dx$$

$$\int_{-\infty}^{\infty} (\hat{X}\psi)^*\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi \, dx$$

$$\int_{-\infty}^{\infty} \psi^* \hat{X}^*\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi \, dx$$

Since $\hat{X}^* \equiv \hat{X}$:

$$\int_{-\infty}^{\infty} \psi^* \hat{X}\psi \, dx = \int_{-\infty}^{\infty} \psi^* \hat{X}\psi \, dx$$

Therefore the Position Operator is Hermitian.

4.31

Prove that the momentum operator is a Hermitian

Solution

Hermitian: $\int \psi_j^* \hat{H} \psi_i dx$

Momentum Operator: $\hat{P} = -i\hbar \frac{d}{dx}$

We will first start by showing you

$$\int_{-\infty}^{\infty} \psi_j (-i\hbar \frac{d}{dx}) psi_i dx$$

$\frac{d\psi_i}{dx} dx = d\psi_i$

$\int_{-\infty}^{\infty} \psi_j (-i\hbar \frac{d}{dx}) psi_i dx$ = iħ $\int_{-\infty}^{\infty} psi_j d\psi_i$

Using integration by parts with u = \psi_{j}*\ and dv = d\psi_{i}

We can notice now that for a confined particle the product \psi_{j}^{*}\psi_{i} will go to zero at each of the endpoints

We get in the end $-i\hbar \frac{d}{dx}$ = $-i\hbar \frac{d}{dx}$ → momentum operator

4.32

Which of the following operators are Hermitian:

a. x,
b. d/dx
c. hd^2/dx^2
d. id^2/dx^2

Solution

A Hermitian Operator $\hat{A}$ satisfies

$$< \Psi^*|A|\Psi >=< \Psi|A^*|\Psi* >$$

x

$$\int \Psi * x\Psi dx = \int \Psi x\Psi* dx$$

where $x^* = x$.

Operator x is Hermitian

d/dx

$$\int \Psi * d/dx\Psi dx$$

$$= \int \Psi* d\Psi$$

Here we can use Integration by Parts *int vdu* = *uv* + *int udv* with v=Ψ* and dv = dΨ

$$= [\Psi * \Psi] - \int \Psi d\Psi*$$

[Ψ*Ψ] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions

$$= -\int \Psi d/dx\Psi * dx$$

Here we inserted dx/dx into the integral

$$= \int \Psi(-d/dx)\Psi* dx$$

d/dx* = d/dx, not -d/dx,so this operator is **not Hermitian.**

hd^2/dx^2

$$\int \Psi * h(d^2/dx^2)\Psi dx$$

$$= h \int \Psi * (d^2/dx)\Psi$$

Here we can use Integration by Parts *int vdu* = *uv* + *int udv* with u=Ψ* and dv=d(dΨ/dx)

$$= h[\Psi * d\Psi/dx] - \int (d\Psi/dx)d\Psi*$$

$$= h[\Psi * d\Psi/dx] - \int (d\Psi * /dx)d\Psi$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ/dx, for example, also approach 0.

$$= -h \int (d\Psi * /dx) d\Psi$$

Here we can use Integration by Parts *int vdu = uv + *int udv* with u=dΨ*/dx and dv=dΨ

$$= -h([\Psi d\Psi * /dx] - \int \Psi d^2\Psi * /dx$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ*/dx, for example, also approaches 0.

$$= h \int \Psi (d^2\Psi * /dx)$$

$$= h \int \Psi (d^2\Psi * /dx^2) dx$$

$$= \int \Psi h (d^2/dx^2) \Psi * dx$$

$h(d^2/dx^2)^* = h(d^2/dx^2)$, so this operator is Hermitian

id^2/dx^2

$$\int \Psi * i (d^2/dx^2) \Psi dx$$

$$= i \int \Psi * (d^2/dx) \Psi$$

Here we can use Integration by Parts

$$\int v du = uv + \int u dv$$

with u=Ψ* and dv=d(dΨ/dx)

$$= i[\Psi * d\Psi/dx] - \int (d\Psi/dx) d\Psi *$$

$$= i[\Psi * d\Psi/dx] - \int (d\Psi * /dx) d\Psi$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ/dx, for example, also approach 0.

$$= -i \int (d\Psi * /dx) d\Psi$$

Here we can use Integration by Parts *int vdu = uv + *int udv* with u=dΨ*/dx and dv=dΨ

$$= -i([\Psi d\Psi * /dx] - \int \Psi d^2\Psi * /dx$$

[Ψ*dΨ/dx] evaluated at infinity and negative infinity is 0, because of the assumption that this wavefunction approaches 0 as one extends to infinity in both directions. This implies that that dΨ*/dx, for example, also approach 0.

$$= i \int \Psi (d^2 \Psi * / dx)$$

$$= i \int \Psi (d^2 \Psi * / dx^2) dx$$

$$= \int \Psi i (d^2 / dx^2) \Psi * dx$$

$$i (d^2 / dx^2) * = -i (d^2 / dx^2)$$

so this operator is NOT Hermitian

4.32

Determine whether the following operators are Hermitian and whether they commute:

$$\hat{A} = i\frac{d}{dx}$$

and

$$\hat{B} = i\frac{d^2}{dx^2}$$

Given that -∞<x<∞ and the operators functions are well behaved.

Solution

If the operator satisfies this condition it is *Hermitian*

$$\int_{-\infty}^{\infty} f^*(x)\,\hat{A}f(x)\,dx = \int_{-\infty}^{\infty} f(x)\,\hat{A}f^*(x)\,dx$$

A)

$$\int_{-\infty}^{\infty} f^*\left(i\frac{df}{dx}\right)dx = i\int_{-\infty}^{\infty} f^*\frac{df}{dx}dx = i\left([_{-\infty}^{\infty} f^*f] - \int_{-\infty}^{\infty} f\frac{df^*}{dx}dx\right)$$

$$= -i\int_{-\infty}^{\infty} f\frac{df^*}{dx}dx = \int_{-\infty}^{\infty} f\left(-i\frac{d}{dx}\right)f^*dx$$

$$\int_{-\infty}^{\infty} f\left(i\frac{d}{dx}\right)^* f^*dx$$

This operator is Hermitian

B)

$$\int_{-\infty}^{\infty} f^*\left(i\frac{d^2f}{dx^2}\right)dx = [_{-\infty}^{\infty} f^*i\frac{df}{dx}] - \int_{-\infty}^{\infty}\frac{df^*}{dx}\frac{df}{dx}dx$$

$$= -i[_{-\infty}^{\infty} f\frac{df^*}{dx}] + i\int_{-\infty}^{\infty} f\frac{d^2f^*}{dx^2}dx$$

$$= -\int_{-\infty}^{\infty} f\frac{id^2}{dx^2}^* f^*dx$$

This operator is **not** Hermitian

If the operators commute they have to satisfy this condition

$$\hat{A}\hat{B}f = \hat{B}\hat{A}f$$

$$\hat{A}\hat{B}f = \frac{id}{dx}\left(\frac{d^2f}{dx^2}\right) = \frac{id^3f}{dx^3}$$

$$\hat{B}\hat{A}f = \frac{id^2}{dx^2}\left(\frac{df}{dx}\right) = \frac{id^3f}{dx^3}$$

This pair of operators commutes.

4.34

Consider two wavefunctions

$$\psi_1(x) = A\sin(k_1 x) + B\cos(k_1 x) \tag{4.E.1}$$

and

$$\psi_2(x) = C\sin(k_2 x) + D\cos(k_2 x)$$

Given the boundary conditions are:

$$\psi(0) = 0$$

and

$$\frac{d\psi_1}{dx} = \frac{d\psi_2}{dx} \quad atx = 0$$

$$A + B = C, k_1(A - B) = k_2 C$$

and given a expression of

$$R = \frac{B^2}{A^2} \tag{4.E.2}$$

Derive the simplest expression of R based on the terms from the boundary conditions provided above.

Solution

Since

$$A + B = C, k_1(A - B) = k_2 C \tag{4.E.3}$$

,

$$k_1(A - B) = k_2(A + B) \tag{4.E.4}$$

$$k_1 A - k_1 B = k_2 A + k_2 B \tag{4.E.5}$$

$$(k_1 - k_2)A = (k_1 + k_2)B \tag{4.E.6}$$

Thus,

$$\frac{B}{A} = \frac{k_1 - k_2}{k_1 + k_2} \tag{4.E.7}$$

$$R = \frac{B^2}{A^2} = \left(\frac{B}{A}\right)^2 = \left(\frac{k_1 - k2}{k_1 + k_2}\right)^2 \tag{4.E.8}$$

4.34

A particle is moving in a field. Half-way through the field, there is a line that represents potential energy. To the left of the line, the potential energy is

$$x < 0$$

and to the right of the line the potential energy is

$$x > 0$$

. If the particle's energy is less than the potential energy line will the particle reflect when the its energy is greater than the Potential energy barrier height?

Solution

When

$$x < 0$$

the Schrödinger equation is as followed:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} = E\psi_1$$

and the solution to this equation is:

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x}$$

where

$$k_1 = (\frac{2mE}{\hbar^2})^{1/2}$$

Region Two where $x > 0$:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + V_0\psi_2 = E\psi_2$$

and the solution to the equation is:

$$\psi_2(x) = Ce^{ik_2x} + De^{-ik_2x}$$

and

$$k_2 = [\frac{2m(E - V_0)}{\hbar^2}]^{1/2}$$

Notice the difference between the two Schrödinger equations. Equation one does not have a potential energy component because it is before the potential energy field hence have zero potential energy. After the potential energy field, the Schrödinger equation has a potential energy component because the particle has potential energy at this moment.

When you solve the differential solutions to the Schrödinger equations you find that the amount that is reflected back of a particle by the line is equal to the amount that is transmitted after the line. This is all we can find out for the information given. However, if we solve this solution for when the Energy of the particle is greater than the potential energy line and compare the differential solutions to all four wave functions then we find that all particles will be reflected by the barrier.

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5: THE HARMONIC OSCILLATOR AND THE RIGID ROTOR

- **The harmonic oscillator is common:** It appears in many everyday examples: Pendulums, springs, electronics (such as the RLC circuit), standing waves on a string, etc. It's trivial to set up demonstrations of these phenomena, and we see them constantly.
- **The harmonic oscillator is intuitive:** We can picture the forces on systems such as pendulum or a plucked string. This makes it simple to study in the classroom. In contrast, there are many "everyday" examples that are not intuitive.
- **The harmonic oscillator is mathematically simple:** Math is part of physics. In studying simple harmonic motion, students can immediately use the formulas that describe its motion. These formulas are understandable: for example, the equation for frequency shows the intuitive result that increasing spring stiffness increases frequency.

5.1: A Harmonic Oscillator Obeys Hooke's Law

5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

5.3: The Harmonic Oscillator Approximates Molecular Vibrations

5.4: The Harmonic Oscillator Energy Levels

5.5: The Harmonic Oscillator and Infrared Spectra

5.6: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials

5.7: Hermite Polynomials are either Even or Odd Functions

5.8: The Energy Levels of a Rigid Rotor

5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

5.E: The Harmonic Oscillator and the Rigid Rotor (Exercises)

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5.1: A Harmonic Oscillator Obeys Hooke's Law

The motion of two atoms in a diatomic molecule can be separated into translational, vibrational, and rotational motions. Both rotation and vibrational motions are internal motions that do not change the center of mass for the molecule (Figure 5.1.1), which is described by translational motion. Quantum translational motions can be modeled with the particle in a box model discussed previously and rotation and vibration can be modeled via the **rigid rotor** and **harmonic oscillator** models, respectively.



Figure 5.1.1 : Two atoms connected by a vibrating bond. There is a rotation around the common center of mass, and oscillation in bond distance. (CC SA-BY, 3.0; www.cleonis.nl).

Before delving into the quantum mechanical harmonic oscillator, we will introduce the classical harmonic oscillator (i.e., involving classical mechanics) to build an intuition that we will extend to the quantum world. A classical description of the vibration of a diatomic molecule is needed because the quantum mechanical description begins with replacing the classical energy with the Hamiltonian operator in the Schrödinger equation. It also is interesting to compare and contrast the classical description with the quantum mechanical picture.

The Classical Harmonic Oscillator

Simple harmonic oscillators about a potential energy minimum can be thought of as a ball rolling frictionlessly in a curved dish or a pendulum swinging frictionlessly back and forth (Figure 5.1.2). The restoring forces are precisely the same in either horizontal direction.

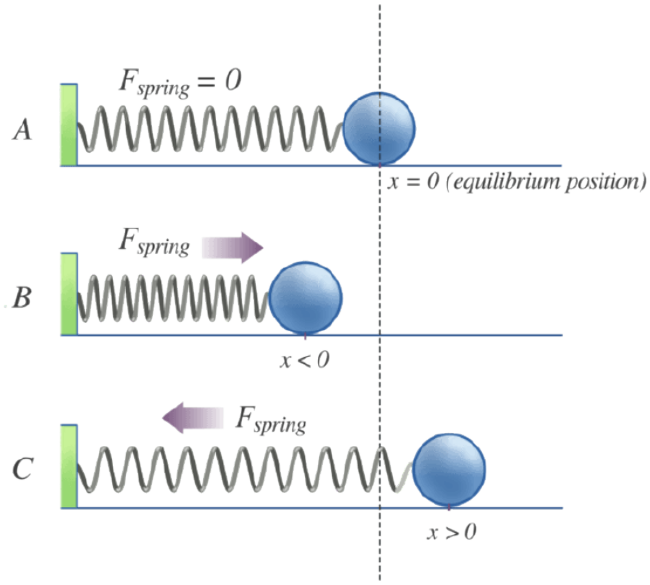


Figure 5.1.2 : A mass connected to a spring that follows Hooke's law is a system that, when displaced from its equilibrium position ($x_o = 0$), experiences a restoring force, F that is proportional to the displacement, x from the equilibrium length (x_o). (CC BY-NC; Ümit Kaya via LibreTexts)

If we consider the bond to behave like a mass on a spring (Figure 5.1.2), then this restoring force (F) is proportional to the displacement (x) from the equilibrium length (x_o) - this is *Hooke's Law*:

$$F = -kx \tag{5.1.1}$$

where k is the force constant. Hooke's Law says that the force is proportional to, but in opposite direction to, the displacement (x). The force constant reflects the **stiffness** of the spring. The idea incorporated into the application of Hooke's Law to a diatomic molecule is that when the atoms move away from their equilibrium positions, a restoring force is produced that increases proportionally with the displacement from equilibrium. The potential energy for such a system increases *quadratically* with the displacement.

$$V(x) = \frac{1}{2}kx^2 \tag{5.1.2}$$

Hooke's Law or the harmonic (i.e. quadratic) potential given by Equation 5.1.2 is an excellent *approximation* for the vibrational oscillations of molecules. The magnitude of the force constant k depends upon the nature of the chemical bond in molecular systems just as it depends on the nature of the spring in mechanical systems. The larger the force constant, the stiffer the spring or the stiffer the bond. Since it is the electron distribution between the two positively charged nuclei that holds them together, a double bond with more electrons has a larger force constant than a single bond, and the nuclei are held together more tightly.

Caution

A stiff bond with a large force constant is not necessarily a strong bond with a large dissociation energy. A harmonic oscillator has no dissociation energy since it CANNOT be broken - there is always a restoring force to keep the molecule together. This is one of many deficiencies in using the harmonic oscillator model to describe molecular vibrations.

Two atoms or one?

You may have questioned the applicability of the harmonic oscillator model involving one moving mass bound to a fix wall via a spring like in Figure 5.1.2 for the vibration of a diatomic molecule with two moving masses like in Figure 5.1.1 . It turned out the two are mathematically the same with internal vibration motion described by a single reduced particle with a reduced mass μ.

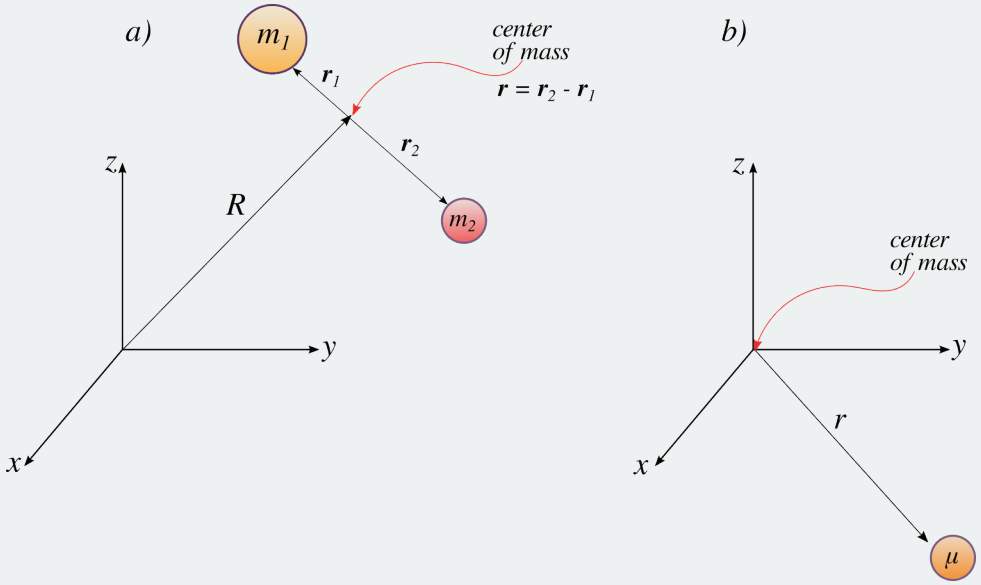


Figure 5.1.3 : Diagrams of the coordinate systems and relevant vectors for the motion of (a) a two-particle diatomic molecule with atoms of mass m_1 and m_2 and (b) the equivalent one-particle pseudo-particle of reduced mass μ. (CC BY-NC; Ümit Kaya via LibreTexts)

For a diatomic molecule, Figure 5.1.3 , the vector $\vec{r}$ corresponds to the internuclear axis. The magnitude or length of r is the bond length, and the orientation of r in space gives the orientation of the internuclear axis in space. Changes in the orientation correspond to rotation of the molecule, and changes in the length correspond to vibration. The change in the bond length from the equilibrium bond length is the **vibrational coordinate** for a diatomic molecule.

Example 5.1.1

a. Show that minus the first derivative of the harmonic potential energy function in Equation 5.1.2 with respect to x is the Hooke's Law force in Equation 5.1.1.
b. Show that the second derivative is the force constant, k.
c. At what value of x is the potential energy a minimum; at what value of x is the force zero?
d. Sketch graphs to compare the potential energy and the force for a system with a large force constant to one with a small force constant.

Solution a

Hooke's Law for a spring entails that the force applied on a spring F is equal to the force constant, $-k$ times the distance compressed or stretched, x (Equation 5.1.1). The derivative of $V(x) = 0.5kx^2$ is

$$V'(x) = (2)\left(\frac{1}{2}\right)kx = kx.$$

The negative of this is $-V'(x) = -kx$ which is exactly equal to Hooke's Law.

Solution b

The second derivative

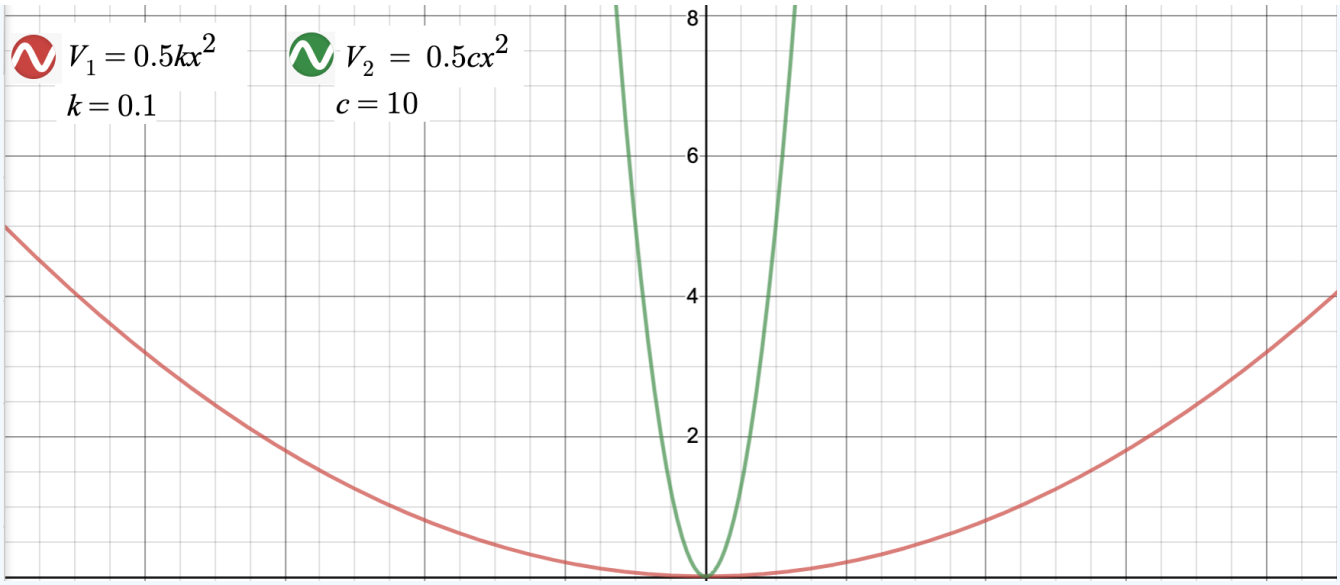
$$V''(x) = \frac{d}{dx}kx = k$$

Thus, the second derivative of this equation for potential energy is equal to the force constant, k.

Solution c

To find the minimum potential energy, it is easiest to set the first derivative equal to zero and solve for x. When $V'(x) = kx = 0$ then x must be equal to zero. Thus, the minimum potential energy is when x=0. Plugging this into Hooke's Law, $F(0) = -k(0) = 0$ so this is also the value for x when the force is zero.

Solution d



The force constant has a drastic effect on both the potential energy and the force. A system with a large force constant requires minimal change in x to have a drastic change in potential energy or force, whereas a system with a small force constant is the exact opposite phenomenon.

Solving the Harmonic Oscillator Model

The classical equation of motion for a one-dimensional simple harmonic oscillator with a particle of mass m attached to a spring having spring constant k is

$$m\frac{d^2x(t)}{dt^2} = -kx(t) \tag{5.1.3}$$

which can be rewritten in the standardform:

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0 \tag{5.1.4}$$

Equation 5.1.3 is a linear second-order differential equation that can be solved by the standard method of factoring and integrating. The resulting solution to Equation 5.1.3 is

$$x(t) = x_o \sin(\omega t + \phi) \tag{5.1.5}$$

with

$$\omega = \sqrt{\frac{k}{m}} \tag{5.1.6}$$

and the momentum has time dependence

$$\begin{aligned} p &= mv \\ &= mx_o\omega\cos(\omega t + \phi) \end{aligned}$$

Figure 5.1.4 show the displacement of the bond from its equilibrium length as a function of time. Such motion is called **harmonic**.

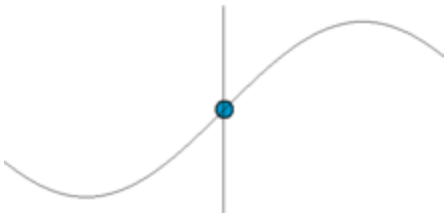


Figure 5.1.4 : Solution to the Harmonic Oscillator. Displacement (y-axis) is plotted as a function of time.

Example 5.1.2

Substitute the following functions into Equation 5.1.4 to demonstrate that they are both possible solutions to the classical equation of motion.

a. $x(t) = x_0 e^{i\omega t}$
b. $x(t) = x_0 e^{-i\omega t}$

where

$$\omega = \sqrt{\frac{k}{m}}$$

Note that the Greek symbol ω for frequency represents the angular frequency $2\pi\nu$.

Solution a

This requires simply placing the given function $x(t) = x_0 e^{i\omega t}$ into Equation 5.1.4.

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

$$\frac{d^2}{dt^2}\left(x_o e^{i\omega t}\right) + \frac{k}{m}x_o e^{i\omega t} = 0$$

$$x_o \frac{d^2}{dt^2}\left(e^{i\omega t}\right) + \frac{k}{m}x_o e^{i\omega t} = 0$$

$$x_o i^2\omega^2\left(e^{i\omega t}\right) + \frac{k}{m}x_o e^{i\omega t} = 0$$

$$x_o i^2\omega^2 e^{i\omega t} + \frac{k}{m}x_o e^{i\omega t} = 0$$

$$x_o i^2\omega^2 + \frac{k}{m}x_o = 0$$

$$-x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \quad \text{with} \quad \omega = \sqrt{\frac{k}{m}}$$

Solution b

This requires simply placing the given function $x(t) = x_0 e^{-i\omega t}$ into Equation 5.1.4.

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

$$\frac{d^2}{dt^2}\left(x_o e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o\frac{d^2}{dt^2}\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 e^{-i\omega t} + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 + \frac{k}{m}x_o = 0$$

$$-x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \quad \text{with} \quad \omega = \sqrt{\frac{k}{m}}$$

Exercise 5.1.1

Show that sine and cosine functions also are solutions to Equation 5.1.4.

Answer available at the end of this section.

Exercise 5.1.2

Identify what happens to the frequency of the motion as the force constant increases in one case and as the mass increases in another case. If the force constant is increased 9-fold and the mass is increased by 4-fold, by what factor does the frequency change?

Answer available at the end of this section.

Harmonic Oscillator Energies

The energy of the vibration is the sum of the kinetic energy and the potential energy. The momentum associated with the harmonic oscillator is

$$p = m\frac{dx}{dt} \tag{5.1.7}$$

so combining Equations 5.1.7 and 5.1.2, the total energy can be written as

$$E = T + V \tag{5.1.8}$$

$$= \frac{p^2}{2m} + \frac{k}{2}x^2 \tag{5.1.9}$$

The total energy of the harmonic oscillator is equal to the maximum potential energy stored in the spring when $x = \pm A$, called the *turning points* (Figure 5.1.5). The total energy (Equation 5.1.9) is continuously being shifted between potential energy stored in the spring and kinetic energy of the mass.

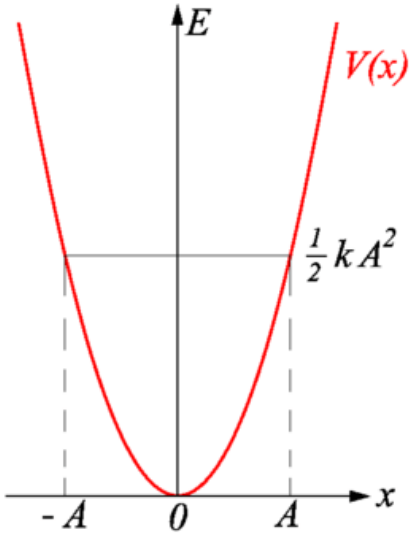


Figure 5.1.5 : The potential $V(x)$ for a harmonic oscillator. Vertical axis energy; horizontal axis displacement x. The potential energy $V(x) = ½kx^2$ is shown in red. (Paul Wormer Wikipedia).

The motion of a classical oscillator is confined to the region where its kinetic energy is nonnegative, which is what the energy relation Equation 5.1.9 says. Physically, it means that a classical oscillator can never be found beyond its turning points, and its energy depends only on how far the turning points are from its equilibrium position. The energy of a classical oscillator changes in a continuous way. The lowest energy that a classical oscillator may have is zero, which corresponds to a situation where an object is at rest at its equilibrium position. The zero-energy state of a classical oscillator simply means no oscillations and no motion at all (a classical particle sitting at the bottom of the potential well in Figure 5.1.5). When an object oscillates, no matter how big or small its energy may be, it spends the longest time near the turning points, because this is where it slows down and reverses its direction of motion. Therefore, the probability of finding a classical oscillator between the turning points is highest near the turning points and lowest at the equilibrium position. (Note that this is not a statement of preference of the object to go to lower energy. It is a statement about how quickly the object moves through various regions.)

Example5.1.3

a. What happens to the frequency of the oscillation as the vibration is excited with more and more energy?
b. What happens to the maximum amplitude of the vibration as it is excited with more and more energy?

Solution

a. Frequency

The energy of the harmonic oscillator can be written as

$$E_v = hv\left(v + \frac{1}{2}\right)$$

and the frequency of oscillation is $\omega = \sqrt{\frac{k}{m}}$. Notice that the frequency depends only on the stiffness (k) and reduced mass (μ) of the oscillator and not on the energy. Hence, increasing the energy of the vibrations does not affects its frequency.

b. Amplitude

The kinetic and potential terms for energy of the harmonic oscillator can be written as

$$\begin{aligned} E &= K + V \\ &= \frac{1}{2}m\omega^2 A^2 \sin^2 \omega t + \frac{1}{2}kA^2 \cos^2 \omega t \end{aligned}$$

with $\omega = \sqrt{\frac{k}{m}}$ so

$$E = \frac{1}{2}kA^2\left(\sin^2\omega t + \cos^2\omega t\right)$$
$$= \frac{1}{2}kA^2$$

The maximum amplitude of the vibration will **increase** as the energy **increases.**

Exercise 5.1.3

If a molecular vibration is excited by collision with another molecule and is given a total energy E_{hit} as a result, what is the maximum amplitude of the oscillation? Is there any constraint on the magnitude of energy that can be introduced?

Answer available at the end of this section.

Answers

Using Equation 5.1.4

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

with $\omega = \sqrt{\frac{k}{m}}$.

For

$$x(t) = x_o\sin(\omega t + \phi)$$

Take the second derivative of $x(t)$

$$\frac{d^2x(t)}{dt} = -\omega^2 x_o\sin(\omega t + \phi)$$
$$= \omega^2 x_o\sin(\omega t + \phi)$$
$$= -\frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right)$$

Plug in $x(t)$ and the second derivative of $x(t)$ into Equation 5.1.4

$$-\frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right) + \frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right) = 0$$

Hence, the sine equation is a solution to Equation 5.1.4

We do the same for the cosine function

$$x(t) = x_o\cos(\omega t + \phi)$$

Take the second derivative of $x(t)$

$$\frac{d^2x(t)}{dt} = -\omega^2 x_o\cos(\omega t + \phi)$$
$$= -\omega^2 x_o\cos(\omega t + \phi)$$
$$= -\frac{k}{m}x_o\cos\left(\sqrt{\frac{k}{m}}t + \phi\right)$$

Plug in $x(t)$ and the second derivative of $x(t)$ into Equation 5.1.4

$$-\frac{k}{m}x_o\cos\left(\sqrt{\frac{k}{m}}t + \phi\right) + \frac{k}{m}x_o\cos\left(\sqrt{\frac{k}{m}}t + \phi\right) = 0$$

The cosine equation is also a solution to Equation 5.1.4.

This is a simple application of Equation 5.1.6. As the force constant increases, the frequency of the motion increases, while as the mass increases, the frequency of the motion decreases. If the force constant increased 9-fold and the mass increased 4-fold,

$$\omega = \sqrt{\frac{9k}{4m}} = \frac{3}{2}\left(\frac{k}{m}\right)$$

The entire frequency of motion would increase by a factor of 3/2.

The equation that defines the energy of a molecular vibration can be approximated is:

$$E_{hit} = T + V = \frac{p^2}{2m} + \frac{k}{2}x$$

The maximum amplitude of a harmonic oscillator is equal to x when the kinetic energy term of total energy equals zero

$$E_{hit} = \frac{k}{2}x$$

Solving for x gives the maximum amplitude:

$$x = \sqrt{\frac{2}{k}E_{hit}}$$

The constraint for the energy that can be introduced cannot be greater than the energy required to break the bond between atoms.

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5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

For studying the energetics of molecular vibration we take the simplest example, a diatomic heteronuclear molecule AB. Let the respective masses of atoms A and B be m_A and m_B. For diatomic molecules, we define the reduced mass μ_{AB} by:

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} \tag{5.2.1}$$

Reduced mass is the representation of a two-body system as a single-body one. When the motion (displacement, vibrational, rotational) of two bodies are only under mutual interactions, the inertial mass of the moving body with respect to the body at rest can be simplified to a reduced mass.

Reduced Mass

Viewing the multi-body system as a single particle allows the separation of the motion: vibration and rotation, of the particle from the displacement of the center of mass. This approach greatly simplifies many calculations and problems.

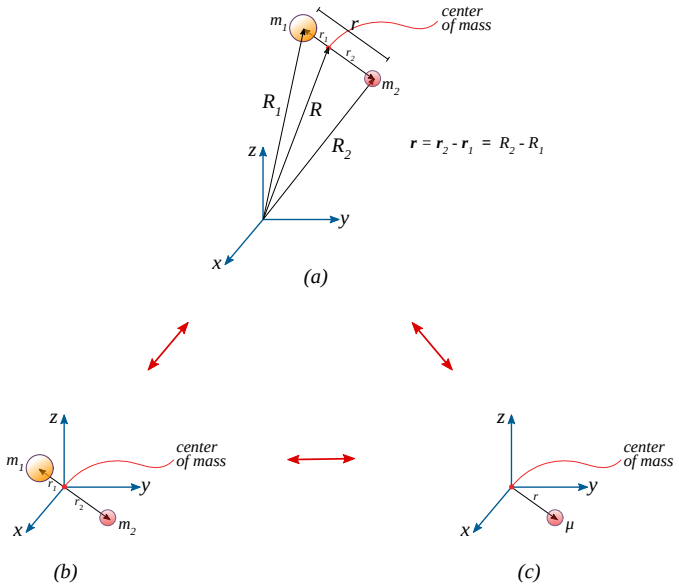


Figure 5.2.1 : a) the individual vectors to the particles m_1 and m_2 in the coordinate space and the resultant vector. b) center of mass. c) reduced mass. (CC BY-NC; Ümit Kaya via LibreTexts)

This concept is readily used in the general motion of diatomics, i.e. simple harmonic oscillator (vibrational displacement between two bodies, following Hooke's Law), the rigid rotor approximation (the moment of inertia about the center of mass of a two-body system), spectroscopy, and many other applications.

Example 5.2.1 : Reduced Mass

Determine the reduced mass of the two body system of a proton and electron with $m_{proton} = 1.6727 \times 10^{-27}\ kg$ and $m_{electron} = 9.110 \times 10^{-31}\ kg$).

Answer available at the end of this section.

The Quantum Harmonic Oscillator

The classical Harmonic Oscillator approximation is a simple yet powerful representation of the energetics of an oscillating spring system. Central to this model is the formulation of the quadratic potential energy

$$V(x) \approx \frac{1}{2}kx^2 \tag{5.2.2}$$

One problem with this classical formulation is that it is not general. We cannot use it, for example, to describe vibrations of diatomic molecules, where quantum effects are important. This require the formulation for Schrödinger Equation using Equation 5.2.2.

$$\hat{H}|\psi\rangle = \left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]|\psi\rangle = E|\psi\rangle$$

Solving this quantum harmonic oscillator is appreciably harder than solving the Schrödinger Equation for the simpler particle-in-the-box model and is outside the scope of this text. However, as with most quantum modules (and in contrast to the classical harmonic oscillator), the energies are quantized in terms of a quantum number (v in this case):

$$E_v = \hbar\left(\sqrt{\frac{k}{\mu}}\right)\left(v + \frac{1}{2}\right) \tag{5.2.3}$$

$$= h\nu\left(v + \frac{1}{2}\right) \tag{5.2.4}$$

with the natural vibrational frequency of the system given as

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{5.2.5}$$

and the mass, μ, is the reduced mass of the system (Equation 5.2.1).

Warning

Be careful to distinguish ν, the symbol for the natural frequency (as a Greek nu) from v the quantum harmonic oscillator quantum number (Latin v).

Caution: Do Not Use Atomic Weights to Calculate Reduced Masses

The vibrational frequencies given by Equation 5.2.5 depend on the force constants (k) and the atomic masses of the vibrating nuclei via the reduced mass (μ). It should be clear that the substitution of one isotope of an atom in a molecule for another isotope will affect the atomic masses and therefore the reduced mass (via Equation 5.2.1) and therefore the vibrational frequencies (via Equation 5.2.5).

It is important to remember that the Periodic Table gives only atomic weights of elements, which are scaled averages of atoms normally encountered in the laboratory (Table 5.2.1). To properly discuss vibrational frequencies of molecules, we need to know (or denote) the specific isotopes in the molecule. Check Table A4 for that information.

Table 5.2.1: Atomic Mass and Isotope Composition. Consult Table A4 for more extensive table.

isotope	atomic mass (in amu)	isotopic abundance (%)
^{1}H	1.007825	99.985
^{2}H	2.0140	0.015
^{35}Cl	35.968852	75.77

isotope	atomic mass (in amu)	isotopic abundance (%)
^{37}Cl	36.965903	24.23
^{79}Br	78.918336	50.69
^{81}Br	80.916289	49.31

Example 5.2.1 : Isotope Effect

What are the reduced mass for $^{1}H\,^{35}Cl$ and $^{1}H\,^{37}Cl$? If the spring constants for vibrations of both molecules are equal and estimated at $478\ N/m$, what are the natural vibrational frequencies of these two molecules?

Solution

The periodic table gives an atomic weight of 35.45 amu for chlorine, but remember this is the the average of the natural abundances of different chlorine isotopes which is dictated primary by two isotopes: ^{35}Cl and ^{37}Cl. For this problem, we need the exact mass of the ^{1}H, ^{35}Cl, and ^{37}Cl isotopes. Check Table A4 for that information.

For $^{1}H\,^{35}Cl$:

$$\begin{aligned}\text{Reduced mass} &= \frac{m_1 m_2}{m_1 + m_2} \\ &= \frac{m_H m_{^{35}Cl}}{m_H + m_{^{35}Cl}} \\ &= \frac{(1.0078)(34.9688)}{1.0078 + 34.9688)}\, amu \\ &= 0.9796\, amu\end{aligned}$$

or when converted into kg is $1.629 \times 10^{-27}\ kg$.

For $^{1}H\,^{37}Cl$:

$$\begin{aligned}\text{Reduced mass} &= \frac{m_1 m_2}{m_1 + m_2} \\ &= \frac{m_H m_{^{37}Cl}}{m_H + m_{^{37}Cl}} \\ &= \frac{(1.0078)(36.965)}{1.0078 + 36.965)}\, amu \\ &= 0.9810\, amu\end{aligned}$$

or when converted into kg is $1.6291 \times 10^{-27}\ kg$. This is only 0.29% bigger.

Equation 5.2.5 is used to predict the respective vibrational frequencies of these two molecules.

For $^{1}H\,^{35}Cl$:

$$\begin{aligned}\nu &= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \\ &= \frac{1}{2\pi}\sqrt{\frac{478\, N/m}{1.629 \times 10^{-27}\, kg}} \\ &= 8.6394 \times 10^{13} s^{-1}\end{aligned}$$

For $^{1}H\,^{37}Cl$:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$
$$= \frac{1}{2\pi}\sqrt{\frac{478\,N/m}{1.629\times10^{-27}\,kg}}$$
$$= 8.621\times10^{13}s^{-1}$$

As with the differences in the reduced masses, the differences in the vibrational frequencies of these two molecules is quite small. However, high resolution IR spectroscopy can easily distinguish the vibrations between these two molecules. Exercise 5.2.1 will demonstrate that this "**isotope effect**" is not always a small effect.

Exercise 5.2.1 : Hydrogen Chloride

The force constant is weakly sensitive to the specific isotopes in a molecule (and we typically assume it is isotope independent). If the $k = 478\ \ N/m$ for both $\mathrm{H}^{35}\mathrm{Cl}$ and $\mathrm{H}^{37}\mathrm{Cl}$. What are the vibration frequencies in these two diatomic molecules.

Answer available at the end of this section.

Answers

$$\mu_{pe} = \frac{(1.6727\times10^{-27})(9.110\times10^{-31})}{1.6727\times10^{-27}+9.110\times10^{-31}}$$
$$= 9.105\times10^{-31}kg$$

$\mathrm{H}^{35}\mathrm{Cl}$: 2886 cm^{-1}

$\mathrm{D}^{35}\mathrm{Cl}$: 2081 cm^{-1}

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5.3: The Harmonic Oscillator Approximates Molecular Vibrations

Learning Objectives

- Understand the utility and limits of using the quantum harmonic oscillator as a model for molecular vibrations

The quantum harmonic oscillator is one of the most important model systems in quantum mechanics. This is due in partially to the fact that an arbitrary potential curve $V(x)$ can usually be *approximated* as a harmonic potential at the vicinity of a stable equilibrium point. Furthermore, it is one of the few quantum-mechanical systems for which an exact, analytical solution exists. Solving other potentials typically require either approximations or numerical approaches to identify the corresponding eigenstates and eigenvalues (i.e., wavefunctions and energies).

A general potential energy ($V(x)$) curve for a molecular vibration can be expanded as a Taylor series

$$V(x) = V(x_0) + \frac{dV(x)}{dx}\bigg|_{x_0}^{x}(x-x_0) + \frac{1}{2!}\frac{d^2V(x)}{dx^2}\bigg|_{x_0}^{x}(x-x_0)^2 + \ldots + \frac{1}{n!}\frac{d^nV(x)}{dx^n}\bigg|_{x_0}^{x}(x-x_0)^n \tag{5.3.1}$$

It is important to note that this approximation is only good for x near x_0, and that x_0 stands for the equilibrium bond distance. $V(x)$ is often (but not always) shortened to the cubic term and can be rewritten as

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 \tag{5.3.2}$$

where $V(x_0) = 0$, k is the harmonic force constant (harmonic term), and γ is the first anharmonic term (i.e., cubic). As Figure 5.3.2 demonstrates, the harmonic oscillator (red curve) is a good approximation for the exact potential energy of a vibration (blue curve).

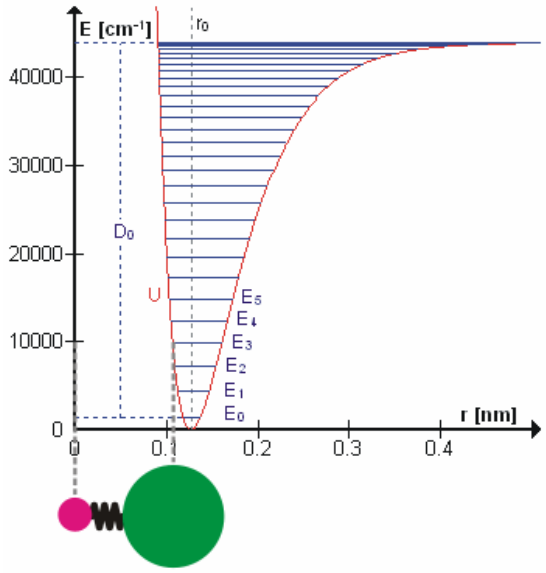


Figure 5.3.1: The vibration of the HCl molecule is really an anharmonic oscillator, but can be approximated as a harmonic oscillator at low energies. In this animation, HCl is vibrating at the E_3 energy level. D_0 is dissociation energy here, r_0 bond length, V potential energy. Energy is expressed in wavenumbers. The hydrogen chloride molecule is attached to the coordinate system to show bond length changes on the curve. (CC BY-SA 3.0; Darekk2 via Wikipedia).

Adding anharmonic perturbations to the harmonic oscillator (Equation 5.3.2) better describes molecular vibrations. Anharmonic oscillation is defined as the deviation of a system from harmonic oscillation, or an oscillator not oscillating in simple harmonic

motion. Anharmonic oscillation is described as the restoring force is no longer proportional to the displacement. Adding the cubic term (Figure 5.3.2 ; green curve) improves the harmonic oscillation approximation especially under greater displacement from equilibrium.

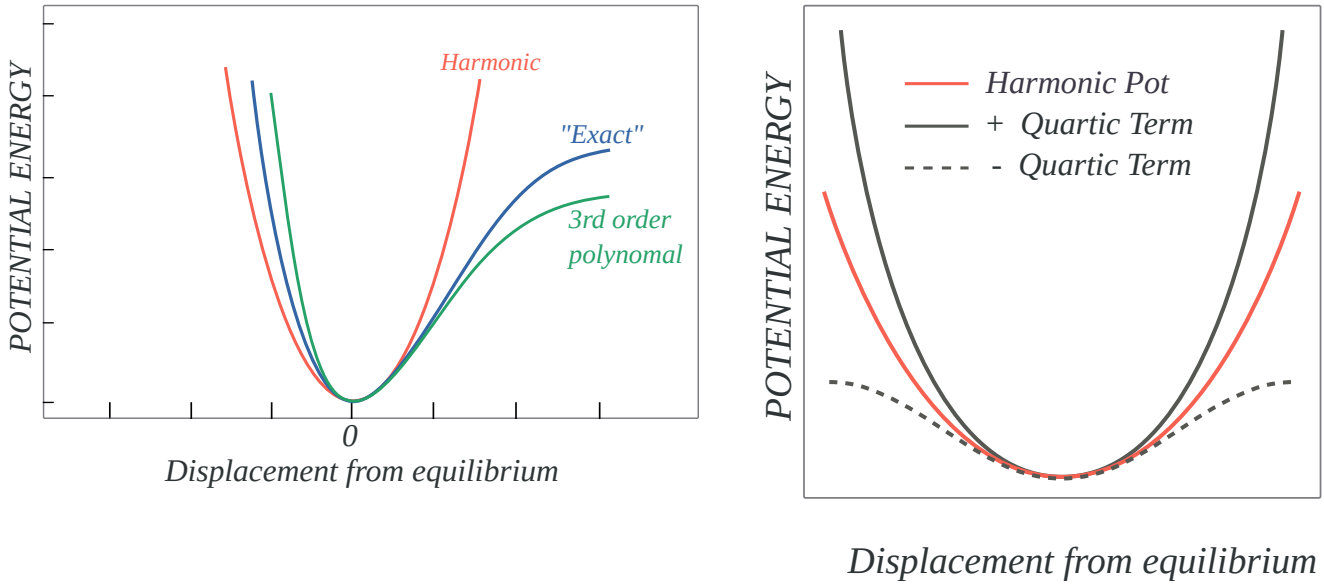


Figure 5.3.2: (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY 4.0; Ümit Kaya via LibreTexts)

Naturally, adding higher order anharmonic terms, like quartic terms (Figure $5.3.2; right$) improve the approximation. Almost all diatomics have experimentally determined potentials for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 with terms up to $n < 10$ determined of Equation 5.3.1.

Figure 5.3.1 shows the the general potential with (numerically) calculated energy levels (E_0, E_1 etc.). D_o is the dissociation energy, which is different from the well depth D_e. These vibrational energy levels of this plot can be calculated using the harmonic oscillator model (i.e., Equation 5.3.1 with the Schrödinger equation) and have the general form

$$E_v = \left(v + \frac{1}{2}\right) v_e - \left(v + \frac{1}{2}\right)^2 v_e x_e + \left(v + \frac{1}{2}\right)^3 v_e y_e + \text{higher terms}$$

where v is the vibrational quantum number and x_e and y_e are the first and second anharmonicity constants, respectively.

The $v = 0$ level is the vibrational ground state. Because this potential is less confining than a parabola used in the harmonic oscillator, the energy levels become **less widely** spaced at high excitation (Figure 5.3.1 ; top of potential).

Limitations of the Harmonic Oscillator Model for Molecular Vibrations

The harmonic oscillation is a great approximation of a molecular vibration, but has key limitations:

- Due to equal spacing of energy, all transitions occur at the **same** frequency (i.e. single line spectrum). However experimentally many lines are often observed (called overtones).
- The harmonic oscillator does not predict bond dissociation; you cannot break it no matter how much energy is introduced.

Morse Potentials are better Approximations of Vibrational Motion

A more powerful approach than just "patching up" the harmonic oscillator solution with anharmonic corrections is to adopt a different potential ($V(x)$). One such approach is the Morse potential, named after physicist Philip M. Morse, and a better approximation for the vibrational structure of the molecule than the harmonic oscillator because it explicitly includes the effects of *bond breaking* and accounts for the anharmonicity of real bonds (Figure 5.3.4).

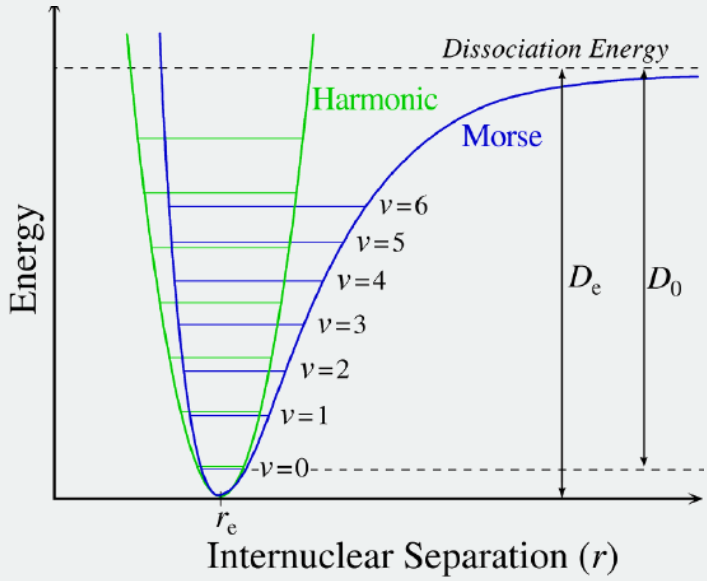


Figure 5.3.4: The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by ħω, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e is larger than the true energy required for dissociation D_0 due to the zero point energy of the lowest ($v = 0$) vibrational level. from Wikipedia.

The Morse Potential is a good approximation to $V(x)$ and is best when looking for a general formula for all x from 0 to ∞, not just applicable for the local region around the x_o:

$$V(x) = D(1 - e^{-\beta(x-x_0)})^2 \tag{5.3.3}$$

with $V(x = x_0) = 0$ and $V(x = \infty) = D$.

The Morse Potential (Figure 5.3.4) approaches zero at infinite r_e and equals $-D_e$ at its minimum (i.e. $r = r_e$). It clearly shows that the Morse potential is the combination of a short-range repulsion term (small r values) and a long-range attractive term (large r values).

Solving the Schrödinger Equation with the Morse Potential (Equation 5.3.3) is not trivial, but can be done analytically.

$$\hat{H}|\psi\rangle = E_n|\psi\rangle$$

with

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} \\ &= \frac{-\hbar^2 d^2}{2m\ dx^2} + D(1 - e^{-\beta(x-x_0)})^2\end{aligned}$$

The solutions and energies for the Morse potential will not be used in this course and will not be discussed in more detail.

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5.4: The Harmonic Oscillator Energy Levels

For a classical oscillator, we know exactly the position, velocity, and momentum as a function of time. The frequency of the oscillator (or normal mode) is determined by the reduced mass μ and the effective force constant k of the oscillating system and does not change unless one of these quantities is changed. There are no restrictions on the energy of the oscillator, and changes in the energy of the oscillator produce changes in the amplitude of the vibrations experienced by the oscillator.

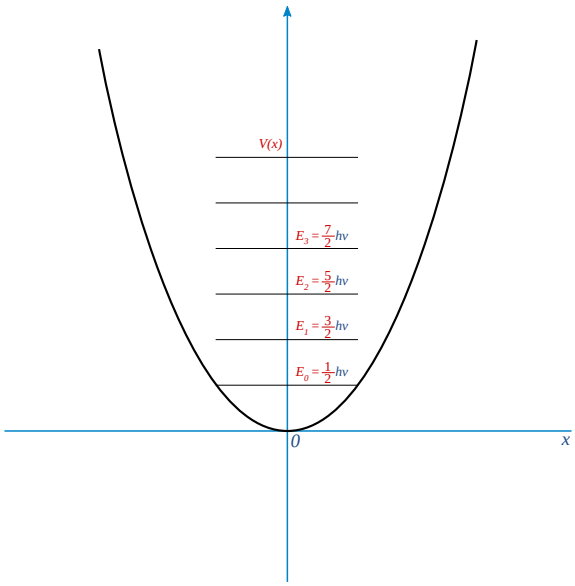


Figure 5.4.1 : Potential energy function and first few energy levels for harmonic oscillator. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

For the quantum mechanical oscillator, the oscillation frequency of a given normal mode is still controlled by the mass and the force constant (or, equivalently, by the associated potential energy function). However, the energy of the oscillator is limited to certain values. The allowed quantized energy levels are equally spaced and are related to the oscillator frequencies as given by Equation 5.4.1 and Figure 5.4.1 .

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega = \left(v + \frac{1}{2}\right)h\nu \tag{5.4.1}$$

with

$$v = 0, 1, 2, 3, \cdots \infty$$

In a quantum mechanical oscillator, we cannot specify the position of the oscillator (the exact displacement from the equilibrium position) or its velocity as a function of time; we can only talk about the probability of the oscillator being displaced from equilibrium by a certain amount. This probability is given by

$$P_{Q\rightarrow Q+dQ} = \int_{Q}^{Q+dQ} \psi_v^*(Q)\psi_v(Q)dQ \tag{5.4.2}$$

We can, however, calculate the average displacement and the mean square displacement of the atoms relative to their equilibrium positions. This average is just $\langle Q\rangle$, the expectation value for Q, and the mean square displacement is $\langle Q^2\rangle$, the expectation value for Q^2. Similarly we can calculate the average momentum $\langle P_Q\rangle$, and the mean square momentum $\left\langle P_Q^2\right\rangle$, but we cannot specify the momentum as a function of time.

Physically what do we expect to find for the average displacement and the average momentum? Since the potential energy function is *symmetric* around $Q = 0$, we expect values of $Q > 0$ to be equally as likely as $Q < 0$. The average value of Q therefore should be zero.

These results for the average displacement and average momentum do not mean that the harmonic oscillator is sitting still. As for

the particle-in-a-box case, we can imagine the quantum mechanical harmonic oscillator as moving back and forth and therefore having an average momentum of zero. Since the lowest allowed harmonic oscillator energy, E_0, is $\frac{\hbar\omega}{2}$ and not 0, the atoms in a molecule must be moving even in the lowest vibrational energy state. This phenomenon is called the zero-point energy or the zero-point motion, and it stands in direct contrast to the classical picture of a vibrating molecule. Classically, the lowest energy available to an oscillator is zero, which means the momentum also is zero, and the oscillator is not moving.

Exercise 5.4.1

Compare the quantum mechanical harmonic oscillator to the classical harmonic oscillator at $v = 1$ and $v = 50$.

Answer available at the end of this section.

Since the average values of the displacement and momentum are all zero and do not facilitate comparisons among the various normal modes and energy levels, we need to find other quantities that can be used for this purpose. We can use the root mean square deviation (see also root-mean-square displacement) (also known as the standard deviation of the displacement) and the root-mean-square momentum as measures of the uncertainty in the oscillator's position and momentum.

For a molecular vibration, these quantities represent the standard deviation in the bond length and the standard deviation in the momentum of the atoms from the average values of zero, so they provide us with a measure of the relative displacement and the momentum associated with each normal mode in all its allowed energy levels. These are important quantities to determine because vibrational excitation changes the size and symmetry (or shape) of molecules. Such changes affect chemical reactivity, the absorption and emission of radiation, and the dissipation of energy in radiationless transitions.

The harmonic oscillator wavefunctions form an orthonormal set; this means that all functions in the set are normalized individually

$$\int_{-\infty}^{\infty} \psi_v^*(x)\psi_v(x)dx = 1 \tag{5.4.3}$$

and are orthogonal to each other.

$$\int_{-\infty}^{\infty} \psi_{v'}^*(x)\psi_v(x)dx = 0 \;\text{ for }\; v' \neq v \tag{5.4.4}$$

The fact that a family of wavefunctions forms an orthonormal set is often helpful in simplifying complicated integrals. We will use these properties when we determine the harmonic oscillator selection rules for vibrational transitions in a molecule and calculate the absorption coefficients for the absorption of infrared radiation.

Finally, we can calculate the probability that a harmonic oscillator is in the classically forbidden region. What does this tantalizing statement mean? Classically, the maximum extension of an oscillator is obtained by equating the total energy of the oscillator to the potential energy, because at the maximum extension all the energy is in the form of potential energy. If all the energy weren't in the form of potential energy at this point, the oscillator would have kinetic energy and momentum and could continue to extend further away from its rest position. Interestingly, as we show below, the wavefunctions of the quantum mechanical oscillator extend beyond the classical limit, i.e. beyond where the particle can be according to classical mechanics.

The lowest allowed energy for the quantum mechanical oscillator is called the **zero-point energy,** $E_0 = \frac{\hbar\omega}{2}$. Using the classical picture described in the preceding paragraph, this total energy must equal the potential energy of the oscillator at its maximum extension. We define this classical limit of the amplitude of the oscillator displacement as Q_0. When we equate the zero-point energy for a particular normal mode to the potential energy of the oscillator in that normal mode, we obtain

$$\frac{\hbar\omega}{2} = \frac{kQ_0^2}{2} \tag{5.4.5}$$

The zero-point energy is the **lowest** possible energy that a quantum mechanical physical system may have. Hence, it is the energy of its ground state.

Recall that k is the effective force constant of the oscillator in a particular normal mode and that the frequency of the normal mode is given by Equation 5.4.1 which is

$$\omega = \sqrt{\frac{k}{\mu}} \tag{5.4.6}$$

Answers

At v=1 the classical harmonic oscillator poorly predicts the results of quantum mechanical harmonic oscillator, and therefore reality. At v=1 the particle will be near the ground state and the classical model will predict the particle to spend most it's time on the outer edges when the KE goes to zero and PE is at a maximum, while the quantum model says the opposite and that the particle will be more likely to be found in the center. At v=50 the quantum model will begin to match the classical much more closely, with the particle most likely to be found at the edges. The quantum model looking more like the classical at higher quantum numbers can be referred to as the correspondence principle.

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5.5: The Harmonic Oscillator and Infrared Spectra

Learning Objectives

- Understand how the quantum harmonic oscillator model can be used to interpret the infrared spectra of diatomic molecules
- Understand the origin of the transition moment integral and selection rules and how they are related

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them. Chemical compounds have different chemical properties due to the presence of different functional groups. IR spectroscopy is one of the most common and widely used spectroscopic techniques. Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds.

IR Spectroscopy

Transitions between vibrational energy levels can be induced about by absorption or emission of radiation. To understand this, knowledge of both the initial and final eigenstates is needed. The energy of the vth eigenstate of a harmonic oscillator can be written as

$$E_v = \left(v + \frac{1}{2}\right) \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{5.5.1}$$

where h is Planck's constant and v is the vibrational quantum number and ranges from 0, 1, 2, 3,..., ∞. Equation 5.5.1 is often rewritten as

$$E_v = \left(v + \frac{1}{2}\right) h\nu_m \tag{5.5.2}$$

where ν_m is the vibrational frequency of the vibration. Equation 5.5.2 is often written as

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega$$

where ω is the angular frequency (i.e., $2\pi\nu$).

Transitions in vibrational energy levels can be brought about by absorption of radiation, provided the energy of the radiation ($h\nu_{photon}$) **exactly** matches the difference in energy ($\Delta E_{vv'}$) between the vibrational quantum state v to quantum state v'. This can be expressed as

$$\begin{aligned} h\nu_{photon} &= \Delta E_{vv'} \\ &= E_{v'} - E_v \\ &= \left(v' + \frac{1}{2}\right) h\nu_m - \left(v + \frac{1}{2}\right) h\nu_m \\ &= (v' - v)\, h\nu_m \end{aligned} \tag{5.5.3}$$

Let's consider only transitions between adjacent eigenstates (discussed in more details below) so

$$v' - v = \pm 1$$

which is positive if an IR photon is absorbed and negative if it is emitted. For the absorption of a IR photon, Equation 5.5.3 simplifies to

$$\begin{aligned} h\nu_{photon} &= h\nu_m \\ &= \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \end{aligned} \tag{5.5.4}$$

The frequency of radiation ν_{photon} that will bring about this change is **identical** to the classical vibrational frequency of the bond ν.

The Wavenumber as a Unit of Energy

The cm^{-1} is the wavenumber scale and it can also be defined as 1/wavelength in cm. A wavenumber is often used due to its direct relationship with both frequency and energy. The frequency of the absorbed radiation causes the molecular vibrational frequency for the absorption process:

$$\bar{\nu}(cm^{-1}) = \frac{1}{\lambda(\mu m)} \times 10^4 \left(\frac{\mu m}{cm}\right) \tag{5.5.5}$$

$$= \frac{\nu\,(Hz)}{c\,(cm/s)} \tag{5.5.6}$$

Equation 5.5.3 can be modified so that the radiation can be expressed in wavenumbers

$$\tilde{\nu}_m = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{5.5.7}$$

where c is the velocity of light (cm/s) and $\tilde{\nu}$ is the wavenumber of an absorption maximum (cm^{-1}).

Example 5.5.1: Hydrogen Halides

The force constants for typical diatomic molecules are in the range between 400 to 2000 $N \cdot m^{-1}$.

Molecule	HF	HCl	HBr	HI	CO	NO
Force constant, k ($N.m^{-1}$)	970	480	410	320	1860	1530

For the diatomic molecules listed above, calculate the following:

a. angular frequency ($\mathrm{rad} \cdot s^{-1}$)
b. natural frequency (Hz)
c. period (s)
d. separation between energy levels
e. wavelength λ of the electromagnetic radiation absorbed in the transition $v = 0 \rightarrow v = 1$.

Solution

For HCl:

a. angular frequency

$$\omega = 5.45 \times 10^{14} \mathrm{rad} \cdot s^{-1}$$

b. natural frequency:

$$\nu = \frac{\omega}{2\pi} = 8.68 \times 10^{13}$$

c. period (s):

$$T = \frac{1}{\nu} = 1.15 \times 10^{-14}$$

d. separation between energy levels:

$$\Delta E = E_{v=1} - E_{v=0} = \hbar\omega = 5.75 \times 10^{-20}\ J$$

e. wavelength λ of the electromagnetic radiation absorbed in the transition $v = 0 \rightarrow v = 1$:

$$3.46 \times 10^{-6}\, m$$

The electromagnetic radiation released (and absorbed) for vibrations is primarily in the infrared (IR) part of the spectrum. Calculating the above properties for the other molecules remains as an exercise.

Note: We did not designate the specific isotopes in the hydrogen halides above because that information was not required to solve these questions.

IR deals with the interaction between a molecule and radiation from the electromagnetic region ranging (4000- 40 cm^{-1}). The IR region of the electromagnetic spectrum ranges in wavelength from 2 -15 μm. Conventionally the IR region is subdivided into three regions (Table 5.5.1): near IR, mid IR and far IR. Most of the IR used originates from the mid IR region.

Table 5.5.1: Regions of the IR Spectrum

Region	Wavelength	Wavenumbers ($\tilde{\nu}$), cm^{-1}	Frequencies (v), HZ
Near	0.78 -2.5	12800 - 4000	3.8 x 10^{14} - 1.2 x 10^{14}
Middle	2.5 - 50	4000 - 200	3.8 x 10^{14} - 1.2 x 10^{14}
Far	50 -100	200 -10	3.8 x 10^{14} - 1.2 x 10^{14}
Most Used	2.5 -15	4000 -670	3.8 x 10^{14} - 1.2 x 10^{14}

Example 5.5.2: Hydrogen Chloride

The $H^{35}Cl$ equilibrium bond length is 0.127 nm and the $v = 0$ to $v = 1$ transition is observed in the infrared at 2,886 cm^{-1}. Compute the vibrational energy of $H^{35}Cl$ in its lowest state.

a. Compute the classical limit for the stretching of the HCl bond from its equilibrium length in this state.
b. What percent of the equilibrium bond length is this extension?

Solution

The $H{-}Cl$ bond length is $0.127\ nm = 1.27 \times 10^{-10} m$ and the IR transition is observed at $2886\ cm^{-1}$. We first convert this to Hertz

$$2886\, cm^{-1}(3 \times 10^{10} cm/s) = 8.646 \times 10^{13} s^{-1} = 8.646 \times 10^{13}\, Hz$$

The equations for the energy of the vth eigenstate of a harmonic oscillator is

$$E_v = (v + 1/2)\hbar\omega$$

So the ground state ($v = 0$) energy is

$$E_0 = \frac{1}{2}\hbar\omega$$

with

$$\begin{aligned}\omega &= 2\pi\nu \\ &= 5.54 \times 10^{14}\, rad/s\end{aligned}$$

We can then extra the ground state vibrational energy (aka zero-point energy) from

$$\begin{aligned}E_o &= \frac{1}{2}\hbar\omega \\ &= \frac{1}{2}\hbar(5.54 \times 10^{14} rad/s) \\ &= 2.916 \times 10^{-20}\, J\end{aligned}$$

The classical limit of the stretch is denoted as Q_0, this can be equated as potential energy in relation to the total E_0 found above as, at E_0, all of the energy would be potential energy in the form of the stretch. In comparison to the classic spring potential

$$V = \frac{1}{2}kQ_0^2$$

As described above, we can relate the two as

$$\frac{1}{2}\hbar\omega = \frac{1}{2}kQ_0^2$$

or,

$$2.916 \times 10^{-20} J = \frac{1}{2}481 Q_0^2$$

where $Q_0 = 1.10 \times 10^{-11} m = 0.0110\ nm$.

Lastly, this classical limit to length can be compared to the equilibrium bond length by a simple relation of

$$\begin{aligned}\text{Percent bond length} &= \frac{Q_0}{x_{eq}} \times 100\% \\ &= \frac{0.0110\, nm}{0.127\, nm} \times 100\% \\ &= 8.66\%\end{aligned}$$

Selection Rules for IR Transitions

Photons can be absorbed or emitted, and the harmonic oscillator can transition from one vibrational energy state to another. Which transitions between vibrational states are allowed? When discussing the Bohr hydrogen atom in Chapter 1, we identified multiple transitions between different states as being responsible for the line spectra emission of the hydrogen atom. No limitations were identified so that any transition between any starting state and ending state was possible and this resulted in a complex pattern in the spectra. As we will identify later on, when considering mulit-electron atoms, there are **selection rules** that limits which transitions will be observed (i.e., are allowed).

A similar situation exist for the harmonic oscillator and IR transitions and a set of selection rules must be satisfied to ensure a particular transition is allowed. Selection rules result from evaluating a **transition moment integral** that expresses the probability of a transition from the v to the v' eigenstates:

$$\mu_T = \langle \psi_{v'} | \hat{\mu}(x) | \psi_v \rangle \tag{5.5.8}$$

$$= \int_{-\infty}^{\infty} \psi^*_{v'}(x) \hat{\mu}(x) \psi_v(x) dx \tag{5.5.9}$$

When the transition moment integral is zero for two specific eigenstates (i.e., $\psi_v(x)$ and $\psi'_v(x)$), then the probability of observing that transition is zero. In this case, this transition is called a **forbidden transition** (i.e., it will not be obversed). Transitions with low probabilities are call "weakly allowed transitions" since they will have small amplitudes in spectra and transitions with high probabilities are "strongly allowed transitions" and will exhibit high amplitudes in spectra.

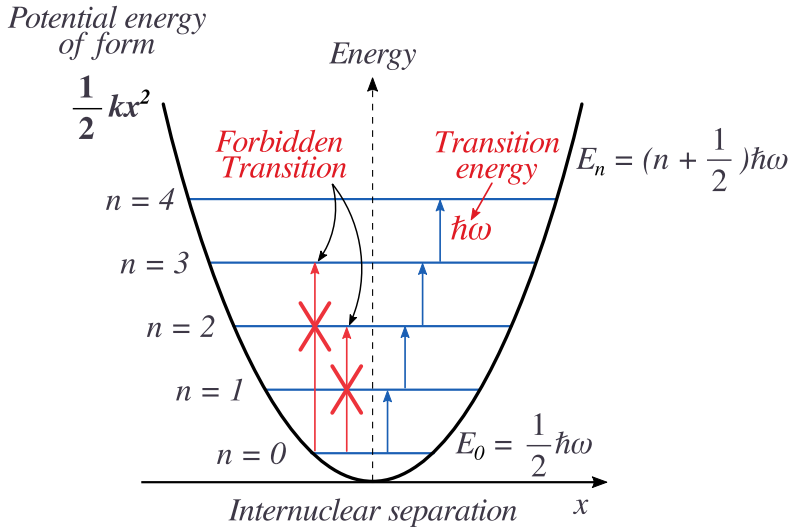


Figure 5.5.1: Possible transitions for a harmonic oscillator. Allowed transitions are labeled with blue arrows and forbidden transitions are labeled with red arrows. (CC BY-NC; Ümit Kaya via LibreTexts)

To evaluate Equation 5.5.9, we need to express the dipole moment operator, $\hat{\mu}$, in terms of the magnitude of the vibration x. The dipole moment operator is defined as

$$\hat{\mu} = \sum_{electrons} e\vec{r} + \sum_{nuclei} q\vec{R} \tag{5.5.10}$$

where the two sums are over all the electrons and nuclei and involve the particle charge ($-e$ or q) multiplying the position vector ($\vec{r}$ or $\vec{R}$, respectively). We can obtain this dipole moment operator in terms of the magnitude of the displacement coordinate, x, in a simple way by using a **Taylor series expansion** for the dipole moment around the equlibrium position ($x = 0$).

$$\hat{\mu}(x) = \mu_{x=0} + \left.\frac{d\mu(x)}{dx}\right|_{x=0} x + \left.\frac{d^2\mu(x)}{dx^2}\right|_{x=0} x^2 + \cdots \tag{5.5.11}$$

Retaining only the first two terms and substituting into Equation 5.5.9 produces

$$\mu_T = \mu_{x=0} \int_{-\infty}^{\infty} \psi_{v'}(x)\psi_v(x)dx + \left.\frac{d\mu(x)}{dx}\right|_{x=0} \int_{-\infty}^{\infty} x\psi^*_{v'}(x)\psi_v(x)dx \tag{5.5.12}$$

where $\mu_{x=0}$ is the **dipole moment** of the molecule when the nuclei are at their equilibrium positions, and

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0}$$

is the *linear* change in the dipole moment due to the displacement of the nuclei in the normal mode. The derivative is the linear change because it multiplies x and not a higher power of x in Equation 5.5.11. Both μ and

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0}$$

are moved outside of the integral because they are constants that no longer depend on x because they are evaluated at $x = 0$.

The integral in the first term in Equation 5.5.12 is 0 because any two harmonic oscillator wavefunctions are *orthogonal*. The integral in the second term of Equation 5.5.12 is zero except when $v' = v \pm 1$ as demonstrated in Exercise 5.5.1 . Also note that the second term is zero if

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0} = 0 \tag{5.5.13}$$

Hence we can identify two "rules" that need to be satisfied for an IR photon to be absorb (or emitted) by a vibrating molecule.

Rules for IR Absorption

For IR absorption to occur two conditions must be met:

1. There must be a **change** in the dipole moment of the molecule as a result of a molecular vibration (or rotation). The change (or oscillation) in the dipole moment allows interaction with the alternating electrical component of the IR radiation. Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment.
2. If the frequency of the radiation ν_{photon} matches the natural frequency of the vibration (ν_m), the IR photon can be absorbed and the amplitude of the vibration increases.

Exercise 5.5.1

Use one of the Hermite polynomial recursion relations to verify that the second integral in Equation 5.5.12 is 0 unless $v' = v \pm 1$.

If we are to observe absorption of infrared radiation due to a vibrational transition in a molecule, the transition moment cannot be zero. This condition requires that the dipole moment derivative Equation 5.5.13 **cannot** be zero and that the vibrational quantum number change by one unit. The normal coordinate motion must cause the dipole moment of the molecule to change in order for a molecule to absorb infrared radiation. If the normal coordinate oscillation does not cause the dipole moment to change then $\mu_T = 0$ and no infrared absorption is observed. So we can

$$\underbrace{\Delta v = \pm 1}_{\text{For allowed transitions}} \tag{5.5.14}$$

Consider oxygen and nitrogen molecules. Because they are symmetrical, their dipole moments are zero, $\mu = 0$. Since the vibrational motion (only bond stretching for a diatomic molecule) preserves this symmetry, the change in the dipole moment due to the vibrational motion also is zero, $\frac{d\mu(x)}{dx} = 0$. Consequently, oxygen and nitrogen do not absorb infrared radiation as a result of vibrational motion.

Exercise 5.5.2

Explain why the molar absorptivity or molar extinction coefficients (ϵ) in Beer's Law for the IR absorption of some vibrations are greater than others.

Answer available at the end of this section.

The case $v' = v + 1$ corresponds to going from one vibrational state to a higher energy one by absorbing a photon with energy $h\nu$. The case $v' = v - 1$ corresponds to a transition that emits a photon with energy $h\nu$. In the harmonic oscillator model infrared spectra are very simple; only the fundamental transitions, $\Delta = \pm 1$, are allowed. The associated transition energy is $\hbar\omega$, according

to Equation 5.5.4. The transition energy is the change in energy of the oscillator as it moves from one vibrational state to another, and it equals the photon energy.

$$\begin{aligned}\Delta E &= E_{final} - E_{initial} \\ &= h\upsilon_{photon} \\ &= \hbar\omega_{oscillator}\end{aligned}$$

For perfect harmonic oscillators, the only possible allowed transitions are $\Delta = \pm 1$ with all other transitions forbidden (Figure 5.5.1). This conclusion predicts that the vibrational absorption spectrum of a diatomic molecule consists of a single line since the energy levels are equally spaced in the harmonic oscillator model (Figure 5.5.1). If the vibration were anharmonic, then the levels would not be equally spaced and then transitions from $\upsilon = 0$ to $\upsilon = 1$ and from $\upsilon = 1$ to $\upsilon = 2$, etc. would occur at different frequencies.

Only the fundamental transitions, $\Delta = \pm 1$, are observed in infrared spectra within harmonic oscillator model.

The actual IR spectrum is more complex, especially at high resolution. There is a fine structure due to the rotational states of the molecule. These states will be discussed in the next chapter. The spectrum is enriched further by the appearance of lines due to transitions corresponding to $\Delta = \pm n$ where $n > 1$. These transitions are called **overtone** transitions and their appearance in spectra despite being forbidden in the harmonic oscillator model is due to the anharmonicity of molecular vibrations. Anharmonicity means the potential energy function is not strictly the harmonic potential. The first overtone, $\Delta\upsilon = 2$, generally appears at a frequency slightly less than twice that of the fundamental, i.e. the frequency due to the $\Delta\upsilon = 1$ transition.

Exercise 5.5.3: Hydrogen Chloride

Compute the approximate transition frequencies in wavenumber units for the first and second overtone transitions in HCl given that the fundamental is at 2,886 cm^{-1}.

Answers

Qualitatively, if the probability of transition is large, then the molar absorptivity is large. And similar if the transition were not allowed, then there will be no intensity and no observed peak in the spectrum. Transitions can be "partially allowed" as well, and these bands appear with a lower intensity than the full allowed transitions.

When looking at the Beer's Law

$$A = \epsilon\ c\ l$$

where A is absorbance. ϵ is the molar absorptivity, c is the molar concentration and l is the optical path length

We are only looking at the change in the molar absorptivity as the IR absorptions of vibrations vary. To do this we have to look at the transition moment integral

$$\mu_T = \langle \psi_{\upsilon'} | \hat{\mu}(x) | \psi_{\upsilon} \rangle$$

When the transition moment integral is zero, there is no transition as it is not allowed under the selection rules. This means that the IR is not absorbing any vibrations and therefore the molar absorptivity is zero, which means that absorbance according to Beer's Law is zero. As the transition moment integral increases, the molar absorptivity also increases and the overall absorbance increases.

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5.6: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials

Learning Objectives

- The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

For a diatomic molecule, there is only one vibrational mode, so there will be only a single set of vibrational wavefunctions with associated energies for this system. For polytatomic molecules, there will be a set of wavefunctions with associated energy associated with each vibrational mode.

The Hamiltonian operator, the general quantum mechanical operator for energy, includes both a kinetic energy term, $\hat{T}$, and a potential energy term, $\hat{V}$.

$$\hat{H} = \hat{T} + \hat{V} \tag{5.6.1}$$

For the free particle and the particle in a box, the potential energy term used in the Hamiltonian was zero. As shown in Equation 5.6.1, the classical expression for the energy of a harmonic oscillator includes both a kinetic energy term and the harmonic potential energy term. Transforming this equation into the corresponding Hamiltonian operator gives,

$$\hat{H}(q) = \frac{1}{2\mu}\hat{P}_q^2 + \frac{k}{2}\hat{q}^2 \tag{5.6.2}$$

where $\hat{q}$ is the operator for the length of the normal coordinate, and $\hat{P}_q$ is the momentum operator associated with the normal coordinate. μ is an effective (reduced) mass, and k is an effective force constant, and these quantities will be different for each of the normal modes (vibrations).

Substituting the definitions for the operators yields

$$\hat{H}(q) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2} + \frac{k}{2}q^2 \tag{5.6.3}$$

since the operator for position or displacement is just the position or displacement. The time-independent Schrödinger Equation then becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_v(q)}{dq^2} + \frac{k}{2}q^2\psi_v(q) = E_v\psi_v(q) \tag{5.6.4}$$

or upon rearranging

$$\frac{d^2\psi_v(q)}{dq^2} + \frac{2\mu}{\hbar^2}\left(E_v - \frac{k}{2}q^2\right)\psi_v(q) = 0 \tag{5.6.5}$$

This differential equation is not straightforward to solve. Rather than fully develop the details of the solution, we will outline the method used because it represents a common strategy for solving differential equations. The steps taken to solve Equation 5.6.5 are to simplify the equation by collecting constants in the parameter β

$$\beta^2 = \frac{\hbar}{\sqrt{\mu k}} \tag{5.6.6}$$

and then changing the variable from q to x where

$$x = \frac{q}{\beta} \tag{5.6.7}$$

so that

$$\frac{d^2}{dq^2} = \frac{1}{\beta^2}\frac{d^2}{dx^2} \tag{5.6.8}$$

After substituting Equations 5.6.6 and 5.6.8 into Equation 5.6.5, the differential equation for the harmonic oscillator becomes

$$\frac{d^2\psi_v(x)}{dx^2} + \left(\frac{2\mu\beta^2 E_v}{\hbar^2} - x^2\right)\psi_v(x) = 0 \tag{5.6.9}$$

Exercise 5.6.1

Make the substitutions given in Equations 5.6.6 and 5.6.8 into Equation 5.6.5 to get Equation 5.6.9.

Solving for the Quantum Wavefunctions

A common strategy for solving differential equations, which is employed here, is to find a solution that is valid for large values of the variable and then develop the complete solution as a product of this asymptotic solution and a power series. Since the potential energy approaches infinity as x and the coordinate q approach infinity, the wavefunctions must approach zero (this is, the wavefunctions must **converge to zero**):

$$\lim_{x\to\infty} \psi_v(x) = 0 \tag{5.6.10}$$

The function that has this property and satisfies the differential equation for large values of x is the exponential function, i.e.,

$$\lim_{x\to\infty} \phi_v(x)\exp\left(\frac{-x^2}{2}\right) = 0 \tag{5.6.11}$$

where the wavefunctions are

$$\psi_v(x) \propto \phi_v(x)\exp\left(\frac{-x^2}{2}\right)$$

The general expression for a power series of $\phi_v(x)$ is

$$\begin{aligned}\phi_v(x) &= \sum_{n=0}^{\infty} c_n(v)x^n \\ &= c_n(v)x + c_n(v)x^2 + c_n(v)x^3 + \cdots\end{aligned}$$

which can be truncated after the first term, after the second term, after the third term, etc. to produce a set of polynomials. There is one polynomial for each value of v where v can be equal to any integer value including zero.

$$\sum_{n=0}^{v} c_n x^n \tag{5.6.12}$$

Each of the truncations of the power series in Equation 5.6.12 can be multiplied by the exponential function in Equation 5.6.11 to create a family of valid solutions to the differential equation in Equation 5.6.9.

$$\psi_v(x) = \sum_{n=0}^{v} c_n x^n \exp\left(\frac{-x^2}{2}\right) \tag{5.6.13}$$

Exercise 5.6.2

Write the first four polynomials, $v = 0$ to $v = 1$, $v = 12$, $v = 13$, $v = 14$ for Equation 5.6.12 and use suitable software to prepare plots of these polynomials. Identify the curves in the plots.

Exercise 5.6.3

Confirm that the wavefunction given by Equation 5.6.13 is a solution to the harmonic oscillator Schrödinger Equation in Equation 5.6.9 for $v = 0$ and $v = 1$.

Hermite Polynomials

While polynomials in general approach ∞ (or $-\infty$) as x approaches ∞, the decreasing exponential term overpowers the polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of x or $-x$. The exact forms of polynomials that solve Equation 5.6.9 are the **Hermite polynomials**, which are standard mathematical functions known from the work of Charles Hermite. The first eight Hermite polynomials, $H_v(x)$, are given below.

- $H_0 = 1$
- $H_1 = 2x$
- $H_2 = -2 + 4x^2$
- $H_3 = -12x + 8x^3$
- $H_4 = 12 - 48x^2 + 16x^4$
- $H_5 = 120x - 160x^3 + 32x^5$
- $H_6 = -120 + 720x^2 - 480x^4 + 64x^6$
- $H_7 = -1680x + 3360x^3 - 1344x^5 + 128x^7$

The first six Hermite polynomials are plotted in Figure 5.6.1 . Hermite polynomials will be discussed in more detail in the following Section.

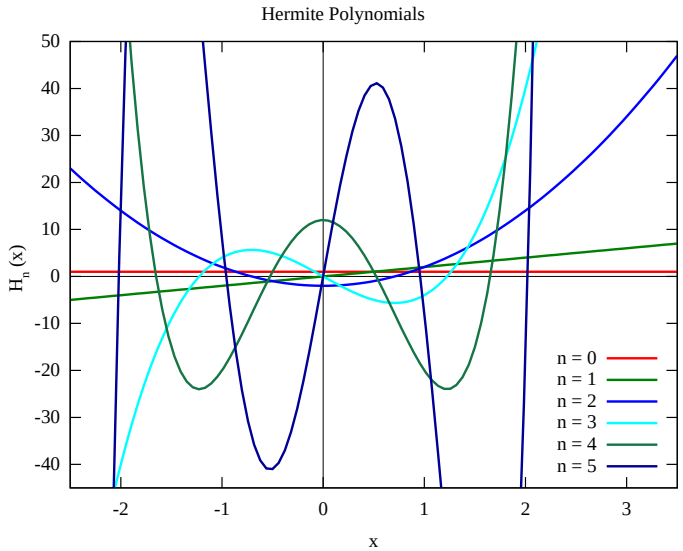


Figure 5.6.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

Exercise 5.6.4

Determine the units of β and the units of x in the Hermite polynomials.

Because of the association of the wavefunction with a probability density, it is necessary for the wavefunction to include a normalization constant, N_v.

$$N_v = \frac{1}{(2^v v! \sqrt{\pi})^{1/2}} \tag{5.6.14}$$

The final form of the harmonic oscillator wavefunctions is thus

$$\psi_v(x) = N_v H_v(x) e^{-x^2/2} \tag{5.6.15}$$

Alternative and More Common Formulation of Harmonic Oscillator Wavefunctions

The harmonic oscillator wavefunctions are often written in terms of Q, the unscaled displacement coordinate (Equation 5.6.7) and a different constant α:

$$\alpha = 1/\sqrt{\beta} = \sqrt{\frac{k\mu}{\hbar^2}}$$

so Equation 5.6.15 becomes

$$\psi_v(x) = N_v'' H_v(\sqrt{\alpha} Q) e^{-\alpha Q^2/2}$$

with a slightly different normalization constant

$$N_v'' = \sqrt{\frac{1}{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

Exercise 5.6.5

Compute the normalization factor for $\psi_v(x)$ where $v = 0$ and $v = 4$. What is the purpose of N_v?

The energy eigenvalues for a quantum mechanical oscillator also are obtained by solving the Schrödinger equation. The energies are restricted to discrete values

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \tag{5.6.16}$$

with $v = 0, 1, 2, 3, \cdots$.

The energies depend both on the quantum number, v, and the oscillator frequency

$$\omega = \sqrt{\frac{k}{\mu}}$$

which in turn depends on the spring constant k and the reduced mass of the vibration μ.

Exercise 5.6.6

Determine the energy for the first ten harmonic oscillator energy levels in terms of $\hbar\omega$. Sketch an energy level diagram of these energies.

1. What insights do you gain from Equation 5.6.16, your calculations, and your diagram?
2. Is it possible to have a molecule that is not vibrating?
3. In terms of $\hbar\omega$, what is the energy of the photon required to cause a transition from one vibrational state to the next higher one?
4. If a transition from energy level $v = 9$ to $v = 10$ were observed in a spectrum, where would that spectral line appear relative to the one for the transition from level $v = 0$ to $v = 1$?
5. If a vibrational transition is observed at 3000 cm-1 in an infrared spectrum, what is the value of $\hbar\omega$ for the normal mode?
6. Identify all the possible meanings of $\Delta E = h\nu$ and the definition of the frequency, ν, in each case.

The normalized wavefunctions for the first four states of the harmonic oscillator are shown in Figure 5.6.2 , and the corresponding probability densities are shown in Figure 5.6.3 . You should remember the mathematical and graphical forms of the first few harmonic oscillator wavefunctions, and the correlation of v with E_v. The number of nodes in the wavefunction will help you to remember these characteristics. Also note that the functions fall off exponentially and that the symmetry alternates. For v equal to an even number, ψ_v is gerade; for v equal to an odd number, ψ_v is ungerade.

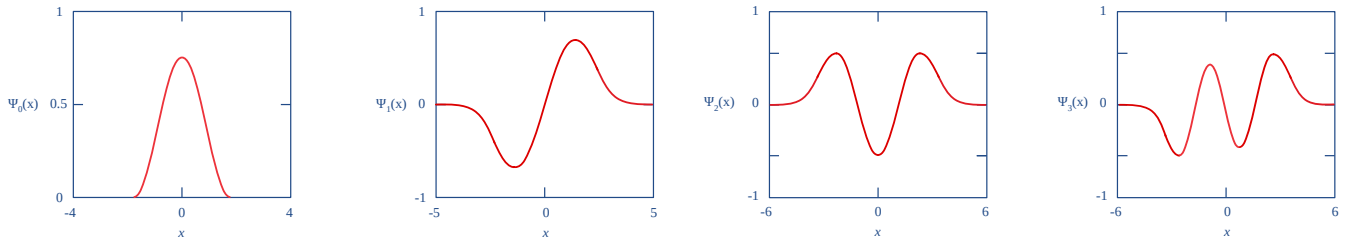


Figure 5.6.2 : The harmonic oscillator wavefunctions describing the four lowest energy states.

Exercise 5.6.7

Write a few sentences describing and comparing the plots in Figure 5.6.2 . How many nodes are there as a function of v? Do the wavefunctions converge at extreme displacement? Where is the most likely displacements for the oscillator to be found?

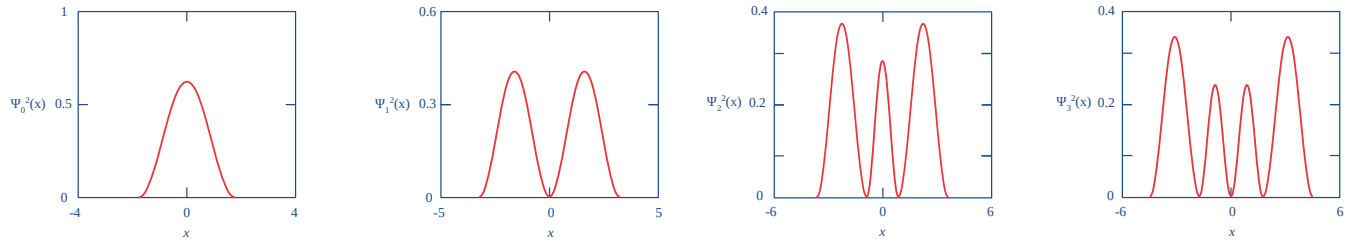


Figure 5.6.3 : The probability densities for the four lowest energy states of the harmonic oscillator.

Exercise 5.6.8

Explain how Figure 5.6.3 is related to Figure 5.6.2 . Explain the physical significance of the plots in Figure 5.6.3 in terms of the magnitude of the normal coordinate Q. Couch your discussion in terms of the HCl molecule. How would you describe the location of the atoms in each of the states? How does the oscillator position correspond to the energy of a particular level?

Answer available at the end of this section.

Exercise 5.6.9

Plot the probability density for energy level 10 of the harmonic oscillator. How many nodes are present? Plot the probability density for energy level 20. Compare the plot for level 20 with that of level 10 and level 1. Compare these quantum mechanical probability distributions to those expected for a classical oscillator. What conclusion can you draw about the probability of the location of the oscillator and the length of a chemical bond in a vibrating molecule? Extend your analysis to include a very high level, like level 50.

In completing Exercise 5.6.9 , you should have noticed that as the quantum number increases and becomes very large, the probability distribution approaches that of a classical oscillator. This observation is very general. It was first noticed by Bohr, and is called the Bohr Correspondence Principle. This principle states that classical behavior is approached in the limit of large values for a quantum number. A classical oscillator is most likely to be found in the region of space where its velocity is the smallest. This situation is similar to walking through one room and running through another. In which room do you spend more time? Where is it more likely that you will be found?

Examination of the quantum mechanical wavefunction for the lowest-energy state reveals that the wavefunction $\psi_0(x)$ extends beyond the classical limit (i.e., outside of the harmonic oscillator well, albeit slightly). Higher energy states have higher total energies, so the classical limits to the amplitude of the displacement will be larger for these states.

Tunneling in the Quantum Harmonic Oscillator

The observation that the wavefunctions are not zero at the classical limit means that the quantum mechanical oscillator has a finite probability of having a displacement that is larger than what is classically possible. The oscillator can be in a region of space where the potential energy is greater than the total energy. Classically, when the potential energy equals the total energy, the kinetic energy and the velocity are zero, and the oscillator cannot pass this point. A quantum mechanical oscillator, however, has a finite probability of passing this point. For a molecular vibration, this property means that the amplitude of the vibration is larger than what it would be in a classical picture. In some situations, a larger amplitude vibration could enhance the chemical reactivity of a molecule.

Exercise 5.6.10

Plot the probability density for $v = 0$ and $v = 1$ states. Mark the classical limits on each of the plots, since the limits are different because the total energy is different for $v = 0$ and $v = 1$. Shade in the regions of the probability densities that extend beyond the classical limit.

We should be able to calculate the probability that the quantum mechanical harmonic oscillator is in the classically forbidden region for the lowest energy state of the harmonic oscillator, the state with $v = 0$. The classically forbidden region is shown by the shading of the regions beyond Q_0 in the graph you constructed for Exercise 5.6.3 . The area of this shaded region gives the probability that the bond oscillation will extend into the forbidden region (Figure 5.6.3). To calculate this probability, we use

$$P[\text{forbidden}] = 1 - P[\text{allowed}] \tag{5.6.17}$$

because the integral from 0 to Q_0 for the allowed region can be found in integral tables and the integral from Q_0 to ∞ cannot. The form of the integral, $P[\text{allowed}]$, to evaluate is

$$P[\text{allowed}] = 2\int_0^{Q_0} \psi_0^*(Q)\psi_0(Q)dQ \tag{5.6.18}$$

The factor 2 appears in Equation 5.6.18 from the chancing the limits of integration from $-Q_0$ to $+Q_0$ into 0 to $+Q_0$; we can do this since the integrand is an even function, i. e., $f(-x) = f(x)$. To evaluate the integral in Equation 5.6.18, use the wavefunction and do the integration in terms of x. Recall that for $v = 0$, $Q = Q_0$ corresponds to $x = 1$. Including the normalization constant, Equation 5.6.18 produces

$$P[\text{allowed}] = \frac{2}{\sqrt{\pi}}\int_0^1 \exp(-x^2)dx \tag{5.6.19}$$

The integral in Equation 5.6.19 is called an error function (ERF) and can only be evaluated numerically. Values can be found in books of mathematical tables. When the limit of integration is 1, ERF(l) = 0.843 and P[forbidden] = 0.157. This result means that the quantum mechanical oscillator can be found in the forbidden region 16% of the time. This effect is substantial and leads to the phenomenon called *quantum mechanical tunneling*.

Exercise 5.6.11

Numerically verify that $P[\text{allowed}]$ in Equation 5.6.19 equals 0.843. To obtain a value for the integral do not use symbolic integration or symbolic equals.

Answers

Figure 5.6.2 is simply the wavefunction in Figure 5.6.1 squared. The normal coordinate is the linear combination of the atomic cartesian coordinates. As Q is often in relation to the energy (kinetic and potential), they would be displaced by a certain amount dependent on Q (energy) along with an increase in nodes. This displacement is apparent when comparing the ascending energy levels of each of the wavefunctions. In the n=0 (first) energy state, it is most probable to be found between -2, 2. (in a range of -4, 4) In the second energy state, it is likely to be between -2.5, 2.5 (range -5, 5), third level: (-3,3) (range -6,6), fourth level (-4,4) (range -6,6).

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5.7: Hermite Polynomials are either Even or Odd Functions

Learning Objectives

- Understand key properties of the Hermite polynomials including orthogonality and symmetry.
- Be proficient at using symmetries of integrands to quickly solve integrals.

Hermite polynomials were defined by Laplace (1810) though in scarcely recognizable form, and studied in detail by Chebyshev (1859). Chebyshev's work was overlooked and they were named later after Charles Hermite who wrote on the polynomials in 1864 describing them as new. They were consequently not new although in later 1865 papers Hermite was the first to define the multidimensional polynomials. The first six Hermite polynomial are plotted in Figure 5.7.1 .

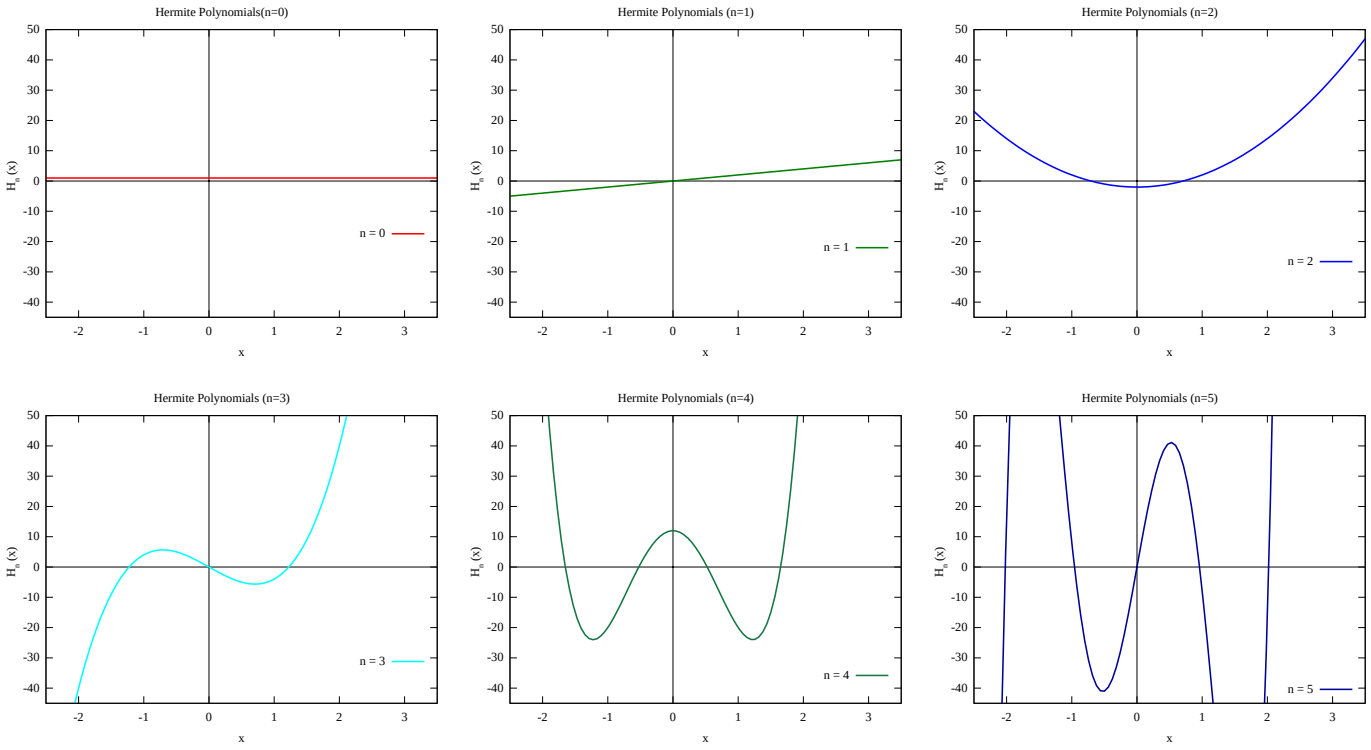


Figure 5.7.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

Generating Formula

Any Hermite polynomial $H_n(x)$ can be generated from a previous one $H_{n-1}(x)$ via the following using the recurrence relation

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x). \tag{5.7.1}$$

Hermite Polynomials are Symmetric

Let $f(x)$ be a real-valued function of a real variable.

- Then f is **even** if the following equation holds for all x and -x in the domain of f

$$f(x) = f(-x)$$

- Then f is **odd** if the following equation holds for all x and -x in the domain of f

$$-f(x) = f(-x)$$

Even and odd are terms used to describe particularly well-behaved functions. An *even* function is symmetric about the y-axis (Figure 5.7.2 ; left). That is, if we reflect the graph of the function in the y-axis, then it does not change. Formally, we say that f is even if, for all x and $-x$ in the domain of f, we have

$$f(-x) = f(x)$$

Two examples of even functions are $f(x) = x^2$ and $f(x) = \cos x$.

An *odd* function has rotational symmetry of order two about the origin (Figure 5.7.2 ; middle). That is, if we rotate the graph of the function 180° about the origin, then it does not change. Formally, we say that ff is odd if, for all x and $-x$ in the domain of f, we have

$$f(-x) = -f(x)$$

Examples of odd functions are $f(x) = x^3$ and $f(x) = \sin x$.

Naturally, not all functions can be classified as even or odd. For example $f = x^3 + 1$ shown in the right side of Figure 5.7.2 , is neither.

> You can also think of these properties as symmetry conditions at the origin. More symmetries in 3D space are discussed in Group Theory.

Without proof, we can identify several key features involving multiplication properties of even and odd functions:

- The product of two **even** functions is an **even** function.
- The product of two **odd** functions is an **even** function.
- The product of an **even** function and an **odd** function is an odd function.

This can be shown graphically as a product table like that in Table 5.7.1 .

Table 5.7.1 : Product table of 1D Functions

Product table	Odd Function (anti-symmetric)	Even Function (symmetric)	No symmetry (neither)
Odd Function (anti-symmetric)	Even Function (symmetric)	Odd Function (anti-symmetric)	who knows
Even Function (symmetric)	Odd Function (anti-symmetric)	Even Function (symmetric)	who knows
No symmetry (neither)	who knows	who knows	who knows

Notice that the Hermite polynomials in Figure 5.7.1 oscillate from even to odd. We can take advantage of that aspect in our calculation of Harmonic Oscillator wavefunctions. Hermite Polynomial is an even or odd function depends on its degree n. Based on

$$H_n(-x) = (-1)^n H_n(x) \tag{5.7.2}$$

- $H_n(x)$ is an even function, when n is even.
- $H_n(x)$ is an odd function, when n is odd.

Integration over Symmetric Functions

You often consider integrals of the form

$$I = \int_{-a}^{a} f(x)\,\mathrm{d}x$$

If f is odd or even, then sometimes you can make solving this integral easier. For example, we can rewrite that integral in the following way:

$$I = \int_{-a}^{a} f(x)\,\mathrm{d}x = \int_{-a}^{0} f(x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{5.7.3}$$

$$= \int_{0}^{a} f(-x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{5.7.4}$$

For an even function, we have $f(-x) = f(x)$ and Equation 5.7.4 can be simplified

$$I = \int_{0}^{a} f(-x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x$$

$$= 2\int_{0}^{a} f(x)\,\mathrm{d}x$$

For an odd function, we have $f(-x) = -f(x)$ and Equation 5.7.4 can be simplified

$$I = -\int_{0}^{a} f(x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x$$

$$= 0$$

That's what it means to simplify the integration: the integral of an odd or even function over the interval $[-L, L]$ can be put into a nicer form (and sometimes we can see that it vanishes without ever computing an integral).

Example 5.7.1

Technically, evaluating the orthogonality of Hermite polynomials requires integrating over the $\exp(-x^2)$ weight function (Equations 5.7.5 and 5.7.6).

Solution

For the Hermite polynomials $H_n(x)$, the relevant inner product (using Dirac Notation)

$$\langle f, g\rangle = \int_{-\infty}^{\infty} f(x)g(x)\exp(-x^2)\,\mathrm{d}x$$

While the $H_2(x)H_3(x)$ product is indeed an odd function (Table 5.7.1), while $exp(-x^2)$ is even. Their product is odd, and thus $\langle f, g\rangle$ certainly ought to be zero.

Symmetry is an important aspect of quantum mechanics and mathematics, especially in calculating integrals. Using this symmetry, integrals can be identified to be equal to zero without explicitly solving them. For example, the integral of an odd integrand over all possible values will **always** be zero irrespective of the exact nature of the function:

$$\int_{-\infty}^{\infty} f(x)\,dx = 0$$

This simplifies calculations greatly as demonstrated in the following chapters.

Hermite Polynomials are Orthogonal

Hermite polynomials $H_n(x)$ are *n*th-degree polynomials for *n* = 0, 1, 2, 3 and form an orthogonal set of functions for the weight function $e^{-x^2/2}$. The exact relation is:

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 0 \tag{5.7.5}$$

if $m \neq n$ and

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 2^n n!\sqrt{\pi} \tag{5.7.6}$$

if $m = n$.

This will not be proved, but can the demonstrated using any of the Hermite polynomials listed in the previous section. The orthogonality property becomes important when solving the Harmonic oscillator problems. Note that the integral of Equation 5.7.6 is important for normalizing the quantum harmonic oscillator wavefunctions discussed in last Section.

Example 5.7.2 : Hermite Polynomials are Orthogonal

Demonstrate that $H_2(x)$ and $H_3(x)$ are orthogonal.

Solution

We need to confirm

$$\int_{-\infty}^{\infty} H_2(x)H_3(x)dx = 0$$

or when substituted

$$\int_{-\infty}^{\infty} (4x^2 - 2)(8x^3 - 12x)dx = 0$$

because it says I need to show it's orthogonal on $[-\infty, \infty]$ or we can just evaluate it on a finite interval $[-L, L]$, where L is a constant.

$$\begin{aligned}\int_{-L}^{L} (4x^2 - 2)(8x^3 - 12x)dx &= 8\left(\frac{2x^6}{3} - 2x^4 + \frac{3x^2}{2}\right)\Bigg|_{-L}^{L} \\ &= 8\left(\frac{2L^6}{3} - 2L^4 + \frac{3L^2}{2}\right) - 8\left(\frac{2(-L)^6}{3} - 2(-L)^4 + \frac{3(-L)^2}{2}\right) \\ &= 0.\end{aligned}$$

Concluding

Hermite polynomials are a component in the harmonic oscillator wavefunction that dictates the symmetry of the wavefunctions. If your integration interval is symmetric around 0, then the integral over *any* integrable odd function is zero, no exception. Therefore as soon as you've found that your integrand is odd and your integration interval is symmetric, you're done. Also, for general functions, if you can easily split them into even and odd parts, you only have to consider the integral over the even part for symmetric integration intervals.

Another important property is that the product of two even or of two odd functions is even, and the product of an even and an odd function is odd. For example, if ff is even, $x \mapsto f(x)\sin(x)$ is odd, and therefore the integral over it is zero (provided it is well defined).

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5.8: The Energy Levels of a Rigid Rotor

Learning Objectives

- Compare the classical and quantum rigid rotor in three dimensions
- Demonstrate how to use the Separation of Variable technique to solve the 3D rigid rotor Schrödinger Equation
- Identify and interpret the two quantum numbers for a 3D quantum rigid rotor including the range of allowed values
- Describe the wavefunctions of the 3D quantum rigid rotor in terms of nodes, average displacements and most probable displacements
- Describe the energies of the 3D quantum rigid rotor in terms of values and degeneracies

Rigid rotor means when the distance between particles do not change as they rotate. A rigid rotor only approximates a rotating diatomic molecular if vibration is ignored.

The Classical Rigid Rotor in 3D

The **rigid rotor** is a mechanical model that is used to explain rotating systems. The linear rigid rotor model consists of two point masses located at fixed distances from their center of mass. The fixed distance between the two masses and the values of the masses are the only characteristics of the rigid model. However, for many actual diatomics this model is too restrictive since distances are usually not completely fixed and corrections on the rigid model can be made to compensate for small variations in the distance. Even in such a case the rigid rotor model is a useful model system to master.

For a rigid rotor, the total energy is the sum of kinetic (T) and potential (V) energies

$$E_{tot} = T + V \tag{5.8.1}$$

The potential energy, V, is set to 0 because the distance between particles does not change within the rigid rotor approximation. However, In reality, $V \neq 0$ because even though the average distance between particles does not change, the particles still vibrate. The rigid rotor approximation greatly simplifys our discussion.

Since $V = 0$ then $E_{tot} = T$ and we can also say that:

$$T = \frac{1}{2}\sum m_i v_i^2 \tag{5.8.2}$$

However, we have to determine v_i in terms of rotation since we are dealing with rotation motion. Since,

$$\omega = \frac{v}{r} \tag{5.8.3}$$

where ω is the **angular velocity**, we can say that:

$$v_i = \omega X r_i \tag{5.8.4}$$

Thus we can rewrite Equation 5.8.2 as:

$$T = \frac{1}{2}\sum m_i v_i \left(\omega X r_i\right) \tag{5.8.5}$$

Since ω is a scalar constant, we can rewrite Equation 5.8.5 as:

$$T = \frac{\omega}{2}\sum m_i \left(v_i X r_i\right) = \frac{\omega}{2}\sum l_i = \omega\frac{L}{2} \tag{5.8.6}$$

where l_i is the **angular momentum** of the ith particle, and L is the angular momentum of the *entire system*. Also, we know from physics that,

$$L = I\omega \tag{5.8.7}$$

where I is the moment of inertia of the rigid body relative to the axis of rotation. We can rewrite Equation 5.8.2 as

$$T = \omega\frac{I\omega}{2} = \frac{1}{2}I\omega^2 \tag{5.8.8}$$

Equation 5.8.8 shows that the energy of the rigid rotor scales with increasing angular frequency (i.e., the faster is rotates) and with increasing moment of inertia (i.e, the inertial resistance to rotation). Also, as expected, the classical rotational energy is not quantized (i.e., all possible rotational frequencies are possible).

The Quantum Rigid Rotor in 3D

It is convenient to discuss rotation with in the spherical coordinate system rather than the Cartesian system (Figure 5.8.1).

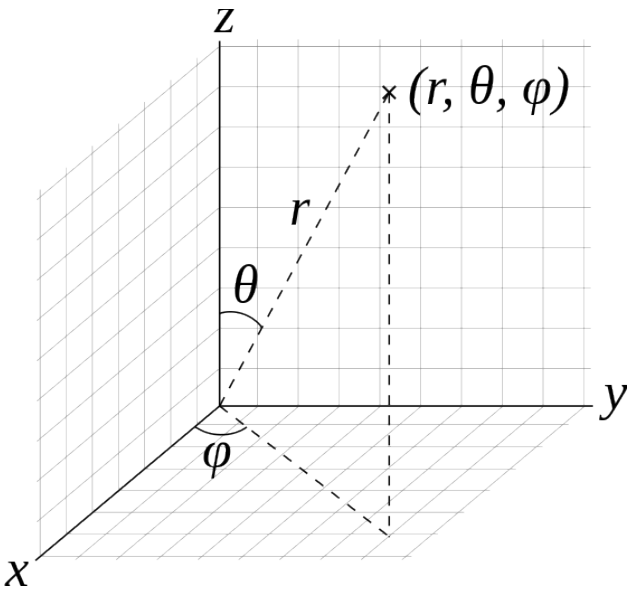


Figure 5.8.1 : The spherical coordinate system in terms of the Cartesian system. (Public Domain; Andeggs via Wikipedia).

To solve the Schrödinger equation for the rigid rotor, we will separate the variables and form single-variable equations that can be solved independently. Only two variables θ and φ are required in the rigid rotor model because the bond length, r, is taken to be the constant r_0. We first write the rigid rotor wavefunctions as the product of a theta-function depending only on θ and a phi-function depending only on φ

$$|\psi(\theta,\varphi)\rangle = |\Theta(\theta)\Phi(\varphi)\rangle \tag{5.8.9}$$

We then substitute the product wavefunction and the Hamiltonian written in spherical coordinates into the Schrödinger Equation 5.8.10

$$\hat{H}|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{5.8.10}$$

to obtain

$$-\frac{\hbar^2}{2\mu r_0^2}\left[\frac{\partial}{\partial r_0}r_0^2\frac{\partial}{\partial r_0} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{5.8.11}$$

Since $r = r_0$ is constant for the **rigid rotor** and does not appear as a variable in the functions, the partial derivatives with respect to r are zero; i.e. the functions do not change with respect to r. We also can substitute the symbol I for the moment of inertia, μr_0^2 in the denominator of the left hand side of Equation 5.8.11, to give

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\Theta(\theta)\Phi(\varphi)\rangle = E|\Theta(\theta)\Phi(\varphi)\rangle \tag{5.8.12}$$

To begin the process of the Separating of Variables technique, multiply each side of Equation 5.8.12 by $\frac{2I}{\hbar^2}$ and $\frac{-\sin^2\theta}{\Theta(\theta)\Phi(\varphi)}$ to give

$$\frac{1}{\Theta(\theta)\psi(\varphi)}\left[\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi)=\frac{-2IE\sin^2\theta}{\hbar^2} \tag{5.8.13}$$

Simplify the appearance of the right-hand side of Equation 5.8.13 by defining a parameter λ:

$$\lambda=\frac{2IE}{\hbar^2}. \tag{5.8.14}$$

Note that this λ has no connection to a wavelength; it is merely being used as an algebraic symbol for the combination of constants shown in Equation 5.8.14.

Inserting λ, evaluating partial derivatives, and rearranging Equation 5.8.13 produces

$$\frac{1}{\Theta(\theta)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta\right)\Theta(\theta)\right]=-\frac{1}{\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) \tag{5.8.15}$$

Exercise 5.8.1

Carry out the steps leading from Equation 5.8.13 to Equation 5.8.15. Keep in mind that, if y is not a function of x,

$$\frac{dy}{dx}=y\frac{d}{dx}$$

Equation 5.8.15 says that the function on the left, depending only on the variable θ, always equals the function on the right, depending only on the variable φ, for all values of θ and φ. The only way two different functions of independent variables can be equal for all values of the variables is if both functions are equal to a constant (review separation of variables). We call this constant m_J^2 because soon we will need the square root of it. The two differential equations to solve are the θ-equation

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta-m_J^2\right)\Theta(\theta)=0 \tag{5.8.16}$$

and the φ-equation

$$\frac{d^2}{d\varphi^2}\Phi(\varphi)+m_J^2\Phi(\varphi)=0 \tag{5.8.17}$$

The partial derivatives have been replaced by total derivatives because only a single variable is involved in each equation.

Often m_J is referred to as just m for convenience.

Exercise 5.8.2

Show how Equations 5.8.16 and 5.8.17 are obtained from Equation 5.8.15.

Solving the φ Equation

The φ-equation is similar to the Schrödinger Equation for the free particle. Since we already solved this previously, we immediately write the solutions:

$$\Phi_m(\varphi)=Ne^{\pm im_J\varphi} \tag{5.8.18}$$

where we introduce the number m to track how many wavelengths of the wavefunction occur around one rotation (similar to the wavelength description of the Bohr atom).

Exercise 5.8.3

Substitute Equation 5.8.18 into Equation 5.8.17 to show that it is a solution to that differential equation.

Answer available at the end of this section.

The normalization condition, Equation 5.8.19 is used to find a value for N that satisfies Equation 5.8.18.

$$\int_0^{2\pi} \Phi^*(\varphi)\Phi(\varphi)d\varphi = 1 \tag{5.8.19}$$

The range of the integral is only from 0 to 2π because the angle φ specifies the position of the internuclear axis relative to the x-axis of the coordinate system and angles greater than 2π do not specify additional new positions.

Exercise 5.8.4

Use the normalization condition in Equation 5.8.19 to demonstrate that $N = 1/\sqrt{2\pi}$.

Answer available at the end of this section.

Values for m are found by using a **cyclic boundary condition**. The cyclic boundary condition means that since φ and $\varphi + 2\varphi$ refer to the same point in three-dimensional space, $\Phi(\varphi)$ must equal $\Phi(\varphi + 2\pi)$, i.e.

$$e^{im_J\varphi} = e^{im_J(\varphi+2\pi)} \tag{5.8.20}$$

$$= e^{im_J\varphi}e^{im_J2\pi} \tag{5.8.21}$$

For the equality in Equation 5.8.21 to hold, $e^{im_J2\pi}$ must equal 1, which is true only when

$$m_J = \cdots, -3, -2, -1, 0, 1, 2, 3, \cdots \tag{5.8.22}$$

In other words m_J can equal **any positive or negative integer or zero.**

Exercise 5.8.5 : Cyclic Boundary Conditions

Use Euler's Formula to show that $e^{im_J2\pi}$ equals 1 for m_J equal to zero or any positive or negative integer.

Thus, the Φ function is

$$\Phi_{m_J}(\varphi) = \sqrt{\frac{1}{2\pi}}e^{\pm im_J\varphi}$$

with

$$m_J = 0, \pm1, \pm2, \cdots$$

Solving the $\Theta(\theta)$ Equation

Finding the $\Theta(\theta)$ functions that are solutions to the θ-equation (Equation 5.8.16) is a more complicated process. Solutions are found to be a set of power series called *Associated Legendre Functions* (Table M2), which are power series of trigonometric functions, i.e., products and powers of sine and cosine functions. The $\Theta(\theta)$ functions, along with their normalization constants, are shown in the third column of Table 5.8.1 .

Table 5.8.1 : Spherical Harmonic Wavefunctions

m_J	J	$\Theta_J^{m_J}(\theta)$	$\Phi(\varphi)$	$Y_J^{m_J}(\theta,\varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$
1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$
-1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$
2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$
-2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$

The solution to the θ-equation requires that λ in Equation 5.8.15 be given by

$$\lambda = J(J+1) \tag{5.8.23}$$

where

$$J \geq |m_J| \tag{5.8.24}$$

J can be 0 or any positive integer greater than or equal to m_J. Each pair of values for the quantum numbers, J and m_J, identifies a rotational state with a wavefunction (Equation 5.8.9) and energy (below). Equation 5.8.24 means that J controls the allowed values of m_J.

> Each pair of values for the quantum numbers, J and m_J, identifies a rotational state and hence a specific wavefunction with associated energy.

The combination of Equations 5.8.14 and 5.8.23 reveals that the energy of this system is quantized.

$$E = \frac{\hbar^2\lambda}{2I} = J(J+1)\frac{\hbar^2}{2I} \tag{5.8.25}$$

Using Equation 5.8.25, you can construct a rotational energy level diagram (Figure 5.8.2). For simplicity, use energy units of $\frac{\hbar^2}{2I}$.

- $J = 0$: The lowest energy state has $J = 0$ and $m_J = 0$. This state has an energy $E_0 = 0$. There is only **one state** with this energy, i.e. one set of quantum numbers, one wavefunction, and one set of properties for the molecule.
- $J = 1$: The next energy level is $J = 1$ with energy $\frac{2\hbar^2}{2I}$. There are **three states** with this energy because m_J can equal +1, 0, or -1. These different states correspond to different orientations of the rotating molecule in space. States with the same energy are said to be degenerate. The degeneracy of an energy level is the number of states with that energy. The degeneracy of the $J = 1$ energy level is 3 because there are three states with the energy $\frac{2\hbar^2}{2I}$.
- $J = 2$: The next energy level is for $J = 2$. The energy is $\frac{6\hbar^2}{2I}$, and there are **five states** with this energy corresponding to $m_J = +2,\ +1,\ 0,$ -1, -2. The energy level degeneracy is five. Note that the spacing between energy levels increases as J increases. Also note that the degeneracy increases. The degeneracy is always $2J + 1$ because m_J ranges from $+J$ to -J in

integer steps, including 0.

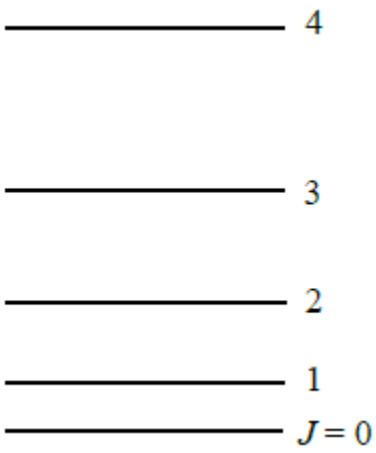


Figure 5.8.2 : Energy spacing for a rigid rotor (in 3D). Notice the energy depends only on J and not depend on m_J. That is, the energy of the rotor is not affected by its orientation.

Each allowed energy of rigid rotor is $(2J+1)$-fold degenerate. Hence, there exist $(2J+1)$ different wavefunctions with that energy.

Exercise 5.8.6

Compute the energy levels for a rotating molecule for $J=0$ to $J=5$ using units of $\frac{\hbar^2}{2I}$.

Answer available at the end of this section.

Exercise 5.8.7

For $J=0$ to $J=5$, identify the degeneracy of each energy level and the values of the m_J quantum number that go with each value of the J quantum number. Construct a rotational energy level diagram including $J=0$ through $J=5$. Label each level with the appropriate values for the quantum numbers J and m_J. Describe how the spacing between levels varies with increasing J.

Answer available at the end of this section.

Interpretation of Quantum Numbers for a Rigid Rotor

The m_J quantum number reflects the component of the angular momentum along the z direction (and hence is sometimes called the azimuthal quantum number). For a fixed value of J, the different values of m_J reflect the different **directions** the angular momentum vector could be pointing – for large, positive m_J the angular momentum is mostly along +z; if m_J is zero the angular momentum is orthogonal to z. Physically, the energy of the rotation does not depend on the direction, which is reflected in the fact that the energy depends only on J (Equation 5.8.25), which measures the length of the vector, not its direction given by m_J.

Example 5.8.7 : Molecular Oxygen

Calculate $J=0$ to $J=1$ rotational transition of the O_2 molecule with a bond length of 121 pm.

Solution

$$E = \frac{\hbar^2}{I} = \frac{\hbar^2}{\mu r^2}$$

$$\mu_{O2} = \frac{m_O m_O}{m_O + m_O} = \frac{(15.9994)(15.9994)}{15.9994 + 15.9994} = 7.9997$$

convert from atomic units to kilogram using the conversion: 1 au = 1.66 x 10^{-27} kg. Plug and chug.

$$E = 5.71 \times 10^{-27}\ Joules$$

Spherical Harmonics

A wavefunction that is a solution to the rigid rotor Schrödinger Equation (Equation 5.8.9) can be written as a single function $Y(\theta, \varphi)$, which is called a spherical harmonic function.

$$Y_J^{m_J}(\theta, \varphi) = \Theta_J^{|m_J|}(\theta)\Phi_{m_J}(\varphi) \tag{5.8.26}$$

The spherical harmonic wavefunction is labeled with m_J and J because its functional form depends on both of these quantum numbers. These functions are tabulated above for $J = 0$ through $J = 2$ and for $J = 3$ in the Spherical Harmonics Table (M4) Polar plots of some of the θ-functions are shown in Figure 5.8.3 .

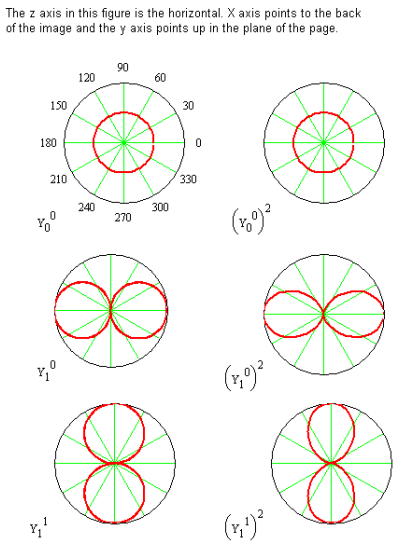


Figure 5.8.3 : Polar plots in which the distance from the center gives the value of the function Y for the indicated angle θ.

The two-dimensional space for a rigid rotor is defined as the surface of a sphere of radius r_0, as shown in Figure 5.8.2 .

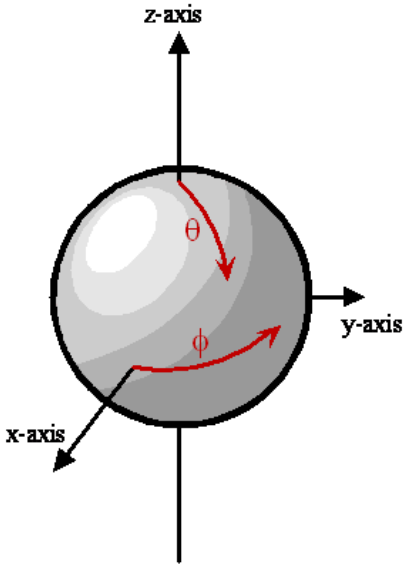


Figure 5.8.4 : Space for a rigid rotor is restricted to the surface of a sphere of radius r_0. The only degrees of freedom are motions along θ or φ on the surface of the sphere.

The probability of finding the internuclear axis at specific coordinates θ_0 and φ_0 within an infinitesimal area ds on this curved surface is given by

$$Pr\left[\theta_0, \varphi_0\right] = Y_J^{m_{J*}}(\theta_0, \varphi_0) Y_J^{m_J}(\theta_0, \varphi_0) ds \tag{5.8.27}$$

where the area element ds is centered at θ_0 and φ_0.

Within the Copenhagen interpretation of wavefunctions, the absolute square (or modulus squared) of the rigid rotor wavefunction $Y_J^{m_{J*}}(\theta, \varphi) Y_J^{m_J}(\theta, \varphi)$ gives the probability density for finding the internuclear axis oriented at θ to the z-axis and φ to the x-axis. In spherical coordinates the area element used for integrating θ and φ is

$$ds = \sin\theta \, d\theta \, d\varphi \tag{5.8.28}$$

Exercise 5.8.8

Use calculus to evaluate the probability of finding the internuclear axis of a molecule described by the $J = 1$, $m_J = 0$ wavefunction somewhere in the region defined by a range in θ of 0° to 45°, and a range in of 0° to 90°. Note that a double integral will be needed. Sketch this region as a shaded area on Figure 5.8.3 .

Consider the significance of the probability density function by examining the $J = 1$, $m_J = 0$ wavefunction. The Spherical Harmonic for this case is

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta \tag{5.8.29}$$

The polar plot of $(Y_1^0)^2$ is shown in Figure 5.8.3 . For $J = 1$ and $m_J = 0$, the probability of finding the internuclear axis is independent of the angle φ from the x-axis, and greatest for finding the internuclear axis along the z-axis, but there also is a probability for finding it at other values of θ as well. So, although the internuclear axis is not always aligned with the z-axis, the probability is highest for this alignment. Also, since the probability is independent of the angle φ, the internuclear axis can be found in any plane containing the z-axis with equal probability.

The $J = 1$, $m_J = 0$ function is 0 when θ = 90°. Therefore, the entire xy-plane is a **node**. This fact means the probability of finding the internuclear axis in this particular horizontal plane is 0 in contradiction to our classical picture of a rotating molecule. In the classical picture, a molecule rotating in a plane perpendicular to the xy-plane must have the internuclear axis lie in the xy-plane

twice every revolution, but the quantum mechanical description says that the probability of being in the xy-plane is zero. This conclusion means that molecules are not rotating in the classical sense, but they still have some, but not all, of the properties associated with classical rotation. The properties they retain are associated with angular momentum.

Exercise 5.8.9

For each state with $J = 0$ and $J = 1$, use the function form of the Y spherical harmonics and Figure 5.8.1 to determine the most probable orientation of the internuclear axis in a diatomic molecule, i.e., the most probable values for θ and θ.

Exercise 5.8.10

Write a paragraph describing the information about a rotating molecule that is provided in the polar plot of $Pr[\theta, \theta]$ for the $J = 1$, $m_J = \pm 1$ state in Figure 5.8.1 . Compare this information to the classical picture of a rotating object.

Summary

There are two quantum numbers that describe the quantum behavior of a rigid rotor in three-deminesions: J is the total angular momentum quantum number and m_J is the z-component of the angular momentum. The spherical harmonics called $Y_J^{m_J}$ are functions whose probability $|Y_J^{m_J}|^2$ has the well known shapes of the s, p and d orbitals etc learned in general chemistry.

References

1. Anderson, J.M. Introduction to Quantum Chemistry, 1969, W.A. Benjamin, Inc, pg.91-100.
2. Atkins, Peter and de Paula, Julio. Physical Chemistry for the Life Sciences. New York: W.H. Freeman and Company. p. 515.

Contributors and Attributions

- Ian Huh
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Mark Tuckerman (New York University)
- MIT OpenCourseWare (Robert Guy Griffin and Troy Van Voorhis)

Answers

Substitute

$$\Phi_m(\varphi) = \mathrm{N}e^{\pm \mathrm{i}m_J\varphi}$$

into

$$\frac{d^2}{d\varphi^2}\Phi(\varphi) + m_J^2\Phi(\varphi) = 0$$

$$\begin{aligned}\frac{d^2}{d\varphi^2}\Phi_{\mathrm{m}}(\varphi) + m_J^2\Phi_{\mathrm{m}}(\varphi) =& \frac{d}{d\varphi}\left(\mathrm{N}\left(\pm \mathrm{i}m_J\right)e^{\pm \mathrm{i}m_J\varphi}\right) + m_J^2\Phi_{\mathrm{m}}(\varphi) \\ &= \mathrm{N}\left(\pm \mathrm{i}m_J\right)^2 e^{\pm \mathrm{i}m_J\varphi}\Big) + m_J^2\left(\mathrm{N}e^{\pm \mathrm{i}m_J\varphi}\right) \\ &= -\mathrm{N}m_J^2 e^{\pm \mathrm{i}m_J\varphi} + \mathrm{N}m_J^2 e^{\pm \mathrm{i}m_J\varphi} = 0\end{aligned}$$

Thus

$$\Phi_m(\varphi) = Ne^{\pm im_J\varphi}$$

is a solution to the differential equations.

We need to evaluate Equation 5.8.19 with $\psi(\varphi) = Ne^{\pm imJ\varphi}$

$$\psi^*(\varphi)\psi(\varphi) = Ne^{+imJ\varphi}Ne^{-imJ\varphi}$$
$$= N^2$$
$$1 = \int_0^{2\pi} N^*Nd\varphi = 1$$
$$N^2(2\pi) = 1$$
$$N = \sqrt{1/2\pi}$$

This rotating molecule can be assumed to be a rigid rotor molecule. From solving the Schrödinger equation for a rigid rotor we have the relationship for energies of each rotational eigenstate (Equation 5.8.25):

$$E = J(J+1)(\hbar^2/2I)$$

Using this equation, we can plug in the different values of the J quantum number so that

For J=0, $E = (0)(1)(\hbar^2/2I) = 0$ For J=1, $E = (1)(2)(\hbar^2/2I) = 2(\hbar^2/2I)$

This shows that as J increases, the energy levels get farther apart (Figure 5.8.2).

- For J=2, $E = (2)(3)(\hbar^2/2I) = 6(\hbar^2/2I)$
- For J=3, $E = (3)(4)(\hbar^2/2I) = 12(\hbar^2/2I)$
- For J=4, $E = (4)(5)(\hbar^2/2I) = 20(\hbar^2/2I)$
- For J=5, $E = (5)(6)(\hbar^2/2I) = 30(\hbar^2/2I)$

This rotating molecule can be assumed to be a rigid rotor molecule. From solving the Schrödinger equation for a rigid rotor, we have:

$$\lambda = 2IE/\hbar^2$$

Where λ is an arbitrary parameter not related to wavelength. Additionally, λ is assigned a quantum relation so that

$$\lambda = J(J+1)$$

Thus, combining the two equations and solving for E yields

$$E = J(J+1)(\hbar^2/2I)$$

Using this equation, we can plug in the different values of J so that

- For J=0, $E = (0)(1)(\hbar^2/2I) = 0$
- For J=1, $E = (1)(2)(\hbar^2/2I) = 2(\hbar^2/2I)$
- For J=2, $E = (2)(3)(\hbar^2/2I) = 6(\hbar^2/2I)$
- For J=3, $E = (3)(4)(\hbar^2/2I) = 12(\hbar^2/2I)$
- For J=4, $E = (4)(5)(\hbar^2/2I) = 20(\hbar^2/2I)$
- For J=5, $E = (5)(6)(\hbar^2/2I) = 30(\hbar^2/2I)$

This shows that as J increases, the energy levels get closer and closer together.

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5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

Learning Objectives

- Demonstrate how to use the 3D regid rotor to describe a rotating diatomic molecules
- Demonstate how microwave spectroscopy can get used to characterize rotating diatomic molecules
- Interprete a simple microwave spectrum for a diatomic molecule

To develop a description of the rotational states, we will consider the molecule to be a rigid object, i.e. the bond lengths are fixed and the molecule cannot vibrate. This model for rotation is called the rigid-rotor model. It is a good approximation (even though a molecule vibrates as it rotates, and the bonds are elastic rather than rigid) because the amplitude of the vibration is small compared to the bond length.

The rotation of a rigid object in space is very simple to visualize. Pick up any object and rotate it. There are orthogonal rotations about each of the three Cartesian coordinate axes just as there are orthogonal translations in each of the directions in three-dimensional space (Figures 5.9.1 and 5.9.2). These rotations are said to be *orthogonal* because one can not describe a rotation about one axis in terms of rotations about the other axes just as one can not describe a translation along the x-axis in terms of translations along the y- and z-axes. For a linear molecule, the motion around the interatomic axis (x-axis) is not considered a rotation.

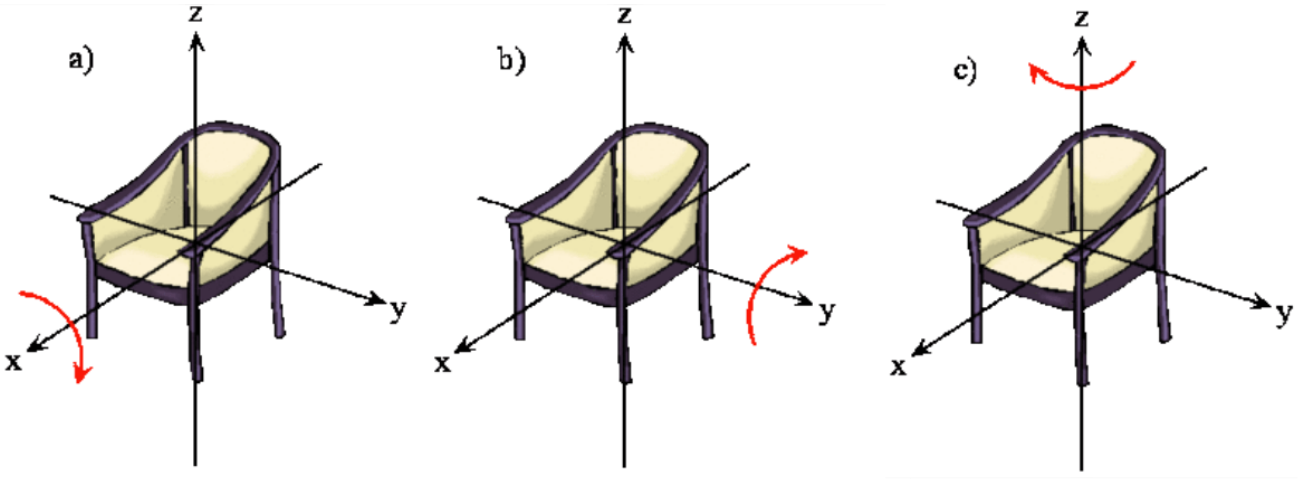


Figure 5.9.1 : Cartesian rotations of a chair. Rotations about the (a) x axis, (b) y axis, and (c) z axis.

In this section we examine the rotational states for a diatomic molecule by comparing the classical interpretation of the angular momentum vector with the probabilistic interpretation of the angular momentum wavefunctions. We want to answer the following types of questions. How do we describe the orientation of a rotating diatomic molecule in space? Is the molecule actually rotating? What properties of the molecule can be physically observed? In what ways does the quantum mechanical description of a rotating molecule differ from the classical image of a rotating molecule?

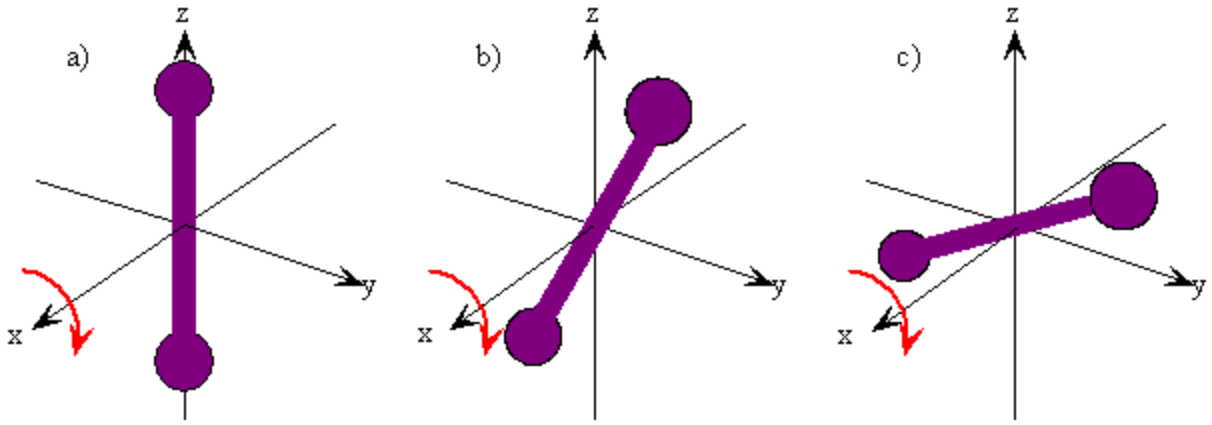


Figure 5.9.2 : Rotation of a diatomic molecule about the x axis.

Introduction to Microwave Spectroscopy

The permanent electric dipole moments of polar molecules can couple to the electric field of electromagnetic radiation. This coupling induces transitions between the rotational states of the molecules. The energies that are associated with these transitions are detected in the far infrared and microwave regions of the spectrum. For example, the microwave spectrum for carbon monoxide spans a frequency range of 100 to 1200 GHz, which corresponds to 3 - 40 cm^{-1}.

The selection rules for the rotational transitions are derived from the transition moment integral by using the spherical harmonic functions and the appropriate dipole moment operator, $\hat{\mu}$.

$$\mu_T = \int Y_{J_f}^{m_f *} \hat{\mu} Y_{J_i}^{m_i} \sin\theta \, d\theta \, d\varphi \tag{5.9.1}$$

or in braket notation

$$\mu_T = \langle Y_{J_f}^{m_f} | \hat{\mu} | Y_{J_i}^{m_i} \rangle \tag{5.9.2}$$

Evaluating the transition moment integral involves a bit of mathematical effort. This evaluation reveals that the transition moment depends on the square of the dipole moment of the molecule, μ^2 and the rotational quantum number, J, of the initial state in the transition,

$$\mu_T = \mu^2 \frac{J+1}{2J+1} \tag{5.9.3}$$

and that the selection rules for rotational transitions are

$$\Delta J = \pm 1 \tag{5.9.4}$$

and

$$\Delta m_J = 0, \pm 1 \tag{5.9.5}$$

A photon is absorbed for $\Delta J = +1$ and emitted for $\Delta J = -1$.

Exercise 5.9.1

Explain why your microwave oven heats water, but not air. Hint: draw and compare Lewis structures for components of air and for water.

The energies of the Jth rotational levels are given by

$$E_J = J(J+1)\frac{\hbar^2}{2I} \tag{5.9.6}$$

with each Jth energy level having a degeneracy of $2J+1$ due to the different possible m_J values.

Microwave Transition Energies

The transition energies for absorption of radiation are given by

$$E_{photon} = \Delta E \tag{5.9.7}$$
$$= E_f - E_i \tag{5.9.8}$$
$$= h\nu \tag{5.9.9}$$
$$= hc\bar{\nu} \tag{5.9.10}$$

Substituting the relationship for energy (Equation 5.9.6) into Equation 5.9.8 results in

$$E_{photon} = E_f - E_i \tag{5.9.11}$$
$$= J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \tag{5.9.12}$$

with J_i and J_f representing the rotational quantum numbers of the initial (lower) and final (upper) levels involved in the absorption transition.

Since microwave spectroscopists use frequency units and infrared spectroscopists use wavenumber units when describing rotational spectra and energy levels, both ν and $\bar{\nu}$ are important to calculate. When we add in the constraints imposed by the selection rules to identify possible transitions, J_f in Equation 5.9.12 can be replaced by J_i+1, since the selection rule requires J_f–$J_i = 1$ for the absorption of a photon (Equation 5.9.4). The equation for absorption transitions (Equation 5.9.12) then can be written in terms of the only the quantum number J_i of the initial state.

$$E_{photon} = h\nu \tag{5.9.13}$$
$$= hc\bar{\nu} \tag{5.9.14}$$
$$= 2(J_i+1)\frac{\hbar^2}{2I} \tag{5.9.15}$$

Equation 5.9.15 can be rewritten as

$$E_{photon} = 2B(J_i+1)$$

where B is the **rotational constant** for the molecule and is defined in terms of the *energy* of the absorbed photon

$$B = \frac{\hbar^2}{2I} \tag{5.9.16}$$

Often spectroscopists want to express the rotational constant in terms of *frequency* of the absorbed photon and do so by dividing Equation 5.9.16 by h

$$B(\text{in freq}) = \frac{B}{h} \tag{5.9.17}$$
$$= \frac{h}{8\pi^2\mu r_0^2} \tag{5.9.18}$$

More often, spectroscopists want to express the rotational constant in terms of *wavenumbers* ($\bar{\nu}$) of the absorbed photon by dividing Equation 5.9.16 by hc,

$$\tilde{B} = \frac{B}{hc} = \frac{h}{8\pi^2 c\mu r_0^2} \tag{5.9.19}$$

The rotational constant depends on the distance (R) and the masses of the atoms (via the reduced mass) of the nuclei in the

diatomic molecule.

Exercise 5.9.2

Construct a rotational energy level diagram for $J = 0$, 1, and 2 and add arrows to show all the allowed transitions between states that cause electromagnetic radiation to be absorbed or emitted.

Exercise 5.9.3

Complete the steps going from Equation 5.9.12 to Equation 5.9.16 and identify the units of B at the end.

Answer available at the end of this section.

Exercise 5.9.4

Infrared spectroscopists use units of wavenumbers. Rewrite the steps going from Equation 5.9.12 to Equation 5.9.16 to obtain expressions for $h\nu$ and B in units of wavenumbers. Note that to convert B in Hz to B in cm^{-1}, you simply divide the former by c.

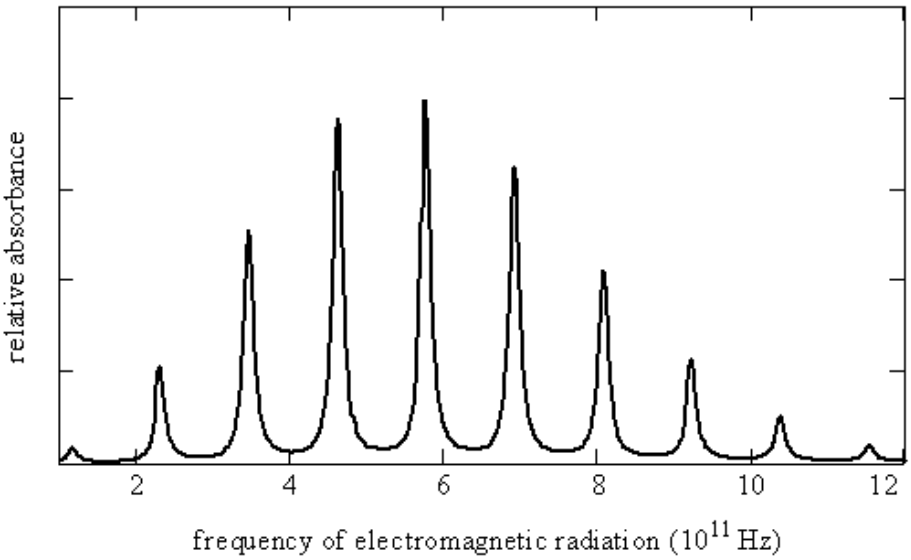


Figure 5.9.3: The rotation spectrum of $^{12}C^{16}O$ at 40 K. The peaks are tabulated in Table 5.9.1.

Figure 5.9.3 shows the rotational spectrum as a series of nearly equally spaced lines. The line positions ν_J, line spacings, and the maximum absorption coefficients (γ_{max}, the absorption coefficients associated with the specified line position) for each line in this spectrum are given here in Table 5.9.1.

Table 5.9.1 : Rotational Transitions in $^{12}C^{16}O$ at 40 K

J	ν_J (MHz)	Spacing from previous line (MHz)	γ_{max}
$0 \rightarrow 1$	115,271.21	0	0.0082
$1 \rightarrow 2$	230,538.01	115,266.80	0.0533
$2 \rightarrow 3$	345,795.99	115,257.99	0.1278
$3 \rightarrow 4$	461,040.76	115,244.77	0.1878

J	ν_J (MHz)	Spacing from previous line (MHz)	γ_{max}
$4 \rightarrow 5$	576,267.91	115,227.15	0.1983
$6 \rightarrow 6$	691,473.03	115,205.12	0.1618
$6 \rightarrow 7$	806,651.78	115,178.68	0.1064
$7 \rightarrow 8$	921,799.55	115,147.84	0.0576
$8 \rightarrow 9$	1,036,912.14	115,112.59	0.0262
$9 \rightarrow 10$	1,151,985.08	115,072.94	0.0103

Let's try to reproduce Figure 5.9.3 from the data in Table 5.9.1 by using the quantum theory that we have developed so far. Equation 5.9.19 predicts a pattern of exactly equally spaced lines. The lowest energy transition is between $J_i = 0$ and $J_f = 1$ so the first line in the spectrum appears at a frequency of $2B$. The next transition is from $J_i = 1$ to $J_f = 2$ so the second line appears at $4B$. The spacing of these two lines is $2B$. In fact the spacing of all the lines is $2B$, which is consistent with the experimental data in Table 5.9.1 showing that the lines are very nearly equally spaced. The difference between the first spacing and the last spacing is less than 0.2%.

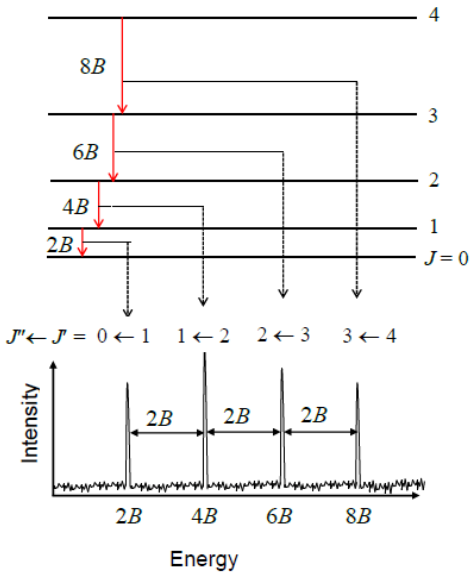


Figure 5.9.4 : Energy levels and line positions calculated in the rigid rotor approximation. (CC BY-SA 3.0; Nrrw via Wikipedia)

Exercise 5.9.5

Use Equation 5.9.19 to prove that the spacing of any two lines in a rotational spectrum is $2B$, i.e. derive:

$$\nu_{J_i+1} - \nu_{J_i} = 2B$$

Answer available at the end of this section.

Example 5.9.1 : Rotation of Sodium Hydride

The molecule NaH undergoes a rotational transition from $J = 0$ to $J = 1$ when it absorbs a photon of frequency $2.94 \times 10^{11}\ Hz$. What is the equilibrium bond length of the molecule?

Solution

We use $J = 0$ in the formula for the transition frequency

$$\nu = 2B = \frac{\hbar}{2\pi I} = \frac{\hbar}{2\pi\mu R_e^2}$$

Solving for R_e gives

$$R_e = \sqrt{\frac{\hbar}{2\pi\mu\nu}}$$

The reduced mass is given by

$$\begin{aligned}\mu &= \frac{m_{Na}m_H}{m_{Na}+m_H} \\ &= \frac{(22.989)(1.0078)}{22.989+1.0078} \\ &= 0.9655\end{aligned}$$

which is in atomic mass units or relative units. To convert to kilograms, we need the conversion factor $1\ au = 1.66 \times 10^{-27}\ kg$. Multiplying this by 0.9655 gives a reduced mass of $1.603 \times 10^{-27}\ kg$. Substituting in for R_e gives

$$\begin{aligned}R_e &= \sqrt{\frac{(1.055 \times 10^{-34}\ J \cdot s)}{2\pi(1.603 \times 10^{-27}\ kg)(2.94 \times 10^{11}\ Hz)}} \\ &= 1.899 \times 10^{-10}\ m \\ &= 1.89\ \mathring{A}\end{aligned}$$

Example 5.9.6

Use the frequency of the $J = 0$ to $J = 1$ transition observed for carbon monoxide to determine a bond length for $^{12}C^{16}O$.

Solution

- J=0: $v_0 = 115271.21\ \text{MHz}$
- J=1: $v_1 = 230538.01\ \text{MHz}$

$$\begin{aligned}\Delta v &= 230538.01\ \text{MHz} - 115271.21\,\text{MHz} \\ &= 115266.8\,\text{MHz} \\ &= 1.153 \times 10^{11}\ \text{Hz} \\ &= \frac{\hbar}{2\pi\mu R_e^2}\end{aligned}$$

The reduced mass is

$$\begin{aligned}\mu &= \frac{m_C m_O}{m_C+m_O} \\ &= \frac{12.01 \times 16.00}{12.01+16.00} \\ &= 6.86\,\text{amu}\end{aligned}$$

Convert to kg

$$6.86amu\left(\frac{1.661 \times 10^{-27}\ \text{kg}}{12\ \text{amu}}\right) = 1.139 \times 10^{-26}\ \text{kg}$$

$$
\begin{aligned}
R_e &= \sqrt{\frac{\hbar}{2\pi\mu\Delta v}} \\
&= \sqrt{\frac{1.055 \times 10^{-34}\ J \cdot s}{2\pi \cdot 1.139 \times 10^{-26}\ \text{kg} \cdot 1.153 \times 10^{11}\ \text{Hz}}} \\
&= 1.131 \times 10^{-10}\text{m} \\
&= 1.131\ \mathring{A}
\end{aligned}
$$

Advanced: Non-Rigid Rotors

Centrifugal stretching of the bond as J increases causes the decrease in the spacing between the lines in an observed spectrum (Table 5.9.1). This decrease shows that the molecule is not really a rigid rotor. As the rotational angular momentum increases with increasing J, the bond stretches. This stretching increases the moment of inertia and decreases the rotational constant (Figure 5.9.5).



Figure 5.9.5 : Two atoms connected by a vibrating bond. There is a rotation around the common center of mass, and oscillation in bond distance. (CC SA-BY 3.0; www.cleonis.nl).

The effect of centrifugal stretching is smallest at low J values, so a good estimate for B can be obtained from the $J = 0$ to $J = 1$ transition. From B, a value for the bond length of the molecule can be obtained since the moment of inertia that appears in the definition of B (Equation 5.9.16) is the reduced mass times the bond length squared. When the centrifugal stretching is taken into account quantitatively, the development of which is beyond the scope of the discussion here, a very accurate and precise value for B can be obtained from the observed transition frequencies because of their high precision. Rotational transition frequencies are routinely reported to 8 and 9 significant figures.

As we have just seen, quantum theory successfully predicts the line spacing in a rotational spectrum. An additional feature of the spectrum is the line intensities. The lines in a rotational spectrum do not all have the same intensity, as can be seen in Figure 5.9.3 and Table 5.9.1. This is related to the populations of the initial and final states. This aspect of spectroscopy will be discussed in more detail in the following chapters

Answers

$$\Delta E_{photon} = E_f - Ei$$

$$E_{r.rotor} = J(J+1)\frac{\hbar^2}{2I}$$

$$E_{photon} = h_\nu = hc\tilde{\nu} = J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I}$$

$$J_f - J_i = 1$$

$$J_f = 1 + J_i$$

$$E_{photon} = h_\nu = hc\tilde{\nu} = (1+J_i)(2+J_i)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I}$$

$$= \frac{\hbar^2}{2I}[2 + 3J_i + J_i^2 - J_i^2 - J_i]$$

$$= \frac{\hbar^2}{2I}2(J_i+1)$$

$$= 2B(J_i+1)$$

Now we do a standard dimensional analysis

$$B = \frac{\hbar^2}{2I} \equiv \left[\frac{kgm^2}{s^2}\right] = [J]$$

$$\frac{B}{h} = B(infreq.) = \frac{h}{8\pi^2\mu r_o^2} \equiv \left[\frac{1}{s}\right]$$

$$\frac{B}{hc} = \widetilde{B} = \frac{h}{8\pi^2\mu c r_o^2} \equiv \left[\frac{s}{m}\right]$$

To prove the relationship, evaluate the LHS. First, define the terms:

$$\nu_{J_i} = 2B(J_i+1), \nu_{J_i+1} = 2B((J_i+1)+1)$$

Substitute into the equation and evaluate:

$$2B((J_i+1)+1) - 2B(J_i+1) = 2B$$

$$2B(J_i+1) + 2B - 2B(J_i+1) = 2B$$

$$2B = 2B$$

LHS equals RHS.Therefore, the spacing between any two lines is equal to $2B$.

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5.E: The Harmonic Oscillator and the Rigid Rotor (Exercises)

Solutions to select questions can be found online.

5.7

Calculate the reduced mass of HCl molecule given that the mass of H atom is 1.0078 amu and the mass of Cl atom is 34.9688 amu. Note that 1 amu = 1.660565*10^{-27} kg.

Solution

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu = \frac{1.0078\ amu \times 34.9688\ amu}{1.0078\ amu + 34.9688\ amu} = 0.9796\ amu$$

$$\mu = 0.9796\ amu \times \frac{1.660565 \cdot 10^{-27}\ kg}{1\ amu} = 1.627 \times 10^{-27} kg$$

5.8

Calculate the reduced mass for the Br_2, Cl_2, and I_2 diatomics.

Solution

From the periodic table, the atomic masses for Br, Cl, and I are 79.904, 35.453, and 126.904 respectively.

Covert the atomic mass to kg.

$Br = (79.904\ amu)(1.6606 \times 10^{-27}\ amu/kg) = 1.327 \times 10^{-25}\ kg\ Cl = (35.453\ amu)(1.6606 \times 10^{-27}\ amu/kg) = 5.887 \times 10^{-26}\ kg\ I = (126.904\ amu)(1.6606 \times 10^{-27}\ amu/kg) = 2.107 \times 10^{-25}\ kg$

$$\mu = \frac{m}{2}$$

therefore

μ_{Br2}=1.327x10^{-25} kg/2=6.635x10^{-26} kg μ_{Cl2}= 5.887x10^{-26}kg/2 = 2.9435x10^{-26}kg μ_{I2}=2.107x10^{-25}kg=1.0535x10-25kg

The equation for a reduced mass (μ) of a diatomic is

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

for a diatomic molecule with identical atoms ($m_1 = m_2 = m$) so

5.14

$^{79}Br^{79}Br$ has a force constant of $240\ N \cdot m^{-1}$. Given this information:

a. Calculate the fundamental vibrational frequency and
b. Calculate the $^{79}Br^{79}Br$ zero point energy.

Solution

We must first know which formula to use which is

$$\nu_{obs} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

calculate the reduced mass

$$\mu = \frac{(79\ amu)^2}{79\ amu + 79\ amu} = 39.5amu$$

and convert to Kg:

$1.66e^{-27}$ kg•amu^{-1}

substitute the given values

$$\nu = \frac{1}{2\pi}\sqrt{\frac{240kg\ m\ s^{-2}\ s}{39.5amu \times 1.66 \times 10^{-27}kg\ amu^{-1}}} = 9.63 \times 10^{12}s^{-1}$$

It can also be convert to wavenumber (inverse centimeter cm^{-1}):

$$\nu_{cm^{-1}} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{9.63 \times 10^{12}s^{-1}}{3.0 \times 10^{10}cm\ s^{-1}} = 321cm^{-1}$$

Zero Point Energy:

$$E_0 = \frac{1}{2}h\nu = \frac{1}{2}hc\nu_{cm^{-1}}$$

(formula to use)

E_0=1/2(6.626e^{-34}J•s)(2.998e^{10}cm•s^{-1})(321cm^{-1})

E_0= 3.19e^{-21}J

5.19

Prove that the second derivative of an even function is even and odd function is odd.

Solution

This is an example..not a proof

The following is an even function:

$$y(x) = a + bx^2 + cx^4 + dx^6$$

so

$$\frac{dy}{dx} = 2bx + 4cx^3 + 6dx^5$$

and

$$\frac{d^2y}{dx^2} = 2b + 12cx^2 + 30dx^4$$

which is an even function.

The following is an odd function:

$$f(x) = ax + bx^3 + cx^5$$

so

$$\frac{df}{dx} = a + 3bx^2 + 5cx^4$$

and

$$\frac{d^2f}{dx^2} = 6bx + 10cx^3$$

which is an odd function.

5.27

The Harmonic oscillator Hamiltonian obeys the reflective property:

$$\hat{H}(x) = \hat{H}(-x)$$

What does this say about the nature of the harmonic oscillator wave function?

Solution

The harmonic oscillator switches from odd to even due to the fact that the reflective property will alternate.

5.28

If $\langle x \rangle$ is an odd function, what does that say about p_x?

Hint: use

$$\frac{d\langle p_x \rangle}{dt} = \left\langle \frac{-dV}{dx} \right\rangle$$

also known as **Ehrenfest's Theorem**, where V is the potential of a one dimensional harmonic oscillator.

Hence, $\langle p_x \rangle$ does not depend on time.

5.32

Convert ∇^2 from Cartesian coordinates to cylindrical coordinates.

Solution

We have to start with the conversion of *Cartesian coordinates* $\{x, y, z\}$ to *cylindrical coordinates* $\{r, \theta, z\}$

$x = r\cos\theta \; y = r\sin\theta \; z = z$

Now putting it all together

$$\nabla^2 = \frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} + \frac{1}{r^2}\frac{d^2}{d\theta^2} + \frac{d^2}{dz^2}$$

$$r = \sqrt{x^2 + y^2}$$

$$\cos\theta = \frac{x}{\sqrt{x^2 + y^2}}$$

$$\sin\theta = \frac{x}{\sqrt{x^2 + y^2}}$$

Now by chain rule we get

$$\frac{d}{dx} = \frac{dr}{dx}\frac{d}{dr} + \frac{d\theta}{dx}\frac{d}{d\theta}$$

$$\frac{d}{dy} = \frac{dr}{dy}\frac{d}{dr} + \frac{d\theta}{dy}\frac{d}{d\theta}$$

$$\frac{dr}{dx} = \frac{x}{r} = \cos\theta$$

$$\frac{dr}{dx} = \sin\theta$$

using **implicit differentiation** and taking the second derivatives will yield

$$\frac{d^2}{dx^2} = \left(\cos\theta\frac{d}{dr} - \frac{\sin\theta}{r}\frac{d}{d\theta}\right)\left(\cos\theta\frac{d}{dr} - \frac{\sin\theta}{r}\frac{d}{d\theta}\right)$$

$$\frac{d^2}{dy^2} = \left(\sin\theta\frac{d}{dr} + \frac{\cos\theta}{r}\frac{d}{d\theta}\right)\left(\sin\theta\frac{d}{dr} + \frac{\cos\theta}{r}\frac{d}{d\theta}\right)$$

$$\frac{d^2}{dz^2} = \frac{d^2}{dz^2}$$

5.37

Find the magnitude of angular momentum and the z component of angular momentum for electrons in a hydrogen-like species with

a. quantum numbers $n = 1, l = 0, m = 0$; and
b. $n = 2, l = 0, m = 0$.

Compare your answers and explain your results.

Solution

The wave function for this problem is given by:

$$\psi_{100} = R(r)_{10}Y(\theta,\phi)_{00} = 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} e^{\frac{-Zr}{a_0}}$$

Using that:

$$\hat{L}^2 Y_{lm}(\theta,\phi) = \hbar^2 l(l+1)Y_{lm}(\theta,\phi),$$

and

$$\hat{L_z} = m\hbar$$

Then $\hat{L}^2 = 0$ and $\hat{L_z} = 0$. Given that the values for l and m are the same as above, the answers would also be the same.

The reason why both answers are the same is that the operators for angular momentum only act on the angular part of the wave function. Since only the quantum number n varied between these two states, the angular momentum eigenvalues did not change.

5.38

Apply the angular momentum operator in the x direction to the following functions ($Y(\theta, \phi)$).

a. $\frac{5\pi}{4} + 7\exp(\pi^2)$
b. $3\pi\sin(\theta)$
c. $\frac{3}{2}\cos(\theta)\exp(i\phi)$

Solution

Let us begin by stating the angular momentum operator in terms of θ and ϕ.

$$\hat{L_x} = i\hbar\Big(\sin(\phi)\frac{\partial}{\partial\theta} + \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}\Big)$$

a) $Y(\theta, \phi) = \frac{5\pi}{4} + 7exp(\pi^2)$

$$\hat{L_x}(\frac{5\pi}{4} + 7exp(\pi^2)) = i\hbar\Big(\sin(\phi)\frac{\partial\frac{5\pi}{4} + 7exp(\pi^2)}{\partial\theta} + \cot(\theta)\cos(\phi)\frac{\partial\frac{5\pi}{4} + 7exp(\pi^2)}{\partial\phi}\Big)$$

$$= 0$$

The function does not depend on θ or ϕ so when the angular momentum operator is applied to the function, it equals 0.

b) $Y(\theta, \phi) = 3\pi\sin(\theta)$

$$\hat{L_x}(3\pi\sin(\theta)) = i\hbar\Big(\sin(\phi)\frac{\partial}{\partial\theta}3\pi\sin(\theta) + \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}3\pi\sin(\theta)\Big)$$

$$= 3i\pi\hbar\sin(\phi)\cos(\theta)$$

c) $Y(\theta, \phi) = \frac{3}{2}\cos(\theta)exp(i\phi)$

$$\hat{L_x}(3\pi\sin(\theta)) = i\hbar\Big(\sin(\phi)\frac{\partial}{\partial\theta}\frac{3}{2}\cos(\theta)exp(i\phi) + \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}\frac{3}{2}\cos(\theta)exp(i\phi)\Big)$$

$$= i\hbar\Big(\frac{-3}{2}\sin(\phi)\sin(\theta)exp(i\phi) + \frac{3i}{2}\cot(\theta)\cos(\phi)\cos(\theta)exp(i\phi)\Big)$$

$$= \frac{3i\hbar exp(i\phi)}{2}(i\cot(\theta)\cos(\phi)\cos(\theta) - \sin(\phi)\sin(\theta))$$

5.41

Use the fact that $\hat{x}$ and $\hat{p}$ are Hermitian in the number operator

$$\hat{a}_- = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{p})$$

$$\hat{a}_+ = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{p})$$

and

$$\hat{H} = \frac{\hbar w}{2}(\hat{a}_-\hat{a}_+ + \hat{a}_+\hat{a}_-)$$

Show that

$$\int \psi_v^*\hat{v}\psi dx \geq 0$$

5.43

Determine the unnormalized wave function $\psi_{\circ}\left(x\right)$ given that $\hat{a}_{-} = 2^{-1/2}\left(\hat{x} + i\hat{p}\right)$ and that $\hat{a_{-}}\psi_{\circ} = 0$ Then find the unnormalized wave function for $\psi_{1}\left(x\right)$ using $\hat{a}_{+}$.

Solution

It was given that $\hat{a}_{-}\psi_{\circ} = 0$, so substituting in $\hat{a}_{-}$ so we know

$$\hat{a_{-}} = 2^{-1/2}\left(\hat{x} + i\hat{p}\right)\psi_{\circ} = 0$$

We can expand and simplify this expression to a first order partial differential equation

$$x\psi_{\circ} + \frac{d\psi_{\circ}}{dx} = 0$$

Solve by separating like terms

$$\frac{d\psi_{\circ}}{\psi_{\circ}} = -xdx$$

Solving this equation for $\psi_{\circ}\left(x\right)$ we find that

$$\psi_{\circ} = e^{\frac{-x^{2}}{2}}$$

To solve for ψ_{1} we understand that $\psi_{1} \backsim \hat{a_{+}}\psi_{\circ} \backsim \hat{x} - i\hat{p}\psi_{\circ}$, as well as that

$$\hat{x} - i\hat{p}\psi_{\circ} = x\psi_{\circ} - \frac{d\psi_{\circ}}{dx} = 2xe^{\frac{-x^{2}}{2}} = 2x\psi_{\circ}$$

So then we can say

$$\boxed{\psi_{1} \backsim xe^{\frac{-x^{2}}{2}}}$$

5.46

Find the reduced mass of an electron in a Tritium atom. Set the mass of the Tritium to be $5.008267 \times 10^{-27}\ kg$. Then find the value of the Rydberg constant for the Tritium atom.

Solution

To solve, use the reduced mass equation, and for mass 1 enter the mass of the electron, and for mass 2 enter the mass of the Tritium atom:

$$\mu = \frac{m_{1}m_{2}}{m_{1} + m_{2}}$$

For which one attains a value of $\mu = 9.1077x10^{-31}kg$

5.46

The mass of a deuterium atom is $3.343586 \times 10^{-27}\ kg$. First calculate the reduce mass of the deuterium atom. Then using the reduced mass calculated find the Rydberg constant for a deuterium atom.

Solution

μ = reduced mass

$$\mu_{deuterium} = \frac{(9.109390 \times 10^{-31} kg)(3.343586 \times 10^{-27} kg)}{(9.109390 \times 10^{-31} kg + 3.343586 \times 10^{-27} kg)}$$

$$\mu_{deuterium} = 9.106909 \times 10^{-31} kg = 0.9997277 m_e$$

R_H = Rydberg constant

$$R_H = (109,737.2 cm^{-1})(0.9997277 m_e) = 109,707.3 cm^{-1}$$

5.47

What is the ratio of the frequency of spectral lines of C-14 that has been ionized 5 times and C-12 that has been ionized 5 times?

Solution

Carbon that has been ionized 5 times is a hydrogen like ion, so we can use the Bohr model to find the desired ratio.

$$E = \frac{uZ^2e^4n^2}{8\varepsilon_0^2h^3c}$$

gives the placement of spectral lines. The coefficient of n^2 is proportional to the frequency of these lines, so the ratio of $E_{C\text{-}14}/E_{C\text{-}12}$ will give the ratio of frequency of the lines. The only difference between these two isotopes is the reduced mass u. So the problem reduces to $\mathbf{u_{C\text{-}14}/\ u_{C\text{-}12}}$. Mass in amu is used below. m_e = mass of electron = $5.4858*10^{-4}$ amu.

$$\mu_{C-14} = \frac{m_e m_{c-14}}{m_e + m_{c-14}} = \frac{(14.003)(5.4858 \times 10^{-4})}{14.003 + 5.4858 \times 10^{-4}} = 5.485585 \times 10^{-4}$$

$$\mu_{C-12} = \frac{m_e m_{c-12}}{m_e + m_{c-12}} = \frac{(12)(5.4858 \times 10^{-4})}{12 + 5.4858 \times 10^{-4}} = 5.485549 \times 10^{-4}$$

$$\frac{\mu_{C-14}}{\mu_{C-12}} = 1.0000065$$

5.47

Calculate the Rydberg constant for a deuterium atom and atomic hydrogen given the reduced mass of a deuterium atom is $9.106909 \times 10^{-31} kg$ and the reduced mass of hydrogen is $9.104431 \times 10^{-31} kg$. Compare both of these answers with the experimental result ($109677.6 cm^{-1}$). Then determine the ratio of the frequencies of the lines in the spectra of atomic hydrogen and atomic deuterium.

Solution

The Rydberg constant is found using

$$R_H = \frac{me^4}{8\epsilon_o^2 ch^3}$$

For a deuterium atom

$$R_H = \frac{(9.104431 \times 10^{-31} kg)(1.602 \times 10^{-19} C)^4}{8(8.854 \times 10^{-12} \frac{F}{m})^2(2.998 \times 10^8 \frac{m}{s})(6.626 \times 10^{-34} J \cdot s)^3}$$

$$R_H = 109707.3 cm^{-1}$$

This is different by $2.7 \times 10^{-2}\%$.

The ratio of the frequencies of the lines in the spectra of atomic hydrogen and atomic deuterium is equivalent to the ratio of the Rydberg constants we just found.

$$\frac{109707.3\ cm^{-1}}{109677.5\ cm^{-1}} = 1.000272$$

$$R_H = \frac{(9.106909 \times 10^{-31} kg)(1.602 \times 10^{-19} C)^4}{8(8.854 \times 10^{-12} \frac{F}{m})^2(2.998 \times 10^8 \frac{m}{s})(6.626 \times 10^{-34} J \cdot s)^3}$$

$$R_H = 109677.5 cm^{-1}$$

This is different by $9.1 \times 10^{-5}\%$.

For a hydrogen atom

5.46

Find the reduced mass of HCl where the mass of hydrogen in 1 amu and the mass of chloride is 35 amu.

Solution

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

$$\mu = \frac{(1.00)(35.00)}{36.00} 1.603 \times 10^{-27} kg = 1.558 \times 10^{-27} kg$$

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6: THE HYDROGEN ATOM

The solution of the Schrödinger equation (wave equation) for the hydrogen atom uses the fact that the Coulomb potential produced by the nucleus is isotropic (it is radially symmetric in space and only depends on the distance to the nucleus). Although the resulting energy eigenfunctions (the orbitals) are not necessarily isotropic themselves, their dependence on the angular coordinates follows completely generally from this isotropy of the underlying potential: the eigenstates of the Hamiltonian (that is, the energy eigenstates) can be chosen as simultaneous eigenstates of the angular momentum operator. This corresponds to the fact that angular momentum is conserved in the orbital motion of the electron around the nucleus. Therefore, the energy eigenstates may be classified by two angular momentum quantum numbers, ℓ and m (both are integers). The angular momentum quantum number $\ell = 0, 1, 2, \ldots$ determines the magnitude of the angular momentum. The magnetic quantum number $m = -\ell, \ldots, +\ell$ determines the projection of the angular momentum on the (arbitrarily chosen) z-axis.

6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly

6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics

6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers

6.5: s-orbitals are Spherically Symmetric

6.6: Orbital Angular Momentum and the p-Orbitals

6.7: The Schrödinger Wave Equation for the Hydrogen Atom

6.8: The Helium Atom Cannot Be Solved Exactly

6.E: The Hydrogen Atom (Exercises)

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6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly

The hydrogen atom, consisting of an electron and a proton, is a two-particle system, and the internal motion of two particles around their center of mass is equivalent to the motion of a single particle with a reduced mass. This reduced particle is located at r, where r is the vector specifying the position of the electron relative to the position of the proton. The length of r is the distance between the proton and the electron, and the direction of r and the direction of r is given by the orientation of the vector pointing from the proton to the electron. Since the proton is much more massive than the electron, we will assume throughout this chapter that the reduced mass equals the electron mass and the proton is located at the center of mass.

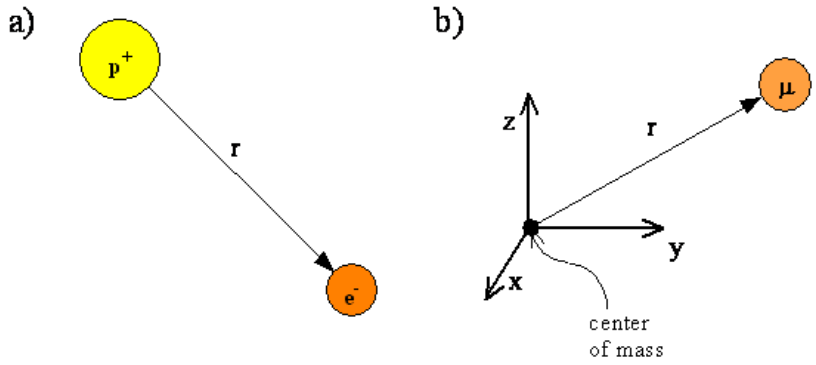


Figure 6.1.1 : (a) The proton (p^+) and electron (e^-) of the hydrogen atom. (b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

Exercise 6.1.1

a. Assuming the Bohr radius gives the distance between the proton and electron, calculate the distance of the proton from the center of mass, and calculate the distance of the electron from the center of mass.
b. Calculate the reduced mass of the electron-proton system.
c. In view of your calculations in (a) and (b), comment on the validity of a model in which the proton is located at the center of mass and the reduced mass equals the electron mass.

Since the internal motion of any two-particle system can be represented by the motion of a single particle with a reduced mass, the description of the hydrogen atom has much in common with the description of a diatomic molecule discussed previously. The time-independent Schrödinger Equation for the hydrogen atom

$$\hat{H}(r,\theta,\varphi)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{6.1.1}$$

employs the same kinetic energy operator, $\hat{T}$, written in spherical coordinates. For the hydrogen atom, however, the distance, r , between the two particles can vary, unlike the diatomic molecule where the bond length was fixed and the rigid rotor model was applicable. The hydrogen atom Hamiltonian also contains a potential energy term, $\hat{V}$, to describe the attraction between the proton and the electron. This term is the Coulomb potential energy,

$$\hat{V}(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{6.1.2}$$

where r is the distance between the electron and the proton. The Coulomb potential energy depends inversely on the distance between the electron and the nucleus and does not depend on any angles. Such a potential is called a **central potential**.

The full expression for $\hat{H}$ in spherical coordinates is

$$\hat{H}(r,\theta,\varphi) = -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r} \tag{6.1.3}$$

The contributions from rotational and radial components of the motion become clearer if we write out the complete Schrödinger equation,

$$\left\{-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\right\}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{6.1.4}$$

multiply both sides of Equation 6.1.4 by $2\mu r^2$, and rearrange to obtain

$$\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right) + 2\mu r^2\left[E + \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(r,\theta,\varphi) =$$

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\varphi) \tag{6.1.5}$$

Manipulating the Schrödinger equation in this way helps us recognize the square of the angular momentum operator in Equation 6.1.5. The square of the angular momentum operator in Equation 6.1.6.

$$\hat{M}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{6.1.6}$$

Substituting Equation 6.1.6 into Equation 6.1.5 produces

$$\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right) + 2\mu r^2[E-\hat{V}]\psi(r,\theta,\varphi) = \hat{M}^2\psi(r,\theta,\varphi) \tag{6.1.7}$$

Exercise 6.1.2

Show the algebraic steps going from Equation 6.1.4 to 6.1.5 and finally to 6.1.7. Justify the statement that the rotational and radial motion are separated in Equation 6.1.7.

Since the angular momentum operator does not involve the radial variable, r, we can separate variables in Equation 6.1.7 by using a product wavefunction, as we did previously for rigid rotors. We know that the eigenfunctions of the angular momentum operator are the Spherical Harmonic functions (Table M4), $Y(\theta,\varphi)$, so a good choice for a product function is

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi) \tag{6.1.8}$$

> The Spherical Harmonic functions provide information about where the electron is around the proton, and the radial function $R(r)$ describes how far the electron is away from the proton.

To separate variables, substitute the product function, Equation 6.1.8 into Equation 6.1.7, evaluate partial derivatives, divide each side by R(r) $Y(\theta,\varphi)$, and set each side of that resulting equation equal to a constant λ.

$$\frac{\hbar^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \frac{2\mu r^2}{R(r)}[E-V]R(r) = \lambda \tag{6.1.9}$$

$$\frac{1}{Y(\theta,\varphi)}\hat{M}^2Y(\theta,\varphi) = \lambda \tag{6.1.10}$$

Equations 6.1.9 and 6.1.10 represent the radial differential equation and the angular differential equation, respectively. As we describe below, they are solved separately to give the $Y(\theta,\varphi)$ angular functions and the R(r) radial functions.

Exercise 6.1.3

Complete the steps leading from Equations 6.1.7 to 6.1.9 and 6.1.10.

Rearranging Equation 6.1.10 yields

$$\hat{M}^2 Y_l^{m_l}(\theta,\varphi) = \lambda Y_l^{m_l}(\theta,\varphi) \tag{6.1.11}$$

where we have added the indices l and m_l to identify a particular spherical harmonic function. Note that the notation has changed from that used with the Rigid Rotor; it is customary to use J and m_J to represent the angular momentum quantum numbers for rotational states, but for electronic states, it is customary to use l and m_l to represent the same thing. Furthermore, the electronic angular momentum is designated by L and the corresponding operator is called $\hat{L}$. In complete electronic notation, Equation 6.1.11 is

$$\hat{L}^2 Y_l^{m_l}(\theta,\varphi) = \lambda Y_l^{m_l}(\theta,\varphi) \tag{6.1.12}$$

Equation 6.1.12 says that $Y_l^{m_l}(\theta,\varphi)$ must be an eigenfunction of the angular momentum operator $\hat{L}^2$ with eigenvalue λ. We know from the discussion of the Rigid Rotor that the eigenvalue λ is $J(J+1)\hbar^2$, or in electronic notation, $l(l+1)\hbar^2$. Consequently, Equation 6.1.12 becomes

$$\hat{L}^2 Y_l^{m_l}(\theta,\varphi) = l(l+1)\hbar^2 Y_l^{m_l}(\theta,\varphi) \tag{6.1.13}$$

Using this value for λ and rearranging Equation 6.1.9, we obtain

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) - E\right]R(r) = 0 \tag{6.1.14}$$

Exercise 6.1.4

Write the steps leading from Equation 6.1.9 to Equation 6.1.14.

The details for solving Equation 6.1.14 are provided elsewhere, but the procedure and consequences are similar to previously examined cases. As for the harmonic oscillator, an asymptotic solution (valid at large r) is found, and then the complete solutions are written as products of the asymptotic solution and polynomials arising from sequential truncations of a power series expansion.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics

The solutions to the hydrogen atom Schrödinger equation are functions that are products of a spherical harmonic function and a radial function:

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_l^{m_l}(\theta,\phi) \tag{6.2.1}$$

The wavefunctions for the hydrogen atom depend upon the three variables r, θ, and ϕ and the three quantum numbers n, l, and m_l. The variables give the position of the electron relative to the nucleus in spherical coordinates. The absolute square of the wavefunction, $|\psi(r,\theta,\phi)|^2$, evaluated at r, θ, and ϕ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r, θ, and ϕ.

Exercise 6.2.1

What is the value of the integral (in braket notation)

$$\langle\psi(r,\theta,\phi)|\psi(r,\theta,\phi)\rangle \ ?$$

or expanded in integral notation (in Cartesian coordinates)

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}|\psi(x,y,z)|^2\,dx\,dy\,dz$$

or expanded in integral notation (in spherical coordinates)

$$\int_{0}^{+\infty}\int_{0}^{\pi}\int_{0}^{+2\pi}|\psi(r,\theta,\phi)|^2 r^2\sin\theta\,d\theta\,d\phi\,dr$$

Answer available at the end of this section.

The quantum numbers have names:

- n is called the principal quantum number,
- l is called the angular momentum quantum number, and
- m_l is called the magnetic quantum number because (as we will see, the energy in a magnetic field depends upon m_l).

Often l is called the azimuthal quantum number because it is a consequence of the θ-equation, which involves the azimuthal angle Θ, referring to the angle to the zenith. These quantum numbers have specific values that are dictated by the physical constraints or boundary conditions imposed upon the Schrödinger equation: n must be an integer greater than 0, l can have the values 0 to n-1, and m_l can have $2l+1$ values ranging from $-l$ to $+l$ in unit or integer steps. The total number of orbitals with a particular value of n is n^2 - i.e., this is the **degeneracy** of the system.

Wavefunction Nomenclature

The values of the quantum number l usually are coded by a letter: s means 0, p means 1, d means 2, f means 3; the next codes continue alphabetically (e.g., g means $l=4$). The quantum numbers specify the quantization of physical quantities. The discrete energies of different states of the hydrogen atom are given by n, the magnitude of the angular momentum is given by l, and one component of the angular momentum (usually chosen by chemists to be the z-component) is given by m_l.

The Φ function is found to have the quantum number m, where

$$\Phi_m(\phi) = A_m e^{im\phi}$$

and A_m is the normalization constant and $m = 0, \pm1, \pm2... \pm\infty$. The Θ function was solved and is known as *Legendre polynomials*, which have quantum numbers m and ℓ. When Θ and Φ are multiplied together, the product is known as **spherical harmonics** with labeling $Y_J^m(\theta, \phi)$.

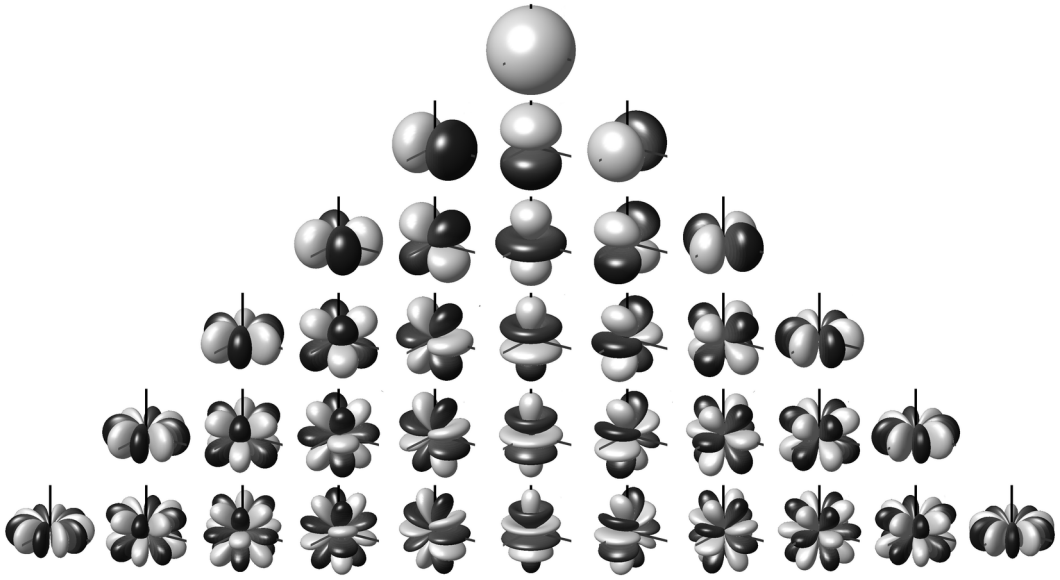


Figure 6.2.1: Spherical Harmonics as commonly displayed, sorted by increasing energies and aligned for symmetry.

Figure 6.2.1 shows the spherical harmonics Y_J^M, which are solutions of the angular Schrödinger equation. These are explicitly written in Table 6.2.1 . Notice that these functions are complex in nature.

Table 6.2.1 : spherical harmonics Y_J^M

m_J	J	$\Theta_J^{m_J}(\theta)$	$\Phi(\varphi)$	$Y_J^{m_J}(\theta, \varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}}(3\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$
1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$
-1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$
2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$
-2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{-2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$

Exercise 6.2.2

Consider several values for n, and show that the number of orbitals for each n is n^2.

Exercise 6.2.3

Construct a table summarizing the allowed values for the quantum numbers n, l, and m_l. for energy levels 1 through 7 of hydrogen.

Exercise 6.2.4

The notation 3d specifies the quantum numbers for an electron in the hydrogen atom.

a. What are the values for n and l?
b. What are the values for the energy and angular momentum?
c. What are the possible values for the magnetic quantum number?
d. What are the possible orientations for the angular momentum vector?

Answer available at the end of this section.

Atomic Orbitals

The hydrogen atom wavefunctions, $\psi(r,\theta,\phi)$, are called **atomic orbitals**. An atomic orbital is a function that describes one electron in an atom. The wavefunction with $n=1$, $l=0$, and $m_l=0$ is called the 1s orbital, and an electron that is described by this function is said to be "in" the 1s orbital, i.e. have a 1s orbital state. The constraints on n, ℓ, and m_ℓ that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

The first few solutions of the Schrödinger equation for the H atom are:

Table 6.2.1 : The solutions to the Schrödinger equation for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho=\frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

	n	l	m_l	ψ_{n,l,m_l}
ψ_{100}	1	0	$m_l=0$	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
ψ_{200}	2	0	$m_l=0$	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(2-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
ψ_{210}	2	1	$m_l=0$	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\cos\theta$
$\psi_{21\pm1}$	2	1	$m_l=\pm1$	$\frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\sin\theta e^{\pm i\phi}$
ψ_{300}	3	0	$m_l=0$	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(27-18\frac{Zr}{a_0}+2\frac{Z^2r^2}{a_0^2}\right) e^{-\frac{Zr}{3a_0}}$
ψ_{310}	3	1	$m_l=0$	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}\cos\theta$
$\psi_{31\pm1}$	3	1	$m_l=\pm1$	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}\sin\theta e^{\pm i\phi}$

	n	l	m_l	ψ_{n,l,m_l}
ψ_{320}	3	2	$m_l = 0$	$\frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \left(3\cos^2\theta - 1\right)$
$\psi_{32\pm1}$	3	2	$m_l = \pm1$	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin\theta\cos\theta e^{\pm i\phi}$
$\psi_{32\pm2}$	3	2	$m_l = \pm2$	$\frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin^2\theta e^{\pm 2i\phi}$

We can take superposition states of the solutions to obtain real wavefunctions that do not have any imaginary components:

Table 6.2.2 : The real solutions to the Schrödinger equation for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

	n	l	m_l	$\psi_{n,l}$
ψ_{1s}	1	0	0	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
ψ_{2s}	2	0	0	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
ψ_{2p_z}	2	1	0	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \cos\theta$
ψ_{2p_x}	2	1	±1	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \sin\theta\cos\phi$
ψ_{2p_y}	2	1	±1	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\frac{Zr}{2a_0}} \sin\theta\sin\phi$
ψ_{3s}	3	0	0	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-\frac{Zr}{3a_0}}$
ψ_{3p_z}	3	1	0	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r \left(6 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}} \cos\theta$
ψ_{3p_x}	3	1	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r \left(6 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}} \sin\theta\cos\phi$
ψ_{3p_y}	3	1	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r \left(6 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}} \sin\theta\sin\phi$
$\psi_{3d_{z^2}}$	3	2	0	$\frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \left(3\cos^2\theta - 1\right)$
$\psi_{3d_{xz}}$	3	2	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin\theta\cos\theta\cos\phi$
$\psi_{3d_{yz}}$	3	2	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin\theta\cos\theta\sin\phi$
$\psi_{3d_{x^2-y^2}}$	3	2	±2	$\frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin^2\theta\cos 2\phi$
$\psi_{3d_{xy}}$	3	2	±2	$\frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}} \sin^2\theta\sin 2\phi$

These are the wavefunctions that are most often depicted. Visualizing the variation of an electronic wavefunction with r, θ, and ϕ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron-deficient part of one molecule is attracted to an electron-rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately do not reveal the shape of an orbital very well. The shape can be revealed better in a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$. Do not confuse such plots with polar plots, which look similar. Probability densities also can be represented by contour maps, as shown in Figure 6.2.2 .

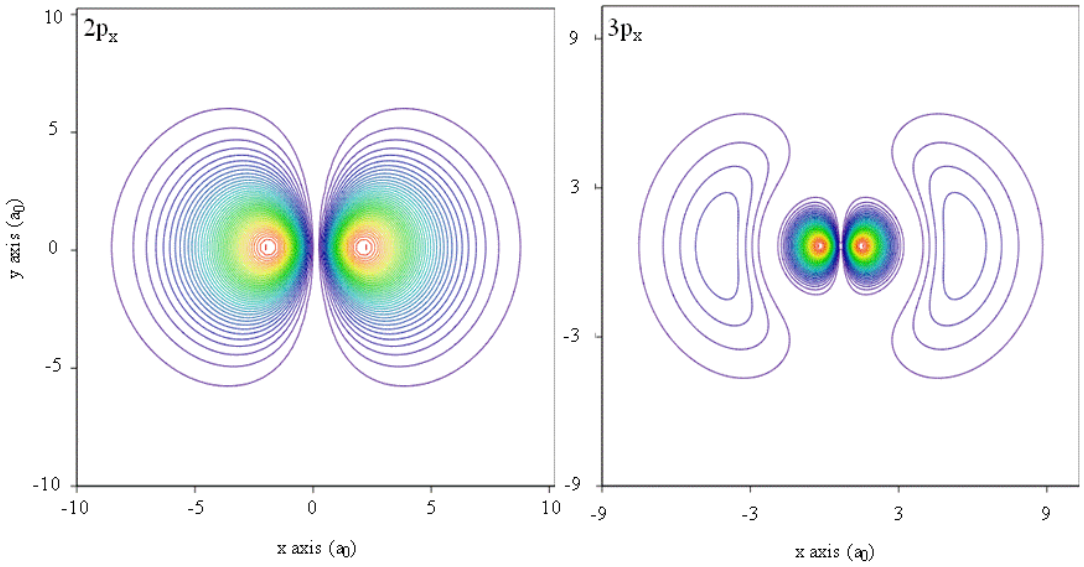


Figure 6.2.2: Contour plots in the x-y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low $R(r)^2$. The angular function used to create the figure was a linear combination of two Spherical Harmonic functions.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, $R(r)$, for the 1s, 2s, and 2p orbitals plotted in Figure 6.2.3 .

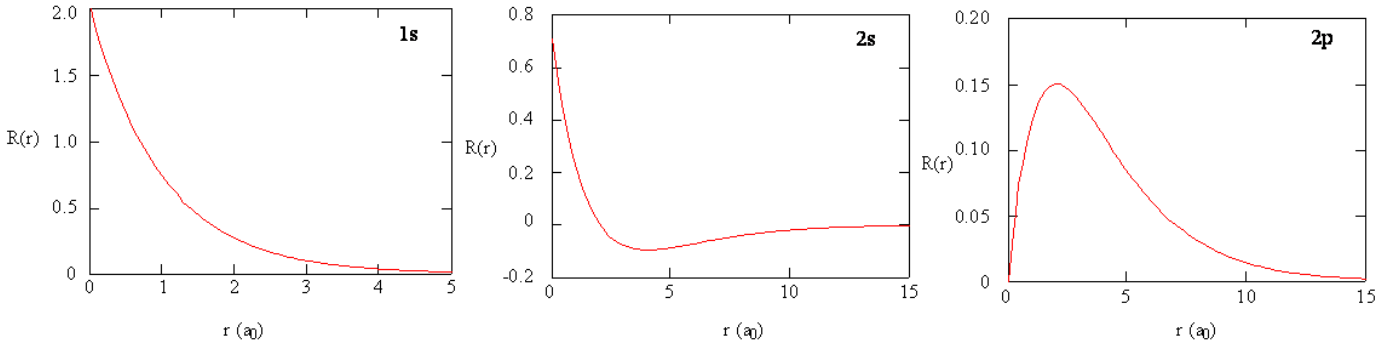


Figure 6.2.3: Radial function, $R(r)$, for the 1s, 2s, and 2p orbitals.

The 1s function in Figure 6.2.3 starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

Next notice how the radial function for the 2s orbital, Figure 6.2.3 , goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$, but p, d, f and all other functions go to zero at the origin. It is useful to remember that there are $n - 1 - l$ radial nodes in a wavefunction, which means that a 1s orbital has no radial nodes, a 2s has one radial node, and so on.

Exercise 6.2.5

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

Exercise 6.2.6

What mathematical feature of each of the radial functions controls the number of radial nodes?

Answer available at the end of this section.

Exercise 6.2.7 : Radial Node

At what value of r does the 2s radial node occur?

Answer available at the end of this section.

Exercise 6.2.8

Make a table that provides the energy, number of radial nodes, and the number of angular nodes and total number of nodes for each function with $n = 1$, $n = 2$, and $n = 3$. Identify the relationship between the energy and the number of nodes. Identify the relationship between the number of radial nodes and the number of angular nodes.

Answer available at the end of this section.

The quantity $R(r)^* R(r)$ gives the radial probability density; i.e., the probability density for the electron to be at a point located the distance r from the proton. Radial probability densities for three atomic orbitals are plotted in Figure 6.2.4 .

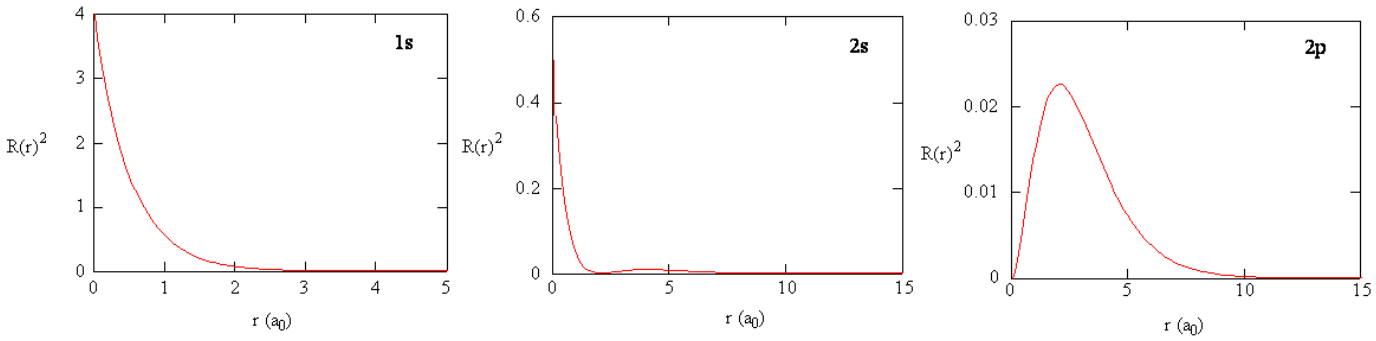


Figure 6.2.4: Radial probability densities for the 1s, 2s, and 2p orbitals.

Probabilities and Distribution Functions

When the **radial probability density** for every value of r is multiplied by the area of the spherical surface represented by that particular value of r, we get the radial distribution function. The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the proton. Since the area of a spherical surface is $4\pi r^2$, the **radial distribution function** is given by

$$\underbrace{4\pi r^2 R(r)^* R(r)}_{\text{radial probability density}}$$

Radial distribution functions are shown in Figure 6.2.5 . At small values of r, the radial distribution function is low because the small surface area for small radii modulates the high value of the radial probability density function near the nucleus. As we increase r, the surface area associated with a given value of r increases, and the r^2 term causes the radial distribution function to increase even though the radial probability density is beginning to decrease. At large values of r, the exponential decay of the radial function outweighs the increase caused by the r^2 term and the radial distribution function decreases.

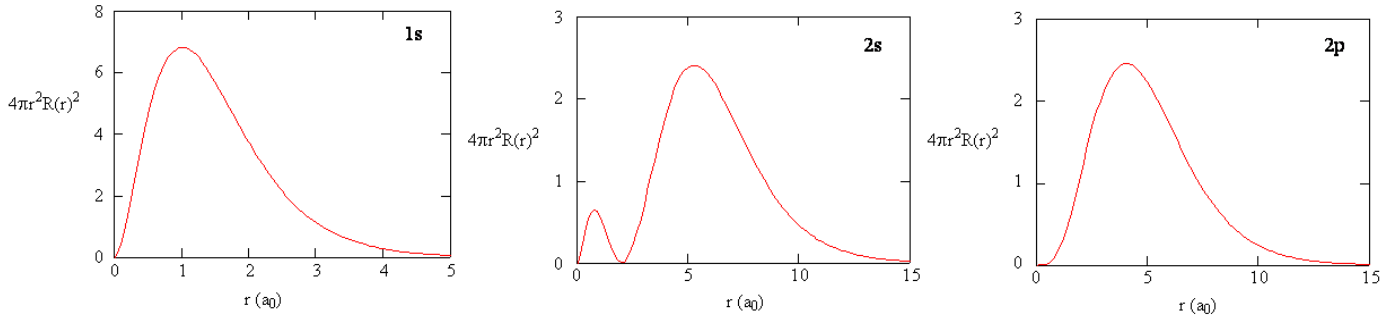


Figure 6.2.5: The radial distribution function for the 1s, 2s, and 2p orbitals.

Exercise 6.2.9

Write a quality comparison of the radial function and radial distribution function for the 2s orbital. See Figure 6.2.6 .

Answer available at the end of this section.

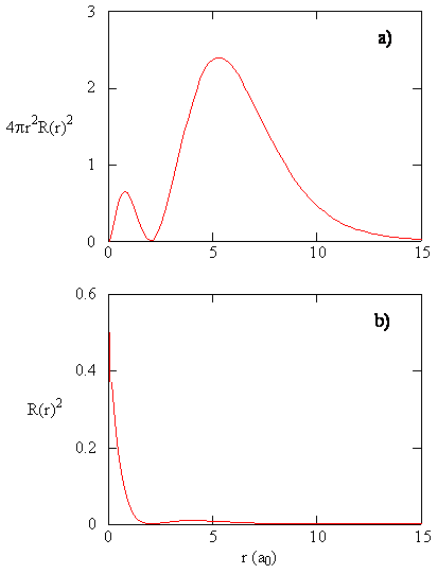


Figure 6.2.6: Comparison of a) the radial distribution function and b) the radial probability density for the 2s orbital.

Answers

No need to know the functional form of the hydrogen atom eigenstates in any coordinate system. If the eigenstates (i.e., solutions to the hydrogen atom Schrödinger equation) are normalized - as we normally like them- then this integral will be 1.

a. $n = 3$ and $l = 2$
b. Energy:

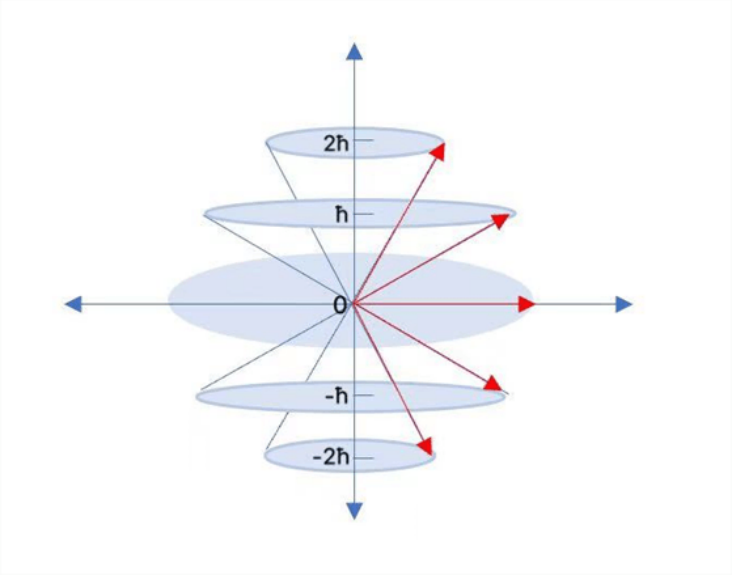
$$E_n = \frac{E_1}{n^2} = \frac{-13.6\text{eV}}{9} = -1.51\text{eV}$$

and angular momentum

$$\sqrt{l(l+1)}\hbar = \sqrt{2 \times 3}\hbar = 2.584 \times 10^{-34} J \cdot S$$

c. Magnetic quantum number:

$$m_l = -2, -1, 0, 1, 2$$



d.

The Laguerre polynomial controls the radial nodes with the number of roots for the Laguerre polynomial is the number of radial nodes.

A node exists when the radial portion of the wavefunction equals 0. The radial portion of the 2s wavefunction is:

$$R(r) = \left(\frac{1}{2\sqrt{2}}\right)\left(\frac{Z}{\alpha_0}\right)^{\frac{3}{2}}(2-\rho)e^{\frac{-\rho}{2}}$$

where $\rho = \frac{Zr}{\alpha_0}$, $Z = 1$ for the hydrogen atom and α_0 is the Bohr radius.

Therefore:

$$R(r) = \left(\frac{1}{2\sqrt{2}}\right)\left(\frac{1}{\alpha_0}\right)^{\frac{3}{2}}\left(2-\frac{r}{\alpha_0}\right)e^{\frac{-2r}{\alpha_0}}$$

For this wavefunction:

- $\left(\frac{1}{\alpha_0}\right)^{\frac{3}{2}}$ is a constant and will never equal 0.
- $e^{\frac{-2r}{\alpha_0}}$ is an exponential, and will also never equal 0.

Therefore, our node is when $\left(2-\frac{r}{\alpha_0}\right) = 0$ and

$$r = 2\alpha_0$$

Wavefunction	Energy	Total Nodes	Radial Nodes	Angular Nodes
1s	13.6 eV	0	0	0
2s	3.4 eV	1	1	0
2p	3.4 eV	1	0	1
3s	1.5 eV	2	2	0
3p	1.5 eV	2	1	1
3d	1.5 eV	2	0	2

The energy of the electron in each wavefunction is

$$E = \frac{Z^2 E_h}{2n^2}$$

The number of total nodes is (N-1\), the number of radial nodes is $N - L - 1$ and the number of angular nodes is L.

$R(r)$ is the radial function of the eigenstate and $4\pi r^2 R(r)^* R(r)$ gives the radial distribution function of the distance of electron at distance r from the nucleus (i.e., the probability integrated over all angles).

The radial probability function is low at small values of r because of a small surface area near nucleus, for example at 2s at a small value of r the radial probability function is low. At higher values of r the surface area increases while radial probability density decreases, this causes the radial distribution function to increase. In contrast the radial probability density is high at small surface area and when r is near the nucleus, i.e low values of r.

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6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

Learning Objectives

- Understand how to measure the orbital angular momentum of an electron around a nucleus.
- Understand how the Heisenburgh Uncertainty Principle extends to orbital angular momenta.
- Manipulate the angular momenta cyclic permutations that allow two of the three projects to be simultaneous measured

Consider a particle described by the Cartesian coordinates $(x, y, z) \equiv \vec{r}$ and their conjugate momenta $(p_x, p_y, p_z) \equiv \vec{p}$. The classical definition of the *orbital angular momentum* of such a particle about the origin is (i.e., via the vector cross product):

$$\vec{L} = \vec{r} \times \vec{p}$$

which can be separated into projections into each of the primary axes :

Multiple \label

Extending this discussion to the quantum mechanics, we can assume that the operators $(\hat{L}_x, \hat{L}_y, \hat{L}_z) \equiv \vec{L}$ - that represent the components of orbital angular momentum in quantum mechanics - can be defined in an analogous manner to the corresponding components of classical angular momentum. In other words, we are going to assume that the above equations specify the angular momentum operators in terms of the position and linear momentum operators.

In Cartesian coordinates, the three operators for the orbital angular momentum components can be written as

$$\hat{L}_x = -\mathrm{i}\,\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \tag{6.3.1}$$

$$\hat{L}_y = -\mathrm{i}\,\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \tag{6.3.2}$$

$$\hat{L}_z = -\mathrm{i}\,\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \tag{6.3.3}$$

These can be transforming to operators in standard spherical polar coordinates,

Multiple \label

we obtain

Multiple \label

We can introduce a new operator $\hat{L^2}$:

$$\hat{L^2} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{6.3.4}$$

$$= -\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right) \tag{6.3.5}$$

The eigenvalue problem for $\hat{L^2}$ takes the form

$$\hat{L^2}|\psi\rangle = \lambda\,\hbar^2|\psi\rangle \tag{6.3.6}$$

where $\psi(r, \theta, \varphi)$ is the wavefunction, and λ is a number. Let us write

$$\psi(r, \theta, \varphi) = R(r)\,Y(\theta, \varphi) \tag{6.3.7}$$

By definition,

$$\boxed{L^2\,Y_l^{m_l} = l\,(l+1)\,\hbar^2\,Y_l^{m_l}} \tag{6.3.8}$$

where l is an integer. This is an important conclusion that argues the angular momentum is quantized with the square of the magnitude of the angular momentum only capable of assume one of the discrete set of values (Equation 6.3.8). From this, the **amplitude** of angular momentum can be expressed

$$\boxed{|\vec{L}| = \sqrt{L^2} = \sqrt{l(l+1)}\hbar} \tag{6.3.9}$$

Warning

We often refer to a particle in a state with angular momentum quantum number l as having angular momentum l, rather than saying that it has angular momentum of $\sqrt{l(l+1)}\hbar$ magnitude, primarily since it is awkward to say quickly.

The properties of spherical harmonics that the z-component of the angular momentum (L_z) is also quantized and can only assume a one of a discrete set of values

$$L_z\,Y_l^{m_l} = m\,\hbar\,Y_l^{m_l} \tag{6.3.10}$$

where m_l is an integer lying in the range $-l \leq m_l \leq l$.

- l is sometimes called "azimuthal quantum number" or "orbital quantum number"
- m_l is sometimes called "magnetic quantum number"

Simultaneous Measurements

Note that observables associated with $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ can, in principle, be measured. However, to determine if they can be measured *simultaneously* with infinite precision, the corresponding operators must **commute**. Remember that the fundamental commutation relations satisfied by the position and linear momentum operators are:

Multiple \label

where i and j stand for either x, y, or z. Consider the commutator of the operators $\hat{L}_x$ and $\hat{L}_z$:

Multiple \label

The **cyclic permutations** of the above result yield the fundamental commutation relations satisfied by the components of an orbital angular momentum:

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\,\hbar\,\hat{L}_z \tag{6.3.11}$$

$$[\hat{L}_y, \hat{L}_z] = \mathrm{i}\,\hbar\,\hat{L}_x \tag{6.3.12}$$

$$[\hat{L}_z, \hat{L}_x] = \mathrm{i}\,\hbar\,\hat{L}_y \tag{6.3.13}$$

The three commutation relations (Equations 6.3.11 - 6.3.13) are the foundation for the whole theory of angular momentum in quantum mechanics. Whenever we encounter three operators having these commutation relations, we know that the dynamical variables that they represent have identical properties to those of the components of an angular momentum (which we are about to derive). In fact, we shall assume that any three operators that satisfy the commutation relations (Equations 6.3.11 - 6.3.13) represent the components of some sort of angular momentum.

> Any three operators that satisfy the cyclic commutation relations represent the components of some sort of angular momentum.

Example 6.3.1 : Commutators

Show that the $\hat{L^2}$ and $\hat{L}_x$ operators commute.

Solution

We want to confirm that $[\hat{L^2}, \hat{L}_x] = 0$ that from Equation 6.3.4 this can be expanded

$$[\hat{L^2}, \hat{L}_x] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x]$$

from the properties of commutators, this can be expanded

$$[\hat{L^2}, \hat{L}_x] = [\hat{L}_x^2, \hat{L}_x] + [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x]$$

However,

$$[\hat{L}_x^2, \hat{L}_x] = \hat{L}_x^2\hat{L}_x - \hat{L}_x\hat{L}_x^2 = \hat{L}_x\hat{L}_x\hat{L}_x - \hat{L}_x\hat{L}_x\hat{L}_x = 0$$

So

$$\begin{aligned}[\hat{L^2}, \hat{L}_x] &= [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\ &= \hat{L}_y^2\hat{L}_x - \hat{L}_x\hat{L}_y^2 + \hat{L}_z^2\hat{L}_x - \hat{L}_x\hat{L}_z^2 \\ &= \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z\end{aligned}$$

Lets look at some related forms which can be used to simplify the above expression. The first two terms can and final two terms can be rewritten as different commutators

$$\begin{aligned}[\hat{L}_y, \hat{L}_x] &= \hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] \\ &= (\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y)\hat{L}_y + \hat{L}_y(\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y) \\ &= \cancel{\hat{L}_y\hat{L}_x\hat{L}_y} - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_y\hat{L}_y\hat{L}_x - \cancel{\hat{L}_y\hat{L}_x\hat{L}_y}\end{aligned}$$

The first & fourth terms cancel, giving

$$[\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] = \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y$$

Similarly,

$$[Lz, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] = \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z$$

So,

$$\begin{aligned}[\hat{L^2}, \hat{L}_x] &= [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] \\ &= -i\hbar\hat{L}_z\hat{L}_y - i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_z\hat{L}_y \\ &= 0\end{aligned}$$

One can also show similarly that

$$[\hat{L^2}, \hat{L}_y] = [\hat{L^2}, \hat{L}_z] = 0$$

Example 6.3.1 shows that while L_z can be known with certainty, L_x and L_y would **unknown**. This means that every vector with the appropriate length and *z*-component can drawn to represent $\vec{L}$, which forms a cone (Figure 6.3.1). The expected value of the angular momentum for a given ensemble of systems in the quantum state characterized by l and m_l could be somewhere on this cone while it cannot be defined for a single system (since the components of L do not commute with each other).

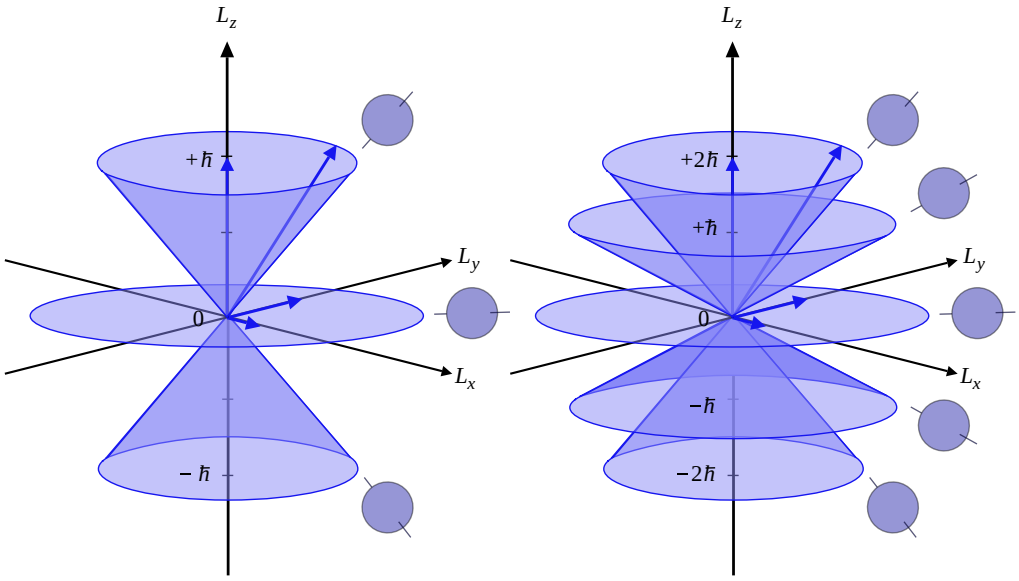


Figure 6.3.1 : Illustration of the vector model of orbital angular momentum. (left) A set of states with quantum numbers $l = 1$, and $m_l = -1, 0, +1$,. (right) A set of states with quantum numbers $l = 2$, and $m_l = -2, -1, 0, +1, +2$. (Public Domain; Maschen via Wikipedia)

The Meaning of Commutation of Two Operators

The mathematics of commutation relations is relatively straightforward, but what does it physically mean for an observable (Hermitian operator) to commute with another observable (Hermitian operator) in quantum mechanics?

If two operators $\hat{A}$ and $\hat{B}$ commute with each other then

$$\hat{A}\hat{B} - \hat{B}\hat{A} = 0,$$

which can be rearranged to

$$\hat{A}\hat{B} = \hat{B}\hat{A}.$$

This is not a trivial statement and many operations do not commute and hence the end-result depends on how you have ordered the operations.

If you recall that operators act on quantum mechanical states and give you a new state in return, then this means that with $\hat{A}$ and $\hat{B}$ commuting, the state you obtain from letting first $\hat{A}$ act and then $\hat{B}$ act on some initial state is the same as if you let first $\hat{B}$ and then $\hat{A}$ act on that state, i.e.,

$$\hat{A}\hat{B}|\psi\rangle = \hat{B}\hat{A}|\psi\rangle.$$

Recall that when you perform a quantum mechanical measurement, you will always measure an eigenvalue of your operator, and after the measurement your state is left in the corresponding eigenstate. The eigenstates to the operator are precisely those states for which there is **no uncertainty** in the measurement: You will **always** measure the eigenvalue.

Therefore, $\hat{B}|a\rangle$ must be an eigenfunction of $\hat{A}$ with eigenvalue a just like $|a\rangle$ itself is. That is essentially saying that $|a\rangle$ is an eigenfunction of $\hat{B}$.

A key example of this is since $\hat{L}^2$ and $\hat{L}_x$ commute (Example 6.3.1) then both operators share the same eigenstates. Hence, we do no need to solve two eignevalue problems:

$$\hat{L}^2|\psi\rangle = \lambda|\psi\rangle$$

and

$$\hat{L}_x|\psi\rangle = \beta|\psi\rangle$$

If we solve one, we then know the eigenvalues ($|\psi\rangle$) for the other!

What does it mean when some observable $\hat{A}$ commutes with the Hamiltonian $\hat{H}$? First, we get all the result from above: There is a simultaneous eigenbasis of the energy-eigenstates and the eigenstates of $\hat{A}$. This can yield a tremendous simplification of the task of solving Schrödinger equations. For example, the Hamiltonian of the hydrogen atom commutes with $\hat{L}$, the angular momentum operator, and with $\hat{L}_z$, its z-component. This tells you that you can classify the eigenstates by an angular- and magnetic quantum number l and m.

Summary

In the quantum world, angular momentum is quantized. The square of the magnitude of the angular momentum (determined by the eigenvalues of the $\hat{L}^2$ operator) can only assume one of the discrete set of values

$$L^2 = l(l+1)\hbar^2$$

or the magnitude of the angular momentum

$$L = \sqrt{l(l+1)}\hbar$$

with $l = 0, 1, 2, ...$

The z-component of the angular momentum (i.e., projection of L onto the z-axis) is also quantized with

$$L_z = m_l\hbar$$

with $m_l = -l, 0-1, ..., 0, ... + l + 1, l$ for a given value of l. Hence, l and m_l are the *angular momentum quantum number* and the *magnetic quantum number,* respectively.

Contributors and Attributions

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6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers

Learning Objectives

- Recognize how the hydrogen atomic orbitals vary as a function of the three primary quantum numbers

The solutions to the hydrogen atom Schrödinger equation discussed previously are functions that are products of a **spherical harmonic function** and a **radial function**.

$$\psi_{n,l,m_l}(r,\theta,\varphi) = \underbrace{R_{n,l}(r)}_{radial}\underbrace{Y_l^{m_l}(\theta,\varphi)}_{angular} \tag{6.4.1}$$

The wavefunctions for the hydrogen atom depend upon the three variables r, θ, and φ and the three quantum numbers n, l, and m_l. The variables give the position of the electron relative to the proton in spherical coordinates. The absolute square of the wavefunction, $|\psi(r,\theta,\varphi)|^2$, evaluated at r, θ, and φ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r, θ, and φ.

Exercise 6.4.1

Evaluate the following integrals

a. $\langle\psi(r,\theta,\varphi)|\psi(r,\theta,\varphi)\rangle$
b. $\langle\psi(r,\theta,\varphi)|\psi(r',\theta',\varphi')\rangle$

Answer available at the end of this section.

Answer available at the end of this section.

The quantum numbers n, l, and m_l have names:

- n is called the **principal quantum number**,
- l is called the **angular momentum quantum number**, and
- m_l is called the **magnetic quantum number** because the energy in a magnetic field depends upon m_l.

Often l is called the azimuthal quantum number because it is a consequence of the θ-equation, which involves the azimuthal angle Θ, referring to the angle to the zenith.

The three quantum numbers have specific values that are dictated by the physical constraints or boundary conditions imposed upon the Schrödinger equation: n must be an integer greater than 0, l can have the values 0 to n-1, and m_l can have $2l+1$ values ranging from $-l$ to $+l$ in unit or integer steps. The values of the quantum number l usually are coded by a letter: s means 0, p means 1, d means 2, f means 3; the next codes continue alphabetically (e.g., g means $l = 4$). The quantum numbers specify the quantization of physical quantities. The discrete energies of different states of the hydrogen atom are given by n, the magnitude of the angular momentum is given by l, and one component of the angular momentum (usually chosen by chemists to be the z-component) is given by m_l. The total number of orbitals with a particular value of n is n^2.

Exercise 6.4.4

Consider several values for n, and show that the number of orbitals for each n is n^2.

Exercise 6.4.5

Construct a table summarizing the allowed values for the quantum numbers n, l, and m_l for energy levels 1 through 7 of hydrogen.

Exercise 6.4.6

The notation 3d specifies the quantum numbers for an electron in the hydrogen atom. What are the values for n and l ? What are the values for the energy and angular momentum? What are the possible values for the magnetic quantum number? What are the possible orientations for the angular momentum vector?

Radial Part of the Wavefunction

The asymptotic behavior (i.e., far away from the nucleus) to the radial part of the wavefunction is

$$R_{\text{asymptotic}}(r) \sim \exp\left(-\frac{r}{n}a_0\right) \tag{6.4.2}$$

where n will turn out to be a quantum number and a_0 is the Bohr radius (~52.9 pm). Note that this function decreases exponentially with distance, in a manner similar to the decaying exponential portion of the harmonic oscillator wavefunctions, but with a different distance dependence, r vs. r^2.

Exercise 6.4.2

What happens to the magnitude of $R_{\text{asymptotic}}(r)$ as the distance r from the proton approaches infinity? Sketch a graph of the function, $R_{\text{asymptotic}}(r)$. Why might this behavior be expected for an electron in a hydrogen atom?

Answer available at the end of this section.

The polynomials produced by the truncation of the power series are related to the associated Laguerre polynomials, $L_{n,l}(r)$, where the set of c_i are constant coefficients.

$$L_{n,l}(r) = \sum_{r=0}^{n-l-1} c_i r^i \tag{6.4.3}$$

These polynomials are identified by two indices or quantum numbers, n and l. Physically acceptable solutions require that n must be greater than or equal to $l+1$. The smallest value for l is zero, so the smallest value for n is 1. The angular momentum quantum number affects the solution to the radial equation because it appears in the radial differential equation, (Equation 6.4.1).

The $R(r)$ functions that solve the radial differential Equation 6.4.1, are products of the associated Laguerre polynomials and the exponential factor, multiplied by a normalization factor $(N_{n,l})$ and $\left(\frac{r}{a_0}\right)^l$.

$$R(r) = N_{n,l}\left(\frac{r}{a_0}\right)^l L_{n,l}(r) e^{-\frac{r}{na_0}} \tag{6.4.4}$$

The decreasing exponential term overpowers the increasing polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of r. The first six radial functions are provided in Table 6.4.1 . Note that the functions in the table exhibit a dependence on Z, the atomic number of the nucleus. As discussed later in this chapter, other one electron systems have electronic states analogous to those for the hydrogen atom, and inclusion of the charge on the nucleus allows the same wavefunctions to be used for all one-electron systems. For hydrogen, $Z = 1$.

Table 6.4.3 : Radial functions for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

	n	l	$R_{n,l}(\rho)$
R_{10}	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$
R_{20}	2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\rho)e^{-\rho/2}$
R_{21}	2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/2}$
R_{30}	3	0	$\frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} (27-18\rho+2\rho^2)e^{-\rho/3}$
R_{31}	3	1	$\frac{1}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} (6\rho+\rho^2)e^{-\rho/3}$
R_{32}	3	2	$\frac{1}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}$

The constraint that n be greater than or equal to $l+1$ also turns out to quantize the energy, producing the same quantized expression for hydrogen atom energy levels that was obtained from the Bohr model of the hydrogen atom.

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2}$$

Bohr Theory vs. Schrödinger Theory

It is interesting to compare the results obtained by solving the Schrödinger equation with Bohr's model of the hydrogen atom. There are several ways in which the Schrödinger and Bohr models differ.

1. First, and perhaps most strikingly, the Schrödinger model does not produce well-defined orbits for the electron. The wavefunctions only give us the probability for the electron to be at various directions and distances from the proton.
2. Second, the quantization of angular momentum is different from that proposed by Bohr. Bohr proposed that the angular momentum is quantized in integer units of $\hbar$, while the Schrödinger model leads to an angular momentum of $\sqrt{(l(l+1)}\hbar$.
3. Third, the quantum numbers appear naturally during solution of the Schrödinger equation while Bohr had to postulate the existence of quantized energy states. Although more complex, the Schrödinger model leads to a better correspondence between theory and experiment over a range of applications that was not possible for the Bohr model.

Exercise 6.4.3

Explain how the Schrödinger equation leads to the conclusion that the angular momentum of the hydrogen atom can be zero, and explain how the existence of such states with zero angular momentum contradicts Bohr's idea that the electron is orbiting around the proton in the hydrogen atom.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

Answers

a. This integral is equal to one since $\psi(r,\theta,\varphi)$ are normalized eigenstates.

b. However, we can explicitly evaluate this integral for any arbitrary pair of eigenstates

$$\langle\psi(r,\theta,\varphi)|\psi(r',\theta',\varphi')\rangle = \int_{allspace} \psi^*(r,\theta,\varphi)\psi(r',\theta',\varphi')d\tau$$

$$= \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\varphi(r^2\sin(\theta)) \overbrace{\psi*(r,\theta,\varphi)}^{R_{n,l}(r)Y_l^{m_l}(\theta,\varphi)} \overbrace{\psi(r,\theta,\varphi)}^{R_{n',l'}(r)Y_{l'}^{m_l'}(\theta,\varphi)}$$

$$= \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\varphi(r^2\sin(\theta))[R_{n,l}(r)Y_l^{m_l}(\theta,\varphi)][R_{n',l'}(r)Y_{l'}^{m_l'}(\theta,\varphi)]$$

$$= \left[\int_0^\infty r^2[R_{n,l}(r)R_{n',l'}(r)]dr\right]\left[\int_0^{2\pi}\int_0^\pi \sin(\theta)[Y_l^{m_l}(\theta,\varphi)Y_{l'}^{m_l'}(\theta,\varphi)]d\theta d\varphi\right]$$

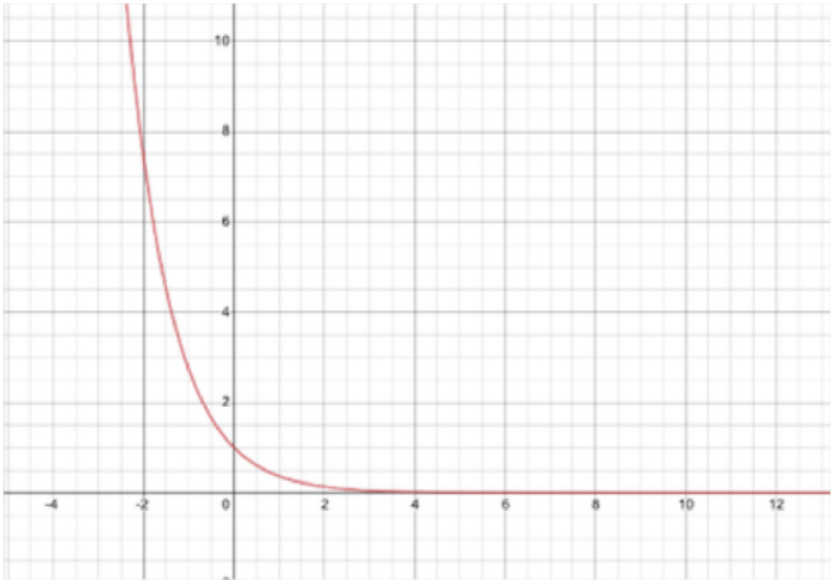
$$= \langle R_{n,l}(r)|R_{n',l'}(r)\rangle\langle Y_l^{m_l}(\theta,\varphi)|Y_{l'}^{m_l'}(\theta,\varphi)\rangle$$

$$= (\delta_{nn'}\delta_{ll'})(\delta_{ll'}\delta_{mm'}) = \delta_{nn'}\delta_{ll'}\delta_{mm'}$$

While part a demonstrates normality of the eigenstates, part b demonstrates the orthogonality of the eigenstate (and normality too).

$$R(r) = e^{-\frac{c}{n}a_0}$$

As r approaches infinity, the exponential decay goes to zero, this is to be expected as the likelihood of an electron being found at an infinite distance away is almost zero too.



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6.5: s-orbitals are Spherically Symmetric

The hydrogen atom wavefunctions, $\psi(r, \theta, \varphi)$, are called atomic orbitals. An atomic orbital is a function that describes one electron in an atom. The wavefunction with $n = 1$, l = 0 is called the 1s orbital, and an electron that is described by this function is said to be “in” the ls orbital, i.e. have a 1s orbital state. The constraints on n, l, and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

Visualizing the variation of an electronic wavefunction with r, θ, and φ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron deficient part of one molecule is attracted to an electron rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

We can obtain an energy and one or more wavefunctions for every value of n, the principal quantum number, by solving Schrödinger's equation for the hydrogen atom. A knowledge of the wavefunctions, or probability amplitudes ψ_n, allows us to calculate the probability distributions for the electron in any given quantum level. When n = 1, the wavefunction and the derived probability function are independent of direction and depend only on the distance r between the electron and the nucleus. In Figure 6.5.1 , we plot both ψ_1 and P_1 versus r, showing the variation in these functions as the electron is moved further and further from the nucleus in any one direction. (These and all succeeding graphs are plotted in terms of the atomic unit of length, $a_0 = 0.529 \times 10^{-8}\ cm$.)

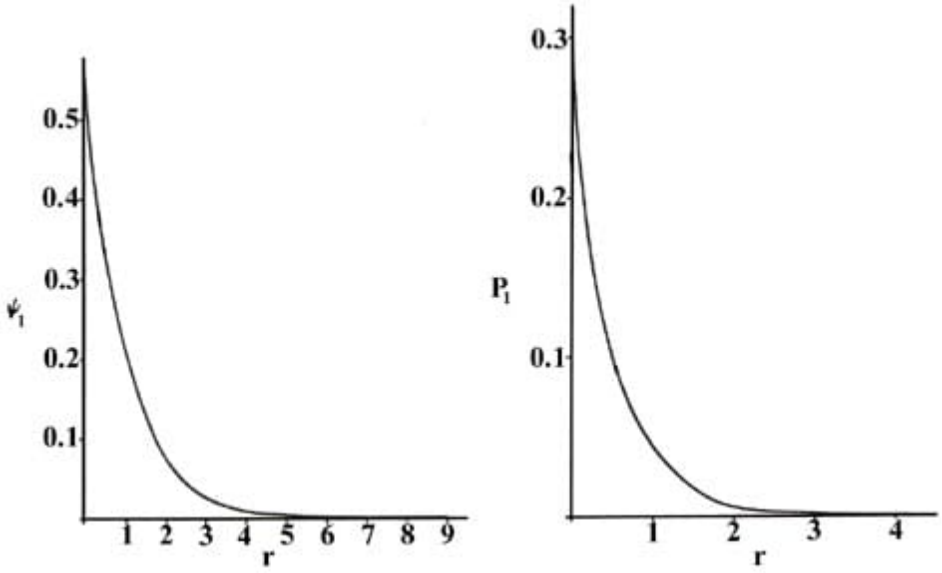


Figure 6.5.1 : The wavefunction and probability distribution as functions of r for the $n = 1$ level of the H atom. The functions and the radius r are in atomic units in this and succeeding figures.

Two interpretations can again be given to the P_1 curve. An experiment designed to detect the position of the electron with an uncertainty much less than the diameter of the atom itself (using light of short wavelength) will, if repeated a large number of times, result in Figure 6.5.1 for P_1. That is, the electron will be detected close to the nucleus most frequently and the probability of observing it at some distance from the nucleus will decrease rapidly with increasing r. The atom will be ionized in making each of these observations because the energy of the photons with a wavelength much less than 10^{-8} cm will be greater than K, the amount of energy required to ionize the hydrogen atom. If light with a wavelength comparable to the diameter of the atom is employed in the experiment, then the electron will not be excited but our knowledge of its position will be correspondingly less precise. In these experiments, in which the electron's energy is not changed, the electron will appear to be "smeared out" and we may interpret P_1 as giving the fraction of the total electronic charge to be found in every small volume element of space. (Recall that the addition of the value of P_n for every small volume element over all space adds up to unity, i.e., one electron and one

electronic charge.)

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately does not reveal the shape of an orbital very well. The shape can be revealed better in a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$.

We could also represent the distribution of negative charge in the hydrogen atom in the manner used previously for the electron confined to move on a plane (Figure 6.5.2), by displaying the charge density in a plane by means of a contour map. Imagine a plane through the atom including the nucleus. The density is calculated at every point in this plane. All points having the same value for the electron density in this plane are joined by a contour line (Figure 6.5.2). Since the electron density depends only on *r*, the distance from the nucleus, and not on the direction in space, the contours will be circular. A contour map is useful as it indicates the "shape" of the density distribution.

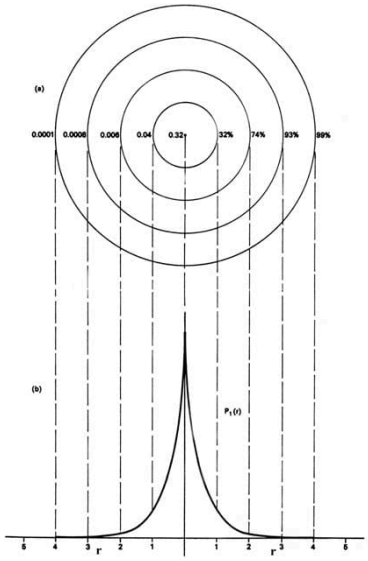


Figure 6.5.2 : (a) A contour map of the electron density distribution in a plane containing the nucleus for the $n = 1$ level of the H atom. The distance between adjacent contours is 1 au. The numbers on the left-hand side on each contour give the electron density in au. The numbers on the right-hand side give the fraction of the total electronic charge which lies within a sphere of that radius. Thus 99% of the single electronic charge of the H atom lies within a sphere of radius 4 au (or diameter = $4.2 \times 10^{-8}\ cm$). (b) This is a profile of the contour map along a line through the nucleus. It is, of course, the same as that given previously in Figure 6.5.1 for P_1, but now plotted from the nucleus in both directions.

When the electron is in a definite energy level we shall refer to the P_n distributions as ***electron density distributions***, since they describe the manner in which the total electronic charge is distributed in space. The electron density is expressed in terms of the number of electronic charges per unit volume of space, e^-/V. The volume *V* is usually expressed in atomic units of length cubed, and one atomic unit of electron density is then e^-/a_0^3. To give an idea of the order of magnitude of an atomic density unit, 1 au of charge density e^-/a_0^3 = 6.7 electronic charges per cubic Ångstrom. That is, a cube with a length of $0.52917 \times 10^{-8}\ cm$, if uniformly filled with an electronic charge density of 1 au, would contain 6.7 electronic charges.

For every value of the energy E_n, for the hydrogen atom, there is a degeneracy equal to n^2. Therefore, for *n* = 1, there is but one atomic orbital and one electron density distribution. However, for *n* = 2, there are four different atomic orbitals and four different electron density distributions, all of which possess the same value for the energy, E_2. Thus for all values of the principal quantum number *n* there are n^2 different ways in which the electronic charge may be distributed in three-dimensional space and still possess the same value for the energy. For every value of the principal quantum number, ***one*** of the possible atomic orbitals is independent of direction and gives a spherical electron density distribution which can be represented by circular contours as has been exemplified above for the case of *n* = 1. The other atomic orbitals for a given value of *n* exhibit a directional dependence and predict density distributions which are not spherical but are concentrated in planes or along certain axes. The angular dependence of the atomic orbitals for the hydrogen atom and the shapes of the contours of the corresponding electron

density distributions are intimately connected with the angular momentum possessed by the electron.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, $R(r)$, for the 1s and 2s orbitals plotted in Figure 6.5.3 . The 1s function in Figure $6.5.3; left$ starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

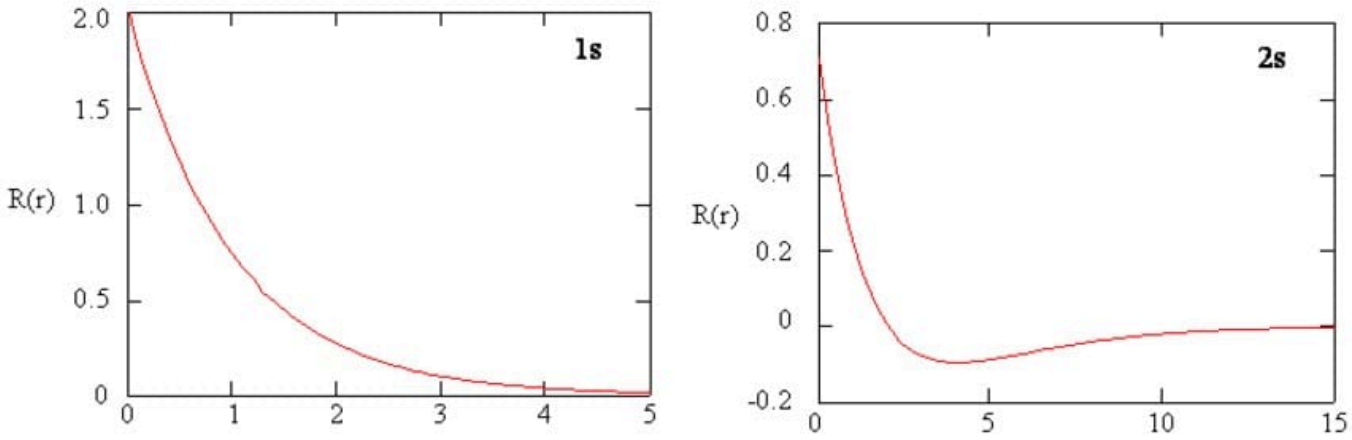


Figure 6.5.3 : Radial function, $R(r)$, for the 1s and 2s orbitals. For an interactive graph click here.

Next notice how the radial function for the 2s orbital, Figure $6.5.3; right$, goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$.

Exercise 6.5.1

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

Exercise 6.5.2

What mathematical feature of each of the radial functions controls the number of radial nodes?

Exercise 6.5.3 : Radial Nodes

At what value of r does the 2s radial node occur?

Exercise 6.5.4

Make a table that provides the energy, number of radial nodes, and the number of angular nodes and total number of nodes for each function with $n = 1$, $n = 2$, and $n = 3$. Identify the relationship between the energy and the number of nodes. Identify the relationship between the number of radial nodes and the number of angular nodes.

Answer available at the end of this section.

Radial probability densities for the 1s and 2s atomic orbitals are plotted in Figure 6.5.4 .

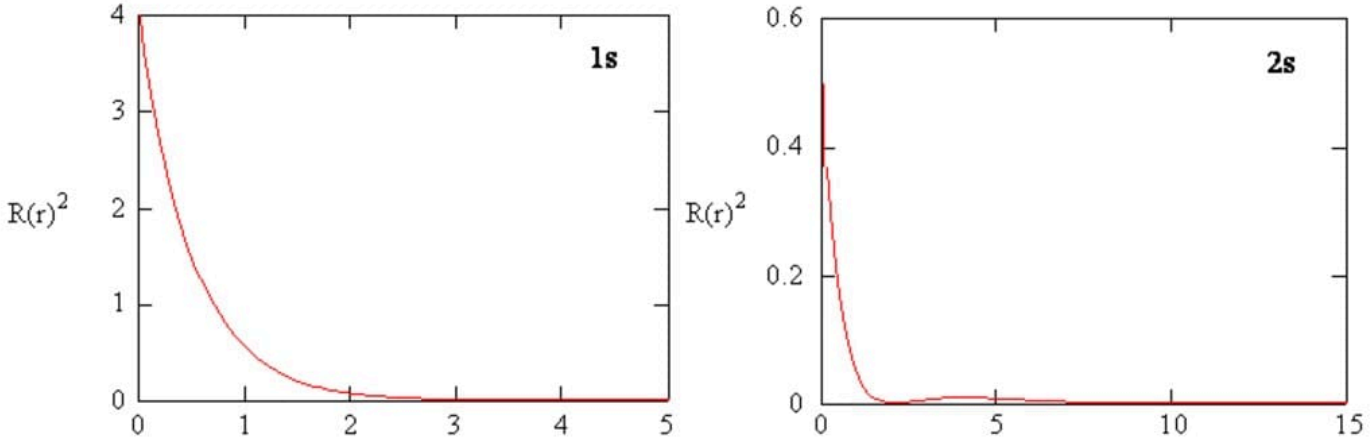


Figure 6.5.4 : Radial densities ($R(r)^*R(r)$) for the 1s and 2s orbitals.

Radial Distribution Functions

Rather than considering the amount of electronic charge in one particular small element of space, we may determine the total amount of charge lying within a thin spherical shell of space. Since the distribution is independent of direction, consider adding up all the charge density which lies within a volume of space bounded by an inner sphere of radius r and an outer concentric sphere with a radius only infinitesimally greater, say $r + \Delta r$. The area of the inner sphere is $4\pi r^2$ and the thickness of the shell is Δr. Thus the volume of the shell is $4\pi r^2 \Delta r$ and the product of this volume and the charge density $P_1(r)$, which is the charge or number of electrons per unit volume, is therefore the total amount of electronic charge lying between the spheres of radius r and $r + \Delta r$. The product $4\pi r^2 P_n$ is given a special name, the **radial distribution function**.

Volume Element for a Shell in Spherical Coordinates

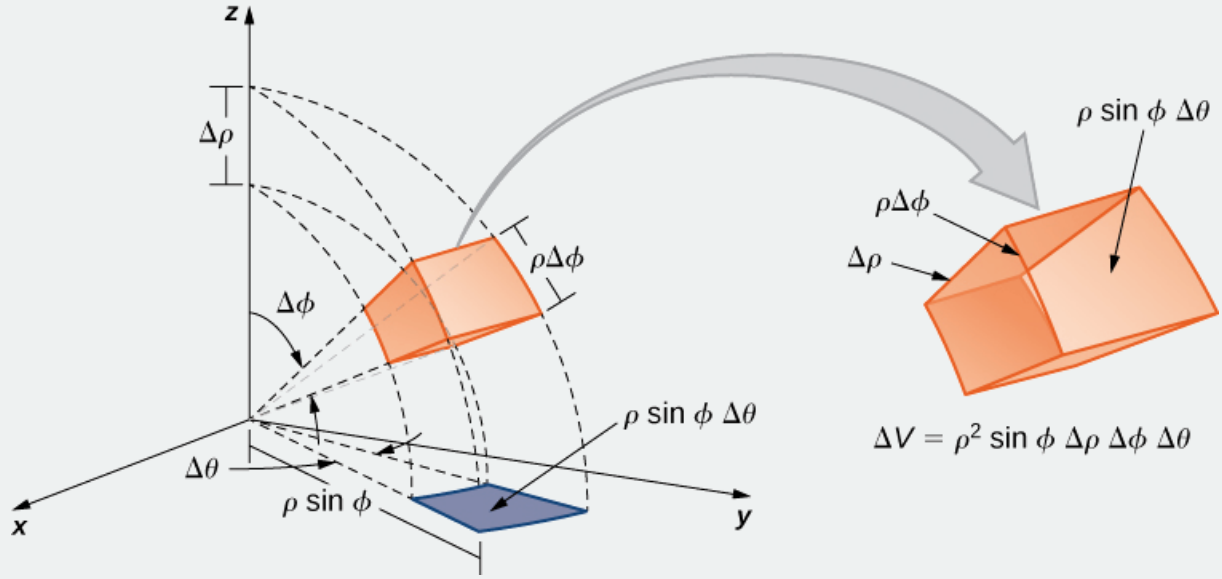
The reader may wonder why the volume of the shell is not taken as:

$$\frac{4}{3}\pi\left[(r+\Delta r)^3 - r^3\right]$$

the difference in volume between two concentric spheres. When this expression for the volume is expanded, we obtain

$$\frac{4}{3}\pi\left(3r^2\Delta r + 3r\Delta r^2 + \Delta r^3\right)$$

and for very small values of Δr the $3r\Delta r^2$ and Δr^3 terms are negligible in comparison with $3r^2\Delta r$. Thus for small values of Δr, the two expressions for the volume of the shell approach one another in value and when Δr represents an infinitesimal small increment in r they are identical.



The volume element of a box in spherical coordinates. (CC BY; OpenStax).

The radial distribution function is plotted in Figure 6.5.5 for the ground state of the hydrogen atom.

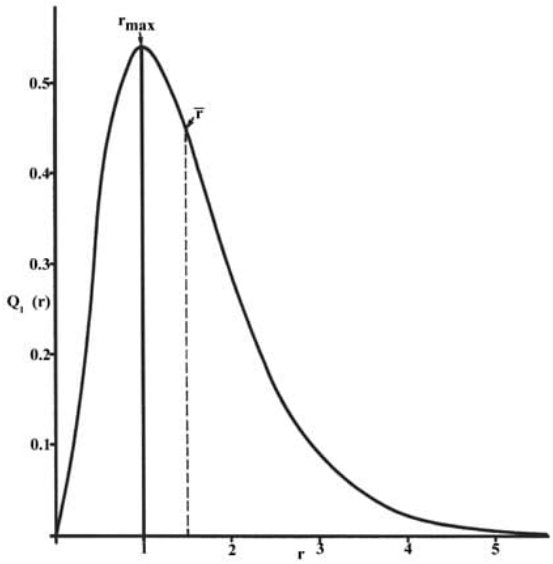


Figure 6.5.5 : The radial distribution function for an H atom. The value of this function at some value of r when multiplied by δr gives the number of electronic charges within the thin shell of space lying between spheres of radius r and $r + \delta r$.

The curve passes through zero at $r = 0$ since the surface area of a sphere of zero radius is zero. As the radius of the sphere is increased, the volume of space defined by $4\pi r^2 Dr$ increases. However, as shown in Figure 6.5.4 , the absolute value of the electron density at a given point decreases with r and the resulting curve must pass through a maximum. This maximum occurs at $r_{max} = a_0$. Thus more of the electronic charge is present at a distance a_o, out from the nucleus than at any other value of r. Since the curve is unsymmetrical, the average value of r, denoted by $\bar{r}$, is not equal to r_{max}. The average value of r is indicated on the figure by a dashed line. A "picture" of the electron density distribution for the electron in the $n = 1$ level of the hydrogen atom would be a spherical ball of charge, dense around the nucleus and becoming increasingly diffuse as the value of r is increased.

> The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the proton. Since the area of a spherical surface is $4\pi r^2$, the radial distribution function is given by $4\pi r^2 R(r)^* R(r)$.

Radial distribution functions are shown in Figure 6.5.6 . At small values of r, the radial distribution function is low because the small surface area for small radii modulates the high value of the radial probability density function near the nucleus. As we

increase r, the surface area associated with a given value of r increases, and the r^2 term causes the radial distribution function to increase even though the radial probability density is beginning to decrease. At large values of r, the exponential decay of the radial function outweighs the increase caused by the r^2 term and the radial distribution function decreases.

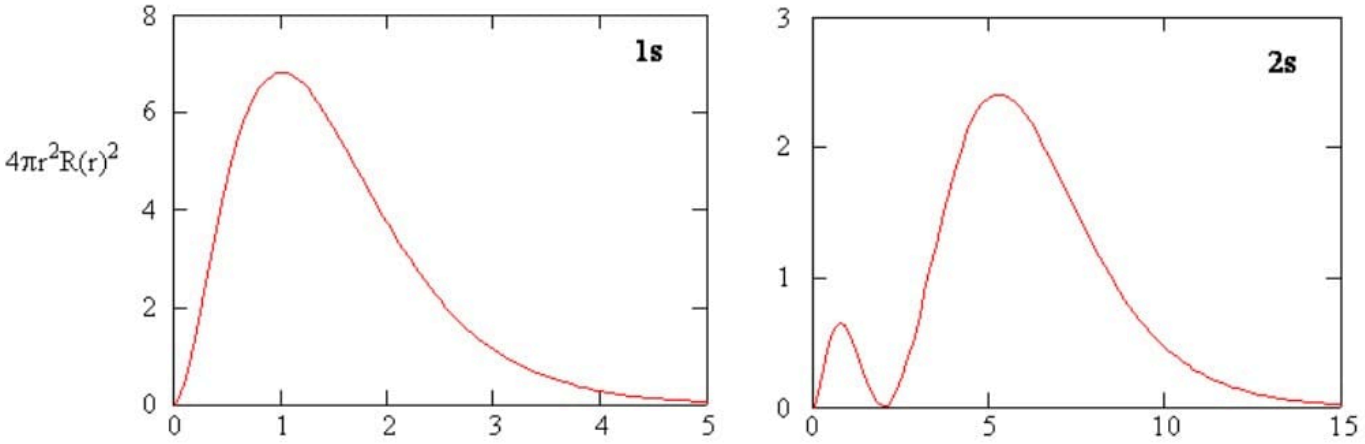


Figure 6.5.6 : The radial distribution function ($4\pi r^2 R(r)^* R(r)$) for the 1s and 2s orbitals. Compare to the radial functions in Figure 6.5.3 or the radial densities in Figure 6.5.4 . For an interactive graph click here.

Example 6.5.1 :

Calculate the probability of finding a 1s hydrogen electron being found within distance $2a_o$ from the nucleus.

Solution available at the end of this section.

Summary

This completes the description of the most stable state of the hydrogen atom, the state for which $n = 1$. Before proceeding with a discussion of the excited states of the hydrogen atom we must introduce a new term. When the energy of the electron is increased to another of the allowed values, corresponding to a new value for n, y_n and P_n change as well. The wavefunctions y_n for the hydrogen atom are given a special name, ***atomic orbitals***, because they play such an important role in all of our future discussions of the electronic structure of atoms. In general the word orbital is the name given to a wavefunction which determines the motion of a single electron. If the one-electron wavefunction is for an atomic system, it is called an atomic orbital.

Do not confuse the word orbital with the classical word and notion of an orbit. First, an orbit implies the knowledge of a definite trajectory or path for a particle through space which in itself is not possible for an electron. Secondly, an orbital, like the wavefunction, has no physical reality but is a mathematical function which when squared gives the physically measurable electron density distribution.

Contributors and Attributions

- Dr. Richard F.W. Bader (Professor of Chemistry / McMaster University)
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

Answers

	Energy 1.Particle in a Box ($h^2n^2/8m_eL^2$) 2.Harmonic Oscillator($(n+0.5)\hbar\omega$) 3.Hydrogen ($-13.6eV/n^2$)	Number of Radial Nodes (n-l-1)	Number of Angular Nodes l = (n-1) l : s =0 p = 1 d = 2	Total Number of Nodes
n = 1	1. 6.02 *10^{-38} J/L^2 2. 1.5$\hbar\omega$ 3. -13.6 eV	-	0	0
n = 2	1. 6.02 *10^{-38} J/L^2 2. 2.5$\hbar\omega$ 3. -3.4 eV	for s: 1 for p: 0	for s: 0 for p: 1	1
n = 3	1. 6.02 *10^{-38} J/L^2 2. 3.5$\hbar\omega$ 3. 1.51 eV	for s: 2 for p: 1 for d: 0	for s: 0 for p:1 for d: 2	2

For a particle in a box the energy is equivalent to $E_n = 6.02 \times 10^{-38} n^2 L^2$ where n is any value greater than and not equal to 0 and L is the length of the box.

Note the wavefunction of hydrogen 1s orbital which is

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\rho}$$

with $\rho = \frac{r}{a_0}$.

The probability of finding the electron within $2a_0$ distance from the nucleus will be:

$$prob = \underbrace{\int_0^{\pi} \sin\theta \, d\theta}_{over\ \theta} \overbrace{\frac{1}{\pi a_0^3} \int_0^{2a_0} r^2 e^{-2r/a_0} dr}^{over\ r} \underbrace{\int_0^{2\pi} d\phi}_{over\ \phi}$$

Since $\int_0^{\pi} \sin\theta d\theta = 2$ and $\int_0^{2\pi} d\phi = 2\pi$, we have

$$\begin{aligned}
prob &= 2 \times 2\pi \times \frac{1}{\pi a_0^3} \int_0^2 a_0(-a_0/2) r^2 de^{-2r/a_0} \\
&= \frac{4}{a_0^3} \left(-\frac{a_0}{2}\right) (r^2 e^{-2r/a_0}|_0^{2a_0} - \int_0^{2a_0} 2re^{-2r/a_0} dr) \\
&= -\frac{2}{a_0^2} [(2a_0)^2 e^{-4} - 0 - 2 \int_0^{2a_0} r \left(-\frac{a_0}{2}\right) de^{-2r/a_0}] \\
&= -\frac{2}{a_0^2} 4a_0^2 e^{-4} + \frac{4}{a_0^2} (-\frac{a_0}{2}) (re^{-2r/a_0}|_0^{2a_0} - \int_0^{2a_0} e^{-2r/a_0} dr) \\
&= -8e^{-4} - \frac{2}{a_0} \left[2a_0 e^{-4} - 0 - (-\frac{a_0}{2}) e^{-2r/a_0}|_0^{2a_0}\right] \\
&= -8e^{-4} - 4e^{-4} - e^{2r/a_0}|_0^{2a_0} \\
&= -12e^{-4} - (e^{-4} - 1) = 1 - 13e^{-4} = 0.762
\end{aligned}$$

There is a 76.2% probability that the electrons will be within $2a_o$ of the nucleus in the 1s eigenstate.

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6.6: Orbital Angular Momentum and the p-Orbitals

Learning Objectives

- To relate the classical orbital angular momentum for an particle to the quantum equivalent
- Characterize the mangnitude and orientation of orbital angular momentum for an electron in terms of quantum numbers

Classical Orbital Angular Momentum

The physical quantity known as angular momentum plays a dominant role in the understanding of the electronic structure of atoms. To gain a physical picture and feeling for the angular momentum it is necessary to consider a model system from the classical point of view. The simplest classical model of the hydrogen atom is one in which the electron moves in a circular orbit with a constant speed or angular velocity (Figure 6.6.1). Just as the linear momentum $m\vec{v}$ plays a dominant role in the analysis of linear motion, so angular momentum (L) plays the central role in the analysis of a system with circular motion as found in the model of the hydrogen atom.

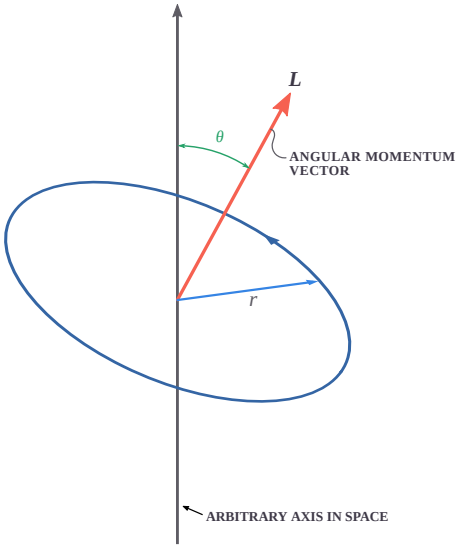


Figure 6.6.1 : The angular momentum vector for a classical model of the atom. (CC BY-NC; Ümit Kaya via LibreTexts)

In Figure 6.6.1 , m is the mass of the electron, $\vec{v}$ is the linear velocity (the velocity the electron would possess if it continued moving at a tangent to the orbit) and r is the radius of the orbit. The linear velocity $\vec{v}$ is a vector since it possesses at any instant both a magnitude and a direction in space. Obviously, as the electron rotates in the orbit the direction of $\vec{v}$ is constantly changing, and thus the linear momentum $m\vec{v}$ is ***not*** constant for the circular motion. This is so even though the speed of the electron (i.e, the magnitude of $\vec{v}$ which is denoted by $|\vec{v}|$) remains unchanged. According to Newton's second law, a force must be acting on the electron if its momentum changes with time. This is the force which prevents the electron from flying on tangent to its orbit. In an atom the attractive force which contains the electron is the electrostatic force of attraction between the nucleus and the electron, directed along the radius *r* at right angles to the direction of the electron's motion.

The angular momentum, like the linear momentum, is a vector and is defined as follows:

$$|\vec{L}| = m\nu r$$

The angular momentum vector $\vec{L}$ is directed along the axis of rotation. From the definition it is evident that the angular momentum vector will remain constant as long as the speed of the electron in the orbit is constant ($|\vec{v}|$ remains unchanged) and the plane and radius of the orbit remain unchanged. Thus for a given orbit, the angular momentum is constant as long as the angular velocity of

the particle in the orbit is constant. In an atom the only force on the electron in the orbit is directed along r; it has no component in the direction of the motion. The force acts in such a way as to change only the linear momentum. Therefore, while the linear momentum is not constant during the circular motion, the angular momentum is. A force exerted on the particle in the direction of the vector $\vec{v}$ would change the angular velocity and the angular momentum. When a force is applied which does change $\vec{L}$, a ***torque*** is said to be acting on the system. Thus angular momentum and torque are related in the same way as are linear momentum and force.

Quantum Angular Momentum

The important point of the above discussion is that both the angular momentum and the energy of an atom remain constant if the atom is left undisturbed. Any physical quantity which is constant in a classical system is both conserved and quantized in a quantum mechanical system. Thus both the energy and the angular momentum are quantized for an atom.

> Any physical quantity which is constant in a classical system is both conserved and quantized in a quantum mechanical system.

There is a quantum number, denoted by l, which governs the magnitude of the angular momentum, just as the quantum number n determines the energy. The ***magnitude*** of the angular momentum may assume only those values given by:

$$|L| = \sqrt{l(l+1)}\hbar \tag{6.6.1}$$

with $l = 0, 1, 2, 3, ...n - 1$.

Furthermore, the value of *n* limits the maximum value of the angular momentum as the value of *l* cannot be greater than *n* - 1. For the state *n* = 1 discussed above, l may have the value of zero only. When *n* = 2, *l* may equal 0 or 1, and for *n* = 3, *l* = 0 or 1 or 2, etc. When *l* = 0, it is evident from Equation 6.6.1 that the angular momentum of the electron is zero. The atomic orbitals which describe these states of zero angular momentum are called s orbitals. The *s* orbitals are distinguished from one another by stating the value of *n*, the principal quantum number. They are referred to as the 1s, 2s, 3s, etc., atomic orbitals.

The preceding discussion referred to the 1s orbital since for the ground state of the hydrogen atom $n = 1$ and $l = 0$. This orbital, and all s orbitals in general, predict spherical density distributions for the electron as discussed previously.

It is common usage to refer to an electron as being "in" an orbital even though an orbital is, but a mathematical function with no physical reality. To say an electron is in a particular orbital is meant to imply that the electron is in the quantum state which is described by that orbital. For example, when the electron is in the 2s orbital the hydrogen atom is in a state for which $n = 2$ and $l = 0$.

Comparing these results with those for the 1s orbital in Figure 6.6.2 we see that as n increases the average value of r increases. This agrees with the fact that the energy of the electron also increases as n increases. The increased energy results in the electron being on the average pulled further away from the attractive force of the nucleus. As in the simple example of an electron moving on a line, nodes (values of r for which the electron density is zero) appear in the probability distributions. The number of nodes increases with increasing energy and equals $n - 1$.

When the electron possesses angular momentum the density distributions are no longer spherical. In fact for each value of l, the electron density distribution assumes a characteristic shapes in Figure 6.6.2 .

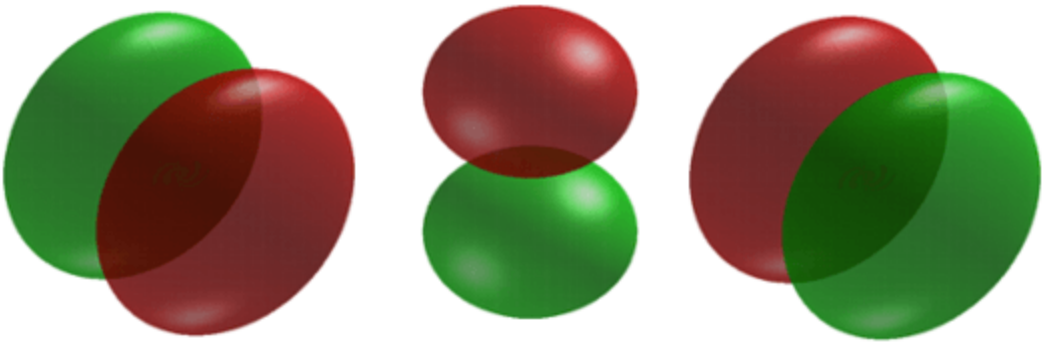


Figure 6.6.2 : The appearance of the three 2p orbitals in three-dimensional space. (CC BY-SA 3.0; I, Sarxos).

When $l = 1$, the orbitals are called *p* orbitals. In this case the orbital and its electron density are concentrated along a line (axis) in space. The 2*p* orbital or wavefunction is positive in value on one side and negative in value on the other side of a plane which is perpendicular to the axis of the orbital and passes through the nucleus. The orbital has a node in this plane, and consequently an electron in a 2*p* orbital does not place any electronic charge density at the nucleus. The electron density of a 1s orbital, on the other hand, is a maximum at the nucleus. The same diagram for the 2*p* density distribution is obtained for any plane which contains this axis. Thus in three dimensions the electron density would appear to be concentrated in two lobes, one on each side of the nucleus, each lobe being circular in cross section Figure 6.6.3 .

An electron possesses orbital angular momentum has a density distributions is no longer spherical.

The m_l Quantum Number and Magnetic Fields

The magnetic quantum number, designated by the letter m_l, is the third quantum numbers which describe the unique quantum state of an electron. The magnetic quantum number distinguishes the orbitals available within a subshell, and is used to calculate the azimuthal component of the orientation of the orbital in space. As with our discussion of rigid rotors, the quantum number m_l refers to the projection of the angular momentum in this arbitrarily chosen direction, conventionally called the z direction or quantization axis. L_z, the magnitude of the angular momentum in the z direction, is given by the formula

$$L_z = m_l \hbar$$

The quantum number m_l refers, loosely, to the direction of the angular momentum vector. The magnetic quantum number m_l only affects the electron's energy if it is in a magnetic field because in the absence of one, all spherical harmonics corresponding to the different arbitrary values of m_l are equivalent. The magnetic quantum number determines the energy shift of an atomic orbital due to an external magnetic field (this is called the Zeeman effect) - hence the name magnetic quantum number. However, the actual magnetic dipole moment of an electron in an atomic orbital arrives not only from the electron angular momentum, but also from the electron spin, expressed in the spin quantum number, which is the fourth quantum number. m_s and discussed in the next chapter.

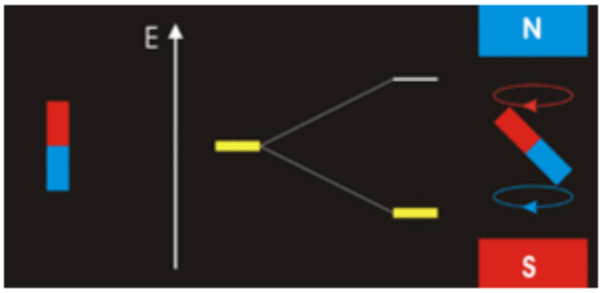


Figure 6.6.3 : The orbiting electron with a non-zero l value acts like a magnetic field with is no energetic difference for any particular orientation (only one energy state, on the left). However, in external magnetic field there is a high-energy state and a low-energy state depending on the relative orientations of the magnet to the external field. (CC SA-BY 3.0; Darekk2).

m_l Which Number Corresponds to which p-Orbital?

The answer is complicated; while $m_l = 0$ corresponds to the p_z, the orbitals for $m_l = +1$ and $m_l = -1$ lie in the xy-plane (see Spherical Harmonics), but not on the axes. The reason for this outcome is that the wavefunctions are usually formulated in spherical coordinates to make the math easier, but graphs in the Cartesian coordinates make more intuitive sense for humans. The p_x and p_y orbitals are constructed via a linear combination approach from radial and angular wavefunctions and converted into xy (this was discussed previously). Thus, it is not possible to directly correlate the values of $m_l = \pm 1$ with specific orbitals. The notion that we can do so is sometimes presented in introductory courses to make a complex mathematical model just a little bit simpler and more intuitive, but it is incorrect.

The three wavefunctions for $n = 2$ and $l = 1$ are as follows.

$$|\psi_{2,1,0}\rangle = r\cos\theta R(r) \tag{6.6.2}$$

$$|\psi_{2,1,+1}\rangle = -\frac{r}{2}\sin\theta e^{i\phi}R(r) \tag{6.6.3}$$

$$|\psi_{2,1,-1}\rangle = +\frac{r}{2}\sin\theta e^{-i\phi}R(r) \tag{6.6.4}$$

The notation is $|\psi_{n,l,m_l}\rangle$ with $R(r)$ is the radial component of this wavefuction, θ is the angle with respect to the z-axis and ϕ is the angle with respect to the xz-plane.

$$R(r) = \sqrt{\frac{Z^5}{32\pi a_0^5}}\mathrm{e}^{-Zr/2a_0}$$

in which Z is the atomic number (or probably better nuclear charge) and a_0 is the Bohr radius.

In switching from spherical to Cartesian coordinates, we make the substitution $z = r\cos\theta$, so:

$$|\psi_{2,1,0}\rangle = zR(r)$$

This is ψ_{2p_z} since the value of ψ is dependent on z: when $z = 0$; $\psi = 0$, which is expected since $z = 0$ describes the xy-plane.

The other two wavefunctions are degenerate in the xy-plane. An equivalent statement is that these two orbitals do not lie on the x- and y-axes, but rather bisect them. Thus it is typical to take linear combinations of them to make the equation look prettier. If any set of wavefunctions is a solution to the Schrödinger equation, then any set of linear combinations of these wavefunctions must also be a solution (Section 2.4). We can do this because of the linearity of the Schrödinger equation.

In the equations below, we're going to make use of some trigonometry, notably Euler's formula:

$$\mathrm{e}^{\mathrm{i}\phi} = \cos\phi + \mathrm{i}\sin\phi \tag{6.6.5}$$

$$\sin\phi = \frac{\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi}}{2\mathrm{i}} \tag{6.6.6}$$

$$\cos\phi = \frac{\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi}}{2} \tag{6.6.7}$$

We're also going to use $x = \sin\theta\cos\phi$ and $y = \sin\theta\sin\phi$.

$$\begin{aligned}\psi_{2p_x} &= \frac{1}{\sqrt{2}}\left(\psi_{2,1,+1} - \psi_{2,1,-1}\right)\\ &= \frac{1}{2}\left(\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi}\right) r\sin\theta f(r)\\ &= r\sin\theta\cos\phi f(r) = x f(r)\\ \psi_{2p_y} &= \frac{\mathrm{i}}{\sqrt{2}}\left(\psi_{2,1,+1} + \psi_{2,1,-1}\right)\\ &= \frac{1}{2\mathrm{i}}\left(\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi}\right) r\sin\theta f(r)\\ &= r\sin\theta\sin\phi f(r) = y f(r)\end{aligned}$$

So, while $m_l = 0$ corresponds to $|p_z\rangle$, $m_l = +1$ and $m_l = -1$ **cannot** be directly assigned to either $|p_x\rangle$ or $|p_y\rangle$, but rather a combination of $|p_x\rangle$ and $|p_y\rangle$. An alternative description is that $m_l = +1$ might correspond to $(|p_x\rangle + |p_y\rangle)$ and $m_l = -1$ might correspond to $(|p_x\rangle - |p_y\rangle)$.

d-Orbitals (even higher angular momenta wavefunctions)

When $l = 2$, the orbitals are called *d* orbitals and Figure 6.6.4 shows the contours in a plane for a 3*d* orbital and its density distribution. Notice that the density is again zero at the nucleus and that there are now two nodes in the orbital and in its density distribution. As the angular momentum of the electron increases, the density distribution becomes increasingly concentrated along an axis or in a plane in space. Only electrons in s orbitals with **zero angular momentum** give spherical density distributions and in addition place charge density at the position of the nucleus.

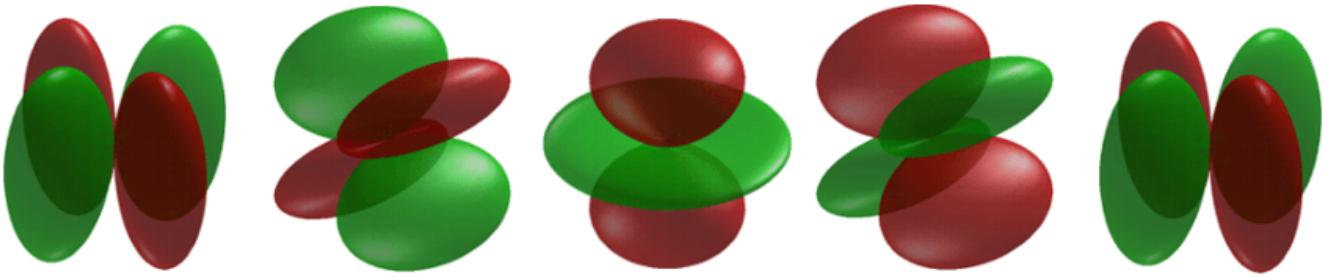


Figure 6.6.4 : The appearance of the 3d electron density distribution in three-dimensional space. (CC BY-SA 3.0; I, Sarxos)

As with the p-orbitals, the only d-orbital that a specific m_l can be ascribed is the d_{z^2} orbitals with $m_l = 0$. The rest are linear combinations of the hydrogen atom wavefunctions with complex spherical harmonic angular components.

There seems to be neither rhyme nor reason for the naming of the states corresponding to the different values of ℓ (s, *p, d, f* for *l* = 0, 1, 2, 3). This set of labels had its origin in the early work of experimental atomic spectroscopy. The letter s stood for sharp, *p* for principal, *d* for diffuse and *f* for fundamental in characterizing spectral lines. From the letter *f* onwards the naming of the orbitals is alphabetical $l = 4, 5, 6 \rightarrow g, h, i, ...$

We have not as yet accounted for the full degeneracy of the hydrogen atom orbitals which we stated earlier to be n^2 for every value of n. For example, when $n = 2$, there are four distinct atomic orbitals. The remaining degeneracy is again determined by the angular momentum of the system. Since angular momentum like linear momentum is a vector quantity, we may refer to the component of the angular momentum vector which lies along some chosen axis. For reasons we shall investigate, the number of values a particular component can assume for a given value of l is $(2l + 1)$. Thus when $l = 0$, there is no angular momentum and there is but a single orbital, an s orbital. When $l = 1$, there are three possible values for the component $(2 \times 1 + 1)$ of the total angular momentum which are physically distinguishable from one another. There are, therefore, three p orbitals. Similarly there are five d orbitals, $(2 \times 2 + 1)$, seven f orbitals, $(2 \times 3 + 1)$, etc. All of the orbitals with the same value of n and l, the three 2p orbitals for example, are similar but differ in their spatial orientations.

To gain a better understanding of this final element of degeneracy, we must consider in more detail what quantum mechanics

predicts concerning the angular momentum of an electron in an atom.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Dr. Richard F.W. Bader (Professor of Chemistry / McMaster University)
- Stack Exchange (Ben Norris and Loong)

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6.7: The Schrödinger Wave Equation for the Hydrogen Atom

Introduction (Schrödinger equation for 1 e- system)

The hydrogen atom, consisting of an electron and a proton, is a two-particle system, and the internal motion of two particles around their center of mass is equivalent to the motion of a single particle with a reduced mass ($m = \frac{m_1 m_2}{m_1+m_2}$). This reduced particle is located at $\vec{r}$, where $\vec{r}$ is the vector specifying the position of the electron relative to the position of the proton. The length r of $\vec{r}$ is the distance between the proton and the electron, and the direction of r is given by the orientation of the vector pointing from the proton to the electron. Since the proton is much more massive than the electron, we will assume that the reduced mass equals the electron mass and the proton is located at the center of mass.

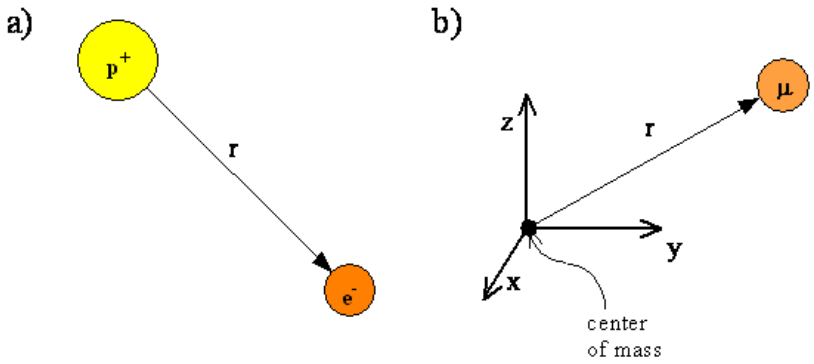


Figure 6.7.1: a) The proton (p^+) and electron (e^-) of the hydrogen atom. b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

Starting with the general Schrödinger equation:

$$\frac{-\hbar^2}{2m}\nabla^2\Psi(\vec{r}) + V(\vec{r})\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{6.7.1}$$

we need an expression for the potential. This is just Coulomb attraction and depends only on the separation distance r:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{6.7.2}$$

where r is the distance between the electron and the proton. The Coulomb potential energy depends inversely on the distance between the electron and the nucleus and does not depend on any angles. Such a potential is called a central potential. Substituting in to equation 6.7.1 this gives us:

$$\frac{-\hbar^2}{2m}\nabla^2\Psi(\vec{r}) + \frac{e^2}{4\pi\epsilon_0 r}\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{6.7.3}$$

Because of the spherical symmetry of the equation it turns out to be better to switch from Cartesian coordinates x, y, z to spherical coordinates in terms of a radius r, as well as angles ϕ, which is measured from the positive x axis in the xy plane and may be between 0 and 2π, and θ, which is measured from the positive z axis towards the xy plane and may be between 0 and π.

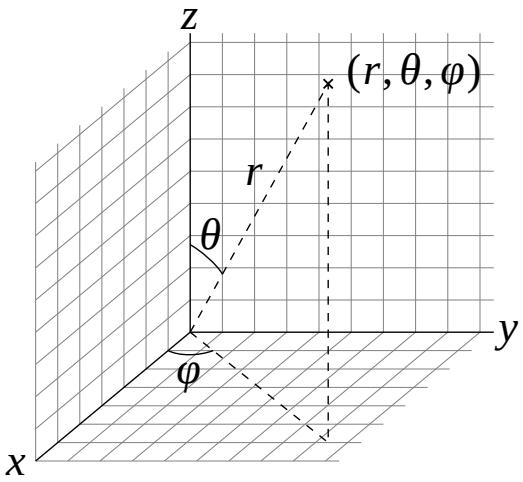


Figure 6.7.2: Spherical Coordinates

This generates a much more complicated, but easier to solve equation:

$$\left\{-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]-\frac{e^2}{4\pi\epsilon_0 r}\right\}\psi(r,\theta,\varphi)=E\psi(r,\theta,\varphi) \tag{6.7.4}$$

The second two terms in the square brackets of this equation only depend on the angles. This lead people to try separating the equation into two parts, one that depends on the angles (θ and φ) and one that depends on the distance (r). This does work, just as the wavefunction for a particle in a multidimensional box can be represented as the product of wavefunctions that depend on each coordinate separately.

Solutions

The solutions to this equation take the form of products of two functions as shown in equation 6.7.5.

$$\psi_{nlm_l}(r,\theta,\varphi)=R_n(r)Y_{lm}(\theta,\varphi) \tag{6.7.5}$$

The $Y_{lm_l}(\theta,\varphi)$ are a the Spherical Harmonic functions (Table M4), which were well known before quantum mechanics was developed. The Spherical Harmonic functions provide information about the angular probability distribution of the electron around the proton, and the radial function $R_n(r)$ describes how far the electron is away from the proton.

The state of the electron is specified by the three quantum numbes n, l, and m_l. For this case of a single electron atom the energy E_n depends only on n, although the other quantum numbers are required for the full description of the wavefunction:

$$E_n=-\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2} \tag{6.7.6}$$

with $n=1,2,3...\infty$.

It is found that the possible values of l are constrained by n and the possible values of m_l are constrained by l. We will see when we consider multi-electron atoms that these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

The Three Quantum Numbers

Schrödinger's approach requires three quantum numbers (n, l, and m_l) to specify a wavefunction for the electron. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer (NOT zero), only certain values of l and m_l are allowed for a given value of n.

The principal quantum number (n): This quantum number indicates the energy of the electron (equation 6.7.6) and the average

distance of an electron from the nucleus. n is restricted to the positive integers:

$$n = 1,\ 2,\ 3,\ 4,\ \ldots \tag{6.7.7}$$

As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wave functions that have the same value of n are said to constitute a principal ***shell***, because those electrons have similar average distances from the nucleus. The principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number (l): This quantum number indicates the shape of the region of space occupied by an electron and the electrons total orbital angular momentum. The allowed values of l are integers that depend on the value of n and can range from 0 to n – 1:

$$l = 0,\ 1,.,2,\ 3,\ ..\ (n-1) \tag{6.7.8}$$

For example, if n = 1, l can be only 0; if n = 2, l can be 0 or 1; and so forth. For a given atom, all wave functions that have the same values of both n and l form a ***subshell***. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

The total angular momentum of the electron has the value:

$$J = \sqrt{l(l+1)}\hbar \tag{6.7.9}$$

Thus the angular momentum of the electron is quantized.

The Magnetic Quantum Number (m_l): This quantum number indicates the orientation of the region of space occupied by an electron with respect to an applied magnetic field. The allowed integer values of m_l depend on the value of l and can range from $-l$ to l:

$$m = -l,\ -l+1,\ldots.0,\ \ldots l-1, l \tag{6.7.10}$$

For example, if $l = 0$, m_l can be only 0; if l = 1, m_l can be –1, 0, or +1; and if l = 2, m_l can be –2, –1, 0, +1, or +2.

Each wave function with an allowed combination of n, l, and m_l values describes an ***atomic orbital***, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

Because the electron is charged and has an angular momentum it can interact with a magnetic field. If the direction of the magnetic field is taken to be along the z-axis then the component (projection) of the angular momentum along the z-axis is:

$$J_z = m_l\hbar \tag{6.7.11}$$

This is the same quantization of J_z as seen for the particle on a ring.

Example 6.7.1: Number of subshells

How many subshells and orbitals are contained within the principal shell with n = 4?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A. Given n = 4, calculate the allowed values of l. From these allowed values, count the number of subshells.

B. For each allowed value of l, calculate the allowed values of ml. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution

A We know that l can have all integral values from 0 to n – 1. If n = 4, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of ml.

B For l = 0, ml can be only 0, and thus the l = 0 subshell has only one orbital. For l = 1, ml can be 0 or ±1; thus the l = 1 subshell has three orbitals. For l = 2, ml can be 0, ±1, or ±2, so there are five orbitals in the l = 2 subshell. The last allowed value of l is l = 3, for which ml can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the l = 3 subshell. The total number of orbitals in the n = 4 principal shell is the sum of the number of orbitals in each subshell and is equal to n2:

$$\underset{(l=0)}{1} + \underset{(l=1)}{3} + \underset{(l=2)}{5} + \underset{(l=3)}{7} = 16 \text{ orbitals} = (4 \text{ principal shells})^2$$

Exercise 6.7.1

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer: three subshells; nine orbitals

Rather than specifying all the values of *n* and *l* every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of *l* for a particular subshell or orbital:

l	0	1	2	3
Designation	s	*p*	*d*	*f*

The principal quantum number is named first, followed by the letter s, *p*, *d*, or *f* as appropriate. These orbital designations are derived from corresponding spectroscopic characteristics of lines involving them: sharp, *p*rincipal, *d*iffuse, and *f*undamental. A 1s orbital has $n = 1$ and $l = 0$; a 2*p* subshell has $n = 2$ and $l = 1$ (and has three 2*p* orbitals, corresponding to $m_l = –1$, 0, and +1); a 3*d* subshell has $n = 3$ and $l = 2$ (and has five 3*d* orbitals, corresponding to $m_l = –2$, –1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 6.7.1):

- Each principal shell has *n* subshells. For $n = 1$, only a single subshell is possible (1s); for $n = 2$, there are two subshells (2s and 2*p*); for $n = 3$, there are three subshells (3s, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with $n \geq 2$ also has an *np* subshell, and any shell with $n \geq 3$ also has an *nd* subshell. Because a 2*d* subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of *l* for $n = 2$, a 2*d* subshell does not exist.
- Each subshell has $2l + 1$ orbitals. This means that all *ns* subshells contain a single s orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

Note

Each principal shell has *n* subshells, and each subshell has $2l + 1$ orbitals.

Table 6.7.1: Allowed values of n, l, and m_l through n = 4

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1s	0	1	1

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
2	0	2s	0	1	4
	1	2p	–1, 0, 1	3	
3	0	3s	0	1	9
	1	3p	–1, 0, 1	3	
	2	3d	–2, –1, 0, 1, 2	5	
4	0	4s	0	1	16
	1	4p	–1, 0, 1	3	
	2	4d	–2, –1, 0, 1, 2	5	
	3	4f	–3, –2, –1, 0, 1, 2, 3	7	

The Radial Component

The first six radial functions are provided in Table 6.7.2. Note that the functions in the table exhibit a dependence on Z, the atomic number of the nucleus. Other one electron systems have electronic states analogous to those for the hydrogen atom, and inclusion of the charge on the nucleus allows the same wavefunctions to be used for all one-electron systems. For hydrogen, $Z = 1$ and for helium, $Z = 2$.

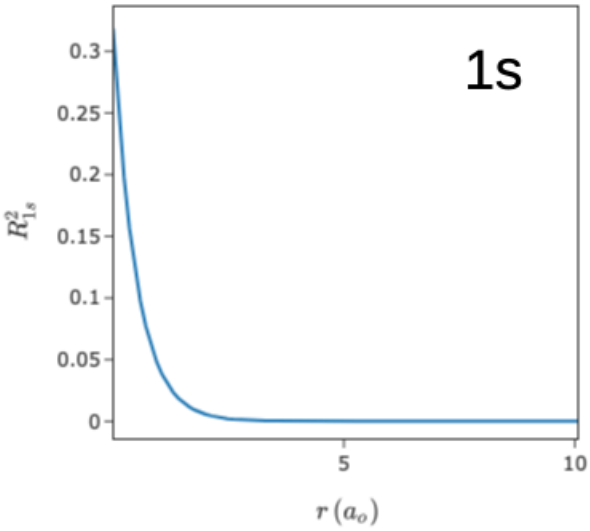
Table 6.7.2: Hydrogen-like atomic wavefunctions for n values $1, 2, 3$: Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

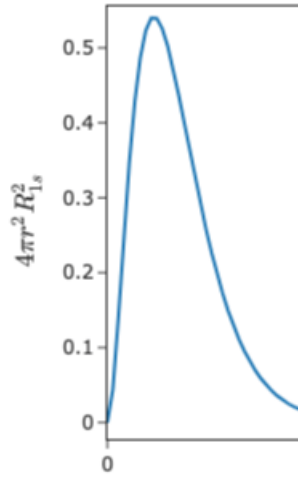
n	l	m_l	Radial Component
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\rho}$
2	0	0	$\psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (2-\rho)e^{\frac{-\rho}{2}}$
2	1	0	$\psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho e^{-\rho/2}\cos(\theta)$
2	1	±1	$\psi_{21\pm 1} = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho e^{-\rho/2}\sin(\theta)e^{\pm i\phi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (27-18\rho+2\rho^2)e^{-\rho/3}$
3	1	0	$\psi_{310} = \frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (6r-\rho^2)e^{-\rho/3}\cos(\theta)$
3	1	±1	$\psi_{31\pm 1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (6\rho-\rho^2)e^{-r/3}\sin(\theta)e^{\pm i\phi}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho^2 e^{-\rho/3}(3cos^2(\theta)-1)$
3	2	±1	$\psi_{32\pm 1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho^2 e^{-\rho/3}\sin(\theta)\cos(\theta)e^{\pm i\phi}$
3	2	±2	$\psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho^2 e^{-\rho/3}\sin^2(\theta)e^{\pm 2i\phi}$

Visualizing the variation of an electronic wavefunction with r, θ, and ϕ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron deficient part of one molecule is attracted to an electron rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

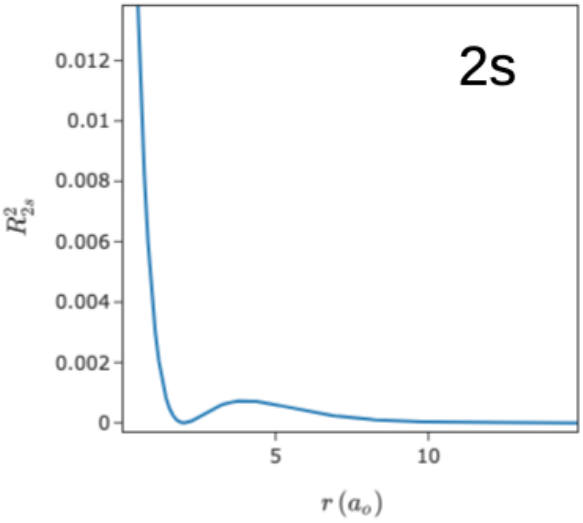
Plots of the radial functions, R(r), for the 1s, 2s, and 2p orbitals plotted in figure $6.7.2$ (left). The quantity $R(r)^*R(r)$ gives the radial probability density; i.e., the probability density for the electron to be at a point located the distance r from the proton. Radial probability densities for three types of atomic orbitals are plotted in figure $6.7.2$ (middle). The probability of finding an electron at a particular distance from the nucleus is the integral of $R(r)^*R(r)$ over the surface of the sphere of radius r, $P(r) = 4\pi r^2 R(r)^*R(r)$, which is plotted in figure $6.7.2$ (right).

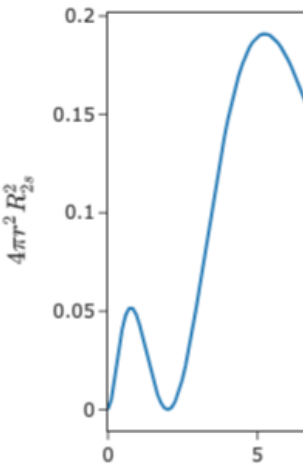

1s
10


1s
0.3
0.25
0.2
0.15
0.1
0.05
0
R_{1s}^2
5
10
$r\,(a_o)$


0.5
0.4
0.3
0.2
0.1
0
$4\pi r^2 R_{1s}^2$
0


2s
10
15


2s
0.012
0.01
0.008
0.006
0.004
0.002
0
R_{2s}^2
5
10
$r\,(a_o)$


0.2
0.15
0.1
0.05
0
$4\pi r^2 R_{2s}^2$
0
5

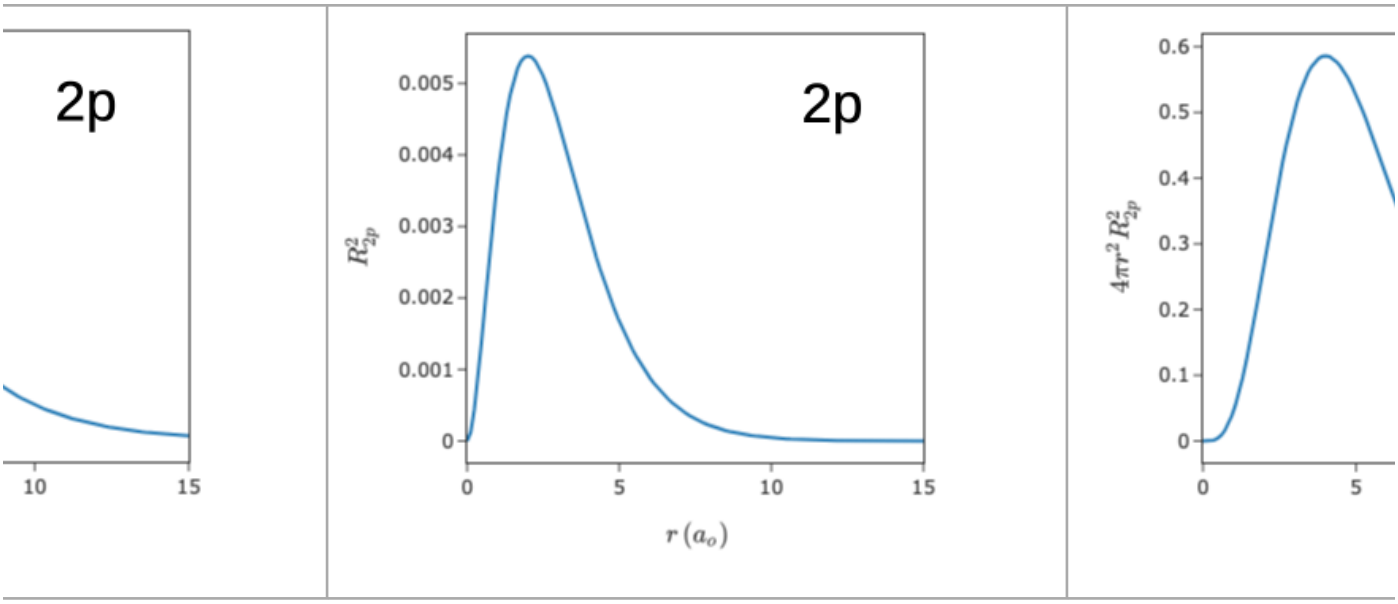


Figure 6.7.2: (left) **Radial function**, R(r), for the 1s, 2s, and 2p orbitals. (middle) **Radial probability densities** for the 1s, 2s, and 2p orbitals.(right) **Radial distribution functions** for the 1s, 2s, and 2p orbitals. Units on the x-axis are Bohrs = 0.529 Å = a_o.

For the hydrogen atom, the peak in the radial probability plot (right colum in figure 6.7.2) occurs at *r* = 0.529 Å (52.9 pm), which is exactly the radius calculated by Bohr for the *n* = 1 orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

> Notice that because the surface area of a sphere with radius of zero is zero, **there is no probability of finding the electron at the nucleus** (r = 0). See the right hand column in figure 6.7.2. This quantum prediction can be thought of as an explanation for why atoms do not collapse into a single uncharged particle.

Figure 6.7.3 compares the electron probability densities for the hydrogen 1s, 2s, and 3s orbitals in 3-D. Note that all three are spherically symmetrical. For the 2s and 3s orbitals, however (and for all other s orbitals as well), the electron probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots (part (c) in Figure 6.7.3). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.

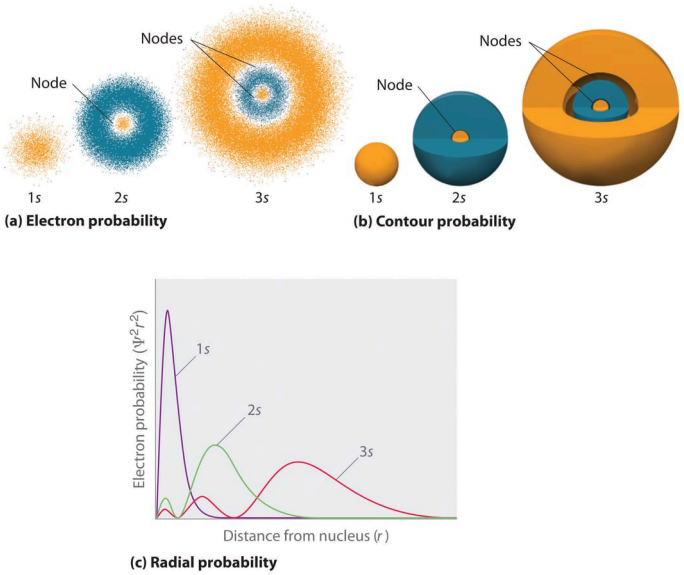


Figure 6.7.3: Probability Densities for the 1 s, 2 s, and 3s Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1s, 2s, and 3s orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (*r*) in all directions (radial probability), the most probable radius increases as*n* increases, but the 2*s* and 3s orbitals have regions of significant electron probability at small values of *r*.

The Angular Component

The angular component of the wavefunction $Y_{lm_l}(\theta, \phi)$ in Equation 6.7.5 does much to give an orbital its distinctive shape. Y is typically normalized so the the integral of Y^2 over the unit sphere is equal to one. In this case, Y^2 serves as a probability function. The probability function can be interpreted as the probability that the electron will be found on the ray emitting from the origin that is at angles (θ, ϕ) from the axes. The probability function can also be interpreted as the probability distribution of the electron being at position (θ, ϕ) on a sphere of radius *r*, given that it is *r* distance from the nucleus. $Y_{l,m_l}(\theta, \phi)$ are also the wavefunction solutions to Schrödinger's equation for a rigid rotor consisting of rotating bodies, for example a diatomic molecule. These are called Spherical Harmonic functions (Table M4).

s Orbitals (l=0)

Three things happen to *s* orbitals as *n* increases (figure 6.7.3):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the *s* orbitals also become higher in energy as *n* increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2*s* and 3*s* orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals (l=1)

Only *s* orbitals are spherically symmetrical. As the value of *l* increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2*p* subshell has *l* = 1, with three values of m_l (–1, 0, and +1), there are three 2*p* orbitals).

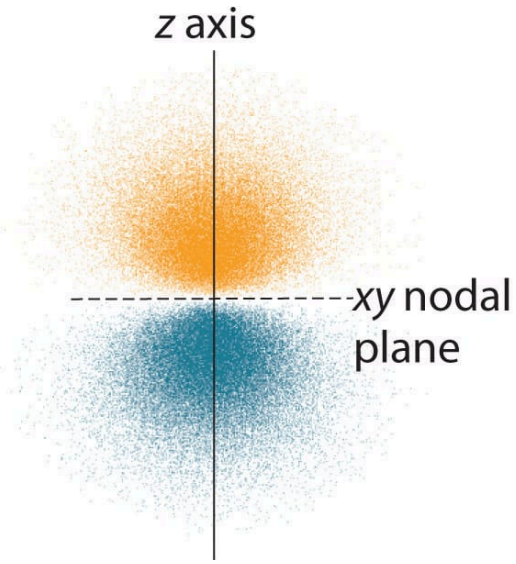


Figure 6.7.4: Illustration of a slice through a p_z orbital, where the dot density indicates the relative probability of finding the electron. The colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure 6.7.4. Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 6.7.5, the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and *y* axis ($2p_y$), respectively. Note that each *p* orbital has just one nodal plane. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

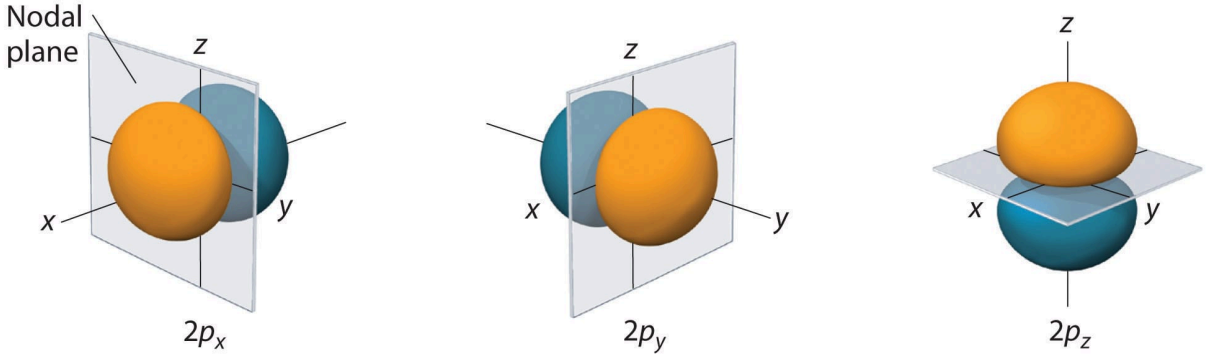


Figure 6.7.5: The Three Equivalent 2 p Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2*p* orbital. The phase of the wave function is positive (orange) in the region of space where *x*, *y*, or *z* is positive and negative (blue) where *x*, *y*, or *z* is negative.

Just as with the s orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in figure 6.7.5, but with additional radial nodes.

Note: Orbitals specified by m_l are not the same as those usually labeled p_x, p_y or p_z

The p_x, p_y and p_z orbitals are **not the solutions to the Schrödinger equation associated with m_l = -1, 0 and 1**. They are valid wavefunctions built from linear combinations of the m_l = -1, 0, 1 wavefunctions in order to get real valued functions. See the table of Spherical Harmonics and Real Valued Spherical Harmonics.

d Orbitals (l=2)

Subshells with l = 2 have five *d* orbitals; the first principal shell to have a *d* subshell corresponds to n = 3. The five *d* orbitals have m_l values of –2, –1, 0, +1, and +2. The surfaces enclosing the 90% probability of finding the electron for the five real-valued linear combinations of the complex orbitals specified by m_l are shown in figure 6.7.6.

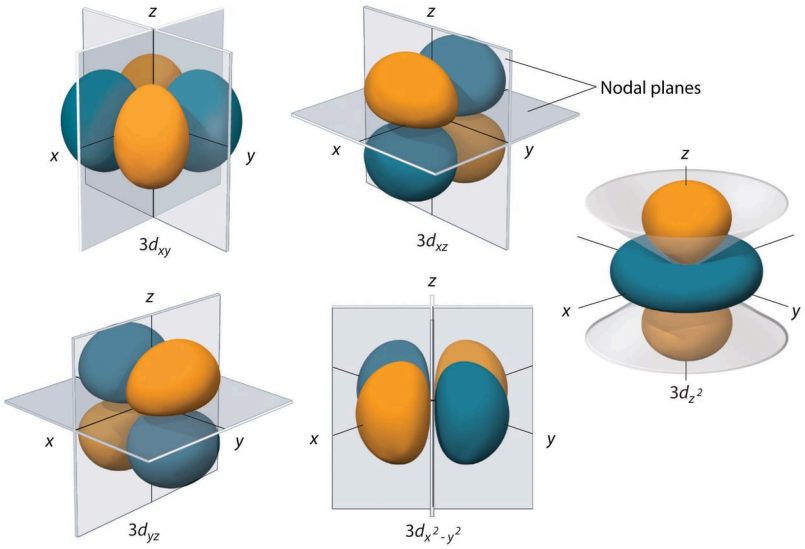


Figure 6.7.6: The five equivalent 3d orbitals of the hydrogen atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The hydrogen 3d orbitals have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the $3d_{x_2-y_2}$ orbital. The fifth 3d orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure 6.7.6, the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in figure 6.7.6.

f Orbitals (l=3)

Principal shells with n = 4 can have subshells with l = 3 and m_l values of –3, –2, –1, 0, +1, +2, and +3. These subshells consist of seven *f* orbitals. Each *f* orbital has three nodal surfaces, so their shapes are complex (not shown).

Energies

As noted previously, the energy for a single electron atom depend only on n, the principal quantum number. The solutions reproduce the same quantized expression for hydrogen atom energy levels that was obtained from the Bohr model of the hydrogen atom.

$$E = -\frac{Z^2}{n^2} Rhc \tag{6.7.12}$$

or

$$E_n = -\frac{Z^2 \mu e^4}{8\epsilon_0^2 h^2 n^2} \tag{6.7.13}$$

The relative energies of the atomic orbitals with $n \leq 4$ for a hydrogen atom are plotted in Figure 6.7.7 ; note that the orbital energies depend on *only* the principal quantum number *n* and are all less than zero, indicating attraction to the nucleus. Consequently, the energies of the 2*s* and 2*p* orbitals of hydrogen are the same; the energies of the 3s, 3*p*, and 3*d* orbitals are the same; and so forth. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are *4* orbitals with different electron density distributions in the $n = 2$ principal shell (one 2*s* and three 2*p* orbitals), *9* in the $n = 3$ principal shell, and *16* in the $n = 4$ principal shell.

> For a single electron atom, the energy of that electron is a function of only the principal quantum number (Equation 6.7.12).

The different values of l and m_l for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. As we have just seen, however, quantum mechanics also predicts that in the hydrogen atom, all orbitals with the same value of *n* (e.g., the three 2*p* orbitals) are degenerate, meaning that they have the same energy. Figure 6.7.7 shows that the energy levels become closer and closer together as the value of *n* increases, as expected because of the $1/n^2$ dependence of orbital energies.

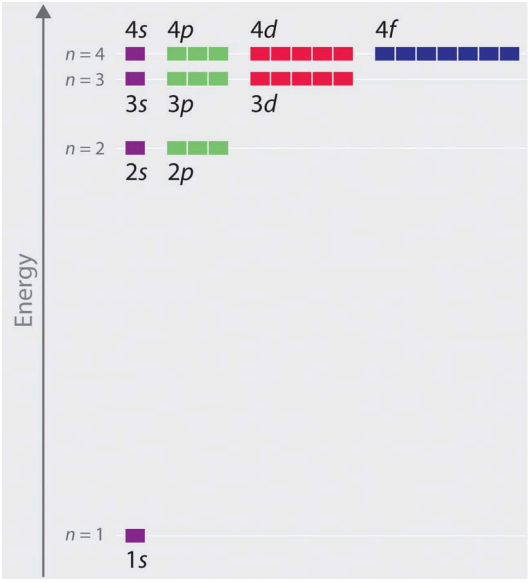


Figure 6.7.7: Orbital energy level diagram for the hydrogen atom. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n.

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the n =

2 orbitals. In ions with only a single electron, the energy of a given orbital depends on only n, and all subshells within a principal shell, such as the p_x, p_y, and p_z orbitals, are degenerate.

Note: Bohr vs. Schrödinger

It is interesting to compare the results obtained by solving the Schrödinger equation with Bohr's model of the hydrogen atom. There are several ways in which the Schrödinger model and Bohr model differ.

1. First, and perhaps most strikingly, the Schrödinger model does not produce well-defined orbits for the electron. The wavefunctions only give us the probability for the electron to be at various directions and distances from the proton.
2. Second, the quantization of angular momentum is different from that proposed by Bohr. Bohr proposed that the angular momentum is quantized in integer units of $\hbar$, while the Schrödinger model leads to an angular momentum of $(l(l+1)\hbar^2)^{\frac{1}{2}}$.
3. Third, the quantum numbers appear naturally during solution of the Schrödinger equation while Bohr had to postulate the existence of quantized energy states. Although more complex, the Schrödinger model leads to a better correspondence between theory and experiment over a range of applications that was not possible for the Bohr model.

Electron Spin: The Fourth Quantum Number

The quantum numbers $n,\ l,\ m_l$ are not sufficient to fully characterize the physical state of the electrons in an atom. In 1926, Otto Stern and Walther Gerlach carried out an experiment that could not be explained in terms of the three quantum numbers $n,\ l,\ m_l$ and showed that there is, in fact, another quantum-mechanical degree of freedom that needs to be included in the theory. The experiment is illustrated in the Figure $6.7.8$. A beam of atoms (e.g. hydrogen or silver atoms) is sent through a spatially inhomogeneous magnetic field with a definite field gradient toward one of the poles. It is observed that the beam splits into two beams as it passes through the field region.

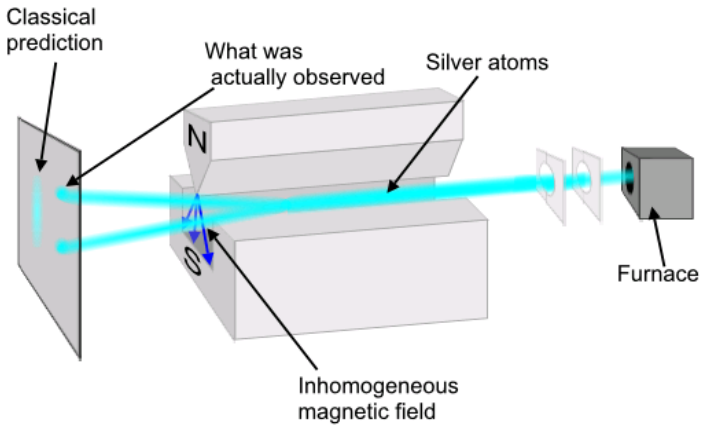


Figure $6.7.8$: The Stern-Gerlach apparatus. from Wikipedia

The fact that the beam splits into 2 beams suggests that the electrons in the atoms have a degree of freedom capable of coupling to the magnetic field. That is, an electron has an *intrinsic magnetic moment* M arising from a degree of freedom that has no classical analog. The magnetic moment must take on only 2 values according to the Stern-Gerlach experiment. The intrinsic property that gives rise to the magnetic moment is called *spin*, S; unlike position and momentum, which have clear classical analogs, spin does not. The implication of the Stern-Gerlach experiment is that we need to include a fourth quantum number, m_s in our description of the physical state of the electron. That is, in addition to give its principal, angular, and magnetic quantum numbers, we also need to say if it is a spin-up electron or a spin-down electron.

Note: Spin is a Quantum Phenomenon

Unlike position and momentum, which have clear classical analogs, spin does not. Spin may be thought of as a relativistic phenomenon. Solutions to the relativistic form of the wave equation for an electron (Dirac equation) do require the inclusion of a spin quantum number.[1] This is related to the relativistic effect that leads to the generation of a magnetic field by moving charged particles.[2] For most situations it is not necessary to use the relativistic formulation and spin is just added as an extra quantum number with two values.

George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Electrons are not spinning as they are a wave, but they do have a magnetic moment. The name electron spin stuck, despite not being particularly accurate.

The magnetic moment has two possible orientations, described by the fourth quantum number, $m_s = +½$ (up) and $m_s = -½$ (down). The subscript *s* is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it. The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist, Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. This is usually referred to as **the Pauli exclusion principle**.

Pauli Exclusion Principle

No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).

By giving the values of *n*, *l*, and m_l, we specify a particular orbital (e.g., 1s with $n = 1$, $l = 0$, $m_l = 0$). Because m_s has only two possible values (+½ or –½), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which was originally based on the physical and chemical properties of the known elements.

Example 6.7.2

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 2*p* orbital and predict the maximum number of electrons the 2*p* subshell can accommodate.

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A. List the quantum numbers (n, l, m_l) that correspond to an $n = 2p$ orbital. List all allowed combinations of (n, l, m_l).
B. Build on these combinations to list all the allowed combinations of (n, l, m_l, m_s).
C. Add together the number of combinations to predict the maximum number of electrons the 2*p* subshell can accommodate.

Solution:

A For a 2*p* orbital, we know that $n = 2$, $l = n - 1 = 1$, and $m_l = -l, (-l + 1),..., (l - 1), l$. There are only three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, –1).

B Because m_s is independent of the other quantum numbers and can have values of only +½ and –½, there are six possible combinations of (n, l, m_l, m_s): (2, 1, 1, +½), (2, 1, 1, –½), (2, 1, 0, +½), (2, 1, 0, –½), (2, 1, –1, +½), and (2, 1, –1, –½).

C Hence the 2*p* subshell, which consists of three 2*p* orbitals ($2p_x$, $2p_y$, and $2p_z$), can contain a total of six electrons, two in each orbital.

Exercise 6.7.2

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a 6s orbital, and predict the total number of electrons it can contain.

Answer: (6, 0, 0, +½), (6, 0, 0, –½); two electrons

References

1. Leonard I. Schiff, *Quantum Mechanics,* 3rd Ed. (McGraw-Hill, New York, 1968) Pp. 480 - 481.

2. Paul Lorain and Dale Corson, *Electromagnetic Fields and Waves*, 2nd Ed. (W. H. Freeman and Co. New York, 1970) Chpt 6.

Contributors and Attributions

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6.8: The Helium Atom Cannot Be Solved Exactly

Learning Objectives

- Adding electrons to the quantum hydrogen atom results in analytically unsolvable Schrödinger Equations (they exist, we just do not have analytical forms for them)
- A basic aspect of the corresponding multi-electron Hamiltonians is that they are NOT separable with respect to the spatial coordinate of each electron
- The solutions to multi-electron Schrödinger Equations are called multi-electron wavefunctions and they are often approximated as a product of single-electron wavefunctions (called the orbital approximation).

Multi-electron Hamiltonians

The second element in the periodic table provides our first example of a quantum-mechanical problem which *cannot* be solved exactly. Nevertheless, as we will show, approximation methods applied to helium can give accurate solutions in perfect agreement with experimental results. In this sense, it can be concluded that quantum mechanics is correct for atoms more complicated than hydrogen. By contrast, the Bohr theory failed miserably in attempts to apply it beyond the hydrogen atom.

Figure 6.7.1 shows a schematic representation of a helium atom with two electrons whose coordinates are given by the vectors r_1 and r_2. The electrons are separated by a distance $r_{12} = |r_1 - r_2|$. The origin of the coordinate system is fixed at the nucleus. As with the hydrogen atom, the nuclei for multi-electron atoms are so much heavier than an electron that the nucleus is assumed to be the center of mass. Fixing the origin of the coordinate system at the nucleus allows us to exclude translational motion of the center of mass from our quantum mechanical treatment.

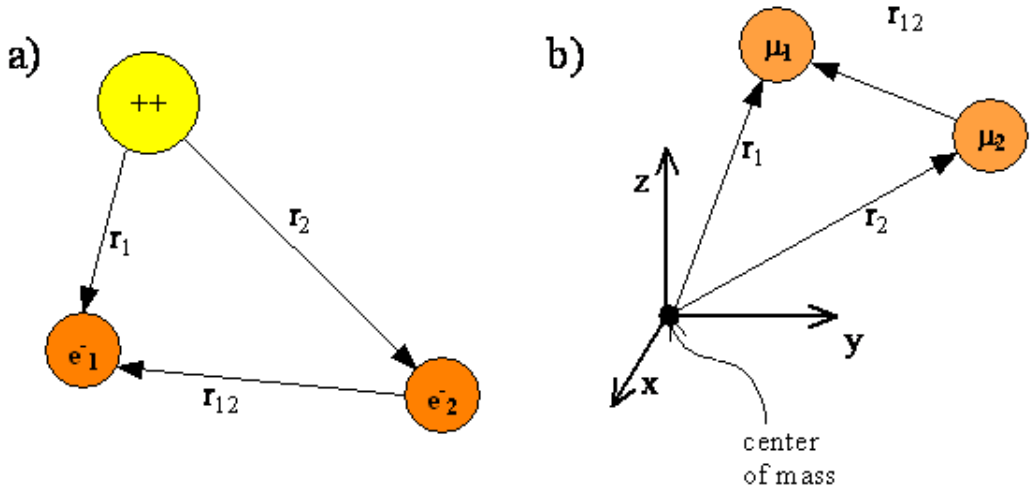


Figure 6.7.1 : (a) The nucleus (++) and electrons (e-) of the helium atom. (b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that μ_1 and $\mu_2 \approx m_e$.

The Hamiltonian operator for the hydrogen atom serves as a reference point for writing the Hamiltonian operator for atoms with more than one electron. Start with the same general form we used for the hydrogen atom Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} \tag{6.8.1}$$

Include a kinetic energy term for each electron and a potential energy term for the attraction of each negatively charged electron for the positively charged nucleus and a potential energy term for the mutual repulsion of each pair of negatively charged electrons. The He atom Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V_1(r_1) + V_2(r_2) + V_{12}(r_{12}) \tag{6.8.2}$$

where

$$V_1(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{6.8.3}$$

$$V_2(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{6.8.4}$$

$$V_{12}(r_{12}) = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{6.8.5}$$

The two-electron Hamiltonian in Equation 6.8.2 can be extended to any atom or ion by replacing the He nuclear charge of +2 with a general charge Z; e.g.

$$V_1(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{6.8.6}$$

and including terms for the additional electrons. The subsequent multi-electron atom with n electron is

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_i^n \nabla_i^2}_{\text{Kinetic Energy}} + \underbrace{\sum_i^n V_i(r_i)}_{\text{Coulombic Attraction}} + \underbrace{\sum_{i\neq j}^{n,n} V_{ij}(r_{ij})}_{\text{electron-electron Repulsion}} \tag{6.8.7}$$

This multi-electron Hamiltonian is qualitatively similar to the 2-electron Hamiltonian (Equation 6.8.1) with each electron having its own kinetic energy and nuclear potential energy terms (Equations 6.8.3 and 6.8.4). The other big difference between single electron systems and multi-electron systems is the presence of the $V_{ij}(r_{ij})$ terms which contain $1/r_{ij}$, where r_{ij} is the distance between electrons i and j. These terms account for the electron-electron repulsion that we expect between like-charged particles.

Exercise 6.7.1 : Multi-electron atom Hamiltonians

For the generalized multi-electron atom Hamiltonian (Equation 6.8.7):

a. Explain the origin of each of the three summations.
b. What do these summations over (i.e., what is the origin of the summing index)?
c. Write expressions for $V_i(r_i)$ and $V_{ij}(r_{ij})$.

Exercise 6.7.2 : Boron Atom

Boron is the fifth element of the periodic table (Z=5) and is located in Group 13.

a. Write the multi-electron Hamiltonian for a $^{11}\mathrm{B}$ atom.
b. Would it be any different for a $^{11}\mathrm{B}^+$ ion?
c. Would it be any different for a $^{10}\mathrm{B}$ atom?

Answer available at the end of this section.

Multi-electron Wavefunctions and the Orbital Approximation

Given what we have learned from the previous quantum mechanical systems we've studied, we predict that exact solutions to the multi-electron Schrödinger equation in Equation 6.8.7 would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the

hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their Coulomb repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends *simultaneously* upon the coordinates of all the electrons; i.e., **a multi-electron wavefunction**,

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \cdots \vec{r}_n)$$

The modulus squared of such a wavefunction would describe the probability of finding the electrons (though not specific ones) at a designated volume (V) in the atom.

$$p(V) = \int_V |\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \cdots \vec{r}_n)|^2 d\tau$$

All of the electrons are described simultaneously by a multi-electron wavefunction, so the total amount of electron density represented by the wavefunction equals the number of electrons in the atom.

$$\int_{\text{all space}} |\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \cdots \vec{r}_i)|^2 d\tau = n$$

Unfortunately, the Coulomb repulsion terms (Equation 6.8.5) make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms and molecules even for two electrons atoms. We have to rely on approximations and the *orbital approximation* is central to basic chemistry concepts.

The Orbital Approximation

The most basic approximations to the exact solutions to a multi-electron atom Hamiltonian, $\hat{H}$, (Equation 6.8.7) involve writing a multi-electron wavefunction ($\psi(r_1, r_2, \cdots, r_n)$) as a simple product of single-electron wavefunctions ($\varphi_i(r_i)$):

$$\psi(r_1, r_2, \cdots, r_n) \approx \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_n(r_n) \tag{6.8.8}$$

or in Dirac notation

$$|\psi(r_1, r_2, \cdots, r_n)\rangle \approx |\varphi_1(r_1)\rangle|\varphi_2(r_2)\rangle\cdots|\varphi_n(r_n)\rangle \tag{6.8.9}$$

The energy of the atom in the state associated with a specific multi-electron wavefunction (E) is obtained from the multi-electron Schrödinger Equation

$$\hat{H}\psi(r_1, r_2, \cdots, r_n) = E\psi(r_1, r_2, \cdots, r_n)$$

Within the approximation in Equation 6.8.8, E can be expressed sum of the energies of the one-electron components (ϵ_i).

$$E \approx \sum_i \epsilon_i$$

This is called the **orbital approximation**.

By writing the multi-electron wavefunction as a product of single-electron functions (Equations 6.8.8 or 6.8.9), we conceptually transform a multi-electron atom into a collection of individual electrons located in individual orbitals whose spatial characteristics and energies can be separately identified. For atoms, these single-electron wavefunctions are called *atomic orbitals* and resemble the wavefunctions for hydrogen-like atoms. For molecules, as we will see in the following chapters, these are called *molecular orbitals*. While a great deal can be learned from such an analysis, it is important to keep in mind that such a discrete, compartmentalized picture of the electrons is an approximation, albeit a powerful one.

Answers

a.

$$\hat{H}_{\mathrm{B}}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\vec{r}_5) = -\frac{\hbar^2}{2m_e}\sum_i^5 \nabla_i^2 + \sum_i^5 \frac{-5e^2}{4\pi\epsilon_0 r_i} + \sum_{i\neq j}^{5,5} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

which expands to 20 terms

$$\begin{aligned}\hat{H}_B(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\vec{r}_5) = &-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2m_e}\nabla_3^2 - \frac{\hbar^2}{2m_e}\nabla_4^2 - \frac{\hbar^2}{2m_e}\nabla_5^2 \\ &- \frac{-5e^2}{4\pi\epsilon_0 r_1} - \frac{-5e^2}{4\pi\epsilon_0 r_2} - \frac{-5e^2}{4\pi\epsilon_0 r_3} - \frac{-5e^2}{4\pi\epsilon_0 r_4} - \frac{-5e^2}{4\pi\epsilon_0 r_5} \\ &+ \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{14}} + \frac{e^2}{4\pi\epsilon_0 r_{15}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} + \frac{e^2}{4\pi\epsilon_0 r_{24}} + \frac{e^2}{4\pi\epsilon_0 r_{25}} + \frac{e^2}{4\pi\epsilon_0 r_{34}} + \frac{e^2}{4\pi\epsilon_0 r_{35}} + \frac{e^2}{4\pi\epsilon_0 r_{45}}\end{aligned}$$

b. Yes, $^{11}\mathrm{B}^+$ has one less electron than $^{11}\mathrm{B}$. Its Hamiltonian is

$$\hat{H}_{\mathrm{B}^+}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4) = -\frac{\hbar^2}{2m_e}\sum_i^4 \nabla_i^2 + \sum_i^4 \frac{-5e^2}{4\pi\epsilon_0 r_i} + \sum_{i\neq j}^{4,4} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

or expanded to 14 terms

$$\begin{aligned}\hat{H}_B(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4) = &-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2m_e}\nabla_3^2 - \frac{\hbar^2}{2m_e}\nabla_4^2 \\ &- \frac{-5e^2}{4\pi\epsilon_0 r_1} - \frac{-5e^2}{4\pi\epsilon_0 r_2} - \frac{-5e^2}{4\pi\epsilon_0 r_3} - \frac{-5e^2}{4\pi\epsilon_0 r_4} \\ &+ \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{14}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} + \frac{e^2}{4\pi\epsilon_0 r_{24}} + \frac{e^2}{4\pi\epsilon_0 r_{34}}\end{aligned}$$

c. No effect. Changing the number of neutrons in the nucleus does not affect kinetic nor potential energies of the electrons. The Hamilitonian for $^{10}\mathrm{B}$ is identical to $^{11}\mathrm{B}$. This is technically correct for this level of discussion, but as we we will see in later, if we expand the Hamiltonian with hyperfine structure the number of neutrons can play a role.

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6.E: The Hydrogen Atom (Exercises)

Solutions to select questions can be found online.

6.5

$$\int_{-1}^{1} T_n(x)T_m(x)\frac{1}{\sqrt{1-x^2}}dx = \begin{cases} 0, & n \neq m \\ \pi, & n = m = 0 \\ \pi/2, & n = m \neq 0 \end{cases}$$

First 6 Chebyshev Polynomials

$$T_0(x) = 1$$
$$T_1(x) = x$$
$$T_2(x) = 2x^2 - 1$$
$$T_3(x) = 4x^3 - 3x$$
$$T_4(x) = 8x^4 - 8x^2 + 1$$
$$T_5(x) = 16x^5 - 20x^3 + 5x$$

Use the orthogonality of Chebyshev polynomials to determine what the following polynomials are equal to

a. $\int_{-1}^{1} x^2 \frac{dx}{\sqrt{1-x^2}}$
b. $\int_{-1}^{1} 4x^3 - 2x \frac{dx}{\sqrt{1-x^2}}$
c. $\int_{-1}^{1} 1 \frac{dx}{\sqrt{1-x^2}}$
d. $\int_{-1}^{1} 4x^4 - 4x^2 + 1 \frac{dx}{\sqrt{1-x^2}}$

Solution

a. x^2= T_1*T_1; therefore the answer is π /2
b. here the following polynomial is not a product of either Chebyshev polynomials; therefore, answer is doesn't follow orthogonality conditions
c. 1=T_0*T_0; therefore, answer is π
d. x^4-4x^2+1= T_2*T_2; therefore the answer is π/2

6.6

Use Eq. 6.47 to generate the radial functions $R_{nl}(r)$ for $n = 1, 2$.

Solution

$$R_{10}(r) = \left\{ \frac{(1-0-1)!}{2(1)[(1+0)!]^3} \right\}^{\frac{1}{2}} \left(\frac{2}{1a_0} \right)^{\frac{0+3}{2}} r^0 e^{-\frac{r}{1a_0}} L_1^1 \left(\frac{2r}{1a_0} \right)$$

$$R_{10}(r) = -\left\{ \frac{1}{2} \right\}^{\frac{1}{2}} \left(\frac{2}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$$

$$R_{20}(r) = \left\{ \frac{(2-0-1)!}{2(2)[(2+0)!]^3} \right\}^{\frac{1}{2}} \left(\frac{2}{2a_0} \right)^{\frac{0+3}{2}} r^0 e^{-\frac{r}{2a_0}} L_2^1 \left(\frac{2r}{2a_0} \right)$$

$$R_{20}(r) = \left\{ \frac{1}{32} \right\}^{\frac{1}{2}} \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{2a_0}} \left(-2! \left(2 - \frac{r}{a_0} \right) \right)$$

$$R_{20}(r) = -2\left\{ \frac{1}{32} \right\}^{\frac{1}{2}} \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{2a_0}} \left(\left(2 - \frac{r}{a_0} \right) \right)$$

$$R_{21}(r) = \left\{ \frac{(2-1-1)!}{2(2)[(2+1)!]^3} \right\}^{\frac{1}{2}} \left(\frac{2}{2a_0} \right)^{\frac{1+3}{2}} r^1 e^{-\frac{r}{2a_0}} L_3^3 \left(\frac{2r}{2a_0} \right)$$

$$R_{21}(r) = -6\left\{ \frac{1}{864} \right\}^{\frac{1}{2}} \left(\frac{1}{a_0} \right)^2 r^1 e^{-\frac{r}{2a_0}}$$

6.29

Compare ψ_{310} and ψ_{311}.

Hint: What do the subscripts tell you about the wave function? What do they denote?

Solution

The first subscript tells you the quantum number n. The second denotes the angular momentum l. The last denotes the magnetic spin number m_l. These two functions have the same n values, and thus they are degenerate.

6.30

What is the probability density of the 3p orbital by evaluating

$$\left(\sum_{m=-1}^{1}\psi_{31m}^{2}\right)$$

Solution

$$\sum_{m=-1}^{1}\psi_{31m}^{2}=\left(\frac{2}{6561\pi}\right)\left(\frac{z^{3}}{a_{o}^{3}}\right)\sigma^{3}\left(6-\sigma\right)^{2}\exp\frac{-2\sigma}{3}\left(\cos^{2}\theta+\sin^{2}\theta\cos^{2}\phi+\sin^{2}\theta\sin^{2}\phi\right)$$

$$\sum_{m=-1}^{1}\psi_{31m}^{2}=\left(\frac{2z^{3}\sigma^{2}\left(6-\sigma\right)^{2}\exp\frac{-2\sigma}{3}}{6561\pi a_{o}^{3}}\right)\left(\cos^{2}\theta+\sin^{2}\theta\left(\cos^{2}\phi+\sin^{2}\phi\right)\right)$$

$$\sum_{m=-1}^{1}\psi_{31m}^{2}=\left(\frac{2z^{3}\sigma^{2}\left(6-\sigma\right)^{2}\exp\frac{-2\sigma}{3}}{6561\pi a_{o}^{3}}\right)$$

6.34

Find the energy, and wavefunction for a single electron located in the 2p orbital of the hydrogen atom. Include all possible wavefunctions.

Solution

Identify the quantum numbers for the electron of interest (in our case, $n=2$; $l=1$). Energy of the electron can be defined as

$$E_{n}=\frac{-m_{e}e^{4}}{8n^{2}\epsilon_{o}^{2}h^{2}}$$

this leads us to

$$E_{2}=\frac{-m_{e}e^{4}}{32\epsilon_{o}^{2}h^{2}}$$

we have two possible wave functions

$$\Psi_{210}=\frac{1}{\sqrt{32}}(\frac{z}{a_{o}})^{3/2}\sigma/e^{-\sigma/2}\cos\theta$$

and

$$\Psi_{21\pm1}=\frac{1}{\sqrt{32}}(\frac{z}{a_{o}})^{3/2}\sigma/e^{-\sigma/2}\sin\theta e^{\pm i\theta}$$

6.37

The Hamiltonian is given by $\hat{H} = \frac{-\hbar}{2m}\nabla^2 + V$ is an Hermitian Operator. Using this fact, show that

$$\int \psi^*[\hat{H}, \hat{A}]\psi d\tau = 0$$

where $\hat{A}$ is any operator.

Solution

Through the commutation relation

$$\int \psi^* \hat{H}\hat{A}\psi d\tau - \int \psi^* \hat{A}\hat{H}\psi d\tau = 0$$

because $\hat{H}$ is a *Hermitian* operator, the above goes to

$$\int (\psi\hat{H})^* \hat{A}\psi d\tau - \int \psi^* \hat{A}(\hat{H}\psi) d\tau = 0$$

$$E\int \psi^* \hat{A}\psi d\tau - E\int \psi^* \hat{A}\psi d\tau = 0$$

6.38

Prove that $\langle \hat{K} \rangle = \langle V \rangle = E/2$ for a harmonic oscillator using the virial theorem

Solution

The virial theorem gives us,

$$\left\langle x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z} \right\rangle = 2\langle \hat{K} \rangle$$

For a three-dimensional harmonic oscillator,

$$V(x, y, z) = \frac{k_x x^2}{2} + \frac{k_y y^2}{2} + \frac{k_z z^2}{2}$$

Therefore,

$$x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z} = k_x x^2 + k_y y^2 + k_z z^2 = 2V$$

and substituting into the equation given by the virial theorem gives us $2\langle V \rangle = 2\langle \hat{K} \rangle$. Because $\langle \hat{K} \rangle + \langle V \rangle = E$, we can also write

$$\langle \hat{K} \rangle = \langle V \rangle = \frac{1}{2}E$$

6.41

Find the expected values of $1/r$ and $1/r^2$ for a hydrogenlike atom in the $2p_z$ orbital.

Solution

The $2p_z$ orbital:

$$\Psi_{210} = \frac{1}{4\sqrt{2\pi}}(Z/a_0)^{3/2}\rho e^{-\rho}\sin\theta\cos\phi\, d\theta$$

where $\rho = Zr/a_o$

$$\langle 1/r\rangle_{\Psi 210} = \int_0^2 \pi\, d\theta \int_0^{\pi} \sin\theta\cos 2\phi d\theta \int_0^{\infty} (Z^{3/2}/a_o^{3/2}4\sqrt{2\pi}^{2*} r^2 p^* e^{-p*}(1/r)dr$$

$$\int_0^{2\pi} d\theta = 2\pi$$

$$\int_0^{\pi} \sin\theta\cos^2\,\phi\, d\theta = \frac{2}{3}$$

$$\int_0^{\infty} (Z^{3/2}/a_o^{3/2}4\sqrt{2\pi})^2 r^2\phi e - \rho(1/r)dr = (Z^3/a_o^3 32\pi)^*[3!/(Z/ao)^4]$$

$$\langle 1/r\rangle_{\Psi 210} = (Z^3/a_o^3 32\pi)(2\pi)(2/3)[3!/(Z/ao)^4]$$

Simplify to get:

$$\left\langle \frac{1}{r} \right\rangle_{\Psi_{210}} = \frac{Z}{4a_o}$$

For the hydrogen atom $Z = 1$, therefore

$$\langle \frac{1}{r} \rangle_{\Psi_{210}} = \frac{1}{4a_o}$$

For $\langle \frac{1}{r^2} \rangle$

$$\langle \frac{1}{r^2} \rangle_{\Psi_{210}} = \int_0^2 \pi\, d\theta \int_0^{\pi} \sin\theta\cos^2\,\phi\, d\theta \int_0^{\infty} (Z^3/2/a_o^3/24\sqrt{2\pi})^2 r^2 p e^{-p}(1/r^2)dr$$

$$\int_0^{2\pi} d\theta = 2\pi$$

$$\int_0^{\pi} \sin\theta\cos^2\phi d\theta = 2/3$$

$$\int_0^{\infty} (Z^{3/2}/a_o^{3/2}4\sqrt{2\pi})^2 r 2pe^{-p}(1/r^2)dr = (Z^3/a_o^3 32\pi)[2!/(Z/ao)^3]$$

$$\langle 1/r^2\rangle \Psi_{210} = (Z^3/a_o^3 32\pi)(2\pi)(2/3)[2!/(Z/a_o)^3]$$

Simplify to get:

$$\langle \frac{1}{r^2} \rangle_{\Psi_{210}} = \frac{Z^2}{12a_o^2}$$

where $Z = 1$

$$\langle \frac{1}{r^2} \rangle_{\Psi_{210}} = \frac{1}{12a_o^2}$$

6.43

Derive the classical magnetic moment of an electron orbiting a nucleus in terms of charge, mass and angular momentum.

Solution

We can begin by recalling the classical expression for a magnetic moment,

$$\mu = IArea$$

Where I is the current the electron makes by revolving around the nucleus. The definition of current is

$$I = \frac{Q}{time}$$

In this case Q is simply the charge (q_e) of the electron and $time$ is the time it takes the electron to orbit the nucleus once. The area is the of loop that the electron takes when revolving around the nucleus. We also know from classical mechanics that $x = vt$. solving for t and evaluating x to be $2\pi r$ for a circle. We can figure out the time of revolution to be,

$$t = \frac{x}{v} = \frac{2\pi r}{v}$$

Our current equations becomes,

$$I = \frac{q_e v}{2\pi r}$$

To introduce angular momentum $L = m_e v r$ we can multiply the right side of our current equation by $\frac{m_e r}{m_e r}$ to arrive at

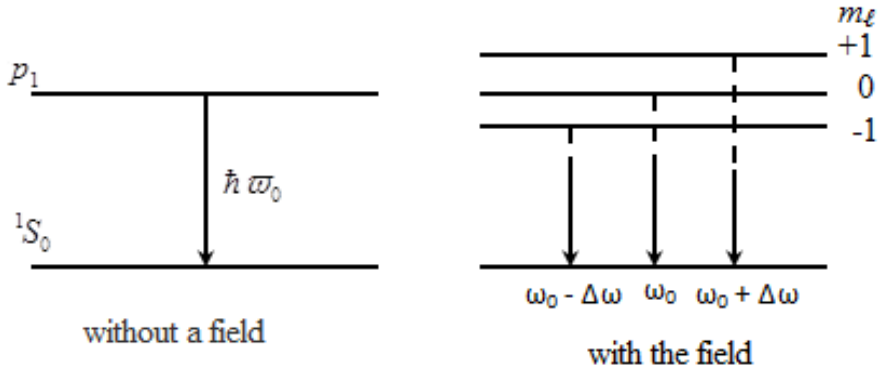
$$I = \frac{q_e m_e v r}{2\pi m_e r^2}$$
$$I = \frac{q_e L}{2\pi m_e r^2}$$

Substituting in the area of a circle (πr^2) we can show that,

$$\boxed{\mu = IArea = \frac{q_e L}{2m_e}}$$

6.46

Find the magnitude of the splitting shown in figure below. The magnetic field in the figure is at 20 T.



Solution

We know from a previous problem that

$$\Delta E = E_2 - E_1 = \beta_e B_z (m_2 - m_1)$$

In the 1\s\ state where m = 0 and in the 2\p\ state where m = 0, \pm\ 1. The condition will cause (m_{2} - m_{1}) become equal to 0, or \pm\ 1 which will affect the magnitude of splitting, calculated below

$$\Delta E = (9.274 * 10^{-24} J * T^{-1})(20T)(1)$$

$$\Delta E = 1.8548 * 10^{-22} J * T^{-1} \text{ or } 0$$

6.47

Consider the transition between the $l = 1$ and the $l = 2$ states for atomic hydrogen. Determine the total number of possible allowed transitions between these two states in an external magnetic field given the following selection rules

a. Light whose electric field vector is parallel to the external magnetic field's direction has a selection rule of $\Delta m = 0$ for allowed transitions.
b. Light whose electric field vector is perpendicular to the external magnetic field's direction has a selection rule of $\Delta m = \pm 1$ for allowed transitions.

Solution

An external magnetic field splits a state with given values n and l into $2l + 1$ levels. So the $l = 1$ state will be split into three states ($m = 0, \pm 1$) and the $l = 2$ state will be split into five states ($m = 0, \pm 1, \pm 2$). This means that the $l = 1 \rightarrow l = 2$ transition will have a possible of 15 transitions (ignoring any selection rules that reduce this number).

Using the selection rule $\Delta m = 0$, then three transitions are possible: $m = 0$, $m = 1$, $m = -1$ Using the selection rule $\Delta m = \pm 1$, then six transitions are possible:

$l = 1$	$\rightarrow$	$l = 2$	Relative Orientation of light Polarization to Magnetic field
m=0		m=1	parallel
m=0		m=-1	parallel
m=1		m=2	perpendicular
m=1		m=0	perpendicular
m=-1		m=-2	perpendicular
m=-1		m=0	perpendicular

6.49

Prove that

$$\hat{L_+}\hat{L_-} - \hat{L_-}\hat{L_+} = 2\hbar\hat{L_z}$$

given that

$$\hat{L_+} = \hat{L_x} + i\hat{L_y}$$

and

$$\hat{L_-} = \hat{L_x} - i\hat{L_y}.$$

Solution

$$\hat{L_+}\hat{L_-} = (\hat{L_x} + i\hat{L_y})(\hat{L_x} - i\hat{L_y}) = \hat{L_x^2} + \hat{L_y^2} - i\hat{L_x^2}\hat{L_y^2} + i\hat{L_y^2}\hat{L_x^2} = \hat{L_x^2} + \hat{L_y^2} + i[\hat{L_y}, \hat{L_x}]$$

$$\hat{L_+}\hat{L_-} = \hat{L^2} - \hat{L_z^2} + \hbar\hat{L_z}$$

and

$$\hat{L_-}\hat{L_+} = (\hat{L_x} - i\hat{L_y})(\hat{L_x} + i\hat{L_y}) = \hat{L_x^2} + \hat{L_y^2} + i\hat{L_x^2}\hat{L_y^2} - i\hat{L_y^2}\hat{L_x^2} = \hat{L_x^2} + \hat{L_y^2} + i[\hat{L_x}, \hat{L_y}]$$

$$\hat{L_-}\hat{L_+} = \hat{L^2} - \hat{L_z^2} - \hbar\hat{L_z}$$

thus

$$\hat{L_+}\hat{L_-} - hatL_-\hat{L_+} = \hat{L^2} - \hat{L_z^2} + \hbar\hat{L_z} - \hat{L^2} + \hat{L_z^2} - \hbar\hat{L_z}$$

$$\hat{L_+}\hat{L_-} - \hat{L_-}\hat{L_+} = 2\hbar\hat{L_z}$$

6.49

Show that the commutative property applies to

$$\hat{L}_-\hat{L}_+$$

Solution

$$\hat{L}_-\hat{L}_+ = \hat{L}_+\hat{L}_-$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y$$

and

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y$$

so

$$\hat{L}_-\hat{L}_+ = [\hat{L}_x - i\hat{L}_y][\hat{L}_x + i\hat{L}_y]$$

$$= \hat{L}_x^2 + i\hat{L}_x\hat{L}_y - i\hat{L}_x\hat{L}_y + \hat{L}_y^2$$

and

$$\hat{L}_+\hat{L}_- = [\hat{L}_x + i\hat{L}_y][\hat{L}_x - i\hat{L}_y]$$

$$= \hat{L}_x^2 - i\hat{L}_y\hat{L}_x + i\hat{L}_x\hat{L}_y + \hat{L}_y^2$$

which shows that

$$\hat{L}_-\hat{L}_+ = \hat{L}_+\hat{L}_-$$

Q7.29

Calculate the ground-state energy for particle in the box model using variational method.

Solution

Variational method equations is:

$$E_\phi = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$$

where the wavefunctions are unnormalized

The unnormalized Schrödinger equation for PIB:

$$\phi(x) = A\sin(\frac{xn\pi}{L})$$

$$\langle\phi|\phi\rangle$$

$$= A = \sqrt{\frac{2}{L}}$$

and

$$\langle\phi|\hat{H}|\phi\rangle$$

$$= \frac{n^2h^2}{8mL^2}\cdot\sqrt{\frac{2}{L}}$$

so

$$E_\phi = \frac{\frac{n^2h^2}{8mL^2}\cdot\sqrt{\frac{2}{L}}}{\sqrt{\frac{2}{L}}}$$

so

$$E_\phi = \frac{n^2h^2}{8mL^2}$$

where n=1 we get

$$E_\phi = \frac{h^2}{8mL^2}$$

6.50

If two functions commute, they have mutual eigenfunctions, such as $\hat{L}^2$ and $\hat{L}_z$. These mutual eigenfunctions are also known as spherical harmonics, $Y_l^m(\theta, \phi)$, however this information is not pertinent in this case. Let

$\psi_{\alpha\beta}$ be a mutual eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ so that

$$\hat{L}_z\,\psi_{\alpha\beta} = \beta^2\backslash_{\alpha\beta}$$

and

$$\hat{L}_z\,\psi_{\alpha\beta} = \alpha\psi_{\alpha\beta}$$

Now let

$$\psi_{\alpha\beta}{}^{+1} = \hat{L}_{+}\psi_{\alpha\beta}$$

Show that

$$\hat{L}_z\psi_{\alpha\beta}{}^{+1} = (\alpha + \hbar)\psi_{\alpha\beta}{}^{+1}$$

and

$$\hat{L}^2\psi_{\alpha\beta}{}^{+1} = \beta^2\psi_{\alpha\beta}{}^{+1}$$

This proves that if α is an eigenvalue of $\hat{L}_z$, then $\alpha + \hbar$ also is an eigenvalue.

Solution

Solve this problem as given below:

$\psi_{\alpha\beta}{}^{+1} = \hat{L}_{+}\psi_{\alpha\beta}$

$\hat{L}_z\ \psi_{\alpha\beta}{}^{+1} = \hat{L}_z\ \hat{L}_{+}\psi_{\alpha\beta}$

$= (\hat{L}_z\ \hat{L}_x + i\hat{L}_z\ \hat{L}_y\ )\psi_{\alpha\beta}$

$z,\ \hat{L}_x] + \hat{L}_x\ \hat{L}_z + i[\hat{L}_z,\ \hat{L}_y] + i\hat{L}_y\ \hat{L}_z)\psi_{\alpha\beta}$

$y + \hat{L}_z\hat{L}_x + i\hbar\hat{L}_x + \hat{L}_y\hat{L}_z)\ \psi_{\alpha\beta}$

$\hat{L}_{+}\hat{L}_z + \hbar\hat{L}_{+})\psi_{\alpha\beta}$

$+(\alpha + \hbar)\psi_{\alpha\beta}$

$\alpha\beta^{+1}$

Therefore proven.

Finally, you can write:

$\hat{L}^2\psi_{\alpha\beta}{}^{+1} = \hat{L}^2\hat{L}_{+}\psi_{\alpha\beta}$

$= (\hat{L}^2\hat{L}_x + i\hat{L}^2\hat{L}_y)\psi_{\alpha\beta}$

$=([\hat{L}^2,\hat{L}_x] + \hat{L}_x\hat{L}^2 + i[\hat{L}^2,\hat{L}_y] + i\hat{L}_y\hat{L}^2)\psi_{\alpha\beta}$

$x\hat{L}^2 + i\hat{L}_y\hat{L}^2)\psi_{\alpha\beta}$

$+\beta^2\psi_{\alpha\beta}$

$2\psi_{\alpha\beta}{}^{+1}$

Therefore proven.

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7: APPROXIMATION METHODS

The Schrödinger equation for realistic systems quickly becomes unwieldy, and analytical solutions are only available for very simple systems - the ones we have described as *fundamental systems* in this module. Numerical approaches can cope with more complex problems, but are still (and will remain for a good while) limited by the available computer power. Approximations are necessary to cope with real systems. Within limits, we can use a pick and mix approach, *i.e.* use *linear combinations* of solutions of the fundamental systems to build up something akin to the real system. There are two mathematical techniques, *perturbation* and *variation* theory, which can provide a good approximation along with an estimate of its accuracy. These two approximation techniques are described in this chapter.

7.1: The Variational Method Approximation

7.2: Linear Variational Method and the Secular Determinant

7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters

7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

7.E: Approximation Methods (Exercises)

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7.1: The Variational Method Approximation

Learning Objectives

- Appreciate the complexity of solving muliti-electron atoms
- Characterize multi-electron interactions within shielding and penetration concepts
- Use the variational method as an approximation to study insolvable problems
- User variational method to evaluate the effective nuclear charge for a specific atom

In this section we introduce the powerful and versatile variational method and use it to improve the approximate solutions we found for the helium atom using the independent electron approximation.

The True (Experimentally Determined) Energy of the Helium Atom

The helium atom has two electrons bound to a nucleus with charge $Z = 2$. The *successive* removal of the two electrons can be considered stepwise:

$$\mathrm{He} \xrightarrow{I_1} \mathrm{He}^+ + e^- \xrightarrow{I_2} \mathrm{He}^{++} + 2e^- \tag{7.1.1}$$

The *first ionization energy* I_1 is the minimum energy required to remove the first electron from helium gas and is experimentally determined:

$$I_1 = -E_{1s}(\mathrm{He}) = 24.59\ eV$$

While the second ionization energy, I_2 can be experimentally determined, it can also be calculated exactly from the hydrogen atom solutions since He^+ is a hydrogen-like ion with $Z = 2$. Hence, we have

$$\begin{aligned} I_2 &= -E_{1s}(\mathrm{He}^+) \\ &= \frac{Z^2}{2n^2} \\ &= 54.42\ \mathrm{eV} \end{aligned}$$

The energy of the three separated particles on the right side of Equation 7.1.1 is zero (by definition). Therefore the ground-state energy of helium atom is given by

$$\begin{aligned} E_{true} &= -(I_1 + I_2) \\ &= -79.02\ \mathrm{eV}. \end{aligned}$$

which can be expressed in terms of the ***Rydberg*** constant ($R_H = 13.6\ \ eV$) that also describes the lowest energy of the hydrogen atom

$$E_{true} = -5.8066\, R_H$$

We will attempt to reproduce this **true value**, as close as possible, by different theoretical approaches (all approximations).

The "Ignorance is Bliss" Approximation

The Hamiltonian for the Helium atom is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \cancel{\frac{e^2}{4\pi\epsilon_0 r_{12}}} \tag{7.1.2}$$

If we simply *ignore* the electron-electron repulsion term, then Equation 7.1.2 can be simplified to

$$\hat{H} \approx -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_2} \tag{7.1.3}$$

$$\approx h_1(r_1) + h_2(r_2) \tag{7.1.4}$$

where h_1 and h_2 are one electron Hamiltonians for electron 1 and 2, respectively, and are just the hydrogen-like Hamiltonians. The approximation in Equation 7.1.4 is convenient since electron 1 is *separable* from electron 2, so that the two-electron wavefunction is approximated as a product to two one-electron wavefunctions:

$$\Psi_{total} = \psi_{el_1}\psi_{el_2} \tag{7.1.5}$$

or in braket notation

$$|\Psi_{total}\rangle = \hat{H}|\psi_{el_1}\psi_{el_2}\rangle \tag{7.1.6}$$

With some operator algebra, something important arises - the one electron energies are **additive**:

$$\hat{H}\Psi_{total} = (\hat{H}_{el_1} + \hat{H}_{el_2})\psi_{n\ el_1}\psi_{n\ el_2} = (E_{n_1} + E_{n_2})\psi_{n\ el_1}\psi_{n\ el_2}$$

or in bra-ket notation

$$\begin{aligned}\hat{H}|\Psi_{total}\rangle &= \hat{H}|\psi_{el_1}\psi_{el_2}\rangle \\ &= (E_{n_1} + E_{n_2})|\psi_1\psi_2\rangle\end{aligned}$$

The energy for a ground state Helium atom (both electrons in lowest state) is then

$$\begin{aligned}E_{He_{1s}} &= \underbrace{E_{n_1}}_{\text{energy of single electron in helium}} + \underbrace{E_{n_2}}_{\text{energy of single electron in helium}} \\ &= -R_H\left(\frac{Z^2}{1}\right) - R_H\left(\frac{Z^2}{1}\right) \\ &= -8R_H\end{aligned}$$

This approximation significantly overestimates the true energy of the helium atom $E_{He_{1s}} = -5.8066\ \ R$. This is a poor approximation and we need to address electron-electron repulsion properly (or better at least).

Shielding and Penetration

One way to take electron-electron repulsion into account is to modify the form of the wavefunction. A logical modification is to change the nuclear charge, Z, in the wavefunctions to an effective nuclear charge (Z_{eff}), from +2 to a smaller value. The rationale for making this modification is that one electron partially shields the nuclear charge from the other electron, as shown in Figure 7.1.1 .

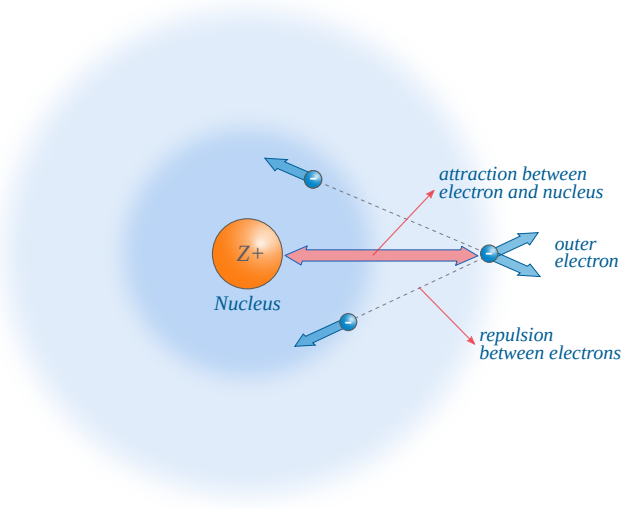


Figure 7.1.1 : Electron-electron shielding leading to a reduced effective nuclear charge. The attractive force of the nucleus on the outer electron is partially countered by the repulsive force between inner electrons and the outer electron. (CC BY-SA; Ümit Kaya via LibreTexts)

A region of negative charge density between one of the electrons and the +2 nucleus makes the potential energy between them more positive (decreases the attraction between them). We can effect this change mathematically by using $\zeta < 2$ in the wavefunction expression. If the shielding were complete, then Z_{eff} would equal 1. If there is no shielding, then $Z_{eff} = 2$. So a way to take into account the electron-electron interaction is by saying it produces a shielding effect. The shielding is not zero, and it is not complete, so the effective nuclear charge varies between one and two.

In general, a theory should be able to make predictions in advance of knowledge of the experimental result. Consequently, a principle and method for choosing the best value for Z_{eff} or any other adjustable parameter that is to be optimized in a calculation is needed. The Variational Principle provides the required criterion and method and says that the best value for any variable parameter in an approximate wavefunction is the value that gives the **lowest energy for the ground state**; i.e., the value that minimizes the energy. The variational method is the procedure that is used to find the lowest energy and the best values for the variable parameters.

A Better Approximation: The Variational Method

The variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. This allows calculating approximate wavefunctions and is the variational principle. The method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an **upper bound** to the ground state energy.

The variational principle means that the expectation value for the binding energy obtained using an approximate wavefunction and the exact Hamiltonian operator will be higher than or equal to the true energy for the system. This idea is really powerful. When implemented, it permits us to find the best approximate wavefunction from a given wavefunction that contains one or more adjustable parameters, called a **trial wavefunction**. A mathematical statement of the variational principle is

$$E_{trial} \geq E_{true} \tag{7.1.7}$$

where

$$E_{trial} = \frac{\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{7.1.8}$$

$$= \frac{\int \psi^*_{trial} \hat{H} \psi_{trial} d\tau}{\int \psi^*_{trial} \psi_{trial} d\tau} \tag{7.1.9}$$

Equation 7.1.7 is called the variational theorem and states that for a time-independent Hamiltonian operator, any trial wavefunction will have an variational energy (i.e., expectation value) that is **greater than or equal** to the true ground state wavefunction corresponding to the given Hamiltonian (Equation 7.1.7). Because of this, the variational energy is an upper bound to the true ground state energy of a given molecule. The general approach of this method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible (Figure 7.1.2).

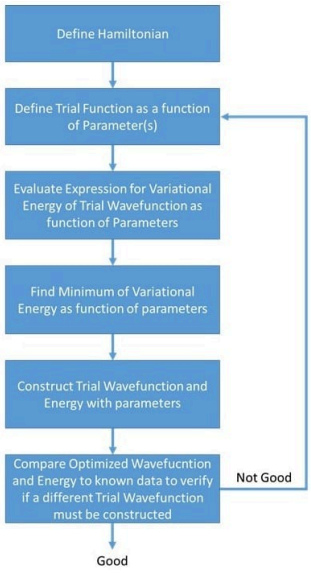


Figure 7.1.2 : Simplified algorithmic flowchart of the Variational Method approximation

The variational energy E_{trial} is only equal to the true energy E_{true} when the the corresponding trial wavefunction ψ_{trial} is equal to the true wavefunction ψ_{true}.

Application to the Helium atom Ground State

Often the expectation values (numerator) and normalization integrals (denominator) in Equation 7.1.9 can be evaluated analytically. For the case of the He atom, let's consider the trial wavefunction as the product wavefunction given by Equation 7.1.10 (this is called the **orbital approximation**),

$$\psi(r_1, r_2) \approx \varphi(r_1)\varphi(r_2) \tag{7.1.10}$$

The adjustable or variable parameter in the trial wavefunction is the effective nuclear charge ζ, and the Hamiltonian is the complete form given below (Note: quantum calculations typically refer to effective nuclear charge as ζ rather than Z_{eff} as we used previously).

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{7.1.11}$$

the adjustable or variable parameter in the trial wavefunction is the effective nuclear charge ζ (would be equal to $\zeta = 2$ if fully unshielded), and the Hamiltonian is the complete form. When the expectation value for the trial energy (Equation 7.1.9) is evaluated for helium, the result is a variational energy that depends on the adjustable parameter, ζ.

$$E_{trial}(\zeta) = \frac{\mu e^4}{4\epsilon_0^2 h}\left(\zeta^2 - \frac{27}{8}\zeta\right) \tag{7.1.12}$$

This function is plotted in Figure 7.1.3 as a function of ζ. According to the variational principle (Equation 7.1.7), the minimum value of the energy on this graph is the best approximation of the true energy of the system, and the associated value of ζ is the best value for the adjustable parameter.

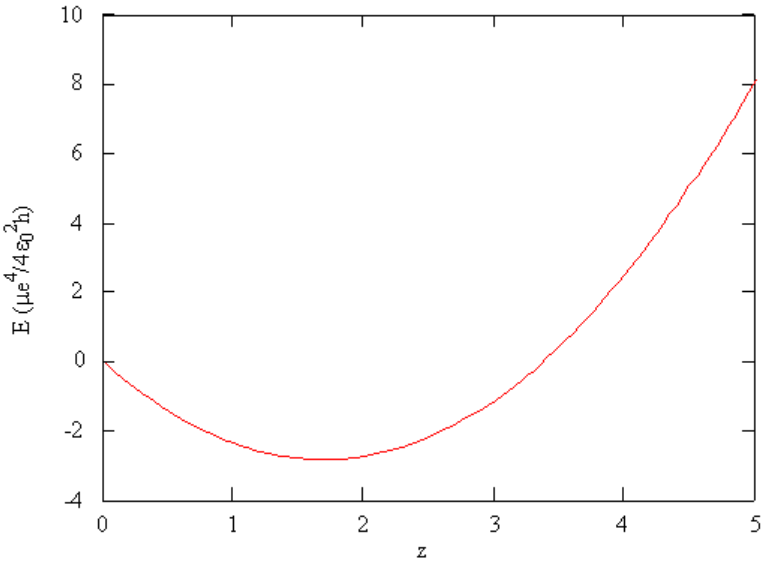


Figure 7.1.3 : Graph of trial energies for helium atom as a function of the adjustable parameter ζ in Equation 7.1.12 that represents the effective nuclear charge felt by the electrons.

Using the mathematical function for the energy of a system, the minimum energy with respect to the adjustable parameter can be found by taking the derivative of the energy with respect to that parameter, setting the resulting expression equal to zero, and solving for the parameter, in this case ζ. This is a standard method in calculus for finding maxima and minima.

Exercise 7.1.1

Find the value for ζ that minimizes the helium binding energy for the product trial wavefunction in Equation 7.1.10 with the Hamiltonian in Equation 7.1.11. and compare the binding energy to the experimental value. What is the percent error in the calculated value?

Solution

The variational method requires following the workflow in Figure 7.1.2 .

- Step 1: Define the Hamiltonian - This is given by Equation 7.1.11.
- Step 2: Define the trial wavefunction as a function of at least one parameter - This is given by Equation 7.1.10.
- Step 3: Evaluate variational energy (E_{trial} integral (Equation 7.1.9) - This procedure was already above in Equation 7.1.12.
- Step 4: Minimize the variational energy as a function of the parameter(s) - Following the standard approach to find extrema in calculus, evaluate the derivative of E_{trial} with respect to ζ and set to zero:

$$\frac{dE_{trial}}{d\zeta} = \frac{\mu e^4}{4\epsilon_0^2 h}\left(2\zeta - \frac{27}{8}\right) = 0$$

then find solve for the roots of this polynomial

$$2\zeta - \frac{27}{8} = 0$$

or

$$\zeta = \frac{27}{16} \approx 1.6875$$

- Step 5-6: The question does not ask for the optimized wavefunction (Step 5) or to compare the result with the true value to evaluate the quality of the approximation (Step 6). We can skip these steps.

From Exercise 7.1.1 , the $\zeta = 1.6875$ and the approximate energy we calculate using this approximation method, E_{approx} = -77.483 eV. Table 7.1.1 show that a substantial improvement in the accuracy of the computed binding energy is obtained by using shielding to account for the electron-electron interaction. Including the effect of electron shielding in the wavefunction reduces the error in the binding energy to about 2%. This idea is very simple, elegant, and significant.

Table 7.1.1 : Comparison of the results of three approximation methods to experiment.

Method	He binding energy (eV)
"Ignorance is Bliss" Approximation (neglect repulsion between electrons)	-108.8
Variational method with variable effective charge	-77.483
Experimental	-79.0

The improvement we have seen in the total energy calculations using a variable parameter ζ indicates that an important contribution of electron-electron interaction or repulsion to the total binding energy arises from the fact that each electron shields the nuclear charge from the other electron. It is reasonable to assume the electrons are independent; i.e., that they move independently, but the shielding must be taken into account in order to fine-tune the wavefunctions. The inclusion of optimizable parameters in the wavefunction allows us to develop a clear physical image of the consequences of our variation calculation. Calculating energies correctly is important, and it is also important to be able to visualize electron densities for multi-electron systems. In the next two sections, we take a temporary break from our consideration of approximation methods in order to examine multi-electron wavefunctions more closely.

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7.2: Linear Variational Method and the Secular Determinant

Learning Objectives

- Understand how the variational method can be expanded to include trial wavefunctions that are a linear combination of functions with coefficients that are the parameters to be varied.
- To be able to construct secular equations to solve the minimization procedure intrinsic to the variational method approach.
- To map the secular equations into the secular determinant
- To understand how the Linear Combination of Atomic Orbital (LCAO) approximation is a specific application of the linear variational method.

A special type of variation widely used in the study of molecules is the so-called **linear variation function**, where the trial wavefunction is a linear combination of N linearly independent functions (often atomic orbitals) that not the eigenvalues of the Hamiltonian (since they are not known). For example

$$|\psi_{trial}\rangle = \sum_{j=1}^{N} a_j |\phi_j\rangle \tag{7.2.1}$$

and

$$\langle\psi_{trial}| = \sum_{j=1}^{N} a_j^* \langle\phi_j| \tag{7.2.2}$$

In these cases, one says that a 'linear variational' calculation is being performed.

Linear Variational Basis Functions

The set of functions $\{\phi_j\}$ are called the 'linear variational' basis functions and are nothing more than members of a set of functions that are convenient to deal with. However, they are typically not arbitrary and are usually selected to address specific properties of the system:

- to obey all of the boundary conditions that the exact state $|\psi_{trial}\rangle$ obeys,
- to be functions of the the same coordinates as $|\psi_{trial}\rangle$,
- to be of the same symmetry as $|\psi_{trial}\rangle$, and
- to be convenient to evaluate Hamiltonian terms elements $\langle\phi_i|H|\phi_j\rangle$.

Beyond these conditions, nothing other than effort can limit the selection and number of such basis functions in the expansions in Equations 7.2.1 and 7.2.2.

As discussed in Section 7.1, the variational energy for a generalized trial wavefunction is

$$E_{trial} = \frac{\langle\psi_{trial}|\hat{H}|\psi_{trial}\rangle}{\langle\psi_{trial}|\psi_{trial}\rangle} \tag{7.2.3}$$

Substituting Equations 7.2.1 and 7.2.2 into Equation 7.2.3 involves addressing the numerator and denominator individually. For the numerator, the integral can be expanded thusly:

$$\langle \psi_{trial}|H|\psi_{trial}\rangle = \sum_{i}^{N}\sum_{j}^{N} a_i^* a_j \langle \phi_i|H|\phi_j\rangle. \tag{7.2.4}$$

$$= \sum_{i,\,j}^{N,\,N} a_i^* a_j \langle \phi_i|H|\phi_j\rangle. \tag{7.2.5}$$

We can rewrite the following integral in Equation 7.2.5 as a function of the basis elements (not the trial wavefunction) as

$$H_{ij} = \langle \phi_i|H|\phi_j\rangle$$

So the numerator of the right side of Equation 7.2.3 becomes

$$\langle \psi_{trial}|H|\psi_{trial}\rangle = \sum_{i,\,j}^{N,\,N} a_i^* a_j H_{ij} \tag{7.2.6}$$

Similarly, the denominator of the right side of Equation 7.2.3 can be expanded

$$\langle \psi_{trial}|\psi_{trial}\rangle = \sum_{i,\,j}^{N,\,N} a_i^* a_j \langle \phi_i|\phi_j\rangle \tag{7.2.7}$$

We often simplify the integrals on the right side of Equation 7.2.7 as

$$S_{ij} = \langle \phi_i|\phi_j\rangle$$

where S_{ij} are **overlap integrals** between the different $\{\phi_j\}$ basis functions. Equation 7.2.7 is thus expressed as

$$\langle \psi_{trial}|\psi_{trial}\rangle = \sum_{i,\,j}^{N,\,N} a_i^* a_j S_{ij} \tag{7.2.8}$$

Orthonormality of Basis Functions

There is no explicit rule that the $\{\phi_j\}$ functions have to be **orthogonal** or **normalized** functions, although they often are selected that way for convenience. Therefore, *a priori*, S_{ij} does not have to be δ_{ij}.

Substituting Equations 7.2.6 and 7.2.8 into the variational energy formula (Equation 7.2.3) results in

$$E_{trial} = \frac{\sum_{i,\,j}^{N,\,N} a_i^* a_j H_{ij}}{\sum_{i,\,j}^{N,\,N} a_i^* a_j S_{ij}} \tag{7.2.9}$$

For such a trial wavefunction as Equation 7.2.1, the variational energy depends quadratically on the 'linear variational' a_j coefficients. These coefficients can be varied just like the parameters in the trial functions of Section 7.1 to find the optimized trial wavefunction ($|\psi_{trial}\rangle$) that approximates the true wavefunction ($|\psi\rangle$) that we cannot analytically solve for.

Minimizing the Variational Energy

The expression for variational energy (Equation 7.2.9) can be rearranged

$$E_{trial}\sum_{i,\,j}^{N,\,N} a_i^* a_j S_{ij} = \sum_{i,\,j}^{N,\,N} a_i^* a_j H_{ij} \tag{7.2.10}$$

The optimum coefficients are found by searching for minima in the variational energy landscape spanned by varying the $\{a_i\}$ coefficients (Figure 7.2.1).

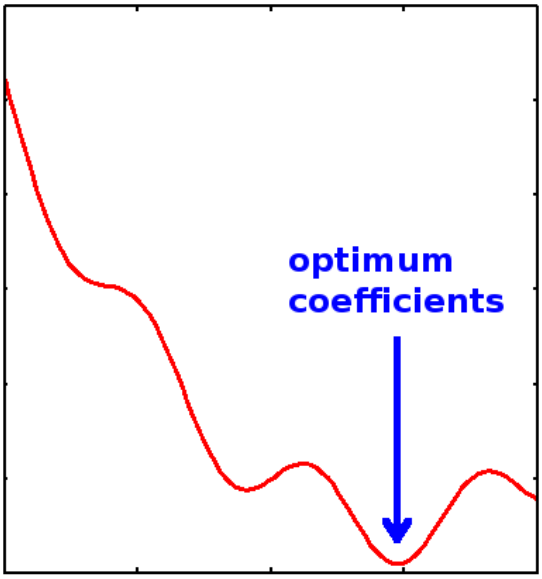


Figure 7.2.1 : Linear Variational Principle in action. Two (or more) wavefunctions are mixed by linear combination. The coefficients a_1, a_2 determine the weight each of them is given. The optimum coefficients are found by searching for minima in the potential landscape spanned by a_1 and a_2. (CC BY-SA-NC; Rudolf Winter; Aberystwyth University).

We want to minimize the energy with respect to the linear coefficients $\{a_i\}$, which requires that

$$\frac{\partial E_{trial}}{\partial a_i} = 0$$

for all i.

Differentiating both sides of Equation 7.2.10 for the kth coefficient gives,

$$\frac{\partial E_{trial}}{\partial a_k} \sum_{i,\,j}^{N,\,N} a_i^* a_j S_{ij} + E_{trial} \sum_i \sum_j \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^* \right] S_{ij} = \sum_{i,\,j}^{N,\,N} \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^* \right] H_{ij} \tag{7.2.11}$$

Since the coefficients are independent

$$\frac{\partial a_i^*}{\partial a_k} = \delta_{ik}$$

and

$$S_{ij} = S_{ji}$$

and also since the Hamiltonian is a Hermitian Operator (see below)

$$H_{ij} = H_{ji}$$

then Equation 7.2.11 simplifies to

$$\frac{\partial E_{trial}}{\partial a_k} \sum_i \sum_j a_i^* a_j S_{ij} + 2 E_{trial} \sum_i a_i S_{ik} = 2 \sum_i a_i H_{ik} \tag{7.2.12}$$

At the minimum variational energy, when

$$\frac{\partial E_{trial}}{\partial a_k} = 0$$

then Equation 7.2.12 gives

$$\sum_{i}^{N} a_i(H_{ik}-E_{trial}S_{ik}) = 0 \tag{7.2.13}$$

for all k. The equations in 7.2.13 are called the **Secular Equations**.

Hermitian Operators

Hermitian operators are operators that satisfy the general formula

$$\langle\phi_i|\hat{A}|\phi_j\rangle = \langle\phi_j|\hat{A}|\phi_i\rangle \tag{7.2.14}$$

If that condition is met, then $\hat{A}$ is a Hermitian operator. For any operator that generates a real eigenvalue (e.g., observables), then that operator is Hermitian. The Hamiltonian $\hat{H}$ meets the condition of a Hermitian operator. Equation 7.2.14 can be rewriten as

$$A_{ij} = A^*_{ji}$$

where

$$A_{ij} = \langle\phi_i|\hat{A}|\phi_j\rangle$$

and

$$A_{ji} = \langle\phi_j|\hat{A}|\phi_i\rangle$$

Therefore, when applied to the Hamiltonian operator

$$H^*_{ij} = H_{ji}.$$

If the functions $\{|\phi_j\rangle\}$ are orthonormal, then the overlap matrix S reduces to the unit matrix (one on the diagonal and zero every where else) and the Secular Equations in Equation 7.2.13 reduces to the more familiar Eigenvalue form:

$$\sum_{i}^{N} H_{ij}a_j = E_{trial}a_i. \tag{7.2.15}$$

Hence, the secular equation, in either form, have as many eigenvalues E_i and eigenvectors {C_{ij}} as the dimension of the H_{ij} matrix as the functions in $|\psi_{trail}\rangle$ (Example 7.2.1). It can also be shown that between successive pairs of the eigenvalues obtained by solving the secular problem at least one exact eigenvalue must occur (i.e.,$E_{i+1} > E_{exact} > E_i$, for all i). This observation is referred to as '*the bracketing theorem*'.

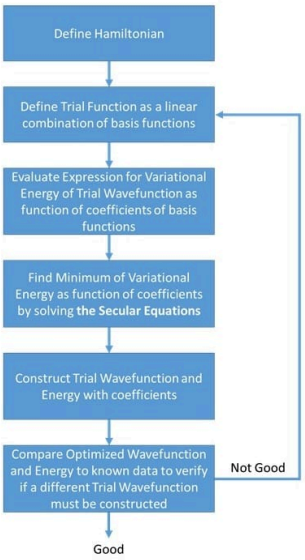


Figure 7.2.2 : Simplified algorithmic flowchart of the linear Variational Method approximation. Compared to the similar algorithmic flowchart for the "normal" Variational Method approximation.

Variational methods, in particular the linear variational method, are the most widely used approximation techniques in quantum chemistry. To implement such a method one needs to know the Hamiltonian H whose energy levels are sought and one needs to construct a trial wavefunction in which some 'flexibility' exists (e.g., as in the linear variational method where the a_j coefficients can be varied). This tool will be used to develop several of the most commonly used and powerful molecular orbital methods in chemistry.

The Secular Determinant

From the secular equations with an orthonormal functions (Equation 7.2.15), we have k simultaneous secular equations in k unknowns. These equations can also be written in matrix notation, and for a non-trivial solution (i.e. $c_i \neq 0$ for all i), the determinant of the secular matrix must be equal to zero.

$$|H_{ik}–ES_{ik}| = 0 \tag{7.2.16}$$

Properties of Determinants

- The determinant is a **real** number, it is **not** a matrix.
- The determinant can be a negative number.
- It is **not** associated with absolute value at all except that they both use vertical lines.
- The determinant **only** exists for square matrices (2×2, 3×3, ..., $n \times n$). The determinant of a 1×1 matrix is that single value in the determinant.
- The inverse of a matrix will exist only if the determinant is not zero.

Expanding Determinants

The determinant can be evaluated using an expansion method involving minors and cofactors. Before we can use them, we need to define them. It is the product of the elements on the main diagonal minus the product of the elements off the main diagonal. In the case of a 2×2 matrix, the specific formula for the determinant is

$$|A| = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc.$$

Similarly, suppose we have a 3×3 matrix A, and we want the specific formula for its determinant $|A|$:

$$|A| = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \begin{vmatrix} d & e \\ g & h \end{vmatrix}$$
$$= aei + bfg + cdh - ceg - bdi - afh.$$

To solve Equation 7.2.16, the determinate should be expanded and then set to zero. That generates a polynomial (called a **characteristic equation**) that can be directly solved with linear algebra methods or numerically.

Example 7.2.1 : A Simple Two Component Basis Set

If $|\psi_{trial}\rangle$ is a linear combination of two functions. In math terms,

$$|\psi_{trial}\rangle = \sum_{n=1}^{N=2} a_n |f_n\rangle = a_1|\phi_1\rangle + a_2|\phi_2\rangle$$

then the secular determinant (Equation 7.2.16), in matrix formulation would look like this

$$\begin{vmatrix} H_{11} - E_{trial}S_{11} & H_{12} - E_{trial}S_{12} \\ H_{12} - E_{trial}S_{12} & H_{22} - E_{trial}S_{22} \end{vmatrix} = 0$$

Solution

Solving the secular equations is done by finding E_{trial} and putting the value into the expansion of the secular determinant

$$a_1^2 H_{11} + 2a_1 a_2 H_{12} + a_2^2 H_{22} = 0$$

and

$$a_1(H_{12} - E_{trial}S_{12}) + a_2(H_{22} - E_{trial}S_{22}) = 0$$

Equation 7.2.16 can be solved to obtain the energies E. When arranged in order of increasing energy, these provide approximations to the energies of the first k states (each having an energy higher than the true energy of the state by virtue of the variation theorem). To find the energies of a larger number of states we simply use a **greater number** of basis functions $\{\phi_i\}$ in the trial wavefunction (Example 7.2.1). To obtain the approximate wavefunction for a particular state, we substitute the appropriate energy into the secular equations and solve for the coefficients a_i.

Using this method it is possible to find all the coefficients $a_1 \ldots a_k$ in terms of one coefficient; normalizing the wavefunction provides the absolute values for the coefficients.

Example 7.2.2 : Linear Combination of Atomic Orbitals (LCAO) Approximation

Trial wavefunctions that consist of linear combinations of simple functions

$$|\psi(r)\rangle = \sum_i a_i |\phi_i(r)\rangle$$

form the basis of the Linear Combination of Atomic Orbitals (LCAO) method introduced by Lennard and Jones and others to compute the energies and wavefunctions of atoms and molecules. The functions $\{|\phi_i\rangle\}$ are selected so that matrix elements can be evaluated analytically. Two basis sets of atomic orbitals functions can be used: Slater type and Gaussian type:

Slater orbitals using Hydrogen-like wavefunctions

$$|\phi_i\rangle = Y_l^m(\theta, \phi)e^{-\alpha r}$$

and Gaussian orbitals of the form

$$|\phi_i\rangle = Y_l^m(\theta,\phi)e^{-\alpha r^2}$$

are the most widely used forms, where $Y_l^m(\theta,\phi)$ are the spherical harmonics that represent the angular part of the atomic orbitals. Gaussian orbitals form the basis of many quantum chemistry computer codes.

Because Slater orbitals give exact results for Hydrogen, we will use Gaussian orbitals to test the LCAO method on Hydrogen, following S.F. Boys, Proc. Roy. Soc. A 200, 542 (1950) and W.R. Ditchfield, W.J. Hehre and J.A. Pople, J. Chem. Phys. Rev. 52, 5001 (1970) with the basis set. Because products of Gaussians are also Gaussian, the required matrix elements are easily computed. The linear variational method is used extensively in molecular orbitals of molecules and further examples will be postponed until that discussion in Chapters 9.

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7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters

Learning Objectives

- Demonstrate that variational problems can include changing parameters within the elements (normal variational method) and changing coefficients of a basis set (linear variational method)

An alternative approach to the general problem of introducing variational parameters into wavefunctions is the construction of a wavefunction as a linear combination of other functions each with one or multiple parameters that can be varied

For hydrogen, the radial function decays, or decreases in amplitude, exponentially as the distance from the nucleus increases. For helium and other multi-electron atoms, the radial dependence of the total probability density does not fall off as a simple exponential with increasing distance from the nucleus as it does for hydrogen. More complex single-electron functions therefore are needed in order to model the effects of electron-electron interactions on the total radial distribution function. One way to obtain more appropriate single-electron functions is to use a sum of exponential functions in place of the hydrogenic spin-orbitals.

An example of such a wavefunction created from a sum or linear combination of exponential functions is written as

$$\varphi_{1s}(r_1) = \sum_j c_j e^{-\zeta_j r_j / a_o} \tag{7.3.1}$$

The linear combination permits weighing of the different exponentials through the adjustable coefficients (c_j) for each term in the sum. Each exponential term has a different rate of decay through the zeta-parameter ζ_j. The exponential functions in Equation 7.3.1 are called **basis functions**. Basis functions are the functions used in linear combinations to produce the single-electron orbitals that in turn combine to create the product multi-electron wavefunctions. Originally the most popular basis functions used were the STO's, but today STO's are not used in most quantum chemistry calculations. However, they are often the functions to which more computationally efficient basis functions are fitted.

Physically, the ζ_j parameters account for the effective nuclear charge (often denoted with Z_{eff}). The use of several zeta values in the linear combination essentially allows the effective nuclear charge to vary with the distance of an electron from the nucleus. This variation makes sense physically. When an electron is close to the nucleus, the effective nuclear charge should be close to the actual nuclear charge. When the electron is far from the nucleus, the effective nuclear charge should be much smaller. See Slater's rules for a rule-of-thumb approach to evaluate Z_{eff} values.

A term in Equation 7.3.1 with a small ζ will decay slowly with distance from the nucleus. A term with a large ζ will decay rapidly with distance and not contribute at large distances. The need for such a linear combination of exponentials is a consequence of the electron-electron repulsion and its effect of screening the nucleus for each electron due to the presence of the other electrons.

Exercise 7.3.1

Make plots of φ in Equation 7.3.1 using three equally weighted terms with ζ = 1.0, 2.0, and 5.0. Also plot each term separately.

Computational procedures in which an exponential parameter like ζ is varied are more precisely called the Nonlinear Variational Method because the variational parameter is part of the wavefunction and the change in the function and energy caused by a change in the parameter is not linear. The optimum values for the zeta parameters in any particular calculation are determined by doing a variational calculation for each orbital to minimize the ground-state energy. When this calculation involves a nonlinear variational calculation for the zetas, it requires a large amount of computer time. The use of the variational method to find values for the coefficients, $\{c_j\}$, in the linear combination given by Equation 7.3.1 above is called the Linear Variational Method because the single-electron function whose energy is to be minimized (in this case φ_{1s}) depends linearly on the coefficients. Although the

idea is the same, it usually is much easier to implement the linear variational method in practice.

Nonlinear variational calculations are extremely costly in terms of computer time because each time a zeta parameter is changed, all of the integrals need to be recalculated. In the linear variation, where only the coefficients in a linear combination are varied, the basis functions and the integrals do not change. Consequently, an optimum set of zeta parameters were chosen from variational calculations on many small multi-electron systems, and these values, which are given in Table 7.3.1 , generally can be used in the STOs for other and larger systems.

Table 7.3.1 : Orbital Exponents for Slater Orbitals

Atom	ζ_{1s}	$\zeta_{2s,2p}$
H	1.24	-
He	1.69	-
Li	2.69	0.80
Be	3.68	1.15
B	4.68	1.50
C	5.67	1.72
N	6.67	1.95
O	7.66	2.25
F	8.56	2.55
Ne	9.64	2.88

Exercise 7.3.2

Compare the value ζ_{1s} = 1.24 in Table 7.3.1 for hydrogen with the value you obtained in Exercise 7.3.1 . and comment on possible reasons for any difference. Why are the zeta values larger for 1s than for 2s and 2p orbitals? Why do the ζ_{1s} values increase by essentially one unit for each element from He to Ne while the increase for the $\zeta_{2s,2p}$ values is much smaller?

Answer available at the end of this section.

The discussion above gives us some new ideas about how to write flexible, useful single-electron wavefunctions that can be used to construct multi-electron wavefunctions for variational calculations. Single-electron functions built from the basis function approach are flexible because they have several adjustable parameters, and useful because the adjustable parameters still have clear physical interpretations. Such functions will be needed in the Hartree-Fock method discussed elsewhere.

Answers

ζ values represent the rate of decay in the radial function of an orbital. ζ values are larger for 1s than 2s and 2p orbitals because 1s orbitals have a smaller radial function. As a result, 1s orbitals decrease faster in radial function as you move further from the nucleus, and have a larger ζ value to represent this faster decay. The ζ values for 1s increase essentially by one unit for each element from He to Ne because the 1s orbital is closest to the nucleus, and experiences the greatest effects from change in electronegativity as nuclear density increases from He to Ne. This increase in electronegativity causes the radial function to decay more and more rapidly as atomic number/nucleus density increase. The 2s and 2p orbitals don't experience as great a change in radial function decay rate because they are shielded by the 1s orbital.

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7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

Learning Objectives

- Use perturbation theory to approximate the energies of systems as a series of perturbation of a solved system.
- Use perturbation theory to approximate the wavefunctions of systems as a series of perturbation of a solved system.

It is easier to compute the changes in the energy levels and wavefunctions with a scheme of successive corrections to the zero-field values. This method, termed **perturbation theory**, is the single most important method of solving problems in quantum mechanics and is widely used in atomic physics, condensed matter and particle physics. Perturbation theory is another approach to finding approximate solutions to a problem, by starting from the exact solution of a related, simpler problem. A critical feature of the technique is a middle step that breaks the problem into "solvable" and "perturbation" parts. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a "small" term to the mathematical description of the exactly solvable problem.

Figure 7.4.1 : Perturbed Energy Spectrum. (CC BY-SA 2.0, Frontier via Wikipedia)

We begin with a Hamiltonian $\hat{H}^0$ having known eigenstates and eigenenergies:

$$\hat{H}^o|n^o\rangle = E_n^o|n^o\rangle \tag{7.4.1}$$

The task is to find how these eigenstates and eigenenergies change if a small term H^1 (an external field, for example) is added to the Hamiltonian, so:

$$(\hat{H}^0 + \hat{H}^1)|n\rangle = E_n|n\rangle \tag{7.4.2}$$

That is to say, on switching on $\hat{H}^1$ changes the wavefunctions:

$$\underbrace{|n^o\rangle}_{\text{unperturbed}} \Rightarrow \underbrace{|n\rangle}_{\text{Perturbed}} \tag{7.4.3}$$

and energies (Figure 7.4.1):

$$\underbrace{E_n^o}_{\text{unperturbed}} \Rightarrow \underbrace{E_n}_{\text{Perturbed}} \tag{7.4.4}$$

> The basic assumption in perturbation theory is that H^1 is sufficiently small that the leading corrections are the same order of magnitude as H^1 itself, and the true energies can be better and better approximated by a successive series of corrections, each of order H^1/H^o compared with the previous one.

The strategy is to **expand** the true wavefunction and corresponding eigenenergy as series in $\hat{H}^1/\hat{H}^o$. These series are then fed into Equation 7.4.2, and terms of the same order of magnitude in $\hat{H}^1/\hat{H}^o$ on the two sides are set equal. The equations thus

generated are solved one by one to give progressively more accurate results.

To make it easier to identify terms of the same order in $\hat{H}^1/\hat{H}^o$ on the two sides of the equation, it is convenient to introduce a dimensionless parameter λ which always goes with $\hat{H}^1$, and then expand both eigenstates and eigenenergies as power series in λ,

$$|n\rangle = \sum_i^m \lambda^i |n^i\rangle \tag{7.4.5}$$

$$E_n = \sum_{i=0}^m \lambda^i E_n^i \tag{7.4.6}$$

where m is how many terms in the expansion we are considering. The ket $|n^i\rangle$ is multiplied by λ^i and is therefore of order $(H^1/H^o)^i$.

> λ is purely a bookkeeping device: we will set it equal to 1 when we are through! It's just there to keep track of the orders of magnitudes of the various terms.

For example, in first order perturbation theory, Equations 7.4.5 are truncated at $m = 1$ (and setting $\lambda = 1$):

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.7}$$

$$E_n \approx E_n^o + E_n^1 \tag{7.4.8}$$

However, let's consider the general case for now. Adding the full expansions for the eigenstate (Equation 7.4.5) and energies (Equation 7.4.6) into the Schrödinger equation for the perturbation Equation 7.4.2 in

$$(\hat{H}^o + \lambda \hat{H}^1)|n\rangle = E_n|n\rangle \tag{7.4.9}$$

we have

$$(\hat{H}^o + \lambda \hat{H}^1)\left(\sum_{i=0}^m \lambda^i |n^i\rangle\right) = \left(\sum_{i=0}^m \lambda^i E_n^i\right)\left(\sum_{i=0}^m \lambda^i |n^i\rangle\right) \tag{7.4.10}$$

We're now ready to match the two sides term by term in powers of λ. Note that the zeroth-order term, of course, just gives back the unperturbed Schrödinger Equation (Equation 7.4.1).

Let's look at Equation 7.4.10 with the first few terms of the expansion:

$$(\hat{H}^o + \lambda \hat{H}^1)\left(|n^o\rangle + \lambda|n^1\rangle\right) = \left(E_n^0 + \lambda E_n^1\right)\left(|n^o\rangle + \lambda|n^1\rangle\right) \tag{7.4.11}$$

$$\hat{H}^o|n^o\rangle + \lambda \hat{H}^1|n^o\rangle + \lambda H^o|n^1\rangle + \lambda^2 \hat{H}^1|n^1\rangle = E_n^0|n^o\rangle + \lambda E_n^1|n^o\rangle + \lambda E_n^0|n^1\rangle + \lambda^2 E_n^1|n^1\rangle \tag{7.4.12}$$

Collecting terms in order of λ and coloring to indicate different orders

$$\underset{\text{zero order}}{\hat{H}^o|n^o\rangle} + \underset{\text{1st order}}{\lambda(\hat{H}^1|n^o\rangle + \hat{H}^o|n^1\rangle)} + \underset{\text{2nd order}}{\lambda^2 \hat{H}^1|n^1\rangle} = \underset{\text{zero order}}{E_n^0|n^o\rangle} + \underset{\text{1st order}}{\lambda(E_n^1|n^o\rangle + E_n^0|n^1\rangle)} + \underset{\text{2nd order}}{\lambda^2 E_n^1|n^1\rangle} \tag{7.4.13}$$

If we expanded Equation 7.4.10 further we could express the energies and wavefunctions in higher order components.

Zero-Order Terms ($\lambda = 0$)

Collecting the zero order terms in the expansion (black terms in Equation 7.4.13) results in just the Schrödinger Equation for the unperturbed system

$$\hat{H}^o|n^o\rangle = E_n^o|n^o\rangle \tag{7.4.14}$$

First-Order Expression of Energy ($\lambda = 1$)

The summations in Equations 7.4.5, 7.4.6, and 7.4.10 can be truncated at any order of λ. For example, the first order perturbation theory has the truncation at $\lambda = 1$. Matching the terms that linear in λ (red terms in Equation 7.4.13) and setting $\lambda = 1$ on both sides of Equation 7.4.13:

$$\hat{H}^o|n^1\rangle + \hat{H}^1|n^o\rangle = E_n^o|n^1\rangle + E_n^1|n^o\rangle \tag{7.4.15}$$

Equation 7.4.15 is the key to finding the first-order change in energy E_n^1. Taking the **inner product** of both sides with $\langle n^o|$:

$$\langle n^o|\hat{H}^o|n^1\rangle + \langle n^o|\hat{H}^1|n^o\rangle = \langle n^o|E_n^o|n^1\rangle + \langle n^o|E_n^1|n^o\rangle \tag{7.4.16}$$

since operating the zero-order Hamiltonian on the bra wavefunction (this is just the Schrödinger equation; Equation 7.4.14) is

$$\langle n^o|\hat{H}^o = \langle n^o|E_n^o \tag{7.4.17}$$

and via the orthonormality of the unperturbed $|n^o\rangle$ wavefunctions both

$$\langle n^o|n^o\rangle = 1 \tag{7.4.18}$$

and Equation 7.4.8 can be simplified

$$\cancel{E_n^o\langle n^o|n^1\rangle} + \langle n^o|H^1|n^o\rangle = \cancel{E_n^o\langle n^o|n^1\rangle} + E_n^1\cancel{\langle n^o|n^o\rangle^1} \tag{7.4.19}$$

since the unperturbed set of eigenstates are orthogonal (Equation 7.4.18) and we can cancel the other term on each side of the equation, we find that

$$E_n^1 = \langle n^o|\hat{H}^1|n^o\rangle \tag{7.4.20}$$

> The first-order change in the energy of a state resulting from adding a perturbing term $\hat{H}^1$ to the Hamiltonian is just the **expectation value** of $\hat{H}^1$ in the **unperturbed** wavefunctions.

That is, the first order energies (Equation 7.4.15) are given by

$$E_n \approx E_n^o + E_n^1 \tag{7.4.21}$$

$$\approx \underbrace{E_n^o + \langle n^o|H^1|n^o\rangle}_{\text{First Order Perturbation}} \tag{7.4.22}$$

7.4.1.A Example : A Perturbed Particle in a Box

Estimate the energy of the ground-state and first excited-state wavefunction within first-order perturbation theory of a system with the following potential energy

$$V(x) = \begin{cases} V_o & 0 \le x \le L \\ \infty & x < 0 \text{ and } x > L \end{cases}$$

Solution

The first step in any perturbation problem is to write the Hamiltonian in terms of a unperturbed component that the solutions (both eigenstates and energy) are known and a perturbation component (Equation 7.4.2). For this system, the unperturbed Hamilonian and solutions is the particle in an infiinitely high box and the perturbation is a shift of the potential within the box by V_o.

$$\hat{H}^1 = V_o$$

Using Equation 7.4.20 for the first-order term in the energy of the ground-state

$$E_n^1 = \langle n^o | H^1 | n^o \rangle$$

with the wavefunctions known from the particle in the box problem

$$|n^o\rangle = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

At this stage we can do two problems independently (i.e., the ground-state with $|1\rangle$ and the first excited-state $|2\rangle$). However, in this case, the first-order perturbation to any particle-in-the-box state can be easily derived.

$$E_n^1 = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) V_o \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) dx$$

or better yet, instead of evaluating this integrals we can simplify the expression

$$E_n^1 = \langle n^o | H^1 | n^o \rangle = \langle n^o | V_o | n^o \rangle = V_o \langle n^o | n^o \rangle = V_o$$

so via Equation 7.4.22, the energy of each perturbed eigenstate is

$$\begin{aligned} E_n &\approx E_n^o + E_n^1 \\ &\approx \frac{h^2}{8mL^2} n^2 + V_o \end{aligned}$$

While this is the first order perturbation to the energy, it is also the exact value.

7.4.1B Example : An Even More Perturbed Particle in a Box

Estimate the energy of the ground-state wavefunction within first-order perturbation theory of a system with the following potential energy

$$V(x) = \begin{cases} V_o & 0 \le x \le L/2 \\ \infty & x < 0 \; and \; x > L \end{cases}$$

Solution

As with Example 7.4.1 , we recognize that unperturbed component of the problem (Equation 7.4.2) is the particle in an infinitely high well. For this system, the unperturbed Hamiltonian and solution is the particle in an infinitely high box and the perturbation is a shift of the potential within half a box by V_o. This is essentially a step function.

Using Equation 7.4.20 for the first-order term in the energy of the any state

$$\begin{aligned} E_n^1 &= \langle n^o | H^1 | n^o \rangle \\ &= \int_0^{L/2} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) V_o \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) dx + \int_{L/2}^{L} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) 0 \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) dx \end{aligned}$$

The second integral is zero and the first integral is simplified to

$$E_n^1 = \frac{2}{L} \int_0^{L/2} V_o \sin^2\left(\frac{n\pi}{L}x\right) dx$$

this is evaluated to

$$E_n^1 = \frac{2V_o}{L}\left[\frac{-1}{2\frac{\pi n}{a}}\cos\left(\frac{n\pi}{L}x\right)\sin\left(\frac{n\pi}{L}x\right) + \frac{x}{2}\right]_0^{L/2}$$
$$= \frac{2V_o}{\cancel{L}}\frac{\cancel{L}}{4} = \frac{V_o}{2}$$

The energy of each perturbed eigenstate, via Equation 7.4.22, is

$$E_n \approx E_n^o + \frac{V_o}{2}$$
$$\approx \frac{h^2}{8mL^2}n^2 + \frac{V_o}{2}$$

First-Order Expression of Wavefunction ($\lambda = 1$)

The general expression for the first-order change in the *wavefunction* is found by taking the inner product of the first-order expansion (Equation 7.4.15) with the bra $\langle m^o|$ with $m \neq n$,

$$\langle m^o|H^o|n^1\rangle + \langle m^o|H^1|n^o\rangle = \langle m^o|E_n^o|n^1\rangle + \langle m^o|E_n^1|n^o\rangle \tag{7.4.23}$$

Last term on right side of Equation 7.4.23

The last integral on the right hand side of Equation 7.4.23 is zero, since $m \neq n$ so

$$\langle m^o|E_n^1|n^o\rangle = E_n^1\langle m^o|n^o\rangle \tag{7.4.24}$$

and

$$\langle m^o|n^0\rangle = 0 \tag{7.4.25}$$

First term on right side of Equation 7.4.23

The first integral is more complicated and can be expanded back into the H^o

$$E_m^o\langle m^o|n^1\rangle = \langle m^o|E_m^o|n^1\rangle = \langle m^o|H^o|n^1\rangle \tag{7.4.26}$$

since

$$\langle m^o|H^o = \langle m^o|E_m^o \tag{7.4.27}$$

so

$$\langle m^o|n^1\rangle = \frac{\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o} \tag{7.4.28}$$

and therefore the wavefunction corrected to first order is:

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.29}$$
$$\approx \underbrace{|n^o\rangle + \sum_{m\neq n}\frac{|m^o\rangle\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o}}_{\text{First Order Perturbation Theory}} \tag{7.4.30}$$

Equation 7.4.30 is essentially is an expansion of the unknown wavefunction correction as a **linear combination** of known unperturbed wavefunctions 7.4.32:

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.31}$$

$$\approx |n^o\rangle + \sum_{m \neq n} c_{m,n}|m^o\rangle \tag{7.4.32}$$

with the expansion coefficients determined by

$$c_{m,n} = \frac{\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o} \tag{7.4.33}$$

This is justified since the set of original zero-order wavefunctions forms a **complete basis set** that can describe any function.

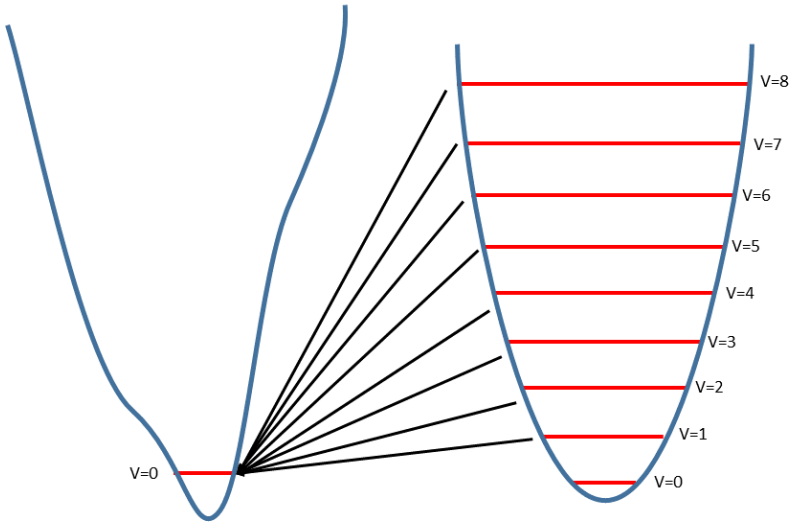


Figure 7.4.2 : The first order perturbation of the ground-state wavefunction for a perturbed (left potential) can be expressed as a linear combination of all excited-state wavefunctions of the unperturbed potential (Equation 7.4.32), shown as a harmonic oscillator in this example (right potential). Note that the ground-state harmonic oscillator wavefunction is not part of this expression and all wavefunctions need to be included in the expression, not just the first eight wavefunctions shown here. (CC BY 4.0; Delmar Larsen)

Calculating the first order perturbation to the wavefunctions is in general an infinite sum of off diagonal matrix elements of H^1 (Figure 7.4.2).

- However, the denominator argues that terms in this sum will be weighted by states that are of **comparable energy**. That means in principle, these sum can be truncated easily based off of some criterion.
- Another point to consider is that many of these matrix elements will equal zero depending on the symmetry of the $\{|n^o\rangle\}$ basis and H^1 (e.g., some $\langle m^o|H^1|n^o\rangle$ integrals in Equation 7.4.30 could be zero due to the integrand having an odd symmetry; see Example 7.4.3).

The denominators in Equation 7.4.30 argues that terms in this sum will be preferentially dictated by states that are of **comparable energy**. That is, eigenstates that have energies significantly greater or lower than the unperturbed eigenstate will weakly contribute to the perturbed wavefunction.

Example 7.4.2 : A Harmonic Oscillator with a Cubic Perturbation

Estimate the energy of the ground-state wavefunction associated with the Hamiltonian using perturbation theory

$$\hat{H} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \epsilon x^3$$

Solution

The first step in a perturbation theory problem is to identify the reference system with the known eigenstates and energies. For this example, this is clearly the harmonic oscillator model.

Energy

The first steps in flowchart for applying perturbation theory (Figure 7.4.1) is to separate the Hamiltonian of the difficult (or unsolvable) problem into a solvable one with a perturbation. For this case, we can rewrite the Hamiltonian as

$$\hat{H}^o + \hat{H}^1$$

where

- $\hat{H}^o$ is the Hamitonian for the standard Harmonic Oscillator with **known** eigenstates and eigenenergies

$$\hat{H}^{(0)} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

- $\hat{H}^1$ is the pertubtiation

$$\hat{H}^1 = \epsilon x^3$$

The first order perturbation is given by Equation 7.4.20, which for this problem is

$$E_n^1 = \langle n^o | \epsilon x^3 | n^o \rangle$$

Notice that the integrand has an odd symmetry (i.e., $f(x) = -f(-x)$) with the perturbation Hamiltonian being odd and the ground state harmonic oscillator wavefunctions being even. So

$$E_n^1 = 0$$

This means to first order pertubation theory, this cubic terms does not alter the ground state energy (via Equation 7.4.22). However, this is not the case if second-order perturbation theory were used, which is more accurate (not shown).

Wavefunction

Calculating the first order perturbation to the wavefunctions (Equation 7.4.30) is more difficult than energy since multiple integrals must be evaluated (an infinite number if symmetry arguments are not applicable). The harmonic oscillator wavefunctions are often written in terms of Q, the unscaled displacement coordinate:

$$|\Psi_v(x)\rangle = N_v'' H_v(\sqrt{\alpha}Q) e^{-\alpha Q^2/2}$$

with α

$$\alpha = 1/\sqrt{\beta} = \sqrt{\frac{k\mu}{\hbar^2}}$$

and

$$N_v'' = \sqrt{\frac{1}{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

Let's consider only the first six wavefunctions that use these Hermite polynomials $H_v(x)$:

- $H_0 = 1$
- $H_1 = 2x$
- $H_2 = -2 + 4x^2$
- $H_3 = -12x + 8x^3$
- $H_4 = 12 - 48x^2 + 16x^4$
- $H_5 = 120x - 160x^3 + 32x^5$

The first order perturbation to the ground-state wavefunction (Equation 7.4.30)

$$|0^1\rangle = \sum_{m\neq 0}^{5} \frac{|m^o\rangle\langle m^o|H^1|0^o\rangle}{E_0^o - E_m^o} \tag{7.4.34}$$

given these truncated wavefunctions (we should technically use the infinite sum) and that we are considering only the ground state with $n = 0$:

$$|0^1\rangle = \frac{\langle 1^o|H^1|0^o\rangle}{E_0^o - E_1^o}|1^o\rangle + \frac{\langle 2^o|H^1|0^o\rangle}{E_0^o - E_2^o}|2^o\rangle + \frac{\langle 3^o|H^1|0^o\rangle}{E_0^o - E_3^o}|3^o\rangle + \frac{\langle 4^o|H^1|0^o\rangle}{E_0^o - E_4^o}|4^o\rangle + \frac{\langle 5^o|H^1|0^o\rangle}{E_0^o - E_5^o}|5^o\rangle$$

We can use symmetry of the perturbation and unperturbed wavefunctions to solve the integrals above. We know that the unperturbed harmonic oscillator wavefunctions $\{|n^0\}\rangle$ alternate between even (when v is even) and odd (when v is odd) as shown previously. Since the perturbation is an odd function, only when $m = 2k + 1$ with $k = 1, 2, 3$ would these integrals be non-zero (i.e., for $m = 1, 3, 5, ...$).

So of the original five unperturbed wavefunctions, only $|m = 1\rangle$, $|m = 3\rangle$, and $|m = 5\rangle$ mix to make the first-order perturbed ground-state wavefunction so

$$|0^1\rangle = \frac{\langle 1^o|H^1|0^o\rangle}{E_0^o - E_1^o}|1^o\rangle + \frac{\langle 3^o|H^1|0^o\rangle}{E_0^o - E_3^o}|3^o\rangle + \frac{\langle 5^o|H^1|0^o\rangle}{E_0^o - E_5^o}|5^o\rangle$$

At this stage, the integrals have to be manually calculated using the defined wavefuctions above, which is left as an exercise. Notice that each unperturbed wavefunction that can "mix" to generate the perturbed wavefunction will have a reciprocally decreasing contribution (w.r.t. energy) due to the growing denominator in Equation 7.4.34.

Exercise 7.4.3 : Harmonic Oscillator with a Quartic Perturbation

Use perturbation theory to estimate the energy of the ground-state wavefunction associated with this Hamiltonian

$$\hat{H} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \gamma x^4.$$

Answer available at the end of this section.

Second-Order Terms ($\lambda = 2$)

There are higher energy terms in the expansion of Equation 7.4.5 (e.g., the blue terms in Equation 7.4.13), but are not discussed further here other than noting the whole perturbation process is an infinite series of corrections that ideally converge to the correct answer. It is truncating this series as a finite number of steps that is the approximation. The general approach to perturbation theory applications is giving in the flowchart in Figure 7.4.1 .

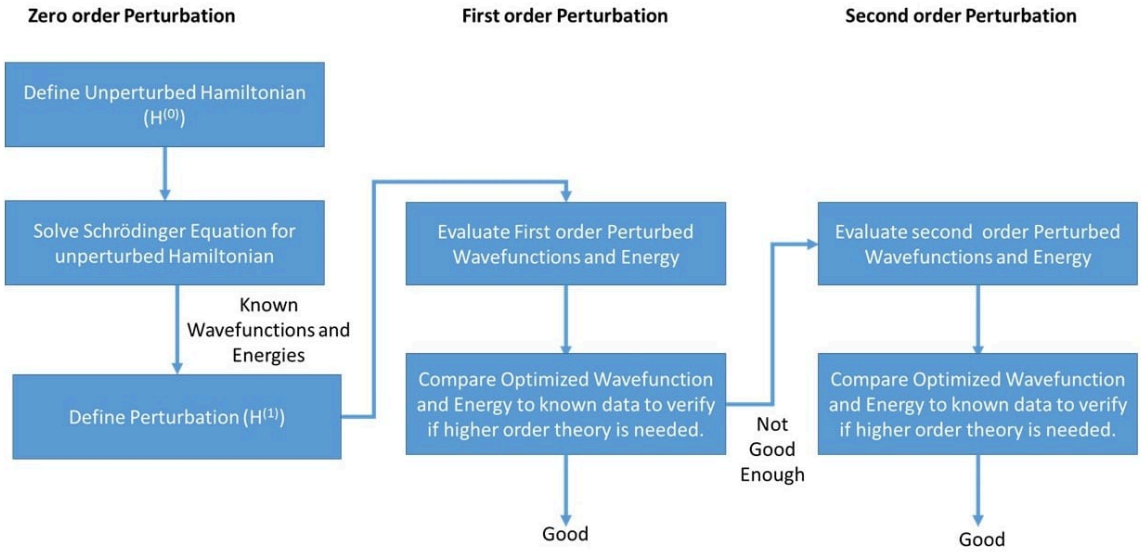


Figure 7.4.1 : Simplified algorithmic flowchart of the Perturbation Theory approximation showing the first two perturbation orders. The process can be continued to third and higher orders. (CC BY 4.0; Delmar Larsen)

Perturbation Theory Does not always Work

It should be noted that there *are* problems that cannot be solved using perturbation theory, even when the perturbation is very weak, although such problems are the exception rather than the rule. One such case is the one-dimensional problem of free particles perturbed by a localized potential of strength λ. Switching on an arbitrarily weak attractive potential causes the $k = 0$ free particle wavefunction to drop below the continuum of plane wave energies and become a localized bound state with binding energy of order λ^2. However, changing the sign of λ to give a repulsive potential there is no bound state, the lowest energy plane wave state stays at energy zero. Therefore the energy shift on switching on the perturbation **cannot** be represented as a power series in λ, the strength of the perturbation.

Answers

The model that we are using is the harmonic oscillator model which has a Hamiltonian

$$H^0 = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

Making the perturbed Hamiltonian

$$H^1 = \gamma x^4$$

To find the perturbed energy we approximate it using Equation 7.4.22

$$E^1 = \langle n^0 \left| H^1 \right| n^0 \rangle$$

where is the wavefunction of the ground state harmonic oscillator

$$n^0 = \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}}$$

When we substitute in the Hamiltonian and the wavefunction we get

$$E^1 = \left\langle \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}} \middle| \gamma x^4 \middle| \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}} \right\rangle$$

Changing this into integral form, and combining the wavefunctions,

$$E^1 = \int_{-\infty}^{\infty} \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} e^{\frac{-ax^2}{2}} \gamma x^4 dx$$

$$= \gamma \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx$$

Now we use the integral table value

$$\int_0^{\infty} x^{2\pi} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \ldots (2n-1)}{2^{n+1} a^n} \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

Where we plug in $\mathrm{n} = 2$ and $\mathrm{a} = \alpha$ for our integral

$$E^1 = 2\gamma \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} \int_0^\infty x^4 e^{-ax^2} dx$$
$$= 2\gamma \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} \frac{1 \cdot 3}{2^3 a^2} \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

This is our perturbed energy.

Now we have to find our ground state energy using the formula for the energy of a harmonic oscillator that we already know,

$$E_r^0 = \left(v + \frac{1}{2}\right) h\nu$$

Where in the ground state $v = 0$ so the energy for the ground state of the quantum harmonic oscillator is

$$E_r^0 = \frac{1}{2} h\nu$$

Putting both of our energy terms together gives us the ground state energy of the wavefunction of the given Hamiltonian,

$$E = E^0 + E^1$$
$$= \frac{1}{2} h\nu + \gamma \frac{3}{4a^2}$$

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7.E: Approximation Methods (Exercises)

Solutions to select questions can be found online.

7.3

Calculate the ground state energy of Harmonic Oscillator using variation method with the following trial wavefunction

$$\phi(x) = |\phi(x)\rangle = \frac{1}{(1+\beta x^2)^2}$$

You may require these definite integrals:

$$\int_{-\infty}^{\infty} \frac{dx}{(1+\beta x^2)^n} = \frac{(2n-3)(2n-5)(2n-7)\ldots(1)}{(2n-2)(2n-4)(2n-6)\ldots(2)\cdot\pi/\beta^{1/2}}$$

$$\int_{-\infty}^{\infty} \frac{dx}{(1-\beta x^2)^n} = \frac{(2n-5)(2n-7)\ldots(1)}{(2n-2)(2n-4)\ldots(2)\cdot\pi/\beta^{3/2}}$$

Solution

First, we must know the Hamiltonian operator for the harmonic oscillator, which is

$$\hat{H} = \frac{-\hbar}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

From this point on, the determination of $E_{\o}$ can be found using the trail function

$$|\phi(x)\rangle = \frac{1}{(1+\beta x^2)^2}$$

which once substitute get the following equation for the numerator portion:

$$\int_{-\infty}^{-\infty} \frac{1}{(1+\backslash\text{betax}^2)^2[\hbar^2/\mu * 2\beta/(1+\backslash\text{betax}^2)^3 - \hbar^2/\mu * 12\beta^2x^2/(1+\backslash\text{betax}^2)^4 + \frac{kx^2}{2}(1+\backslash\text{betax}^2)^2]}$$

$$= 2\beta\hbar^2/\mu * (7*5*3*1*\pi/8*6*4*2*\beta 1/2) - 12\beta^2\hbar^2/\mu * (7*5*3*1*\pi/10*8*6*4*2*\beta 1/2) + k/2 * (3*1*\pi$$

$$= \frac{7\pi\beta^{1/2}\hbar}{32\mu + k\pi/32\beta^{3/2}}$$

Now solving the denominator:

$$\int_{\infty}^{\infty} \phi^*\phi\, dx = \int_{\infty}^{\infty} \frac{1}{(1+\beta x^2)^4} = \frac{5*3*1*\pi}{6*4*2*\beta^{1/2}} = \frac{5\pi}{/16\beta^{1/2}}$$

After this we will find

$$E_\phi = \frac{7\pi\beta^{1/2}\hbar^2}{32\mu * (16\beta^{1/2}/5\pi)} + \frac{k\pi}{32\beta^{3/2} * (16\beta^{1/2}/5\pi)} = \frac{7/10 * \beta\hbar 2}{\mu} + \frac{1}{10}\frac{k}{\beta}$$

Then find minimum value

\[\dfrac{dE_\phi}{d \beta}= \dfrac{7 \hbar^2}{10μ} -\dfrac{ k}{10 \beta^2_{min} = 0\nonumber \]

therefore

$$\beta_{min} = \sqrt{\frac{\mu k}{7\hbar^2}}$$

\[E_{min}= \dfrac{7^{1/2} \hbar }{5 * (k/μ)^{1/2}} + \dfrac{7^{1/2} \hbar }{5 (k/μ)^{1/2} }= 71/2 \hbar /5 (k/μ)^{1/2} = 0.53 \hbar *(k/μ)^{1/2}\nonumber \]

Therefore overall get

$$E_{exact} = 0.500\hbar\sqrt{(k/\mu)}$$

⇒ this value differs by 6%.

7.8

What is the variational (trial) energy of the trial function

$$|\phi\rangle = e^{-ax^2}$$

for the ground-state of a harmonic oscillator? Just set up the integral, but do not evaluate. Use

$$\hat{H} = \frac{\hbar^2}{2m}\nabla n^2 + \frac{kx^2}{2}$$

Solution

The variational energy:

$$E_{trial}(a) = \frac{\langle\phi(a)|\hat{H}|\phi(a)\rangle}{\langle\phi(a)|\phi(a)\rangle} \geq E_{true}$$

numerator:

$$\langle\phi|\phi\rangle = \int_{-\infty}^{\infty} e^{-2ax^2}dx$$

All combined together to extract the trial energy as a function of a:

$$E_{trial}(a) = \frac{\int_{-\infty}^{\infty} e^{-ax^2}\left[\frac{\hbar^2}{2m}\frac{d^2(e^{-ax^2})}{dx^2} + \frac{kx^2}{2}\right]e^{-ax^2}dx}{\int_{-\infty}^{\infty} e^{-2ax^2}dx}$$

Use the components of $\hat{H}$ to operate on ϕ

$$\langle\phi|\hat{H}|\phi\rangle = \int_{-\infty}^{\infty} e^{-ax^2}\left[\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{kx^2}{2}\right]e^{-ax^2}dx$$

denominator:

$$\langle\phi|\phi\rangle = \int_{-\infty}^{\infty} e^{-ax^2}e^{-ax^2}dx$$

7.9

Use the trial function

$$|\exp^{\frac{-\alpha x^2}{2}}\rangle$$

to set up the integrals to find the ground state energy of a anharmonic oscillator whose potential is $V(x) = cx^5$, but do not evaluate.

Solution

$$E = \frac{\int_{-\infty}^{\infty} \phi^* \hat{H} \phi d\tau}{\int_{-\infty}^{\infty} \phi^* \phi d\tau}$$

$$\int_{-\infty}^{\infty} \phi^* \phi d\tau = \int_{-\infty}^{\infty} \exp^{-\alpha x^2} dx$$

$$\int_{-\infty}^{\infty} \phi^* \hat{H} \phi d\tau = \int_{-\infty}^{\infty} (\frac{\hbar^2}{2m}\nabla^2 + \frac{kx^2}{2} + cx^5) \exp^{-\alpha x^2} dx$$

$$E = \frac{\int_{-\infty}^{\infty} (\frac{\hbar^2}{2m}\nabla^2 + \frac{kx^2}{2} + cx^5) \exp^{-\alpha x^2} dx}{\int_{-\infty}^{\infty} \exp^{-\alpha x^2} dx}$$

7.12

Consider a particle of mass m in a box from $x = -a$ to $x = a$ with $V(x) = -V_0$ for $|x| \geq a$. Assume a trial function of the form

$$|\phi(x)\rangle = l^2 - x^2$$

for $-l < x < l$ and $\psi(x) = 0$ otherwise. l is the parameter. Does the trial function satisfy the requirements of a particle in a box wavefunction?

The result of the variational method was

$$E_\phi(s) = \frac{5}{16}\frac{\hbar^2}{ma^2}\left[\frac{4}{s^2} + \frac{4}{5}\left(8 - \frac{15}{s} + \frac{10}{s^3} - \frac{3}{s^5}\right)\right]$$

Where $s = \dfrac{l}{a}$ is a new variational parameter for convenience of expression. Derive a polynomial expression for s that can be solved to obtain the value of s that yields the ground state energy, but do not attempt to solve for this value of s .

Solution

Yes, it is finite over all x values, it's first and second derivatives are continuous, and it meets the boundary conditions $\psi(-a) = \psi(a) = 0$, and it is normalizable for a choice of l.

Taking the derivative of E with respect to s,

$$\frac{\partial E}{\partial s} = 0 = -\frac{8}{s^3} + \frac{4}{5}\left(\frac{15}{s^2} - \frac{30}{s^4} + \frac{15}{s^6}\right)$$

With some algebra, this becomes,

$$3s^4 - 2s^3 - 6s^2 + 3 = 0$$

With a calculator or other root finding procedure, s can be solved for.

7.13

Given a trial wavefunction equal to $\sin\lambda(x)$, explain in words a stepwise procedure on how you would go about solving for the energy of this trial wavefunction as well as how to minimize the error.

Solution

1. Denote $\sin(\lambda(x)) = \phi_n$

2. Solve the integral $\langle\phi_n^*|\phi_n\rangle$

3. Solve the integral $\langle\phi_n^*|\hat{H}|\phi_n\rangle$

4. Now that you solved for steps 2 and 3, plug into the equation

$$E_n = \frac{\langle\phi_n^*|\hat{H}|\phi_n\rangle}{\langle\phi_n^*|\phi_n\rangle}$$

5. Take the derivative of E_n with respect to λ and set equal to 0.

$$\frac{dE_n}{d\lambda}$$

6. Solve for λ and plug back into equation in step 4.

7.16

Using the variational method approximation, find the ground state energy of a particle in a box using this trial function:

$$|\phi\rangle = N\cos\left(\frac{\pi x}{L}\right)$$

How does is it compare to the true ground state energy?

Solution

The problem asks that we apply variational methods approximation to our trial wavefunction.

$$E_\phi = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} \geq E_o$$

$$\langle\phi|\phi\rangle = 1 = \int_0^L N^2\cos^2\left(\frac{\pi x}{L}\right)$$

Performing this integral and solving for N yields

$$N = \sqrt{\frac{2}{L}}$$

The Hamiltonian for a particle in a one dimensional box is $\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$

$$\begin{aligned}\langle\phi|\hat{H}|\phi\rangle &= \langle N\cos\left(\frac{\pi x}{L}\right)\Big|\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\Big|N\cos\left(\frac{\pi x}{L}\right)\rangle \\ &= \int_0^L N\cos\left(\frac{\pi x}{L}\right)\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}N\cos\left(\frac{\pi x}{L}\right)dx \\ &= \frac{N^2\pi^2\hbar^2}{2mL^2}\int_0^L\cos^2\left(\frac{\pi x}{L}\right)dx\end{aligned}$$

where $N = \sqrt{\frac{2}{L}}$. The above equation after the integral becomes

$$\frac{\pi^2\hbar^2}{mL^3}\left(\frac{L}{2}\right)$$

$$E_\phi = \frac{\pi^2\hbar^2}{2mL^2}$$

This is equal to the ground state energy of the particle in a box that we calculated from the Schrodinger equation using

$$\psi = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})$$

7.17

For the three-electron detrimental wavefunction

$$\psi = \begin{vmatrix} \phi_A(1) & \phi_A(2) & \phi_A(3) \\ \phi_B(1) & \phi_B(2) & \phi_B(3) \\ \phi_C(1) & \phi_C(2) & \phi_C(3) \end{vmatrix}.$$

confirm that:

a. the interchange of two columns changes the sign of the wavefunction,
b. the interchange of two rows changes the sign of the wavefunction, and
c. the three electrons cannot have the same spin orbital.

Solution

First find the determinant

$$\psi = \phi_A(1) \begin{vmatrix} \phi_B(2) & \phi_B(3) \\ \phi_C(2) & \phi_C(3) \end{vmatrix} - \phi_A(2) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(1) & \phi_B(2) \\ \phi_C(1) & \phi_C(2) \end{vmatrix}$$

$$= \phi_A(1)\ (\phi_B(2)\phi_C(3) - \phi_C(2)\phi_B(3)) - \phi_A(2)\ (\phi_B(1)\phi_C(3) - \phi_C(1)\phi_B(3)) + \phi_A(3)\ (\phi_B(1)\phi_C(2) - \phi_C(1)\phi_B(2))$$

$$\psi = \phi_A(1)\phi_B(2)\phi_C(3) - \phi_A(1)\phi_C(2)\phi_B(3) - \phi_A(2)\phi_B(1)\phi_C(3) + \phi_A(2)\phi_C(1)\phi_B(3) + \phi_A(3)\phi_B(1)\phi_C(2) - \phi_A(3)\phi_C(1)\phi_B$$

a) Switch column 1 with column 2

$$\psi_{(a)} = \begin{vmatrix} \phi_A(2) & \phi_A(1) & \phi_A(3) \\ \phi_B(2) & \phi_B(1) & \phi_B(3) \\ \phi_C(2) & \phi_C(1) & \phi_C(3) \end{vmatrix}$$

Now find the determinant

$$\phi_{(a)} = \phi_A(2) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} - \phi_A(1) \begin{vmatrix} \phi_B(2) & \phi_B(3) \\ \phi_C(2) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(2) & \phi_B(1) \\ \phi_C(2) & \phi_C(1) \end{vmatrix}$$

$$\phi_{(a)} = \phi_A(2)\phi_B(1)\phi_C(3) - \phi_A(2)\phi_C(1)\phi_B(3) - \phi_A(1)\phi_B(2)\phi_C(3) + \phi_A(1)\phi_C(2)\phi_B(3) + \phi_A(3)\phi_B(2)\phi_C(1) - \phi_A(3)\phi_C(2)\phi$$

Comparing equation (5) with equation (6) we see that $\phi = -\phi_{(a)}$

b) Switch row 2 with row 3

$$\phi_{(b)} = \begin{vmatrix} \phi_A(1) & \phi_A(2) & \phi_A(3) \\ \phi_C(1) & \phi_C(2) & \phi_C(3) \\ \phi_B(1) & \phi_B(2) & \phi_B(3) \end{vmatrix}.$$

Now find the determinant

$$\phi_{(b)} = \phi_A(1) \begin{vmatrix} \phi_C(2) & \phi_C(3) \\ \phi_B(2) & \phi_B(3) \end{vmatrix} - \phi_A(2) \begin{vmatrix} \phi_C(1) & \phi_C(3) \\ \phi_B(1) & \phi_B(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_C(1) & \phi_C(2) \\ \phi_B(1) & \phi_B(2) \end{vmatrix}$$

$$\phi_{(b)} = \phi_A(1)\phi_C(2)\phi_B(3) - \phi_A(1)\phi_B(2)\phi_C(3) - \phi_A(2)\phi_C(1)\phi_B(3) + \phi_A(2)\phi_B(1)\phi_C(3) + \phi_A(3)\phi_C(1)\phi_B(2) - \phi_A(3)\phi_B(1)\phi$$

Comparing equation (5) with equation (7) we see that $\phi = -\phi_{(b)}$

c) Replace column 2 with column 1

$$\phi_{(c)} = \begin{vmatrix} \phi_A(1) & \phi_A(1) & \phi_A(3) \\ \phi_B(1) & \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(1) & \phi_C(3) \end{vmatrix}$$

Now find the determinant

$$\phi_{(c)} = \phi_A(1) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} - \phi_A(1) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(1) & \phi_B(1) \\ \phi_C(1) & \phi_C(1) \end{vmatrix}$$

The first two terms are identical but opposite so they cancel one another. The third has a determinant of zero.

$$\phi_{(c)} = 0 + \phi_A(3) \cdot (0) = 0$$

7.20

a. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for an oscillator that has a potential of

$$V(x) = (1/2)kx^2 + x^3 + x^4 + x^5?$$

b. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for a particle in a box that has a potential of $V(x) = 0$ between 0<x<L?

c. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for a hydrogenlike atom that has a potential of

$$V(x) = \frac{-e^2}{4\pi\epsilon_o r} + \frac{1}{2}\epsilon r\cos\theta?$$

Solution

For an oscillator:

$$\hat{H} = \frac{-\hbar 2}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}kx^2 + x^3 + x^4 + x^6$$

$\hat{H}^{(0)}$ is the Hamiltonian for a simple harmonic oscillator, therefore

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}kx^2$$

$\hat{H}^{(1)}$ is what is added to the Hamiltonian for a simple harmonic oscillator. therefore

$$\hat{H}^{(1)} = x^3 + x^4 + x^5$$

$\Psi^{(0)}$ is the wave function for a simple harmonic oscillator, therefore

$$\Psi^{(0)} = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

$E^{(0)}$ is the energy for a simple harmonic oscillator, therefore

$$E^{(0)} = h\nu\left(v + \frac{1}{2}\right)$$

where v= 0,1, 2... ∞

Particle in a box

Using this as an example, we find that for a particle in a box with potential V(x) = 0 between 0<x<L

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$\hat{H}^{(0)} = -\frac{\hbar 2}{2m}\frac{\partial^2}{\partial x^2}$$

\[\hat{H}^{(1)} = 0\nonumber \]

$\Psi^{(0)}$ =B*sin(nπx/L)

$E^{(0)} = n^2h^2 / 8mL^2$ where n= 1, 2, 3 ... ∞

Hydrogen like Atom

For a hydrogen like atom that has a potential of

$$V(x) = -\frac{e^2}{4\pi\epsilon_o r} + (1/2)\epsilon r\cos\theta$$

\[\hat{H} = - ħ ^{2}/2μ ∂2 /∂x2 ∇^2 -e^2/(4πϵ$_o$r) + (1/2)ϵrcosθ\nonumber \]

\[\hat{H}^{(0)} = - ħ ^2/2μ ∂2 /∂x2 ∇^2 -e^2/(4πϵ_0r)\nonumber \]

\[\hat{H}^{(1)} =(1/2)ϵrcosθ\nonumber \]

$Ψ^{(0)} = Ψ_{n,l,m} (r,θ,ϕ)$

$E^{(0)} = μe^4 / 8ϵ_o^2h^2n^2$

7.21

Using a harmonic oscillator as the unperturbed problem, calculate the first-order correction to the energy of the $v = 0$ level for the system described as

$$V(x) = \frac{k}{2}x^2 + \frac{m}{6}x^3 + \frac{b}{24}x^4$$

7.22

Using the first order perturbation theory for particle in a box, calculate the ground-state energy for the system

$$V(x) = ax^3 \qquad 0 < x < b$$

Solution

$$\psi_1 = \sqrt{\frac{2}{b}}\sin(\frac{\pi x}{b})$$

$$\widehat{H} = \widehat{H}^0 + \widehat{H}^1$$

$$\widehat{H}^1 = ax^3$$

$$E_1 = E_1^0 + E_1^1$$

$$E_1^0 = \frac{h^2}{8mb^2}$$

$$E_1^1 = \langle\psi^1|\widehat{H}^1|\psi^1\rangle$$

$$= \int_0^b \frac{2a}{b}x^3\sin^2(\frac{\pi x}{b})dx$$

$$= \frac{2a}{b}\frac{(\pi^2-3)b^4}{8\pi^2}$$

$$= \frac{(\pi^2-3)ab^3}{4\pi^2}$$

$$E_1 = \frac{h^2}{8mb^2} + \frac{(\pi^2-3)ab^3}{4\pi^2}$$

7.23

In your chemistry lab you were able to manipulate an external electric field to have the strength κ. You're supervisor wants you to figure out what the first-order correction to the ground state energy of a hydrogen like atom of charge N in this electric field.

Solution

You should remember, or look up the ground state wavefunction for a hydrogen atom and find that

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{Z_\circ} \right)^{\frac{3}{2}} e^{-r/a_\circ}$$

Our change in energy equation has a familiar form

$$\Delta E = \int \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} d\tau$$

For this problem you construct a Hamiltonian for a Hydrogen atom in an electron field with strength κ.

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ne^2}{4r\pi\kappa_\circ} + er\kappa \cos\theta$$

Luckily you have previously calculated $\hat{H}^{(1)}$ for this system in a previous experiment, simply allowing you to substitute your variables into your expressions to find that

$$\Delta E = \frac{Ne\kappa}{\pi} \left(\frac{1}{Z_\circ} \right)^3 \int_0^\infty r^3 e^{\frac{-r}{a_\circ}} dr \int_0^{2\pi} d\phi \int_0^\pi \sin\theta \cos\theta d\theta$$

Notice that the problem gets simplified by the fact that

$$\int_0^\pi \sin\theta \cos\theta d\theta = 0$$

So your answer is a trivial solution.

$$\boxed{\Delta E = 0}$$

7.25A

Use first-order perturbation theory to calculate ground-state energy of a harmonic oscillator with a cx^7 added to the end of the potential.

Solution

The Hamiltonian to the system can be formulated as

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^7$$

we then solve

$$E^1 = \langle\psi_0|cx^7|\psi_0\rangle$$

We know that the integral is of an odd function over a symmetric boundary is 0, so by symmetry we can conclude that the energy is 0.

7.25B

In order to calculate the first-order correction to the ground-state energy of the quartic oscillator, use first-order perturbation theory. The potential energy is $V(x) = cx^4$. For this potential use the harmonic oscillator as the unperturbed system. Solve for the perturbing potential as well.

Solution

The Hamiltonian operator is given below:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + cx^4$$

To use a harmonic oscillator as the reference system, add and subtract $\frac{1}{2}kx^2$ from $\hat{H}$.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d}{dx^2} + \frac{1}{2}kx^2 \ + cx^4 - \frac{1}{2}kx^2$$

Hence we get :

$$\hat{H}^{(0)} = cx^4 - \frac{1}{2}kx^2$$

Now we have:

$$\Delta E = \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)} \ d\tau \ldots.$$

By putting the values in the equation above, we get:

$$\Delta E = \left(\frac{\alpha}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} dx e^{-x^2\alpha}\left(cx^4 - \frac{1}{2}kx^2\right)$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} 2\left[\frac{3c}{8\alpha^2}\left(\frac{\pi}{\alpha}\right)^{1/2} - \frac{k}{8\alpha}\left(\frac{\pi}{\alpha}\right)^{1/2}\right]$$

$$= \frac{3c}{4\alpha^2} - \frac{k}{4\alpha}$$

7.26

Solve the following integrals using this trial wavefunction

$$|\phi\rangle = c_1 x(a-x) + c_2 x^2 (a-x)^2$$

For simplicity purposes, we can assume that a = 1.

$$H_{11} = \frac{\hbar^2}{6m} \; S = \frac{1}{30}$$

$$H_{12} = H_{22} = \frac{\hbar^2}{30m} \; S_{12} = S_{21} = \frac{1}{140}$$

$$H_{22} = \frac{\hbar^2}{105m} \; S_{22} = \frac{1}{630}$$

Solution

We know that for a particle in a box

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$$

We also know the two components of the trial function that was given are

$$\phi_1 = x(a-x)$$

and

$$\phi_2 = x^2 (a-x)^2$$

Using this we will have

$$\hat{H}\phi_1 = \frac{\hbar^2}{2m}$$

and

$$\hat{H}\phi_2 = \frac{\hbar^2}{m}(a^2 - 6ax + 6x^2)$$

Using this we can solve for H_{ii} and S_{ij} using this integral

$$\int_0^1 x^m (1-x)^n dx = \frac{m!n!}{(m+n+1)!}$$

Letting $a = 1$, we can now solve for

$$H_{11} = \frac{\hbar^2}{m}$$

$$\int_0^1 x(1-x)dx = \frac{\hbar^2}{6m}$$

$$H_{12} = \frac{\hbar^2}{m}$$

$$\int_0^1 x(1-x)(1-6x+6x^2)dx = \frac{\hbar^2}{30m}$$

$$H_{21} = \frac{\hbar^2}{m}$$

$$\int_0^1 x^2(1-x)^2 dx = \frac{\hbar^2}{30m}$$

$$H_{22} = \frac{\hbar^2}{105m}$$

$$S_{11} = \int_0^1 x^2(1-x)^2 dx = \frac{4}{5!} = \frac{1}{30}$$

$$S_{12} = S_{21} = \int_0^1 x^3(1-x)^3 dx = \frac{36}{7!} = \frac{1}{140}$$

$$S_{22} = \int_0^1 x^4(1-x)^4 dx = \frac{576}{9!} = \frac{1}{630}$$

7.27

Use Perturbation Theory to add cubic and quartic perturbations to the SHO and find the first three SHO energy levels. Do this by expanding the Morse potential:

$$V(x) = D(1 - e^{-Bx})^2$$

into polynomials (i.e., a Taylor expansion). Show that the Hamiltonian can be written as

$$\frac{-h^2\nabla^2}{8\pi^2 m} + ax^2 + bx^3 + cx^4$$

Note which terms can be associated with H^0 and which are the H^1 perturbation. What are the relationships between a, b, c, and D, B? How do the new energy levels compare to the old ones?

Solution

The e^{-Bx} function can be expanded noting that

$$e^x \approx 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + ... + Ox^n$$

So e^{-Bx} will expand similarly, replacing x in the above expansion with -Bx, so

\[e^{-Bx] = 1 - Bx + B^2x^2/2 - B^3x^3/6 + ... + Ox^n\nonumber \]

The Morse Potential therefore is

$$D(1 - (1 - Bx + B^2\frac{x^2}{2} - B^3\frac{x^3}{6})^2$$

The expansion is shortened to 4 terms only.

$$= D(Bx - B^2x^2/2 + B^3x^3/6)^2$$

$$=D (B^6x^6/36 - B^5x^5/6 + 7B^4x^4/12 - B^3x^3 + B^2x^2)$$

$$= DB^6x^6/36 - DB^5x^5/6 + 7DB^4x^4/12 - DB^3x^3 + DB^2x^2$$

$$= 7DB^4x^4/12 - DB^3x^3 + DB^2x^2$$

(We have truncated above the quartic term)

Here, it is seen that DB^2x^2 corresponds to the H^0 potential, and $7DB^4x^4/12 - DB^3x^3$ is H^1

We can also see that $a = DB^2$, $b = - DB^3$, $c = 7DB^4/12$ in in the Hamiltonian potential: $ax^2 + bx^3 + cx^4$

Perturbation theory states that

$$E_n = E_n^0 + E_n^1 = E_n^0 + \int \Psi_n^0 H^1 \Psi_n^0 \, d\tau$$

Therefore, with $E^0_0 = h\nu/2$ and $\Psi^0_0 = (\alpha/\pi)^{1/4}e^{-\alpha(x^2)/2}$

$E^0_1 = 3h\nu/2$ and $\Psi^0_1 = (4\alpha^3/\pi)^{1/4}xe^{-\alpha(x^2)/2}$

$E^0_2 = 5\ h\nu/2$ and $\Psi^0_2 = (\alpha/4\pi)^{1/4}(2\alpha x^2 - 1)e^{-\alpha(x^2)/2}$

$H^1 = bx^2 + cx^2$

the first three energy levels are:

$E_0 = hv/2 + \int (\alpha/\pi)^{1/4} e^{-\alpha(x^2)/2} (bx^3 + cx^4)(\alpha/\pi)^{1/4} e^{-\alpha(x^2)/2} dx$

$= hv/2 + (\alpha/\pi)^{1/2} \int e^{-\alpha(x^2)} (bx^3 + cx^4) dx$

$= hv/2 + (\alpha/\pi)^{1/2} [\int e^{-\alpha(x^2)} bx^3 dx + \int e^{-\alpha(x^2)} cx^4 dx]$ (The cubic integral is odd so evaluates to 0)

$= hv/2 + (\alpha/\pi)^{1/2} \int e^{-\alpha(x^2)} cx^4 dx$

We can use $\int x^{2n} e^{-\alpha x^2} dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= hv/2 + 2 * c(\alpha/\pi)^{1/2} * 3/(2^3\alpha^2) * (\pi/\alpha)^{1/2}$

$= hv/2 + 3c/(4\alpha^2)$

$E_1 = 3hv/2 + \int (4\alpha^3/\pi)^{1/4} x e^{-\alpha(x^2)/2} (bx^3 + cx^4)(4\alpha^3/\pi)^{1/4} x e^{-\alpha(x^2)/2} dx$

$= 3hv/2 + (4\alpha^3/\pi)^{1/2} \int x^2 e^{-\alpha(x^2)} (bx^3 + cx^4) dx$

$= 3hv/2 + (4\alpha^3/\pi)^{1/2} [\int x^2 e^{-\alpha(x^2)} bx^3 dx + \int x^2 e^{-\alpha(x^2)} cx^4 dx]$ (First integral evaulates to 0)

$= 3hv/2 + c(4\alpha^3/\pi)^{1/2} \int x^6 e^{-\alpha(x^2)} dx$

We can use $\int x^{2n} e^{-\alpha x^2} dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= 3hv/2 + 2* c(4\alpha^3/\pi)^{1/2} * 15/(2^4\alpha^3) * (\pi/\alpha)^{1/2}$

$= 3hv/2 + 15c/(4\alpha^2)$

$E_{2o} = 5hv/2 + \int (\alpha/4\pi)^{1/4} (2\alpha x^2 - 1) e^{-\alpha(x^2)/2} (bx^3 + cx^4) (\alpha/4\pi)^{1/4} (2\alpha x^2 - 1) e^{-\alpha(x^2)/2} dx$

$= 5hv/2 + (\alpha/4\pi)^{1/2} \int (bx^3 + cx^4)(2\alpha x^2 - 1)^2 e^{-\alpha(x^2)} dx$

$= 5hv/2 + (\alpha/4\pi)^{1/2} [\int bx^3 (2\alpha x^2 - 1)^2 e^{-\alpha(x^2)} dx + \int cx^4 e^{-\alpha(x^2)} (2\alpha x^2 - 1)^2 dx$

$= 5hv/2 + (\alpha/4\pi)^{1/2} \int cx^4 e^{-\alpha(x^2)} (2\alpha x^2 - 1)^2 dx$ (First integral evaluates to 0)

$= 5hv/2 + (\alpha/4\pi)^{1/2} \int 4c\alpha^2 x^8 e^{-\alpha(x^2)} - 4\alpha c x^6 e^{-\alpha(x^2)} + cx^4 e^{-\alpha(x^2)} dx$

We can use $\int x^{2n} e^{-\alpha x^2} dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= 5hv/2 + (\alpha/4\pi)^{1/2} [4c\alpha^2 * 2 * (105/(32\alpha^4)) * (\pi/\alpha)^{1/2} - \alpha c * 2 * 15/(2^4\alpha^3) * (\pi/\alpha)^{1/2} + c * 2 * 3/(2^3\alpha^2) * (\pi/\alpha)^{1/2}]$

$= 5hv/2 + 39c/4\alpha^2$

It is evident that as the energy levels increase, the perturbation to the energy increases as well, making the Hooke potential increasingly bad as an approximation of intramolecular potential.

7.27

Use the perturbation theory to calculate the first - order corrections to the ground state energy of

a. A harmonic oscillator that arises from a cubic and quartic term.
b. A quartic oscillator that arises from only using a quartic term cx^4

and compare the results.

Solution

A) The Hamiltonian for this problem is

$$\hat{H} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2 + bx^3 + cx^4$$

We use the harmonic oscillator Hamiltonian for $\hat{H}^{(0)}$

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2$$

$$\hat{H}^{(1)} = bx^3 + cx^4$$

$$\psi^{(0)} = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

$$E^{(0)} = h\mu(v + \frac{1}{2})$$

$$E_0 = E_0^{(0)} + \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}\, d\tau$$

$$E_0 = \frac{\hbar\mu}{2} + b(\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx x^3 e^{-x^2\alpha} + c(\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx x^4 e^{-x^2\alpha}$$

$$E_0 = \frac{\hbar\mu}{2} + 0 + 2c\frac{\alpha}{\pi}^{1/2}\int_0^{\infty} dx x^4 e^{-x^2\alpha}$$

$$E_0 = \frac{\hbar\mu}{2} + \frac{3c}{4\alpha^2}$$

B) The Hamiltonian for this problem is

$$\hat{H} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + cx^4$$

We use the harmonic oscillator Hamiltonian for $\hat{H}^{(0)}$

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2$$

$$\hat{H}^{(1)} = cx^4 - \frac{kx^2}{2}$$

$$E = \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}\, d\tau$$

$$E = (\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx e^{-x^2\alpha}(cx^4 - \frac{kx^2}{2})$$

$$E = (\frac{\alpha}{\pi})^{1/2}2(\frac{3c}{8\alpha^2}(\frac{\alpha}{\pi})^{1/2} - \frac{k}{8\alpha}(\frac{\alpha}{\pi})^{1/2})$$

$$E = \frac{3c}{4\alpha^2} + \frac{k}{4\alpha}$$

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8: MULTIELECTRON ATOMS

Electrons with more than one atom, such as Helium (He), and Nitrogen (N), are referred to as multi-electron atoms. Hydrogen is the only atom in the periodic table that has one electron in the orbitals under ground state. We will learn how additional electrons behave and affect a certain atom.

8.1: Atomic and Molecular Calculations are Expressed in Atomic Units

8.2: Perturbation Theory and the Variational Method for Helium

8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method

8.4: An Electron has an Intrinsic Spin Angular Momentum

8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants

8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

8.8: Term Symbols Gives a Detailed Description of an Electron Configuration

8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number

8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States

8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

8.E: Multielectron Atoms (Exercises)

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8.1: Atomic and Molecular Calculations are Expressed in Atomic Units

Learning Objectives

- Demonstrate how solving electron structure problems are less cluttered by switching to atomic units instead of SI units.

Atomic units (au or a.u.) form a system of natural units which is especially convenient for atomic physics calculations. Atomic units, like SI units, have a unit of mass, a unit of length, and so on. However, the use and notation is somewhat different from SI. Suppose a particle with a mass of *m* has 3.4 times the mass of electron. The value of mass m can be written in three ways:

- $m = 3.4\ \ m_e$: This is the clearest notation (but least common), where the atomic unit is included explicitly as a symbol.
- $m = 3.4\ \ a.u.$: This notation is ambiguous, but is common. Here, it means that the mass m is 3.4 times the atomic unit of mass. If considering a length L of 3.4 times the atomic unit of length, the equation would look the same, $L = 3.4\ \ a.u.$ The dimension needs to be inferred from context, which is sloppy.
- $m = 3.4$: This notation is similar to the previous one, and has the same dimensional ambiguity. It comes from formally setting the atomic units to 1 (Table 8.1.1).

This article deals with "Hartree type" of atomic units, where the numerical values of the following four fundamental physical constants are all unity by definition:

Table 8.1.1 : Fundamental atomic units

Dimension	Name	Symbol/Definition	Value in SI units	Value in Atomic Units
mass	electron rest mass	m_e	9.109×10^{-31} kg	1
charge	elementary charge	e	1.602×10^{-19} C	1
action	reduced Planck's constant	$\hbar = \frac{h}{2\pi}$	1.054×10^{-34} J·s	1
electric constant^{-1}	Coulomb force constant	$k_e = \frac{1}{4\pi\epsilon_o}$	8.987×10^{9} kg·m^3·s^{-2}·C^{-2}	1

Example 8.1.1 : Simplifying the Hamiltonian

Use the atomic units definitions in Table 8.1.1 to contrast the Hamiltonian for a Helium atom in Si units and in atomic units.

Solution

In SI units, the Hamiltonian for a Helium atom is

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

In atomic units, the same Hamiltonian

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

All the units that make the SI version of the Hamiltonian disappear to emphasize the key aspects of the operator.

Atomic units are derived from certain fundamental properties of the physical world, and are free of anthropocentric

considerations. It should be kept in mind that atomic units were designed for atomic-scale calculations in the present-day universe, with units normalize the reduced Planck constant and also mass and charge of the electron are set to 1, and, as a result, the speed of light in atomic units is a large value, $1/\alpha \approx 137$. For example, the orbital velocity of an electron around a small atom is of the order of 1 in atomic units. Table 8.1.2 give a few derived units. Some of them have proper names and symbols assigned, as indicated in the table.

Table 8.1.2 : Derived atomic units

Dimension	Name	Symbol	Expression	Value in SI units	Value in more common units
length	bohr	a_o	$4\pi\epsilon_0\hbar^2/(m_e e^2) = \hbar/(m_e c\alpha)$	5.291×10^{-11} m	0.052 nm = 0.529 Å
energy	hartree	E_h	$m_e e^4/(4\pi\epsilon_0\hbar)^2 = \alpha^2 m_e c^2$	4.359×10^{-18} J	27.2 eV = 627.5 kcal·mol^{-1}
time			$\hbar/E_\mathrm{h}$	2.418×10^{-17} s	
velocity			$a_0 E_\mathrm{h}/\hbar = \alpha c$	2.187×10^{6} m·s^{-1}	

Bohr model in atomic units

Atomic units are chosen to reflect the properties of electrons in atoms. This is particularly clear from the classical Bohr model of the hydrogen atom in its ground state. The ground state electron orbiting the hydrogen nucleus has (in the classical Bohr model):

- Orbital velocity = 1
- Orbital radius = 1
- Angular momentum = 1
- Orbital period = 2π
- Ionization energy = $^1/_2$
- Electric field (due to nucleus) = 1
- Electrical attractive force (due to nucleus) = 1

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8.2: Perturbation Theory and the Variational Method for Helium

Learning Objectives

- Demonstrate that both perturbation theory and variational methods can be used to solve the electron structure of the helium atom.

Both perturbation theory and variation method (especially the linear variational method) provide good results in approximating the energy and wavefunctions of multi-electron atoms. Below we address both approximations with respect to the helium atom.

Perturbation Theory of the Helium Atom

We use perturbation theory to approach the analytically unsolvable helium atom Schrödinger equation by focusing on the Coulomb repulsion term that makes it different from the simplified Schrödinger equation that we have just solved analytically. The electron-electron repulsion term is conceptualized as a correction, or perturbation, to the Hamiltonian that can be solved exactly, which is called a **zero-order Hamiltonian**. The perturbation term corrects the previous Hamiltonian to make it fit the new problem. In this way the Hamiltonian is built as a sum of terms, and each term is given a name. For example, we call the simplified or starting Hamiltonian, $\hat{H}^0$, the zero order term, and the correction term $\hat{H}^1$.

$$\hat{H} = \hat{H}^0 + \hat{H}^1 \tag{8.2.1}$$

The Hamilonian for the helium atom (in atomic units) is:

$$\hat{H}^0 = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}}_{\text{H atom Hamiltonian}} - \underbrace{\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}}_{\text{H atom Hamiltonian}} \tag{8.2.2}$$

$$\hat{H}^1 = \frac{1}{r_{12}} = \frac{1}{|r_1 - r_2|} \tag{8.2.3}$$

The expression for the first-order correction to the energy is

$$\begin{aligned} E^1 &= \langle \psi^0 | \hat{H}^1 | \psi^0 \rangle \\ &= \int \psi^{0*} \hat{H}^1 \psi^0 \, d\tau \end{aligned}$$

Equation ??? is a general expression for the first-order perturbation energy, which provides an improvement or correction to the zero-order energy we already obtained. Hence, E^1 is the average interaction energy of the two electrons calculated using wavefunctions that assume there is no interaction.

The solution to $\hat{H}^0$ (Equation 8.2.2) is the product of two single-electron hydrogen wavefunctions (scaled by the increased nuclear charge) since $\hat{H}^0$ can be separated into independent functions of each electron (i.e., Separation of Variables).

$$|\psi^0\rangle = |\varphi_{1s}(r_1)\varphi_{1s}(r_2)\rangle$$

So the integral in Equation ??? is

$$E^1 = \iint \varphi_{1s}(r_1)\varphi_{1s}(r_2)\frac{1}{r_{12}}\varphi_{1s}(r_1)\varphi_{1s}(r_2)\, d\tau_1 d\tau_2 \tag{8.2.4}$$

where the double integration symbol represents integration over all the spherical polar coordinates of both electrons $r_1, \theta_1, \varphi_1, r_2, \theta_2, \varphi_2$. The evaluation of these six integrals is lengthy. When the integrals are done, the result is E^1 = +34.0 eV so that the total energy calculated using our second approximation method, first-order perturbation theory, is

$$E_{approx2} = E^0 + E^1 = -74.8eV \tag{8.2.5}$$

The new approximate value for the binding energy represents a substantial (~30%) improvement over the zero-order energy:

$$E^0 = \frac{2}{n^2} + \frac{2}{n^2} = 4 \underbrace{E_h}_{hartrees} = 108.8\, eV$$

so the interaction of the two electrons is an important part of the total energy of the helium atom. We can continue with perturbation theory and find the additional corrections, E^2, E^3, etc. For example,

$$E^0 + E^1 + E^2 = -79.2\, eV.$$

So with two corrections to the energy, the calculated result is within 0.3% of the experimental value of -79.01 eV. It takes thirteenth-order perturbation theory (adding E^1 through E^{13} to E^0) to compute an energy for helium that agrees with experiment to within the experimental uncertainty. Interestingly, while we have improved the calculated energy so that it is much closer to the experimental value, we learn nothing new about the helium atom wavefunction by applying the first-order perturbation theory to the energy above. He need to expand the wavefunctions to first order perturbation theory, which requires more effort. Below, we will employ the variational method approximation to modify zero-order wavefunctions to address one of the ways that electrons are expected to interact with each other.

The Hartree Unit of Energy

The hartree is the atomic unit of energy (named after the British physicist Douglas Hartree) and is defined as

$$E_h = 2R_H hc$$

where R_H is the Rydberg constant, h is the Planck constant and c is the speed of light.

$$\begin{aligned} E_h &= 4.359 \times 10^{-18}\, J \\ &= 27.21\, eV. \end{aligned}$$

The hartree is usually used as a unit of energy in atomic physics and computational chemistry. As discussed before for hydrogen emission, IR, and microwave spectroscopies, experimental measurements prefer the electronvolt (eV) or the wavenumber (cm^{-1}).

Variational Method Applied to the Helium Method

As discussed in Section 6.7, because of the electron-electron interactions, the Schrödinger's Equation cannot be solved exactly for the helium atom or more complicated atomic or ionic species. However, the ground-state energy of the helium atom can be estimated using approximate methods. One of these is the variational method which requires the minimizing of the following variational integral.

$$E_{trial} = \frac{\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{8.2.6}$$

$$= \frac{\int_0^\infty \psi^*_{trial} \hat{H} \psi_{trial} d\tau}{\int_0^\infty \psi^2_{trial}\, d\tau} \tag{8.2.7}$$

The five trial wavefunctions discussions below are equally "valid" trial wavefunctions that describe the probability of finding each electron (technically the wavefunction squared). What separates the "poor" approximations from the "good" approximation is whether the trial wavefunction predicts experimental results. Consequently, for all the approximations used for the rest of this TextMap, it is important to compare the theoretical results to the "true" (i.e., experimental) results. No matter how complicated an approximation is, it is only as good as the accuracy of its predicted values to experimental values.

Trial Wavefunction #1: Simple Orbital Approximation with One Parameter

As is clear from Equation 8.2.6, the variational method approximation requires that a trial wavefunction with one or more adjustable parameters be chosen. A logical first choice for such a multi-electron wavefunction would be to assume that the electrons in the helium atom occupy two identical, but scaled, hydrogen 1s orbitals.

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{8.2.8}$$

$$= \exp\left[-\alpha(r_1 + r_2)\right] \tag{8.2.9}$$

The variational energy obtained after minimizing Equation 8.2.7 after substituting the trial wavefunction (Equation 8.2.9) by varying α is

$$E_{trial} = -2.84766\ E_h$$

and the experimentally determined ground-state energy for the helium atom is the sum of first and second ionization energies

$$E_{\text{exp}} = I_1 + I_2 = -2.90372\ E_h \tag{8.2.10}$$

The deviation of energy for the optimized trial wavefunction from the experimental value is

$$\left|\frac{E_{trial}(\alpha) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.84766\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.11}$$

$$= 1.93\% \tag{8.2.12}$$

The value of -2.8477 hartrees is within 2% of the known ground-state energy of the helium atom. The error in the calculation is attributed to the fact that the wavefunction is based on the orbital approximation and, therefore, does not adequately take electron-electron interactions into account. In other words, this wavefunction gives the electrons too much independence, given that they have like charges and tend to avoid one another.

Trial Wavefunction #2: Orbital Approximation with Two Parameters

Some electron-electron interactions can be built into the multi-electron wavefunction by assuming that each electron is in an orbital which is a linear combination of two different and scaled hydrogen 1s orbitals.

$$\phi(r_1) = \exp(-\alpha r_1) + \exp(-\beta r_1) \tag{8.2.13}$$

Under the orbital approximation this assumption gives a trial wavefunction of the form

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{8.2.14}$$

$$= \exp(-\alpha r_1)\exp(-\alpha r_2) + \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) + \exp(-\beta r_1)\exp(-\beta r_2) \tag{8.2.15}$$

Inspection of this trial wavefunction indicates that 50% of the time the electrons are in different orbitals, while for the first trial wavefunction the electrons were in the same orbital 100% of the time. Notice the enormous increase in the complexity of the variational expression for the energy for this trial wavefunction (Equation 8.2.7). However, the calculation is very similar to that using the previous trial wavefunction. The differences are that in this case the expression for the energy is more complex and that it is being minimized simultaneously with respect to two parameters (α and β) rather than just one (α).

The variational energy obtained after minimizing Equation 8.2.7 after substituting the trial wavefunction (Equation 8.2.15) by varying α and β is

$$E_{trial} = -2.86035\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.86035\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.16}$$

$$= 1.49\% \tag{8.2.17}$$

Clearly introducing some electron-electron interactions into the trial wavefunction has improved the agreement between theory

and experiment (Equation 8.2.12 vs. 8.2.17).

Trial Wavefunction #3: Orbital Approximation with Two Parameters

The extent of electron-electron interactions can be increased further by eliminating the first and last term in the second trial wavefunction (Equation 8.2.15). This yields a multi-electron wavefunction of the form,

$$|\psi(1,2)\rangle_{trial} = \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) \tag{8.2.18}$$

This trial wavefunction places the electrons in different scaled hydrogen 1s orbitals 100% of the time this adds further improvement in the agreement with the literature value of the ground-state energy is obtained. The variational energy obtained after minimizing Equation 8.2.7 after substituting the trial wavefunction (Equation 8.2.18) by varying α and β is

$$E_{trial} = -2.87566\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.87566\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.19}$$

$$= 0.97\% \tag{8.2.20}$$

This result is within 1% of the actual ground-state energy of the helium atom.

Trial Wavefunction #4: Approximation with Two Parameters

The third trial wavefunction, however, still rests on the orbital approximation and, therefore, does not treat electron-electron interactions adequately. Hylleraas took the calculation a step further by introducing electron-electron interactions directly into the first trial wavefunction by adding a term, r_{12}, involving the inter-electron separation.

$$|\psi_{trial}(1,2)\rangle = (\exp[-\alpha(r_1 + r_2)])\,(1 + \beta r_{12}) \tag{8.2.21}$$

In the trial multi-electron wavefunction of Equation 8.2.21, if the electrons are far apart, then r_{12} is large and the magnitude of the wavefunction increases to favor that configuration. The variational energy obtained after minimizing Equation 8.2.7 after substituting the trial wavefunction (Equation 8.2.21) by varying α and β is

$$E_{trial} = -2.89112\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.89112\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.22}$$

$$= 0.43\% \tag{8.2.23}$$

This modification of the trial wavefunction has further improved the agreement between theory and experiment to within 0.5%.

Fifth Trial Wavefunction #5: Approximation with Three Parameters

Chandrasakar brought about further improvement by adding Hylleraas's r_{12} term to the third trial wavefunction (Equation 8.2.18) as shown here.

$$|\psi(1,2)\rangle_{trial} = [\exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2)]\,[1 + \gamma r_{12}] \tag{8.2.24}$$

Chandrasakar's three parameter wavefunction gives rise to a fairly complicated variational expression for ground-state energy. The variational energy obtained after minimizing Equation 8.2.7 after substituting the trial wavefunction (Equation 8.2.24) by varying α, β and γ is

$$E_{trial} = -2.90143\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta,\gamma)-E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.90143+2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.25}$$

$$= 0.0789\% \tag{8.2.26}$$

Chandrasakar's wavefunction gives a result for helium that is within 0.07% of the experimental value for the ground-state energy.

Summary

The purpose of this section is to examine five trial wavefunctions for the helium atom used within the Perturbation Theory and Variational method approximation. For the Variational method approximation, the calculations begin with an uncorrelated wavefunction in which both electrons are placed in a hydrogenic orbital with scale factor α. The next four trial functions use several methods to increase the amount of electron-electron interactions in the wavefunction. As the summary of results that is appended shows this gives increasingly more favorable agreement with the experimentally determined value for the ground-state energy of the species under study. The detailed calculations show that the reason for this improved agreement with experiment is due to a reduction in electron-electron repulsion.

Five variational method calculations that have been outlined above for the helium atom ($Z = 2$) can be repeated for two-electron atoms (e.g., H^-, Li^+, Be^{2+}, etc). The hydride anion is a particularly interesting case because the first two trial wavefunctions do not predict a stable ion (i.e., they are poor approximations). This indicates that electron-electron interactions is an especially important issue for atoms and ions with small nuclear charge.

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8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method

Learning Objectives

- Show how the Hartree approximation can be used to solve for the wavefunctions and energies of multi-electron atoms.
- Understand the orbital approach of independent orbitals is an approximation to a mutlti-electron system with the motions of all electrons coupled together.
- Demonstate how the Self-Consistant Field (SCF) calculation is needed to support the Hartree approximation

The Hartree method is used to approximate the wavefunction and the energy of a quantum multi-electron system in a stationary state. This approximation assumes that the exact N-body wavefunction of the system can be approximated by a product of single-electron wavefunctions. By invoking the variational method, one can derive a set of N-coupled equations for the N spin orbitals. A solution of these equations yields the Hartree wavefunction and energy of the system. It is one step better than the "Ignorance is Bliss" approach, discussed previously, but still far from modern state-off-the-art methods.

Unsolvable Systems

The Hamiltonian for a generic multielectron atom includes nucleus-electron attraction terms for the additional electrons with a general charge Z; e.g.

$$V_{\text{nuclear-electron}}(r_1) = -\frac{Z}{|\mathbf{r}-\mathbf{R}|} \tag{8.3.1}$$

in atomic units with $|\mathbf{r}-\mathbf{R}|$ is the distance between the electron and the nucleus, The Hamiltonian must also have terms for electron-electron repulsion (also in atomic units)

$$V_{\text{electron-electron}}(r_{12}) = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

with $|\mathbf{r}-\mathbf{r}'|$ is the distance between electron 1 and electron 2. So the proper multi-electron Hamiltonian can be constructed

$$\hat{H}(r_1, r_2, ...r_n) = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V_{\text{nuclear-electron}}(r_i) + \sum_{i\neq j} V_{\text{electron-electron}}(r_{ij}) \tag{8.3.2}$$

Given what we have learned from the previous quantum mechanical systems we've studied, we predict that exact solutions to the multi-electron Schrödinger equation would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their electron-electron repulsion (final term in Equation 8.3.2) means that an exact wavefunction for a multi-electron system would be a single function that depends **simultaneously** upon the coordinates of all the electrons; i.e., a multi-electron wavefunction:

$$|\psi(r_1, r_2, \cdots r_i)\rangle \tag{8.3.3}$$

Unfortunately, the electron-electron repulsion terms make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms.

The Hartree Approximation

The method for finding best possible one-electron wavefunctions that was published by Douglas Hartree in 1948 and improved two years later by Vladimir Fock. For the Schrödinger equation to be analytically solvable, the variables must be separable - the variables are the coordinates of the electrons. To separate the variables in a way that retains information about electron-electron interactions, the electron-electron term (Equation 8.3.1) must be approximated so it depends only on the coordinates of one electron. Such an approximate Hamiltonian can account for the interaction of the electrons in **an average way**. The exact one-electron eigenfunctions of this approximate Hamiltonian then can be found by solving the Schrödinger equation. These functions are the best possible **one-electron functions**.

The Hartree approximation starts by invoking an initial *ansatz* that the multi-electron wavefunction in Equation 8.3.3 can be expanded as a product of single-electron wavefunctions (i.e., orbitals)

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)\rangle \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N)$$

from which it follows that the electrons are *independent*, and interact only via the mean-field Coulomb potential. This yields one-electron Schrödinger equations of the form

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

or

$$H_e(r)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

where $V(r)$ is the potential in which the electron moves; this includes both the nuclear-electron interaction

$$V_{nucleus}(\mathbf{r}) = -Ze^2\sum_R \frac{1}{|\mathbf{r}-\mathbf{R}|}$$

and the mean field arising from the $N-1$ other electrons. We smear the other electrons out into a smooth negative charge density $\rho(\mathbf{r}')$ leading to a potential of the form

$$V_{electron}(\mathbf{r}) = -e\int d\mathbf{r}'\rho(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

where

$$\rho(\mathbf{r}) = \sum_i^{\text{occupied}} |\psi(\mathbf{r})|^2.$$

The sum over runs over all occupied states; i.e., only the states of electrons that exist in the atom. The wavefunctions that from this approach with the Hamiltonian $H_e(r)$ involve possess three kinds of energies discussed below.

Three Energies within the Hartree Approximation

The total energy ϵ_j of the orbital ϕ_j, is the sum of the above three contributions:

1. **Kinetic Energy:** The Kinetic energy of the electron has an average value is computed by taking the expectation value of the kinetic energy operator

   $$\frac{-\hbar^2}{2m}\nabla^2$$

   with respect to any particular solution $\phi_j(r)$ to the Schrödinger equation:

   $$KE = \langle\phi_j|\frac{-\hbar^2}{2m}\nabla^2|\phi_j\rangle$$

2. **Nuclear-Electron Coulombic Attraction Energy:** Coulombic attraction energy with the nucleus of charge Z:

$$\langle \phi_j | \frac{-Ze^2}{|\mathbf{r}-\mathbf{R}|} | \phi_j \rangle$$

3. **Electron-Electron Coulombic Repulsion Energy:** Coulomb repulsion energies with all of the $N-1$ other electrons, which are assumed to occupy other atomic orbitals denoted ϕ_K, with this energy computed as

$$\sum_{j \neq k} \langle \phi_j(r)\phi_k(r') | \frac{e^2}{|r-r'|} | \phi_j(r)\phi_k(r') \rangle. \tag{8.3.4}$$

The Dirac notation $\langle \phi_j(r)\phi_k(r') | \frac{e^2}{|r-r'|} | \phi_j(r)\phi_k(r') \rangle$ is used to represent the two-electron (six-dimensional) Coulomb integral

$$J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr'$$

that describes the Coulomb repulsion between the charge density $|\phi_j(r)|^2$ for the electron in ϕ_j and the charge density $|\phi_k(r')|^2$ for the electron in ϕ_k. Of course, the sum over k must be limited to exclude $k = j$ to avoid counting a "self-interaction" of the electron in orbital ϕ_j with itself.

Adding these all together to get the total energy ϵ_j of the orbital ϕ_j:

$$\epsilon_J = \langle \phi_j | \frac{-\hbar^2}{2m} \nabla^2 | \phi_j \rangle + \langle \phi_j | \frac{-Ze^2}{|\mathbf{r}-\mathbf{R}|} | \phi_j \rangle + \sum_{j \neq k} \langle \phi_j(r)\phi_k(r') | \frac{e^2}{|r-r'|} | \phi_j(r)\phi_k(r') \rangle.$$

This treatment of the electrons and their orbitals is referred to as the **Hartree-level of theory**.

When screened hydrogenic atomic orbitals are used to approximate the ϕ_j and ϕ_K orbitals, the resultant ϵ_J values do **not** produce accurate predictions. For example, the negative of ϵ_J should approximate the ionization energy for removal of an electron from the orbitals ϕ_j. Such ionization potentials (IP s) can be measured, and the measured values do not agree well with the theoretical values when a crude screening approximation is made for the atomic orbitals.

The Self-Consistant Field (SCF) Approach to the Variational Method

The Hartree Equations are nonlinear and must be solved iteratively. This is because if particles interact, that interaction must be in the Hamiltonian. So until we know where the particles are, we cannot write down the Hamiltonian, but until we know the Hamiltonian, we cannot tell where the particles are.

The idea is to solve the Schrödinger equation for an electron moving in the potential of the nucleus and all the other electrons. We start with a guess for the trial electron charge density, solve N/2 one-particle Schrödinger equations (initially identical) to obtain N electron wavefunctions. Then we construct the potential for each wavefunction from that of the nucleus and that of all the other electrons, symmetrize it, and solve the N/2 Schrödinger equations again. This method is ideal for a computer, because it is easily written as an algorithm (Figure 8.3.1).

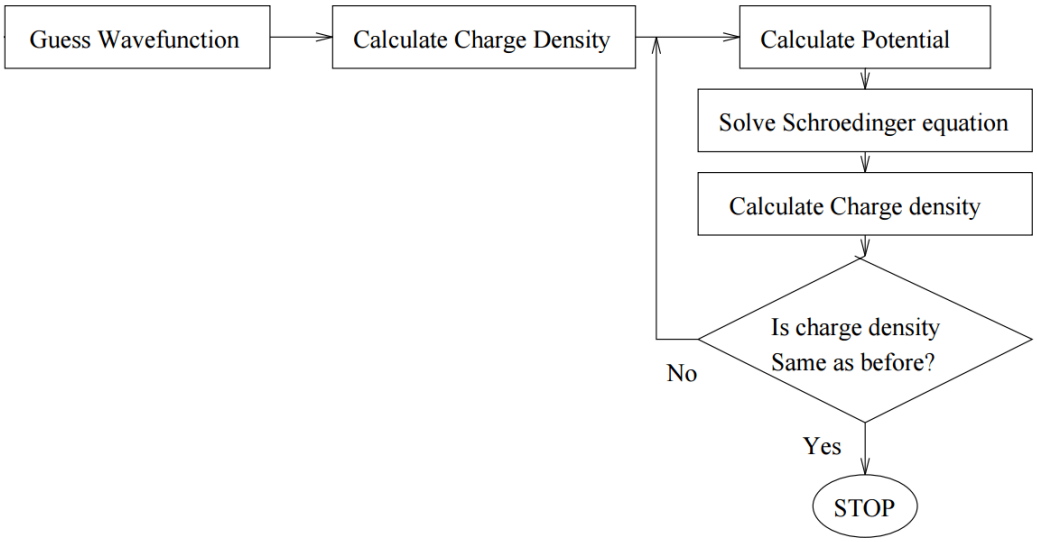


Figure 8.3.1 : Algorithm for Self-consistent field theory.

Although we are concerned here with atoms, the same methodology is used for molecules or even solids (with appropriate potential symmetries and boundary conditions). This is a variational method, so wherever we refer to wavefunctions, we assume that they are expanded in some appropriate basis set.

> Fock improved on Hartree's method by using proper "antisymmetrized wavefunctions" (called the Hartree-Fock method) instead of simple one-electron wavefunctions.

Shielding and Effective Charges Concepts are Useful

The hydrogen-like orbitals provide qualitative descriptions of orbitals of atoms with more than a single electron. By introducing the concept of screening as a way to represent the repulsive interactions among the electrons of an atom, an effective nuclear charge Z_{eff} can be used in place of Z in the hydrogenic $\psi_{n,l,m}$ and $E_{n,l}$ formulas to generate approximate atomic orbitals to be filled by electrons in a many-electron atom. For example, in the crudest approximation of a carbon atom, the two $1s$ electrons experience the full nuclear attraction so $Z_{\text{eff}} = 6$ for them, whereas the $2s$ and $2p$ electrons are screened by the two $1s$ electrons, so $Z_{\text{eff}} = 4$ for them. Within this approximation, one then occupies two $1s$ orbitals with $Z = 6$, two $2s$ orbitals with $Z = 4$ and two $2p$ orbitals with $Z = 4$ in forming the full six-electron product wavefunction of the lowest-energy state of carbon

$$|\psi(1,2,\ldots,6)\rangle = |\psi_{1s}(1)\psi_{1s}(2)\psi_{2s}(3)\ldots\psi_{1p}(6)\rangle. \tag{8.3.5}$$

However, such approximate orbitals are not sufficiently accurate to be of use in quantitative simulations of atomic and molecular structure. In particular, their energies do not properly follow the trends in atomic orbital (AO) energies that are taught in introductory chemistry classes (Figure 8.3.2).

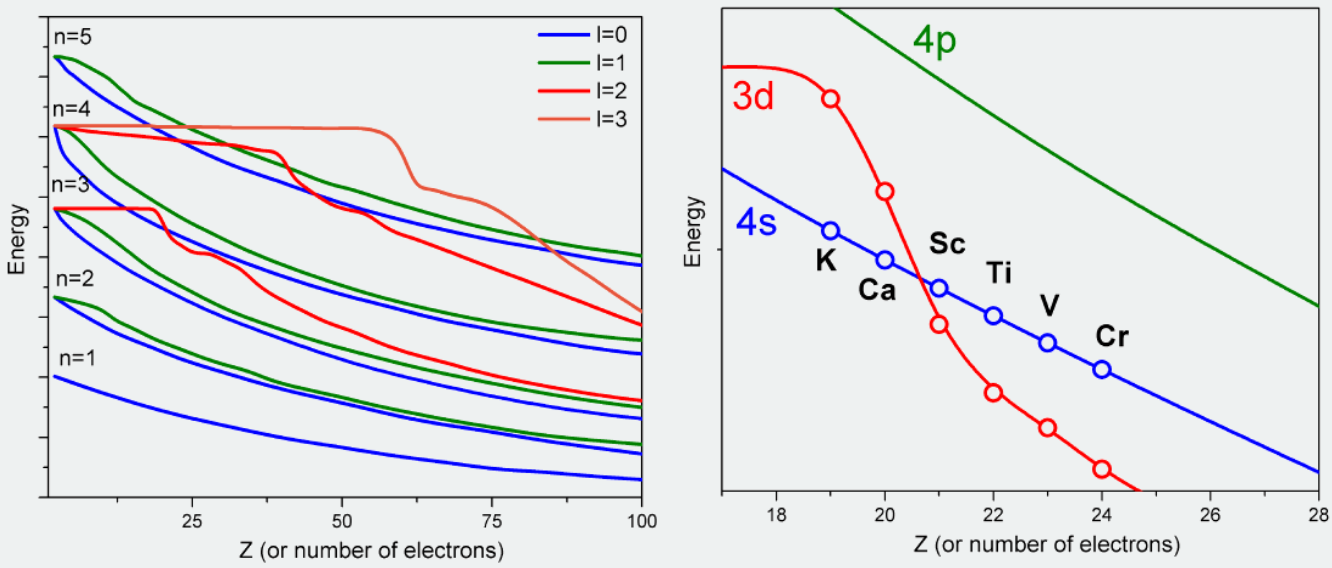


Figure 8.3.2 : Energies of Atomic Orbitals as Functions of the number of electrons in Neutral Atoms. (CC BY 4.0; Delmar Larsen).

For example, the relative energies of the $3d$ and $4s$ orbitals are not adequately described in a model that treats electron repulsion effects in terms of a simple screening factor. So, now it is time to examine how we can move beyond the screening model and take the electron repulsion effects, which cause the inter-electronic couplings that render the Schrödinger equation insolvable, into account in a more reliable manner.

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8.4: An Electron has an Intrinsic Spin Angular Momentum

Learning Objectives

- Understand the forth quantum number for electrons - spin.
- Understand how spin is connected to magnetic properties of the electrons and atoms.
- Understand how to break degeneracy via externally applied magnetic fields in electrons and atoms.

Imagine doing a hypothetical experiment that would lead to the discovery of electron spin. Your laboratory has just purchased a microwave spectrometer with variable magnetic field capacity. We try the new instrument with hydrogen atoms using a magnetic field of 10^4 Gauss and look for the absorption of microwave radiation as we scan the frequency of our microwave generator (Figure 8.4.1).

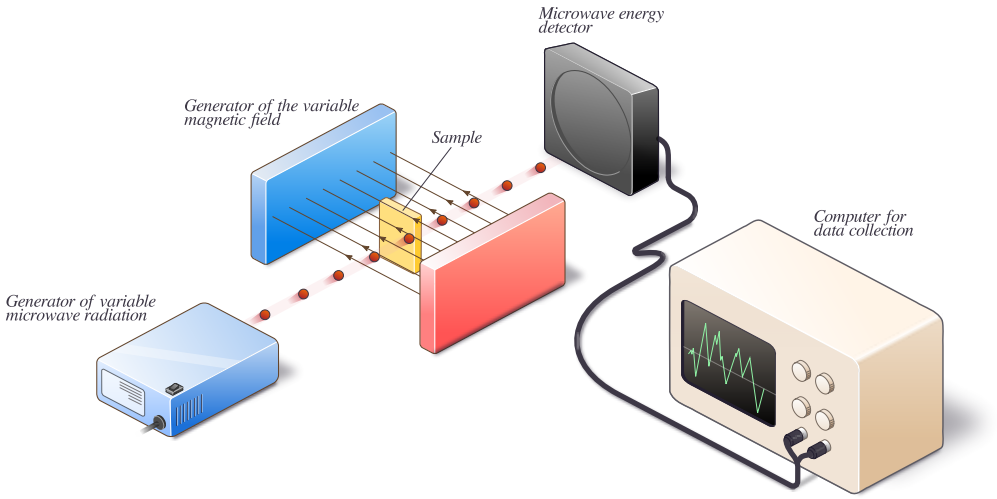


Figure 8.4.1 : Schematic diagram of a microwave spectrometer with the sample in a variable magnetic field. The strength of the magnetic field is set, and the sample's absorption of microwave photons is measured for a range of microwave photon energies (or frequencies). (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Finally we see absorption at a microwave photon frequency of $28 \times 10^9\ Hz$ (28 gigahertz). This result is really surprising from several perspectives. Each hydrogen atom is in its ground state, with the electron in a 1s orbital. The lowest energy electronic transition that we predict based on existing theory (the electronic transition from the ground state (ψ_{100} to ψ_{21m}) requires an energy that lies in the vacuum ultraviolet (the lower Lyman line at 121 nm), not the microwave, region of the spectrum. Furthermore, when we vary the magnetic field we note that the frequency at which the absorption occurs varies in proportion to the magnetic field.

The Zeeman Effect: Breaking Degeneracies with Magnetic Fields

Magnetism results from the circular motion of charged particles. This property is demonstrated on a macroscopic scale by making an electromagnet from a coil of wire and a battery. Electrons moving through the coil produce a magnetic field, which can be thought of as originating from a magnetic dipole or a bar magnet. Electrons in atoms also are moving charges with angular momentum so they too produce a magnetic dipole, which is why some materials are magnetic. A **magnetic dipole** interacts with a magnetic field, and the energy of this interaction is given by the scalar product of the magnetic dipole moment, and the magnetic field, $\vec{B}$.

$$E_B = -\vec{\mu}_m \cdot \vec{B} \tag{8.4.1}$$

Pieter Zeeman was one of the first to observe the splittings of spectral lines in a magnetic field caused by this interaction. Consequently such splittings are known as the Zeeman effect. (Figure 8.4.2). The expectation value calculated for the total energy in this case is the sum of the energy in the absence of the field, E_n, plus the Zeeman energy:

$$\langle E \rangle = E_n + \frac{e\hbar B_z m_l}{2m_e} \tag{8.4.2}$$

$$= E_n + \mu_B B_z m_l \tag{8.4.3}$$

The factor

$$\frac{e\hbar}{2m_e} = -\gamma_e \hbar = \mu_B \tag{8.4.4}$$

defines the constant μ_B, called the **Bohr magneton**, which is taken to be the fundamental magnetic moment. It has units of 9.2732×10^{-21} erg/Gauss or 9.2732×10^{-24} Joule/Tesla. This factor will help you to relate magnetic fields, measured in Gauss or Tesla, to energies, measured in ergs or Joules, for any particle with a charge and mass the same as an electron.

Equation 8.4.3 demonstrates that that m_l quantum number degeneracy of the hydrogen atom is removed by the externally applied magnetic field. For example, the three hydrogen atom eigenstates $|\psi_{211}\rangle$, $|\psi_{21-1}\rangle$, and $|\psi_{210}\rangle$ are degenerate in zero magnetic field, but have different energies in an externally applied magnetic field (Figure 8.4.2).

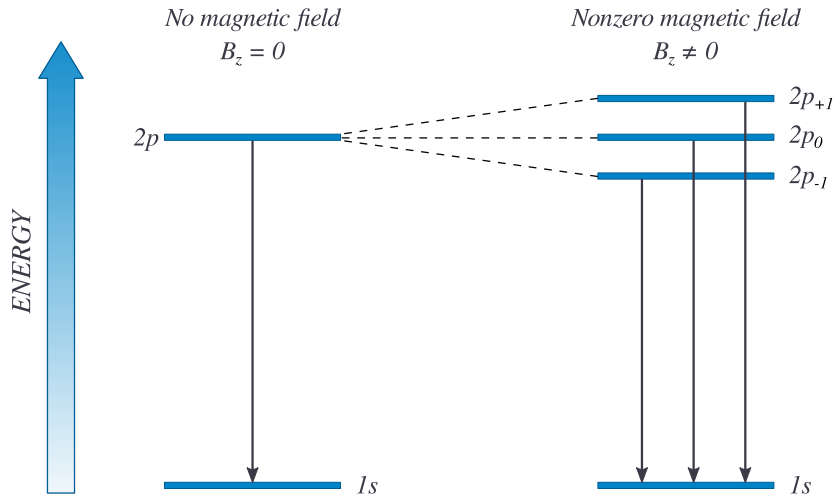


Figure 8.4.2 : The Zeeman effect for the $2s \rightarrow 1s$ transition. Emission when an electron switches from a 2p orbital to a 1s orbital occurs at only one energy in the absence of a magnetic field, but can occur at three different energies in the presence of a magnetic field. (CC BY-NC; Ümit Kaya via LibreTexts)

The $m_l = 0$ state, for which the component of angular momentum and hence also the magnetic moment in the external field direction is zero, experiences no interaction with the magnetic field. The $m_l = +1$ state, for which the angular momentum in the z-direction is +ħ and the magnetic moment is in the opposite direction, against the field, experiences a raising of energy in the presence of a field. Maintaining the magnetic dipole against the external field direction is like holding a small bar magnet with its poles aligned exactly opposite to the poles of a large magnet. It is a higher energy situation than when the magnetic moments are aligned with each other.

Electron Spin and the Stern-Gerlach Experiment

To discover new things, experimentalists sometimes must explore new areas in spite of contrary theoretical predictions. Our theory of the hydrogen atom at this point gives no reason to look for absorption in the microwave region of the spectrum. By doing the crazy experiment outlines above, we discovered that when an electron is in the $|1s\rangle$ orbital of the hydrogen atom, there are two different states that have the same energy. When a magnetic field is applied, this degeneracy is removed, and microwave radiation can cause transitions between the two states. In the rest of this section, we see what can be deduced from this experimental observation. This experiment actually could be done with electron spin resonance spectrometers available today (Figure 8.4.1). To

explain our observations, a new model for the hydrogen atom. Our original model for the hydrogen atom accounted for the motion of the electron and proton in our three-dimensional world; the new model needs something else that can give rise to an additional Zeeman-like effect. We need a charged particle with angular momentum to produce a magnetic moment, just like that obtained by the orbital motion of the electron. We can postulate that our observation results from a motion of the electron that was not considered in the last section - electron spin. We have a charged particle spinning on its axis. We then have charge moving in a circle, angular momentum, and a magnetic moment, which interacts with the magnetic field and gives us the Zeeman-like effect that we observed (Figure 8.4.2).

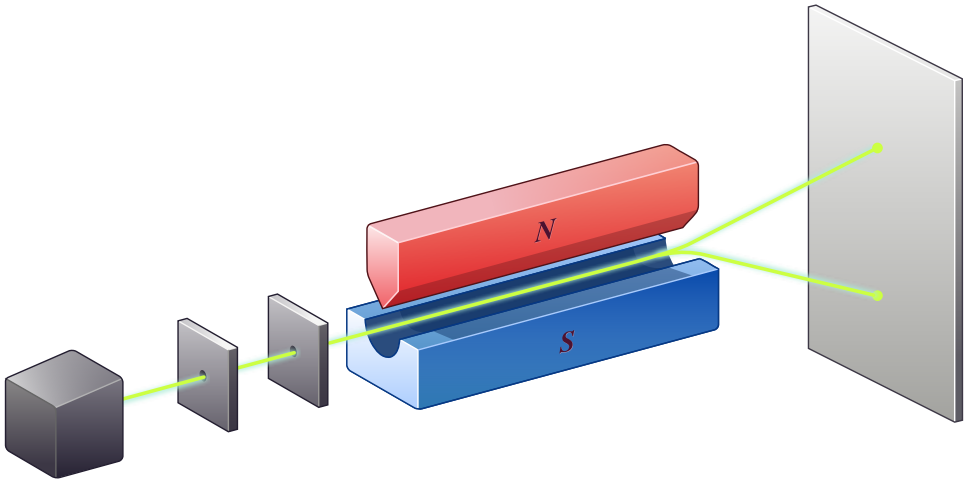


Figure 8.4.2 : Stern–Gerlach experiment: silver atoms travel through an inhomogeneous magnetic field and are deflected up or down depending on their spin. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

In 1920, Otto Stern and Walter Gerlach designed an experiment, which unintentionally led to the discovery that electrons have their own individual, continuous spin even as they move along their orbital of an atom. Today, this electron spin is indicated by the fourth quantum number, also known as the **Electron Spin Quantum Number** and denoted by m_s. In 1925, Samuel Goudsmit and George Uhlenbeck made the claim that features of the hydrogen spectrum that were unexamined might by explained by assuming electrons act as if it has a spin, which can be denoted by an arrow pointing up, which is +1/2, or an arrow pointing down, which is -1/2. The Stern and Gerlach experiment which demonstrated this was done with a beam of vaporized silver atoms that split into two beams after passing through a magnetic field (Figure 8.4.2). An explanation of this is that an electron has a magnetic field due to its spin. When electrons that have opposite spins are put together, there is no net magnetic field because the positive and negative spins cancel each other out. The silver atom used in the experiment has a total of 47 electrons, 23 of one spin type, and 24 of the opposite. Because electrons of the same spin cancel each other out, the *one unpaired electron* in the atom will determine the spin.

Spin Eigenstates and Eigenvalues

To describe electron spin from a quantum mechanical perspective, we must have spin wavefunctions and spin operators. The properties of the spin states are deduced from experimental observations and by analogy with our treatment of the states arising from the orbital angular momentum of the electron. The important feature of the spinning electron is the spin angular momentum vector, which we label S by analogy with the orbital angular momentum L. We define spin angular momentum operators with the same properties that we found for the rotational and orbital angular momentum operators. After all, angular momentum is angular momentum, no matter if it is *orbital* or *spin* in nature.

We found that

$$\hat{L}^2|Y_l^{m_l}\rangle = l(l+1)\hbar^2|Y_l^{m_l}\rangle$$

so by analogy for the spin states, we must have

$$\hat{S}^2|\sigma_s^{m_s}\rangle = s(s+1)\hbar^2|\sigma_s^{m_s}\rangle$$

where σ is a spin wavefunction with quantum numbers s and m_s that obey the same rules as the quantum numbers l and m_l associated with the spherical harmonic wavefunction Y. We also found the project of the orbital angular momentum on the z-axis is

$$\hat{L}_z|Y_l^{m_l}\rangle = m_l\hbar|Y_l^{m_l}\rangle$$

so by analogy, we must have a similar projection for the spin angular momentum:

$$\hat{S}_z|\sigma_s^{m_s}\rangle = m_s\hbar|\sigma_s^{m_s}\rangle \tag{8.4.5}$$

Since m_l ranges in integer steps from $-l$ to $+l$, also by analogy m_s ranges in integer steps from $-s$ to $+s$. In our hypothetical experiment, we observed one absorption transition, which means there are two spin states. Consequently, the two values of m_s must be $+s$ and $-s$, and the difference in m_s for the two states, labeled f and i below, must be the smallest integer step, i.e., 1. The result of this logic is that

$$\begin{aligned} m_{s,f} - m_{s,i} &= 1 \\ (+s) - (-s) &= 1 \\ 2s &= 1 \\ s &= \frac{1}{2} \end{aligned} \tag{8.4.6}$$

Therefore our conclusion is that the magnitude of the spin quantum number is 1/2 and the values for m_s are +1/2 and -1/2. The two spin states correspond to spinning clockwise and counter-clockwise with positive and negative projections of the spin angular momentum onto the z-axis (Figure 8.4.3). The state with a positive projection, m_s = +1/2, is called α; the other is called β. These spin states are arbitrarily labeled α and β, and the associated spin wavefunctions also are designated by $|\alpha\rangle$ and $|\beta\rangle$.

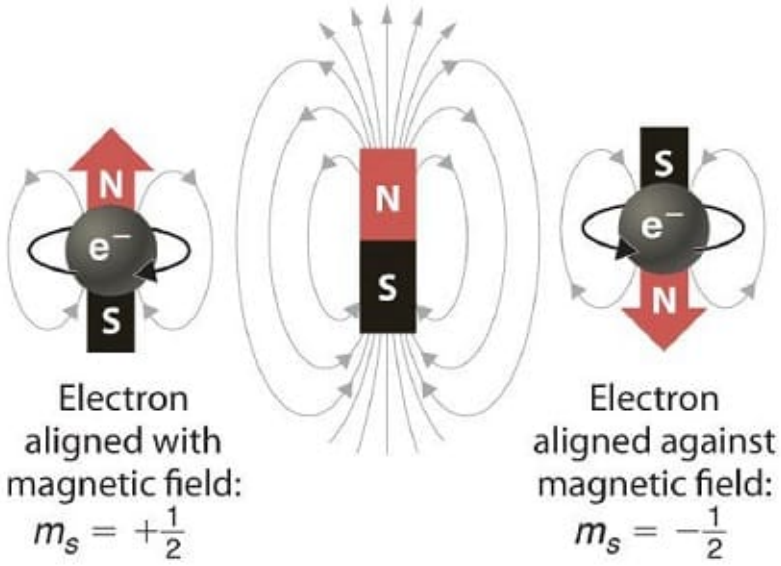


Figure 8.4.3 : Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden. (CC BY-SA-NC 3.0; Anonymous).

From Equation 8.4.5, the magnitude of the z-component of spin angular momentum, S_z, is given by

$$S_z = m_s\hbar \tag{8.4.7}$$

so the value of S_z is $+\hbar/2$ for spin state α and $-\hbar/2$ for spin state β. Hence, we conclude that the α spin state, where the magnetic moment is aligned against the external field direction, has a **greater energy** than the β spin state.

Electrons are not Actually Spinning

Electron's hypothetical surface would have to be moving *faster* than the speed of light for it to rotate quickly enough to produce the observed angular momentum. Hence, an electron is not simply a spinning ball or ring and electron spin appears to be an *intrinsic angular moment* of the particle rather than a consequence of the rotation of a charge particle like Figure 8.4.3 suggests. Despite this, the term "electron spin" persists in quantum vernacular.

Properties of Spin Eigenstates

Even though we do not know their functional forms, the spin wavefunctions are taken to be normalized and orthogonal to each other.

$$\int \alpha^* \alpha \, d\tau_s = \int \beta^* \beta \, d\tau_s = 1 \tag{8.4.8}$$

or in braket notation

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \tag{8.4.9}$$

and

$$\int \alpha^* \beta \, d\tau_s = \int \beta^* \alpha \, d\tau_s = 0 \tag{8.4.10}$$

or in braket notation

$$\langle \alpha | \beta \rangle = \langle \alpha | \beta \rangle = 0 \tag{8.4.11}$$

where the integral is over the spin variable τ_s.

Now let's apply these deductions to the experimental observations in our hypothetical microwave experiment in Figure 8.4.1 . We can account for the frequency of the transition (ν= 28 gigahertz) that was observed in this hypothetical experiment in terms of the magnetic moment of the spinning electron and the strength of the magnetic field. The photon energy, $h\nu$, is given by the difference between the energies of the two states, E_α and E_β

$$\Delta E = h\nu \tag{8.4.12}$$

$$= E_\alpha - E_\beta \tag{8.4.13}$$

The energies of these two states consist of the sum of the energy of an electron in a 1s orbital, E_{1s}, and the energy due to the interaction of the spin magnetic dipole moment of the electron, μ_s, with the magnetic field, B.

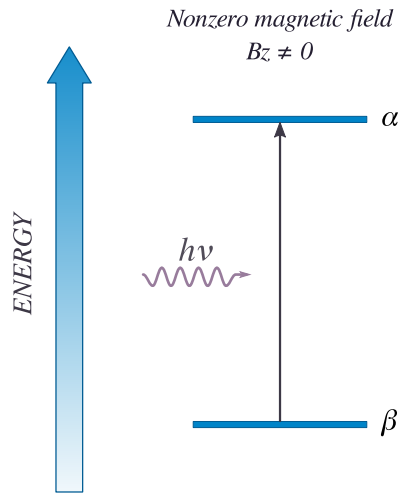


Figure 8.4.4 : Absorption of a photon to cause a transition from the β to the α state. (CC BY-NC; Ümit Kaya via LibreTexts)

The two states with distinct values for spin magnetic moment μ_s are denoted by the subscripts α and β (the spin version of Equation 8.4.1.

$$E_\alpha = E_{1s} - \mu_{s,\alpha} \cdot B$$
$$E_\beta = E_{1s} - \mu_{s,\beta} \cdot B$$

Substituting the two equations above into the expression for the photon (Equation 8.4.13) energy gives

$$h\nu = E_\alpha - E_\beta \tag{8.4.14}$$
$$= (E_{1s} - \mu_{s,\alpha} \cdot B) - (E_{1s} - \mu_{s,\beta} \cdot B) \tag{8.4.15}$$
$$= (\mu_{s,\beta} - \mu_{s,\alpha}) \cdot B \tag{8.4.16}$$

Again by analogy with the orbital angular momentum and magnetic moment discussed above, we take the spin magnetic dipole of each spin state, $\mu_{s,\alpha}$ and $\mu_{s,\beta}$, to be related to the total spin angular momentum of each state, S_α and S_β, by a constant **spin gyromagnetic ratio**, γ_s, as shown below.

$$\mu_s = \gamma_s S$$

or each of the two states

$$\mu_{s,\alpha} = \gamma_s S_\alpha$$
$$\mu_{s,\beta} = \gamma_s S_\beta$$

With the magnetic field direction defined as z, the scalar product in Equation 8.4.16 becomes a product of the z-components of the spin angular momenta, $S_{z,\alpha}$ and $S_{z,\beta}$, with the external magnetic field.

Inserting the values for $S_{z,\alpha} = +\frac{1}{2}\hbar$ and $S_{z,\alpha} = -\frac{1}{2}\hbar$ from Equation 8.4.7 and rearranging Equation 8.4.16 yields

$$\frac{h\nu}{B} = -\gamma_s \hbar$$

Calculating the ratio $\frac{h\nu}{B}$ from our experimental results, $\nu = 28 \times 10^9 \ Hz$ when $B = 10^4 \ gauss$, gives us a value for

$$-\gamma_s \hbar = 18.5464 \times 10^{-21} \, erg/gauss.$$

This value is about twice the Bohr magneton,$-\gamma_e \hbar$, found in Equation 8.4.4 i.e. $\gamma_s \hbar = 2.0023, \gamma_e \hbar$, or

$$\gamma_s = 2.0023\gamma_e \tag{8.4.17}$$

The factor of 2.0023 is called the **g-factor** and accounts for the deviation of the spin gyromagnetic ratio from the value expected for orbital motion of the electron. In other words, it accounts for the spin transition being observed where it is instead of where it would be if the same ratio between magnetic moment and angular momentum held for both orbital and spin motions. The value 2.0023 applies to a freely spinning electron; the coupling of the spin and orbital motion of electrons can produce other values for g.

Exercise 8.4.1

Carry out the calculations that show that the g-factor for electron spin is 2.0023.

Interestingly, the concept of electron spin and the value g = 2.0023 follow logically from *Dirac*'s *relativistic quantum theory*, which is beyond the scope of this discussion. Electron spin was introduced here as a postulate to explain experimental observations. Scientists often introduce such postulates parallel to developing the theory from which the property is naturally deduced.

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8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

Learning Objectives

- Interprete the consequence of exchanging two electrons in a multi-electron atom on the wavelengths
- Connect the Pauli's Exclusion Principle to the permutation symmetry of multi-electron atoms

Quantum mechanics allows us to predict the results of experiments. If we conduct an experiment with indistinguishable particles a correct quantum description cannot allow anything which distinguishes between them. For example, if the wavefunctions of two particles overlap, and we detect a particle, which one is it? The answer to this is not only that we do not know, but that we cannot know. Quantum mechanics can only tell us the probability of finding a particle in a given region. The wavefunction must therefore describe both particles.

The Schrödinger equation for the helium atom is then:

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_1^2)-V(\mathbf{r}_1)-V(\mathbf{r}_2)+V_{12}(\mathbf{r}_1,\mathbf{r}_2)\right]\psi(\mathbf{r}_1,\mathbf{r}_2)=E\psi(\mathbf{r}_1,\mathbf{r}_2)$$

where the subscripts label each particle, and there are six coordinates, three for each particle. While $|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ is a six dimensional wavefunction (three for each electron) and contains all the information we can measure (a Postulate of Quantum Mechanics), it only provide the probability of finding the electron at a specific volume element, and does **not** tell us which particle is which (e.g., is it electon 1 or electron 2?).

What basis states would be appropriate for $|\psi\rangle$? If we consider the orbital approximation that uses a product wavefunction

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle=|\varphi_a(\mathbf{r}_1)\rangle|\varphi_b(\mathbf{r}_2)\rangle$$

where $|\varphi_a(\mathbf{r}_1)\rangle$ and $|\varphi_b(\mathbf{r}_2)\rangle$ are one-particle spin-orbitals (with both spin and spatial components) of atoms 1 and 2. This approximation allows us to separate the two particle equation into two one-electron equations:

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2+V(\mathbf{r}_1)\right]|\varphi_a(\mathbf{r}_1)\rangle=E|\varphi_a(\mathbf{r}_1)\rangle$$

$$\left[-\frac{\hbar^2}{2m}\nabla_2^2+V(\mathbf{r}_2)\right]|\varphi_b(\mathbf{r}_2)\rangle=E|\varphi_a(\mathbf{r}_2)\rangle$$

provided that the particles do not interact (e.g., ∇_1^2 does not act on $|\varphi_b(\mathbf{r}_2)\rangle$ and $V_{12}=0$).

Unfortunately, by doing this we have introduced unphysical *labels* to the indistinguishable particles. And this is wrong: the effect of it is that the particles do not interfere with each other because they are in different dimensions (six dimensional space - remember?). When we construct a two particle wavefunction out of two one-particle wavefunctions we must be ensure that the probability density (the measurable quantity $|\psi|^2$) is independent of the **artificial** labels.

The Exchange Operator

We can deepen our understanding of the quantum mechanical description of multi-electron atoms by examining the concepts of electron indistinguishability and the Pauli Exclusion Principle in detail. We will use the following statement as a guide to keep our explorations focused on the development of a clear picture of the multi-electron atom: "When a multi-electron wavefunction is built as a product of single-electron wavefunctions, the corresponding concept is that exactly one electron's worth of charge density is described by each atomic spin-orbital."

A subtle, but important part of the conceptual picture, is that the electrons in a multi-electron system are not distinguishable

from one another by any experimental means. Since the electrons are indistinguishable, the probability density we calculate by squaring the modulus of our multi-electron wavefunction also cannot change when the electrons are interchanged (permuted) between different orbitals. In general, if we interchange two identical particles, the world does not change. As we will see below, this requirement leads to the idea that the world can be divided into two types of particles based on their behavior with respect to permutation or interchange.

In order for the probability density to remain unchanged when two particles are permuted, the wavefunction itself can change only by a factor of $e^{i\varphi}$, which represents a complex number, when the particles described by that wavefunction are permuted. As we will show below, the $e^{i\varphi}$ factor is possible because the probability density depends on the absolute square of the function and all expectation values involve $\psi\psi^*$. Consequently $e^{i\varphi}$ disappears in any calculation that relates to the real world because $e^{i\varphi}e^{-i\varphi} = 1$.

We could symbolically write an approximate two-particle wavefunction as $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 ($\mathbf{r}_1$) for the coordinates of particle 2 ($\mathbf{r}_2$) and vice versa, to get the new wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This new wavefunction must have the property that

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = \psi(\mathbf{r}_2, \mathbf{r}_1)^*\psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.1}$$

since the probability density of the electrons in the atom does **not** change upon permutation of the electrons.

Exercise 8.5.1

Permute the electrons the product function for He wavefunction:

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = |\varphi_{1s}(\mathbf{r}_1)\rangle|\varphi_{1s}(\mathbf{r}_2)\rangle$$

Equation 8.5.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.2}$$

so that

$$\left(e^{-i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right)\left(e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.3}$$

If we exchange or permute two identical particles twice, we are (by definition) back to the original situation. If each permutation changes the wavefunction by $e^{i\varphi}$, the double permutation must change the wavefunction by $e^{i\varphi}e^{i\varphi}$. Since we then are back to the original state, the effect of the double permutation must equal 1; i.e.,

$$e^{i\varphi}e^{i\varphi} = e^{i2\varphi} = 1 \tag{8.5.4}$$

which is true only if $\varphi = 0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature.

Exercise 8.5.2

Use Euler's Equality

$$e^{i\pi} + 1 = 0$$

to show that $e^{i2\varphi} = 1$ when $\varphi = 0$ or $n\pi$ and consequently $e^{i\varphi} = \pm 1$.

We can introduce the *exchange operator* $\hat{P}_{12}$: an operator which permutes the labels of the particles in a multi-particle wavefucntion. This is a rather strange operator, because it only changes the *unphysical* labels which we have attached to the one-particle wavefunctions in order to make the maths more easy. For a meaningful solution we must have a wavefunction which has a probability amplitude unchanged by $\hat{P}_{12}$: it must be either symmetric or antisymmetric with respect to exchange:

$$\hat{P}_{12}|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \pm|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle \tag{8.5.5}$$

Bosons and femions

Physical solutions must be eigenfunctions of $\hat{P}_{12}$ (i.e., $\hat{H}$ and $\hat{P}_{12}$ commute). Moveover, Equation 8.5.5 argues that the eigenvalues of the Exchange Operator are either +1 (bosons) or –1 (fermions).

Bosons

Wavefunctions for which $e^{i\varphi} = +1$ are defined as symmetric with respect to permutation, because the wavefunction is identical before and after a single permutation. Wavefunctions that are symmetric with respect to interchange of the particles obey the following mathematical relationship,

$$\hat{P}_{12}|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = +|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$

The behavior of some particles requires that the wavefunction be symmetric with respect to permutation. These particles are called bosons and have integer spin such as deuterium nuclei, photons, and gluons.

Fermions

The behavior of other particles requires that the wavefunction be antisymmetric with respect to permutation $(e^{i\varphi} = -1)$. A wavefunction that is antisymmetric with respect to electron interchange is one whose output changes sign when the electron coordinates are interchanged, as shown below.

$$\hat{P}_{12}|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = -|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$

These particles are called fermions and have half-integer spin and include electrons, protons, and neutrinos. Since electrons are fermion, any wavefunction used to describe multiple electrons **must** be antisymmetric with respect to permutation of the electrons. The requirement that the wavefunction be antisymmetric applies to all multi-electron functions $\psi(\mathbf{r}_1,\mathbf{r}_2,\cdots r_i)$, including those approximated as products of single electron functions

$$|\psi(\mathbf{r}_1,\mathbf{r}_2,\cdots r_i)\rangle \approx \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\cdots\varphi_i(r_i) \tag{8.5.6}$$

Exercise 8.5.4

What is meant by the term permutation symmetry?

Exercise 8.5.5

Explain why the product function $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ could describe two bosons (deuterium nuclei), but can not describe two fermions (e.g. electrons).

Answer available at the end of this section.

The Pauli's Exclusion Principle

Any physically meaningful Hamiltonian must commute with $\hat{P}_{12}$, otherwise $\hat{H}$ and $\hat{P}_{12}$ could not have common eigenfunctions and the system could not remain in an eigenstate of exchange. A simple product wavefunction like that in Equation 8.5.6 does **not** satisfy this (unless $\varphi_a = \varphi_b$). A **linear combination of all permutations** is required to satisfy indistinguishability constraints.

For a two particle system (e.g., Helium) there is the asymmetric combination

$$|\psi^{-}\rangle = \frac{1}{\sqrt{2}}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.7}$$

and symmetric combination

$$|\psi^{+}\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle + C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle + C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.8}$$

where the C_{ab} terms are expansion and normalization parameters.

> Note that the antisymmetric combination (Equation 8.5.7) **cannot** include terms where both particles are in the same state (spin-orbital), but there are three possibilities for the symmetric state (Equation 8.5.8).

Although any linear combinations of C_{ab}, C_{bb}, and C_{aa} in Equation 8.5.8 is possible, there are three limiting expressions for possible symmetric combinations:

$$|\psi_1^{+i}\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.9}$$

$$|\psi_2^{+i}\rangle = C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle \tag{8.5.10}$$

$$|\psi_3^{+i}\rangle = C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.11}$$

If $\varphi_a(\mathbf{r}_1) = \varphi_a(\mathbf{r}_2)$, then $|\varphi^{-i}\rangle = 0$. Thus there is no possible antisymmetric combination involving electrons in the same state (spin-orbit). This is the **Pauli exclusion principle**.

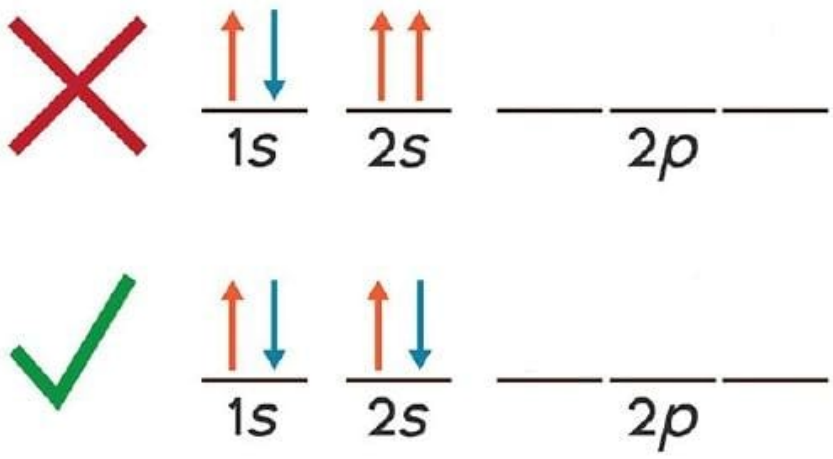


Figure 8.5.1 : The 1s and 2s subshells for beryllium atoms can hold only two electrons and when filled, since each electrons is described by a specific spin-orbital and each orbital (spatial) can hold either an α or a β electron (i.e., they must have opposite spins). Otherwise they will have the same four quantum numbers, in violation of the Pauli Exclusion Principle.

The Pauli Exclusion Principle argues that two electrons **could not** be described by the same spin-orbital. To see the relationship between this statement and the requirement that the wavefunction be antisymmetric for electrons, try to construct an anti-symmetric wavefunction for two electrons that are described by the same spin-orbital

$$|\varphi_b(\mathbf{r}_1)\rangle = \varphi_a(\mathbf{r}_2)\rangle$$

For example, if this were the case for the anti-symmetric combination for helium (Equation 8.5.7), then the wavefunction collapses to zero. We can only constructs wavefunctions that are antisymmetric with respect to permutation symmetry only if each electron is described by a different function.

> The Pauli Exclusion Principle is simply the requirement that the wavefunction be antisymmetric for electrons, since they are fermions.

Answers

Because if we switch $\mathbf{r}_1$ and $\mathbf{r}_2$, the product function becomes $\varphi(r_2)\varphi(r_1)$, which is equal to $\varphi(r_1)\varphi(r_2)$, which is consistent with the wavefunctions of bosons, because boson wavefunctions are symmetric. However, fermion wavefunctions are antisymmetric, which means that if switch r_1 and r_2, the result should be -1×the original wavefunction. Therefore, the product function $\varphi(r_1)\varphi(r_2)$ **cannot** describe fermions.

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8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants

Learning Objectives

- Understand how the Pauli Exclusion principle affects the electronic configuration of mulit-electron atoms
- Understand how determinantal wavefunctions (Slater determinents) ensure the proper symmetry to electron permutation required by Pauli Exclusion Principle.
- Connect the electron permutation symmetry requirement to multi-electron wavefunctions to the Aufbau principle taught in general chemistry courses

Let's try to construct an antisymmetric function that describes the two electrons in the ground state of helium. Blindly following the first statement of the Pauli Exclusion Principle, then each electron in a multi-electron atom **must** be described by a different spin-orbital. For the ground-state helium atom, this gives a $1s^2 2s^0 2p^0$ configuration (Figure 8.6.1).

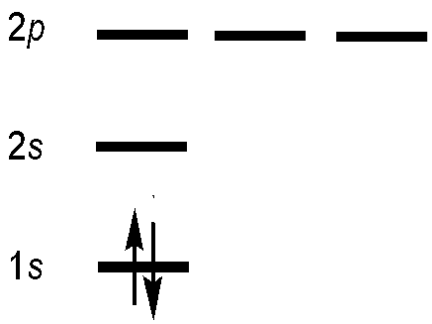


Figure 8.6.1 : Electron configuration for ground state of the helium atom.

We try constructing a simple product wavefunction for helium using two different spin-orbitals. Both have the 1s spatial component, but one has spin function α and the other has spin function β so the product wavefunction matches the form of the ground state electron configuration for He, $1s^2$.

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \varphi_{1s}\alpha(\mathbf{r}_1)\varphi_{1s}\beta(\mathbf{r}_2) \tag{8.6.1}$$

After permutation of the electrons, this becomes

$$|\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle = \varphi_{1s}\alpha(\mathbf{r}_2)\varphi_{1s}\beta(\mathbf{r}_1) \tag{8.6.2}$$

which is different from the starting function since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are different spin-orbital functions. Hence, the simple product wavefunction in Equation 8.6.1 does not satisfy the indistinguishability requirement since an antisymmetric function must produce the same function multiplied by (–1) after permutation of two electrons, and that is not the case here. We must try something else.

To avoid getting a totally different function when we permute the electrons, we can make **a linear combination of functions**. A very simple way of taking a linear combination involves making a new function by simply adding or subtracting functions. The function that is created by subtracting the right-hand side of Equation 8.6.2 from the right-hand side of Equation 8.6.1 has the desired antisymmetric behavior. The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s}\alpha(\mathbf{r}_1)\varphi_{1s}\beta(\mathbf{r}_2) - \varphi_{1s}\alpha(\mathbf{r}_2)\varphi_{1s}\beta(\mathbf{r}_1)] \tag{8.6.3}$$

In this orbital approximation, a single electron is held in a single s*pin-orbital* with an orbital component (e.g., the $1s$ orbital) determined by the n, l, m_l quantum numbers and a spin component determined by the m_s quantum number.

The wavefunction in Equation 8.6.3 can be decomposed into spatial and spin components:

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{1s}(2)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)-\alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.4}$$

Example 8.6.1 : Symmetry to Electron Permutation

Show that the linear combination of spin-orbitals in Equation 8.6.3 is antisymmetric with respect to permutation of the two electrons.

Hint

Replace the minus sign with a plus sign (i.e. take the positive linear combination of the same two functions) and show that the resultant linear combination is symmetric.

Solution

First a reminder of permutation symmetries:

- If the wavefunction is symmetric with respect to permutation of the two electrons then
$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = |\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$
- If the wavefunction is antisymmetric with respect to permutation of the two electrons then
$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = -|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$

We start with the original wavefunction

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)-\varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

and flip the position of electron 1 with electron 2 and vice versa

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)-\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)] \tag{8.6.5}$$

We then we ask if we can rearrange the left side of Equation 8.6.5 to either become $+|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ (symmetric to permutation) or $-|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ (antisymmetric to permutation).

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = \frac{1}{\sqrt{2}}[-\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)+\varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

or

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = -\frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)-\varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

This is just the negative of the original wavefunction, therefore

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = -|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$$

The wavefunction is antisymemtric.

Exercise 8.6.1 : Symmetry

Is this linear combination of spin-orbitals

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)+\varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

symmetric or antisymmetric with respect to permutation of the two electrons?

Answer available at the end of this section.

The electronic configuration of the first excited state of He is $1s^1 2s^1 2p^0$ and we can envision four microstates for this configuration (Figure 8.6.2). As spected, the wavefunctions associated for of these microstate must satisfy indistinguishability requirement just like the ground state.

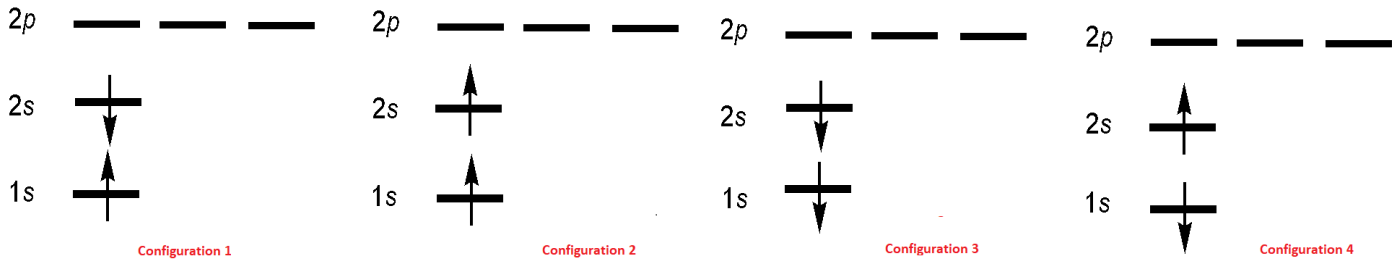


Figure 8.6.2 : Electron configurations for first-excited state of the helium atom.

These electron configurations are used to construct four possible excited-state two-electron wavefunctions (but not necessarily in a one-to-one correspondence):

$$|\psi_1(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)+\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)-\alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.6}$$

$$|\psi_2(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\alpha(2)]}_{\text{spin component}} \tag{8.6.7}$$

$$|\psi_3(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)+\alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.8}$$

$$|\psi_4(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\beta(1)\beta(2)]}_{\text{spin component}} \tag{8.6.9}$$

All four wavefunctions are antisymmetric as required for fermionic wavefunctions (which is left to an exercise). Wavefunctions $|\psi_2\rangle$ and $|\psi_4\rangle$ correspond to the two electrons both having spin up or both having spin down (Configurations 2 and 3 in Figure 8.6.2 , respectively). Wavefunctions $|\psi_1\rangle$ and $|\psi_3\rangle$ are more complicated and are antisymmetric (Configuration 1 - Configuration 4) and symmetric combinations (Configuration 1 + 4). That is, a single electron configuration does not describe the wavefunction. For many electrons, this ad hoc construction procedure would obviously become unwieldy. However, there is an elegant way to construct an antisymmetric wavefunction for a system of N identical particles.

Determinantal Wavefunctions

A linear combination that describes an appropriately antisymmetrized multi-electron wavefunction for any desired orbital configuration is easy to construct for a two-electron system. However, interesting chemical systems usually contain more than two electrons. For these multi-electron systems a relatively simple scheme for constructing an antisymmetric wavefunction from a product of one-electron functions is to write the wavefunction in the form of a determinant. John Slater introduced this idea so the determinant is called a **Slater determinant**.

John C. Slater introduced the determinants in 1929 as a means of ensuring the antisymmetry of a wavefunction, however the determinantal wavefunction first appeared three years earlier independently in Heisenberg's and Dirac's papers.

The Slater determinant for the two-electron ground-state wavefunction of helium is

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2)\end{vmatrix} \tag{8.6.10}$$

A shorthand notation for the determinant in Equation 8.6.10 is then

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = 2^{-\frac{1}{2}} Det|\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)| \tag{8.6.11}$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is $(N!)^{-\frac{1}{2}}$ for N electrons.

The generalized Slater determinant for a multi-electrom atom with N electrons is then

$$\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\varphi_1(\mathbf{r}_1) & \varphi_2(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_1)\\ \varphi_1(\mathbf{r}_2) & \varphi_2(\mathbf{r}_2) & \cdots & \varphi_N(\mathbf{r}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \varphi_1(\mathbf{r}_N) & \varphi_2(\mathbf{r}_N) & \cdots & \varphi_N(\mathbf{r}_N)\end{vmatrix} \tag{8.6.12}$$

Example 8.6.2 : Helium Atom

Expand the Slater determinant in Equation 8.6.10 for the He atom.

Solution

To expand the Slater determinant of the Helium atom, the wavefunction in the form of a two-electron system:

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2)\end{vmatrix}$$

This is a simple expansion exercise of a 2×2 determinant

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\left[\varphi_{1s}(1)\alpha(1)\varphi_{1s}(2)\beta(2) - \varphi_{1s}(2)\alpha(2)\varphi_{1s}(1)\beta(1)\right]$$

It is not unexpected that the determinant wavefunction in Equation 8.6.10 is the same as the form for the helium wavefunction that is given in Equation 8.6.3.

Exercise 8.6.2 : Lithium Atom

Write and expand the Slater determinant for the ground-state Li atom.

Answer available at the end of this section.

Now that we have seen how acceptable multi-electron wavefunctions can be constructed, it is time to revisit the "guide" statement of conceptual understanding with which we began our deeper consideration of electron indistinguishability and the Pauli Exclusion Principle. What does a multi-electron wavefunction constructed by taking specific linear combinations of product wavefunctions mean for our physical picture of the electrons in multi-electron atoms? Overall, the antisymmetrized product function describes the configuration (the orbitals, regions of electron density) for the multi-electron atom. Because of the requirement that electrons be indistinguishable, we cannot visualize specific electrons assigned to specific spin-orbitals. Instead, we construct functions that allow each electron's probability distribution to be dispersed across each spin-orbital. The total charge density described by any one spin-orbital cannot exceed one electron's worth of charge, and each electron in the system is contributing a portion of that charge density.

The four configurations in Figure 8.6.2 for first-excited state of the helium atom can be expressed as the following Slater Determinants

$$|\phi_a(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix} \tag{8.6.13}$$

$$|\phi_b(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix} \tag{8.6.14}$$

$$|\phi_c(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1)\\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix} \tag{8.6.15}$$

$$|\phi_d(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1)\\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix} \tag{8.6.16}$$

Slater determinants are constructed by arranging spinorbitals in columns and electron labels in rows and are normalized by dividing by $\sqrt{N!}$, where N is the number of occupied spinorbitals. As you can imagine, the algebra required to compute integrals involving Slater determinants is extremely difficult. It is therefore most important that you realize several things about these states so that you can avoid unnecessary algebra:

- A Slater determinant corresponds to a single electron configuration diagram (Figure 8.6.2). Furthermore, recall that for the excited states of helium we had a problem writing certain stick diagrams as a (space)x(spin) product and had to make linear combinations of certain states to force things to separate (Equation 8.6.7 and 8.6.9). Because of the direct correspondence of configuration diagrams and Slater determinants, the same pitfall arises here: Slater determinants sometimes may not be representable as a (space)x(spin) product, in which case a linear combination of Slater determinants must be used instead. This generally only happens for systems with unpaired electrons (like several of the Helium excited-states).
- A Slater determinant is anti-symmetric upon exchange of any two electrons. We recall that if we take a matrix and interchange two its rows, the determinant changes sign.

The wavefunctions in 8.6.6-8.6.9 can be expressed in term of the four determinants in Equations 8.6.13-8.6.16.

$$\begin{aligned}|\psi_2\rangle &= |\phi_b\rangle\\ &= \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix}\\ |\psi_4\rangle &= |\phi_d\rangle\\ &= \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1)\\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix}\end{aligned}$$

but the wavefunctions that represent combinations of spinorbitals and hence combinations of electron configurations (e.g., igure 8.6.2) are combinations of Slater determinants (Equation 8.6.13-8.6.15)

$$\begin{aligned}|\psi_1\rangle &= |\phi_a\rangle - |\phi_c\rangle\\ &= \frac{1}{2}\left(\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix} - \begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1)\\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix}\right)\\ |\psi_3\rangle &= |\phi_a\rangle + |\phi_c\rangle\\ &= \frac{1}{2}\left(\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix} + \begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1)\\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix}\right)\end{aligned}$$

Note the expected change in the normalization constants.

Example 8.6.3 : Carbon Atom

Write the Slater determinant for the ground-state carbon atom. If you expanded this determinant, how many terms would be in the linear combination of functions?

Solution

Carbon has 6 electrons which occupy the 1s 2s and 2p orbitals. Each row in the determinant represents a different electron and each column a unique spin-obital where the electron could be found. There are 6 rows, 1 for each electron, and 6 columns, with the two possible p orbitals both alpha (spin up), in the determinate. There are two columns for each s orbital to account for the alpha and beta spin possibilities. There are two different p orbitals because the electrons in their ground state will be in the different p orbitals and both spin up. N=6 so the normalization constant out front is 1 divided by the square-root of 6!

$$\psi(1,2,3,4,5,6) = \frac{1}{6!^{1/2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) & \varphi_{2px}(1)\alpha(1) & \varphi_{2py}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) & \varphi_{2px}(2)\alpha(2) & \varphi_{2py}(2)\alpha(2) \\ \varphi_{1s}(3)\alpha(3) & \varphi_{1s}(3)\beta(3) & \varphi_{2s}(3)\alpha(3) & \varphi_{2s}(3)\beta(3) & \varphi_{2px}(3)\alpha(3) & \varphi_{2py}(3)\alpha(3) \\ \varphi_{1s}(4)\alpha(4) & \varphi_{1s}(4)\beta(4) & \varphi_{2s}(4)\alpha(4) & \varphi_{2s}(4)\beta(4) & \varphi_{2px}(4)\alpha(4) & \varphi_{2py}(4)\alpha(4) \\ \varphi_{1s}(5)\alpha(5) & \varphi_{1s}(5)\beta(5) & \varphi_{2s}(5)\alpha(5) & \varphi_{2s}(5)\beta(5) & \varphi_{2px}(5)\alpha(5) & \varphi_{2py}(5)\alpha(5) \\ \varphi_{1s}(6)\alpha(6) & \varphi_{1s}(6)\beta(6) & \varphi_{2s}(6)\alpha(6) & \varphi_{2s}(6)\beta(6) & \varphi_{2px}(6)\alpha(6) & \varphi_{2py}(6)\alpha(6) \end{vmatrix}$$

Expanding this determinant would result in a linear combination of functions containing 720 terms. An expanded determinant will contain N! factorial terms, where N is the dimension of the matrix.

8.6.3A Exercise : Excited-State of Helium Atom

Write the Slater determinant for the $1s^1 2s^1$ excited state orbital configuration of the helium atom.

Answer available at the end of this section.

8.6.3B Exe

Critique the energy level diagram and shorthand electron configuration notation from the perspective of the indistinguishability criterion. Can you imagine a way to represent the wavefunction expressed as a Slater determinant in a schematic or shorthand notation that more accurately represents the electrons? (This is not a solved problem!)

Answers

Symmetric

Slater determinant for Li atom:

$$\psi(1,2,3) = \frac{1}{\sqrt{6}} \det \begin{pmatrix} \varphi_{1s}\alpha(1) & \varphi_{1s}\beta(1) & \varphi_{2s}\alpha(1) \\ \varphi_{1s}\alpha(2) & \varphi_{1s}\beta(2) & \varphi_{2s}\alpha(2) \\ \varphi_{1s}\alpha(3) & \varphi_{1s}\beta(3) & \varphi_{2s}\alpha(3) \end{pmatrix}$$

Expansion of Slater determinant:

$$\psi(1,2,3) = \frac{1}{\sqrt{6}}[\varphi_{1s}\alpha(1)\varphi_{1s}\beta(2)\varphi_{2s}\alpha(3) - \varphi_{1s}\alpha(1)\varphi_{1s}\beta(3)\varphi_{2s}\alpha(2) + \varphi_{1s}\alpha(3)\varphi_{1s}\beta(1)\varphi_{2s}\alpha(2) - \varphi_{1s}\alpha(3)\varphi_{1s}\beta(2)\varphi_{1s}\alpha(1) + \varphi_{1s}\alpha(2)\varphi_{1s}\beta(3)\varphi_{2s}\alpha(3)]$$

Note that this is also a valid ground state wavefunction

$$\psi(1,2,3) = \frac{1}{\sqrt{6}} \det \begin{pmatrix} \varphi_{1s}\alpha(1) & \varphi_{1s}\beta(1) & \varphi_{2s}\beta(1) \\ \varphi_{1s}\alpha(2) & \varphi_{1s}\beta(2) & \varphi_{2s}\beta(2) \\ \varphi_{1s}\alpha(3) & \varphi_{1s}\beta(3) & \varphi_{2s}\beta(3) \end{pmatrix}$$

What is the difference between these two wavefunctions?

Since there are 2 electrons in question, the Slater determinant should have 2 rows and 2 columns exactly. Additionally, this means the normalization constant is $1/\sqrt{2}$.

Each element of the determinant is a different combination of the spatial component and the spin component of the $1s^1 2s^1$ atomic orbitals

$$\frac{1}{\sqrt{2}} \begin{bmatrix} \varphi_{1_s}(1)\alpha(1) & \varphi 2_s(1)\beta(1) \\ \varphi 1_s(2)\alpha(2) & \varphi 2_s(2)\beta(2) \end{bmatrix}$$

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8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

Learning Objectives

- Understand how the Hartree method is expanded to include symmetrized mulit-electron determential wavefunctions via the Hartree-Fock equations.
- Understand how to calculate the orbital energies from HF theory.
- Apply HF theory with Koopman's theory to estimate ionization energies and electron affinities.

The Hartree method discussed previously is useful as an introduction to the solution of many-particle system and to the concepts of self-consistency and of the self-consistent-field calculations, but its importance is confined to the history of physics. In fact the Hartree method is not just approximate, it is fundamentally wrong since its wavefunction is not antisymmetric to electron permutation! The Hartree-Fock approach discussed below is a better approach, which correctly takes into account the antisymmetric character of the trial wavefunctions.

Although the *Hartree equations* are numerically tractable via the self-consistent field method, it is not surprising that such a crude approximation fails to capture elements of the essential physics. The Pauli exclusion principle demands that the many-body wavefunction be antisymmetric with respect to interchange of any two electron coordinates, e.g.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) \tag{8.7.1}$$

which clearly cannot be satisfied by the multi-electron wavefunctions of the form used in the Hartree Approximation, i.e., the orbital approximation (Equation 8.7.2).

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N) \tag{8.7.2}$$

This indistinguishability condition can be satisfied by forming a Slater determinant of single-particle orbitals

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N}} |\psi(\mathbf{r}_1)\psi(\mathbf{r}_2) \dots \psi(\mathbf{r}_N)| \tag{8.7.3}$$

This decouples the electrons resulting in N single-particle **Hartree-Fock** equations:

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r})}_{\text{kinetic energy}} + \underbrace{V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{electron-nucleus potential}} + \underbrace{V_{electron}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{Hartree Term}} - \sum_j \int d\mathbf{r}' \frac{\psi_j^\star(\mathbf{r}')\psi_i^\star(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = \epsilon_i\psi_i(\mathbf{r}). \tag{8.7.4}$$

As with the *Hartree equations*, the first term is the kinetic energy of the ith electron

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r})$$

and the second term is the electron-nucleus potential between the ith electron and nucleus

$$V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r})$$

The third term (sometimes called the “Hartree” term) is the electrostatic potential between the ith electron and the **average** charge distribution of the other $N-1$ electrons.

$$V_{electron}(\mathbf{r})\psi_i(\mathbf{r}) = J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr' \tag{8.7.5}$$

These three terms are identical to Hartree Equations with the product wavefunction ansatz (i.e., orbital approximation). The fourth term of Equation 8.7.4 is not in the Hartree Equations:

$$\sum_j \int d\mathbf{r}' \frac{\psi_j^\star(\mathbf{r}')\psi_i^\star(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

and is the *exchange* term. This term resembles the direct Coulomb term, but for the exchanged indices. It is a manifestation of the Pauli exclusion principle, and acts so as to separate electrons of the same spin. This "exchange" term acts only on electrons with the same spin and comes from the Slater determinant form of the wavefunction (Equation 8.7.3). Physically, the effect of exchange is for like-spin electrons to avoid each other. The exchange term adds considerably to the complexity of these equations.

The Hartree-Fock Equations in Equation 8.7.4 can be recast as series of Schrödinger-like equations:

$$\hat{F}|\varphi_i\rangle = \epsilon_i|\varphi_i\rangle \tag{8.7.6}$$

where $\hat{F}$ is called the **Fock operator** and $\{|\varphi_i\rangle\}$ are the Hatree-Fock orbitals with corresponding energies ϵ_i.

The Fock operator is a one-electron operator and solving a Hartree-Fock equation gives the energy and Hartree-Fock orbital for one electron. For a system with 2N electrons, the variable i will range from 1 to N; i.e there will be one equation for each orbital. The reason for this is that only the spatial wavefunctions are used in Equation 8.7.6. Since the spatial portion of an orbital can be used to describe two electrons, each of the energies and wavefunctions found by solving Equation 8.7.6 will be used to describe two electrons.

The nature of the Fock operator reveals how the Hartree-Fock (HF) or Self-Consistent Field (SCF) Method accounts for the electron-electron interaction in atoms and molecules while preserving the idea of **independent atomic orbitals**. The wavefunction written as a Slater determinant of spin-orbitals is necessary to derive the form of the Fock operator, which is

$$\begin{aligned}\hat{F} &= \hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) \\ &= -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j)\end{aligned} \tag{8.7.7}$$

As shown by the expanded version on the far right, the first term in this equation, $\hat{H}^0$, is the familiar hydrogen-like operator that accounts for the kinetic energy of an electron and the potential energy of this electron interacting with the nucleus. The next term accounts for the potential energy of one electron in an average field created by all the other electrons in the system. The $\hat{J}$ and $\hat{K}$ operators result from the electron-electron repulsion terms in the full Hamiltonian for a multi-electron system. These operators involve the one-electron orbitals as well as the electron-electron interaction energy.

The Fock operator (Equation 8.7.7) depends on **all occupied** orbitals (because of the exchange and Coulomb operators). Therefore, a specific orbital can only be determined if all the others are known. One must use iterative methods to solve the HF equations like the Self-consistent field method discussed previously for the Hartree Approximation.

Exchange Energy

The exchange interaction is a quantum mechanical effect that only occurs between identical particles. Despite sometimes being called an exchange force in analogy to classical force, **it is not a true force**, as it lacks a force carrier. The effect is due to the wavefunction of indistinguishable particles being subject to exchange symmetry, that is, either remaining unchanged (symmetric) or changing its sign (antisymmetric) when two particles are exchanged. Both bosons and fermions can experience the exchange interaction. For fermions, it is sometimes called Pauli repulsion and related to the Pauli exclusion principle. For bosons, the exchange interaction takes the form of an effective attraction that causes identical particles to be found closer together, as in Bose–Einstein condensation.

Example 8.7.1 : Hartree-Fock Energy of Helium

For example, the electron 1 in helium (with $Z = 2$), then

$$\hat{H}^0(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}$$

The Fock operator is couched in terms of the coordinates of the one electron whose perspective we are taking (which we will call electron 1 throughout the following discussion), and the **average field created by all the other electrons** in the system is built in terms of the coordinates of a generic "other electron" (which we'll call electron 2) that is considered to occupy each orbital in turn during the summation over the N spatial orbitals. The best possible one-electron wavefunctions, by definition, will give the **lowest possible total energy** for a multi-electron system used with the complete multielectron Hamiltonian to calculate the expectation value for the total energy of the system. These wavefunctions are called the **Hartree-Fock wavefunctions** and the calculated total energy is the Hartree-Fock energy of the system.

As with the Hartree Equations, solving the Hartree-Fock Equations is mathematically equivalent to assuming each electron interacts only with the average charge cloud of the other electrons. This is how the electron-electron repulsion is handled. This also why this approach is also called the **Self-Consistant Field (SCF)** approach.

Hartree-Fock Energy

The Hartree-Fock equations $h_e\phi_i = \epsilon_i\phi_i$ imply that the orbital energies ϵ_i can be written as:

$$\begin{aligned}\epsilon_i &= \langle\phi_i|h_e|\phi_i\rangle \\ &= \langle\phi_i|T+V|\phi_i\rangle + \sum_{j(\text{occupied})}\langle\phi_i|J_j - K_j|\phi_i\rangle \\ &= \langle\phi_i|T+V|\phi_i\rangle + \sum_{j(\text{occupied})}[J_{i,j} - K_{i,j}],\end{aligned}$$

where $T+V$ represents the kinetic (T) and nuclear attraction (V) energies, respectively. Thus, ϵ_i is the average value of the kinetic energy plus Coulombic attraction to the nuclei for an electron in ϕ_i plus the sum over all of the spin-orbitals occupied in ψ of Coulomb minus Exchange interactions of these electrons with the electron in ϕ_i.

If ϕ_i is an occupied spin-orbital, the $j = i$ term $[J_{i,i} - K_{i,i}]$ disappears in the above sum and the remaining terms in the sum represent the Coulomb minus exchange interaction of ϕ_i with all of the $N-1$ other occupied spin-orbitals. If ϕ_i is a virtual spin-orbital, this cancelation does not occur because the sum over j does not include $j = i$. So, one obtains the Coulomb minus exchange interaction of ϕ_i with all N of the occupied spin-orbitals in ψ. Hence the energies of occupied orbitals pertain to interactions appropriate to a total of N electrons, while the energies of virtual orbitals pertain to a system with $N+1$ electrons. This difference is very important to understand and to keep in mind.

To give an idea of how well HF theory can predict the ground state energies of several atoms, consider Table 8.7.1 below:

Table 8.7.1 : Hartree-Fock Calculations of Ground Energies of Select Atoms (all energies are in R_H)

Atom	Hartree-Fock Energy	Experiment
He	-5.72	-5.80
Li	-14.86	-14.96
Ne	-257.10	-257.88
Ar	-1053.64	-1055.20

Koopmans' Theorem

Koopmans' theorem states that the first ionization energy is equal to the negative of the orbital energy of the highest occupied molecular orbital. Hence, the ionization energy required to generated a cation and detached electron is represented by the removal of an electron from an orbital without changing the wavefunctions of the other electrons. This is called the "frozen orbital approximation." Let us consider the following model of the detachment or attachment of an electron in an N-electron system.

1. In this model, both the parent molecule and the species generated by adding or removing an electron are treated at the

single-determinant level.
2. The Hartree-Fock orbitals of the parent molecule are used to describe both species. It is said that such a model neglects orbital relaxation (i.e., the re-optimization of the spin-orbitals to allow them to become appropriate to the daughter species).

Within this model, the energy difference between the daughter and the parent can be written as follows (ϕ_k represents the particular spin-orbital that is added or removed:

- for electron detachment (vertical ionization energies)

$$E_{N-1} - E_N = -\epsilon_k \tag{8.7.8}$$

- and for electron attachment (electron affinities)

$$E_N - E_{N+1} = -\epsilon_k. \tag{8.7.9}$$

The Hartree-Fock equations deal with exchange exactly; however, the equations neglect more detailed correlations due to many-body interactions. The effects of electronic correlations are not negligible; indeed the failure of Hartree-Fock theory to successfully incorporate correlation leads to one of its most celebrated failures.

Example 8.7.2 : Electron Affinity

Let's derive this result for the case in which an electron is added to the $N+1^{st}$ spin-orbital. The energy of the N-electron determinant with spin-orbitals ϕ_1 through f_N occupied is

$$E_N = \sum_{i=1}^{N} \langle \phi_i | T + V | \phi_i \rangle + \sum_{i=1}^{N} [J_{i,j} - K_{i,j}]$$

which can also be written as

$$E_N = \sum_{i=1}^{N} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N} [J_{i,j} - K_{i,j}].$$

Likewise, the energy of the $N+1$-electron determinant wavefunction is

$$E_{N+1} = \sum_{i=1}^{N+1} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N+1} [J_{i,j} - K_{i,j}].$$

The difference between these two energies is given by

$$\begin{aligned} E_N - E_{N+1} &= -\langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \frac{1}{2} \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ &\quad - \frac{1}{2} \sum_{j=1}^{N+1} [J_{N+1,j} - K_{N+1,j}] \\ &= -\langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ &= -\epsilon_{N+1}. \end{aligned}$$

That is, the energy difference is equal to minus the expression for the energy of the $N+1^{st}$ spin-orbital, which was given earlier.

Advanced: Electron Correlation and the "Exchange Hole"

In the Copenhagen Interpretation, the squared modulus of the wavefunction gives the probability of finding a particle in a given place. The many-body wavefunction gives the N-particle distribution function, i.e. $|\Phi(r_1, ..., r_N)|^2$ is the probability density that particle 1 is at r_1, ..., and particle N is at r_N. However, when trying to work out the interaction between electrons, what we want to know is the probability of finding an electron at r, given the positions of all the other electrons $\{r_i\}$. This implies that the electron behaves quantum mechanically when we evaluate its wavefunction, but as a classical point particle when it contributes to the potential seen by the other electrons.

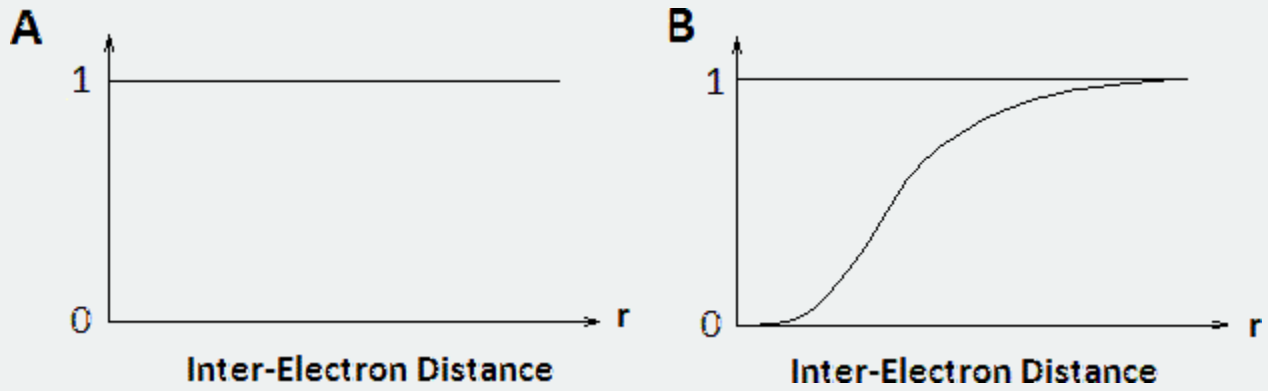


Figure 8.7.2 : Normalized Conditional Probability for from electron-electron interactions (excluding coulomb effects) in (A) the Hartree approximation and (B) the Hartree-Fock approximation.

The contributions of electron-electron interactions in N-electron systems within the Hartree and Hartree-Fock methods are shown in Figure 8.7.2 . The conditional electron probability distributions $n(r)$ of $N-1$ electrons around an electron with given spin situated at $r = 0$. Within the Hartree approximation, all electrons are treated as independent, therefore $n(r)$ is structureless. However, within the Hartree-Fock approximation, the N-electron wavefunction reflects the Pauli exclusion principle and near the electron at $r = 0$ the exchange hole can be seen where the the density of spins equal to that of the central electron is reduced. Electrons with opposite spins are **unaffected** (not shown).

Summary

So, within the limitations of the HF, frozen-orbital model, the ionization potentials (IPs) and electron affinities (EAs) are given as the negative of the occupied and virtual spin-orbital energies, respectively. This statement is referred to as Koopmans' theorem; it is used extensively in quantum chemical calculations as a means of estimating ionization potentials (Equation 8.7.8) and Electron Affinities (Equation 8.7.9) and often yields results that are qualitatively correct (i.e., ± 0.5 eV). In general Hartree-Fock theory gives a great first order solution (99%) to describing multi-electron systems, but that last 1% is still too great for quantitatively describing many aspects of chemistry and more sophisticated approaches are necessary. These are discussed elsewhere.

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8.8: Term Symbols Gives a Detailed Description of an Electron Configuration

Learning Objectives

- Understand how electron configurations results in different manifestations of angular momenta (both oribital and spin)
- Describe the manifestations in atoms via atomic term symbols

Atoms have quantum numbers that are directly analogous to the electronic quantum numbers.

The Total Orbital Angular Momentum Quantum Number: L

One might naively think that you could get the total angular momentum of an atom (L) by simply adding up the l values of the individual electrons. The problem with this idea is that the angular momenta of the various electrons are not necessarily pointing in the same direction. Let's consider the case of adding two 2p-orbitals together (i.e., with $l = 1$ quantum numbers).

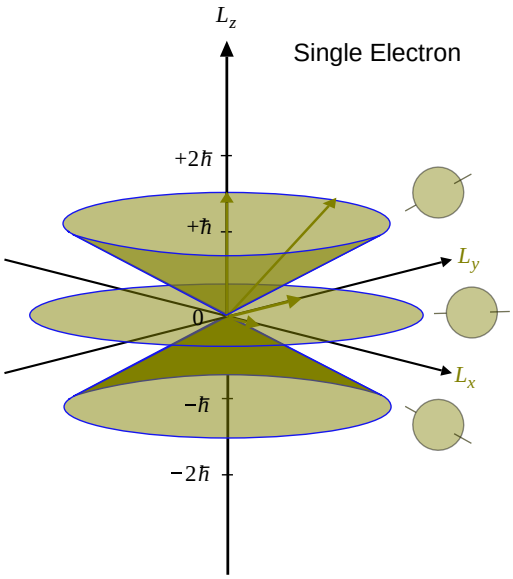


Figure 8.8.1 : The three possible angular momenta vectors for a p-orbital.

As discussed in Section 6.3, each of these electrons has $\sqrt{2}\hbar$ of angular momentum, but oriented in three different directions given by three different m_l values of 1, 0, and -1 (Figure 8.8.1).

$$L = \sum_{i}^{n} l_i \tag{8.8.1}$$

However, we must recognize that while the magnitude of angular momentum is a scalar (represented by l), angular momenta are really vector quantities and to add them together will require vector addition (vs. scalar addition) to do properly and must address all possible orientations of l for each electron.

For example, if two electrons are revolving in the same direction as each other (i.e., same m_l values), one would add just their l values together

$$L(\text{same direction}) = \sqrt{2}\hbar + \sqrt{2}\hbar = 2\hbar$$

If the two elections were revolving in opposites direction (e.., opposite m_l values, you subtract their values.

$$L(\text{same direction}) = \sqrt{2}\hbar - \sqrt{2}\hbar = 0$$

If they are revolving at some off-angle relative to each other (one revolving in a plane and one off plane), you would partially subtract them.

$$L(\text{same direction}) = \sqrt{2}\hbar + 0 = \sqrt{2}\hbar$$

To figure out all of the possible combinations of l for a pair of electrons, simply add them together to get the co-aligned case, subtract them to get the opposing case, and then fill in all the numbers in between to get the off-angle cases. For the two p-orbital case, there are no other possibilities (remember that l and hence L must be non-negative since they represent the magnitude of angular momenta (addressing the m_l values is a different story as we discuss below).

If you prefer to have a formula for the possibilities of L, you can use this:

$$L = |l_1 + l_2|, |l_1 + l_2\text{-}1|, \ldots, |l_1\text{-}l_2| \tag{8.8.2}$$

Technically, Equation 8.8.2 should include all electrons in a system, not just two, to account for all possible combinations of orbital angular momenta, however, there are some tricks that aid in applying this equations to address larger multi-electron atoms. First, electrons in s-orbitals have no orbital angular momentum, so they can be ignored. Second, if block of orbitals are completely filled (e.g., all six p-block spin-orbitals or all 10 d-block spin-orbitals), then the orbital angular momentum vector of each electron will be countered by another electron in the system; these are called **closed-shell** systems. Systems with partially unfilled blocks are called **open-shell** systems.

Hence, conveniently for chemists, an atom's electronic state depends entirely on its unfilled sub shells. Because electrons distribute themselves in a symmetric manner, the inner shell electrons end up canceling out each other's momenta. For an atom in the configuration $1s^2 2s^2 p^2$, only the two p-electrons matter. For an atom in the configuration $1s^2 2s^1 2p^1$, we have to examine only the 2s and 2p electrons (and can ignore the s electrons too).

Example 8.8.1 : Total Orbital Angular Momentum of Carbon

What are the possible L values for the electrons in the $1s^2 2s^2 2p^2$ configuration of carbon?

Solution

Both open-shell electrons (i.e., the 2p electrons) are $l = 1$. The possible combinations are 2, 1, 0.

Example 8.8.2 : Total Orbital Angular Momentum of Unknown Species

What are the possible L values for the electrons in the $[Xe]6s^2 4f^1 5d^1$?

Solution

We can ignore the electrons in the $[Xe]$ core and the electrons in the $6s$ block. So all we have to consider is the f electron $l = 3$ and d electron $l = 2$.

The two extremes possible (Equation 8.8.2) are

$$3 + 2 = 5$$

and

$$3\text{-}2 = 1$$

The possible combinations are thus 5, 4, 3, 2, and 1.

The Total Magnetic Quantum Number: M_l

The Total Magnetic Quantum Number M_l is the total z-component of all of the relevant electrons' orbital momentum. Where L told you how much total angular momentum there is in the system, M_l tells you which direction it is pointing. Like L, a given configuration can have several possible values of M_l, depending on the electrons' relative orientation. Unlike L, M_l is allowed to have negative values. To list the possible M_l values for a two electron system, take the case where both m_l are positive, then take the case where they are both negative, and then fill in the numbers in between (Figure 8.8.1).

$$M_l = m_{l1} + m_{l2}, m_{l1} + m_{l2}\text{-}1, ..., \text{-}m_{l1}\text{-}m_{l2} \tag{8.8.3}$$

Note that there is no absolute value function in Equation 8.8.3 like in Equation 8.8.2.

Example 8.8.3 : Total Magnetic Quantum Number of the Zirconium Ground State

What are the possible values M_l of a zirconium atom with the $[Kr]5s^24d^2$ electron configuration?

Solution

Both open-shell electrons (i.e., the 4d electrons) are $l = 2$, so the values are 4, 3, 2, 1, 0, -1, -2, -3, -4.

The Total Spin Magnetic Quantum Number: M_s

M_s is the sum total of the z-components of the electrons' inherent spin. Do not confuse it with M_l, which is the sum total of the z-component of the **orbital angular momentum**. It is easily computed by finding all of the possible combinations of m_s. Since m_s for each individual electron can only be +1/2 or - 1/2, this isn't too complicated.

$$M_s = m_{s1} + m_{s2}, m_{s1} + m_{s2}\text{-}1, ..., m_{s1}\text{-}m_{s2} \tag{8.8.4}$$

Example 8.8.4 : Total Spin Magnetic Quantum Number of the Carbon Ground State

What are the M s values for $1s^22s^22p^2$?

Solution

$M_s = 1, 0, \text{-}1$

The Total Intrinsic Spin Quantum Number: S

The sum total of the spin vectors of all of the electrons is called S. The difference between S and M_s is subtle, but vital for understanding multiplicity. M_s measures the total z-component of the electrons' spins, while S measures the entire resultant vector. The values of S are computing in a manner very similar to M_s. Because S measures the magnitude of a vector, it cannot ever be negative.

$$S = |s_1 + s_2|, |s_1 + s_2\text{-}1|, ..., |s_1\text{-}s_2| \tag{8.8.5}$$

Example 8.8.5 : The Hydrogen Ground State

Find S for $1s^1$.

Solution

S clearly has to be ½ since that's the spin of a single electron and there's only one electron to worry about.

Example 8.8.6 : The Beryllium Excited State

Find S for $1s^2 2s^1 2p^1$.

Solution

$S = 1, 0$

Example 8.8.7 : The Carbon Ground State

Find S for carbon atoms with the $1s^2 2s^2 2p^2$ electron configuration.

Solution

$S = 1, 0$ This is the same as the previous problem. Notice that S is not affected by which orbitals the electrons are in. S only cares about how many **open-shell electrons** (i.e., unpaired electrons) there are, not about where they are. This is because S measures an inherent property of the electrons themselves

Example 8.8.8

Find S for nitrogen atoms with the $1s^2 2s^2 2p^3$ electron configuration.

Solution

We have not done a three electron case yet, but they are not hard. Find all the combinations for a single pair first, and then factor in the third electron. For two electrons, we already know that the two possible S values are S=1,0. A third electron can either add or subtract ½ from these values, so the final S can be $S = 3/2, 1, 1/2$.

The Total Angular Momentum Quantum Number J

The total orbital angular momentum of an atom (measured in terms of l), and the total spin angular momentum of an atom (measure in S) combine to form total angular momentum, a number that is quantized by the number J. L and S do not necessarily have to be pointing in the same direction (Figure 8.8.1), so J can range from $L + S$ to $|L–S|$.

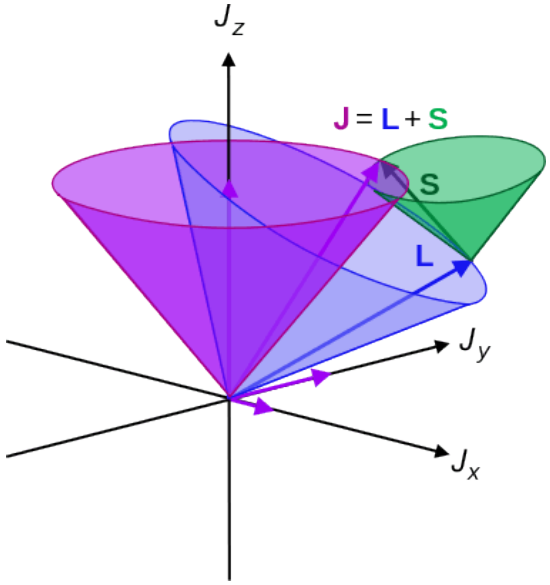


Figure 8.8.1 : Illustration of L-S coupling. Total angular momentum J is purple, orbital L is blue, and spin S is green.

Table 8.8.1 : Quantum Numbers and associated ranges

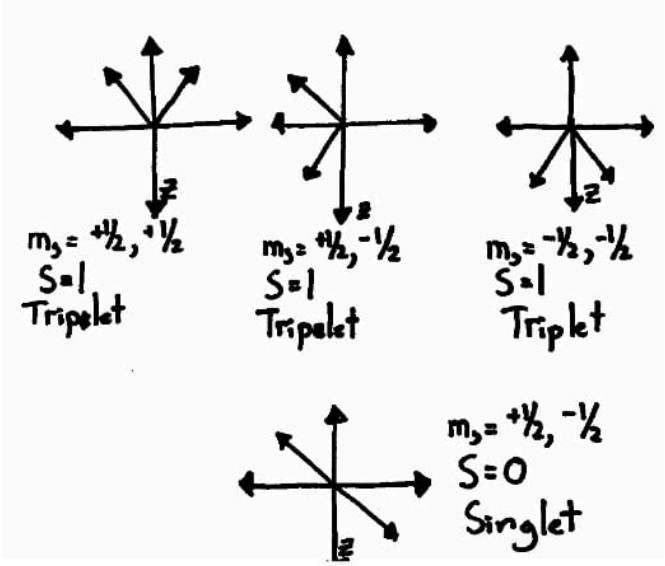
Symbol	Name	Allowed Range
l	Total orbital angular momentum	$\|l_1 + l_2\|, ..., \|l_1\text{-}l_2\|$
M_l	Magnet Quantum number	$[m_{l1} + m_{l2}, ..., \text{-}m_{l1}\text{-}m_{l2}]$
M_s	Spin Magnetic Quantum Number	$\|m_{s1} + m_{s2}\|, ..., \|m_{s1}\text{-}m_{s2}\|$
S	Inherent Spin Number	$\|s_1 + s_2\|, ..., \|s_1\text{-}s_2\|$
M	Multiplicity	2S+1
J	Total Angular Momentum	$L + S, ..., \|L - S\|$

Multiplicity

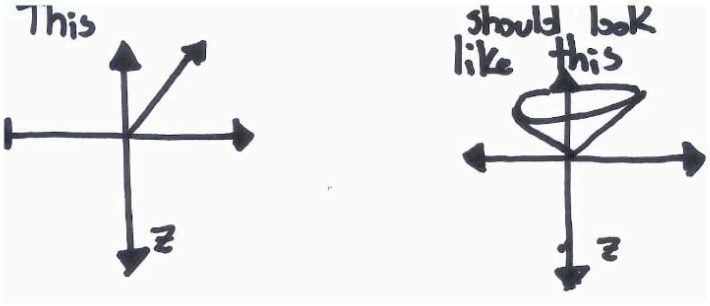
Multiplicity is a simple - sounding concept that defies simple explanations. You know from your first - year education that a singlet is when the net spin (S) is equal to zero (e.g. all the electrons are spin paired), and a triplet happens when the net spin is equal to 1 (e.g. two electrons are pointing in the same direction). They are called “singlet” and “triplet” because there are 3 ways to combine a pair of electron spins to get S=1, but only one way to get $S = 0$. If you draw a picture of the possible ways that two electrons can arrange their spins, you get something like this:



Figure 8.8.1 : When we call an electron spin “up,” what we really mean is that it has a positive z-component (e.g. $m_s = +½$).



While this picture is an improvement over the simple up-down model, it is still misleading. The three spin axes of an electron share a Heisenberg Uncertainty Principle. The more you know about S_x, the less you can know about either S_y or S_z. The same is true for all other combinations of x, y and z. Since we have defined S_z as a known and fixed value, the values of S_x and S_y must be **completely unknown**. This causes the x and y orientations of the electrons to become smeared out across all possible values:



Constructing Term Symbols

Atomic term symbols contain two pieces of information. They tell you the total orbital angular momentum of the atom (l), and they tell you the multiplicity (M). l is denoted by a simple code, similar to the code used to delineate the types of atomic orbitals:

- $L = 0 \rightarrow S$
- $L = 1 \rightarrow P$
- $L = 2 \rightarrow D$
- $L = 3 \rightarrow F$

Note that while the notation is similar, L does NOT say anything about what types of orbitals the electrons are in. A state that has the term symbol P does NOT necessarily have an open p-shell. The multiplicity is indicated by appending a number to the upper left of the symbol. A $L = 2$, $M = 3$ state would be represented by ${}^3D$. The secret to writing the term symbols for an atom is to discover what combinations of l and M are possible for that atom with that specific electronic configuration. An atom that only has closed shells will always be $1S$.

Each term symbol represents a discrete energy level. We can place these levels in the correct order by using these simple rules:

- 1: High multiplicity values mean low energy
- 2: If there is a tie, high l values mean low energy

- 3a: If there is still a tie and the shell is less than half full, then low J means low energy
- 3b: If the shell is more than half full, then high J means low energy

These rules reliably predict the ground state. They have only erratic agreement with experiment when ordering the other levels.

Example 8.8.9 : Hydrogen Ground State

What are the term symbols for the microstates possible for $1s^1$ electronic configuration of hydrogen?

Solution

Since there is only one electron, this is a simple problem. $L = 0$ and $M = 1$, so the only possible term symbol is ^2S. With only one electron, $S = ½$, so $J = 0 + ½ = ½$. Only one microstate exists for this configuration and it has a term symbol of $^2S_{½}$.

Example 8.8.10 : Boron

What are the term symbols for the microstates possible for $1s^2 2s^2 2p^1$ electronic configuration of boron?

Solution

There still only one open shell electron, so $L = 1$, $M = 1$ and $S = ½$. We get a term symbol of the type ^2P, which gets split into separate symbols because $J = 3/2$ and $1/2$. Two possible microstates exist for this system with term symbols of $^2P_{3/2}$ and $^2P_{1/2}$.

Example 8.8.11 : Beryllium Excited State

What are the term symbols for the microstates possible for the $1s^2 2s^1 2p^1$ excited-state electronic configuration of Beryllium?

Solution

Now we have two electrons to worry about. Since $l_1 = 0$ and $l_2 = 1$, the only possible combination is $L = 1$. The possible combinations of S are: $S = 1, 0$. This means that $M = 3$ or $M = 1$. The term symbols will be of the form ^1P and ^3P. For the ^1P state, $L = 1$ and $S = 0$, so $J = 1$. For the second state, $L = 1$ and $S = 1$, so $J = 2, 1, 0$. There are four microstates for this configuration with term symbols of $^1P_1$ and $^3P_2$, $^3P_1$, and $^3P_0$.

Example 8.8.12 : Zirconium

What are the term symbols for the microstates possible for the $[Kr]5s^2 4d^2$ ground-state electronic configuration of zirconium?

Solution

This is a much harder problem. We will need to use a special technique to disentangle all of the possible combinations of l and M. Let's start be listing the relevant quantum numbers for the two open-shell electrons:

$l_1 = 2$	$l_2 = 2$
$m_{l1} = 2, 1, 0, -1, -2$	$m_{l2} = 2, 1, 0, -1, -2$
$m_{s1} = ½, -½$	$m_{s1} = ½, -½$

Let's combine these numbers to generate the atomic quantum numbers:

$$L = 4, 3, 2, 1, 0$$

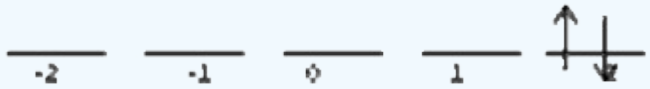
$$M_l = 4, 3, 2, 1, 0, -1, -2, -3, -4$$

$$M_s = 1, 0$$

We know that there will at least one each of S, P, D, F and G. It isn't immediately clear which of these will be singlets and which will be triplets. To figure this out, we need to systematically examine the possible microstates. It turns out that there are **45** possible ways to put distribute two electrons between 5 d orbitals. That's a lot! The easiest way to list the states is to organize them into a chart:

$M_s = -1$	$M_s = 0$	$M_s = +1$

Attacking the chart one row at a time. Ask yourself, how many ways can I arrange the two electrons to give me $M_l = 4$? It turns out there is only one possible combination that does this:

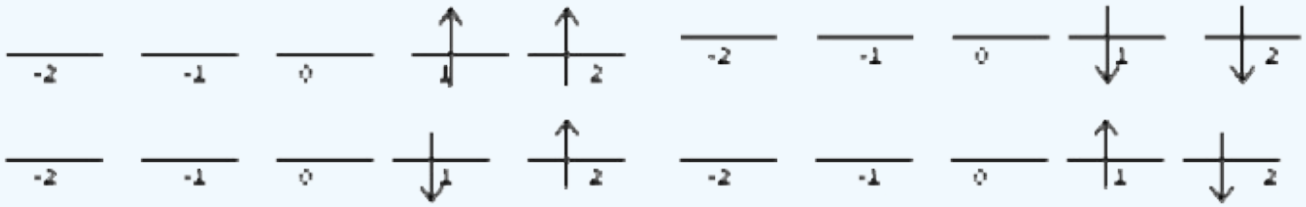


alt

This state is has $M_s = 0$. This means that there is only 1 microstate that corresponds to $M_l = 4$ and $M_s = 0$, and none that correspond to $M_l = 4$ and $M_s = \pm$-1. We add this microstate to the chart like this:

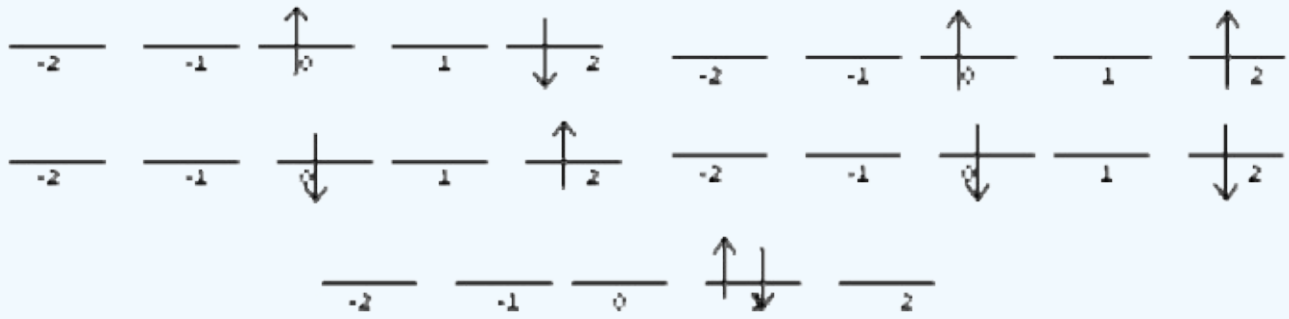
M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0

Now, how many ways are there to get $M_l = 3$?



M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1

For $M_l = 2$, we find the following states:



M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1

You should be able to draw the microstates on your own by now. You should find 8 states, four of which are singlet and four of which are triplets.

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1
1	2	4	2

There are only nine possible ways to arrange the electrons to get $M_l = 0$

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2

The rest of the chart will be symmetric to the first half, so we do not need to do any more work:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	~~0~~	1	~~0~~
3	1	2	1
2	1	3	1
1	2	4	2
~~0~~	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
-4	~~0~~	1	~~0~~

Now that we have a listing of all of the microstates, we need to figure out how to divide them up between the term symbols. It turns out that each term symbol can have, at most, one microstate from each box on the chart. The term symbols always end up claiming a “box” of microstates, centered on the middle of the chart. This is easier shown than said.

Attacking the chart from the top, we can see that the $M_l = 4$ $M_s = 0$ state clearly belongs to a ${}^1G$ symbol. The M_l = -4 $M_s = 0$ box also clearly belongs to this symbol. If I connect these states with a “box,” I get this:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
~~4~~	~~0~~	~~1~~	~~0~~
3	1	2	1
2	1	3	1
1	2	4	2
~~0~~	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
~~-4~~	~~0~~	~~1~~	~~0~~

The strickthough configurations all belong to the ${}^1G$ state. Let's subtract them from the chart to indicate that they are not available for other term symbols.

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
3	1	2	1
2	1	3	1
1	2	4	2
~~0~~	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1

The next row indicates a $L = 3$ state. Because there are three M_s values available, this is a **triplet**. The term symbol will be ${}^3F$, which reduces the chart down to

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	2	4	2
0	2	5	2
-1	2	4	2

The next state will be ^1D. Leaving us with

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	1	1	1
0	1	2	1
-1	1	1	1

Next is a ^3P state. The chart is getting pretty small now wtih

M_l	$M_s = 0$
	0

The last remaining microstate comprises the ^1S term symbol.

The total listing is

$$^1G,\ ^3F,\ ^1D,\ ^3P,\ ^1S.$$

Assigning J values, we get

$$^1G_4,\ ^3F_4,\ ^3F_3,\ ^3F_2,\ ^1D_2,\ ^3P_2,\ ^3P_1,\ ^3P_0,\ ^1S_0$$

If you can do this problem, you can do almost any atomic term symbol.

Note

The secret to writing the term symbols for an atom is to discover what combinations of l and M are possible for that atom with that specific electronic configuration.

Shortcuts

There is a deep symmetry that connects different electronic configurations. It turns out that a p^1 configuration has the same term symbols as a p^5. Similarly, $p^2 = p^4$. A similar relationship can be used to figure out high electron number term symbols for the d and f orbitals.

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8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number

Learning Objectives

- Compate two spin-orbit coupling schemes that couple the total spin angular momenta and total orbital angular momenta of a multi-electron spectra

We need to be able to identify the electronic states that result from a given electron configuration and determine their relative energies. An electronic state of an atom is characterized by a specific energy, wavefunction (including spin), electron configuration, total angular momentum, and the way the orbital and spin angular momenta of the different electrons are coupled together. There are two descriptions for the coupling of angular momentum. One is called **j-j coupling**, and the other is called **L-S coupling**. The j-j coupling scheme is used for heavy elements (z > 40) and the L-S coupling scheme is used for the lighter elements. Only L-S coupling is discussed below.

L-S Coupling of Angular Momenta

L-S coupling also is called R-S or Russell-Saunders coupling. In L-S coupling, the orbital and spin angular momenta of all the electrons are combined separately

$$L = \sum_i l_i \tag{8.9.1}$$

$$S = \sum_i s_i \tag{8.9.2}$$

The total angular momentum vector then is the sum of the total orbital angular momentum vector and the total spin angular momentum vector.

$$J = L + S \tag{8.9.3}$$

The total angular momentum quantum number parameterizes the total angular momentum of a given particle, by combining its orbital angular momentum and its intrinsic angular momentum (i.e., its spin). Due to the spin-orbit interaction in the atom, the orbital angular momentum no longer commutes with the Hamiltonian, nor does the spin.

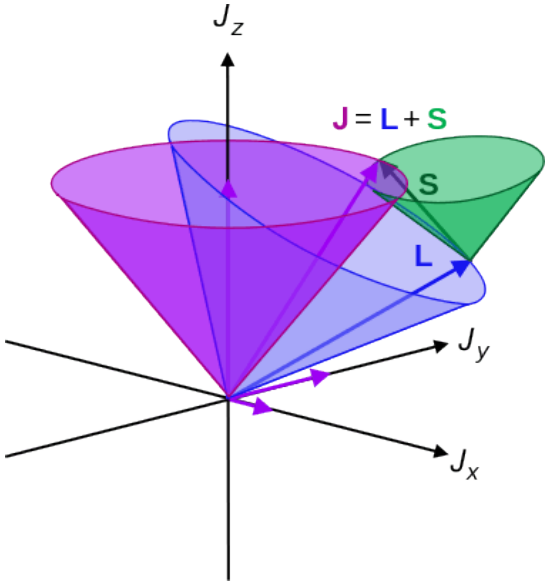


Figure 8.9.1 : "Vector cones" of total angular momentum J (purple), orbital L (blue), and spin S (green). The cones arise due to quantum uncertainty between measuring angular momentum components (see vector model of the atom). (Public Domain; Maschen).

However the total angular momentum J does commute with the Hamiltonian and so is a constant of motion (does not change in time). The relevant definitions of the angular momenta are:

Orbital Angular Momentum

$$|\vec{L}| = \hbar\sqrt{\ell(\ell+1)}$$

with its projection on the z-axis

$$L_z = m_\ell \hbar$$

Spin Angular Momentum

$$|\vec{S}| = \hbar\sqrt{s(s+1)}$$

with its projection on the z-axis

$$S_z = m_s \hbar$$

Total Angular Momentum

$$|\vec{J}| = \hbar\sqrt{j(j+1)}$$

with its projection on the z-axis

$$J_z = m_j \hbar$$

where

- l is the azimuthal quantum number of a single electron,
- s is the spin quantum number intrinsic to the electron,
- j is the total angular momentum quantum number of the electron,

The quantum numbers take the values:

$$m_\ell \in \{-\ell, -(\ell-1)\cdots \ell-1, \ell\}, \quad \ell \in \{0, 1\cdots n-1\} \tag{8.9.4}$$
$$m_s \in \{-s, -(s-1)\cdots s-1, s\}, \tag{8.9.5}$$
$$m_j \in \{-j, -(j-1)\cdots j-1, j\}, \tag{8.9.6}$$
$$m_j = m_\ell + m_s, \quad j = |\ell + s| \tag{8.9.7}$$

and the magnitudes are:

$$|\mathbf{J}| = \hbar\sqrt{j(j+1)} \tag{8.9.8}$$
$$|\mathbf{J}_1| = \hbar\sqrt{j_1(j_1+1)} \tag{8.9.9}$$
$$|\mathbf{J}_2| = \hbar\sqrt{j_2(j_2+1)} \tag{8.9.10}$$

in which

$$j \in \{|j_1 - j_2|, |j_1 - j_2| - 1 \cdots j_1 + j_2 - 1, j_1 + j_2\}$$

This process may be repeated for a third electron, then the fourth etc. until the total angular momentum has been found.

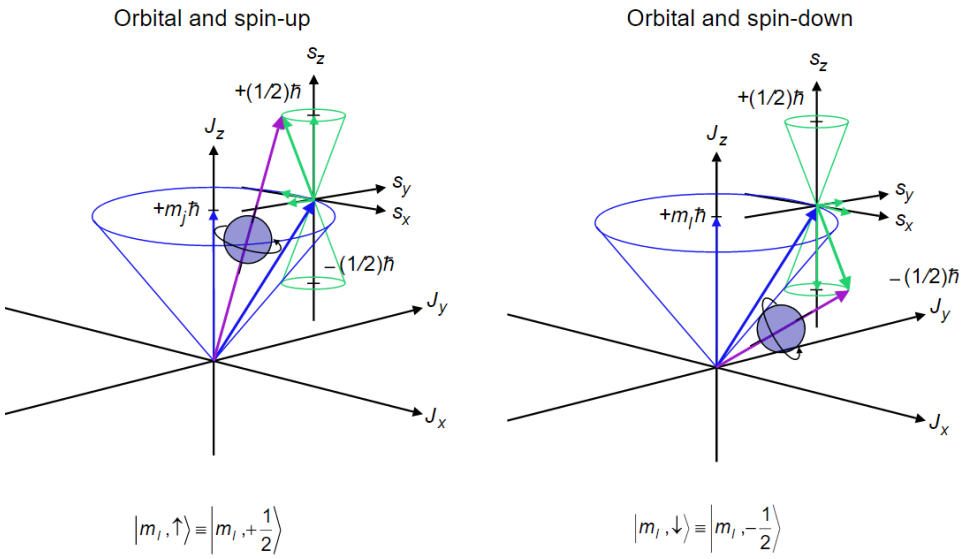


Figure 8.9.2 : Vector model of total angular momentum: spin and orbital coupling (spin-1/2 particles). (Public Domain; Maschen).

The result of these vector sums is specified in a code that is called a Russell-Saunders term symbol, and each term symbol identifies an energy level of the atom. Consequently, the energy levels also are called terms. A term symbol has the form ${}^{2s+1}L_J$ where the code letter that is used for the total orbital angular momentum quantum number L = 0, 1, 2, 3, 4, 5 is S, P, D, F, G, H, respectively. Note how this code matches that used for the atomic orbitals. The superscript $2S+1$ gives the spin multiplicity of the state, where S is the total spin angular momentum quantum number. The spin multiplicity is the number of spin states associated with a given electronic state. In order not to confuse the code letter S for the orbital angular momentum with the spin quantum number S, you must examine the context in which it is used carefully. In the term symbol, the subscript J gives the total angular momentum quantum number. Because of spin-orbit coupling, only J and M_j are valid quantum numbers, but because the spin-orbit coupling is weak L, M_l, S, and m_s still serve to identify and characterize the states for the lighter elements.

For example, the ground state, i.e. the lowest energy state, of the hydrogen atom corresponds to the electron configuration in which the electron occupies the 1s spatial orbital and can have either spin α or spin β. The term symbol for the ground state is ${}^2S_{1/2}$, which is read as “doublet S 1/2”. The spin quantum number is 1/2 so the superscript 2S+1 = 2, which gives the spin multiplicity of the state, i.e. the number of spin states equals 2 corresponding to α and β. The S in the term symbol indicates that the total orbital angular momentum quantum number is 0 (For the ground state of hydrogen, there is only one electron and it is in an s-orbital with $l = 0$). The subscript ½ refers to the total angular momentum quantum number. The total angular momentum is the sum of the spin and orbital angular momenta for the electrons in an atom. In this case, the total angular momentum quantum number is just the spin angular momentum quantum number, ½, since the orbital angular momentum is zero. The ground state has a degeneracy of two because the total angular momentum can have a z-axis projection of $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$, corresponding to m_J

= +1/2 or -1/2 resulting from the two electron spin states α and β. We also can say, equivalently, that the ground state term or energy level is two-fold degenerate.

Exercise 8.9.1

Write the term symbol for a state that has 0 for both the spin and orbital angular momentum quantum numbers.

Exercise 8.9.2

Write the term symbol for a state that has 0 for the spin and 1 for the orbital angular momentum quantum numbers

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8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States

Learning Objectives

- Define Hund three rules
- Use Hunds three rules to predict the lowest energy configuration and term symbols for multi-electron systems

The Aufbau section discussed how that electrons fill the lowest energy orbitals first, and then move up to higher energy orbitals only after the lower energy orbitals are full. However, there a problem with this rule. Certainly, 1s orbitals should be filled before 2s orbitals, because the 1s orbitals have a lower value of n, and thus a lower energy. What about the three different 2p orbitals? In what order should they be filled? The answer to this question involves Hund's rule, which make a lot more sense in the context of generated term symbols that are used to combine the various L and S values represent vector additions of possible microstates.

Hund's Rules

1. State with the largest value of S is most stable and stability decreases with decreasing S.
2. For states with same values of S, the state with the largest value of L is the most stable.
3. If states have same values of L and S then, for a subshell that is less than half filled, state with smallest J is most stable; for subshells that are more than half filled, state with largest value of J is most stable.

Example 8.10.1

Rank these terms associated with an electronic configuration of an atom based on energy (via Hund's rules):

$$^3D,\ ^3P,\ ^3S,\ ^1D,\ ^1P,\ ^1S$$

Hund's First Rule (Maximize Spin Multiplicity)

According to the first rule, electrons always enter an empty orbital before they pair up. Electrons are negatively charged and, as a result, they repel each other. Electrons tend to minimize repulsion by occupying their own orbitals, rather than sharing an orbital with another electron. Furthermore, quantum-mechanical calculations have shown that the electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus.

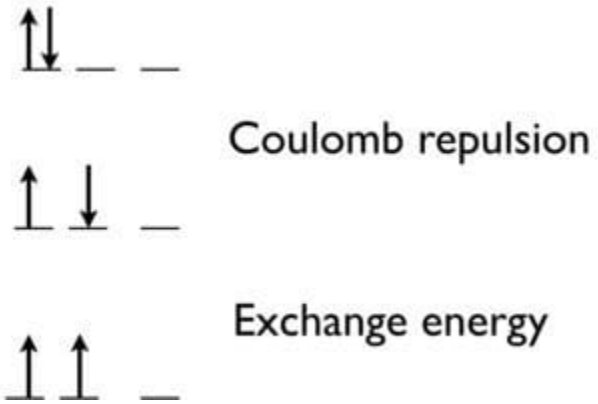


Figure 8.10.1 : Origin of Hund's First Rule. Hund's first rule is that for a given electron configuration, a state in which the spins are unpaired has lower total energy than one in which the spins are paired.

There's a Coulomb repulsion between two electrons to put them in the same orbital (a spin pairing energy often discussed in Crystal Field Theory). However, there's also a quantum mechanical effect. The *exchange energy* (which is favorable) increases with the number of possible exchanges between electrons with the same spin and energy. In transitioning from the top state to the middle state of Figure 8.10.1 , we remove the Coulomb repulsion between electrons in the same orbital. Moreover, In transitioning from the middle state to the bottom state (most stable state predicted by Hund's first rule), we *gain* the *exchange energy*, because these two electrons are indistinguishable.

Hund's Second Rule (Maximize Orbital Angular Multiplicity)

What matters is the total (scalar) angular momentum, not the direction. The negative and positive signs refer only to the direction of the angular momentum, not the magnitude. The direction is furthermore arbitrary (except in, say, a magnetic or electric field). So is the spin direction, incidentally. By convention we usually draw the first electron in each orbital as "up" (positive spin). However we could just as easily draw it "down". It makes no difference - in the absence of an external EM field, the energy is the same, if only because molecules/atoms are rotating with respect to the lab frame anyway. "Up" and "down", in other words, is artificial. What matters is the *relative* momentum vectors of the various electrons in the system, and hence their sum total.

Hund's Third Rule (Minimize less than half filled or maximize greater than half filled shells)

A long time ago someone offering a reasonably simple explanation related to the fact that when the shell is more than half full, it's easier to visualize the system as an interaction between the spin and orbital momenta of holes rather than electrons, in which case the energetic stabilization term is reversed in sign. This would be because the spin angular momentum of a single hole would be opposite in sign compared to the spin angular momentum of a single electron. Taking as an example - the three p-orbitals. A situation with 1 electron and 5 electrons are functionally similar, except that one has a single electron and one has a single hole. All things being equal, the total spin angular momentum of the 1 electron system would be opposite in sign to whatever the total spin angular momentum of the 5 electron system is. So the expectations for Hund's rules would be switched. You can kind of see this if you draw out all the microstates of the 1-electron and 5-electron configurations: the everything is pretty much changed in sign in the latter case.

Example 8.10.2

What terms and levels can arise from an atom with the ground-state configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^1 3d^1$? Which is the most stable (lowest in energy) state?

Solution

Possible states include:

$$^1F_3,\ ^1D_2,\ ^1P_1,\ ^3F_4,\ ^3F_3,\ ^3F_2,\ ^3D_3,\ ^3D_2,\ ^3D_1,\ ^3P_2,\ ^3P_1,\ ^3P_0.$$

There are two unpaired electrons in this system from the electron configuration.

- Rule 1 predicts that the ground state will be a triplet with $S = 1$ so $2S + 1 = 3$. So the ground state is from this more narrowed list: $^3F_4,\ ^3F_3,\ ^3F_2,\ ^3D_3,\ ^3D_2,\ ^3D_1,\ ^3P_2,\ ^3P_1,\ ^3P_0$.
- Rule 2 predicts a F state since that is the highest multiplicity with $L = 3$: So the ground state is from this more narrowed list: $^3F_4,\ ^3F_3,\ ^3F_2$
- Rule 3 predicts the lowest J term since the d shell is less than half full. That is the $J = 2$ state.

Therefore for this system, the atom will have a ground-state structure of

$$^3F_2$$

Example 8.10.3 : Titanium cation

The ground configuration of a Ti^{2+} ion is $[Ar]3d^2$. What is the term of lowest energy state?

Solution

- Rule 1: two unpaired electrons ⇒ highest S = 1 ⇒ 2S + 1 = 3
- Rule 2: two in d in parallel spin ⇒ highest L = 1 + 2 = 3 ⇒ 3F
- Rule 3:.L = 3, S = 1 ⇒ J = 4, 3, 2; less than half-filled ⇒ $^3F_2$

Exercise 8.10.3

What is the term of lowest energy state for the following atoms and ions.

- C: $[He]2s^22p^2$
- N: $[He]2s^22p^3$
- O: $[He]2s^22p^4$
- Cr^{3+}: $[Ar]3d^3$
- Mn^{3+}: $[Ar]3d^4$
- Fe^{3+}: $[Ar]3d^5$

Answer available at the end of this section.

Answers

$^3P_0$, $^4S_{3/2}$, $^3P_2$, $^4F_{3/2}$, $^5D_0$, and $^6S_{5/2}$, respectively.

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8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

Learning Objectives

- Demonstrate how spin-orbit coupling is experimentally observed in atomic spectra
- Use atomic terms symbols to ascribe transitions to specific angular momenta states described by atomic term symbols

Around 1930, several spectroscopists using high resolution instruments found that lines in the hydrogen atom spectrum actually are not single lines but they are multiplets as shown for an isotopic mixture of hydrogen,(H_α^1) and deuterium, (H_α^2), in Figure 8.11.1 . A multiplet consists of two or more closely spaced lines. Two lines together form a doublet, three a triplet, etc. Multiplets also are called fine structure. The term fine structure means the lines are spaced close together, i.e. finely spaced. Such fine structure also was found in spectra of one-electron ions such as He^+.

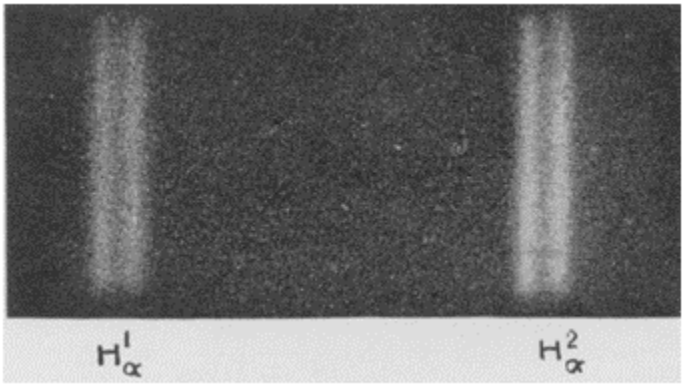


Figure 8.11.1 : Photograph of the first line in the Balmer series for atomic hydrogen and deuterium. These lines are identified as H_α^1 (hydrogen) and H_α^2 (deuterium), respectively. From H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) p. 132 and G.N. Lewis and F.H. Spedding, Phys. Rev. 43, 964 (1933). The doublet splitting for H_α^1 at 656.279 nm was measured to be 0.326 cm^{-1}.

You should recall that the H_α^1 line in the Balmer series at 656.279 nm was understood as resulting from a single transition of an electron from the n = 3 energy level to the n = 2 level. The observation of fine structure revealed that an orbital energy level diagram does not completely describe the energy levels of atoms. This fine structure also provided key evidence at the time for the existence of electron spin, which was used not only to give a qualitative explanation for the multiplets but also to furnish highly accurate calculations of the multiplet splittings.

Spin-Orbit Coupling

Specifying the orbital configuration of an atom does not uniquely identify the electronic state of the atom because the orbital angular momentum, the spin angular momentum, and the total angular momentum are not precisely specified. For example in the hydrogen $2p^1$ configuration, the electron can be in any of the three p-orbitals, m_l = +1, 0, and –1, and have spins with m_s = +1/2 or –1/2. Thus, there are 3 times 2 different possibilities or states. Also, the orbital and spin angular momentum of the electrons combine in multiple ways to produce angular momentum vectors that are characteristic of the entire atom not just individual electrons, and these different combinations can have different energies. This coupling of orbital and spin angular momentum occurs because both the electron spin and orbital motion produce magnetic dipole moments. As we have seen previously, the relationship between the angular momentum and the magnetic moment is given by the gyromagnetic ratio. These magnetic dipoles interact just like two tiny bar magnets attracting and repelling each other. This interaction is called **spin-orbit interaction**. The interaction energy is proportional to the scalar product of the magnetic dipole moments, which are proportional to the angular momentum vectors.

$$E_{s-o} \propto S \cdot L$$

with the following terms added to the Hamiltonian

$$\hat{H}_{s-o} \propto \hat{S} \cdot \hat{L}$$

where the constant of proportionality is called the spin-orbit coupling constant. The spin-orbit interaction couples the spin motion and orbital motion of all the electrons together. This coupling means that exact wavefunctions are not eigenfunctions of the spin and orbital angular momentum operators separately. Rather the total angular momentum $J = L + S$, the vector sum of the spin and orbital angular momentum, is required to be coupled for a completely accurate description of the system. Trying to describe the coupled system in terms of spin and orbital angular momentum separately is analogous to trying to describe the positions of two coupled bar magnets independently. It cannot be done; their interaction must be taken into account (Figure 8.11.1).

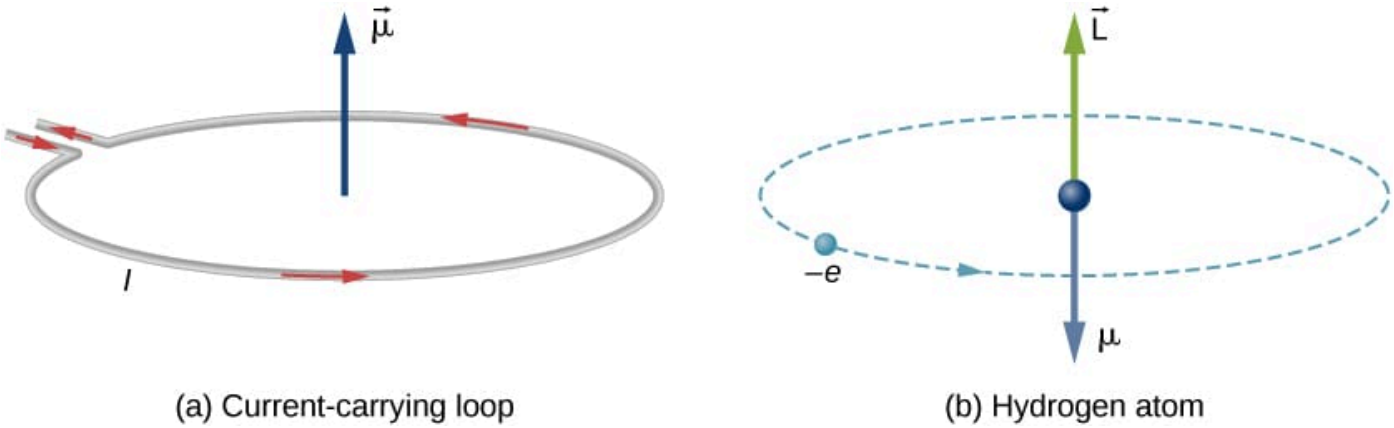


Figure 8.11.1 : An electron that orbits the nucleus induces a "current" and a magnetic field. Similarly, the rotating electron (really intrinsic spin) of the electron induces a different magnet. Both a magnetic (dipole) moments will interact with each other via spin-orbit coupling to generate fine structure atomic spectra.(CC-SA OpenStax).

Atomic Spectroscopy

Higher energy or excited orbital configurations also exist. The hydrogen atom can absorb energy, and the electron can be promoted to a higher energy orbital. The electronic states that result from these excited orbital configurations also are characterized or labeled by term symbols. The details of how to determine the term symbols for multi-electron atoms and for cases where both the orbital and spin angular momentum differ from zero are given elsewhere, along with rules for determining the relative energies of the terms.

We have found that the selection rules for promoting a single electron moving from one atomic orbital to another via the absorption or emission of light are

$$\Delta l = \pm 1$$
$$\Delta m_l = 0, \pm 1$$

These selection rules arise from the conservation fo angular momentum during a spectroscopic transition and the fact that a photon has a spin 1. Within the limits of L-S coupling, these rules can be expressed in terms of atomic term symbols resulting in the resulting Russell-Saunders selection rules:

$$\Delta S = 0 \tag{8.11.1}$$
$$\Delta L = 0, \pm 1 \tag{8.11.2}$$
$$\Delta J = 0, \pm 1, \tag{8.11.3}$$

but the $J = 0$ to $J = 0$ transition is forbidden

$$\Delta m_J = 0, \pm 1 \tag{8.11.4}$$

but the $m_J = 0$ to $m_J = 0$ transition is forbidden if $\Delta J = 0$.

These selection rules result from the general properties of angular momentum such as the conservation of angular momentum

and commutation relations. The $\Delta L = 0$ option in Equation 8.11.2 does not violate the conservation of angular momentum discussed previously, since $\Delta l = \pm 1$ is still required. The orbital angular momentum of an electron must change upon absorption, but this does not necessarily affect the overall momentum of the state given by Equation 8.11.2.

The selection rules apply only to atoms that can be described with Russell-Saunders (LS) coupling. These rules fail as the atomic number increases because the S and L quantum numbers become "bad" quantum numbers; this occurs when the jj-coupling coupling approach is more applicable. For example, the transition between single ($S = 1/2$ and triplet $S = 1$ states (violation of selection rule in Equation 8.11.1) are allowed and experimentally observed, in heavy atoms.

Example 8.11.1 : Sodium Atoms

An example of this fine structure is the emission of sodium atoms.

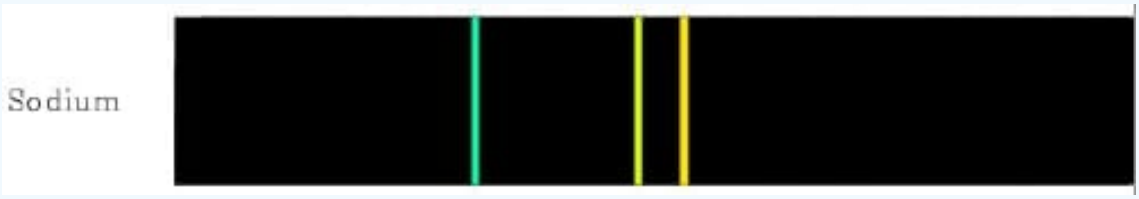


Figure above does not show this splitting).

616.07 nm	615.42 nm	589.00 nm	589.59 nm	568.82 nm	568.26 nm

How can these transitions be described in terms of transitions between microstates

Solution

We need to discussed states in terms of not only electron configurations, but in terms of microstates (i.e., term symbols) and the principal quantum number of the valence electron, n:

- The ground state has a $(Ne]ns^1$ configuration, which has only one microstate $^2S_{1/2}$
- The excited state with the valence electron in the p-orbitals has an electron configuration of $[Ne]np^1$, which has two microstates: $^2P_{3/2}$ and $^2P_{1/2}$
- The excited state with the valence electron in the p-orbitals has an electron configuration of $[Ne]nd^1$, which has two microstates of $^2D_{5/2}$ and $^2D_{3/2}$

Observed lines can be explained:

- $5S \rightarrow 3P$ gives two lines since the initial configuration has two microstates: 616.07, 615.42 nm
- $3P \rightarrow 3S$ gives two lines since the terminal configuration has two microstates: 589.00, 589.59 nm
- $4D \rightarrow 3P$ gives two lines since the terminal configuration has two microstates: 568.82, 568.26 nm

Splitting of the Sodium D Line

One notable atomic spectral line of sodium vapor is the so-called D-line, which may be observed directly as the sodium flame-test line and also the major light output of low -pressure sodium lamps (these produce pressure sodium lamps (these produce an unnatural yellow). The D-line is one of the classified Fraunhofer lines in Sodium vapor in the upper layers of lines. Sodium vapor in the upper layers of the sun creates a dark line in the emitted spectrum of electromagnetic radiation by absorbing visible light in a band of wavelengths around 589.5 nm. This wavelength corresponds to transitions in atomic sodium in which the valence-electron transitions from a 3s to 3p electronic state.

Closer examination of the visible spectrum of atomic sodium reveals that the D-line actually consists of two lines called the D_1 and D_2 lines at 589 6 nm and 589.0 nm, respectively. The splitting between these lines arises because of spin-orbit coupling. Na has one unpaired electron ($S = ½$). If we consider the $S \rightarrow P$ transition, then for the excited state, P, we have $L = 1$. Thus, $J = 3/2$ or $J = 1/2$.

Now we want to apply these ideas to understand why multiplet structure is found in the luminescence spectrum of hydrogen and single electron ions. As we have said, the H_α line in the Balmer series at 656.279 nm can be understood via a transition of an electron in a n = 3 atomic orbital to a n = 2 atomic orbital. When this spectral line was examined using high-resolution instruments, it was found actually to be a doublet, i.e. two lines separated by 0.326 cm^{-1}.

There are 9 degenerate orbitals associated with the n = 3 level, and 4 associated with the n = 2 level. Since an electron can be in any orbital with any one of two spins, we expect the total number of states to be twice the number of orbitals. The number of orbitals is given by n^2 so there should be 8 states associated with n = 2 and 18 states associated with n = 3. Using the ideas of vector addition of angular momentum, the terms that result from having an electron in any one of these orbitals are given in Table 8.11.1 .

Table 8.11.1 : H Atom Terms Originating from n = 1, 2, and 3

Orbital Configuration	Term Symbols	Degeneracy
$1s^1$	$^2S_{1/2}$	2
$2s^1$	$^2S_{1/2}$	2
$2p^1$	$^2P_{1/2}$, $^2P_{3/2}$	2, 4
$3s^1$	$^2S_{1/2}$	2
$3p^1$	$^2P_{1/2}$, $^2P_{3/2}$	2, 4
$3d^1$	$^2D_{3/2}$, $^2D_{5/2}$	4, 6

Table 8.11.1 shows that there are three terms associated with n = 2, and 5 terms associated with n = 3. In principle, each term can have a different energy. The degeneracy of each term is determined by the number of projections that the total angular momentum vector has on the z-axis. These projections depend on the m_J quantum number, which ranges from $+J$ to $-J$ in integer steps. J is the total angular momentum quantum number, which is given by the subscript in the term symbol. This relationship between m_J and J (m_J varies from $+J$ to $-J$ in integer steps) is true for any angular momentum vector.

Exercise 8.11.3

Confirm that the nine term symbols in Table 8.11.1 are correct.

Exercise 8.11.4

Confirm that the values for the degeneracy in Table 8.11.1 are correct and that the total number of states add up to 8 for n = 2 and 18 for n = 3.

The energies of the terms depend upon spin-orbit coupling and relativistic corrections that need to be included in the Hamiltonian operator in order to provide a more complete description of the hydrogen atom. As a consequence of these effects, all terms with the same n and (J\) quantum numbers have the **same energy,** while terms with different values for n or J have different energies. The theoretical term splittings as given by H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) pp. 132-137 and are shown in Figure 8.11.2 .

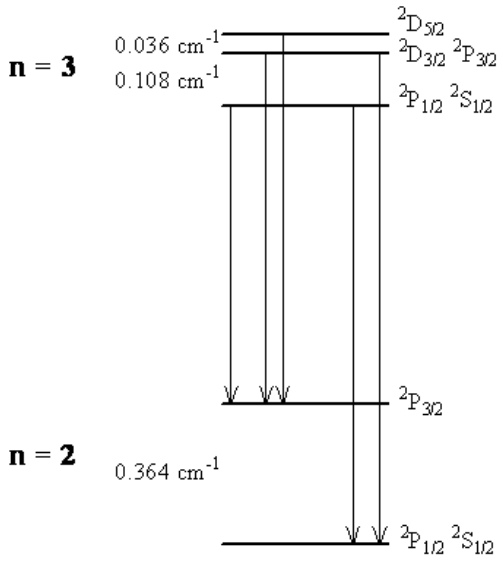


Figure 8.11.2 : Energy level diagram for the electronic states of hydrogen corresponding to an electron with the principal quantum number n = 3 and n = 2. While the relative energies of the terms are drawn to scale, the energy of n = 3 relative to n = 2 is not. Transitions to the $2P_{3/2}$ and ($2P_{1/2}$ and $2S_{1/2}$) levels correspond to the two lines in the H_α^1 band, which have a measured separation of 0.326 cm^{-1}.

Figure 8.11.2 shows 5 allowed transitions for the electron in the states associated with n = 3 to the states associated with n = 2. Of these five, two are most intense and are responsible for the doublet structure. These two transitions are indicated by the wide black lines at the bottom of the figure to correspond to the lines observed in the photographic spectrum shown in Figure 8.11.2 . The other transitions contribute to the width of these lines or are not observed. The theoretical value for the doublet splitting is 0.328 cm^{-1}, which is in excellent agreement with the measured value of 0.326 cm^{-1}. The value of 0.328 cm^{-1} is obtained by taking the difference, 0.364 – 0.036 cm^{-1},in the term splittings.

As we have just seen, the electronic states, as identified by the term symbols, are essential in understanding the spectra and energy level structure of atoms, but it also is important to associate the term symbols and states with the orbital electron configurations. The orbital configurations help us understand many of the general or coarse features of spectra and are necessary to produce a physical picture of how the electron density changes because of a spectroscopic transition.

Exercise 8.11.5

Use the Russell-Saunders selection rules to determine which transitions contribute to the H_α line in the hydrogen spectrum.

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8.E: Multielectron Atoms (Exercises)

Solutions to select questions can be found online.

8.4

Prove the speed of electron in first Bohr orbit is $e^2/4\pi\epsilon_0\hbar = 2.188 \times 10^6 m \bullet s^{-1}$. The speed is in atomic units.

Solution

Use following formula in order to make the calculations

$$v = \frac{\hbar}{m_e a_0}$$

$$v = \frac{\hbar}{m_e}\left(\frac{m_e e^2}{4\pi\epsilon_0\hbar^2}\right)$$

$$v = \frac{e^2}{4\pi\epsilon_0\hbar}$$

Substituting values get the following:

$$v = \frac{(1.6022 \times 10^{-19}\ C)^2}{(1.1127 \times 10^{-10} C^2 \cdot J^{-1} \cdot m^{-1})(1.0546 \times 10^{-34}\ J \cdot s)}$$

$$v = 2.1877 \times 10^6\ m \cdot s^{-1}$$

This is the speed in atomic units. Are either of the two separate terms in the two term helium Hartree-Fock Orbital acceptable wavefunctions by themselves?

$$\psi(r) = 0.81839e^{-1.44608r} + 0.52072e^{-2.86222r}$$

8.15

Explain why:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1 dr_2 d\sigma_1 d\sigma_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1 dr_2 d\sigma_1 d\sigma_2}$$

can be rewritten as:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1 dr_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1 dr_2}$$

Solution

The Hamiltonian does not depend on spin, so the spin integral can be factored out.

8.16

Why must you distinguish the two electrons in separated hydrogen atoms?

Solution

They must be distinguished from one another because they each belong to a separate nucleus, not to an individual one.

8.17

In both the Hartree-Fock approximation and hydrogen atomic wavefunction, why is the angular dependence the same?

Solution

Since the Hamiltonian used in the approximation only depends on r, the angular dependence is not affected in the Hartree-Fock approximation. So both the Hartree-Fock approximation and hydrogen atom will have the same angular dependence.

8.20

Given the two electron determinate wavefunction below, determine if the spin component of the system is symmetric, anti-symmetric, or neither.

$$\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\alpha(2) \end{vmatrix}$$

Solution

We have to solve the determinate.

$$1s1\alpha(2)1s2\beta(2) - 1s1\beta(2)1s1\alpha(2)$$

Now we have to factor out the spatial part from the spin part.

$$1s11s2[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

We are focused on the spin part and by observation, we can tell that the spin component is anti-symmetric.

8.23

Given $\hat{S}_z\alpha = \frac{\hbar}{2}\alpha$ and $\hat{S}_z\alpha = \frac{-\hbar}{2}\beta$, show that Ψ_{200} is an eigenfunction of $S_{z,total} = \hat{S}_{za} + \hat{S}_{zB}$.

Solution

Start with $\Psi_{200} = C(\psi_{2sa} + \psi_{2sB})$.

$$\hat{S}_{z.total}\Psi = C(\hat{S}_{za} + \hat{S}_{zB})[\psi_{2sa} + \psi_{2sB}]$$

$$= C\left(\frac{\hbar}{2} - \frac{\hbar}{2}\right)[\psi_{2sa} + \psi_{2sB}]$$

$$= 0$$

8.24

For the wavefunction:

$$\psi = \begin{vmatrix} \psi_A(1) & \psi_A(2) \\ \psi_B(1) & \psi_B(2) \end{vmatrix}$$

discuss the effect on the wavefunction of (a) swapping rows of the matrix and (b) swapping columns of the matrix.

Solution

Let's expand the determinant to inspect the complete multi-electron wavefunction:

$$\psi = \psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1)$$

If we swap rows:

$$\psi_{RowSwap} = \psi_A(2)\psi_B(1) - \psi_A(1)\psi_B(2) = -\psi$$

If we swap columns:

$$\psi_{ColumSwap} = \psi_A(2)\psi_B(1) - \psi_A(1)\psi_B(2) = -\psi$$

Conclusion: swapping the either two rows or two columns of a Slater determinant changes the sign of the wavefunction.

8.27

What are the term symbols for carbon and oxygen atoms in the ground state?

Solution

Carbon: The electron configuration for carbon at ground state (lowest energy) is $1s^2 2s^2 2p^2$

Since the 1s and 2s orbitals are completely filled, they can be neglected when calculating for S. For the lowest energy, you need to use the highest values of S and L, therefore we find that S= 1/2 +1/2=1 and L=1 which corresponds to the letter P. Since the 2p orbital is less than half-way filled, we use J=|L-S|=|1-1|=0.

The term symbol is ${}^{2S+1}L_J$ which is ${}^3\mathrm{P}_0$ for the ground-state of carbon atoms.

Oxygen: The electron configuration for oxygen at ground state (lowest energy) is $1s^2 2s^2 2p^4$

Again, the 1s and 2s orbitals may be neglected when calculating for S.

$$S = 1/2 + 1/2 + 1/2 - 1/2 = 1$$

The last electron has a spin down due to the Pauli Exclusion Principle.

L=1 which corresponds to the letter P.

Since the 2p orbital for oxygen is more than half-filled,

$$J = L + S = 2$$

The term symbol for the ground-state oxygen atom is ${}^3\mathrm{P}_2$

8.28

Show that the number of sets of magnetic quantum number (m_l) and spin quantum number (m_s) associated with any term symbol is equal to $(2L+1)(2S+1)$. Apply this result to the np^2 case and show that symbol ${}^1S$, ${}^3P$ and ${}^1D$ account for all the possible sets of magnetic quantum numbers and spin quantum numbers

8.29

Calculate all possible numbers of term symbol for an np^1 electron configuration.

Solution

$$N = \frac{G!}{e!(G-e)!}$$

where G is the highest number of electrons that an orbital can hold and e is the highest number of electrons that a subshell can hold

$$N = \frac{6!}{2!(6-2)!} = 15$$

8.30

Determine the ground state term symbol for the electron configuration of the Halogens.

Solution

Halogens have the electron configurationnp^5 we can determine the term symbols for this configuration by mapping out all possible configurations the electrons can fit into the six spin orbitals. To quickly determine how many possible combinations there are we can use a statistical method of $N_{Comb.} = \binom{spinorbitals}{electrons}$

$$N_{comb} = \binom{6}{5} = \frac{6!}{5!(6!-5!)} = 6$$

Now we know that there are 6 different configurations that we can map out to determine the term symbols. Since we are working with the p orbital we know $l = 1$ and $m_s = -1,\ 0,\ 1$. I will denote spin using α as spin up $+\frac{1}{2}$ and β as spin down $-\frac{1}{2}$. M_L is the sum of the m_s values corresponding to the number of electrons in that energy level. For example if you have $\alpha\beta$ in $m_s = +1$ only, you then have 2 electrons in $m_s = +1$ resulting in $M_L = +1 + 1 = 2$. M_s is the sum of the spin up and spin down values.

+1	0	-1	M_L	M_s
$\alpha\beta$	$\alpha\beta$	α	+1	$+\frac{1}{2}$
$\alpha\beta$	α	$\alpha\beta$	0	$+\frac{1}{2}$
α	$\alpha\beta$	$\alpha\beta$	-1	$+\frac{1}{2}$
$\alpha\beta$	$\alpha\beta$	β	+1	$-\frac{1}{2}$
$\alpha\beta$	β	$\alpha\beta$	0	$-\frac{1}{2}$
β	$\alpha\beta$	$\alpha\beta$	-1	$-\frac{1}{2}$

Now we need to determine the maximum value of M_L andM_s. Looking at the table we see that

$$max\ M_L = 1$$
$$max\ M_s = \frac{1}{2}$$

From this we know our maximum value of L and S

$$L_{max} = 1$$
$$S_{max} = \frac{1}{2}$$

Our possible values for L and S are

$$L = 1,\ 0$$
$$S = \frac{1}{2}$$

Since S is only $\frac{1}{2}$ we know we can only have doublet term symbols since $2\left(\frac{1}{2}\right) + 1 = 2$. L ranges from 1 to 0 so our possible corresponding symbols will be P and S. This leaves us with the possibility of having

$$^2P,\ ^2S$$

To figure out what is there we start with the term symbol that has the largest L value, with is the P. We see that for P, $L = 1$ and $S = \frac{1}{2}$. For a value of $L = 1$ our m_l can be $+1,\ 0,\ -1$ and for an $S = \frac{1}{2}$ our $m_s = +\frac{1}{2},\ -\frac{1}{2}$. In the table above all rows that contain these possible combination include every row. Therefore all of the configurations are contained in this doublet P term symbol. Including values of J we know that $L + S \geq J \geq |L - S|$. Since $L = 1$ and $S = \frac{1}{2}$ our final term symbols are

$$^2P_{\frac{3}{2}},\ ^2P_{\frac{1}{2}}$$

Hund's rules say that when L and S are the same with a subshell more than half filled, you look to the largest J value to be the most stable. Therefore our final answer and the ground state term symbol for halogens is

$$\boxed{^2P_{\frac{3}{2}}}$$

8.33

^2P, ^2D, and ^4S are the term symbols for an atom with the np^3 electron configuration. Using the term symbols for the np^3 electron configuration, calculate the J values associated with each of the term symbol. Then find out which term symbol represent the ground state.

Solution

To calculate J we use this equation

$$J = L + S$$

This equation can be further expanded to be

$$J = L + S, L + S - 1, L + S - 2, \ldots |L - S|$$

Term Symbol	L	S	J	Full Term Symbol
^2P	1	$\frac{1}{2}$	$\frac{3}{2}, \frac{1}{2}$	$^2P_{3/2}$ and $^2P_{1/2}$
^2D	2	$\frac{1}{2}$	$\frac{5}{2}\ \frac{3}{2}$	$^4D_{5/2}$ and $^4D_{3/2}$
^4S	0	$\frac{3}{2}$	$\frac{3}{2}$	$^4S_{3/2}$

8.34

What are the ground state electron configuration and term symbol for Calcium?

Solution

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

or

$$[Ar]4s^2$$

For the term symbol:

Spin Multiplicity: S = 0 (all electrons paired)

$$J = S + L = 0$$

There is only one valid value of J, so the term symbol for this configuration is

$$^{2S+1}L_J = {}^1S0$$

$$2S + 1 = 1$$

Orbital Angular Multiplicity: L = 0 because we consider an s orbital. This corresponds to S.

8.34

Find the ground state term symbol for Ca.

Solution

ns^2 electron configurations have the term symbol $^1S_0$, so the term symbol for Ca in the ground state is $^1S_0$.

8.36

Write the electron configuration for vanadium and use this information to find the ground-state term symbol for V.

Solution

The electron configuration for vanadium is $[Ar]3d^3 4s^3$

Spin Multiplicity: The electron configuration predicts three unpaired electrons, so

$$S = 1/2 + 1/2 + 1/2 = 3/2$$

and the multiplicity of $2S + 1$ predicts that this will be a quartet. Orbital Angular Momentum: The electron configuration predicts three electrons with $l = 2$ and the rest so not contribute, so $L = 1 + 1 + 1 = 3$, which is an F state

The ground-state term symbol for vanadium is $^4F_{3/2}$ since vanadium has a half-filled 3d subshell.

- Total Angular Momentum: The shell is half full

8.36

What is the ground-state term symbol for Ne.

Solution

The term symbol is ${}^{2S+1}L_J$

where

S is the total electron spin L is the total orbital angular momentum

so $2S+1 = 2 \cdot 0 + 1 = 1$ and $J = 0 + 0 = 0$. So the term symbol for Ne is ${}^1S_0$.

and

$$J = L + S$$

The electron configuration for:Ne is $1s^2 2s^2 2p^6$ since Ne has spherical symmetry, we get:

$$L = 0 + 0 = S$$

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} = 0$$

8.37

Looking at the $1s2p$ electron configuration for He. Solve for the term symbols (states) of the Helium configuration and the degeneracies. If electron spin orbit coupling is included, what effect will this have?

Solution

There are two possible sets of m_l and m_s for the ns electron and six possible sets of m_l and m_s for the np electron, so there are 2 × 6 = 12 possible sets of m_l and m_s for the system. We can denote values for the electron in the ns orbital as m_{1j} and those for the electron in the np orbital as m_{2j}. The allowed values are given below:

Microstate	$m_l(1)$	$m_s(1)$	$m_l(2)$	$m_s(2)$	M_L	M_S	M_J
	Electron 1 in $1s$ orbital		*Electron 2 in $2p$ orbital*		*Combined Angular Momenta of both Electrons*		
1	0	+ 1/2	1	+ 1/2	1	1	2
2	0	- 1/2	1	+ 1/2	1	0	0
3	0	+ 1/2	1	- 1/2	1	0	0
4	0	- 1/2	1	- 1/2	1	-1	1
5	0	+ 1/2	0	+ 1/2	0	1	0
6	0	- 1/2	0	+ 1/2	0	0	1
7	0	+ 1/2	0	- 1/2	0	0	0
8	0	- 1/2	0	- 1/2	0	-1	0
9	0	+ 1/2	-1	+ 1/2	-1	1	0
10	0	- 1/2	-1	+ 1/2	-1	0	-1
11	0	+ 1/2	-1	- 1/2	-1	0	-2
12	0	- 1/2	-1	- 1/2	-1	-1	-2

Entries 1, 2, 4, 5, 6, 8, 9, 10, and 12 correspond to L = 1 and S = 1, or ^{3}P term symbol, and entries 3, 7, and 11

correspond to L = 1 and S = 0, which is a ^{1}P term symbol. The values of J can be derived from the table or by using

$$J = (L + S), (L + S - 1), (L + S - 2), \ldots\ldots, (|L + S|),$$

The final results given the term symbols below:

$^3P_2$ $^3P_1$ $^3P_0$ $^1P_1$

$(L + S)$ $(L + S - 1)$ $(|L - S|)$ $(|L + S|)$

The states corresponding to this electron configuration and their degeneracies are:

Term symbol: $^3P_2$ $^3P_1$ $^3P_0$ $^1P_1$

Degeneracy: 5 3 1 3

According to Hund's rule, the ground state $^3P_0$. Including the effect of spin-orbit coupling removes the degeneracy of the electronic states, and no spin orbit coupling splits the lines in an atomic spectra.

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9: COMPUTATIONAL QUANTUM CHEMISTRY

Computational chemistry is the field of chemistry that uses mathematical approximations and computer programs to solve problems of chemical interest. Quantum chemistry is a subfield that addresses the equations and approximations derived from the postulates of quantum mechanics; specifically involving solving the Schrödinger equation for molecular systems. Quantum chemistry is typically separated into a*b initio,* which uses methods that do not include any empirical parameters or experimental data and semi-empirical which do.

9.1: Overview of Quantum Calculations

9.2: Gaussian Basis Sets

9.3: Extended Basis Sets

9.4: Orbital Polarization Terms in Basis Sets

9.E: Computational Quantum Chemistry (Exercises)

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9.1: Overview of Quantum Calculations

Multielectron Electronic Wavefunctions

We could symbolically write an approximate two-particle wavefunction as $\psi(r_1, r_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 (r_l) for the coordinates of particle 2 (r_2) and vice versa, to get the new wavefunction $\psi(r_1, r_2)$. This new wavefunction must have the property that

$$|\psi(r_1, r_2)|^2 = \psi(r_2, r_1)^* \psi(r_2, r_1) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{9.1.1}$$

Equation 9.1.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(r_1, r_2) = e^{i\varphi} \psi(r_1, r_2)$$

so that

$$\left(e^{-i\varphi} \psi(r_1, r_2)^*\right) \left(e^{i\varphi} \psi(r_1, r_2)^*\right) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{9.1.2}$$

If we exchange or permute two identical particles twice, we are (by definition) back to the original situation. If each permutation changes the wavefunction by $e^{i\varphi}$, the double permutation must change the wavefunction by $e^{i\varphi} e^{i\varphi}$. Since we then are back to the original state, the effect of the double permutation must equal 1; i.e.,

$$e^{i\varphi} e^{i\varphi} = e^{i2\varphi} = 1$$

which is true only if $\varphi = 0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature, but the behavior of elections is that the wavefunction be antisymmetric with respect to permutation ($e^{i\varphi} = -1$). A wavefunction that is antisymmetric with respect to electron interchange is one whose output changes sign when the electron coordinates are interchanged, as shown below.

$$\psi(r_2, r_1) = e^{i\varphi} \psi(r_1, r_2) = -\psi(r_1, r_2)$$

Blindly following the first statement of the Pauli Exclusion Principle, that each electron in a multi-electron atom **must** be described by a different spin-orbital, we try constructing a simple product wavefunction for helium using two different spin-orbitals. Both have the 1s spatial component, but one has spin function α and the other has spin function β so the product wavefunction matches the form of the ground state electron configuration for He, $1s^2$.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) \tag{9.1.3}$$

After permutation of the electrons, this becomes

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1) \tag{9.1.4}$$

which is different from the starting function since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are different spin-orbital functions. However, an antisymmetric function must produce the same function multiplied by (–1) after permutation, and that is not the case here. We must try something else.

To avoid getting a totally different function when we permute the electrons, we can make a linear combination of functions. A very simple way of taking a linear combination involves making a new function by simply adding or subtracting functions. The function that is created by subtracting the right-hand side of Equation 9.1.4 from the right-hand side of Equation 9.1.3 has the desired antisymmetric behavior. The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1)]$$

A linear combination that describes an appropriately antisymmetrized multi-electron wavefunction for any desired orbital configuration is easy to construct for a two-electron system. However, interesting chemical systems usually contain more than two electrons. For these multi-electron systems a relatively simple scheme for constructing an antisymmetric wavefunction from

a product of one-electron functions is to write the wavefunction in the form of a determinant. John Slater introduced this idea so the determinant is called a Slater determinant.

The Slater determinant for the two-electron wavefunction for the ground state H_2 system (with the two electrons occupying the σ_{1s} molecular orbital)

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_{1s}(1)\alpha(1) & \sigma_{1s}(1)\beta(1) \\ \sigma_{1s}(2)\alpha(2) & \sigma_{1s}(2)\beta(2) \end{vmatrix}$$

We can introduce a shorthand notation for the arbitrary **spin-orbital**

$$\chi_{i\alpha}(\mathbf{r}) = \varphi_i\alpha$$

or

$$\chi_{i\beta}(\mathbf{r}) = \varphi_i\beta$$

as determined by the m_s quantum number. A shorthand notation for the determinant in Equation 8.6.4 is then

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = 2^{-\frac{1}{2}} Det|\chi_{1s\alpha}(\mathbf{r}_1)\alpha\chi_{1s\beta}(\mathbf{r}_2)\beta|$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is

$$(N!)^{-\frac{1}{2}}$$

for a system of N electrons.

The generalized Slater determinant for a multe-electrom atom with N electrons is then

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{r}_1)\alpha & \chi_1(\mathbf{r}_1)\beta & \cdots & \chi_{N/2}(\mathbf{r}_1)\beta \\ \chi_1(\mathbf{r}_2)\alpha & \chi_2(\mathbf{r}_2)\beta & \cdots & \chi_{N/2}(\mathbf{r}_2)\beta \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{r}_N)\alpha & \chi_2(\mathbf{r}_N)\beta & \cdots & \chi_{N/2}(\mathbf{r}_N)\beta \end{vmatrix} \tag{9.1.5}$$

In a modern *ab initio* electronic structure calculation on a closed shell molecule, the electronic Hamiltonian is used with a single determinant wavefunction. This wavefunction, Ψ, is constructed from molecular orbitals, ψ that are written as linear combinations of contracted Gaussian basis functions, φ

$$\varphi_j = \sum_k c_{jk}\psi_k \tag{9.1.6}$$

The contracted Gaussian functions are composed from primitive Gaussian functions to match Slater-type orbitals. The exponential parameters in the STOs are optimized by calculations on small molecules using the nonlinear variational method and then those values are used with other molecules. The problem is to calculate the electronic energy from

$$E = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \tag{9.1.7}$$

or in bra-ket notation

$$E = \frac{\left\langle \Psi | \hat{H} | \Psi \right\rangle}{\langle \psi | \psi \rangle}$$

The the optimum coefficients c_{jk} for each molecular orbital in Equation 9.1.6 by using the Self Consistent Field Method and the Linear Variational Method to minimize the energy as was described previously for atoms.

The variational principle says an approximate energy is an upper bound to the exact energy, so the lowest energy that we calculate

is the most accurate. At some point, the improvements in the energy will be very slight. This limiting energy is the lowest that can be obtained with a single determinant wavefunction (e.g., Equation 9.1.5). This limit is called the *Hartree-Fock limit*, the energy is the *Hartree-Fock energy*, the molecular orbitals producing this limit are called *Hartree-Fock orbitals*, and the determinant is the *Hartree-Fock wavefunction*.

Hartree-Fock Calculations

You may encounter the terms *restricted* and *unrestricted* Hartree-Fock. The above discussion pertains to a restricted HF calculation. In a restricted HF calculation, electrons with α spin are restricted or constrained to occupy the same spatial orbitals as electrons with β spin. This constraint is removed in an unrestricted calculation. For example, the spin orbital for electron 1 could be $\psi_A(r_1)\alpha(1)$, and the spin orbital for electron 2 in a molecule could be $\psi_B(r_2)\beta(2)$, where both the spatial molecular orbital and the spin function differ for the two electrons. Such spin orbitals are called *unrestricted*. If both electrons are constrained to have the same spatial orbital, e.g. $\psi_A(r_1)\alpha(1)$ and $\psi_A(r_2)\beta(2)$, then the spin orbital is said to be *restricted*. While unrestricted spin orbitals can provide a better description of the electrons, twice as many spatial orbitals are needed, so the demands of the calculation are much higher. Using unrestricted orbitals is particular beneficial when a molecule contains an odd number of electrons because there are more electrons in one spin state than in the other.

Example 11.1.1 : Carbon Monoxide

It is well known that carbon monoxide is a poison that acts by binding to the iron in hemoglobin and preventing oxygen from binding. As a result, oxygen is not transported by the blood to cells. Which end of carbon monoxide, carbon or oxygen, do you think binds to iron by donating electrons? We all know that oxygen is more electron-rich than carbon (8 vs 6 electrons) and more electronegative. A reasonable answer to this question therefore is *oxygen*, but experimentally it is carbon that binds to iron.

A quantum mechanical calculation done by Winifred M. Huo, published in J. Chem. Phys. 43, 624 (1965), provides an explanation for this counter-intuitive result. The basis set used in the calculation consisted of 10 functions: the ls, 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of C and O. Ten molecular orbitals (mo's) were defined as linear combinations of the ten atomic orbitals (Equation 9.1.6. The ground state wavefunction Ψ is written as the Slater Determinant of the five lowest energy molecular orbitals ψ_k. Equation 9.1.7 gives the energy of the ground state, where the denominator accounts for the normalization requirement. The coefficients C_{kj} in the linear combination are determined by the variational method to minimize the energy. The solution of this problem gives the following equations for the molecular orbitals. Only the largest terms have been retained here. These functions are listed and discussed in order of increasing energy.

- $1s \approx 0.941s_o$. The 1 says this is the first σ orbital. The σ says it is symmetric with respect to reflection in the plane of the molecule. The large coefficient, 0.94, means this is essentially the 1s atomic orbital of oxygen. The oxygen 1s orbital should have a lower energy than that of carbon because the positive charge on the oxygen nucleus is greater.
- $2s \approx 0.921s_c$. This orbital is essentially the 1s atomic orbital of carbon. Both the 1σ and 2σ are "nonbonding" orbitals since they are localized on a particular atom and do not directly determine the charge density between atoms.
- $3s \approx (0.722s_o + 0.182p_{zo}) + (0.282s_c + 0.162p_{zc})$. This orbital is a "bonding" molecular orbital because the electrons are delocalized over C and O in a way that enhances the charge density between the atoms. The 3 means this is the third σ orbital. This orbital also illustrates the concept of hybridization. One can say the 2s and 2p orbitals on each atom are hybridized and the molecular orbital is formed from these hybrids although the calculation just obtains the linear combination of the four orbitals directly without the *à priori* introduction of hybridization. In other words, hybridization just falls out of the calculation. The hybridization in this bonding LCAO increases the amplitude of the function in the region of space between the two atoms and decreases it in the region of space outside of the bonding region of the atoms.
- $4s \approx (0.372s_c + 0.12p_{zc}) + (0.542p_{zo} - 0.432s_0)$. This molecular orbital also can be thought of as being a hybrid formed from atomic orbitals. The hybridization of oxygen atomic orbitals, because of the negative coefficient with $2s_O$, decreases the electron density between the nuclei and enhances electron density on the side of oxygen facing away from the carbon atom. If we follow how this function varies along the internuclear axis, we see that near carbon the function is positive whereas near oxygen it is negative or possibly small and positive. This change means there must be a node between the two nuclei or at the oxygen nucleus. Because of the node, the electron density between the two nuclei is

low so the electrons in this orbital do not serve to shield the two positive nuclei from each other. This orbital therefore is called an “antibonding” molecular orbital and the electrons assigned to it are called antibonding electrons. This orbital is the antibonding partner to the 3σ orbital.

- $1\pi \approx 0.322p_{xc} + 0.442p_{xo} \text{and} 2\pi \approx 0.322p_{yc} + 0.442p_{yo}$. These two orbitals are degenerate and correspond to bonding orbitals made up from the p_x and p_y atomic orbitals from each atom. These orbitals are degenerate because the x and y directions are equivalent in this molecule. π tells us that these orbitals are antisymmetric with respect to reflection in a plane containing the nuclei.
- $5\sigma \approx 0.382_{sC} - 0.382_{pC} - 0.292p_{zO}$. This orbital is the sp hybrid of the carbon atomic orbitals. The negative coefficient for $2p_C$ puts the largest amplitude on the side of carbon away from oxygen. There is no node between the atoms. We conclude this is a nonbonding orbital with the nonbonding electrons on carbon. This is not a “bonding” orbital because the electron density between the nuclei is lowered by hybridization. It also is not an antibonding orbital because there is no node between the nuclei. When carbon monoxide binds to Fe in hemoglobin, the bond is made between the C and the Fe. This bond involves the donation of the 5σ nonbonding electrons on C to empty d orbitals on Fe. Thus molecular orbital theory allows us to understand why the C end of the molecule is involved in this electron donation when we might naively expect O to be more electron-rich and capable of donating electrons to iron.

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9.2: Gaussian Basis Sets

The problem is that STOs do not perform well with numerical integration methods: in most cases, numerical integrals involving these functions requires very large grid sizes and limits. To overcome this problem, computational chemists have developed *Gaussian-type orbitals* (GTOs), which can be numerically integrated in a much more efficient manner. Some integrals become solvable analytically, and other multidimensional integrals can be transformed into products of single-dimensional ones, dramatically reducing the computational cost for evaluating them.

Gaussian Type Orbitals (GTO)

Although any basis set that sufficiently spans the space of electron distribution could be used, the concept of Molecular Orbitals as **Linear Combinations of Atomic Orbitals** **(LCAO)** suggests a very natural set of basis functions: AO-type functions centered on each nuclei. One obvious choice are the exact hydrogen AO's, known as **Slater-type orbitals (STO)** -describing the radial component of the functions. However, the computation of the integrals is greatly simplified by using **Gaussian-type orbitals (GTO)** for basis functions.

While the STO basis set was an improvement over hydrogenic orbitals in terms of computational efficiency, representing the STOs with Gaussian functions produced further improvements that were needed to accurately describe molecules. The GTOs are most frequently expressed in Cartesian coordinates:

$$|\phi_{abc}^{GTO}(x,y,z;\alpha)\rangle = Ne^{-\alpha r^2}(x-x_0)^a(y-y_0)^b(z-z_0)^c, \tag{9.2.1}$$

where α is the shape term that can be optimized, x, y, and z are Cartesian coordinates for an electron in an orbital whose center is located at position (x_0, y_0, z_0), and a, b, and c are nonnegative integers that serve a similar function to the ℓ and m quantum numbers for selecting the shape of the orbital. An orbital with angular momentum ℓ is created by choosing $a+b+c=\ell$. For instance, a p_x orbital shape can be approximated by letting $a=1$, $b=0$, and $c=0$, and a d_{zz} orbital by $a=0$, $b=0$, and $c=2$. Once again N is a normalization constant, and $r=\sqrt{x^2+y^2+z^2}$.

Limitation: Overdetermined Basis

One significant point to note about Cartesian Gaussian functions is that when $\ell \geq 2$, there are more Cartesian functions than atomic orbitals with the same value of ℓ. As a simple example, when $\ell = 2$ (i.e., a d orbital), there are 5 spherical harmonic functions: those with $m = 2, 1, 0, -1$, and -2. However, there are 6 ways to make Cartesian Gaussian functions with $\ell = 2$: x^2, y^2, z^2, xy, yz, and xz. This means that if a set of Cartesian functions is used to represent d orbitals, the set of 6 functions is contaminated by a contribution from one or more orbitals of different ℓ (in this case, the linear combination of Cartesian Gaussians $d_{xx}+d_{yy}+d_{zz}$ is actually an s-type orbital with $\ell = 0$). In general, the number of Cartesian functions that can be formed for a given ℓ is $(\ell+1)(\ell+2)/2$, while the number of "spherical harmonic" Gaussian functions is $2\ell+1$. Nevertheless, it is possible to apply a mathematical transformation to the Cartesian Gaussian functions to extract combinations equivalent to the corresponding spherical-harmonic Gaussian functions, so for the purposes of this course, we will assume that this is always done. Therefore, we will assume that if a basis set includes a set of d functions, for instance, the number of functions in the set is 5, not 6.

The biggest limitation of GTOs is that they do not have quite the right shape close to the nucleus (near $r = 0$): the exponential term goes as $-\alpha r^2$ rather than $-\alpha r$. The "cusp" that is obtained by an exponential with an r^{-1} dependence is not well reproduced by an exponential function that goes as r^{-2}. (Figure $9.2.1$).

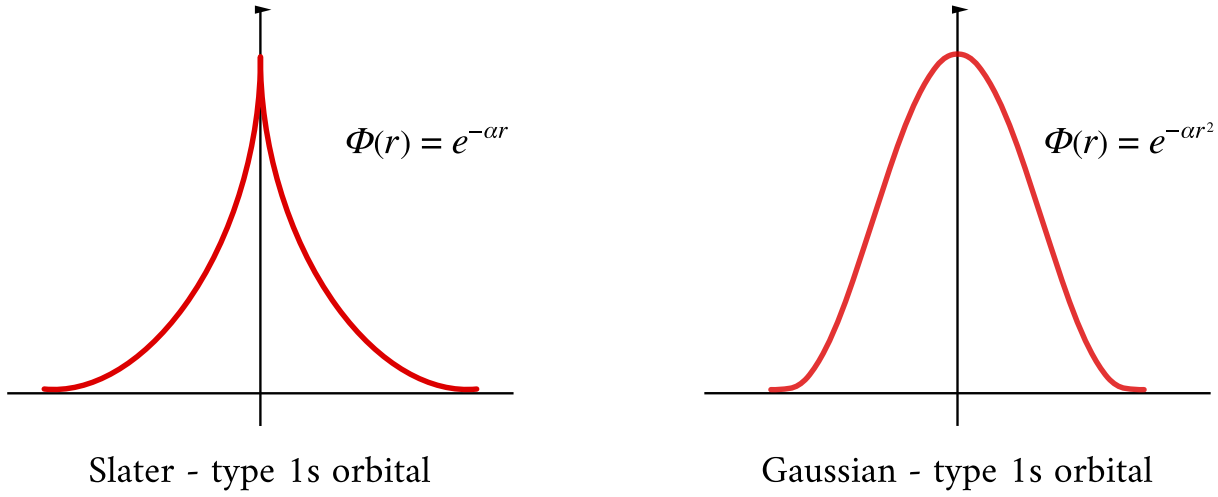


Figure 9.2.1: Radial Dependence of Slater and Gaussian Basis Functions. (CC BY 4.0; Ümit Kaya via LibreTexts)

Multiple Gaussian Representation

This can be partially overcome by using a linear combination of GTOs to approximate an STO; these are called “contracted” basis functions. One of the first of these basis sets to be developed was the \(STO-NG\) family, in which a single STO is expressed as a contracted function involving N GTOs (see Figure 9.2.2):

$$|\psi_i^{\text{STO-NG}}\rangle = \sum_n^N d_{in}|\phi^{GTO}(\alpha_{in})\rangle \tag{9.2.2}$$

where i is the type of STO being approximated (eg $1s$), d_{in} are the optimized expansion coefficients for each GTO in the linear combination for orbital i, and α_{in} are the optimized α terms for each GTO. The d and α terms are varied to maximize overlap with the corresponding STO; tabulations of these are available, though they’re not difficult to calculate. When these STO-NG basis functions are used in a molecular calculation, the d and α coefficients are not adjusted any further; once those constants are set, the entire linear combination $|\psi_i^{\text{STO-NG}}\rangle$ acts like a single STO atomic orbital.

The linear combination in Equation 9.2.2 is not optimized in the energy variational calculation, but rather is frozen and treated as a single function. The linear combination of **primitive Gaussian functions** is called a **contracted Gaussian function**.

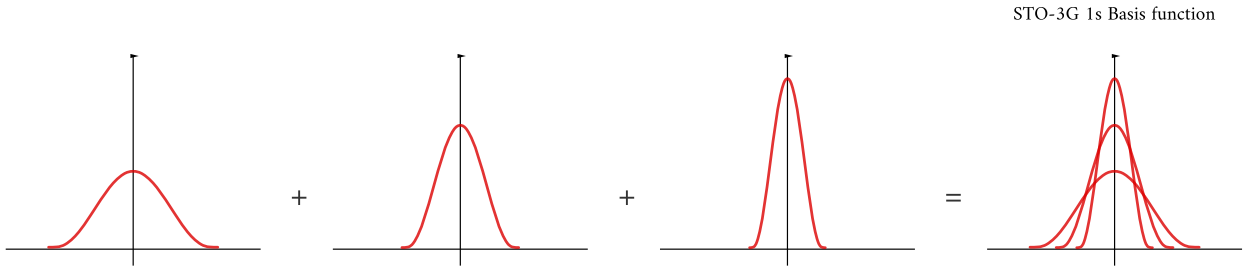


Figure 9.2.2: To better represent the cusp in the electron density at the nuclei, GTO basis sets are constructed from fixed linear-combinations of Gaussian functions, contracted GTOs (CGTO). The earliest CGTO basis sets, where constructed from N GTOs that best fit the desired STO. These are called STO-NG basis sets. (CC BY 4.0; Ümit Kaya via LibreTexts)

Although multiple GTOs are required to approximate a single STO, electronic structure calculations involving GTOs are much faster than with STOs. All overlap integrals can be evaluated analytically, and for most other types of integrals (Coulomb and exchange integrals, both one-electron and two-electron), the full 3D or 6D integral can be split into a product of 3 or 6 one-dimensional integrals. For a 6D integral with 100 grid points, an STO may require 100^6 function evaluations, while the same

integral over a single GTO may require only 600. Moreover, there are several clever quadrature strategies for integrals involving products of Gaussians which reduce the number of quadrature points required for accurate evaluation. Thus, despite the need for using a combination of several GTOs to create an orbital function of comparable quality to a single STO, a calculation involving GTOs can achieve the same accuracy as one involving STOs in a much shorter time.

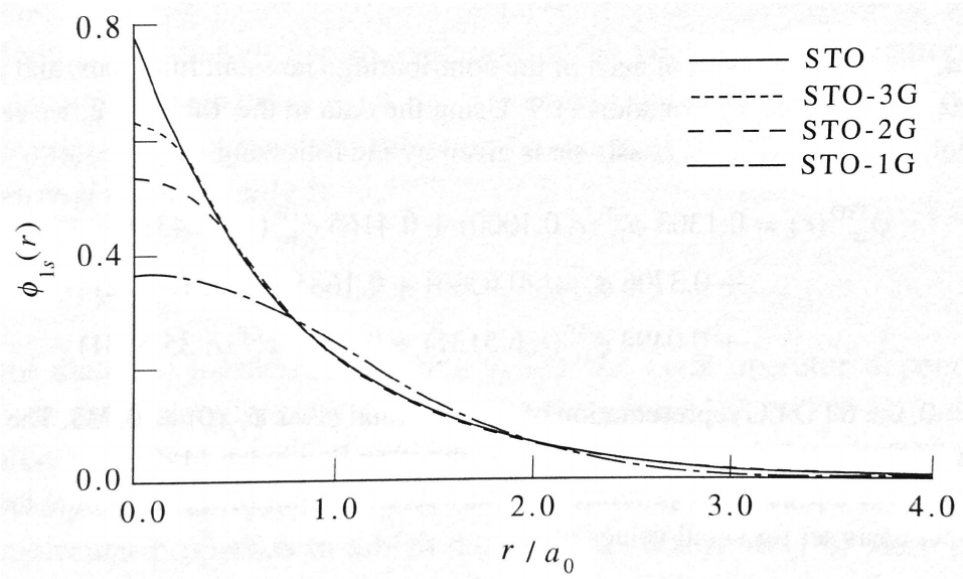


Figure $9.2.3$: STO-NG basis functions for the $1s$ STO.

For this reason, almost all modern electronic structure calculations are performed using basis sets built from combinations of GTOs. Basis set development is undertaken by a variety of theoretical chemists in an effort to make calculations of certain types of molecules or molecular properties more efficient; these groups perform tedious optimizations of various parameters (α, N, d , etc.) for each orbital representing each atom in order to reproduce experimentally measured quantities or quantities calculated at very high levels of theory. The results of these benchmarks are published, and the optimized coefficients are made available to standard quantum chemical packages. One of the main sources for obtaining and learning about basis sets is the Basis Set Exchange website (https://bse.pnl.gov); most basis sets used in the chemical literature have been deposited there.

Basis Notation

Many types of basis sets exist, and their designations (e.g., 6-311++G**, aug-cc-pCV5Z, etc.) can look like alphabet soup to the uninitiated. Nevertheless, with many electronic structure packages, choosing a basis set is often as simple as typing in its name; most common basis sets are pre-loaded into these programs, and if you require a basis set that is not already there, the Basis Set Exchange website has many available in a variety of input formats. Because of the ease of choosing a basis set, it can be tempting to overlook the details, but knowledge of what kinds of functions are included in different classes of basis sets, as well as which basis sets are optimal for what types of molecular problems, can save a lot of time. Here we will introduce a couple of commonly used classes of basis functions, along with some of the terminology used to describe them.

Gaussian basis sets are identified by abbreviations such as N-MPG*. N is the number of Gaussian primitives used for each inner-shell orbital. The hyphen indicates a split-basis set where the valence orbitals are double zeta. The M indicates the number of primitives that form the large zeta function (for the inner valence region), and P indicates the number that form the small zeta function (for the outer valence region). G identifies the set a being Gaussian. The addition of an asterisk to this notation means that a single set of Gaussian 3d polarization functions (discussed elsewhere) is included. A double asterisk means that a single set of Gaussian 2p functions is included for each hydrogen atom.

For example, 3G means each STO is represented by a linear combination of three primitive Gaussian functions. 6-31G means each inner shell (1s orbital) STO is a linear combination of 6 primitives and each valence shell STO is split into an inner and outer part (double zeta) using 3 and 1 primitive Gaussians, respectively (see Table $9.2.1$ for other examples).

Table 9.2.1: Different Gaussian Basis sets

Basis set	# functions		Basis set	# functions		Basis set	# functions
STO-3G	5		6-31G	9		6-311G	13
3-21G	9		6-31G*	15		6-311G*	18*
4-31G	9		6-31+G*	19		6-311+G*	22*

Example 11.2.2

The 1s Slater-type orbital $S_1(r) = \sqrt{4\zeta_1 e^{-\zeta_1 r}}$ with $\zeta_1 = 1.24$ is represented as a sum of three primitive Gaussian functions,

$$S_G(r) = \sum_{j=1}^{3} C_j e^{-\alpha_j r^2}$$

This sum is the contracted Gaussian function for the STO.

a. Make plots of the STO and the contracted Gaussian function on the same graph so they can be compared easily. All distances should be in units of the Bohr radius. Use the following values for the coefficients, C, and the exponential parameters, α.

index j	α_j	C_j
1	0.1688	0.4
2	0.6239	0.7
3	3.425	1.3

b. Change the values of the coefficients and exponential parameters to see if a better fit can be obtained.
c. Comment on the ability of a linear combination of Gaussian functions to accurately describe a STO.

Summary

STOs are computationally difficult and it was later realized by Frank Boys that these Slater-type orbitals could in turn be approximated as linear combinations of Gaussian orbitals instead. Because it is easier to calculate overlap and other integrals with Gaussian basis functions, this led to huge computational savings

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9.3: Extended Basis Sets

Minimal Basis

It is useful to begin a study of basis sets by thinking of the smallest possible number of orbitals required to calculate the electronic structure of a molecule. From chemical intuition, it seems reasonable that since molecules are made from atoms, we should at least include all occupied orbitals from the constituent atoms in the basis set, and it is probably also good to include all the orbitals in partially-filled shells. For example, the electron configuration for hydrogen is $1s^1$, so the minimal basis for a molecule would involve a $1s$ orbital from each hydrogen atom. Carbon's electron configuration is $1s^2 2s^2 2p^2$, so each carbon atom in a molecule would contribute $1s$, $2s$, and three $2p$ orbitals (even though only two of the three are occupied, it makes most sense to include the entire $2p$ shell since those orbitals are degenerate in carbon). As another example, sulfur's electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^4$, so each sulfur atom would contribute three s-type orbitals ($1s$, $2s$, and $3s$) and six p-type orbitals (the three $2p$ orbitals and the three $3p$ ones). Finally, it is conventional to include the p shell for all alkali and alkaline earth metals, even though those orbitals are not occupied in the atom. Leaving out the p orbitals for these metals tends to yield exceptionally poor results.

The simplest way to construct a minimal basis set would be to use a single Slater-type orbital to represent each orbital in the minimal basis. Because each atom has different orbital shapes (i.e., the $2p$ orbitals of a carbon atom are different than those of an oxygen atom), the STO for each atom's orbital will have its own value of ζ associated with it. Some examples of values of ζ are shown in Table $9.3.1$. As can be seen in the table, the value of ζ tends to increase with atomic number as the larger nuclear charge of the atom holds the electrons closer to the nucleus. Using such a minimal basis of Slater-type orbitals, the wavefunction is expressed as:

$$|\psi\rangle = \sum_i c_i |\phi_{\mathrm{STO}}(\zeta_i)\rangle,$$

where $|\phi_{\mathrm{STO}}(\zeta_i)\rangle$ is the STO corresponding to orbital i. The total number and type of orbitals in the basis depends on which atoms make up the molecule.

Table $9.3.1$: ζ values for selected atoms and orbitals, from McQuarrie.

Atom	ζ_{1s}	$\zeta_{2s} = \zeta_{2p}$
H	1.24	...
He	1.69	...
Li	2.69	0.80
C	5.67	1.72
F	8.56	2.55

Multiple Gaussian Representation

Because of the difficulties with performing efficient numerical integration of STOs, it is extremely rare for these to be used, even as a minimal basis. The simplest minimal basis set encountered is the aforementioned STO-NG family, in which each Slater-type orbital is built from a linear combination of GTOs. As we go forward, it will important to be very clear with the terminology used to discuss the "orbitals." At this point, we introduce the concept of an *orbital function*: this is a mathematical function that is analogous to an atomic orbital in an LCAO-MO calculation. The dimensionality of the Hamiltonian matrix depends on the number of orbital functions, and the solutions to the electronic Schrödinger equation are linear combinations of these orbital functions. However, each orbital function may itself be built up from multiple simpler functions. In the present case, a single STO-NG orbital function is built from a linear combination of *Gaussian primitives*: the individual GTOs with their own values of d and α. When the Hamiltonian is being solved, the d and α values of the Gaussian primitives remain fixed; only the weights of the orbital functions themselves are adjusted.

As a simple example, let us use the STO-3G basis to represent the orbitals in $\mathrm{H_2}$. Instead of a linear combination of atomic orbitals $|\psi\rangle = c_1|1s_A\rangle + c_2|1s_B\rangle$, the electronic wavefunction is given by the linear combination:

$$|\psi\rangle = c_1|\phi_{\text{STO-3G},A}\rangle + c_2|\phi_{\text{STO-3G},B}\rangle$$

$$|\phi_{\text{STO-3G},A}\rangle = 0.15432897e^{-3.42525091(r-r_A)^2} + 0.53532814e^{-0.62391373(r-r_A)^2} + 0.44463545e^{-0.16885540(r-r_A)^2}$$

$$|\phi_{\text{STO-3G},A}\rangle = 0.15432897e^{-3.42525091(r-r_B)^2} + 0.53532814e^{-0.62391373(r-r_B)^2} + 0.44463545e^{-0.16885540(r-r_B)^2}.$$

The STO-3G basis set is still a minimal basis set because, as we can see in this example, only one orbital function is used to represent the $|1s\rangle$ orbital of the hydrogen atom. The fact that each orbital function is built from three Gaussian primitives does not increase the size of the Hamiltonian matrix; the three primitive functions are used to approximate a single STO with a certain value of ζ.

When a single orbital function is represented by multiple Gaussian primitives, that orbital function is called a **contraction**. Contractions are represented using a notation that tells how many primitives are contracted into how many orbital functions. It is easiest to see this by example. Consider a carbon atom in an STO-3G basis. As a minimal basis, the STO-3G basis includes carbon's $1s$, $2s$, and three $2p$ orbitals, and each is represented by three Gaussian primitives. The contraction is denoted $(6s3p) \rightarrow [2s1p]$. The numbers and orbital types in parentheses tell the number of Gaussian primitives that contribute to each type of orbital (s, p, d, etc.), and the numbers in square brackets tell how many "shells" of orbital functions of each type those primitives are contracted into. In this example, 6 s-type GTOs are contracted into 2 s-type orbital functions, and three p-type primitives are contracted into a single p-type orbital function shell (but there are still 3 p-type orbital functions in that shell). By examining the numbers in square brackets, we can quickly see the total number of orbital functions is 5 (2×1) s-type and (1×3) p-type. Contractions come in two types: *segmented contractions*, in which each Gaussian primitive appears only in a single orbital function, and *general contractions*, where a given Gaussian primitive may appear in more than one orbital function to save memory. We will revisit the contraction concept in Section 1.5.3.2.

A minimal basis is a specific case of a more general category: *Single zeta* basis sets. In a single zeta basis set, each atomic orbital is represented by a single orbital function (i.e., one value of ζ for an STO, or one linear combination of GTOs that approximate an STO with that value of ζ). All minimal basis sets are single zeta, but not all single zeta basis sets are necessarily minimal. For example, we could choose to also include the $2s$ and $2p$ orbitals for hydrogen atoms, each represented by a single orbital function. The resultant basis set would still be single zeta, though not minimal. Nevertheless, it is rare to encounter a single zeta basis that is not also a minimal basis because there are more efficient ways to improve the quality of a basis set.

Multiple Zeta Basis sets

Over the course of basis set development, researchers realized that minimal basis sets could be improved in a number of ways. As with the discussion of the STOs, one improvement to the minimal basis sets was the development of *multiple zeta* basis sets (e.g., double zeta (DZ), triple zeta (TZ), etc.). For instance, in a double zeta basis, instead of using a single orbital function to represent the $1s$ orbital, two STOs with different values of ζ would be added to the basis to represent that single atomic orbital (Figure 9.3.2).

In an STO-3G-DZ basis for H_2, the electronic wavefunction would be:

$$|\psi\rangle = c_1|\phi_{\text{STO-3G},A}(\zeta_1)\rangle + c_2|\phi_{\text{STO-3G},A}(\zeta_2)\rangle + c_3|\phi_{\text{STO-3G},B}(\zeta_1)\rangle + c_4|\phi_{\text{STO-3G},B}(\zeta_2)\rangle,$$

where each $|\phi_{\text{STO-3G}}\rangle$ function (on atom A or B) is a fixed linear combination of three Gaussian primitives. Because two different ζ values are used to represent each $1s$ orbital, the $1s$ orbital can take on different radial shapes (i.e., become more diffuse or more compact) as their relative weights change. The basis set gains additional *flexibility* as the wavefunction amplitude around each nucleus can take on a greater variety of shapes compared with a single zeta basis. Flexibility confers a superior ability for the basis set to reproduce the shapes of the molecular wavefunction. As an example, it is easy to imagine that if a hydrogen atom is bonded to an electronegative atom like fluorine, the electron density around the hydrogen atom in will be quite different than that around each nucleus in H_2. The double zeta basis is more flexible in that it can alter the shape of the $1s$ orbital around the hydrogen atom in a way that the single zeta basis cannot.

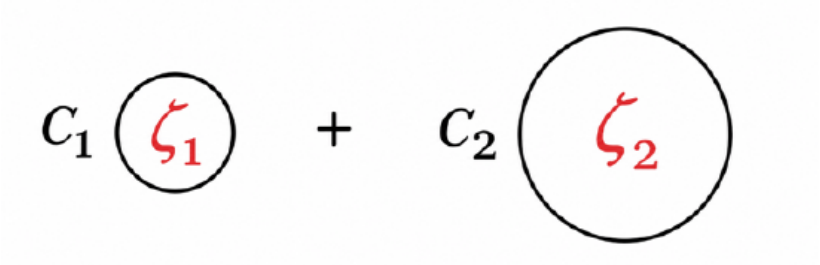


Figure 9.3.1: A "double zeta" basis set with each Atomic Orbital is represented by 2 orbital functions with different ζ values.

However, the increased flexibility comes at a cost: a double zeta basis contains twice as many orbital functions as a single zeta basis. If a molecule has N orbital functions in a single basis, its Hamiltonian is an $N \times N$ matrix. To represent the same molecule in a double zeta basis requires $2N$ orbital functions, so the Hamiltonian becomes a $2N \times 2N$ matrix– even accounting for the Hermiticity of the Hamiltonian, there will be about 3–4 times more matrix elements to evaluate! Because of this steep computational penalty, true multiple-zeta basis sets are not used often for reasons that will soon be apparent.

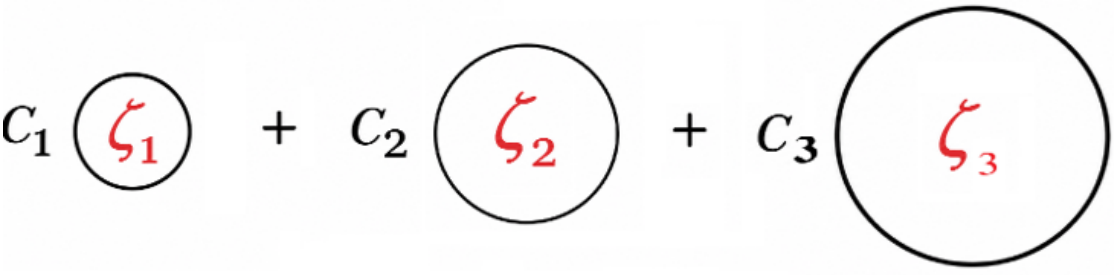


Figure 9.3.2: A "triple zeta" basis with each Atomic Orbital is represented by 3 orbital functions with different ζ values.

In a multiple zeta basis set, the individual orbital functions begin **lose their original meaning as atomic orbitals**. This presents a challenge: how is it possible to optimize the weights and exponents of the Gaussian primitives? In the single zeta basis, this was straightforward: an atomic structure calculation could be performed with STO functions to optimize the value of ζ, and then the coefficients in the Gaussian primitives could be adjusted to optimize the overlap of the contracted orbital functions with the corresponding STO. With a multiple zeta basis set, this is no longer possible. Instead, atomic structure calculations are performed directly with GTO contractions, and the GTO parameters optimized directly in an effort to minimize the atomic orbital energies. This is a highly nonlinear multivariate optimization problem, and requires an extensive, careful exploration of parameter space, so development of multiple-zeta basis sets is challenging, and still an active area of research today.

Split-valence basis sets

Chemical intuition tells us a large portion of molecular structure and reactivity involves only the valence electrons in a molecule. Electrons in atomic “core” orbitals tend to remain close to the nucleus and participate very little in bonding interactions; they effectively just screen a portion of the nuclear charge from electrons in the outer valence shells, allowing those valence electrons to more easily move around. This suggests that core orbitals in a molecule require little flexibility, and this realization led to the development of *split-valence* basis sets: in which a single orbital function is used to represent a core atomic orbital, and multiple orbital functions are used to represent valence atomic orbitals. In other words, each atom has a single zeta representation of its core orbitals, and a multiple zeta representation of its valence orbitals. By using a split-valence basis, additional flexibility is gained in the regions where the electron density is likely to be distorted away from the nucleus through interactions with other atoms, while the cost of the calculation is kept lower than a true multiple-zeta basis set by sacrificing flexibility near the atomic centers. It is common for modern electronic structure calculations to employ split-valence basis sets. Here, we will explore two of the more frequently used general purpose families of split-valence basis sets: the Pople basis sets and Dunning’s correlation consistent basis sets.

John Pople was the co-recipient of the 1998 Nobel Prize in chemistry for “for his development of computational methods in quantum chemistry.” This was due in part to his work developing split-valence basis sets, and in part to his work developing the *Gaussian* quantum chemical software package. Pople’s split valence basis sets can be recognized by their designation of the form X-YG, where X is usually a one-digit number and Y is a two or three digit number. X indicates the number of Gaussian primitives that are contracted into a single orbital function to describe core orbitals. The number of digits in Y indicates the number of

orbital functions per valence orbital, and each digit in Y denotes how many Gaussian primitives are in each. For example, the basis set 3-21G uses a contraction of 3 GTOs to represent each core orbital, and two orbital functions to represent each valence orbital. Of these two, the first one (made of 2 primitives) corresponds to a larger effective value of ζ (i.e., a narrower function), while the second (made of 1 primitive) is more diffuse. Once the third row of the periodic table is reached, it becomes common for the contractions to be general rather than segmented, so in the larger basis sets the total number of Gaussian primitives may be less than the number suggested by a straightforward count of core and valence orbitals. The exponents and coefficients of the primitives for most Pople-style basis sets are optimized using HF/SCF calculations of the respective atoms. More examples are shown in Table $9.3.2$.

Table $9.3.2$: Summary of contractions, number of orbital functions (OF), and number of Gaussian primitives (GTO) for selected Pople-style split valence basis sets.

(l)2-4 (l)5-7 (l)8-10 Atoms	Contraction	OF	GTO	Contraction	OF	GTO	Contraction	OF	GTO
H–He	$(3s)\rightarrow[2s]$	2	3	$(4s)\rightarrow[2s]$	2	4	$(5s)\rightarrow[3s]$	3	5
Li–Ne	$(6s3p)\rightarrow[3s2p]$	9	15	$(10s4p)\rightarrow[3s2p]$	9	22	$(11s5p)\rightarrow[4s3p]$	13	26
Na–Ar	$(9s6p)\rightarrow[4s3p]$	13	27	$(16s10p)\rightarrow[4s3p]$	13	46	$(17s11p)\rightarrow[5s4p]$	17	50

Extended Basis Set Notation

The notation of this sort of basis set (with a Gaussian basis) is

$$N-MPG$$

for describing split-valence basis set. N is the number of Gaussian functions describing inner-shell orbitals, while the hyphen denotes a split-valence set. M and P designate the number of Gaussian functions used to fit the two orbitals of the valence shell:

- M corresponds to number of Gaussian functions used to describe the smaller orbital
- P corresponds to number of Gaussian functions used to describe the larger orbital (e.g., 6-31G and 3-21G).

There are hundreds of basis sets composed of Gaussian-type orbitals (Table $9.3.3$). The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The largest of these can contain dozens to hundreds of basis functions on each atom.

Table $9.3.3$: Commonly used split-valence basis sets

3-21G	3-21G	3-21G	3-21G* - Polarized	3-21+G - Diffuse functions	3-21+G* - With polarization and diffuse functions
4-21G	4-31G	4-31G	4-31G	4-31G	
6-21G	6-31G	6-31G*	6-31+G*	6-31G(3df, 3pd)	6-311G
6-311G	6-311G*	6-311+G*			

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9.4: Orbital Polarization Terms in Basis Sets

Polarization Functions

As it turns out, even the additional flexibility afforded by split-valence basis sets is not quite enough to provide a good, efficient description of chemical bonding for most atoms. This is because the electron density in a molecule is more anisotropic around each atom than the electron density in a bare atom. This is an important result when considering accurate representations of bonding between atoms, because the very presence of the bonded atom makes the energetic environment of the electrons spherically asymmetric. In order to better account for the shapes of molecular orbitals, is is almost mandatory to supplement the split-valence basis sets with additional *polarization functions*: orbital functions with greater ℓ values than the valence orbitals of the atom.

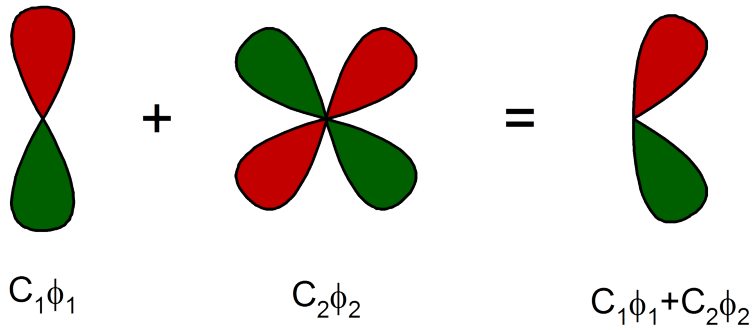


Figure 9.4.1: A d-polarization function added to a p orbital. (CC-BY-SA-3.0; Rifleman 82)

Similarly, d-type functions can be added to a basis set with valence p orbitals, and f-functions to a basis set with d-type orbitals, and so on.

Notation

In the Pople basis sets, polarization functions are indicated with "stars": for instance, 6-31G* or 6-311G**. A single star indicates that $\ell + 1$ functions are added to all second-row and higher atoms (e.g., carbon gets a set of d orbitals), and a double star indicates that hydrogen and helium also receive p functions. The polarization functions are each built just from a single Gaussian primitive. Most Pople style basis sets with polarization functions are optimized through HF/SCF calculations; however, the 6-311G** basis set was optimized by second order Møller Plesset perturbation theory (MP2) calculations, which partially account for dynamic electron correlation. A summary of some common Pople-style basis sets with polarization functions is shown in Table 9.4.1. For more on these basis sets, see R. Krishnan et al., *J. Chem. Phys.* (1980), 72, 650 and the other papers in that series.

Table 9.4.1: Summary of contractions, number of orbital functions (OF), and number of Gaussian primitives (GTO) for selected Pople-style split valence basis sets with polarization functions.

(l)2-4 (l)5-7 Atoms	Contraction	OF	GTO	Contraction	OF	GTO
H–He	$(4s)\rightarrow[2s]$	2	4	$(5s1p)\rightarrow[3s1p]$	4	6
Li–Ne	$(10s5p1d)\rightarrow[3s2p1d]$	14	30	$(11s5p1d)\rightarrow[4s3p1d]$	18	31
Na–Ar	$(16s10p1d)\rightarrow[4s3p1d]$	18	51	$(13s9p1d)\rightarrow[5s4p1d]^{\dagger}$	22	45

Diffuse Functions

Accurately describing negatively charged species presents a particular challenge. For example, anions tend to have very diffuse electron distributions and very large basis functions (with very small exponents) are often needed for accurate results. The additional electrons associated with anions often occupy spatially extended regions, causing the electron density to spread much farther from the nuclei than in neutral or positively charged species. Similar issues apply to radicals, van der Waals or hydrogen-

bonded complexes, electronically excited states and others. Conventional split-valence basis sets generally lack the flexibility needed to represent these diffuse electron distributions adequately, potentially limiting the accuracy of the calculated electronic structure and properties.

To address this, basis sets are often supplemented with additional **diffuse functions**. Diffuse functions supplement a basis set in a similar manner to polarization functions by adding extra $n+1$ orbital functions.

Notation

The presence of diffuse functions in a Pople basis set is denoted with a $+$ symbol, such as 6-31+G. A single plus indicates that one extra $n+1$ function, built from a single Gaussian primitive, is added for each orbital in the valence shell for all atoms except H and He. Two plus symbols (e.g., 6-311++G) indicate that H and He also receive $n+1$ functions. To illustrate this, in a 6-311++G basis set, a hydrogen atom's $1s$ (valence) orbital is represented by 3 orbital functions (built from 3, 1, and 1 GTOs, respectively), and an extra orbital function consisting of just one Gaussian primitive is added to represent the $2s$ orbital. The contraction, therefore, is $(6s)\rightarrow[4s]$. A carbon atom in the same basis set receives diffuse functions to represent the $3s$ and three $3p$ orbitals. The coefficients of the Gaussian primitives in basis sets with diffuse functions are optimized by calculations of either atomic excited states or atomic anions. Diffuse and polarization functions are very often combined to effectively include the next shell after the valence shell; such basis sets are essential for calculating accurate properties of loosely-bound species. Additional examples are given in Table $9.4.2$.

Table $9.4.2$: Summary of contractions, number of orbital functions (OF), and number of Gaussian primitives (GTO) for selected Pople-style split valence basis sets with diffuse and polarization functions.

(l)2-4 (l)5-7 Atoms	Contraction	OF	GTO	Contraction	OF	GTO
H–He	$(6s)\rightarrow[4s]$	4	6	$(6s1p)\rightarrow[4s1p]$	7	9
Li–Ne	$(12s6p)\rightarrow[5s4p]$	17	30	$(12s6p1d)\rightarrow[5s4p1d]$	18	31
Na–Ar	$(14s10p)\rightarrow[6s5p]^{\dagger}$	21	44	$(14s10p1d)\rightarrow[7s6p1d]^{\dagger}$	26	49

In the end, the accuracy of a calculation depends on the basis set chosen, and there are tradeoffs to be made. For the best answer, the basis set must be flexible enough to fit the shape of the "true" wavefunction, which can be accomplished by adding additional functions with different shape parameters or polarization properties to the set. The more functions that are added, though, the more time is required to complete the calculation. The farther down the periodic table the atoms are, the more functions need to be included in the basis, and the more difficult the calculations will be. In fact, for many 4th-row and higher atoms, it is common to use basis sets that include *effective core potentials*: mathematical functions that represent a classical potential that is added to the Hamiltonian in place of many of the core electrons. These basis sets reduce considerably the numbers of integrals that need to be calculated, and can make calculations of very heavy atoms with many electrons tractable. However, there are limitations, particularly for molecular properties that are sensitive to the electronic wavefunction near the nucleus (e.g., X-ray spectroscopy, NMR shielding coefficients).

Summary

For atoms whose ground-state electronic configurations include occupied s and p orbitals, a common approach is to introduce a set of d-type **polarization functions** that allow the electron density to deform beyond the shapes described by the original s- and p-type functions, providing a more flexible description of the electronic distribution during chemical bonding.

The addition of **diffuse functions** improve the representation of electron density that extends far from the atomic nuclei. They are typically added as an extra set of uncontracted Gaussian functions with the same angular momentum types as the valence orbitals. These are very shallow Gaussian basis functions, which more accurately represent the "tail" portion of the atomic orbitals, which are distant from the atomic nuclei. These additional basis functions can be important when considering anions and other large, "soft" molecular systems.

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9.E: Computational Quantum Chemistry (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook
Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 11 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

What is meant by the expression ab initio calculation?
List all the terms in a complete molecular Hamiltonian.
Why are calculations on closed-shell systems more easily done than on open-shell systems?
How is it possible to reduce a multi-electron Hamiltonian operator to a single-electron Fock operator?
Why is the calculation with the Fock operator called a self-consistent field calculation?
What is the physical meaning of a SCF one-electron energy?
Why is the nonlinear variational method not used in every case to optimize basis functions, and what usually is done instead?
Why is it faster for a computer to use the variational principle to determine the coefficients in a linear combination of functions than to determine the parameters in the functions?
Identify the characteristics of hydrogenic, Slater, and Gaussian basis sets.
What is meant by the Hartree-Fock wavefunction and energy?
What is neglected that makes the Hartree-Fock energy necessarily greater than the exact energy?
What is meant by correlation energy?
What purpose is served by including configuration interaction in a calculation?

Q11.1

Prove that a three dimensional Gaussian function centered at r_1 = x_1i + y_1j + z_1k is a product of three one-dimensional Gaussian functions centered on x_1, y_1, z_1.

S11.1

$$e^{-a(r-r_0)^2} = e^{-a[(x-x_1)i+(y-y_1)j+(z-z_1)k]^2}$$

$$= e^{-a[(x-x_1)^2+(y-y_1)^2+(z-z_1)^2]}$$
$$= e^{-a(x-x_1)^2}\ e^{-a(y-y_1)^2}\ e^{-a(z-z_1)^2}$$

Q11.2

Show that

$$\int_0^\infty e^{-(x-x_0)^2}dx = \int_0^\infty e^{-x^2}dx = \frac{1}{2}\int_{-\infty}^\infty e^{-x^2}dx = \sqrt{\pi} \tag{9.E.1}$$

S11.2

The equalities are all equivalent since in the first integral x_0 is a constant and the second and third are even.

Q11.3

The Gaussian Integral

$$I_0 = \int_{-\infty}^\infty e^{-4x^2}dx \tag{9.E.2}$$

Convert the integration variables from Cartesian coordinates to polar coordinates and show that

$$I_0 = \frac{\sqrt{\pi}}{2} \tag{9.E.3}$$

S11.3

We first write

$$I_0^2 = \left(\int_{-\infty}^{\infty} e^{-4x^2} dx\right)^2 = \int_{-\infty}^{\infty} e^{-4x^2} dx \int_{-\infty}^{\infty} e^{-4y^2} dy \tag{9.E.4}$$

the product of two integrals can be expressed as a double integral

$$I_0^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-4(x^2+y^2)} dxdy \tag{9.E.5}$$

In polar coordinates $x^2 + y^2 = r^2$ and $dxdy = rdrd\theta$. The limits of integration in polar coordinates corresponding to the limits in Cartesian coordinates are $0 \leq r < \infty$ and $0 \leq \theta \leq 2\pi$.

The double integral becomes

$$I_0^2 = \int_0^{\infty} \int_0^{2\pi} e^{-4r^2} rdrd\theta = 2\pi \int_0^{\infty} e^{-4r^2} rdr. \tag{9.E.6}$$

The integration over θ gives a factor of 2π.The integral over r can be done using a **U substitution**, $u = 4r^2$ and $du = 8rdr$.

Therefore

$$\int_0^{\infty} e^{-4r^2} rdr = \frac{1}{8} \int_0^{\infty} e^{-u^2} du = \frac{1}{8} \tag{9.E.7}$$

meaning that $I^2 = 2\pi \times \frac{1}{8}$, so $I_0 = \frac{\sqrt{\pi}}{2}$.

Q11.4

Show that the integral

$$I_{2n} = \int_{-\infty}^{\infty} x^{2n} e^{-ax^2} dx$$

can be obtained from I_o

$$I_o = \int_{-\infty}^{\infty} e^{-ax^2} dx$$

by differentiating n times with respect to a when I_o is

$$I_0 = \tfrac{1}{2}\left(\tfrac{\pi}{a}\right)^{\frac{1}{2}}$$

gives in a general form:

$$I_{2n} = \tfrac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n}\left(\tfrac{a}{2}\right)^{\frac{1}{2}}$$

S11.4

The first step is to take the derivative of I_o about 3 times with respect to a:

$$I_o = \int_{-\infty}^{\infty} e^{-ax^2} dx$$

$$\frac{dI_o}{da} = \int_{-\infty}^{\infty} -x^2 e^{-ax^2} dx = -\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx$$

$$\frac{d^2 I_o}{da^2} = \int_{-\infty}^{\infty} -x^{2\cdot 2} e^{-ax^2} dx = \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx$$

solve the integrals for the first I_{2n} starting with I_o,

$$I_o = \int_{-\infty}^{\infty} e^{-ax^2} dx = \frac{1}{2}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

$$I_2 = \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{dI_o}{da} = \frac{1}{4a}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

$$I_4 = \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx = \frac{d^2 I_o}{da^2} = -\frac{dI_2}{da} = \frac{3}{8a}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

$$I_6 = \int_{-\infty}^{\infty} x^6 e^{-ax^2} dx = -\frac{d^3 I_o}{da^3} = -\frac{dI_4}{da} = \frac{3\cdot 5}{16a}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

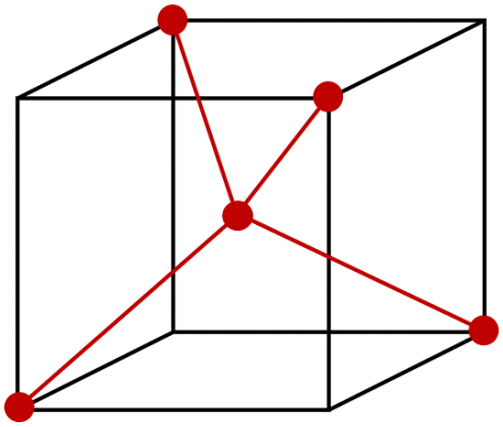
in general

$$I_{2n} = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\left(\frac{a}{2}\right)^{\frac{1}{2}}$$

(note: if you look at the equations sheet provided in the Gaussian integrals sections the limits of integration from -∞ to +∞ and from 0 to +∞ give the same end result with a minor difference in the exponent for the two in the denominator)

Q11.17

Using the Figure below, specify the coordinates of the atoms that comprise the molecule methane. Determine a set of Cartesian coordinates of the atoms in the molecule. The HCH bond angle is 110.0° and the C-H bond length is 109.1 pm.



S11.17

This figure can represent methane if and only if the central atom is carbon and the 4 atoms at the vertices are hydrogen atoms. We then must assign the origin of our coordinate system to be at the carbon atom. Considering the length of the edge of this cube is 2a, then the bond length from the vertices (hydrogen atoms) to the center (carbon atom) is $\sqrt{3}$ times the length of one edge of the cube, so

$$\frac{109.1\ pm}{\sqrt{3}} = 63\ pm = a \tag{9.E.8}$$

Diagonal of cube length 2a would be $2a\sqrt{(3)}$ - but we need half that.

Q11.18

Determine a rough set of Cartesian coordinates of the atoms in the molecule SiH_3F given the bond angle of $H-Si-H$ is 109.5° and the $Si-H$ and $Si-F$ bond lengths are 146.0 and $159.5\ pm$, respectively. (Hint: locate the origin at the Silicon.)

S11.18

For a simpler case of SiH_4, The four hydrogen would be equally far from the central atom (origin). The coordinates can be calculated as (a,a,a) ,$(-a,-a,a)$,$(a,-a,-a)$, and $(-a,-a,-a)$. The value of a can be determined by $a=\frac{l}{\sqrt{3}}$ where l is the bond length. For hydrogen:

$$a=\frac{146\,pm}{\sqrt{3}}=84.29\,pm \tag{9.E.9}$$

For florine:

$$a=\frac{159.5\,pm}{\sqrt{3}}=92.09\,pm \tag{9.E.10}$$

One set of solutions is:

	x/pm	y/pm	z/pm
C	0	0	0
H	84.29	84.29	84.29
H	-84.29	-84.29	84.29
H	84.29	-84.29	-84.29
F	-92.09	-92.09	-92.09

Q11.19

Molecule	Frequency [cm^{-1}]	R_e [pm]
H_2	4647	73.2
CO	2438	111.4
HCl	2886	130

Given the above table of calculated vibrational frequencies and bond lengths, calculate the vibrational force constant of each of the molecules. Do you expect that the calculated values are higher or lower than the experimental values? Are bond length calculations or vibrational-frequency calculations more accurate? Why?

S11.19

The relationship between wave number and harmonic force constant can be expressed as

$$\tilde{\nu}=(2c\pi)^{-1}\sqrt{\frac{k}{\mu}} \tag{9.E.11}$$

which can be rewritten as

$$k = 4\mu(\tilde{\nu}c\pi)^2. \tag{9.E.12}$$

The reduced masses can be found to be

$$\mu_{H_2} = 8.38 \times 10^{-28}\text{kg}, \mu_{CO} = 1.14 \times 10^{-26}\text{kg}, \text{ and } \mu_{HCl} = 1.626 \times 10^{-27}\text{kg}.$$

Now we can find our force constants by plugging in the given values.

- $k_{H_2} = 642N/m$
- $k_{CO} = 2404N/m$
- $k_{HCl} = 481N/m$

We should expect that the values we found are higher than what is experimentally measured, as other forces are unaccounted for. Bond length calculations are more accurate because it requires a smaller basis set to calculate accurately.

Q11.20

Normalize the following Gaussian function:

$$\phi(r) = xe^{-\alpha r^2} \tag{9.E.13}$$

S11.20

We write $\phi(r)$ in spherical coordinates and then apply the normalization condition of the normalized function $A\phi(r)$

The normalization condition is

$$\int A^2x^2e^{-2\alpha r^2}d\tau = 1 \tag{9.E.14}$$

or in bra-ket notation

$$\langle\phi(r)|\phi(r)\rangle = 1.$$

where A is the normalization constant. In spherical coordinates,

$$1 = \int A^2r^2\sin^2\theta\cos^2\phi e^{-2\alpha r^2}d\tau \tag{9.E.15}$$

$$= A^2\int_0^\infty r^4e^{-2\alpha r^2}dr\int_0^\pi \sin^3\theta d\theta\int_0^{2\pi}\cos^2\phi d\phi \tag{9.E.16}$$

$$\frac{1}{A^2} = \frac{3}{8(2\alpha)^2}\left(\frac{\pi}{2\alpha}\right)^{1/2}\left(\frac{4}{3}\right)(\pi) \tag{9.E.17}$$

$$= \frac{\pi^{3/2}}{2^{7/2}\alpha^{5/2}} \tag{9.E.18}$$

Therefore, the nomalization constant will the inverse of this result:

$$A = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} \tag{9.E.19}$$

Q11.21

Which hydrogen atomic orbital corresponds to the following normalized Gaussian orbital?

$$G(x,y,z;\alpha) = \left(\frac{128\alpha^5}{\pi^3}\right)^{0.25}ye^{-\alpha r^2} \tag{9.E.20}$$

How many radial and angular nodes does the above function have? Is this result what you would expect for the corresponding hydrogen function?

S11.21

The typical form is:

$$G_{nlm}(r,\theta,\phi) = N_n r^{n-1} e^{-\alpha r^2} Y_l^m(\theta,\phi) \tag{9.E.21}$$

.

From this, we can see the function in the question shows n = 2 and l = 1. Because n = 2, there is 1 node and l = 1 tells us that there is 1 angular node. Therefore, there are no radial nodes.This is consistent with the $2p_y$ orbital in a hydrogenic function.

Q11-22

Slater type orbitals have the form,

$$\chi_{nlm} = R_n(r) Y_{lm}(\theta,\phi) \tag{9.E.22}$$

where the second term is the spherical harmonic given by

$$R_n(r) = \frac{(2\alpha)^{(n+1/2)}}{\sqrt{(2n)!}} r^{(n-1)} e^{(-\alpha r)} \tag{9.E.23}$$

Define the 1s-slater type orbital.

S11-22

For n=1, the slater-type orbital is

$$\phi_{nlm} = \frac{(2\zeta)^{(n+1/2)}}{\sqrt{(2n)!}} r^{(n-1)} e^{(-\zeta r)} Y_{lm}(\theta,\phi) \tag{9.E.24}$$

$$\phi_{1s}(r,\zeta) = S_{100}(r,\zeta) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r} \tag{9.E.25}$$

11.23

Consider the normalized functions

$$G_1(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})(\frac{1}{4}) x^2 e^(- \alpha r^2) \tag{9.E.26}$$

$$G_2(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})(\frac{1}{4}) y^2 e^(- \alpha r^2) \tag{9.E.27}$$

$$G_3(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})(\frac{1}{4}) z^2 e^(- \alpha r^2) \tag{9.E.28}$$

$$G_4(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})(\frac{1}{4}) (x^2 - y^2) e^(- \alpha r^2) \tag{9.E.29}$$

Which hydrogen atomic orbital corresponds to the linear combination

$$G_3(x,y,z;\alpha) + G_1(x,y,z;\alpha)? \tag{9.E.30}$$

S11.23

$$G_3(x,y,z;\alpha)+G_1(x,y,z;\alpha)=(\frac{2048\alpha^7}{9\pi^3})^(\frac{1}{4})(z^2+x^2)e^(-\alpha r^2) \tag{9.E.31}$$

Corresponds to the

$$3d_{z^2+x^2} \tag{9.E.32}$$

hydrogen atomic orbital.

This is a good tricky question because usually people would think that

$$H_2 \tag{9.E.33}$$

only has two energy levels, but really there are more, just not occupied. Once you excite/add a good amount of energy, it could change to different orbitals.

(The math is right but Hydrogen has only five 3d orbitals and they are $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{y^2}$, and $3d_{(x^2-y^2)}$ so the $3d_{z^2+x^2}$ is not consistent . -RM)

Q11.27

Scientists are trying to theoretically predict the dipole moment of a CO molecule using the STO-3G and 6-31G* basis sets. When compared to their experimental data, the 6-31G* basis set provided a more accurate calculation than did the STO-3G basis set. Why is this?

S11.27

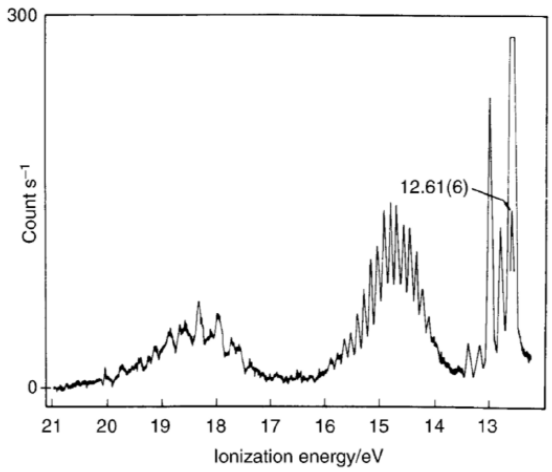
To calculate the dipole moment of a molecule, one needs an accurate description of the electron densities and molecular orbitals. This description becomes **more accurate when a larger basis set is used**, which is why the 6-31G* basis set gave more accurate calculations than did the STO-3G basis set.

Q11.28

The orbital energies calculated for formaldehyde using STO-3G an 3-21G basis sets are given below.

Orbital	energy/E_h	energy/E_h
$1a_1$	-20.3217	-20.4856
$2a_1$	-11.1250	-11.2866
$3a_1$	-1.3373	-1.4117
$4a_1$	-0.8079	-0.8661
$1b_2$	-0.6329	-0.6924
$5a_1$	-0.5455	-0.6345
$1b_1$	-0.4431	-0.5234
$2b_2$	-0.3545	-0.4330
$2b_1$	0.2819	0.1486
$6a_1$	0.6291	0.2718
$3b_2$	0.7346	0.3653
$7a_1$	0.9126	0.4512

Determine the ground-state electronic configuration of water. The photoelectron spectrum of water is shown below.



Assign the bands. Which calculated set of energies shows the best agreement with the photoelectron spectrum? Predict the ionization energy and electron affinity of water for each calculated set of energy levels. How do these compare with the experimental values?

S11.28

There are 8 electrons in water (2 from water and 6 from oxygen). This gives use the ground-state electronic configuration of

$$1a_1^2 2a_1^2\ 1b_2^2\ 3a_1^2\ 1b_1^2$$

The band at approx. 15 eV corresponds to the $1b_1^2$ electrons, the bands at 15.5 eV correspond to $1b_2^2\ 3a_1^2$ electrons. 18.5 ev = $1a_1^2 2a_1^2$.

IE = $-E_{2h2}$ = 0.6924*15 ev = 10.386 ev

EA = $-E_{2h1}$ = 0.5234*18.5 ev = 9.6829 ev

Q11.29

The units of dipole moment given by Gaussian 94 are called debyes (D), after the Dutch-American chemist, Peter Debye, who was awarded the Nobel Prize for chemistry in 1936 for his work on dipole moments. One dehye is equal to 10^{-18} esu•cm where esu (electrostatic units) is a non-SI unit for electric charge. Given that a 9v battery is 3.0 x 10^{-2} esu, show that the conversion factor between debyes and C • m (coulomb • meters) is 1 D = 5.34 x 10^-38 C•m.

S11.29

$$1D = 1 * 10^{-18} esu \bullet cm \left(\frac{1.6022 * 10^{-19}\, C}{4.803 * 10^{-10}\, esu} * \frac{1m}{100cm} \right) = 3.3407 * 10^{-30}\, C \bullet m \tag{9.E.34}$$

Q11.30

Determine the dipole moment $SnCl_2$ by using the geometry and charges:

$$z = e \sum X_i r_i \tag{9.E.35}$$

S11.30

$$e((0.41sin(52.57)i + .041cos(52.75)j)94.7 * 10^{-12}m + (0.41sin(52.57)i + 0.41cos(52.75)j)94.7x10^{-12}m) \tag{9.E.36}$$

$$= 2.3D \tag{9.E.37}$$

Notes:

The equation I found for dipole moment is:

$$\vec{\mu} = \sum_i q_i \vec{r}_i \tag{9.E.38}$$

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10: CHEMICAL BONDING IN DIATOMIC MOLECULES

Our basis for understanding chemical bonding and the structures of molecules is the electron orbital description of the structure and valence of atoms, as provided by quantum mechanics. We assume an understanding of the periodicity of the elements based on the nuclear structure of the atom and our deductions concerning valence based on electron orbitals.

10.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules

10.2: The H_2^+ Prototypical Species

10.3: The Overlap Integral

10.4: Chemical Bond Stability

10.5: Bonding and Antibonding Orbitals

10.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital

10.7: Molecular Orbitals Can Be Ordered According to Their Energies

10.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

10.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle

10.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic

10.11: Photoelectron Spectroscopy

10.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

10.13: Molecular Term Symbols Describe Electronic States of Molecules

10.14: Molecular Term Symbols Designate Symmetry

10.E: Chemical Bond in Diatomic Molecules (Exercises)

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10.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules

Learning Objectives

- Understand the need to introduce an approximation like the Born-Oppenheimer approximation to solve multi-electron systems
- Understand the basis of parameterization involved in using the Born-Oppenheimer approximation

Using quantum mechanics to predict the chemical bonding patterns, optimal geometries, and physical and chemical properties of molecules is a large and active field of research known as *molecular quantum mechanics* or more commonly as *quantum chemistry*. The density functional theory referred to in the previous lecture, for which the chemistry Nobel prize was given in 1998, has had a tremendous impact in quantum chemistry, with some of the papers in this subject having acquired some 10,000 citations each since their publication. In fact, the 1998 chemistry Nobel prize was shared between Walter Kohn, one of the inventors of density functional theory and John Pople, the developer of a commonly used quantum chemistry software package.

Quantum chemistry calculations allow the geometries of molecules to be computed as well as a wide range of properties. Quantum chemistry can also be used in a novel way, in which the electrons are treated using quantum mechanics but the nuclei are treated as classical particles. We use quantum mechanics to calculate the internuclear forces but then use these forces in Newton's Second Law to study the motion of the nuclei during chemical reactions. This gives us a microscopic window into the specific motions, the complex dance, executed by the nuclei during a simple or complex chemical process.

The methods of quantum chemistry have become very sophisticated, and there are various software packages that can be downloaded for carrying out the calculations of quantum chemistry. It should be noted that these packages use a series of approximations to solve the Schrödinger equation because for all but the simplest of molecules, exact solutions are not available. We will discuss some of these methods, but first we need to introduce some of the underlying theory.

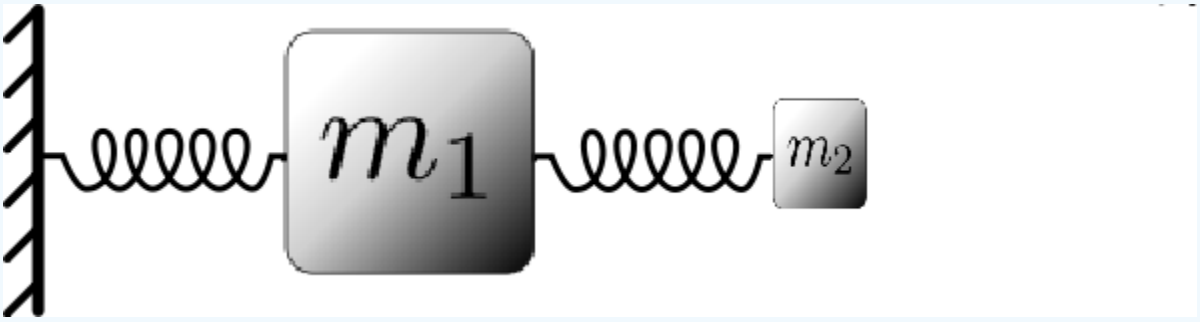
The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is one of the basic concepts underlying the description of the quantum states of molecules. This approximation makes it possible to separate the motion of the nuclei and the motion of the electrons. This is not a new idea for us. We already made use of this approximation in the particle-in-a-box model when we explained the electronic absorption spectra of cyanine dyes without considering the motion of the nuclei. Then we discussed the translational, rotational and vibrational motion of the nuclei without including the motion of the electrons. In this chapter we will examine more closely the significance and consequences of this important approximation. Note, in this discussion nuclear refers to the atomic nuclei as parts of molecules not to the internal structure of the nucleus.

The Born-Oppenheimer approximation neglects the motion of the atomic nuclei when describing the electrons in a molecule. The physical basis for the Born-Oppenheimer approximation is the fact that the mass of an atomic nucleus in a molecule is much larger than the mass of an electron (more than 1000 times). Because of this difference, the nuclei move much more slowly than the electrons. In addition, due to their opposite charges, there is a mutual attractive force of Ze^2/r^2 acting on an atomic nucleus and an electron. This force causes both particles to be accelerated. Since the magnitude of the acceleration is inversely proportional to the mass, a = F/m, the acceleration of the electrons is large and the acceleration of the atomic nuclei is small; the difference is a factor of more than 2000. Consequently, the electrons are moving and responding to forces very quickly, and the nuclei are not. You can imagine running a 100-yard dash against someone whose acceleration is a 2000 times greater than yours. That person could literally run circles around you.

Example 9.1.1 : Coupled Oscillators with Dissimilar Masses

If two particles interact in some way, and one is much heavier than the other, the light particle will move essentially as a "slave" of the heavy particle. That is, it will simply follow the heavy particle wherever it goes, *and*, it will move rapidly in response to the heavy particle motion. As an illustration of this phenomenon, consider the simple mechanical system pictured below:



(CC BY-SA 3.0 Unported; Jim.belk via Wikipedia).

Considering this as a classical system, we expect that the motion will be dominated by the large heavy particle (m_1), which is attached to a fixed wall by a spring. The small, light particle (m_2, which is attached to the heavy particle by a spring will simply follow the heavy particle and execute rapid oscillations around it.

So a good approximation is to describe the electronic states of a molecule by thinking that the nuclei are not moving, i.e. that they are stationary. The nuclei, however, can be stationary at different positions so the electronic wavefunction can depend on the positions of the nuclei even though their motion is neglected.

Now we look at the mathematics to see what is done in solving the Schrödinger equation after making the Born-Oppenheimer approximation. For a diatomic molecule as an example, the Hamiltonian operator is grouped into three terms

$$\hat{H}(r,R) = \hat{T}_{nuc}(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} + \hat{H}_{elec}(r,R) \tag{10.1.1}$$

where

$$\hat{T}_{nuc}(R) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 \tag{10.1.2}$$

and

$$\hat{H}_{elec}(\vec{r},\vec{R}) = \frac{-\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left(-\sum_i \frac{Z_A}{r_{Ai}} - \sum_i \frac{Z_B}{r_{Bi}} + \frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{r_{ij}}\right) \tag{10.1.3}$$

In Equation 10.1.1, the first term represents the kinetic energy of the nuclei, the second term represents the Coulomb repulsion of the two nuclei, and the third term represents the contribution to the energy from the electrons, which consists of their kinetic energy, mutual repulsion for each other, and attraction for the nuclei. $\vec{r}$ and $\vec{R}$ are vectors specifying the positions of all the electrons and all the nuclei, respectively.

Exercise 9.1.1

Define all the symbols in Equations 10.1.1 through 10.1.3.

Answer available at the end of this section.

Exercise 9.1.2

Explain why the factor of 1/2 appears in the last term in Equation 10.1.3.

Answer available at the end of this section.

The Born-Oppenheimer approximation says that the nuclear kinetic energy terms in the complete Hamiltonian, Equation 10.1.1, can be neglected in solving for the electronic wavefunctions and energies. Consequently, the electronic wavefunction $\varphi_e(r, R)$ is found as a solution to the electronic Schrödinger equation

$$\hat{H}_{elec}(r, R)\varphi_e(r, R) = E_e(R)\varphi_e(r, R) \tag{10.1.4}$$

Even though the nuclear kinetic energy terms are neglected, the Born-Oppenheimer approximation still takes into account the variation in the positions of the nuclei in determining the electronic energy and the resulting electronic wavefunction depends upon the nuclear positions, R. As a result of the Born-Oppenheimer approximation, the molecular wavefunction can be written as a product

$$\psi_{ne}(r, R) = X_{ne}(R)\varphi_e(r, R) \tag{10.1.5}$$

This product wavefunction is called the Born-Oppenheimer wavefunction. The function $X_{ne}(R)$ is the vibrational wavefunction, which is a function of the nuclear coordinates R and depends upon both the vibrational and electronic quantum numbers or states, n and e, respectively. The electronic function, $\varphi_e(r, R)$, is a function of both the nuclear and electronic coordinates, but only depends upon the electronic quantum number or electronic state, e. Translational and rotational motion is not included here. The translational and rotational wavefunctions simply multiply the vibrational and electronic functions in Equation 10.1.5 to give the complete molecular wavefunction when the translational and rotational motions are not coupled to the vibrational and electronic motion.

In the *Crude Born-Oppenheimer Approximation*, R is set equal to R_o, the equilibrium separation of the nuclei, and the electronic wavefunctions are taken to be the same for all positions of the nuclei (i.e., the nuclei never move). The electronic energy, $E_e(R)$, in Equation 10.1.4 combines with the repulsive Coulomb energy of the two nuclei, to form the potential energy function that controls the nuclear motion as shown in Figure 9.1.1 .

$$V_e(R) = E_e(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} \tag{10.1.6}$$

Consequently the Schrödinger equation for the vibrational motion is

$$(\hat{T}_{nuc}(R) + V(R))X_{ne}(R) = E_{ne}X_{ne}(R) \tag{10.1.7}$$

Potential Energy Curves and Surfaces

Previously, the potential energy was approximated as a harmonic potential or Morse potential depending on the displacement, R , of the nuclei from their equilibrium positions.

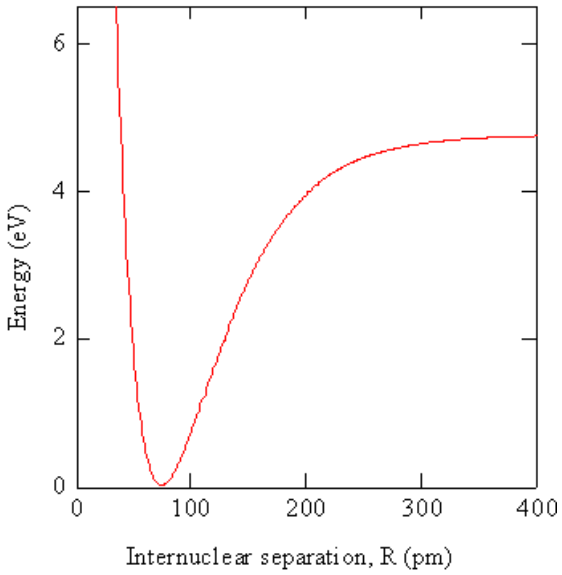


Figure 9.1.1 : The potential energy function for a diatomic molecule.

In practice the electronic Schrödinger equation is solved using approximations at particular values of R to obtain the wavefunctions $\varphi_e(r, R)$ and potential energies $V_e(R)$. The potential energies can be graphed as illustrated in Figure 9.1.1 .

The graph in Figure 9.1.1 is the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When R is very large there are two atoms that are weakly interacting. As R becomes smaller, the interaction becomes stronger, the energy becomes a large negative value, and we say a bond is formed between the atoms. At very small values of R, the internuclear repulsion is very large so the energy is large and positive. This energy function controls the motion of the nuclei. Previously, we approximated this function by a harmonic potential to obtain the description of vibrational motion in terms of the harmonic oscillator model. Other approximate functional forms could be used as well, e.g. the Morse potential. The equilibrium position of the nuclei is where this function is a minimum, i.e. at $R = R_0$. If we obtain the wavefunction at $R = R_0$ and use this function for all values of R, we have employed the *Crude Born-Oppenheimer* approximation.

Exercise 9.1.3

Relate Equation 10.1.7 to the one previously used in our description of molecular vibrations in terms of the harmonic oscillator model.

While the potential energy function, $V_e(R)$, for a diatomic molecule is a 1-D curve (Figure 9.1.1), molecules with more than two atoms will have multi-dimensional **potential energy surfaces** with 3N-6 (or 3N-5 for linear molecule) dimensions for the number of internal degrees of freedom.

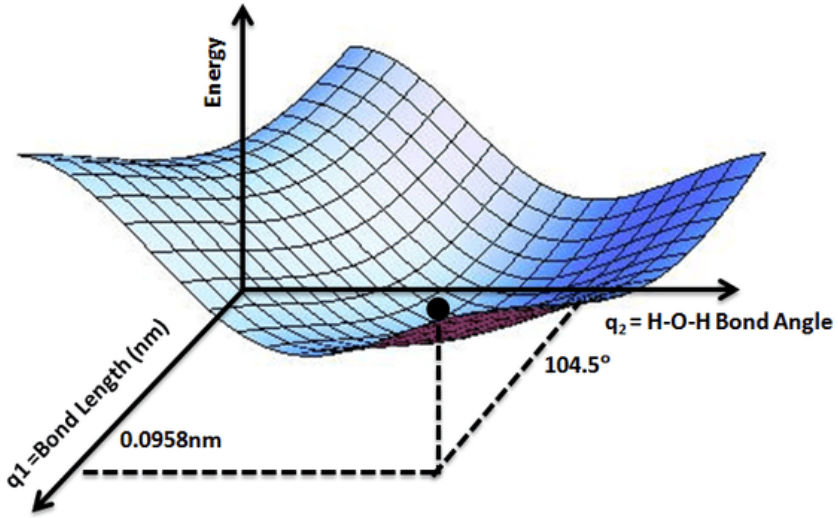


Figure 9.1.2 : The potential energy surface for a water molecule: Shows the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958 nm and H-O-H bond angle of 104.5°. from Wikipeda (AimNature)

The potential energy surface concept can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction. Qualitatively the reaction coordinate diagrams (one-dimensional slices through the potential energy surfaces) have numerous applications. Chemists use reaction coordinate diagrams as both an analytical and pedagogical aid for rationalizing and illustrating kinetic and thermodynamic events. The purpose of energy profiles and surfaces is to provide a qualitative representation of how potential energy varies with molecular motion for a given reaction or process.

Exercise 9.1.4

Explain the difference between the Born-Oppenheimer approximation and the Crude Born-Oppenheimer approximation.

Summary

In this section we started with the Schrödinger equation for a diatomic molecule and separated it into two equations, an electronic Schrödinger equation and a nuclear Schrödinger equation. In order to make the separation, we had to make an approximation. We had to neglect the effect of the nuclear kinetic energy on the electrons. The fact that this assumption works can be traced to the fact that the nuclear masses are much larger than the electron mass. We then used the solution of the electronic Schrödinger equation to provide the potential energy function for the nuclear motion. The solution to the nuclear Schrödinger equation provides the vibrational wavefunctions and energies.

Contributors and Attributions

David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

Answers

$$\hat{H}(r,R) = \underbrace{\hat{T}_{nuc}(R)}_{\text{Kinetic Energy Term for nuclei}} + \underbrace{\frac{e^2}{4\pi\epsilon_o}\frac{Z_A Z_B}{R}}_{\text{Repulsion Term for nuclei}} + \underbrace{\hat{H}_{elec}(r,R)}_{\text{Hamiltonian for electrons}}$$

$$\hat{T}_{nuc}(R) = \underbrace{\frac{\hbar^2}{2m_A}\nabla_A^2}_{\text{Kinetic Energy Term for nuclei A}} - \underbrace{\frac{\hbar^2}{2m_b}\nabla_B^2}_{\text{Kinetic Energy Term for nuclei B}}$$

$$\hat{H}_{elec}(\vec{r},\vec{R}) = \underbrace{\frac{-\hbar^2}{2m}\sum_i \nabla_i^2}_{\text{Kinetic Energy Term for electrons}} + \frac{e^2}{4\pi\epsilon_o}\left(- \underbrace{\sum_i \frac{Z_A}{r_{Ai}}}_{\text{Attraction Term between nuclei A and electron i}} - \underbrace{\sum_i \frac{Z_B}{R_{Bi}}}_{\text{Attraction Term between nuclei B and electron i}} + \underbrace{\frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{r_{ij}}}_{\text{Repulsion Term between electrons}} \right)$$

where, $Z_x$is the charge of particle x, m_x is the mass of particle x and r_{xz} is the distance between particle x and z.

The 1/2 term is there to make sure we do not double count the potential energies via the two summations. Otherwise, we would independently add the potential energy of electron 1 with electron 2 and the potential energy of electron 2 with electron 1. These are the same and hence one has to be removed.

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10.2: The H_2^+ Prototypical Species

Molecular orbital theory is a conceptual extension of the orbital model, which was so successfully applied to atomic structure. As was once playfully remarked, "a molecule is nothing more than an atom with more nuclei." This may be overly simplistic, but we do attempt, as far as possible, to exploit analogies with atomic structure. Our understanding of atomic orbitals began with the exact solutions of a prototype problem – the hydrogen atom. We will begin our study of homonuclear diatomic molecules beginning with another exactly solvable prototype, the hydrogen molecule-ion $\mathrm{H_2}^+$.

The Hydrogen Molecular Ion

The simplest conceivable molecule would be made of two protons and one electron, namely $\mathrm{H_2}^+$. This species actually has a transient existence in electrical discharges through hydrogen gas and has been detected by mass spectrometry and it also has been detected in outer space. The Schrödinger equation for $\mathrm{H_2}^+$ can be solved exactly within the Born-Oppenheimer approximation (i.e., fixed nuclei). This ion consists of two protons held together by the electrostatic force of a single electron. Clearly the two protons, two positive charges, repeal each other. The protons must be held together by an attractive Coulomb force that opposes the repulsive Coulomb force. A negative charge density between the two protons would produce the required counter-acting Coulomb force needed to pull the protons together. So intuitively, to create a chemical bond between two protons or two positively charged nuclei, a high density of negative charge between them is needed. We expect the molecular orbitals that we find to reflect this intuitive notion.

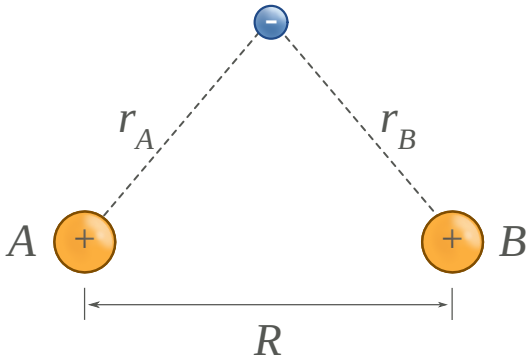


Figure 9.2.1 : Hydrogen molecular ion $\mathrm{H_2}^+$ with fixed nuclei A and B, internuclear distance R. (CC BY-NC; Ümit Kaya via LibreTexts)

The electronic Hamiltonian for $\mathrm{H_2}^+$ is

$$\hat{H}_{elec}(r,R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \tag{10.2.1}$$

where r_A and r_B are the distances electron from the A and B hydrogen nuclei, respectively and R is the distance between the two protons.

Although the Schrödinger equation for $\mathrm{H_2}^+$ can be solved exactly (albeit within the Born-Oppenheimer approximation where the nuclei are fixed) because there is only one electron, we will develop approximate solutions in a manner applicable to other diatomic molecules that have more than one electron.

Linear Combination of Atomic Orbitals

For the case where the protons in H_2^+ are infinitely far apart, we have a hydrogen atom and an isolated proton when the electron is near one proton or the other. The electronic wavefunction would just be $1s_A(r)$ or $1s_B(r)$ depending upon which proton, labeled A or B, the electron is near. Here $1s_A$ denotes a 1s hydrogen atomic orbital with proton A serving as the origin of the spherical polar coordinate system in which the position r of the electron is specified. Similarly $1s_B$ has proton B as the origin. A useful approximation for the molecular orbital when the protons are close together therefore is a linear combination of the two atomic orbitals. The general method of using

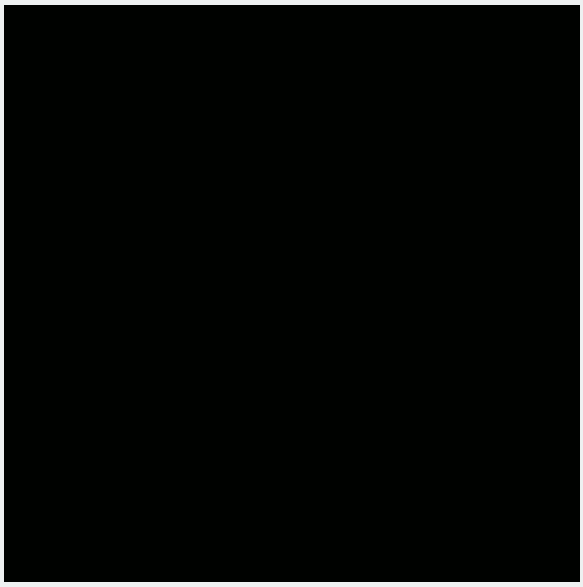
$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \tag{10.2.2}$$

i.e. of finding molecular orbitals as linear combinations of atomic orbitals is called the *Linear Combination of Atomic Orbitals - Molecular Orbital (LCAO-MO) Method*. In this case we have two basis functions in our basis set, the hydrogenic atomic orbitals $1s_A$ and $1s_B$.

The Linear Combination of Atomic Orbitals (LCAO) Approximation and Interference

The LCAO approximation is an example of the linear variational method discussed previously with the true molecular orbital wavefunction approximated as an expansion of a basis set of atomic orbitals on each atom of the molecule with variable coefficients that can be optimized (e.g., via the secular equations). As discussed previously, the number of wavefunctions (solutions) extracted from solving the secular determinant is equal the number of elements in the expansion. So for the expansion in Equation 10.2.2 with two atomic orbitals contributing result in two molecule orbitals.

This method yields a approximate picture of the molecular orbitals in a molecules. The figure below shows two atoms approaching along the axis of one of their $2p$ states. In the top row, the two lobes facing one another have the same sign; in the bottom row they have opposite sign. These are two different linear combinations of the same two atomic states, on different atoms and with difference phases (i.e., signs of C_A vs. C_B in the expansion). In the first example, the electron density increases between the nuclei and in the second example, a very steep-sided node between the two nuclei causes all the probability density to face away from the atom opposite.



For H_2^+, the simplest molecule, the starting function is given by Equation 10.2.2. We must determine the values for the coefficients, C_A and C_B. We could use the variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition $|C_A|^2 = |C_B|^2$; namely, $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\psi_+ = C_+(1s_A + 1s_B) \tag{10.2.3}$$

$$\psi_- = C_-(1s_A - 1s_B) \tag{10.2.4}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for ψ_+ is enhanced (Figure 9.2.2 (bottom) between the two protons, whereas it is diminished for ψ_- as shown in Figures 9.2.2 (top). ψ_- has a node in the middle while ψ_+ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons.

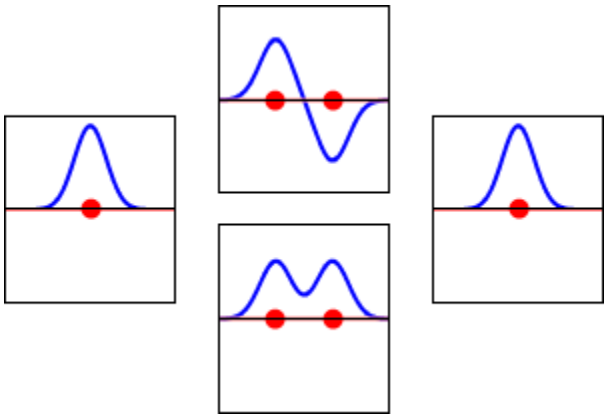


Figure 9.2.2 : Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H_2^+ ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red dots mark the locations of the nuclei. The electron wavefunction oscillates according to the Schrödinger wave equation, and orbitals are its standing waves. The standing wave frequency is proportional to the orbital's kinetic energy. (This plot is a one-dimensional slice through the three-dimensional .)

So ψ_+ is called a **bonding molecular orbital**. If the electron were described by ψ_-, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so ψ_- is called an **antibonding molecular orbital**.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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10.3: The Overlap Integral

For $H_2{}^+$, the simplest molecule, we must determine the values for the coefficients, C_A and C_B for the LCAO approximation for the molecular orbital as a linear combination of the two atomic orbitals

$$|\psi(r)\rangle = C_A 1s_A(r) + C_B 1s_B(r)$$

We could use the linear variational method to find a value for these coefficients, but for the case of $H_2{}^+$ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition

$$|C_A|^2 = |C_B|^2$$

so $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\underbrace{|\psi_+\rangle = C_+(1s_A + 1s_B)}_{\text{bonding molecular orbital}} \tag{10.3.1}$$

and

$$\underbrace{|\psi_-\rangle = C_-(1s_A - 1s_B)}_{\text{antibonding molecular orbital}} \tag{10.3.2}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for $|\psi_+\rangle$ is enhanced between the two protons, whereas it is diminished for $|\psi_-\rangle$ as shown in Figures 9.3.1 . ψ_- has a node in the middle while $|\psi_+\rangle$ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons. So $|\psi_+\rangle$ is called a *bonding molecular orbital*. If the electron were described by $|\psi_-\rangle$, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so $|\psi_-\rangle$ is called an *antibonding molecular orbital*.

Now we want to evaluate C_+ and C_- and then calculate the energy. The bonding and antibonding character of ψ_+ and ψ_- also should be reflected in the energy. If $|\psi_+\rangle$ indeed describes a bonding orbital, then the energy of this state should be less than that of a proton and hydrogen atom that are separated. The calculation of the energy will tell us whether this simple theory predicts $H_2{}^+$ to be stable or not and also how much energy is required to dissociate this molecule.

The constants C_+ and C_- are evaluated from the standard normalization condition:

$$\int \psi_\pm^* \psi_\pm d\tau = \langle \psi_\pm | \psi_\pm \rangle = 1 \tag{10.3.3}$$

$$\langle C_\pm(1s_A \pm 1s_B) | C_\pm(1s_A \pm 1s_B) \rangle = 1 \tag{10.3.4}$$

$$|C_\pm|^2[\underbrace{\langle 1s_A|1s_A\rangle}_{1} + \underbrace{\langle 1s_B|1s_B\rangle}_{1} \pm \underbrace{\langle 1s_B|1s_A\rangle}_{S} \pm \underbrace{\langle 1s_A|1s_B\rangle}_{S^*}] = 1 \tag{10.3.5}$$

Since the atomic orbitals are normalized, the first two integrals are just 1. The last two integrals are called *overlap integrals* and are symbolized by S and S^*, respectively, since one is the complex conjugate of the other.

The overlap integrals are telling us to take the value of $1s_B$ at a point multiply by the value of $1s_A$ at that point and sum (integrate) such a product over all of space (Figure 9.3.1). If the functions do not overlap, i.e. if one is zero when the other one is not and vice versa, these integrals then will be zero. It also is possible in general for such integrals to be zero even if the functions overlap because of the cancelation of positive and negative contributions.

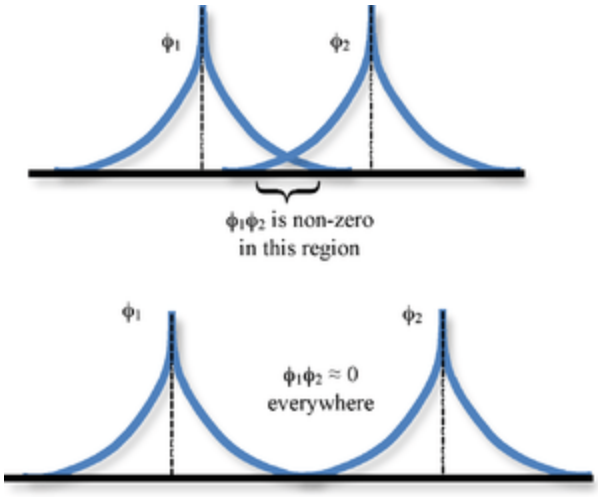


Figure 9.3.1 : The wavefunctions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case both S is close to zero.

If the overlap integral is zero, for whatever reason, the functions are said to be *orthogonal*. Notice that the overlap integral ranges from 0 to 1 as the separation between the protons varies from $R = \infty$ to $R = 0$. Clearly when the protons are infinite distance apart, there is no overlap, and when $R = 0$ both functions are centered on one nucleus and $\langle 1s_A|1s_B\rangle$ becomes identical to $\langle 1s_B|1s_A\rangle$, which is normalized to 1, because $1s_A = 1s_B$.

With these considerations and using the fact that $1s$ wavefunctions are real so

$$\langle 1s_A|1s_B\rangle = \langle 1s_B|1s_A\rangle = S \tag{10.3.6}$$

Equation 10.3.5 becomes

$$|C_{\pm}|^2(2 \pm 2S) = 1 \tag{10.3.7}$$

The solution to Equation 10.3.7 is given by

$$C_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} \tag{10.3.8}$$

Hence, the normalized molecular orbitals in Equations 10.3.1 and 10.3.1 are

$$|\psi_+\rangle = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B) \tag{10.3.9}$$

and

$$|\psi_-\rangle = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B) \tag{10.3.10}$$

The energies associated with these wavefunctions requires a bit more effort to calculate though as demonstrated in the following section.

For the overlap integral of two 1s orbitals from the hydrogen dimer discussed above is difficult to evaluate analytically and is explained here. The final answer is:

$$S(R) = \langle 1s_A|1s_B\rangle \tag{10.3.11}$$

$$= e^{-R/a_o}\left(1 + \frac{R}{a_o} + \frac{R^2}{3a_o^2}\right) \tag{10.3.12}$$

The overlap integral for two 1s atomic orbitals of hydrogen is graphically displayed below

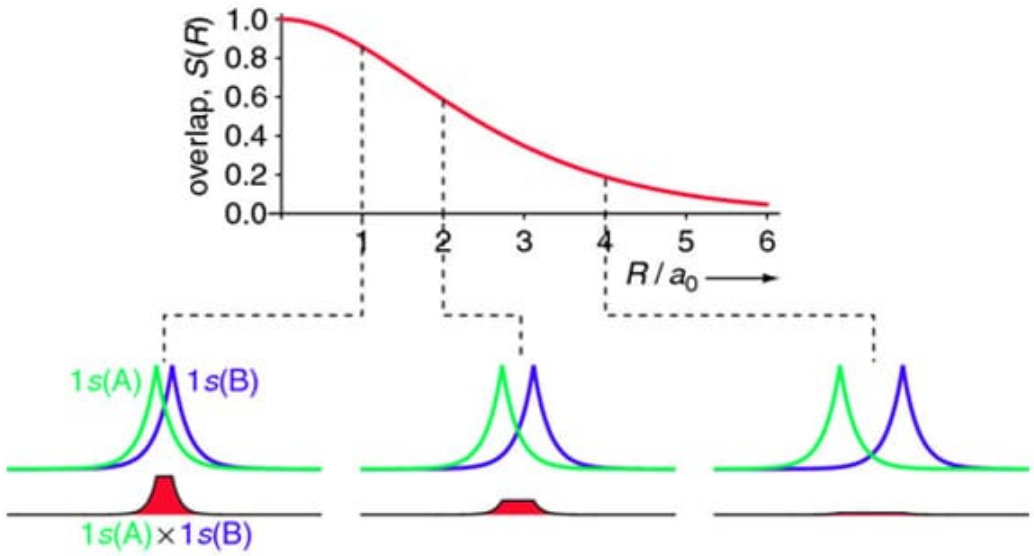


Figure 9.3.2 : The overlap integral at different proton separations.

Example 9.3.1

Calculate the difference in the electronic charge density (C/pm^3) at a point halfway between the two nuclei for H_2^+ for an electron in the bonding molecular orbital compared to one in the antibonding molecular orbital.

Solution

The electronic charge density is calculated with the formula $|e\psi^2|$ where $e = 1.602 \times 10^{-19} C$

a: Bonding Molecular Orbital

First, squaring the bonding molecular orbital (Equation 10.3.9) gives us:

$$\begin{aligned}\psi_+^2 &= \frac{1}{2(1+S)}(1s_A + 1s_B)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3}\left(e^{-r_A/a_0} + e^{-r_B/a_0}\right)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3} \\ &= (0.561)^2 \times \left(\frac{1}{\pi \times (52.9\text{ pm})^3}\right) = 6.7672 \times 10^{-7}\text{ pm}^{-3}\end{aligned}$$

(Note: The value of C^2 is obtained from equation 9.3.12 and the value of S is from Equation 10.3.12)

To find the density at halfway between A and B for the bonding orbital evalulate at 1/2 R,

$$r_A = \frac{1}{2}R \text{ and } r_B = \frac{1}{2}R$$

$$\psi_+^2 = 3.7 \times 10^{-7}\text{ pm}^{-3}$$

Now multiply this answer by e to generate the electronic charge density,

$$P = \left(3.7 \times 10^{-7}\text{ pm}^{-3}\right) \times \left(1.602 \times 10^{-19}\right)\text{ C} = 5.93 \times 10^{-26} C/pm^3$$

b: Antibonding Molecular Orbital

To find the halfway between A and B for the anti-bonding orbital at $r_A = \frac{1}{2}R$ and $r_B = \frac{1}{2}R$. However, simple inspection of Equation 10.3.10 or Figure 9.3.1 shows this will be zero.

$$e\psi_-^2 = 0$$

Obviously, when multiplied by e, the answer is still zero. This makes logical sense as there would be no charge density between the two atoms as there lies a node with no probability of finding an electron.

Exercise 9.3.1

Show that for two arbitrary functions $\langle\varphi_B|\varphi_A\rangle$ is the complex conjugate of $\langle\varphi_A|\varphi_B\rangle$ and that these two integrals are equal if the functions are real.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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10.4: Chemical Bond Stability

Learning Objectives

- Identify the nature of the energy of molecular orbitals of a diatomic as a function of intermolecular distance
- Identify the three integrals involved in calculation the total Molecular Orbital Energy: coulomb Integral, exchange integral, and overlap integral

As shown previously, we can construct two molecular orbitals for the H_2^+ system using the LCAO approximation with a basis set of two 1s atomic orbitals (i.e., the $1s$ orbitals on hydrogen A ($1s_A$) and hydrogen B ($1s_B$):

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2(1 \pm S)}}(1s_A \pm 1s_B) \tag{10.4.1}$$

The energy of these two molecular orbitals can be calculated from the expectation value integral of the Hamiltonian,

$$E_\pm = \left\langle \psi_\pm | \hat{H}_{elec} | \psi_\pm \right\rangle \tag{10.4.2}$$

which can be expanded using the expanded molecular orbital wavefunctions in Equations 10.4.1 to give

$$E_\pm = \frac{1}{2(1 \pm S)} \left[\underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{BA}} \right] \tag{10.4.3}$$

where S is the overlap integral between the two atomic orbitals of the basis. The four integrals in Equation 10.4.3 can be represented by H_{AA}, H_{BB}, H_{AB}, and H_{BA}, respectively.

$$E_\pm = \frac{1}{2(1 \pm S)} \left[H_{AA} + H_{BB} \pm H_{AB} \pm H_{BA} \right] \tag{10.4.4}$$

Exercise 9.4.1

Show that Equation 10.4.2 expands to give Equation 10.4.3 within the LCAO approximation that uses a basis set of only two 1s atomic orbitals.

Answer available at the end of this section.

Notice that A and B appear equivalently in the Hamiltonian operator for H_2^+. This equivalence means that integrals involving $1s_A$ must be the same as corresponding integrals involving $1s_B$, i.e.

$$H_{AA} = H_{BB} \tag{10.4.5}$$

and since the wavefunctions are real

$$|A\rangle = \langle A|$$

so

$$H_{AB} = H_{BA} \tag{10.4.6}$$

These two equalities simplify Equation 10.4.4:

$$E_{\pm} = \frac{1}{1 \pm S}(H_{AA} \pm H_{AB}) \tag{10.4.7}$$

Now examine the details of H_{AA} after inserting the Hamiltonian operator for $H_2{}^+$ (Equation 9.2.1):

$$H_{AA} = \underbrace{\left\langle 1s_A \left| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} \right| 1s_A \right\rangle}_{E_H} + \frac{e^2}{4\pi\epsilon_0 R}\cancelto{1}{\langle 1s_A | 1s_A \rangle} - \underbrace{\left\langle 1s_A \left| \frac{e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle}_{J_{AB}} \tag{10.4.8}$$

- The first term is just the integral for the energy of the hydrogen atom of the 1s orbital, E_H.
- The second integral is equal to 1 by normalization; the prefactor is just the Coulomb repulsion of the two protons.
- The last integral, *including the minus sign*, is represented by J and is called the **Coulomb integral**.

Physically J_{AB} is the potential energy of interaction of the electron located around proton A with proton B. It is negative because it is an attractive interaction. It is the average interaction energy of an electron described by the $1s_A$ function with proton B.

The Coulomb Integral () J

The **Coulomb Integral** is the potential energy of electrostatic repulsion between the electron with the electron density in $1S_A$ and the the electron with the electron density function $1S_B$

Now consider H_{AB}.

$$H_{AB} = \underbrace{\left\langle 1s_A \left| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_B} \right| 1s_B \right\rangle}_{E_H S} + \frac{e^2}{4\pi\epsilon_0 R}\cancelto{S}{\langle 1s_A | 1s_B \rangle} - \underbrace{\left\langle 1s_A \left| \frac{e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle}_{K_{AB}} \tag{10.4.9}$$

- In the first integral we have the hydrogen atom Hamiltonian and the H atom function $1s_B$. The function $1s_B$ is an eigenfunction of the operator with eigenvalue E_H. Since E_H is a constant it factors out of the integral, which then becomes the overlap integral, S. The first integral therefore reduces to $E_H S$.
- The second term is just the Coulombic energy of the two protons times the overlap integral.
- The third term, *including the minus sign*, is given the symbol K and is called the *exchange integral* because the electron is described by the $1s_A$ orbital on one side and by the $1s_B$ orbital on the other side of the operator. The electron changes or exchanges position in the molecule.

The Exchange Integral () K

In a **coulomb integral**, the electron always is in the same orbital; whereas, in an *Exchange Integral*, the electron is in one orbital on one side of the operator and in a different orbital on the other side.

Using the expressions for H_{AA} (Equation 10.4.8) and H_{AB} (Equation 10.4.9) and substituting into Equation 10.4.7 produces:

$$E_{\pm} = \frac{1}{1 \pm S}\left[\left(E_H + \frac{e^2}{4\pi\epsilon_0 R}\right)(1 \pm S) + J \pm K\right] \tag{10.4.10}$$

$$= E_H + \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{10.4.11}$$

Equation 10.4.11 tells us that the energy of the $H_2{}^+$ molecule is the energy of a hydrogen atom plus the repulsive energy of two protons plus some additional electrostatic interactions of the electron with the protons. These additional interactions are given by the last term

$$\frac{J \pm K}{1 \pm S}.$$

If the protons are infinitely far apart then only E_H is nonzero, which we can set to zero by subtracting off:

$$\Delta E_{\pm} = E_{\pm} - E_H \tag{10.4.12}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{10.4.13}$$

To get a chemical bond and a stable $H_2{}^+$ molecule $\Delta E_{\pm}$ must be less than zero and have a minimum, i.e. $\frac{J \pm K}{1 \pm S}$ must be sufficiently negative to overcome the positive repulsive energy of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ for some value of R. For large R, these terms are zero, and for small R, the **Coulomb repulsion of the protons rises to infinity.**

Exercise 9.4.2

Show that Equation 9.2.1 follows from Equation 10.4.7

The Coulomb and Exchange Integrals

We will examine more closely how the Coulomb repulsion term and the integrals J, K, and S depend on the separation of the protons, but first we want to discuss the physical significance of J, the Coulomb integral, and K, the exchange integral. J and K have been defined as

$$J_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_A}(r)\frac{e^2}{4\pi\epsilon_0 r_B}d\tau \tag{10.4.14}$$

$$K_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_B}(r)\frac{e^2}{4\pi\epsilon_0 r_A}d\tau \tag{10.4.15}$$

Figure 9.4.2 shows graphs of the four terms contributing to the energy of $H_2{}^+$ (Equation 10.4.13). In Figure 9.4.2 , you can see that as the internuclear distance R approaches zero,

- the Coulomb repulsion of the two protons goes from near zero to a large positive number,
- the overlap integral goes for zero to one, and
- J and K become increasingly negative.

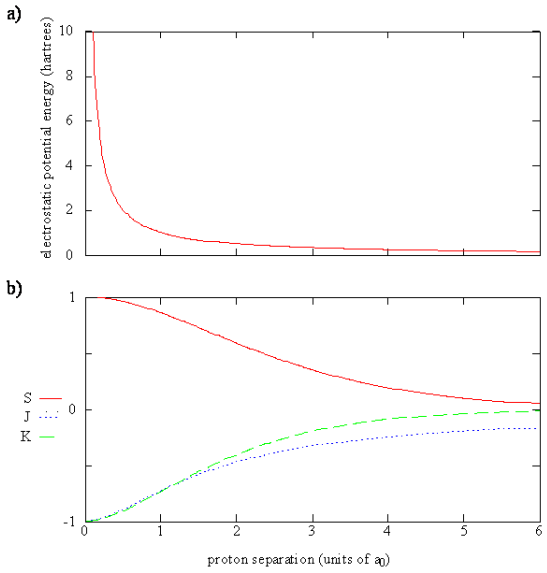


Figure 9.4.2 : (a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance R in units of the Bohr radius (52.92 pm). (b) The overlap (S), Coulomb (J), and exchange (K) integrals at different proton separations. The units for J and K are hartrees; S has no units.
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Note that both J and K integrals are **negative** since all quantities in the integrands of Equation 10.4.14 and 10.4.15 are positive. In the Coulomb integral, $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the charge density of the electron around proton A, since **r** represents the coordinates of the electron relative to proton A. Since r_B is the distance of this electron to proton B, the Coulomb integral gives the potential energy of the charge density around proton A interacting with proton B. J can be interpreted as an average potential energy of this interaction because $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the probability density for the electron at point r, and $\frac{e^2}{4\pi\epsilon_0 r_B}$ is the potential energy of the electron at that point due to the interaction with proton B. Essentially, J accounts for the attraction of proton B to the electron density of hydrogen atom A. As the two protons get further apart, this integral goes to zero because all values for r_B become very large and all values for $1/r_B$ become very small.

In the **exchange integral**, K, the product of the two functions is nonzero **only** in the regions of space where the two functions overlap. If one function is zero or very small at some point then the product will be zero or small. The exchange integral also approaches zero as internuclear distances increase because the both the overlap and the $1/r$ values become zero. The product $e\varphi^*_{1s_A}(r)\varphi_{1a_B}(r)$ is called the *overlap charge density*. Since the overlap charge density is significant in the region of space between the two nuclei, it makes an important contribution to the chemical bond. The exchange integral, K, is the potential energy due to the interaction of the overlap charge density with one of the protons. While J accounts for the attraction of proton B to the electron density of hydrogen atom A, K accounts for the added attraction of the proton due the build-up of electron charge density between the two protons.

Exercise 9.4.3

Write a paragraph describing in your own words the physical significance of the Coulomb and exchange integrals for H_2^+.

Figure 9.4.3 shows the energy of H_2^+ relative to the energy of a separated hydrogen atom and a proton as given by Equation 10.4.11. For the electron in the ψ_- orbital, the energy of the molecule, $E_{el}(R)$, **always** is greater than the energy of the separated atom and proton.

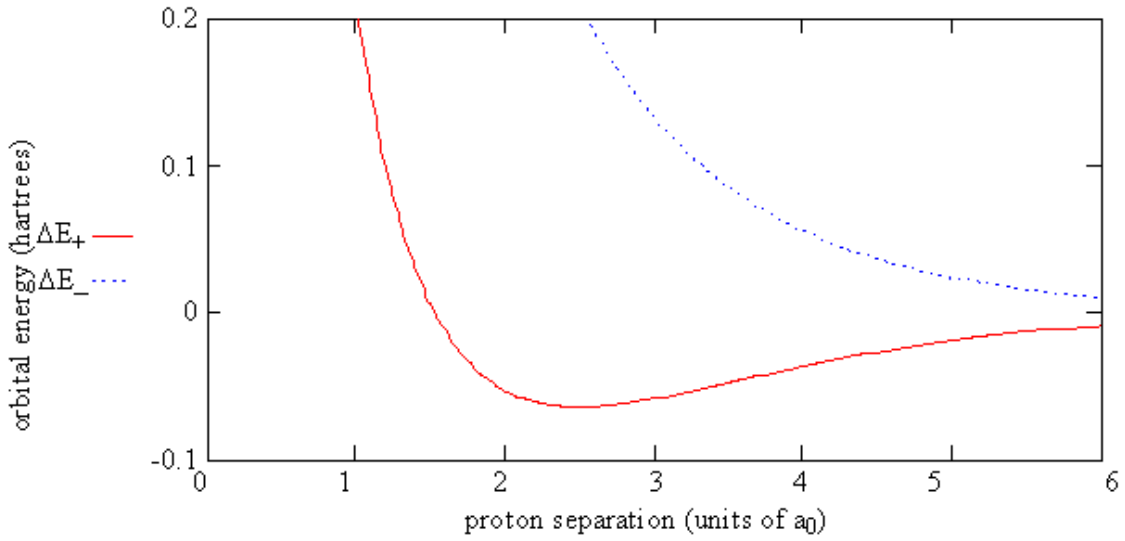


Figure 9.4.3 : Energy of the H_2^+ bonding molecular orbital ΔE_+ and the molecular orbital ΔE_-, relative to the energy of a separated hydrogen atom and proton.

For the electron in the ψ_+ orbital, you can see that the big effect for the energy of the bonding orbital, $E_+(R)$, is the balance between the repulsion of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ and J and K, which are both negative. J and K manage to compensate for the repulsion of the two protons until their separation is less than 100 pm (i.e the energy is negative up until this point), and a minimum in the energy is produced at 134 pm. This minimum represents the formation of a chemical bond. The effect of S is small. It only causes the denominator in Equation 10.4.11 to increase from 1 to 2 as R approaches 0.

For the antibonding orbital, $-K$ is a positive quantity and essentially cancels J so there is not sufficient compensation for the Coulomb repulsion of the protons. The effect of the -K in the expression, Equation 10.4.11, for E_- is to account for the absence of overlap charge density and the enhanced repulsion because the charge density between the protons for ψ_- is even lower than that given by the atomic orbitals.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

Answers

Here we have the wavefunction within the LCAO approximation that uses a basis set of only two 1s atomic orbitals (Equation 10.4.1).

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2(1 \pm S)}} \left(1_{Sa} \pm 1_{Sb}\right)$$

And our LCAO approximation is equivalent to this if we plug in the wavefunction directly.

$$E_\pm = \langle \psi_\pm | \hat{H} | \psi_\pm \rangle = N^2 \langle \left(1_{Sa} \pm 1_{Sb}\right) | \hat{H} | \left(1_{Sa} - 1_{Sb}\right) \rangle$$

We can see form above that the normalization constant squared results in:

$$N^2 = \frac{1}{2(1 \pm S)}$$

We now FOIL the mulitple (i.e., expaned term by term):

$$\langle 1_{Sa} | \hat{H} | 1_{Sa} \rangle + \langle 1_{Sb} | \hat{H} | 1_{Sb} \rangle \pm \langle 1_{Sa} | \hat{H} | 1_{Sb} \rangle \pm \langle 1_{Sb} | \hat{H} | 1_{Sa} \rangle$$

Now we can see this is now equivalent to Equation 10.4.3 if the equation above is inserted (and adding a subscript to emphasize this only applies to the electronic wavefunction):

$$E_\pm = \frac{1}{2(1 \pm S)} \left[\underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{BA}} \right]$$

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10.5: Bonding and Antibonding Orbitals

Learning Objectives

- Characterize the bonding and anti-bonding molecular orbitals in H^+

The two molecular orbitals of the H^+ ion were created via the linear combinations of atomic orbitals (LCAOs) approximation were created from the sum and the difference of two atomic orbitals. Within this approximation, the j[th] molecular orbital can be expressed as a linear combination of many atomic orbitals $\{\phi_i\}$:

$$|\psi_J\rangle = \sum_i^N c_{J,i}|\phi_i\rangle \tag{10.5.1}$$

A molecule will have as many molecular orbitals as there are atomic orbitals used in the basis set (N in Equation 10.5.1). Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1s orbitals is called a σ_{1s} combination (parts (a) and (b) of Figure 9.5.1).

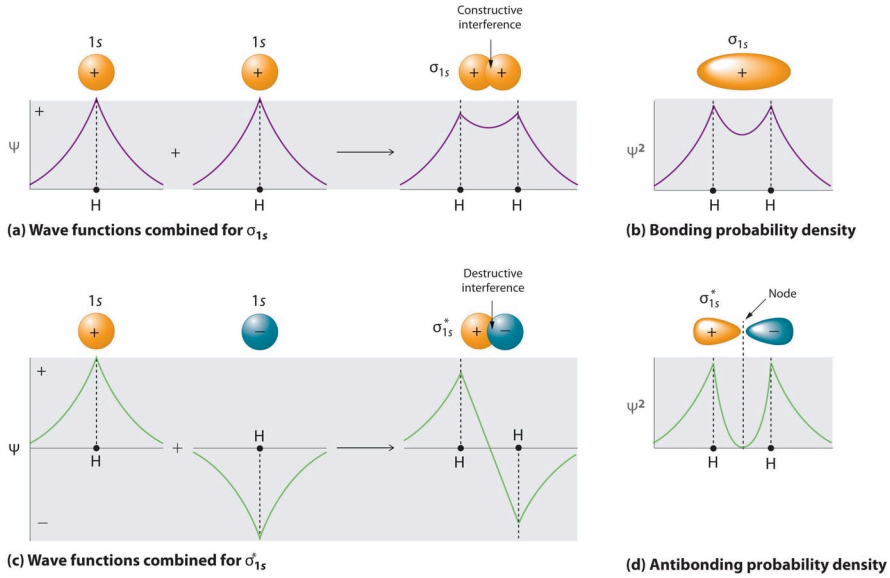


Figure 9.5.1 : Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wavefunctions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wavefunction (Ψ^2) for the bonding σ1s molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wavefunction.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the atomic orbital wavefunctions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wavefunction (Ψ2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei. (CC BY-SA-NC; anonymous).

In the sigma (σ) orbital, the electron density along the internuclear axis and between the nuclei has *cylindrical symmetry*; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1s denotes the atomic orbitals from which the molecular orbital was derived.

$$|\sigma_{1s}\rangle = \frac{1}{\sqrt{2(1+S)}}\left(|1s_A\rangle + |1s_B\rangle\right) \tag{10.5.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 9.5.1

). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ_{1s}^{*} and has a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$|\sigma_{1s}^{*}\rangle = \frac{1}{\sqrt{2(1-S)}}\left(|1s_A\rangle - |1s_B\rangle\right) \tag{10.5.3}$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wavefunctions. In contrast, electrons in the $\sigma_{1s}^{\star}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma_{1s}^{\star}$ orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wavefunctions).

> Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1s atomic orbitals. Conversely, electrons in the $\sigma_{1s}^{\star}$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1s atomic orbitals. Consequently, the $\sigma_{1s}^{\star}$ molecular orbital has a *higher* energy than either of the hydrogen 1s atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1s atomic orbitals, and the $\sigma_{1s}^{\star}$ (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure 9.5.2

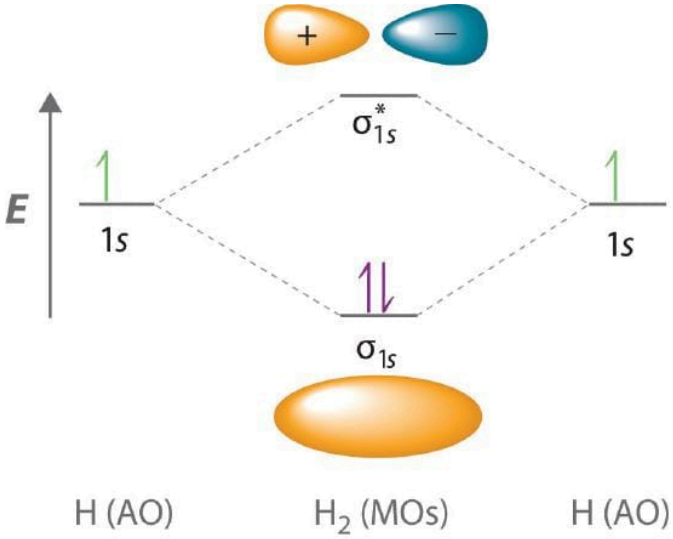


Figure 9.5.2 : Molecular Orbital Energy-Level Diagram for H2. The two available electrons (one from each H atom) in this diagram fill the bonding σ1s molecular orbital. Because the energy of the σ1s molecular orbital is lower than that of the two H 1s atomic orbitals, the H2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).

Expanding Beyond the 1s Orbital Basis Set

This picture of bonding in H_2^+ in the previous section is very simple, but gives reasonable results when compared to an exact calculation. The equilibrium bond distance is 134 pm compared to 106 pm (exact), and a dissociation energy is 1.8 eV compared to 2.8 eV (exact). To better describe chemical bonding we need to account for the increase in electron density between the two nuclei. The 1s orbitals alone are not particularly good for this purpose because they are spherically symmetric and show no preference for the space between the atomic nuclei. The use of additional atomic orbitals can correct this situation and provide

additional parameters, which can be optimized by the linear variational method, to give a better function with a lower energy and more accurate description of the charge density.

The energy of the non-normalized molecular orbital can be calculated from the expectation value integral of the Hamiltonian,

$$E_J = \frac{\left\langle \psi_J | \hat{H}_{elec} | \psi_J \right\rangle}{\langle \psi_J | \psi_J \rangle} \tag{10.5.4}$$

This is the variational energy using $|\psi_J\rangle$ as the trail wavefunction. After substituting the LCAO expansion for $|\psi_J\rangle$ (Equation 10.5.1) into the energy expression of Equation 10.5.4 results in:

$$E_J = \frac{\left\langle \sum_i c_{J,i}^* \phi_i \middle| \hat{H}_{elec} \middle| \sum_j c_{J,i} \phi_j \right\rangle}{\left\langle \sum_i c_{J,i}^* \phi_j \middle| \sum_j c_{J,j} \phi_j \right\rangle} \tag{10.5.5}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} \langle \phi_i | \hat{H}_{elec} | \phi_j \rangle}{\sum_{i,j} c_{J,i}^* c_{J,j} \langle \phi_i | \phi_j \rangle} \tag{10.5.6}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} H_{ij}}{\sum_{i,j} c_{J,i}^* c_{J,j} S_{ij}} \tag{10.5.7}$$

where H_{ij} is the Hamiltonian matrix element.

$$H_{ij} = \langle \phi_i | \hat{H}_{elec} | \phi_j \rangle$$

Following the variational theorem, to determine the coefficients of the LCAO expansion c_i, we need to minimize E_J

$$\frac{\partial E_J}{\partial c_k} = 0 \tag{10.5.8}$$

for all k. This requires solving N linear equations to hold true (where N is the number of atomic orbitals in the basis)

$$\sum_{i=1}^{N} c_i (H_{ki} - E S_{ki}) = 0 \tag{10.5.9}$$

These equations are the **secular equations** and were discussed previously in the context of the linear variational method approximation. For the two basis set expansion (N) in Figure 9.5.1 , these are

$$\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) &= 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) &= 0 \end{aligned} \tag{10.5.10}$$

where c_1 and c_2 are the coefficients in the linear combination of the atomic orbitals used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{10.5.11}$$

Solving these secular equations with N different atomic orbitals in the expansion (Equation 10.5.1) requires finding the N roots of an N order polynomial.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \ldots \\ H_{12} - ES_{12} & H_{22} - ES_{22} & \ldots \\ \ldots & \ldots & \ldots \end{vmatrix} = 0 \tag{10.5.12}$$

Each molecular orbital ($|\psi_J\rangle$) from this treatment has an energy E_J that is given by a different set of coefficients, $\{c_{ij}\}$ where i runs over all N functions in the basis (i.e., number of the atomic orbitals in the LCAO approximation of Equation 10.5.1), and J runs over molecular orbitals. Solve the set of linear equations using that specific E_J to determine c_{ij} values.

Steps in a Solving the Secular Equations

1. Select a set of N basis functions
2. Determine all N(N –1)/2 values of both H_{ij} and S_{ij}
3. Form the secular determinant; determine N roots E_j of secular equation
4. For each E_J solve the set of linear equations to determine the basis set coefficients \(c_{ij\}) for the j-th molecular orbital

For more information on solving the Secular equations check here.

The greater the number of atomic orbitals N that combine to genera the molecular orbitals (Equation 10.5.1), the more accurate the LCAO approximation is. This is expected based on our discussions of the variational method examples. Hence, the ψ_+ and ψ_- molecular orbitals for H_2^+ are better expressed with higher energy hydrogenic wavefunctions

$$|\psi_J\rangle = c_{J,1}1s_A + c_{J,2}1s_B + c_{J,3}2s_A + c_{J,4}2s_B + c_{J,5}2p_{z,A} + c_{J,6}2p_{z,B} \tag{10.5.13}$$

The reasons that only the p_z atomic orbitals are included in this expansion are discussed later.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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10.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, ψ_i, as a linear combination of other functions, φ_j, which are called basis functions because they provide the basis for representing the molecular orbital.

$$|\psi_i\rangle = \sum_j c_{ij}\varphi_j \tag{10.6.1}$$

where

- j is the index for the jth basis function (e.g., atomic orbital)
- i is the ith molecular orbitals and
- c_{ij} is the expansion coefficient of the jth basis function for the ith molecular orbital.

The variational method is used to find values for parameters in the basis functions and for the constant coefficients in the linear combination that optimize these functions, i.e. make them as good as possible. The criterion for quality in the variational method is making the ground state energy of the molecule as low as possible. Here and in the rest of this chapter, the following notation is used: σ is a general spin function (can be either α or β), φ is the basis function (this usually represents an atomic orbital), ψ is a molecular orbital, and Ψ is the electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. Just as for atoms, each electron in a molecule can be described by a product of spin-orbitals. Since electrons are fermions, the electronic wavefunction must be **antisymmetric** with respect to the permutation of any two electrons. A Slater determinant containing the molecular spin orbitals produces the antisymmetric wavefunction. For example for two electrons,

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_A(r_1)\alpha(1) & \psi_B(r_1)\beta(1) \\ \psi_A(r_2)\alpha(2) & \psi_B(r_2)\beta(2) \end{vmatrix} \tag{10.6.2}$$

Solving the Schrödinger equation in the orbital approximation will produce a set of spatial molecular orbitals, each with a specific energy, ϵ. Following the Aufbau Principle, two electrons with different spins (α and β, consistent with the Pauli Exclusion Principle discussed for muliti-electron atoms) are assigned to each spatial molecular orbital in order of increasing energy. For the ground state of the 2n electron molecule, the n lowest energy spatial orbitals will be occupied, and the electron configuration will be given as $\psi_1^2\psi_2^2\psi_3^2 \ldots \psi_n^2$. The electron configuration also can be specified by an orbital energy level diagram as shown in Figure 9.6.1 . Higher energy configurations exist as well, and these configurations produce excited states of molecules. Some examples are shown in Figure 9.6.1 .

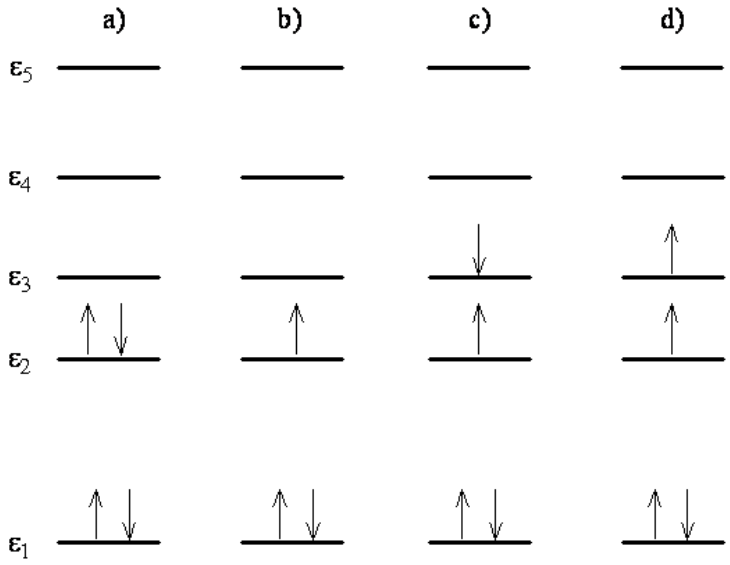


Figure 9.6.1 : a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration.

Symmetry

Molecular orbitals usually are identified by their symmetry or angular momentum properties. For example, a typical symbol used to represent an orbital in an electronic configuration of a diatomic molecule is $2\sigma_g^2$. The superscript in symbol means that this orbital is occupied by two electrons; the prefix means that it is the second sigma orbital with *gerade* symmetry.

Diatomic molecules retain a component of angular momentum along the internuclear axis. The molecular orbitals of diatomic molecule therefore can be identified in terms of this angular momentum. A Greek letter, e.g. σ or π, encodes this information, as well as information about the symmetry of the orbital. A σ means the component of angular momentum is 0, and there is no node in any plane containing the internuclear axis, so the orbital must be symmetric with respect to reflection in such a plane. A π means there is a node and the wavefunction is antisymmetric with respect to reflection in a plane containing the internuclear axis. For homonuclear diatomic molecules, a *g* or a *u* is added as a subscript to designate whether the orbital is symmetric or antisymmetric with respect to the center of inversion of the molecule.

A homonuclear diatomic molecule has a center of inversion in the middle of the bond. This center of inversion means that $\psi(x,y,z) = \pm\psi(-x,-y,-z)$ with the origin at the inversion center. Inversion takes you from (x,y,z) to $(-x,-y,-z)$. For a heteronuclear diatomic molecule, there is no center of inversion so the symbols g and u are not used. A prefix 1, 2, 3, etc. simply means the first, second, third, etc. orbital of that type. We can specify an electronic configuration of a diatomic molecule by these symbols by using a superscript to denote the number of electrons in that orbital, e.g. the lowest energy configuration of N_2 is

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 \tag{10.6.3}$$

Contrasting LCAO with other Quantum Chemistry Methods

As we have already seen, the LCAO approach is very approximate, yielding only qualitative results. It should be noted that the Hartree-Fock method discussed earlier for atoms can also be used for molecules. For example, the molecule He_2^+ has three electrons, and the Li atom also has three electrons. As usual with Hartree-Fock, the idea is to optimize the shapes of the single-electron orbitals $\psi_1(r)$, $\psi_2(r)$ and $\psi_3(r)$ by minimizing the guess to the ground state energy E_g. Of course, we will not get the same answer as for Li because there is a different V_{en} energy for He_2^+ due to the presence of two positively charge nuclei $(charge = +2e)$ separated by a distance R in contrast to the single $+3e$ charged nucleus for Li. When the shapes of the orbitals are optimized, we also obtain three energy ε_1, ε_2 and ε_3. Not unexpectedly, we find that two of the HF orbitals resemble $1\sigma_g$ while the third resembles $1\sigma_u^*$ and the first two energies ε_1 and ε_2 will be nearly equal, while the third ε_3 will

be noticeably higher. To contrast with the LCAO approach, in LCAO, we do not optimize the shapes of the orbitals (these are assumed *a priori* to be $1s$ shaped). All we do is choose the mixing coefficients so as to minimize the guess to the ground-state energy E_g.

We note, finally, that the density functional theory alluded to earlier can also be used for molecules. It is often the case that density functional theory yields a more accurate description than Hartree-Fock, but this depends on the molecule. In any case, both are more accurate than LCAO. There is also a hierarchy of methods called *post Hartree-Fock* methods, all of which are based on the wavefunction rather than the electron density, that can be used to improve upon the HF approximation systematically. The greater the accuracy that is desired for the calculation, the more costly computationally the post HF methods become, so quantum chemistry is often a trade-off between accuracy and efficiency, an issue that becomes more critical to take into account when calculations on large molecules must be carried out!

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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10.7: Molecular Orbitals Can Be Ordered According to Their Energies

The LCAO-MO method that we used for H_2^+ can be applied qualitatively to homonuclear diatomic molecules to provide additional insight into chemical bonding. A more quantitative approach also is helpful, especially for more complicated situations, like heteronuclear diatomic molecules and polyatomic molecules. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they are often ignored in constructing molecular orbitals. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

Molecular Orbitals Formed from *ns* Orbitals

The molecular orbitals diagrams formatted for the dihydrogen species are similar to the diagrams to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 9.7.1 , where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

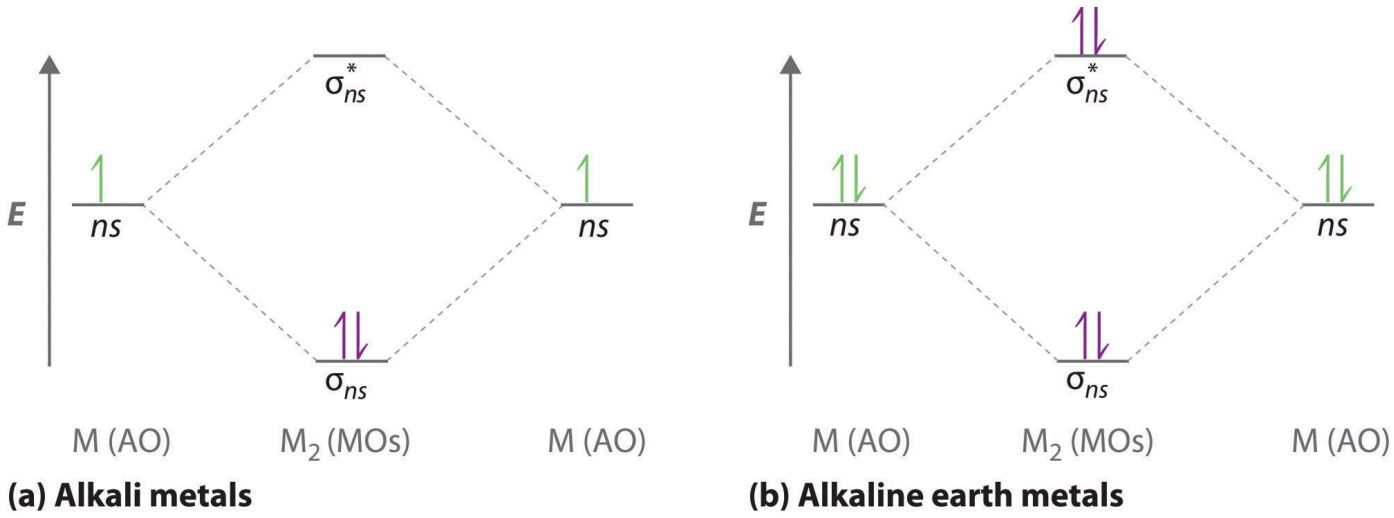


Figure 9.7.1 : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σns (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ^*_{ns} (nonbonding) levels, leading to a predicted bond order of 0. (CC BY-SA-NC; anonymous).

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule. As shown in Figure $10.7.1b$, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

Example 9.7.1 : Sodium Dimer Ion

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

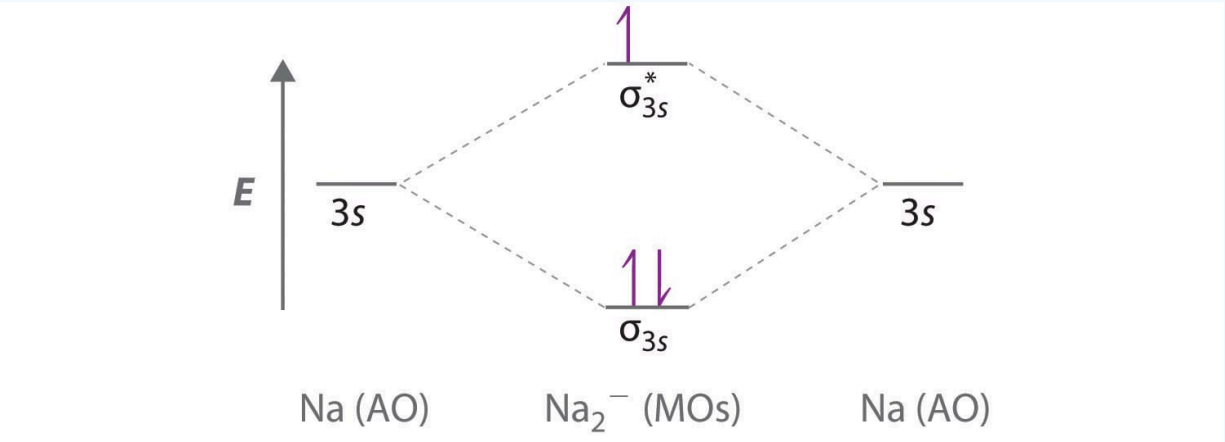
Strategy

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1s atomic orbitals.

B The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s^*} and a $(\sigma_{3s})^2(\sigma_{3s}^\star)^1$ electron configuration.



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C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

Exercise 9.7.1 : Calcium Dimer Cation

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer available at the end of this section.

Molecular Orbitals Formed from n*p* Orbitals

Atomic orbitals other than *n*s orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{10.7.1}$$

Just as with *n*s orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 9.7.2 , it is the mathematical *difference* of their wavefunctions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{10.7.2}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z\,(A) + np_z\,(B) \tag{10.7.3}$$

In this combination, shown in part (b) in Figure 9.7.2 , the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z\,(A) - np_z\,(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

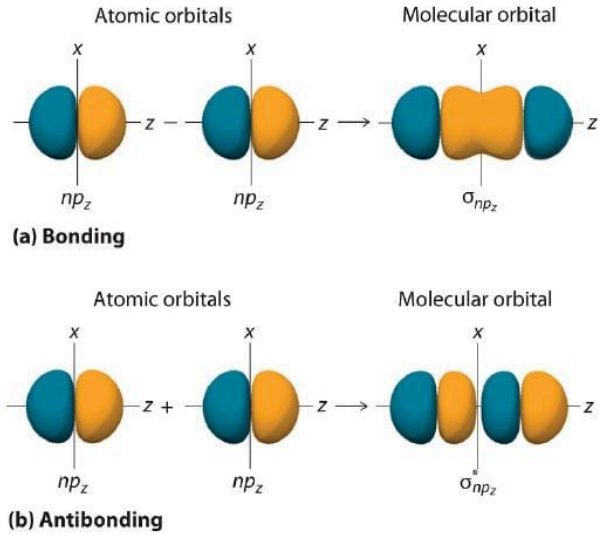


Figure 9.7.2 : Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the z-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate – + – +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 9.7.3 , we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on

one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{10.7.4}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{10.7.5}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^{\star}_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y}molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

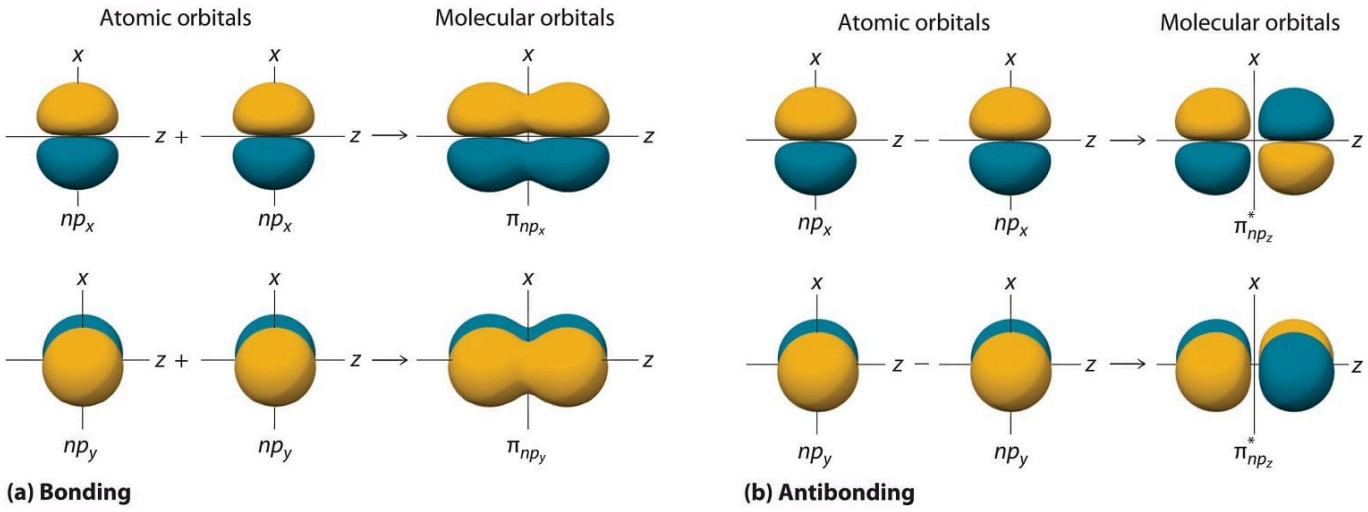


Figure 9.7.3 : Formation of π Molecular Orbitals from npx and npy Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the npx and the npy atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

Energies for Homonuclear Diatomic Molecules

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

Figure 9.7.4 is an energy-level diagram that can be applied to two *identical* interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a

σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

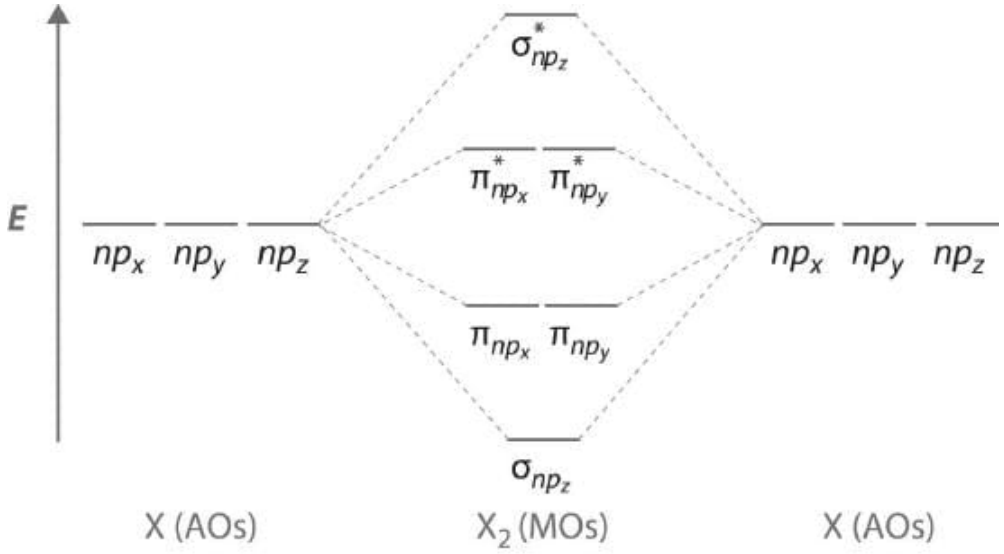


Figure 9.7.4 : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals. (CC BY-SA-NC; anonymous).

The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in Figure $10.7.5a$; the n = 1 orbitals (σ_{1s} and σ_{1s}*) are located well below those of the n = 2 level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^\star_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^\star_{2p_x}$ and $\pi^\star_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rules. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons.

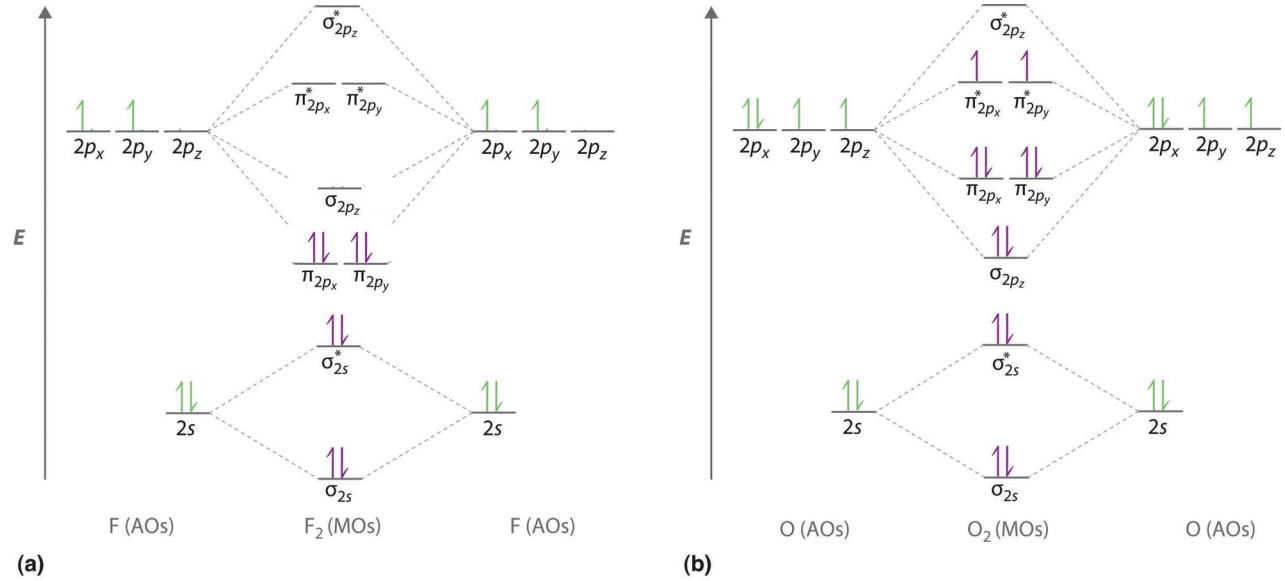


Figure 9.7.5 : Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For C_2, with 8 valence electrons (4 from each F atom). This diagram shows 6 electrons in bonding orbitals and 2 in antibonding orbitals, resulting in a bond order of 2. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^{\star}_{np_x}, \pi^{\star}_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. (CC BY-SA-NC; anonymous).

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the $2p_z$ orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 9.7.6 . Experimentally, the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 9.7.6). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

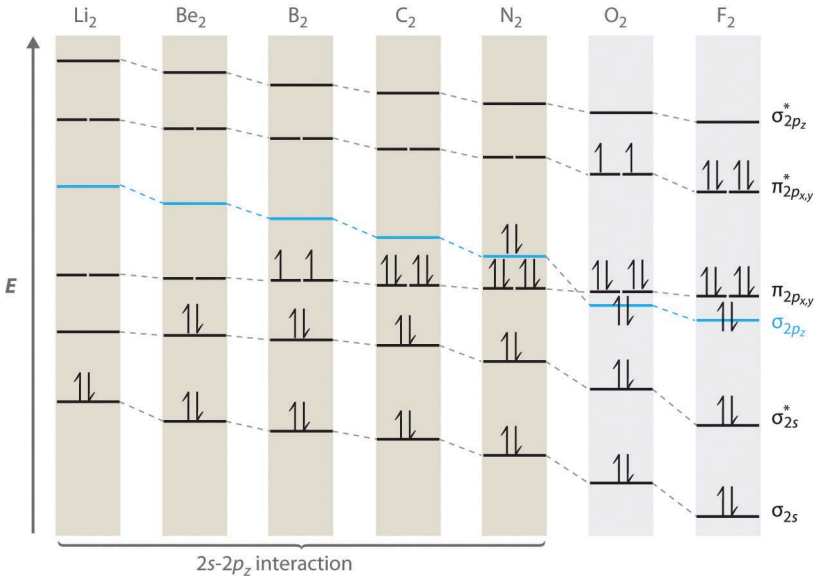


Figure 9.7.6 : Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is lower in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2s and 2*p* atomic orbitals as the nuclear charge increases across the row. (CC BY-SA-NC; anonymous).

Example 9.7.2 : Diatomic Sulfur

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

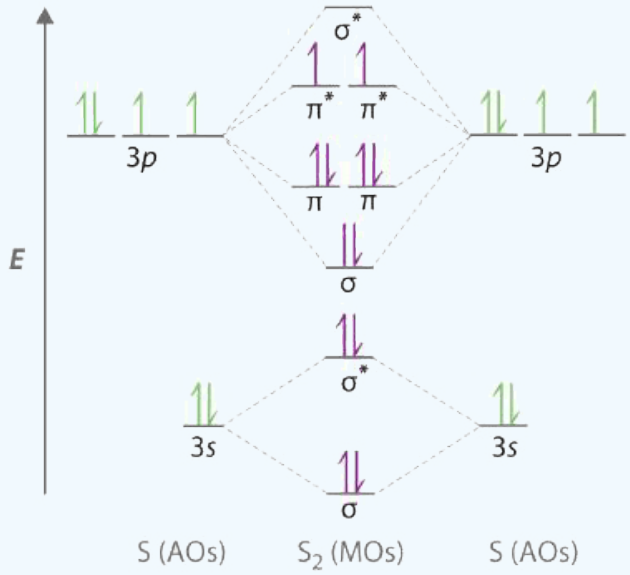
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a [Ne]$3s^2 3p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figures 9.7.6 and 9.7.7 , we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases, the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



(CC BY-SA-NC; anonymous).

Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^{\star}_{3p_x}$ and $\pi^{\star}_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2 (\sigma^{\star}_{3s})^2 (\sigma_{3p_z})^2 (\pi_{3p_{x,y}})^4 (\pi_{3p^{\star}_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 – 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise 9.7.2

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer available at the end of this section.

Molecular Orbitals Formed from *ns* with n*p* Orbitals

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 9.7.7 , the sum of the two atomic wavefunctions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

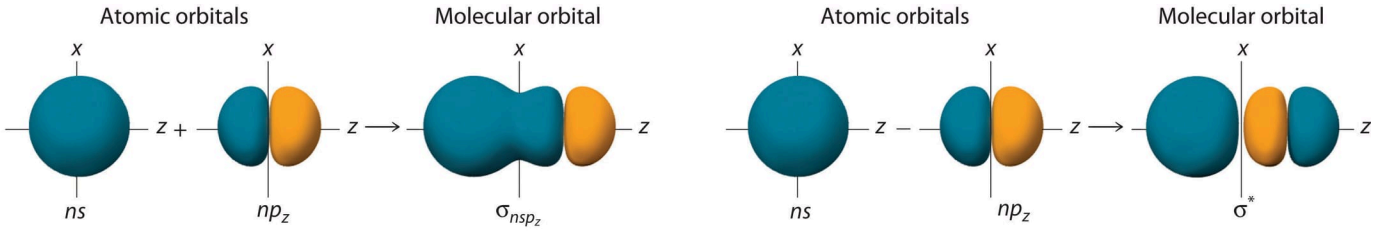


Figure 9.7.7 : Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

Answers

Ca_2^+ has a $(\sigma_{4s})^2 (\sigma_{4s}^\star)^1$ electron configurations and a bond order of 1/2 and should exist.

$(\sigma_{2s})^2 (\sigma_{2s}^\star)^2 (\sigma_{2p_z})^2 (\pi_{2p_{x,y}})^4 (\pi_{2p_{x,y}^\star})^4$ bond order of 1; no unpaired electrons

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10.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

Learning Objectives

- Using bond order as a metric for the existance of molecules

Bond Order

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. Within the molecular orbital approach, *bond order* is defined as one-half the *net* number of bonding electrons:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \tag{10.8.1}$$

To calculate the bond order of H_2, we know that the σ_{1s} (bonding) molecular orbital contains two electrons, while the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\text{bond order} = \frac{2-0}{2} = 1 \tag{10.8.2}$$

This result corresponds to the single covalent bond; double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams to describe the bonding in other pairs of atoms and ions where *n* = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's Rules.

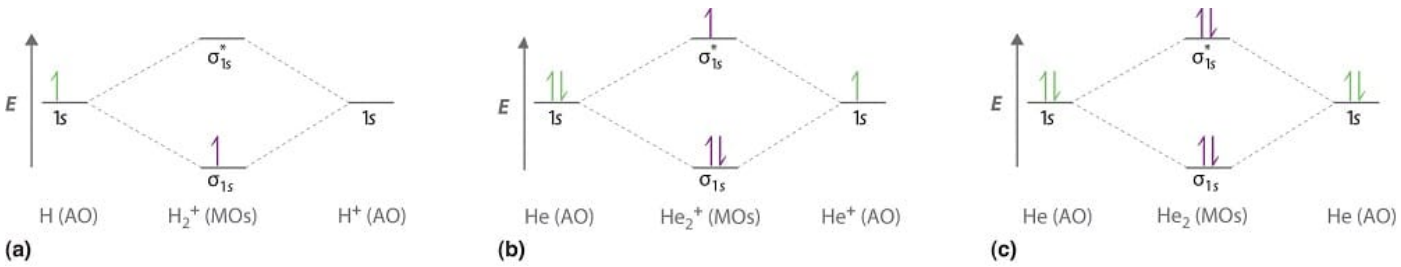


Figure 9.8.1 : Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here. (CC BY-SA-NC; anonymous)

Figure $10.8.1a$ shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (via Equation 10.8.1)

$$\text{bond order} = \frac{1-0}{2} = 1/2$$

Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 9.8.1 , these predictions agree with the experimental data.

Table 9.8.1 : Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Species	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2 (\sigma^\star_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2 (\sigma^\star_{1s})^2$	0	5,500	4.6×10^{-5}

Figure $10.8.1b$ is the molecular orbital energy-level diagram for $\mathrm{He_2}^{2+}$. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the $\sigma^\star_{1s}$ antibonding orbital, giving a $(\sigma_{1s})^2 (\sigma^\star_{1s})^1$ electron configuration. This electron configuration gives a bond order (via Equation $10.8.1$) of

$$\text{bond order} = \frac{2-1}{2} = 1/2$$

As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 9.8.1).

Example 9.8.1 : The ion $\mathrm{He_2}^{2+}$

Use a molecular orbital energy-level diagrams to predict the bond order and stability of the $\mathrm{He_2}^{2+}$ ion.

Given: chemical species

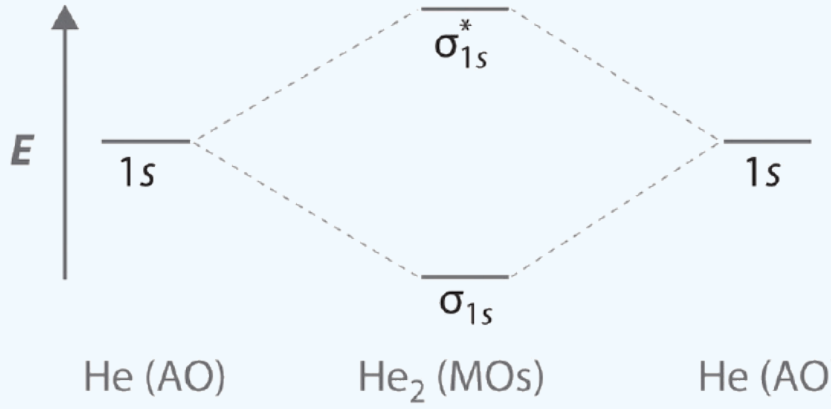
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

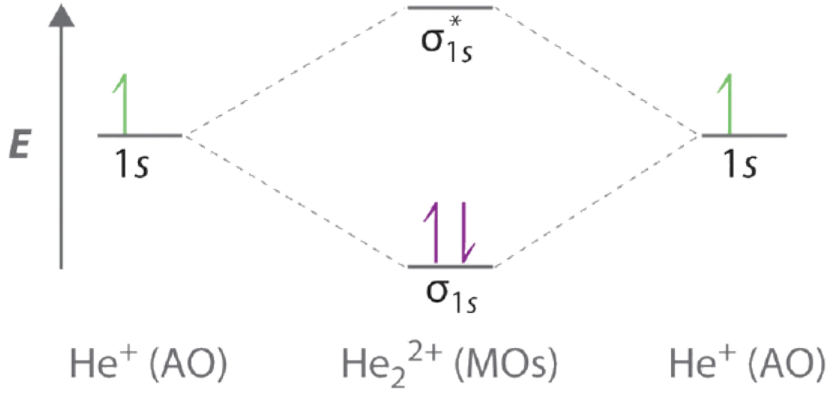
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1s atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a $\sigma^\star_{1s}$ antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1s atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired.

C So the bond order is (via Equation 10.8.1)

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise 9.8.1 : The Ion H_2^{2-}

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer available at the end of this section.

The Helium Dimer

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure 10.8.1c is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and $\sigma_{1s}^{\star}$ antibonding orbitals must

contain two electrons. This gives a $(\sigma_{1s})^2 (\sigma^\star_{1s})^1$ electron configuration, with a predicted bond order (via Equation 10.8.1) of

$$\text{bond order} = \frac{2-2}{2} = 0 \tag{10.8.3}$$

which indicates that the He_2 molecule has no net covalent bond and is not a stable species.

The ability to track bond order to bond strength is due to the fact that the energy difference between the anti-bonding $\sigma^\star_{1s}$ molecular orbital and the original $1s$ atomic orbital is *larger* than the energy difference between the bonding σ_{1s} molecular orbital and the $1s$ atomic orbitals. This was derived previously where the stabilization energy (ΔE_+) of the σ_{1s} molecular orbital is less than the destabilization energy (ΔE_-) of the anti-bonding $\sigma^\star_{1s}$ molecular orbital:

$$\Delta E_\pm = E_\pm - E_H \tag{10.8.4}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{10.8.5}$$

Hence, the anti-bonding $\sigma^\star_{1s}$ molecular orbital is more destabilized relative to the atomic orbitals than the bonding σ_{1s} molecular orbital is stabilized relative to the $1s$ atomic orbitals (E_H.

The fact that the anti-bonding MO energy difference is larger than the bonding σ_{1s} molecular orbital energy difference is the true reason that helium dimer is not predicted to exist with a covalent bond. Of the four valence electrons in helium dimer, two will fill the bonding σ_{1s} molecular orbital, and the other two will fill the anti-bonding $\sigma^\star_{1s}$ molecular orbital. The two electrons in the bonding σ_{1s} molecular orbital will achieve some stabilization relative to the $1s$ atomic orbitals, but the two electrons in the anti-bonding $\sigma^\star_{1s}$ molecular orbital will achieve *greater* de-stabilization relative to their position in the atomic orbitals. The net result is a less stable molecule than if the electrons remained in their respective $1s$ atomic orbitals.

> The *electrons in antibonding orbitals cancel (and exceed) the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature (at least as a covalently bonding complex).

However, Van der Waals Helium Dimers do exist

Based on molecular orbital theory discussed above, the $\mathrm{He_2}$ molecule should not exist since no covalent bond formed between the helium atoms (Equation 10.8.3). However, the molecular orbital description above neglects the van der Waals force that exists between the atoms as demonstrated by the existence of liquid helium (at 4 K). So a "molecule" composed of two helium atoms bound by the van der Waals force may exist by this attractive force instead - and it does.

A helium dimer molecule bound by Van der Waals forces was first proposed by John Clarke Slater in 1928 and observed in 1993 by Gentry and coworkers. Interestingly, $\mathrm{He_2}$ is the largest known molecule of two atoms when in its ground state with an extremely long bond length with a separation of about 5,200 pm. The binding energy is only $4.6 \times 10^{-5}\ kJ/mol$, so the $\mathrm{He—He}$ bond is 5,000 times weaker than the covalent bond in the hydrogen molecule (Table 9.8.1).

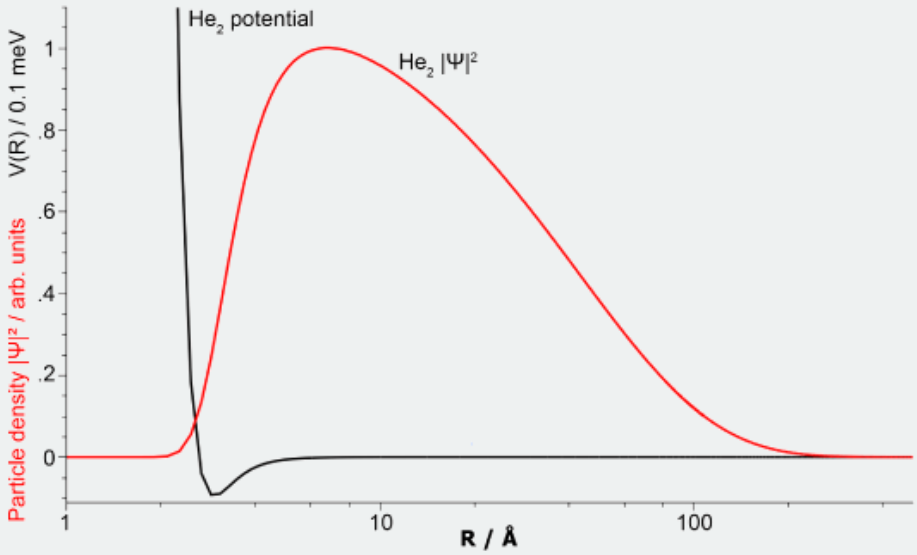


Figure 9.8.2 : The weak helium-helium Van der Waals potential decrease leads to the particle probability density distribution leaking more into the classically forbidden region (i..e, tunneling). This effect allows the wavefunction to extend to sizes of fullerenes, the diameter of DNA and even small viruses ($\mathrm{He_2}$ potential and wavefunction taken from Przybytek 2010), while the classical turning point is located at 13.6 Å, the overall wavefunction extends to more than 200 Å. (Inspire; http://inspirehep.net/record/1415151/plots)

Conclusion

The decrease in energy caused by the bonding orbital (constructive interference of the atomic orbitals) is canceled by the increase in energy caused by the antibonding orbital (destructive interference of the atomic orbitals), so it is not energetically favorable for the helium atoms to be in such proximity, so if that situation arises, they'll separate quickly since there's no force keeping them there.

Answers

$\mathrm{H_2}^{2-}$ has a valence electron configuration of $(\sigma_{1s})^2 (\sigma_{1s}^*)^2$ with a bond order of 0. It is therefore predicted to be unstable.

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10.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle

Just like with multielectron atoms, there are restrictions on how electrons occupy molecular orbitals. The most important of these rules is the Pauli exclusion principle, which we will not try to prove but will take as a fact. In general chemistry, you were told that the Pauli exclusion principle means that electrons in the same orbital must have opposite spin, and that only two electrons can be in each orbital. That is close, but not entirely accurate. The true statement of the Pauli exclusion principle is this: wavefunctions must be antisymmetric with respect to exchange of identical fermions, and symmetric with respect to exchange of identical bosons. A is a particle with half-integer spin, and a is a particle with integer spin. Recall that electrons are fermions (spin 1/2): we represent the two possible spin states as $|\alpha\rangle$ ($m_z = 1/2$) and $|\beta\rangle$ ($m_z = -1/2$), according to their spin projections.

Because all electrons are identical, the Pauli exclusion principle requires that the electronic wavefunction be antisymmetric with respect to exchanging any of them.[2] The word “antisymmetric” in this context means that if we swap two electrons (i.e., exchange their labels), the wavefunction must change sign. To denote both the orbital of an electron and its spin, we use a product of , each of the form $|\psi\sigma\rangle$, where ψ depends only on the spatial coordinates of the electrons, and σ depends only on their spins.

In the ground electronic state of , the electrons both occupy the $|1\sigma\rangle$ spatial orbital. Naively, we could write the following product of spin orbitals:

$$|\psi\rangle = |1\sigma^1\alpha^1\rangle|1\sigma^2\beta^2\rangle \tag{10.9.1}$$

where the superscript refers to the electron number. Note that since the spatial and spin coordinates are independent of one another, we can group them into kets in whichever way is most convenient for us at the time. Let us define the permutation operator $\hat{p}_{12}$, which swaps the labels of electrons 1 and 2, in order to test the wavefunction for asymmetry in accordance with the **Pauli Exclusion Principle**. It is clear that the electronic wavefunction we wrote above does not change sign under this permutation operation!

$$\hat{p}_{12}|\psi\rangle = |1\sigma^2\alpha^2\rangle|1\sigma^1\beta^1\rangle \neq -|\psi\rangle. \tag{10.9.2}$$

Instead, we can take a linear combination of spin functions to make a new wavefunction:

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle - |1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle\right) \tag{10.9.3}$$

Since the Hamiltonian did not contain any terms that depend on spin, the energy of this new wavefunction is equal to the energy of our original wavefunction.[3] We can use the permutation operator $\hat{p}_{12}$ to see that this wavefunction is in fact antisymmetric:

$$\begin{aligned}\hat{p}_{12}|\psi\rangle &= \frac{1}{\sqrt{2}}\left(|1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle - |1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle\right)\\ &= -\frac{1}{\sqrt{2}}\left(|1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle - |1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle\right)\\ &= -|\psi\rangle.\end{aligned} \tag{10.9.4}$$

We see here that the orbital is not occupied by one electron of each spin, but in fact it is occupied electrons in a superposition of spin states. In larger systems, antisymmetrized wavefunctions show that each orbital is occupied by a superposition of all electrons in the system in both spin states. Although that is difficult to conceptualize, in most practical cases the electrons can still be thought of as localized in one particular orbital with one particular spin.

There is a standard procedure to generate an appropriately antisymmetrized electronic wavefunction from any set of single-electron functions. Like in multi-electron atoms, the general method for doing this is by use of a Slater determinant: a determinant in which each column contains the product of one molecular orbital and spin function for each possible labeling of the electrons. For our system above (two electrons in $|1\sigma\rangle$, one with spin α, and the other with spin β), we would write

$$|\psi\rangle = \frac{1}{\sqrt{2!}}\begin{vmatrix} |1\sigma^1\alpha^1\rangle & |1\sigma^1\beta^1\rangle \\ |1\sigma^2\alpha^2\rangle & |1\sigma^2\beta^2\rangle \end{vmatrix}, \tag{10.9.5}$$

where once again the superscript indicated the label on the electron. The Slater determinant therefore contains all of the possible ways that we could assign numbers to the electrons in the system.

Note

A few things to know about Slater determinants:

- If two columns are swapped, the determinant changes sign (this is why it satisfies the exclusion principle!).
- If any two columns in a determinant are the same, the determinant is 0. This is why the Pauli exclusion principle only allows one electron of each spin to occupy a single orbital, which you learned way back in Gen Chem. It also directly leads to the "Aufbau" principle: when populating molecular orbitals, we fill up orbitals in order of increasing energy with two electrons each.
- The energy of a Slater determinant (in the independent particle approximation) is simply the sum of the orbitals that make it up (i.e., add up the energy of each electron in the MO diagram).
- The wavefunction described by a Slater determinant is normalized if the individual orbitals that make it up are normalized.
- Two Slater determinants are orthogonal if they differ in any single orbital.

Given an MO diagram, it is easy to generate a Slater determinant for the ground electronic state of a closed-shell molecule using general chemistry rules: the Aufbau principle and the Pauli exclusion principle. Each orbital can accommodate one electrons of each spin, and electrons are placed into orbitals from lowest to highest energy. A system with N electrons in the orbitals $|\phi_1\rangle$, $|\phi_2\rangle$, etc., will generate an $N \times N$ dimensional Slater determinant, and the general form is (if N is even):

$$|\psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\phi_1^1\alpha^1\rangle & |\phi_1^1\beta^1\rangle & |\phi_2^1\alpha^1\rangle & |\phi_2^1\beta^1\rangle & \cdots & |\phi_{N/2}^1\alpha^1\rangle & |\phi_{N/2}^1\beta^1\rangle \\ |\phi_1^2\alpha^2\rangle & |\phi_1^2\beta^2\rangle & |\phi_2^2\alpha^2\rangle & |\phi_2^2\beta^2\rangle & \cdots & |\phi_{N/2}^2\alpha^2\rangle & |\phi_{N/2}^2\beta^2\rangle \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ |\phi_1^N\alpha^N\rangle & |\phi_1^N\beta^N\rangle & |\phi_2^N\alpha^N\rangle & |\phi_2^N\beta^N\rangle & \cdots & |\phi_{N/2}^N\alpha^N\rangle & |\phi_{N/2}^N\beta^N\rangle \end{vmatrix} \tag{10.9.6}$$

Once again, each column contains the orbital and spin state of one of the electrons in the diagram, and each row in the column corresponds to a different choice of label (1, 2, 3, etc...). Evaluating the determinant yields a normalized, antisymmetrized wavefunction. Therefore, an MO diagram can stand as an effective substitute for an electronic wavefunction; it is implied that the true wavefunction used in calculations comes from the Slater determinant described by the diagram.

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10.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic

Learning Objectives

- To describe the connection between bond order, bond length and bond energy in diatomic molecules
- To explain the observed paramagnetic properties of molecular oxygen with Molecular Orbital theory

In general chemistry courses, students learn that covalent bonds can come as either single, double or triple bonds, which are identifies by their bond order. Both bond length and bond energy changes as the bond order increases and as the number of electrons shared between two atoms in a molecule increases, the bond order of a bond increases, the strength of the bond increases and the distance between nuclei decreases (Table 9.10.1).

Table 9.10.1 : General Correlation between Bond Strength, length and order in Covalent bonds

Bond	Bond Order	Bond Enthalpy (kJ/mol)	Bond Length (Å)
C−C	1	348	1.54
C=C	2	614	1.34
C≡C	3	839	1.20
N−N	1	163	1.47
N=N	2	418	1.24
N≡N	3	941	1.10

The above trend can be observed in the first row diatomics in Figure 9.10.1 . The bond order can be determined directly form the molecular orbital electron configurations. For diatomics, the occupations can correlate to bond length, bond energies (Figure 9.10.1).

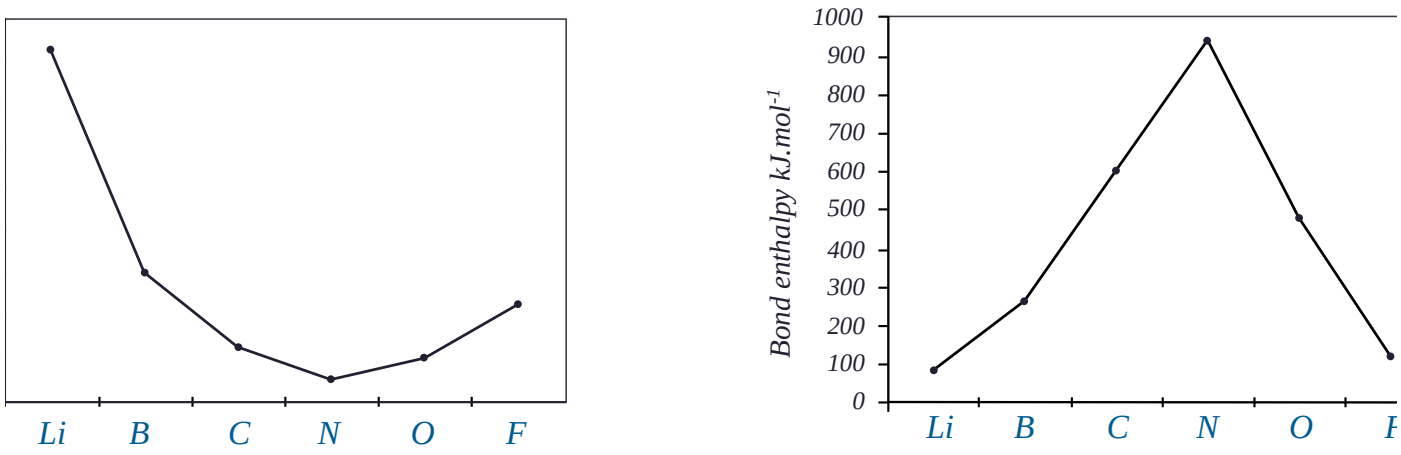


Figure 9.10.1 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

The trends in Figure 9.10.1 and Table 9.10.1 extend to molecular ions.

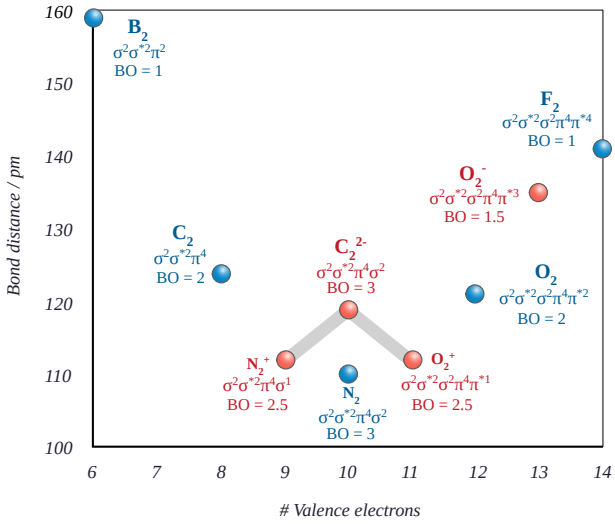


Figure 9.10.2 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

Example 9.10.1 : Molecular Oxygen

Arrange the following four molecular oxygen species in order of increasing bond length: O_2^+, O_2, O_2^-, and O_2^{2-}.

Solution

The bond length in the oxygen species can be explained by the positions of the electrons in molecular orbital theory. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in Figure 9.10.1 . We again fill the orbitals according to Hund's rules and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}^* orbitals, two more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. According to Hund's first rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving a multiplicity of 3 (a triplet state) with two unpaired electrons. This leads to a predicted bond order of

$$\frac{8-4}{2}=2$$

which corresponds to a double bond, in agreement with experimental data: the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

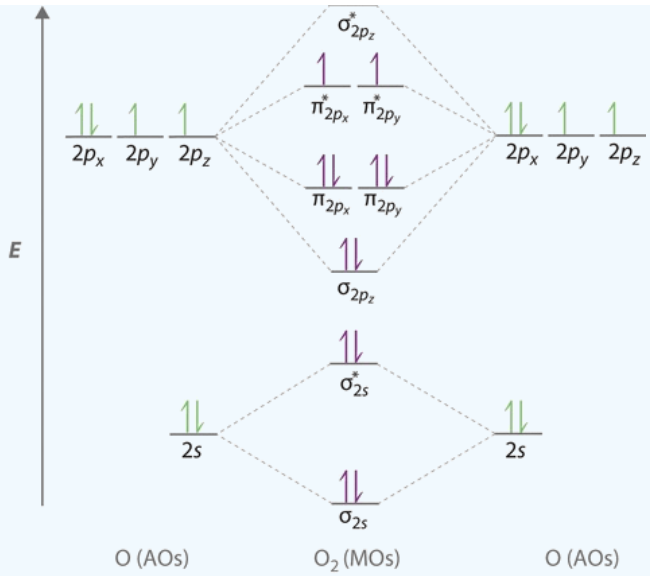


Figure 9.10.3 : Molecular Orbital Energy-Level Diagrams for O_2. With 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^\star_{np_x},\ \pi^\star_{np_y}\right)$ pair of orbitals. Hund's first rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. (CC BY-SA-NC; Anonymous by request).

The bond order is determined from the the electron configurations. The electron configurations for the four species are contrasted below.

- O_2:

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^1\pi_{2p_y}^{*\,1}$$

  From Equation ???, the bond order for O_2 is 2 (i.e., a double bond).
- $O_2{}^+$:

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^1\pi_{2p_y}^{*\,0}$$

  From Equation ???, the bond order for $O_2{}^+$ is 2.5. An alternative and equally valid configuration is

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^0\pi_{2p_y}^{*\,1}$$
- $O_2{}^-$:

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^2\pi_{2p_y}^{*\,1}$$

  From Equation ???, the bond order for $O_2{}^-$ is 1.5. An alternative and equally valid configuration is

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^1\pi_{2p_y}^{*\,2}$$
- $O_2{}^{2-}$:

  $$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_x}^2\pi_{2p_y}^{*\,2}$$

  From Equation ???, the bond order for $O_2{}^{2-}$ is 1.

The bond order decreases and the bond length increases in the order. The predicted order of increasing bondlength then is $O_2{}^+ < O_2 < O_2{}^- < O_2{}^{2-}$. This trend is confirmed experimentally with $O_2{}^+$ (112.2 pm), O_2 (121 pm), $O_2{}^-$ (128 pm) and $O_2{}^{2-}$ (149 pm).

Molecular Oxygen is Paramagnetic

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. None of the other bonding models (e.g., Valence Bond theory or Lewis bonding) can predict the presence of two unpaired electrons in O_2

. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Video 9.10.1 , it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 9.10.1 : Liquid O_2 Suspended between the Poles of a Magnet. Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

Advanced: Spin Barriers

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*.

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10.11: Photoelectron Spectroscopy

Learning Objectives

- Demonstrate how photoelectron spectroscopy can be used to resolve the absolute energies of molecular orbitals.

Photoelectron spectroscopy (PES) utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample.

- **X-ray Photoelectron Spectroscopy** (XPS) uses soft x-rays (with a photon energy of 200-2000 eV) to examine electrons in *core*-levels.
- **Ultraviolet Photoelectron Spectroscopy** (UPS) using vacuum UV radiation (with a photon energy of 10-45 eV) to examine electrons in *valence* levels.

Both photoelectron spectroscopies are based upon a single photon in/electron out process. The energy of a photon of all types of electromagnetic radiation is given by the Planck–Einstein relation:

$$E = h\nu \tag{10.11.1}$$

where h is Planck constant and ν is the frequency (Hz) of the radiation. UPS is a powerful technique to exam molecular electron structure since we are interested in the molecular orbitals from polyatomic molecules (especially the valence orbitals) and is the topic of this page.

Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy). In UPS the photon interacts with valence levels of the molecule or solid, leading to ionization by removal of one of these valence electrons. The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.

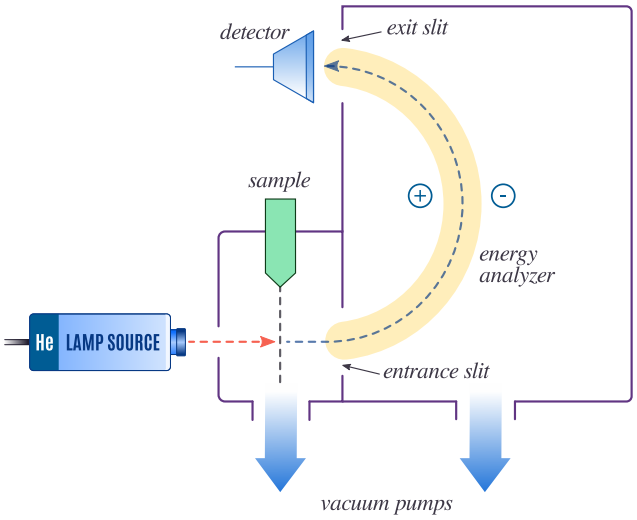


Figure 10.4.1: Diagram of a basic, typical PES instrument used in UPS, where the radiation source is an UV light source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit. (CC BY 4.0; Ümit Kaya via LibreTexts)

The process of photoionization can be considered in several ways. One way is to look at the overall process for a species A:

$$A + \text{photon} \rightarrow A^{+} + e^{-} \tag{10.11.2}$$

Conservation of energy then requires that (after using Equation 10.11.1):

$$E(A) + h\nu = E(A^+) + E(e^-) \tag{10.11.3}$$

Since the free electron's energy is present solely as kinetic energy (KE) (i.e., there is no internal energy in a free electron)

$$E(e^-) = KE$$

Equation 10.11.3 can then be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - \left[E(A^+) - E(A)\right] \tag{10.11.4}$$

The final term in brackets represents the difference in energy between the ionized and neutral species and is generally called the **vertical ionization energy** (IE) of the ejected electron; this then leads to the following commonly quoted equations:

$$KE = h\nu - IE \tag{10.11.5}$$

or

$$IE = h\nu - KE \tag{10.11.6}$$

The vertical ionization energy is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (i.e., a free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

Note

Equation 10.11.5 may look familiar to you as it the same equation Einstein used to describe the photoelectric effect except the vertical ionization energy (IE) is substituted for workfunction Φ. Both vertical ionization energy and workfunctions are metrics for the binding energy of an electron in the sample.

At a fundamental level, ionization energies are well-defined thermodynamic quantities related to the heats of protonation, oxidation/reduction chemistry, and ionic and covalent bond energies. Ionization energies are closely related to the concepts of electronegativity, electron-richness, and the general reactivity of molecules. The energies and other characteristic features of the ionization bands observed in photoelectron spectroscopy provide some of the molecular orbitals detailed and specific quantitative information regarding the electronic structure and bonding in molecules.

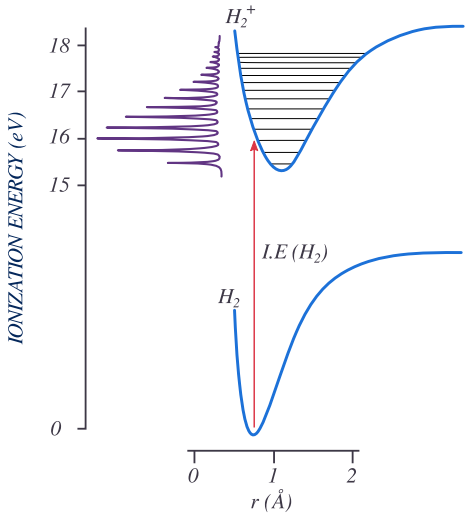


Figure 10.4.2: Vertical ionization process for molecular hydrogen. (CC BY 4.0; Ümit Kaya via LibreTexts)

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states as shown in Equation 10.11.6 and as illustrated in the Figure 10.4.2. Nonetheless, the information obtained from photoelectron spectroscopy is typically discussed in terms of the electronic structure and bonding in the ground states of neutral molecules, with ionization of electrons occurring from bonding molecular orbitals, lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals by Koopmans' theorem, which states that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the *vertical ionization energy* to the ion state formed by removal of an electron from that orbital (Figure 10.4.3), provided the distributions of the remaining electrons do not change (i.e., frozen).

$$I_j = -\epsilon_j \tag{10.11.7}$$

There are many limitations to Koopmans' theorem, but in a first order approximation each ionization of a molecule can be considered as removal of an electron from an individual orbital. The ionization energies can then be considered as measures of orbital stabilities, and shifts can be interpreted in terms of orbital stabilizations or destabilizations due to electron distributions and bonding. Koopmans' theorem is implicated whenever an orbital picture is involved, but is not necessary when the focus is on the total electronic states of the positive ions.

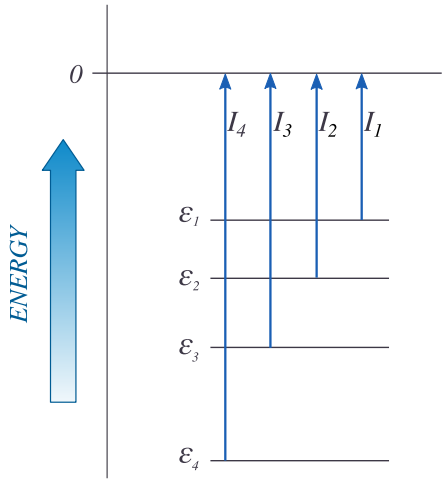


Figure 10.4.3: Within Koopmans' Theorem, the energies of the orbitals ϵ have an attractively simple physical interpretation: they give the amount of energy necessary to remove (ionize) the electron out of the molecular orbital, which corresponds to the negative of the experimentally observable ionization potential (I). (CC BY 4.0; Ümit Kaya via LibreTexts)

Koopmans' Theorem

Koopmans' theorem argues that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the vertical ionization energy to the ion state formed by removal of an electron from that orbital.

Several different ionization energies can be defined, depending on the degree of vibrational excitation of the cations. In general, the following two types of ionization energies are considered (Figure 10.4.4):

- Adiabatic ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v''= 0) + h\nu \rightarrow M^+(x, v' = 0) + e^-$$

  Adiabatic ionization energy that is, the minimum energy required to eject an electron from a molecule in its ground vibrational state and transform it into a cation in the lowest vibrational level of an electronic state x of the cation.
- Vertical ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v''= 0) + h\nu \rightarrow M^+(x, v' = n) + e^-$$

where, the value n of the vibrational quantum number v' corresponds to the vibrational level whose wavefunction gives the largest overlap with the v" = 0 wavefunction. This is the most probable transition and usually corresponds to the vertical transition where the internuclear separations of the ionic state are similar to those of the ground state.

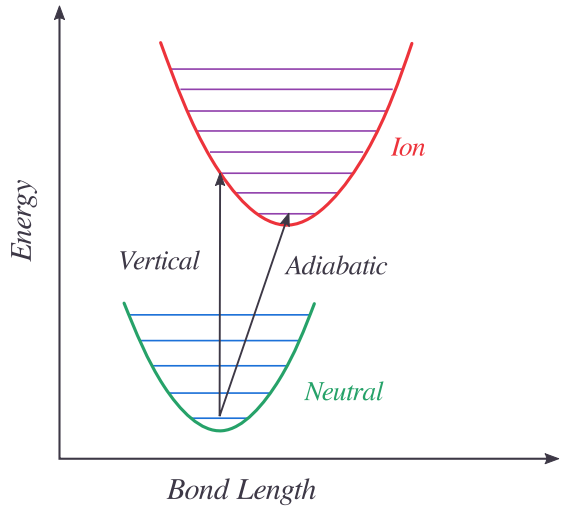


Figure 10.4.4: Difference between vertical and adiabatic ionization energies for a simple harmonic oscillator system. (CC BY 4.0; Ümit Kaya via LibreTexts)

The geometry of an ion may be different from the neutral molecule. The measured ionzation energy in a PES experiment can refer to the vertical ionization energy, in which case the ion is in the same geometry as the neutral, or to the adiabatic ionzaiton energy, in which case the ion is in its lowest energy, relaxed geometry (mostly the former though). This is illustrated in the Figure 10.4.4. For a diatomic the only geometry change possible is the bond length. The figure shows an ion with a slightly longer bond length than the neutral. The harmonic potential energy surfaces are shown in green (neutral) and red (ion) with vibrational energy levels. The vertical ionzation energy is **always greater** than the adiabatic ionzation energy.

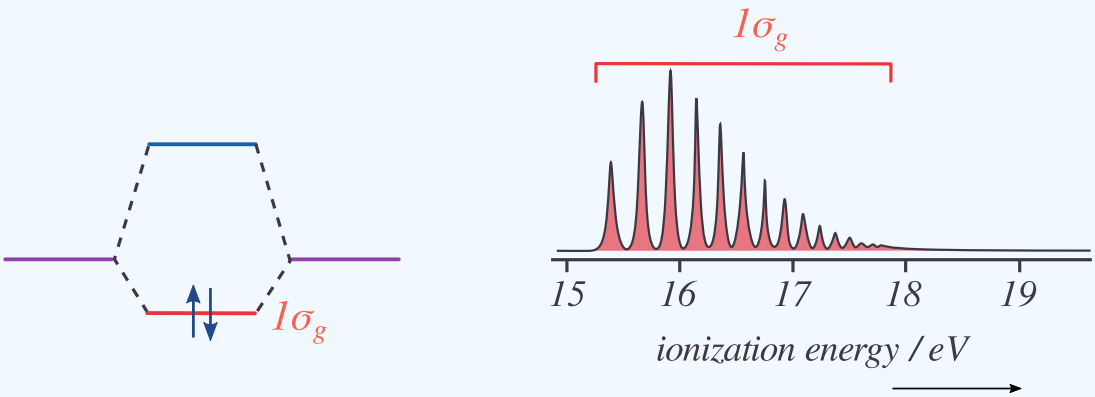
Differing Ionization Energies

You have been exposed to three metrics of ionization energies already, which are similar, but with distinct differences:

- The *ionization energy* (also called *adiabatic ionization energy*) is the lowest energy required to effect the removal of an electron from a molecule or atom, and corresponds to the transition from the lowest electronic, vibrational and rotational level of the isolated molecule to the lowest electronic, vibrational and rotational level of the isolated ion.
- The *binding energy* (also called *vertical ionization energy*) is the energy change corresponding to an ionization reaction leading to formation of the ion in a configuration which is the same as that of the equilibrium geometry of the ground state neutral molecule.
- The *workfunction* is the minimum energy needed to remove an electron from a (bulk) solid to a point in the vacuum.

Example 10.4.1: Molecular Hydrogen

As you remember, the molecular orbital description of molecular hydrogen involves two $|1s\rangle$ atomic orbitals generating a bonding $1\sigma_g$ and antibonding $2\sigma_u^*$ molecular orbitals. The two electrons that are responsible for the H_2 bond are occupied in the $1\sigma_g$.

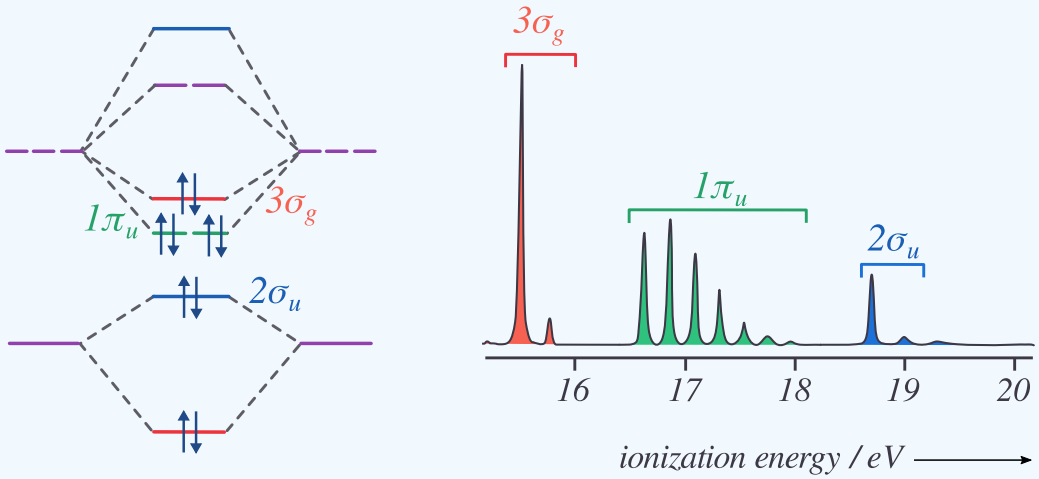


MO diagram and PES spectrum of H_2. (CC BY 4.0; Ümit Kaya via LibreTexts)

The PES spectrum has a single band that corresponds to the ionization of a $1\sigma_g$ electron. The multiple peaks are due to electrons ejecting from a range of stimulated vibrational energy levels. When extensive vibrational structure is resolved in a PES molecular orbital, then the removal of an electron from that molecular orbital induces a significant change in the bonding (in this case an increase in the bond length since the bond order has been reduced).

Example 10.4.2: Molecular Nitrogen

Diatomic nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Four molecular orbitals are occupied (the two $1\pi_u$ orbitals are both occupied). The UV photoelectron spectrum of N_2, has three bands corresponding to $3\sigma_g$, $1\pi_u$ and $2\sigma_u$ occupied molecular orbitals. Both $3\sigma_g$ and $2\sigma_u$ are weakly bonding and antibonding. The $1\sigma_g$ orbital is not resolved in this spectrum since the incident light $h\nu$ used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital.



MO diagram and PES spectrum of N_2. (CC BY 4.0; Ümit Kaya via LibreTexts)

Note that extensive vibrational structure for the $1\pi_u$ band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.

Hydrogen Chloride

The molecular energy level diagram for HCl is reproduced in Figure 10.4.5

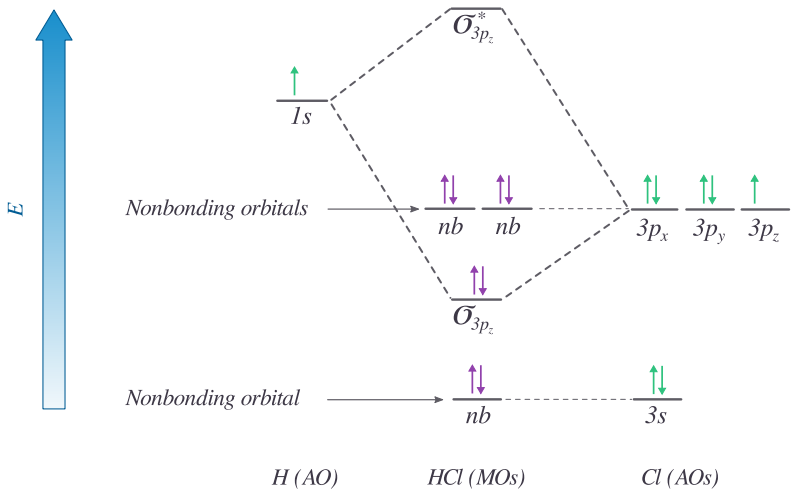


Figure 10.4.5: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts molecular orbitals strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1. (CC BY 4.0; Ümit Kaya via LibreTexts)

Important aspects of molecular orbital diagram in Figure 10.4.5:

- The H 1s energy lies well above the Cl 2*s* and 2*p* atomic orbitals;
- The valence electron configuration can be written $3\sigma^2 1\pi^4$;
- The H 1s orbital contributes only to the σ molecular orbitals, as does one of the Cl 2*p* orbitals (hence the lines in Figure 10.4.5 connecting these atomic orbitals and the 3σ and 4σ molecular orbitals);
- The remaining Cl 2*p* orbitals (ie those perpendicular to the bond axis) are unaffected by bonding, and these form the 1π molecular orbitals;
- The 1π orbitals are nonbonding - they are not affected energetically by the interaction between the atoms, and are hence neither bonding nor antibonding;
- The 3σ orbital is weakly bonding, and largely Cl 2*p*;
- The 3σ* orbital is antibonding, and primarily of H 1s character;

Figure 10.4.6 shows the analogous MO diagram and photoelectron spectrum for HCl. The spectrum has two bands corresponding to non-bonding 1*p* (or 1π) molecular orbitals (with negligible vibrational structure) and the 3s bonding molecular orbital (vibrational structure).

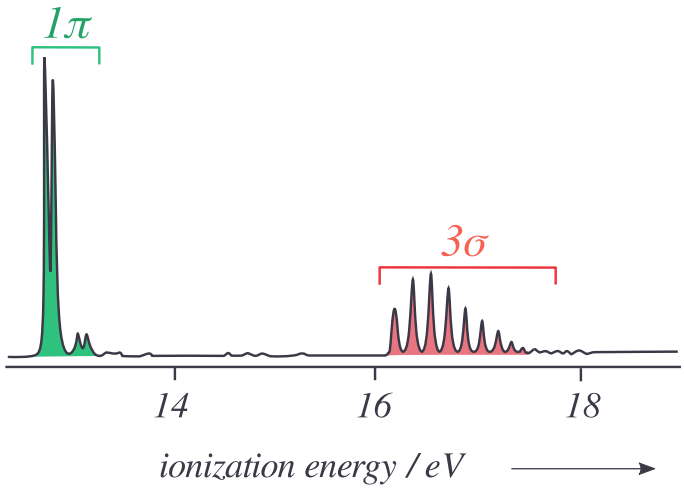


Figure 10.4.6: Photoelectron spectrum HCl. (CC BY 4.0; Ümit Kaya via LibreTexts)

The higher energy (more stabilized) core molecular orbitals are not observed since the incident photon energy $h\nu$ is below their ionization energies.

Water

In the simplified valence bond theory perspective of the water molecule, the oxygen atom form four sp^3 hybrid orbitals. Two of these are occupied by the two lone pairs on the oxygen atom, while the other two are used for bonding. Within the molecular orbital picture, the electronic configuration of the H_2O^+ molecule is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ where the symbols a_1, b_2 and b_1 are orbital labels based on molecular symmetry that will be discussed later (Figure 10.4.7). Within Koopmans' theorem:

- The energy of the $1b_1$ HOMO corresponds to the ionization energy to form the H_2O^+ ion in its ground state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1$.
- The energy of the second-highest molecular orbitals $3a_1$ refers to the ion in the excited state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^2$.

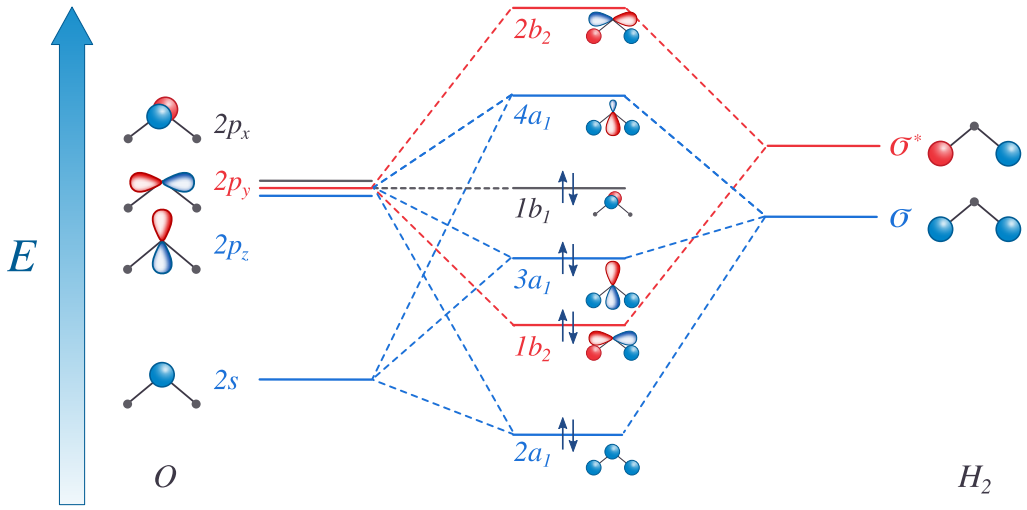


Figure 10.4.7: MO diagram for water. (CC BY 4.0; Ümit Kaya via LibreTexts)

The Hartree–Fock orbital energies (with sign changed) of these orbitals are tabulated below and compared to the experimental ionization energies.

Molecular orbital	Hartree–Fock orbital Energies (eV)	Experimental Ionization Energies (eV)
$2a_1$	36.7	32.2
$1b_2$	19.5	18.5
$3a_1$	15.9	14.7
$1b_1$	13.8	12.6

As explained above, the deviations between orbital energy and ionization energy is small and due to the effects of orbital relaxation as well as differences in electron correlation energy between the molecular and the various ionized states.

The molecular orbital perspective has the lone pair in different orbitals (one in a non-bonding orbital ($1b_1$ and one in the bonding orbitals). We tern to the photoelectron spectroscopy to help identify which theory is more accurate (i.e., describes reality better). The photoelectron spectrum of water in Figure 10.4.6 can be interpreted as having three major peaks with some fine structure arises from vibrational energy changes. The light source used in this experiment is not sufficiently energetic to ionize electrons from the lowest lying molecular orbitals.

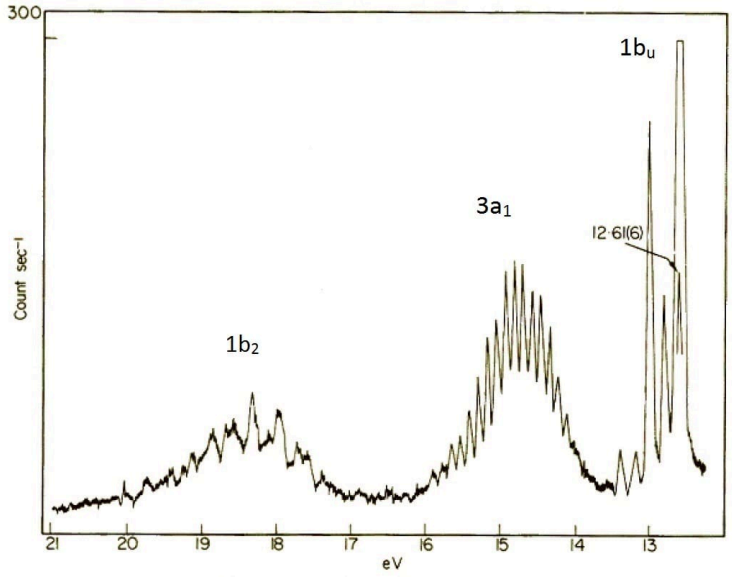


Figure 10.4.8: Photoelectron spectrum of water. Note the energy axes is flipped compared to other spectra on this page. This spectrum does not go to high enough energy to show the deep $2a_1$ molecular orbital.

If water was formed two identical O-H bonds and two lone pairs on the oxygen atom line valence bond theory predicts, then the PES in Figure 10.4.8 would have two (degenerate) peaks, one for the two bonds and one for the two lone pairs. The photoelectron spectrum clearly shows three peaks in the positions expected for the molecular orbitals in Figure 10.4.8.

If the molecular orbitals in Figure 10.4.7 represent the real electronic structure, how do we view the bonding? These molecular orbitals are delocalized and bare little relationship to the familiar 2-center bonds used in valence bond theory. For example, the $2a_1$ $1b_1$ and $3a_1$ molecular orbitals all have contributions from all three atoms, they are really 3-centered molecular orbitals. The bonds however can be thought of as representing a build up of the total electron density which loosely put is a total of all the orbital contributions. Despite this, we keep the ideas of hybridization and 2-center bonds because they are useful NOT because they represent reality

Summary

A photoelecton spectrum can show the relative energies of occupied molecular orbitals by ionization. (i.e. ejection of an electron). A photoelectron spectrum can also be used to determine energy spacing between vibrational levels of a given electronic state. Each orbital energy band has a structure showing ionization to different vibrational levels.

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10.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 10.12.4. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

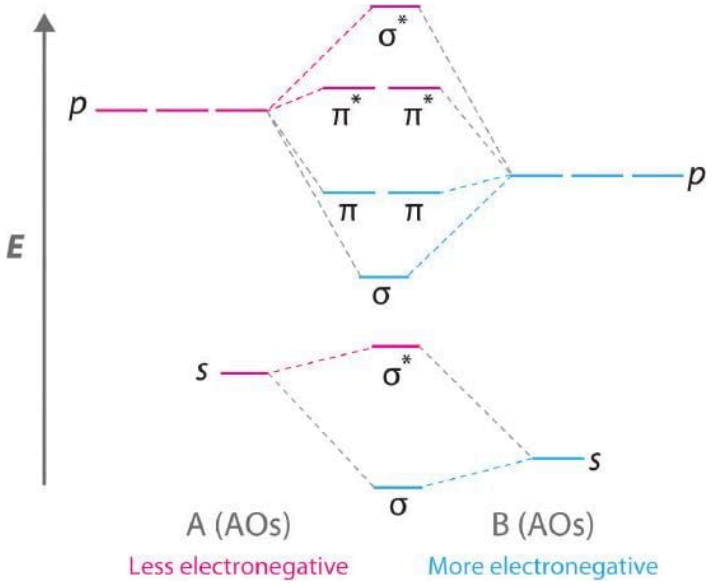


Figure 10.12.4: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 10.12.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 10.12.11). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

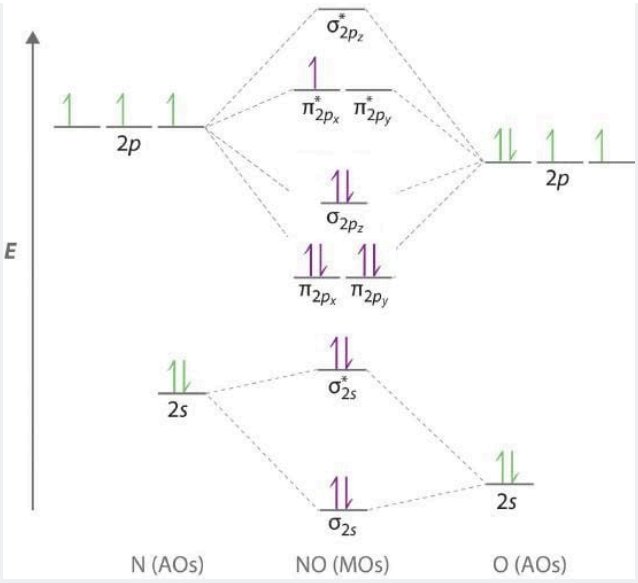


Figure 10.12.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_z},\ \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2\,(\sigma^{\star}_{2s})^2\,\left(\pi_{2p_{x,y}}\right)^4\,(\sigma_{2p_z})^2\,\left(\pi_{2p^{\star}_{x,y}}\right)^1$ in order of increasing energy. Hence, the $\pi_{2p_{x,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the NO molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure 10.12.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 10.12.13, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 10.12.6 that the 1s orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3s atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1s and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1s orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1s orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3s, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 – 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1s atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+} - -Cl^{\delta-}$.

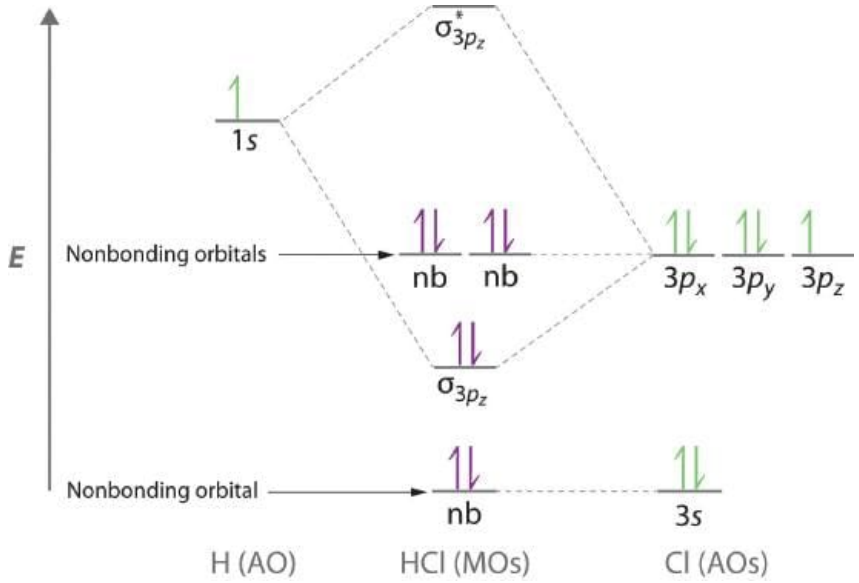


Figure 10.12.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

Electrons in nonbonding molecular orbitals have no effect on bond order.

Example 10.12.4: The Cyanide Ion

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 10.12.4 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

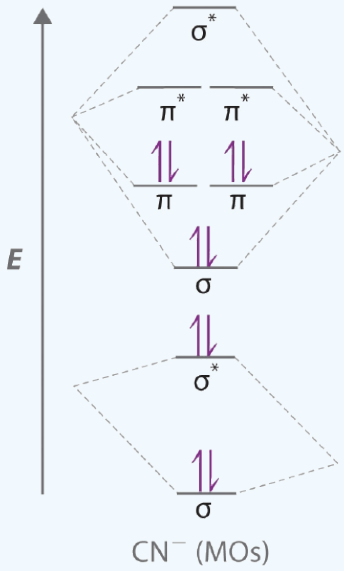
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 10.12.4 in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the –1 charge. Placing these electrons in an energy-level diagram like Figure 10.12.4 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C.

B The resulting valence electron configuration gives a predicted bond order of (8 – 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

Exercise 10.12.4: The Hypochlorite Ion

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer available at the end of this section.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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Summary

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With

such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

Answers

Exercise 10.12.4**: The Hypochlorite Ion**

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

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10.13: Molecular Term Symbols Describe Electronic States of Molecules

Molecular term symbols specify molecular electronic energy levels. Term symbols for diatomic molecules are based on irreducible representations in linear symmetry groups, derived from spectroscopic notations. They usually consist of four parts: spin multiplicity, azimuthal angular momentum, total angular momentum and symmetry. All molecular term symbols discussed here are based on Russel-Saunders coupling.

Introduction

Molecular term symbols mark different electronic energy levels of a diatomic molecule. These symbols are similar to atomic term symbols, since both follow the Russell-Saunders coupling scheme. Molecular term symbols employ symmetry labels from group theory. The possibility of an electronic transition can be deducted from molecular term symbols following selection rules. For multi-atomic molecules, symmetry labels play most of term symbols' roles.

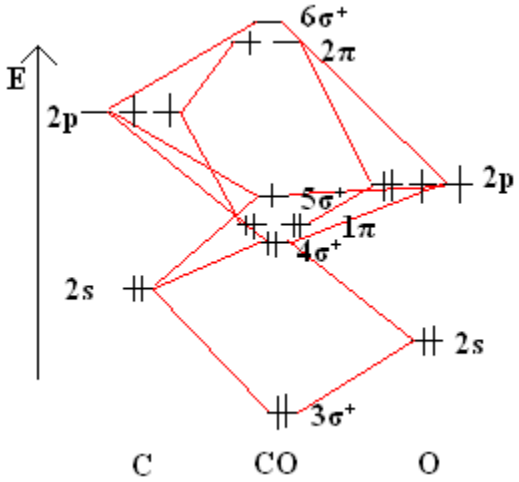
For homonuclear diatomics, the term symbol has the following form:

$$^{2S+1}\Lambda_{\Omega,(g/u)}^{(+/-)} \tag{10.13.1}$$

whereas Λ is the projection of the orbital angular momentum along the internuclear axis: Ω is the projection of the total angular momentum along the internuclear axis; *g*/*u* is the parity; and +/− is the reflection symmetry along an arbitrary plane containing the internuclear axis. Λ may be one of the greek letters in the sequence: Σ Π Δ Φ... when Λ = 0, 1, 2, 3..., respectively. For heteronuclear diatomics, the term symbol does not include the *g*/*u* part, for there is not inversion center in the molecule.

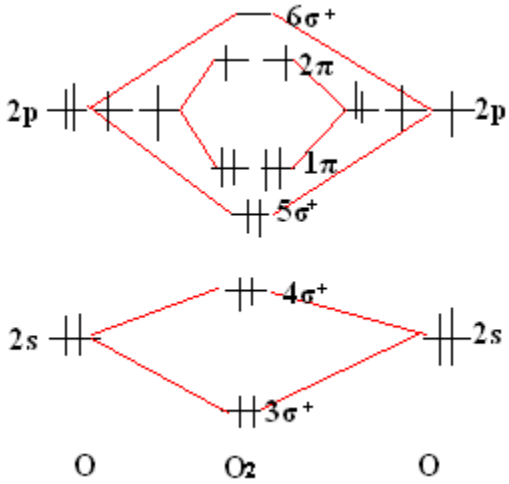
Determining term symbols of diatomics

Let's start with CO again. As we have seen before, the molecule has a close-shell configuration. Its ground state is a totally symmetric singlet, $^1\Sigma^+$, since the only possible values of (S, Λ) are (0, 0). If one of the HOMO electrons on the $5\sigma^+$ orbital has jumped to the LUMO, this molecule will be in an excited state as follows.



Suppose a CO molecule is in the excited state shown above. In order to know the term symbol of this state, a direct product of the labels is required for the two MO's with unpaired electrons. The multiplication is such as $\Pi \times \Sigma^+ = \Pi$. According to Pauli's exclusion rule, these two unpaired electrons can never share the same set of quantum numbers, therefore the spin degeneracy S can reach its maximum 3. The resulting term symbols are $^1\Pi$ and $^3\Pi$.

Now if we look at O_2, it does not have a close-shell configuration at its ground state. There are two unpaired electrons each occupying one of the two degenerate 2π orbitals, which can be seen in the diagram below.



The term symbol for oxygen molecule at its ground state is therefore derived such as $\Pi \times \Pi = \Sigma^+ + \Sigma^- + [\Delta]$, as the symbol in brackets does not allow the oxygen atoms to commute.

Transition between electronic states of diatomics

We'll focus on selection rules. Like atomic electronic states, different selection rules apply when differently incurred transitions occur. Usually for electric dipole field induced transitions, the selection rules are the same as for atoms.

1. $\Delta\Lambda = 0, \pm 1$ except $\Lambda = 0 \ddagger \Lambda' = 0$
2. $\Delta S = 0$
3. $\Delta\Omega = 0; \pm 1$ except $\Omega = 0 \ddagger \Omega' = 0$

References

1. Harris, Daniel C. (republished in 1989). *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy*. Dover Publications. pp. 421-478. ISBN 0-486-66144-X
2. D. J. Willock (2009). *Molecular Symmetry*. John Wiley & Sons Ltd. ISBN 0-470-85348-4

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10.14: Molecular Term Symbols Designate Symmetry

The quantum numbers for diatomic molecules are similar from the atomic quantum numbers. Be cautious, because the rules for finding the possible combinations are different. The total orbital angular momentum quantum number For the molecular case, this number is called Λ instead of L. It follows the same naming convention as L, except that instead of using capital English letters, it uses capital Greek letters:

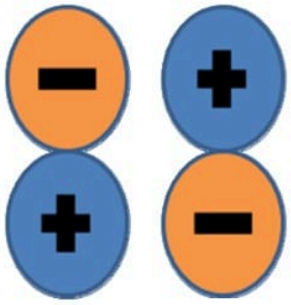
- $\Lambda = 0 \rightarrow \Sigma$
- $\Lambda = 1 \rightarrow \Pi$
- $\Lambda = 2 \rightarrow \Delta$
- $\Lambda = 3 \rightarrow \Phi$

Unlike L, there is not a general formula for finding the possible combinations of Λ. You have to examine the individual microstates. This is easier than it sounds.

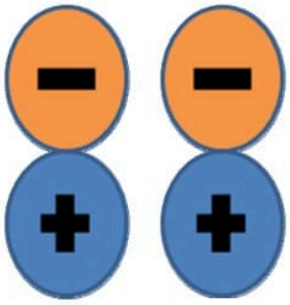
- **The total magnetic quantum number** M_L: M_L works like M_l with atoms, except that there is no formula for finding the combinations.
- **The total spin magnetic quantum number** M_S: M_S works exactly like M_s. Electrons can either point with or against the z -axis, and being in a molecular orbital versus an atomic orbital doesn't change this. M_S can range from $m_{s1} + m_{s2}$ to m_{s1}-m_{s2}.

Two New Symmetries: Parity and Reflection

Molecular orbitals are more complex than atomic ones and require more modifiers to completely define. **Parity** (sometimes called "inversion") tells you if the orbital is *symmetric* or *anti-symmetric* when an inversion operation is performed. The symmetry notation **u** and **g** are sometimes used when describing molecular orbitals. This refers to the operation of inversion, which requires starting at an arbitrary point in the orbital, traveling straight through the center, and then continuing outwards an equal distance from the center. The orbital is designated **g** (for gerade, even) if the phase is the same, and **u** (for ungerade, uneven) if the phase changes sign.



This pi orbital is gerade



This pi orbital is ungerade

To determine whether or not a given state is g or u, find the parity of each individual open-shell electron and uses these simple (Laporte rules):

- $g + g \rightarrow g$
- $g + u \rightarrow u$
- $u + u \rightarrow g$

Example 9.15.1: Closed Shell Configuration

What is the parity of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

Solution

Since both open shell electrons are ungerade, the overall parity is g. Helpful hint: bonding sigma orbitals and anti - bonding pi orbitals are always gerade. Anti - bonding sigmas and bonding pis are always ungerade. Draw them and see for yourself.

Reflection determines if a given orbital is symmetric or anti-symmetric upon reflection through a plane that contains both nuclei. The choice of symmetry planes is arbitrary. As long as you pick a plane and stick with it, you will always get the right answer. When an orbital is symmetric, it is labeled +. When an orbital is anti - symmetric, it is labeled - . To find the overall reflection of a state, use these rules:

- (+)(+) \rightarrow +
- (+)(-) \rightarrow -
- (-)(-) \rightarrow +

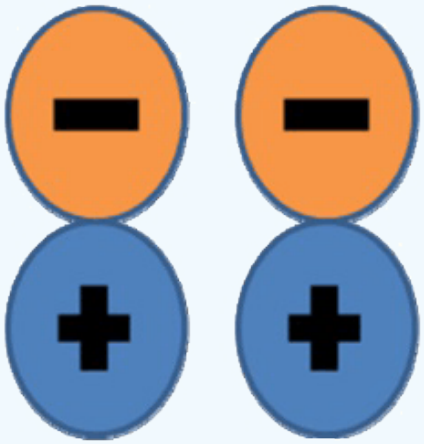
Reflection only applies to Σ states! For Λ > 0, there are no reflection labels! If you experiment with the rules, you will quickly realize why this is the case.

Example 9.15.2

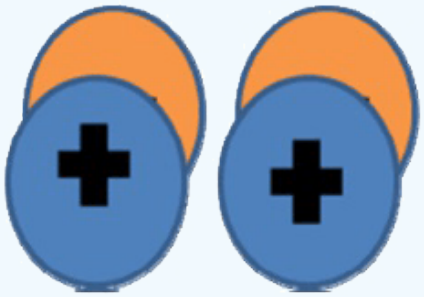
What is the reflection of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

Solution

You need to know what the orbitals look like. Draw a picture and then pick a plane. For this example, the plane of the page is selcted, but the orthogonal plane would have worked just as well.



The “vertical” orbital is +



The “horizontal” orbital is -

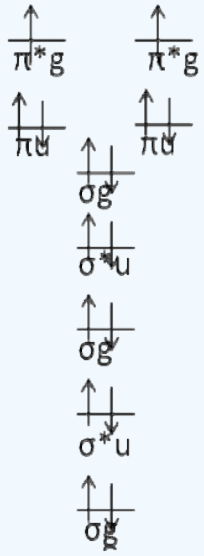
The “vertical” orbital is + The “horizontal” orbital is - Since one is + and one is - , the overall reflection is - . Try using the orthogonal plane and convince yourself that you still get the same answer.

Example 9.15.3: Oxygen

What are the term symbols for O_2 ?

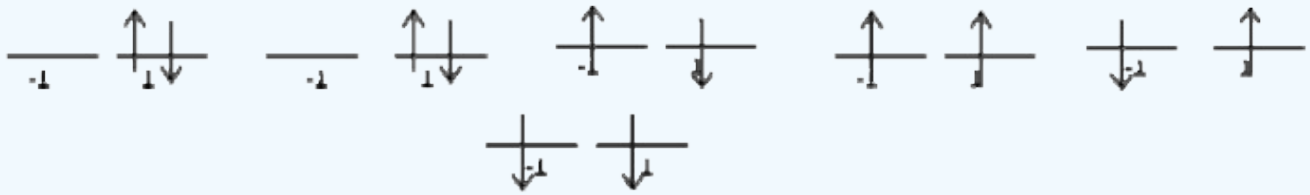
Solution

The molecular orbital diagram for O_2 is



Where I chose arbitrary configurations for the last two electrons.

There are two open - shell electrons occupying the anti-bonding π_g orbitals. These are the only electrons that matter. It is easiest to simply draw all of the permutations and figure out the bounds on Λ and M_L by inspection. If we do this, it is easy to see that $\Lambda = 2, 0$ and that $M_L = 2, 0, -2$



$M_s = -1$	$M_s = 0$	$M_s = 2$
0	**1**	0
1	2	1
0	1	0

The top row is a $\Lambda = 2$ $M_S = 0$ state, so it is $^1\Delta$. Both electrons are in the rightmost orbital. This orbital is gerade, and (g)(g) = g, so the parity label is g. We do not assign reflection labels to non Σ states, so the term symbol is $^1\Delta_g$. After removing the used up microstates, the chart becomes

$M_s = -1$	$M_s = 0$	$M_s = 2$
1	**1**	0

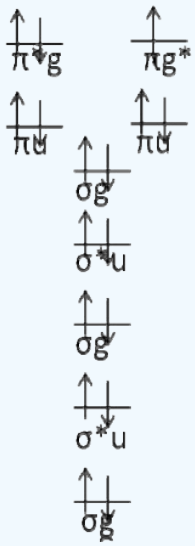
This is a Λ =0 state with three possible spin configurations, so it is $^3\Sigma$. We know that the electrons are in different sub-orbitals (if you cannot see this, try drawing all of the possible combinations that give $\Lambda = 0$). Both of the orbitals are gerade, so the overall parity is gerade. One of the orbitals will be +, the other will be - . The final answer is $^1\Delta_g \backslash (^3\Sigma_g^+$

Exercise 9.15.1

Write the term symbols for O_2^-

Solution

First draw the electron configuration diagram.



There are only two possible configurations. It should be easy to see that the term symbol is ${}^2\Pi_g$.

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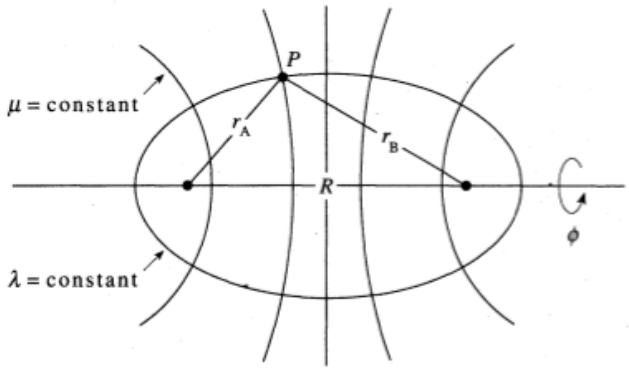
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10.E: Chemical Bond in Diatomic Molecules (Exercises)

Solutions to select questions can be found online.

9.3

The overlap integral and other integrals that arise in two-center systems like that of H_2 which is called a **two-center integral**. The two center integrals are much easier being evaluated by simply using the coordinate system, elliptic coordinates. In the coordinate system, where there are simply two fixed points which are separated by distance R.



A point P is given by three coordinates which are

- $\lambda = r_A + r_B/R$
- $\mu = r_A + r_B/R$

the angle ø is the angle that (r_A, r_B, R) triangle makes the interfocal axis. The differential volume element (elliptic coordinates) $\Leftrightarrow dr = R^3/8(\lambda^2 - \mu^2)d\lambda\ d\mu\ d\phi$

Given definitions λ, μ, ϕ → prove that

- $1 \leq \lambda < \infty$
- $-1 \leq \mu \leq 1$
- $0 \leq \phi \leq 2\pi$

Use elliptic coordinates to evaluate the overlap integral.

Use Equation:

$$S = \int dr\, 1s_A 1s_B = \frac{Z^3}{\pi} \int dr\, e^{-Zr_A} e^{-Zr_B}$$

Solution

From simple inspection of the figure:

- Have $r_A + r_B$ is never less than that of R. Therefore, $1 \leq \lambda < \infty$.
- $r_A - r_B$ can never have a of magnitude greater that that of R, therefore have $-1 \leq \mu \leq 1$.
- The variable ϕ can undergo 1 complete revolution therefore have/get $0 \leq \phi \leq 2\pi$.

Knowing all of this information, we can now solve for this equation:

$$
\begin{aligned}
S &= \frac{Z^3}{\pi}\int dr e^{-ZrA} e^{-Zr)B} \\
&= \frac{Z^3}{\pi}\int_0^{2\pi} d\phi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu R^3/8(\lambda^2-\mu^2)e^{-Z(r_A+r_B)} \\
&= \frac{R^3Z^3}{4}\int_1^{\infty} d\lambda \int_{-1}^{1} d\mu(\lambda^2-\mu^2)e^{-ZR\lambda} \\
&= \frac{R^3Z^3}{4}\int_1^{\infty} d\lambda e^{-ZR\lambda} \int_{-1}^{1} d\mu(\lambda^2-\mu^2) \\
&= \frac{R^3Z^3}{4}\int_1^{\infty} d\lambda e^{-ZR\lambda}(2\lambda^2-2/3) \\
&= \frac{R^3Z^3}{2}\left[(1/ZR+2/Z^2R^2+2/Z^3R^3)e^{-ZR}-1/3ZRe^{-ZR}\right] \\
&= e^{-ZR}(1+ZR+Z^2R^2/3)
\end{aligned}
$$

9.4

Repeat the calculation in 9.3 for $\psi_- = 1s_A - 1s_B$

Solution

$$E_- = \frac{\int dr\psi_-^* H\psi_-}{\int dr\psi_-^*\psi_-}$$

The denominator is

$$\int dr\psi_-^*\psi_- = 2(1-S)$$

The numerator can be evaluated using equations 9.18, 9.19, 9.20, 9.21 with a simple exchange of a minus sign in equations 9.18 and 9.21,

$$\int dr\psi_-^* H\psi_- = 2E_{1s}(1+S)+2J-2K$$

So

$$E_- = \frac{2E_{1s}(1+S)+2J-2K}{2(1-S)}$$

9.9

Show that the $2p_x$ and the $2p_y$ orbitals do not overlap. Use $2p_x \equiv C\cos\theta$ and $2p_y \equiv C\sin\theta\cos\theta$ and $f(r)$ as the radial component.

Solution

If $\int \Psi_1\Psi_2 dr \neq 0$ then the orbitals overlap.

Substituting in:

$$\int C\cos^2\theta\sin\theta f(r)$$

$$C\int_0^{\pi} cos^2\theta\sin\theta\int_0^{\infty} f(r) \neq 0$$

This orbitals do not overlap.

9.10

what does the overlap integral represent?

Solution

The overlap integral represents the amount of overlap there is between the orbitals of 2 or more different nuclei. It is only significant for orbitals that have a large overlap. It is a component of the energy integral of the nuclei.

9.14

Which of the three species is the is the least stable due to bond order: O_2, ${O_2}^+$, ${O_2}^{2-}$. Hint it may be helpful to draw molecular orbitals for each species although it is not required.

Solution

We have to use the bond order formula for each of the situations.

$$\text{Bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of anti-bonding electrons})}{2}$$

For O_2: We have 12 valence electrons. Therefore

$$\text{Bond order} = \frac{10-8}{2} = 1$$

From the bond orders, we can see that ${O_2}^{2-}$ is the least stable.

$$\text{Bond order} = \frac{10-5}{2} = \frac{5}{2}$$

For ${O_2}^{2-}$: We have 14 valence electrons. Therefore

$$\text{Bond order} = \frac{10-6}{2} = 2$$

For ${O_2}^{+}$: We have 11 valence electrons. Therefore

9.17

Write the electron configuration and bond order of carbon monoxide.

Solution

The electron configuration for carbon monoxide

$$CO : KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma 2_{p_z})^2$$

The bond order of CO is three.

9.17

Determine the bond order diphosphorus P_2.

Solution

Each phosphorus atom will contribute 5 valence electrons, so there will be a total of 10 valence electrons. We use these ten valence electrons to fill up atomic orbitals and we learn that the ground state electron configuration has 8 electron in bonding orbitals and 2 electrons in antibonding orbitals. To find bond order we take bonding electrons(8 electrons) minus antibonding (2 electrons) and divide by 2 to find the bond order of 3.

9.18

Determine the bond order for the bond in nitrogen oxide cation, NO^{+}.

Solution

The equation for bond order is

Misplaced '#'

There are 10 electrons total in the $2p$ level that have to fill the $\sigma_1, \sigma_1^*, \pi, \sigma_2, \pi^* \sigma_2^*$ in order of increasing energy, respectively. If one fills out the MO diagram, they will find that the number of bonding electrons is 8 and the number of antibonding electrons is 2.

Thus, the bond order is

$$\frac{1}{2}[8-2]=3$$

This indicates that there is triple bond for NO^{+}

9.18

What is the electron configuration and bond order of nitric oxide ion?

Solution

The electron configuration of NO^{+} is

$$NO^{+}: KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^1$$

The bond order of NO^{+} is $2\frac{1}{2}$

9.21

Determine the bond order for the NO molecule.

Solution

Bond Order = [(# of binding electrons) - (# of anitbonding electrons)] /2

From drawing the Molecular Orbital Diagram, we find that there are 6 binding electrons and 1 antibonding electron, therefore,

Bond Order = (6-1)/2 =5/2

9.22

How is the energy-level diagram for diatomic OH radical differ from that of NH? What is the highest occupied molecular orbital of OH?

9.23

If a light source generates a light at 73.4 nm while a photoelectron spectrometer is measuring the kinetic energy of the electrons ionized when the molecule absorbs this light, what is the largest electron binding energy that can be measured? Also, is it possible to determine the energy of the occupied molecular orbitals of a molecule using the kinetic energy of the ionized electrons measured? If yes, explain. *Hint* : Recall the photoelectron effect discussed in lecture 2.

Solution

The energy of the source light is

$$E = \frac{hc}{\lambda} = 2.71 \times 10^{-18}\ J$$

So 2.71 x 10^{-18} J is the largest electron binding energy that can be measured using this radiation source.

Using Einstein's explanation of the photoelectric effect, we know that

$$\varphi + KE = h\nu$$

Hence, if we know the kinetic energy of the ionized electrons, as well as the energy absorbed by the electron *v*, we can find φ, which is the energy of the molecular orbital occupied by the electron being ionized.

9.24

Why would the ionization energy of a $3p$ electron from HCl molecule be lower than a $3p$ electron from a chlorine atom?

Solution

The electrons that are shared between the two atoms in HCl are pulled closer to the Chlorine atom because it has a greater electronegativity than hydrogen. This creates a dipole moment and the bonding electrons become localized in such a way that they shield the nonbonding $3p$ electrons on the chlorine atom more than the inner shells of just a chlorine atom. Since shielding is greater for HCl the electrons require less energy to be pulled away from the molecule. Less shielded valence electrons will experience a greater attractive force decreasing the radius and increasing ionization energy.

9.27

Photoelectron spectroscopy involves the measurement of kinetic energy of photoelectrons to determine the binding energy, intensity and angular distributions of these electrons and use the information obtained to examine the electronic structure of molecules. It differs from the conventional methods of spectroscopy in that it detects electrons rather than photons to study electronic structures of a material. The O_2 photoelectron spectrum emits two bands of 52.3898 MJ* mol^{-1} and 52.311 MJ*mol^{-1}. This emission corresponds to the 1\(\s) ionization of the oxygen electron. In your own words explain the observation.

Solution

The two bands that oxygen is emitted corresponds to the spin $(+\frac{1}{2}, -\frac{1}{2})$ ionization in the $1s$ electron. The marginal difference in energy is due to the spin-orbit coupling, which is also known as spin-pairing. Spin-orbit coupling describes the weak magnetic interaction between the orbital motion and the particle spin in a particle

9.28

Would the ionization energies of non-bonding 1s electrons be different for HCl and Cl_2?

Solution

The shielding effects for the 1s electrons are different for these two systems. In HCl, the bonding electron is localized on the more electronegative Cl, while in Cl_2 the bonding electrons are right in between the two atoms. This means that the 1s electrons are more shielded in HCl than in Cl_2 , and so the electron is easier to rip off in HCl. So the ionization energy for 1s electrons in HCl is smaller than in Cl_2.

9.28

First write out the ground-state electron configuration for the homonuclear diatomic molecule F_2. Then given the experimental ionization energies for a 1s fluorine electron for HF and F_2 as 66.981 and 67.217 $MJ \cdot mol^{-1}$, explain why even though the 1s electrons of fluorine are not involved in the chemical bonds their ionization energies are different.

Solution

The ground state configuration is

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g)^2(1\pi_g)^2$$

The ionization energies are different because the 1s electrons affect the attraction of those electrons to the nucleus, even though they are not involved in the actual bond. The F_2 bonding electrons are equally distributed between two atoms, whereas the HF bonding electrons are localized on the fluorine atom. Therefore there is increased shielding of the 1s orbital on HF which causes a smaller ionization energy.

9.30

Try to solve for the ground-state term symbols for the diatomic molecules H_2^+ and H_2, given that the ground-state electron configuration for H_2^+ is $(\sigma_g 1s)^1$ and for H_2 is $(\sigma_g 1s)^2$.

Solution

$(1\sigma_g)^1$ corresponds to M_L=0 and M_s=1/2, meaning that there is an unpaired electron in the symmetric molecular orbitals of g and there is change in the $1\sigma_g$ wavefunction. The ground-state term symbol for H_2^+ will then be

$$^2\Sigma_g^+ \tag{10.E.1}$$

$(1\sigma_g)^2$ corresponds to M_L=0 and M_s=0, meaning that there is an unpaired electron in the molecular orbitals of g and there is change in the $1\sigma_g$ wavefunction. The ground-state term symbol for H_2 will then be

$$^1\Sigma_g^+ \tag{10.E.2}$$

9.30

Find the ground-state term symbols for B_2.

Solution

The ground state electron configuration is

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^1(1\pi_u)^1$$

We do not care about the filled orbitals because their

$$M_L = M_S = 0$$

The two unfilled orbitals are

$$(1\pi_u)^1(1\pi_u)^1$$

all possible combinations of

$$m_{l1}, m_{s1}, m_{l2}, m_{s2}$$

for B_2 are:

$$M_S, M_L :$$

$$(0, 2) : 1^+, 1^-$$

$$(0, 0) : 1^-, -1^+$$

$$(0, -2) : -1^+, -1^-$$

With these possible combinations we find the following to be possible ground state term symbols:

$$^1\Delta, ^3\Sigma, ^1\Sigma$$

Following Hund's Rule we detect $^3\Sigma$ to be our ground-state term symbol because the largest spin multiplicity will be the ground state of B_2. Now we take the two unoccupied orbitals and take the product to get the symmetry of the molecular orbital.

$$u \cdot u = g$$

So the ground-state term symbol for

$$B_2$$

is: $^3\Sigma_g^-$

9.31

Solve for the ground-state molecular term symbols for O_2, N_2, N_2^+, and O_2^+.

Solution

The ground state molecular term symbols are given below:

O_2

The molecular term symbol of O_2 without the ± designation is $^3\Sigma_g$. The electron configuration is (filled orbital) (1$\pi_g 2p_x$)^1(1$\pi_g 2p_y$)^1, so the symmetry with respect to a reflection through the x-z plane is (+) (-) = (-); therefore, the complete molecular term symbol of O_2 is $^3\Sigma_g^-$.

N_2

$(1\sigma_g)^2$ $(1\sigma u)^2$ $(2\sigma_g)^2(2\sigma u)^2(1\pi u)^2(1\pi u)^2(3\sigma_g)^2$ Corresponds to | M_L | = 0 and | M_S | = 0 of a $^1\Sigma$ term symbol. The symmetry of the molecule is g. The complete ground state term symbol of N_2 is $^1\Sigma_g{}^+$ because the molecular wave function does not change when reflected through a plane containing the two nuclei.

$N_2{}^+$

$(1\sigma_g)^2$ $(1\sigma u)^2$ $(2\sigma_g)^2(2\sigma u)^2(1\pi u)^2(1\pi u)^2(3\sigma_g)^1$ Corresponds to | M_L | = 0 and | M_S | = 0.5 of a $^2\Sigma$ term symbol. The symmetry of the molecule is g. The complete ground state term symbol of $N_2{}^+$ is $^2\Sigma_g{}^+$ because the molecular wave function does not change when reflected through a plane containing the two nuclei.

$O_2{}^+$

$(1\sigma_g)^2$ $(1\sigma u)^2$ $(2\sigma_g)^2(2\sigma u)^2(3\sigma_g)^2(1\pi u)^2(1\pi u)^2(1\pi g)^1$ Corresponds to | M_L | = 1 and | M_S | = 0.5 of a $^2\Pi$ term symbol. The symmetry of the molecule is g, since the only unfilled molecular orbital has symmetry g, so the complete ground state term symbol of $O_2{}^+$ is $^2\Pi_g$.

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11: BONDING IN POLYATOMIC MOLECULES

The concept of a molecular orbital is readily extended to provide a description of the electronic structure of a polyatomic molecule. Indeed molecular orbital theory forms the basis for most of the quantitative theoretical investigations of the properties of large molecules. In general a molecular orbital in a polyatomic system extends over all the nuclei in a molecule and it is essential, if we are to understand and predict the spatial properties of the orbitals, that we make use of the symmetry properties possessed by the nuclear framework.

11.1: Hybrid Orbitals Account for Molecular Shape

11.2: Hybrid Orbitals in Water

11.3: BeH_2 is Linear and H_2O is Bent

11.4: The pi-Electron Approximation of Conjugation

11.5: Butadiene is Stabilized by a Delocalization Energy

11.6: Benzene and Aromaticity

11.E: Bonding in Polyatomic Molecules (Exercises)

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11.1: Hybrid Orbitals Account for Molecular Shape

Learning Objectives

- Introduce hybrid orbital to explain non-linear molecular structure

Valence bond (VB) theory is one of two basic theories, along with **molecular orbital** (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory, which will be discussed elsewhere, predict wavefunctions that cover the entire molecule.

Review of Diatomics

Let us consider H_2. Recall that the Lewis structure for a single H atom is $H\cdot$ and for H_2, it is $H:H$. Thus, each hydrogen brings one unpaired electron to the bond. Let the two protons be denoted A and B and the two electrons 1 and 2. Now, consider the potential energy

$$V = V_{ee} + V_{en} + V_{nn} \tag{11.1.1}$$

$$= \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{R_{AB}}\right] \tag{11.1.2}$$

But as $R_{AB} \to \infty$, the $1/r_{12}$, $1/r_{1B}$, $1/r_{2A}$, and $1/R_{AB}$ terms vanish and the potential energy becomes simply that of two noninteracting hydrogen atoms

$$V \to -\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{1A}} + \frac{1}{r_{2B}}\right]$$

Since the potential energy becomes a simple sum of separate energies for electrons 1 and 2, the wavefunction should simply be a product $\psi_{1s}(r_1 - r_A)\psi_{1s}(r_2 - r_B)$. But as we let $R_{AB} \to R_e$, where R_e is the equilibrium bond length, the electrons mix, and we can no longer tell if electron 1 belongs to atom A or atom B and the same for electron 2. Thus, we need to construct a combination of products that is consistent with the Pauli exclusion principle. If we just consider the coordinates r_1 and r_2 of the electrons, then the only wavefunction we can construct from a product of 1s orbitals is

$$\psi_u(r_1, r_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)]$$

where the u designator indicates that this is an odd function. The constant C_u is the overall noramlization constant. Unfortunately, like in the LCAO method, such a wavefunction is antibonding and is not a good representation of the ground state. If, however, we construct the wavefunction

$$\psi_g(r_1, r_2) = C_g[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)]$$

where g designates that this is an even function (even in German is *gerade*), we violate the Pauli exclusion principle, even though such a wavefunction leads to a stable chemical bond.

What is missing here is the fact that we have not considered the spins of the electrons. Since the electrons are identical, if we exchange coordinates *and* spins, then the wavefunction should change sign. Thus, we can make both wavefunctions above consistent with the Pauli exclusion principle by multiplying by an appropriate spin wavefunction. We obtain

$$\psi_u(r_1, r_2, s_1, s_2) = \psi_u(x_1, x_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{11.1.3}$$

$$\psi_g(r_1, r_2, s_1, s_2) = \psi_g(x_1, x_2) = C_g[\psi^A_{1s}(r_1)\psi_{1s}B(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{11.1.4}$$

where s_1 and s_2 are the z-components of spin for electrons 1 and 2, respectively. We can now use ψ_g as an approximate 2-electron wavefunction that leads to a stable chemical bond in H_2.

The fact that ψ_u is antibonding can be easily determined by looking for a nodal plane between the two atoms, in this case, in the plane that exactly bisects the line joining the two atoms, midway between them. That this is, indeed, a nodal plane can be seen by considering two points r_1 and r_2 for the two electrons that are taken to lie in this plane. By symmetry, the functions $\psi^A_{1s}(r_1)$ and $\psi^B_{1s}(r_1)$ have the same value for r_1 in this plane, and the same for $\psi^B_{1s}(r_2)$ and $\psi^A_{1s}(r_2)$. Let us assign the following values:

$$\psi^A_{1s}(r_1) = \psi^B_{1s}(r_1) = A \tag{11.1.5}$$

$$\psi^B_{1s}(r_2) = \psi^A_{1s}(r_2) = A' \tag{11.1.6}$$

Substituting these into $\psi_u(x_1, x_2)$, we obtain

$$\psi_u(x_1, x_2) = C_u[AA' - A'A][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] = 0$$

Since the wavefunction has a node midway between the two atoms, it is clearly antibonding and should have a *higher energy* than the corresponding bonding wavefunction ψ_g.

A similar argument can be used for the molecule F_2. Each F has an electronic configuration

$$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$$

and the Lewis structure of F_2 is



Figure 10.1.1 : Lewis structure of F_2.

Most of the electrons are in lone pairs, but the $2p_z$ electrons, which are unpaired in each F atom come together to form the bond. Thus, the bonding wavefunction should be a **2-electron wavefunction** constructed from $2p_z$ orbitals. The bonding wavefunction takes the "gerade" form as in H_2:

$$\psi_g(r_1, r_2, s_1, s_2) = C_g[\psi^A_{2p_z}(r_1)\psi^B_{2p_z}(r_2) + \psi^A_{2p_z}(r_2)\psi^B_{2p_z}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]$$

For HF, the $2p_z$ orbital on F and $1s$ orbital on H come together to form the bonding wavefunction. To be consistent with the Pauli principle, we need a wavefunction of the form

$$\psi(r_1, r_2, s_1, s_2) = [\psi^H_{1s}(1)\psi^F_{2p_z}(2) + \psi^H_{1s}(2)\psi^F_{2p_z}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]) \tag{11.1.7}$$

Looking at the HF example, it becomes clear how much valence bond theory attempts to appear as a "quantum version" of the Lewis dot structure model. Valence bond theory attempts to construct very approximate wavefunctions for the bonding electrons in a Lewis structure, leaving the orbitals unused in the construction of the valence bond wavefunctions for the lone pair electrons. In the case of HF, we use the $2p_z$ orbitals of F, which leaves the $2s$, $2p_x$ and $2p_y$ orbitals unused. Since there are three lone pairs, these three orbitals are sufficient to hold each of the lone pairs as spin-up/spin-down couples.

Hybridization

For polyatomic molecules, the valence bond theory becomes a very poor approximation because the directionalities of the $2s$ and $2p$ orbitals is too restrictive to describe molecules with steric numbers ranging between 2 and 4. The example considered above of $\mathrm{H_2O}$ illustrates this rather dramatically! Let us consider an even simpler molecule, $\mathrm{BeH_2}$, which has a steric number of 2 and is linear. Let the atoms lie entirely along the z-axis in the arrangement $\mathrm{H{-}Be{-}H}$.

Although the Be atom has a ground-state electronic configuration of $1s^2 2s^2$, but if we "promote" one of the $2s$ electrons to a state with higher energy and allow its electronic structure to be $1s^2 2s 2p_z$, then the unpaired electrons in the $2s$ and $2p_z$ orbitals can combine with the unpaired electrons in each of the hydrogen atoms to form bonds. The energy needed to excite the electron in Be would be "repaid" by the energy gained in the formation of stable bonds. The two valence-bond wavefunctions we would construct would be

$$\psi_1(1,2) = C_1 \left[\psi_{1s}^{H_1}(1)\psi_{2s}^{Be}(2) + \psi_{1s}^{H_1}(2)\psi_{2s}^{Be}(1)\right] [\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{11.1.8}$$

$$\psi_2(1,2) = C_2 \left[\psi_{1s}^{H_2}(1)\psi_{2p_z}^{Be}(2) + \psi_{1s}^{H_2}(2)\psi_{2p_z}^{Be}(1)\right] [\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{11.1.9}$$

Unfortunately, even this simple scheme does not work entirely because the two $\mathrm{Be{-}H}$ bonds would be different due to their construction from different combinations of orbitals. By symmetry, however, we can see that the two $\mathrm{Be{-}H}$ bonds should be equivalent. A solution to this problem was proposed by Linus Pauling in the 1930s in the form of **orbital hybridization**, a scheme that we still use today.

Pauling used the fact that in the first and second periods, the $2s$ and $2p$ orbitals have similar energies. Indeed, for the H atom, the energies are exactly the same. Given that these energies are not that different, we can combine s and p orbitals and still have a valid solution of the Schrödinger equation. That is, a general orbital

$$\chi(r) = C_1\psi_{2s}(r) + C_2\psi_{2p_x}(r) + C_3\psi_{2p_y}(r) + C_4\psi_{2p_z}(r)$$

is also a solution of the Schrödinger equation with the same energy as a $2s$ or $2p$ orbitals individually (this is exactly true for H). In the case of $\mathrm{BeH_2}$, the external potential on the electrons in Be by the two hydrogens changes the energy levels and creates a near degeneracy between the $2s$ and $2p_z$ orbitals, hence, we are now free to combine the into linear combinations that are more suitable to the construction both of valence bond wavefunctions *and* MOs via the LCAO procedure.

sp Hybrid Orbitals

For Be, we now allow the s and p orbitals to mix and create two *hybrid* orbitals known as sp orbitals. The two new hybrid wavefunctions as linear combination of the functions for 2s and $2p_z$ (using Dirac Notation):

$$|\chi_i\rangle = a_1|2s\rangle + b_1|2p_z\rangle \tag{11.1.10}$$

$$|\chi_j\rangle = a_2|2s\rangle + b_2|2p_z\rangle \tag{11.1.11}$$

These two wavefunctions must be orthogonal.

$$\langle\chi_i|\chi_j\rangle = \delta_{ij}$$

Which can be separated into the following relationships:

$$\langle\chi_i|\chi_i\rangle = 1 \tag{11.1.12}$$

and

$$\langle\chi_j|\chi_j\rangle = 1 \tag{11.1.13}$$

and

$$\langle\chi_i|\chi_j\rangle = \langle\chi_j|\chi_i\rangle = 0 \tag{11.1.14}$$

Equations 11.1.12 and 11.1.13 are the **normality requirement** and Equation 11.1.14 is the **orthogonality requirement** for the new hybrid wavefunctions. Substituting 11.1.10 into 11.1.12 results in

$$\langle\chi_i|\chi_i\rangle = a_1^2 \cancelto{1}{\langle 2s|2s\rangle} + a_1b_1 \cancelto{0}{\langle 2s|2p_z\rangle} + a_1b_1 \cancelto{0}{\langle 2p_z|2s\rangle} + b_1^2 \cancelto{1}{\langle 2p_z|2p_z\rangle} = 1$$

and similarly for $\langle\chi_j|\chi_j\rangle$

$$\langle\chi_j|\chi_j\rangle = a_2^2 \cancelto{1}{\langle 2s|2s\rangle} + a_2b_2 \cancelto{0}{\langle 2s|2p_z\rangle} + a_2b_2 \cancelto{0}{\langle 2p_z|2s\rangle} + b_2^2 \cancelto{1}{\langle 2p_z|2p_z\rangle} = 1$$

results in the following relationships

$$\langle\chi_i|\chi_i\rangle = a_1^2 + b_1^2 = 1 \tag{11.1.15}$$

$$\langle\chi_j|\chi_j\rangle = a_2^2 + b_2^2 = 1 \tag{11.1.16}$$

and

$$\langle \chi_i | \chi_j \rangle = a_1 a_2 + b_1 b_2 = 0 \tag{11.1.17}$$

These are four unknowns and three equations. The fourth "constraint" is that we assume contribution of $|s\rangle$ is the same for both hybrid orbitals.

$$a_1 = a_2$$

Equations 11.1.15 to 11.1.17 revert to

$$a_1^2 + b_1^2 = 1 \tag{11.1.18}$$

$$a_1^2 + b_2^2 = 1 \tag{11.1.19}$$

$$b_1^2 = b_2^2 \tag{11.1.20}$$

Therefore

$$b_1 = -b_2$$

and

$$a_1 = b_1 \tag{11.1.21}$$

Insert Equation 11.1.21 into 11.1.20 to get

$$a_1 = \frac{1}{\sqrt{2}}$$

and the two hybrid orbitals are

$$\chi_1(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) + \psi_{2p_z}(r)] \tag{11.1.22}$$

$$\chi_2(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) - \psi_{2p_z}(r)] \tag{11.1.23}$$

Note that these orbitals are both normalized and orthogonal:

$$\int |\chi_1(r)|^2 dV = 1 \; ; \; \int |\chi_2(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_2(r) dV = 0$$

These orbitals appear as shown in Figure 10.1.3

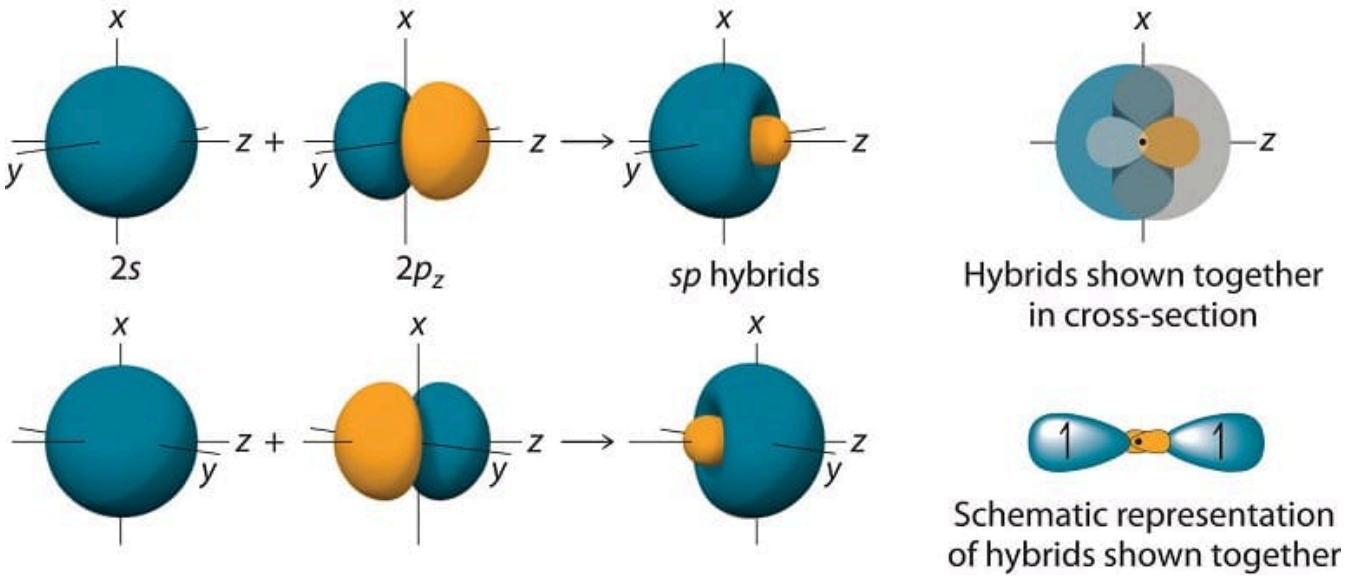


Figure 10.1.3 : The Formation of sp Hybrid Orbitals. Taking the sum and difference of an ns and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

Given that the two sp hybrid orbitals are mirror images of each other, they can overlap with the $1s$ orbital of H (shown in the figure) and create two equal bonds, as needed for BeH_2. Using the valence bond formulation, now, one of the BeH bonds will be described by a wavefunction of the form:

$$\psi_1(1,2) = C_1[\psi_{1s}^{H_1}(1)\chi_1^{Be}(2) + \psi_{1s}^{H_1}(2)\chi_1^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{11.1.24}$$

$$\psi_2(1,2) = C_2[\psi_{1s}^{H_2}(1)\chi_2^{Be}(2) + \psi_{1s}^{H_2}(2)\chi_2^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{11.1.25}$$

In the above wavefunctions, it is clear that H_1 is on the right and H_2 is on the left, based on the directionalities of χ_1 and χ_2.

sp^2 Hybrid Orbitals

For trigonal planar molecules such as BH_3, we start with the electronic configuration of B, which is $1s^2 2s^2 2p_x$, and we promote one of the $2s$ electrons to a $2p_y$ orbital, so that we have $1s^2 2s 2p_x 2p_y$. Suppose the geometry of BH_3 is such that one of the hydrogen atoms lies along the positive x axis. The remaining hydrogen atoms would be in the 3rd and 4th quadrants, respectively (Figure 10.1.4).

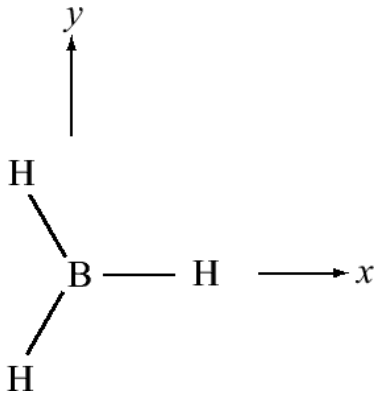


Figure 10.1.4: Geometry of BH_3.

If we simply combine the $2s$ with the $2p_x$ and $2p_y$ orbitals of boron, the resulting hybrid orbitals will not point in the correct direction. For this reason, we will create rotated versions of the p_x and p_y orbitals, which, as we will see are tantamount to taking new combinations of $2p_x$ and $2p_y$ orbitals to combine with the $2s$. Since the rotation occurs in the xy plane, the coordinate that controls this is the azimuthal angle ϕ. For the p_x and p_y orbitals, the ϕ dependence is

$$\psi_{2p_x} \sim \cos\phi \ ; \ \psi_{2p_y} \sim \sin\phi$$

If we rotate $2p_y$ by -30 degrees (Figure 10.1.5 ; blue is positive and red is negative), the ϕ dependence becomes

$$\psi_{2p_y}^{(rot)} \sim \sin(\phi + 30)$$

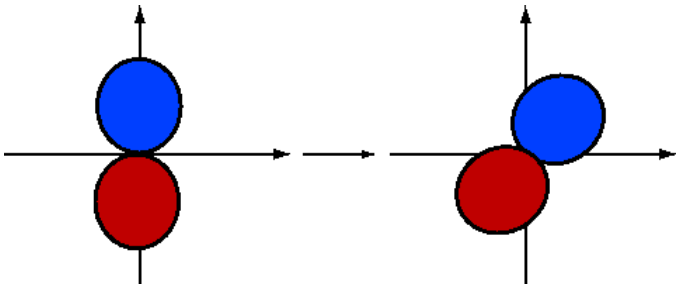


Figure 10.1.5: Rotation of a $2p_y$ orbital by -30 degrees.

Using the fact that

$$\sin(\alpha \pm \beta) = \sin\alpha\cos\beta \pm cos\alpha sin\beta$$

this rotation gives

$$\psi_{2p_y}^{(rot,1)} \sim \sin\phi\cos 30 + \cos\phi\sin 30 \tag{11.1.26}$$

$$\sim \left[\frac{\sqrt{3}}{2}\sin\phi + \frac{1}{2}\cos\phi\right] \tag{11.1.27}$$

$$\sim \left[\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x}\right] \tag{11.1.28}$$

Similarly, consider rotating $-\psi_{2p_y}$ by $+30$ degrees (Figure 10.1.6). This gives

$$-\psi_{2p_y}^{(rot,2)} \sim -\sin(\phi - 30) \tag{11.1.29}$$

$$\sim -\left[\frac{\sqrt{3}}{2}\sin\phi - \frac{1}{2}\cos\phi\right] \tag{11.1.30}$$

$$\sim -\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x} \tag{11.1.31}$$

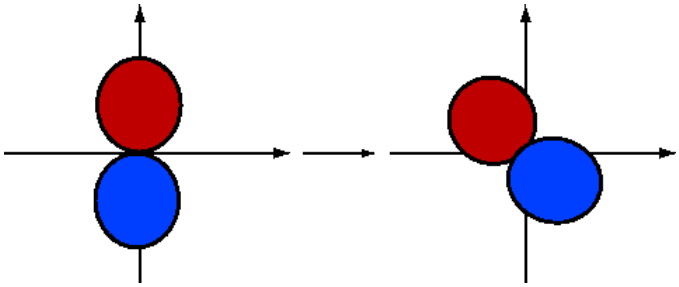


Figure 10.1.6: Rotation of a $-2p_y$ orbital by 30 degrees.

So, we now take the hybrid orbitals to be of the form

$$\chi_1(r) = a\psi_{2s}(r) - b\psi_{2p_x} \tag{11.1.32}$$

$$\chi_2(r) = c\psi_{2s}(r) + d\psi_{2p_y}^{(rot,1)}(r) \tag{11.1.33}$$

$$\chi_3(r) = c\psi_{2s}(r) - d\psi_{2p_y}^{(rot,2)}(r) \tag{11.1.34}$$

The coefficients a, b, and c are determined by requiring that the orbitals are normalized and mutually orthogonal:

$$\int |\chi_1(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_2(r)dV = 0 \tag{11.1.35}$$

$$\int |\chi_2(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_3(r)dV = 0 \tag{11.1.36}$$

$$\int |\chi_3(r)|^2 dV = 1 \; ; \; \int \chi_2^*(r)\chi_3(r)dV = 0 \tag{11.1.37}$$

Carrying out the algebra, we obtain the following sp^2 hybrid orbitals:

$$\chi_1(r) = \frac{1}{\sqrt{3}}[\psi_{2s}(r) - \sqrt{2}\psi_{2p_x}(r)] \tag{11.1.38}$$

$$\chi_2(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) + \sqrt{3}\psi_{2p_y}(r)] \tag{11.1.39}$$

$$\chi_3(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) - \sqrt{3}\psi_{2p_y}(r)] \tag{11.1.40}$$

The sp^2 hybrids allow bonding at 120° degrees, and these orbitals appear as shown in Figure 10.1.7:

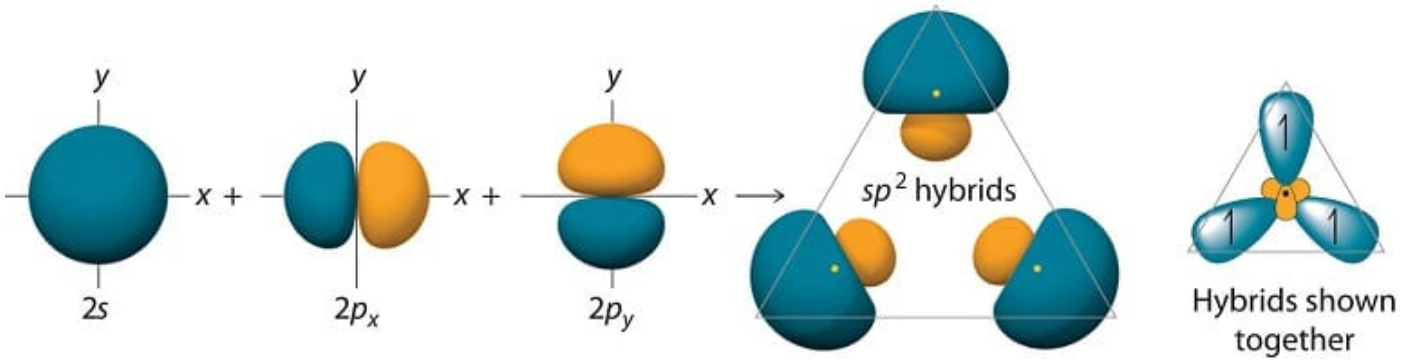


Figure 10.1.7: Formation of sp^2 Hybrid Orbitals. Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

The figure also shows the overlaps of these orbitals with the $1s$ orbitals of H.

sp^3 Hybrid Orbitals

Finally, we consider the case of methane CH_4. The electronic configuration of C is $1s^2 2s^2 2p_x 2p_y$. We now promote one of the $2s$ orbitals to the $2p_z$ orbital and write C as $1s^2 2s 2p_x 2p_y 2p_z$. We can now hybridize the $2s$ orbital with each of the $2p$ orbitals to create four hybrids:

$$\chi_1(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{11.1.41}$$

$$\chi_2(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{11.1.42}$$

$$\chi_3(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{11.1.43}$$

$$\chi_4(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{11.1.44}$$

The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 10.1.8). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

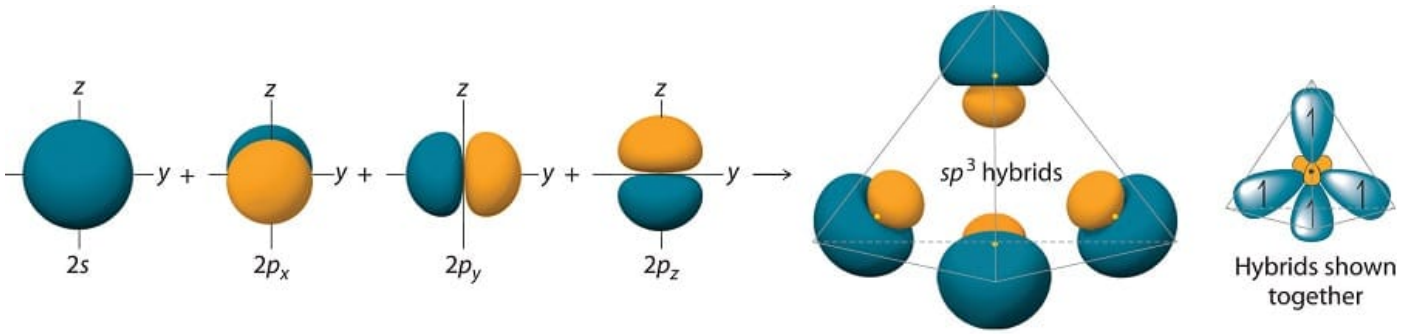


Figure 10.1.8 : Formation of sp^3 Hybrid Orbitals. Combining one ns and three np atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

Are hybrid orbitals Real?

Hybridization is an often misconceived concept. It only is a mathematical interpretation, which explains a certain bonding situation (in an intuitive fashion). In a molecule the equilibrium geometry will result from various factors, such as steric and electronic interactions, and further more interactions with the surroundings like a solvent or external field. The geometric arrangement will not be formed because a molecule is hybridized in a certain way, it is the other way around, i.e. a result of the geometry or more precise and interpretation of the wavefunction for the given molecular arrangement.

The justification we gave for invoking hybridization in molecules such as BeH_2, BF_3 and CH_4 was that the bonds in each are geometrically and chemically equivalent, whereas the atomic *s*- and *p*-orbitals on the central atoms are not. By combining these into new orbitals of *sp*, sp^2 and sp^3 types we obtain the required number of completely equivalent orbitals. This seemed easy enough to do on paper; we just drew little boxes and wrote "sp^2" or whatever below them. But what is really going on here?

The full answer is beyond the scope of this course, so we can only offer the following very general explanation. First, recall what we mean by "orbital": a mathematical function ψ having the character of a standing wave whose square ψ^2 is proportional to the probability of finding the electron at any particular location in space. The latter, the *electron density distribution*, can be observed (by X-ray scattering, for example), and in this sense is the only thing that is "real".

A given standing wave (ψ-function) can be synthesized by combining all kinds of fundamental wave patterns (that is, atomic orbitals) in much the same way that a color we observe can be reproduced by combining different sets of primary colors in various proportions. In neither case does it follow that these original orbitals (or colors) are actually present in the final product. So one could well argue that hybrid orbitals are not "real"; they simply turn out to be convenient for understanding the bonding of simple molecules at the elementary level, and this is why we use them.

Summary

The shape and bonding valecies of polyatomic molecules can be accounted for by hybrid orbitals. Molecular orbitals are formed from linear combinations of atomic orbitals which are similar in energy. These atomic orbitals could come from different atoms, or from the same atom. For example, the 2 sand 2patomic orbitals are very close energetically. When a linear combo of more than one atomic orbital from the **same atom** is formed, we have a hybrid orbital.

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11.2: Hybrid Orbitals in Water

The goal of applying Valence Bond Theory to water is to describe the bonding in $\mathrm{H_2O}$ and account for its structure (i.e., appropriate bond angle and two lone pairs predicted from VSEPR theory).

The ground state electronic configuration of atomic oxygen atom is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ and of course the ground state electronic configuration of atomic hydrogen atom is $1s^1$, i.e., a spherical atomic orbital with no preferential orientation. If only the unfilled $2p_y$ and $2p_z$ atomic orbitals of the oxygen were used as bonding orbitals, then two bonds would be predicted. These bonding wavefunctions would be mixture of only $|2p_y\rangle$ and $|2p_z\rangle$ orbitals on oxygen and the $|1s\rangle$ orbitals on the hydrogens (H_1 and H_2):

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + b_1|2p_y\rangle_O \tag{11.2.1}$$

$$|\chi_2\rangle = a_2|1s\rangle_{H_2} + b_2|2p_z\rangle_O \tag{11.2.2}$$

However, with a $\mathrm{H{-}O{-}H}$ bond angle for these bonds would be expected to be 90° since $2p_y$ and $2p_z$ are oriented 90° with respect to each other. Note that $|\chi_1\rangle$ and $|\chi_2\rangle$ are two-center bonding orbitals common to Valence Bond theory.

alt

Figure 10.2.1 : The three p-orbitals are aligned along perpendicular axis (CC-SA-BY-NC; Nick Greeves via ChemTube3D);

Using the oxygen atomic orbitals directly is obviously not a good model for describing bonding in water, since we know from experiment that the bond angle for water is 104.45° (Figure 10.2.2), which is also in agreement with VSEPR theory. Since the $2s$ orbital is spherical, mixing some $2s$ character into the $2p_z$ orbitals can adjust the bond angle as discussed previously by creating new hybrid orbitals.

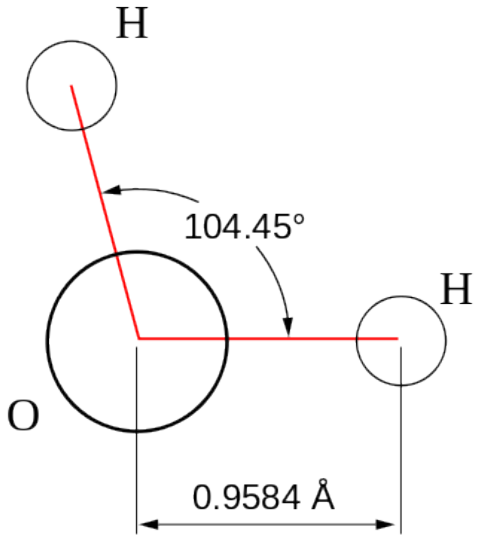


Figure 10.2.2 : Experimentally determined geometry of the water molecule (CC BY-SA 3.0; Booyabazooka).

Historically, Valence Bond theory was used to explain bend angles in small molecules. Of course, it was only qualitatively correct in doing this, as the following example shows. Let us construct the Valence Bond wavefunctions for the two bonding pairs in H_2O by mixing the $|2s\rangle$, $|2p_x\rangle$, $|2p_y\rangle$, and $|2p_z\rangle$ into four new sp^3 hybrid orbitals:

$$\chi_1(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right]$$
$$\chi_2(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right]$$
$$\chi_3(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right]$$
$$\chi_4(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right]$$

Hence, the three $2p$ orbitals of the oxygen atom combined with the $2s$ orbitals of the oxygen to form four sp^3 hybrid orbitals (Figure 10.2.3).



Figure 10.2.4: This would leave the $2s$ and $2p_z$ orbitals of oxygen left over for the two lone pairs on the oxygen.

The bond angle for four groups of electrons around a central atom is 109.5 degrees. However, for water the experimental bond angle is 104.45°. The VSPER picture (general chemistry) for this is that the smaller angle can be explained by the presence of the two lone-pairs of electrons on the oxygen atom. Since they take up more volume of space compared to a bonding pair of electrons the repulsions between lone pairs and bonding pairs is expected to be greater causing the H-O-H bond angle to be smaller than the ideal 109.5°.

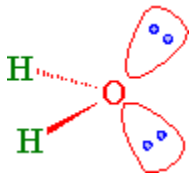


Figure 10.2.4 : Among the four hybrid orbitals, two are half filled and the remaining two are completely filled.

We can rationalize this by thinking about the s and p characters of the hybrids. In a perfectly sp^3 hybridized set of hybrid orbitals, each sp^3 orbital should have: 25% s character and and 75% p character. Since the bond angle is not 109.5° in water, the hybrid orbitals cannot have exactly this ratio of s and p character. So there there is uneven distribution of s and p character between the 4 hybrid orbitals. First we will write down the wavefunction and see what this means and then we will rationalize it.

Estimating Character of Hybrid Orbitals

The terminology we use for hybridization actually is just an abbreviation:

$$\mathrm{sp}^x = \mathrm{s}^{\frac{1}{x+1}}\mathrm{p}^{\frac{x}{x+1}}$$

In theory x can have any value, hence any of the following combinations constitute valid hybridization schemes for 1 s orbital and 3 p orbitals:

$$\begin{aligned} 1\times\mathrm{s}, 3\times\mathrm{p} &\rightsquigarrow 4\times\mathrm{sp}^3 \\ &\rightsquigarrow 3\times\mathrm{sp}^2, 1\times\mathrm{p} \\ &\rightsquigarrow 2\times\mathrm{sp}, 2\times\mathrm{p} \\ &\rightsquigarrow 2\times\mathrm{sp}^3, 1\times\mathrm{sp}, 1\times\mathrm{p} \\ &\rightsquigarrow \text{etc. pp.} \\ &\rightsquigarrow 2\times\mathrm{sp}^4, 1\times\mathrm{p}, 1\times\mathrm{sp}^{(2/3)} \end{aligned}$$

There are virtually infinite possibilities of combinations. Which one is "valid" is only determined by experiment (e.g., structure or spectroscopy). The generic sp^x hybrid orbitals wavefunction can be roughly written in terms of atomic orbital character:

$$|\chi_i\rangle = N(p + \gamma s) \tag{11.2.3}$$

where N is a normalization constant and γ is the relative contribution of s character to the hybrid orbital. For a pure sp^3 hybrid, γ would be 0.25 and for a pure sp hybrid, γ would be 1. The question is how to determine γ to get a better picture of the hybridization of water. Starting with the normalization criteria for wavefunctions:

$$\langle \chi_i | \chi_i \rangle = 1$$

and substituting Equation 11.2.3 into to get

$$\langle N(p + \gamma s) | N(p + \gamma s) \rangle = 1$$

which in integral notation is

$$\int N^2 (p + \gamma s)^2 d\tau = 1$$

where $d\tau$ represents all space. This is then expanded to

$$N^2 \cancelto{1}{\int p^2 d\tau} + N^2 2\gamma \cancelto{0}{\int sp\, d\tau} + N^2 \gamma^2 \cancelto{1}{\int s^2 d\tau} = 1 \tag{11.2.4}$$

These terms simplify either due to orthogonality or normality of the constitute atomic orbitals. Equation 11.2.4 simplifies to

$$N^2 + N^2 \gamma^2 = 1$$

and thus the normalization factor can be expressed in terms of γ

$$N = \frac{1}{\sqrt{1 + \gamma^2}}$$

and the generic normalized sp^x hybrid orbital (Equation 11.2.3) is

$$|\chi_i\rangle = \frac{1}{\sqrt{1 + \gamma^2}} (p + \gamma s) \tag{11.2.5}$$

The s and p characters to a hybrid orbital are now easy to obtain by squaring $|\chi_i\rangle$

- The magnitude of p-character is

$$\left(\frac{1}{\sqrt{1 + \gamma^2}} \right)^2 = \frac{1}{1 + \gamma^2} \tag{11.2.6}$$

  as $\gamma \to 0$, then the p character of the hybrid goes to 100%
- The magnitude of s-character is

$$\left(\frac{1}{\sqrt{1 + \gamma^2}} \gamma^2 \right)^2 = \frac{\gamma^2}{1 + \gamma^2} \tag{11.2.7}$$

  as $\gamma \to 1$, then the s character of the hybrid goes to 50%

As mentioned above, the geometric arrangement will **not** be formed because a molecule is hybridized in a certain way, it is the other way around. How do we choose the correct value of γ for the hybrid orbitals? The mixing coefficient γ is clearly related to the bond angle θ. Using some simple trigonometric relationships, it can be proven that:

$$\cos\theta = -\gamma^2 \tag{11.2.8}$$

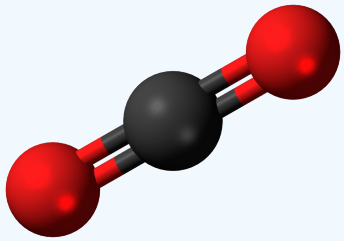
Equation 11.2.8 is an important equation as it related experimentally determined structure to the nature of the bonding and specifically, the composition of the atomic orbitals that create the hybrid orbitals used in the bonding.

Example 10.2.1 : Carbon Dioxide

What is the s-character in the hybrid orbitals for CO_2.

Solution

We know from simple VSEPR theory that the geometry of CO_2 is a linear triatomic molecule.



Thus $\theta = 180\,^\circ$ and via Equation 11.2.8, $\gamma = 1$ since $\cos 180\,^\circ = -1$. Hence, Equation 11.2.7 argues that the hybrid orbitals used in the bonding of CO_2 have 50% character; i.e., they are sp hybrid orbitals

$$|\chi_1\rangle = \frac{1}{\sqrt{2}}(s+p)$$

and

$$|\chi_2\rangle = \frac{1}{\sqrt{2}}(s-p)$$

Now, let's apply Equation 11.2.7 to water to find the character of the hybrid orbitals in water. The bond angle in water is 104.45° (Figure 10.2.2) hence

$$\cos 104.5^\circ = -0.25$$

and

$$\gamma = \sqrt{0.25} = 0.5$$

From Equation 11.2.6, then the amount of p character in the hybrid orbitals are

$$\frac{1}{1+\gamma^2} = \frac{1}{1+0.5^2} = 0.80\%$$

which leave 20% for s character (Equation 11.2.7).

$$\frac{\gamma^2}{1+\gamma^2} = \frac{0.5^2}{1+0.5^2} = 0.20$$

The two hybridized atomic orbitals of oxygen involved in bonding are each 80% p and 20% s character. This are not perfect sp^3 hybrid orbitals, as expected. Actually, the orbitals involved in the bonds would be better described as sp^4 hybridized. It does not mean that there are 4 p-orbitals in the hybrid orbital, but that each hybrid consists of 20% of s and 80% of p atomic orbitals.

Lone Pairs

Water has two sets of non-bonding electron pairs (Figure 10.2.4). Without a bond angle to start from, we cannot derive γ that describes the nonbonding hybrid orbitals that they occupy. However, we do know that the O atom has three p orbitals. So the TOTAL absolute p-character in all hybrid orbitals must be 3.

Let x be the p-character in the lone pairs hybrid orbitals:

$$0.8 + 0.8 + x + x = 3$$

This is assuming the lone pairs are **identical**. Solving for this, x = 0.7 (i.e. 70% p and 30% s). From this we can estimate the angle between the lone pair using Equations 11.2.6 and 11.2.8

- p-character:

$$\frac{1}{1+\gamma^2} = 0.7$$

so

$$-\gamma^2 = \frac{1}{0.7-1} = -0.42$$

and $\theta = 115\ °$.

The angle between the lone pairs is greater (115°) than the bond angle (104.5°). The sp^3 hybrid atomic orbitals of the lone pairs have > 25% s-character. These hybrid orbitals are less directional and held more tightly to the O atom. The sp^3 hybrid atomic orbitals of the bonding pairs have < 25% s-character. They are more directional (i.e., more p-character) and electron density found in the bonding region between O and H.

Warning

It should be noted that the valence bond theory application described above predicts that the two lone electron pairs are in the same hybrid orbitals and hence have the same energies. As discussed in the next sections, that is not experimentally observed in photoelectron spectroscopy, which is a shortcoming of valence bond theory's application to water.

Contributors and Attributions

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11.3: BeH_2 is Linear and H_2O is Bent

In this section, we will construct approximate molecular orbitals for a water molecule by considering a simple linear triatomic of the general form HXH, where X is a second row element. We will take a multi-centered molecular orbital approach instead of the two-centered valence bond/hybrid approach discussed previously. As with previous discussions of Molecular Orbitals, we approximate them as a linear combinations of atomic orbitals (LCAO). In molecular orbital theory linear combinations of **all** available (atomic) orbitals will form molecular orbitals. These are spread over the whole molecule, or delocalized, and in a quantum chemical interpretation they are called canonical orbitals. Since it is absolutely wrong to assume that there are only three types of sp^x hybrid orbitals, it is possible, that there are multiple different types of orbitals involved in bonding for a certain atom.

AH_2 Molecules

We want to construct a reasonable argument for the energetic ordering and structure of the molecular orbitals. We first note that each H will donate a $1s$ orbital in the LCAO scheme, and A will likely donate at least $2s$ and possible $2p$ orbitals, depending on its chemical identity. In general, if we consider only the first row A elements, the molecule orbitals (via the LCAO) can be expressed as combination of $1s$ orbitals on the two Hydrogens (H_1 and H_2) and the four n=2 orbitals ($2s$ $2p_x$ $2p_y; 2p_z$) on the A atom:

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_2|1s\rangle_{H_2} + a_3|2s\rangle_A + a_4|2p_x\rangle_A + a_5|2p_y\rangle_A + a_6|2p_z\rangle_A \tag{11.3.1}$$

These molecular orbitals were created with six atomic orbitals and hence six different $|\chi\rangle$ molecular orbitals can be created. As with previous molecular orbitals problems, the coefficients of this expansion ($\{a_i\}$) are determined by solving the secular determinant.

If we consider only linear AH_2 molecules, then Equation 11.3.1 can be simplified by ignoring $2p_x$ and $2p_y$ atomic orbitals since they are perpendicular to the bonds and are hence non-bonding (only for linear AH_2 molecules). Moreover, the molecule is symmetric about the center (the position of A), hence the orbitals have to have the same symmetry.

Only the $2p$ orbital of A that will overlap with $1s$ of H is the $2p_z$. Hence, Equation 11.3.1 can be simplified to consider the combination

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A + a_6|2p_z\rangle_A \tag{11.3.2}$$

Note that the two coefficients in front of the $1s$ orbitals of hydrogen are the same by symmetry. This since no hydrogen is "special" and they must have the same contribution to the molecular orbital.

Mixing Amplitudes

How big should the $2s$ orbital contributors of A be compared to the $1s$ orbital of H?

This depends on several things. First, is the nuclear charge on A and the second is the **electronegativity** difference between H and A. The first determines how quickly the $2s$ orbitals, remembering that the exponential part is $exp(-Zr/a_0)$, and the electronegativity difference determines the relative magnitude of H_1 compared to H_2.

The six $|\chi\rangle$ molecular orbitals from Equation 11.3.1 are shown in Figure 10.3.1 .

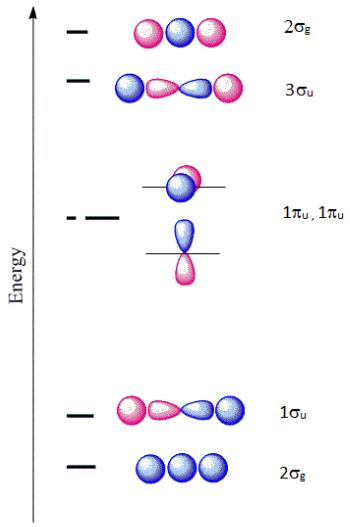


Figure 10.3.1 : The six molecular orbitals for the $\mathrm{AH_2}$ molecule constrained to a linear geometry. The symmetry labels for each molecular orbital are indicated.

The first molecular orbital $|\chi_1\rangle$ constructed from Equation 11.3.1 is purely bonding because the $2s$ orbital is positive near the A nucleus, but becomes negative as we go away from the nucleus. This orbital is also even (*garade symmetry*), so we can denote it as a $2\sigma_g$ orbital signifying that it is constructed from a $2s$ orbital of A combined with the two $1s$ orbitals of H. The only other MO that can be constructed that has the right symmetry is $|\chi_6\rangle$ which is denoted as $2\sigma_u$. This is an antibonding molecular orbital and is also even (*garade symmetry*). The corresponding wavefunctions are:

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A$$

$$|\chi_6\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} - a_3|2s\rangle_A$$

Next, if we combine a $2p_z$ orbital of A with the $1s$ of H, there are two possibilities that have the right symmetry. The first is

$$|\chi_2\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A$$

which is a bonding orbital and denoted as $1\sigma_u$. This is purely antibonding and has an odd symmetry (*ungarede*). The other combination is

$$|\chi_5\rangle = a_1|1s\rangle_{H_1} - a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A$$

Hence, we denote this as $2\sigma_g$. The orbitals $2p_x$ and $2p_y$ from X are nonbonding and become π_{2p_x} and π_{2p_y} nonbonding orbitals and designated as $1\pi_u$ orbitals:

$$|\chi_3\rangle = |2p_x\rangle_A$$

$$|\chi_4\rangle = |2p_y\rangle_A$$

Beryllium Hydride (BeH_2) is Linear

Consider the $\mathrm{BeF_2}$ molecule: Be has a $1s^2\ 2s^2$ electron configuration with is no unpaired electrons available for bonding. From a perspective of using only atomic orbitals to generate the bonding orbitals, we would conclude that the molecule could not exist since no free orientals exist on Be atom to bond. Clearly, atomic orbitals are not adequate to describe orbitals in molecules, but this can be solved by allowing the 2s and one 2p orbital on Be to mix to form sp hybrid orbitals. The experimental $\mathrm{H{-}Be{-}H}$ bond angle is 180°. Presumably, one electron from Be is shared with each unpaired electrons from H. We could promote and electron from the 2s orbital on Be to the 2p orbital to get two unpaired electrons for bonding (predicting 90° bond angles, not 180°). Thus the geometry is still not explained with atomic orbitals alone.

Be has 2s and 2p orbitals, and it is in the middle. H has 1s orbitals; there are two H atoms on the outside. We initially make

combinations of the H atomic orbitals that we previously used to make diatomic hydrogen, except there is no overlap (i.e., $S = 0$). These combinations will mix with the 2s and $2p_z$ on Be, as shown in Figure 10.3.2.

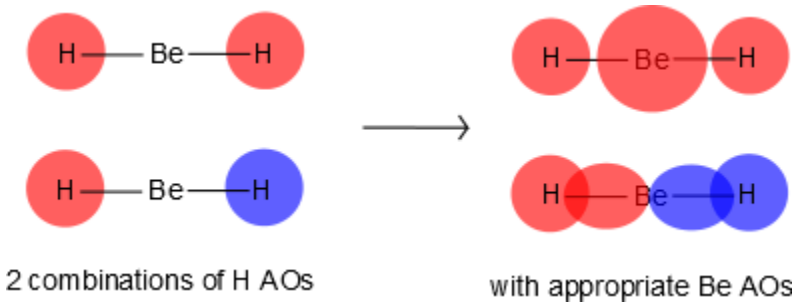


Figure 10.3.2: Forming molecular orbitals for $\mathrm{BeH_2}$.

Then we can put the Molecular Orbital diagram together, starting with the outside, drawing in bonding, non-bonding and anti-bonding MOs, and filling the electrons (Figure 10.3.3). The bond order is 2.

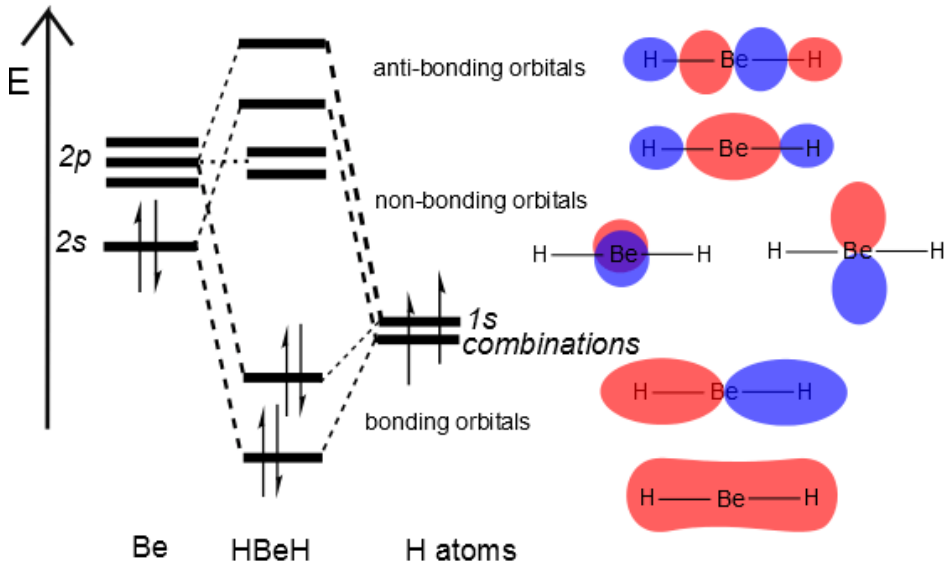


Figure 10.3.3: Molecular orbitals diagram for $\mathrm{BeH_2}$.

Walsh diagrams, often called angular coordinate diagrams or correlation diagrams, are representations of calculated orbital energies of a molecule versus a distortion coordinate, used for making quick predictions about the geometries of small molecules. By plotting the change in molecular orbital levels of a molecule as a function of geometrical change, Walsh diagrams explain why molecules are more stable in certain spatial configurations (i.e. why water adopts a bent conformation).

Walsh Correlation Diagrams

A major application of Walsh diagrams is to explain the regularity in structure observed for related molecules having identical numbers of valence electrons (i.e. why $\mathrm{H_2O}$ and $\mathrm{H_2S}$ look similar), and to account for how molecules alter their geometries as their number of electrons or spin state changes. Additionally, Walsh diagrams can be used to predict distortions of molecular geometry from knowledge of how the LUMO (Lowest Unoccupied Molecular Orbital) affects the HOMO (Highest Occupied Molecular Orbital) when the molecule experiences geometrical perturbation. Walsh's rule for predicting shapes of molecules states that a molecule will adopt a structure that best provides the most stability for its HOMO. If a particular structural change does not perturb the HOMO, the closest occupied molecular orbital governs the preference for geometrical orientation.

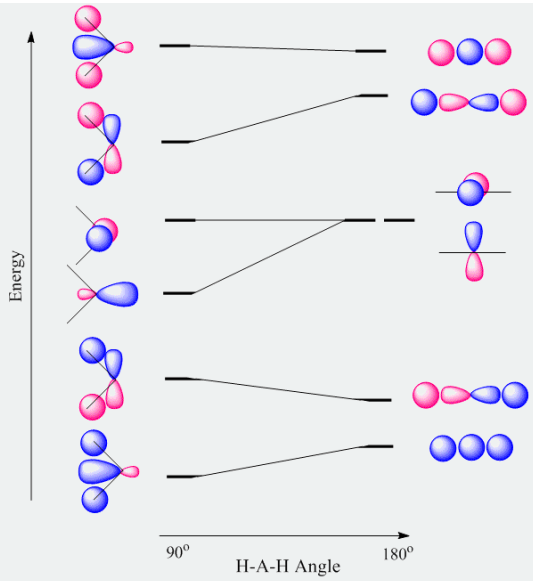


Figure 10.3.4: A Walsh diagram for an AH_2 molecule. (public domain).

For the AH_2 molecular system, Walsh produced the first angular correlation diagram by plotting the orbital energy curves for the canonical molecular orbitals while changing the bond angle from 90° to 180° (Figure 10.3.4). As the bond angle is distorted, the energy for each of the orbitals can be followed along the lines, allowing a quick approximation of molecular energy as a function of conformation.

A typical prediction result for water is an bond angle of 90°, which is not even close to the experimental value of 104°. At best, the method is able to differentiate between a bent and linear molecule.

> Walsh's rule for predicting shapes of molecules states that a molecule will adopt a structure that best provides the most stability for its HOMO. If a particular structural change does not perturb the HOMO, the closest occupied molecular orbital governs the preference for geometrical orientation.

Figure 10.3.4 illustrates the difference between the actual linear case we just analyzed and the truly bent molecule, e.g. H_2O. The geometry changes the ordering somewhat, but the qualitative picture we obtain from the linear case makes it a useful construction. The oxygen atomic orbitals are labeled according to their symmetry (Figure 10.3.5) as a_1 for the 2s orbital and b_1 ($2p_x$), b_2 ($2p_y$) and a_1 ($2p_z$) for the three 2p orbitals. The two hydrogen 1s orbitals are premixed to form a_1 and b_2 molecular orbitals.

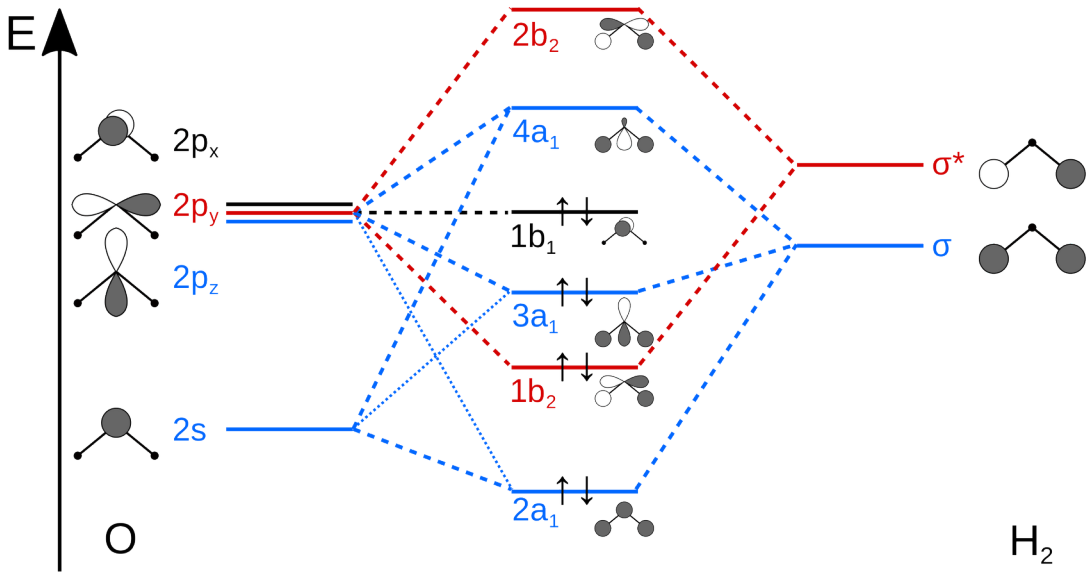


Figure 10.3.5: MO diagram for water. (CC-SA-BY-3.0; Officer781 via Wikipedia).

Mixing takes place between same-symmetry orbitals of comparable energy resulting a new set of MO's for water:

- $2a_1$ MO from mixing of the oxygen 2s atomic orbital and the hydrogen σ MO. Small oxygen $2p_z$ atomic orbital admixture strengthens bonding and lowers the orbital energy.
- $1b_2$ MO from mixing of the oxygen $2p_y$ atomic orbital and the hydrogen σ* MO.
- $3a_1$ MO from mixing of the oxygen $2p_z$ atomic orbital and the hydrogen σ MO. Small oxygen 2s atomic orbital admixture weakens bonding and raises the orbital energy.
- $1b_1$ nonbonding MO from the oxygen $2p_x$ atomic orbital (the p-orbital perpendicular to the molecular plane).

In the water molecule the highest occupied orbital, $(1b_1)$ is non-bonding and highly localized on the oxygen atom, similar to the non-bonding orbitals of hydrogen fluoride. The next lowest orbital $(2a_1)$ can be thought of as a non-bonding orbital, as it has a lobe pointing away from the two hydrogens. From the lower energy bonding orbitals, it is possible to see that oxygen also takes more than its "fair share" of the total electron density. The electronic configuration of water in the ground state (Figure 10.3.5) is therefore

$$(a_1)^2(b_2)^2(a_1)^2(b_1)^2$$

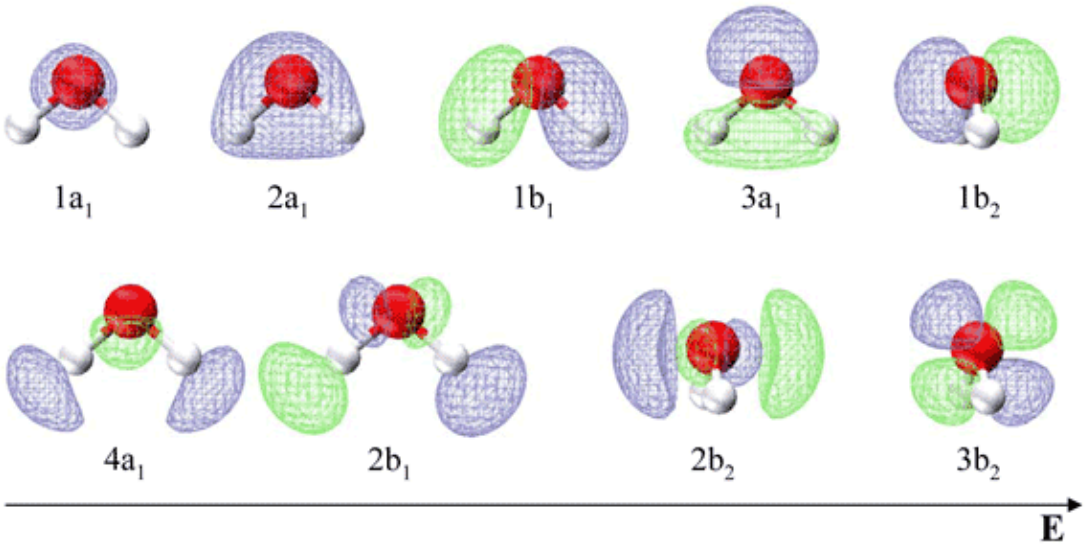


Figure 10.3.5. Image from Anna Krylov (USC)

Table 10.3.1 list the respective LCAO coefficients for the six atomic orbitals. Table 10.3.1 combines the energy values with the description derived from the character table for molecules of point group C_{2v}

Table 10.3.1: LCAO Coefficients of first six molecular orbitals of water

Energy	Symbol	s(H)	s(O)	p_x(O)	p_y(O)	p_z(O)	s(H)
6.728	$2b_2$	0.525	0	0	-0.669	0	-0.525
5.440	$3a_1$	-0.553	0.306	0	0	-0.544	0.553
-12.191	$1b_1$	0	0	-1.000	0	0	0
-14.467	$2a_1$	-0.309	0.354	0	0	0.827	-0.309
-19.113	$1b_2$	-0.473	0	0	-0.743	0	0.473
-40.032	$1a_1$	0.315	0.884	0	0	-0.143	0.315

Note in contrast to the valence bond theory discussed previous for water, the two lone electron pairs are **not in identical orbitals**. The $1b_1$ MO is a lone pair, while the $3a_1$, $1b_2$ and $2a_1$ MO's can be localized to give two O–H bonds and an in-plane lone pair. This is in agreement with the experimentally measured photoelectron spectrum discussed in the next section.

Summary

Walsh correlation diagram is a plot of molecular orbital energy as a function of some systematic change in molecular geometry. For example, the correlation between orbital energies and bond angle for an $\mathrm{AH_2}$ molecule. The geometry of a molecule is determined by which possible structure is lowest in energy. We can use the Walsh diagram to determine the energy trends based on which orbitals are occupied.

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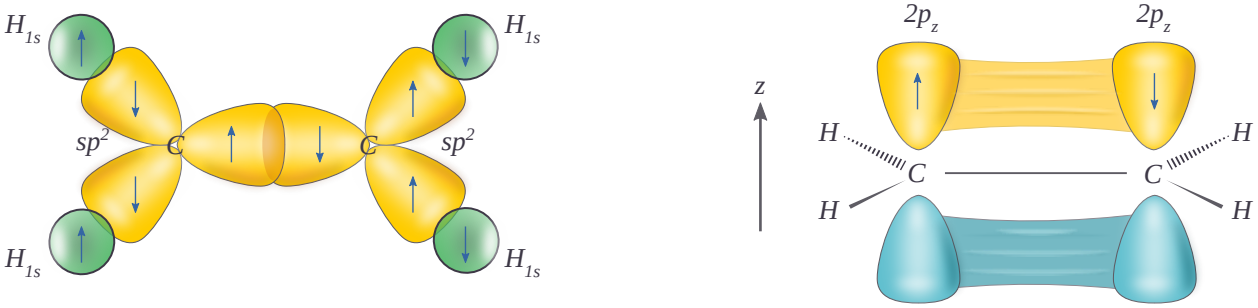
11.4: The pi-Electron Approximation of Conjugation

Learning Objectives

- Demonstrate how Hückel's theory approximates the full molecular orbital picture of molecules by treating the σ-bonding and π-bonding networks independently.

Molecular orbital theory has been very successfully applied to large conjugated systems, especially those containing chains of carbon atoms with alternating single and double bonds. An approximation introduced by Hückel in 1931 considers only the delocalized *p* electrons moving in a framework of π-bonds. This is, in fact, a more sophisticated version of a free-electron model.

The simplest hydrocarbon to consider that exhibits π bonding is ethylene (ethene), which is made up of four hydrogen atoms and two carbon atoms. Experimentally, we know that the $\mathrm{H-C-H}$ and $\mathrm{H-C-C}$ angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied s orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H (sp^2 + s) and one C–C (sp^2 + sp^2) (part a of Figure 10.5.1).



(a) C_2H_4 σ - bonded framework *(b) C_2H_4 π bonding*

Figure 10.5.1 : (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the *z*-axis.) (CC BY-NC; Ümit Kaya via LibreTexts)

The Hückel approximation is used to determine the energies and shapes of the π molecular orbitals in conjugated systems. Within the Hückel approximation, the covalent bonding in these hydrocarbones can be separated into two independent "frameworks": the σ-bonding framework and the the σ-bonding framework. The wavefunctions used to describe the bonding orbitals in each framework results from different combinations of atomic orbitals. The method limits itself to addressing conjugated hydrocarbons and specifically only π electron molecular orbitals are included because these determine the general properties of these molecules; the sigma electrons are ignored. This is referred to as *sigma-pi separability* and is justified by the orthogonality of σ and π orbitals in planar molecules. For this reason, the Hückel method is limited to planar systems. Hückel approximation assumes that the electrons in the π bonds “feel” an electrostatic potential due to the entire σ-bonding framework in the molecule (i.e. it focuses only on the formation of π bonds, given that the σ bonding framework has already been formed).

Conjugated Systems

A conjugated system has a region of overlapping p-orbitals, bridging the interjacent single bonds, that allow a *delocalization* of π electrons across all the adjacent aligned p-orbitals. These π electrons do not belong to a single bond or atom, but rather to a group of atoms.

Ethylene

Before considering the Hückel treatment for ethylene (C_2H_4), it is beneficial to review the general bonding picture of the molecule. Bonding in ethylene involves the sp^2 hybridization of the $2s$, $2p_x$, and $2p_y$ atomic orbitals on each carbon atom; leaving the $2p_z$ orbitals untouched (Figure 10.5.2).

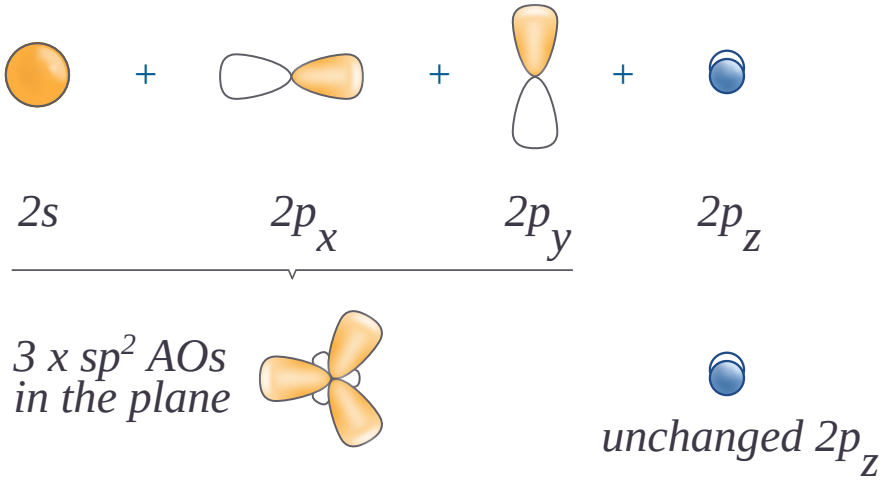


Figure 10.5.2 : Hybridizing of the carbon atomic orbitals to give sp^2 hybrid orbitals for bonding to hydrogen atoms in ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

The use of hybrid orbitals in the molecular orbital approach describe here is merely a convenience and not invoking valence bond theory (directly). An identical description can be extracted using exclusively atomic orbitals on carbon, but the interpretation of the resulting wavefunctions is less intuitive. For example, the ith molecular orbital can be described via hybrid orbitals

$$|\psi_1\rangle = c_1|sp_1^2\rangle + c_2|1s_a\rangle$$

or via atomic orbitals.

$$|\psi_1\rangle = a_1|2s\rangle + a_1|2p_x\rangle + a_1|2p_y\rangle + a_4|1s_a\rangle$$

where $\{a_i\}$ and $\{c_i\}$ are coefficients of the expansion. Either describe will work and both are identical approaches since

$$|sp_1^2\rangle = b_1|2s\rangle + b_1|2p_x\rangle + b_1|2p_y\rangle$$

where $\{c_i\}$ are coefficients describing the hybridized orbital.

The bonding occurs via the mixing of the electrons in the sp^2 hybrid orbitals on carbon and the electrons in the $1s$ atomic orbitals of the four hydrogen atoms (Figure 10.5.1 ; left) resulting in the σ-bonding framework. The π-bonding framework results from the unhybridized $2p_z$ orbitals (Figure 10.5.2 ; right). The independence of these two frameworks is demonstrated in the resulting molecular orbital diagram in Figure 10.5.3 ; Hückel theory is concerned only with describing the molecular orbitals and energies of the π bonding framework.

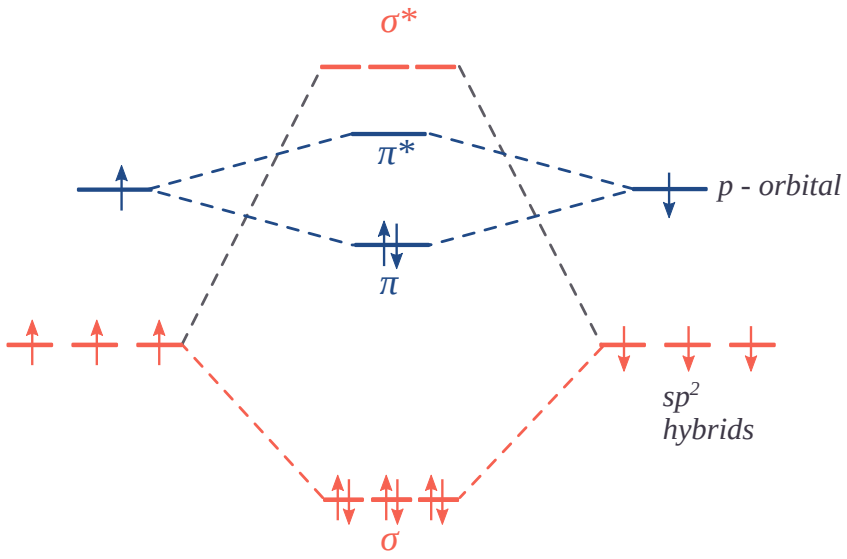


Figure 10.5.3 : Molecular orbitals demonstrating the sigma-pi separability of the π-bonding framework (blue) and the σ-bonding frameworks (red) of ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

Hückel treatment is concerned only with describing the molecular orbitals and energies of the π bonding framework.

Since Hückel theory is a special consideration of molecular orbital theory, the molecular orbitals $|\psi_i\rangle$ can be described as a linear combination of the $2p_z$ atomic orbitals ϕ at carbon with their corresponding $\{c_i\}$ coefficients:

$$|\psi_i\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \tag{11.4.1}$$

This equation is substituted in the Schrödinger equation:

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$$

with $\hat{H}$ the Hamiltonian and E_i the energy corresponding to the molecular orbital to give:

$$\hat{H}c_1|\phi_1\rangle + \hat{H}c_2|\phi_2\rangle = Ec_1|\phi_1\rangle + Ec_2|\phi_2\rangle \tag{11.4.2}$$

If Equation 11.4.2 is multiplied by $\langle\phi_1|$ (and integrated), then

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{11.4.3}$$

where H_{ij} are the Hamiltonian matrix elements (see note below)

$$H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle\phi_i|\phi_j\rangle = \int \phi_i \phi_j \mathrm{d}v$$

If Equation 11.4.2 is multiplied by $\langle\phi_2|$ (and integrated), then

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \tag{11.4.4}$$

Both Equations 11.4.3 and 11.4.4 can better represented in matrix notation,

$$\begin{bmatrix} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) \\ c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) \end{bmatrix} = 0$$

or more simply as a product of matrices.

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{11.4.5}$$

All diagonal Hamiltonian integrals H_{ii} are called **Coulomb integrals** and those of type H_{ij} are called **resonance integrals**. Both integrals are negative and the resonance integrals determines the strength of the bonding interactions. The equations described by Equation 11.4.5 are called the ***secular equations*** and will also have the trivial solution of

$$c_1 = c_2 = 0$$

Within linear algebra, the secular equations in Equation 11.4.5 will also have a non-trivial solution, if and only if, the secular determinant is zero

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{11.4.6}$$

or in shorthand notation

$$\det(H - ES) = 0$$

Everything in Equation 11.4.6 is a known number except E. Since the secular determinant for ethylene is a 2×2 matrix, finding E , requires solving a quadratic equation (after expanding the determinant)

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{21} - ES_{21})(H_{12} - ES_{12}) = 0$$

There will be two values of E which satisfy this equation and they are the molecular orbital energies. For ethylene, one will be the bonding energy and the other the antibonding energy for the π-orbitals formed by the combination of the two carbon $2p_z$ orbitals (Equation 11.4.1). However, if more than two $|\phi\rangle$ atomic orbitals were used, e.g., in a bigger molecule, then more energies would be estimated by solving the secular determinant.

Solving the secular determinant is simplified within Hückel method via the following four assumptions:

1. All overlap integrals S_{ij} are set equal to zero. This is quite reasonable since the $\pi -$ orbitals are directed perpendicular to the direction of their bonds (Figure 10.5.1). This assumption is often call neglect of differential overlap (NDO).
2. All resonance integrals H_{ij} between non-neighboring atoms are set equal to zero.
3. All resonance integrals H_{ij} between neighboring atoms are equal and set to β.
4. All coulomb integrals H_{ii} are set equal to α.

These assumptions are mathematically expressed as

$$H_{11} = H_{22} = \alpha$$

$$H_{12} = H_{21} = \beta$$

Assumptions 1 means that the overlap integral between the two atomic orbitals is 0

$$S_{11} = S_{22} = 1$$

$$S_{12} = S_{21} = 0$$

Matrix Representation of the Hamiltonian

The Coulomb integrals

$$H_{ii} = \langle \phi_i | H | \phi_i \rangle$$

and resonance integrals.

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \;\; (i \neq i)$$

are often described within the matrix representation of the Hamiltonian (specifically within the $|\phi\rangle$ basis):

$$\hat{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}$$

or within the Hückel assumptions

$$\hat{H} = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix}$$

The Hückel assumptions reduces Equation 11.4.5 in two homogeneous equations:

$$\begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{11.4.7}$$

if Equation 11.4.7 is divided by β:

$$\begin{bmatrix} \frac{\alpha - E}{\beta} & 1 \\ 1 & \frac{\alpha - E}{\beta} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

and then a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{11.4.8}$$

then Equation 11.4.7 simplifies to

$$\begin{bmatrix} x & 1 \\ 1 & x \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{11.4.9}$$

The trivial solution gives both wavefunction coefficients equal to zero and the other (non-trivial) solution is determined by solving the secular determinant

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

which when expanded is $x^2 - 1 = 0$ so $x = \pm 1$.

Knowing that $E = \alpha - x\beta$ from Equation 11.4.8, the energy levels can be found to be

$$E = \alpha - \pm 1 \times \beta$$

or

$$E = \alpha \mp \beta$$

Since β is negative, the two energies are ordered (Figure 10.5.4)

- For π_1: $E_1 = \alpha + \beta$
- For π_2: $E_2 = \alpha - \beta$

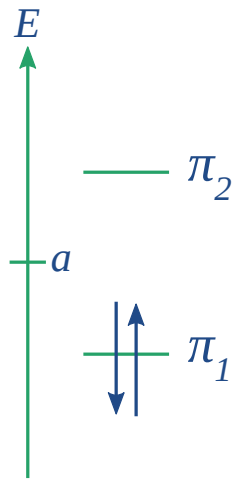


Figure 10.5.4 : π energies of ethylene with occupation. (CC BY-NC; Ümit Kaya via LibreTexts)

To extract the coefficients attributed to these energies, the corresponding x values can be substituted back into the Secular Equations (Equation 11.4.9). For the lower energy state ($x = -1$)

$$\begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 11.4.1):

$$|\psi_1\rangle = N_1(\phi_1\rangle + |\phi_2\rangle) \tag{11.4.10}$$

where N_1 is the normalization constant for this molecular orbital; this is the **bonding** molecular orbital.

For the higher energy molecular orbital ($x = -1$) and then

$$\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = -c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 11.4.1):

$$\psi_2\rangle = N_2(\phi_1\rangle - |\phi_2\rangle) \tag{11.4.11}$$

where N_2 is the normalization constant for this molecular orbital; this is the **anti-bonding** molecular orbital.

The normalization constants for both molecular orbitals can obtained via the standard normalization approach (i.e., $\langle\psi_i|\psi_i\rangle = 1$) to obtain

$$N_1 = N_2 = \frac{1}{\sqrt{2}}$$

These molecular orbitals form the π-bonding framework and since each carbon contributes one electron to this framework, only the lowest molecular orbital ($|\psi_1\rangle$) is occupied (Figure 10.5.5) in the ground state. The corresponding electron configuration is then π_1^2.

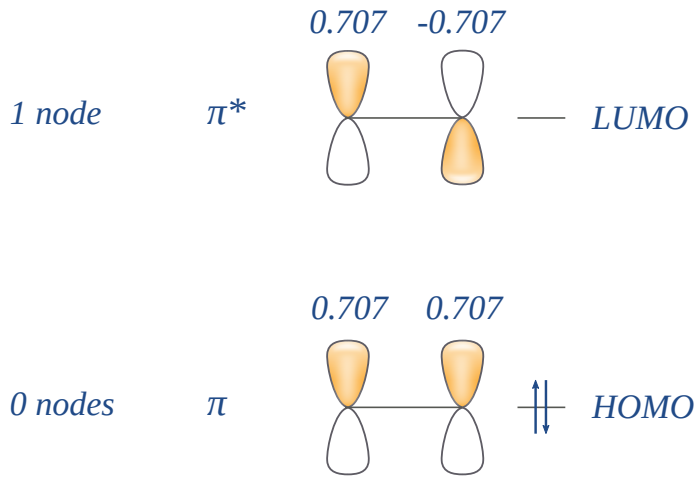


Figure 10.5.5 : Schemetic representation of the π molecular orbitals framework for ethylene . Notice that the antibonding molecular orbital has one more node than the bonding molecular orbital as expected since it is higher in energy. (CC BY-NC; Ümit Kaya via LibreTexts)

HOMO and LUMO are acronyms for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively and are often referred to as frontier orbitals. The energy difference between the HOMO and LUMO is termed the HOMO–LUMO gap.

The 3-D calculated π molecular orbitals are shown in Figure 10.5.6 .

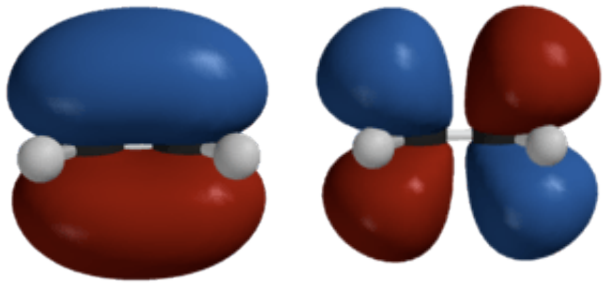


Figure 10.5.6 : Calculated π molecular orbitals for ethylene . (left) the bonding orbital (|\psi_1 \rangle\) and (right) the antibonding $(|\psi_2\rangle$ orbital.

Limitations of Hückel Theory

Hückel theory was developed in the 1930's when computers were unavailable and a simple mathematical approaches were very important for understanding experiment. Although the assumptions in Hückel theory are drastic they enabled the early calculations of molecular orbitals to be performed with mechanical calculators or by hand. Hückel Theory can be extended to address other types of atoms in conjugated molecules (e.g., nitrogen and oxygen). Moreover, it can be extended to also treat σ orbitals and this "Extended Hückel Theory" is still used today. Despite the utility of Hückel Theory, it is highly qualitative and we should remember the limitations of Hückel Theory:

- Hückel Theory is very approximate
- Hückel Theory cannot calculate energies accurately (electron-electron repulsion is not calculated)
- Hückel Theory typically overestimates predicted dipole moments

Hückel Theory is best used to provide simplified models for understanding chemistry and for a detailed understanding modern *ab initio* molecular methods discussed in Chapter 11 are needed.

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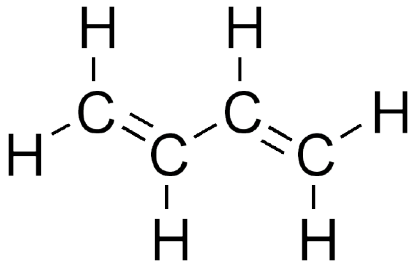
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11.5: Butadiene is Stabilized by a Delocalization Energy

Learning Objectives

- Apply Hückel theory to an extended π-bonding network
- Identify the origin of delocalization energy from Hückel theory and relate it to resonances structures in valence bond theory

1,3-Butadiene is a simple conjugated diene with the formula $\mathrm{C_4H_6}$ and can be viewed structurally as two vinyl groups ($\mathrm{CH_2{=}CH_2}$) joined together with a single bond. Butadiene can occupy either a cis or trans conformers and at room temperature, 96% of butadiene exists as the trans conformer, which is 2.3 kcal/mole more stable than the cis structure.



trans-1,3-Butadiene

For the simple application of applying Hückel theory for understanding the electronic structure of butadiene, we will ignore the energetic differences between the two conformers. As discussed previously, the molecular orbitals are linear combination of the four $|p\rangle$ atomic orbitals on the carbon atoms that are not participating in the σ bonding network:

$$|\psi_i\rangle = \sum_j^4 c_{ij}|p_i\rangle$$

or explicitly

$$|\psi_i\rangle = c_{i1}|p_1\rangle + c_{i2}|p_2\rangle + c_{i3}|p_3\rangle + c_{i4}|p_4\rangle \tag{11.5.1}$$

for the ith molecular orbital $|\psi_i\rangle$. The secular equations that need to be solved are

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{11.5.2}$$

If the standard Hückel theory approximations were used

$$H_{ii} - ES_{ii} = \alpha$$

and

$$H_{ij} - ES_{ij} = \beta$$

when $i = j \pm 1$, otherwise

$$H_{ij} - ES_{ij} = 0$$

then the secular equations for butadiene in Equation 11.5.2 become

$$\begin{bmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{11.5.3}$$

Solving Equation 11.5.3 for $\{c_i\}$ coefficients and energy secular equation requires extracting the roots of the secular determinant:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{11.5.4}$$

If both sides of Equation 11.5.4 were divided by β^4 and a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{11.5.5}$$

then Equation 11.5.4 simplifies further to

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{11.5.6}$$

This is essentially the connection matrix for the butadiene molecule. Each pair of connected atoms is represented by 1, each non-connected pair by 0 and each diagonal element by x. Expansion of the determinant in Equation 11.5.6 gives the 4th order polynomial equation

$$x^4 - 3x^2 + 1 = 0 \tag{11.5.7}$$

While solving 4th order equations typically require numerical estimation, Equation 11.5.7 can be further simplified by recognizing that it is a quadratic equation in terms of x^2. Therefore, the roots are

$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

or $x = \pm\ 0.618$ and $x = \pm\ 1.618$. Since α and β are negative, these molecular orbital energies can ordered in terms of energy (from lowest to highest):

$$E_1 = \alpha + 1.618\beta \tag{11.5.8}$$

$$E_2 = \alpha + 0.618\beta \tag{11.5.9}$$

$$E_3 = \alpha - 0.618\beta \tag{11.5.10}$$

$$E_4 = \alpha - 1.618\beta \tag{11.5.11}$$

This sequence of energies is displayed in the energy diagram of Figure 10.6.1 .

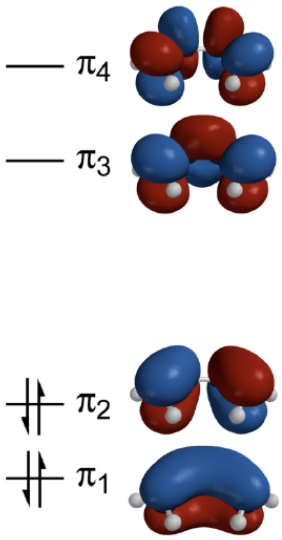


Figure 10.6.1 : The π molecular orbital energies from Hückel theory for butadiene with ground-state configuration. Structures calculated and images produced using HF/6-31G* (Public Domain; Ben Mills).

Each p atomic orbital of carbon contributes a single electron to the π manifold, so the ground-state occupation of the resulting four π electrons have a $\pi_1^2\pi_2^2$ configuration (Figure 10.6.1). The the total π-electron energy is then determined by adding up the energies in Equations 11.5.8-11.5.11 and scaling by their occupations to get

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_1 + 2\times E_2 + 0\times E_3 + 0\times E_4 \\ &= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) \\ &= 4\alpha + 4.472\beta \end{aligned} \tag{11.5.12}$$

If the bonding of butadiene were described only as two localized double bond as in its dominant valence-bond structure (Figure 10.6.1), then its π-electron energy would be given by twice the E_π predicted for the ethlyene molecule:

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_\pi(\text{ethylene}) \\ &= 2\times 2(\alpha+\beta) \\ &= 4\alpha + 4\beta \end{aligned} \tag{11.5.13}$$

Comparing Equation 11.5.12 with Equation 11.5.12, the total π energy of butadiene lies lower than the total π energy of two double bonds by 0.48β (the σ bond does not contribute). This difference is known as the **delocalization energy**; a typical estimate of β is around -75 kJ/mol, which results in a *delocalization energy* for butadiene of -35 kJ/mol.

The delocalization energy is the extra stabilization resulting from the electrons extending over the whole molecule.

Delocalization Energy in Valence Bond Theory

Delocalization energy is intrinsic to molecular orbital theory, since it results from breaking the two-center bond concept with the molecular orbitals that spread over more that just one pair of atoms. However, within the two-center theory of valence bond theory, the delocalization energy results from a stabilization energy attributed to resonance. Several conventional valence bond resonance structures that can be written for 1,3-butadiene, four of which are shown in Figure 10.6.2 . However, while structure $2a$ dominates, the other resonance structures also contribute to describing the total molecule and hence predict a corresponding stabilization energy akin to the delocalization energy in molecular orbital theory.

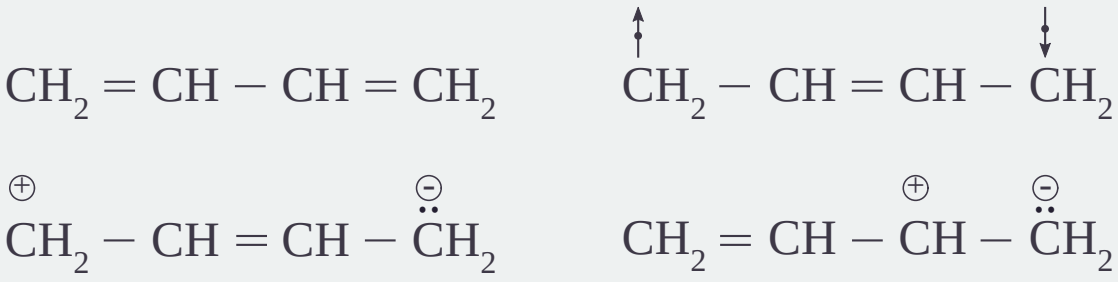


Figure 10.6.2 : Several resonance structures that can be written for 1,3-butadiene. The resonance structure in the upper left dominates, but does not exclusively describe the system since a delocalization energy is experimentally observed compared to two ethylene molecules. (CC BY-NC; Ümit Kaya via LibreTexts)

In general, the true description of the bonding within the valence bond theory is a superposition of resonance structures with amplitudes that are determined via a variational optimization to find the lowest possible energy for the valence bond wavefunctions.

The solving the secular equations (Equation 11.5.2) gives the $\{c_{ij}\}$ coefficients for the molecular orbitals in Equation 11.5.1 (not demonstrated):

$$|\psi_1\rangle = 0.37|p_1\rangle + 0.60|p_2\rangle + 0.60|p_3\rangle + 0.37|p_4\rangle \tag{11.5.14}$$

$$|\psi_3\rangle = 0.60|p_1\rangle + 0.37|p_2\rangle - 0.37|p_3\rangle - 0.60|p_4\rangle \tag{11.5.15}$$

$$|\psi_3\rangle = 0.60|p_1\rangle - 0.37|p_2\rangle - 0.37|p_3\rangle + 0.60|p_4\rangle \tag{11.5.16}$$

$$|\psi_4\rangle = 0.37|p_1\rangle - 0.60|p_2\rangle + 0.60|p_3\rangle - 0.37|p_4\rangle \tag{11.5.17}$$

These are depicted in Figure 10.6.3 .

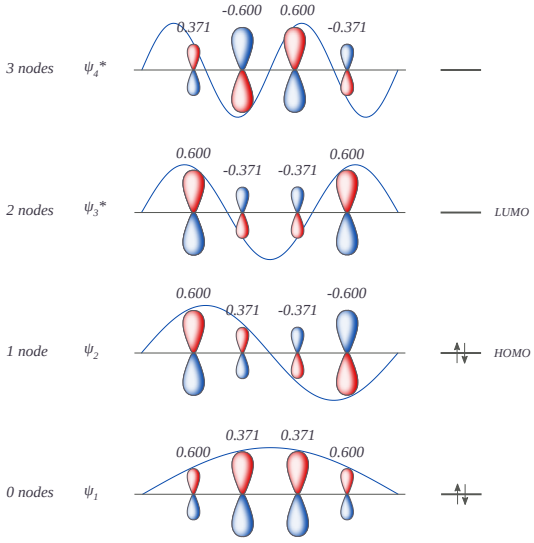


Figure 10.6.3 : Energy level diagram and decomposition of the π molecular orbitals of butadiene. This is view three-dimensionally in Figure 10.6.1 . (CC BY-NC; Ümit Kaya via LibreTexts)

Note the correlation of the energy of the π molecular orbitals of butadiene to the number of nodes in the wavefunction; this is the general trend observed in previous systems like the particle in the box and atomic orbitals. The four 3-D calculated molecular orbitals are contrasted in Figure 10.6.1 .

Exercise 10.6.1

What would Hückel theory predict for the energy levels and π molecular orbitals of cis-butadiene? Do you believe this approach adequately describes the energy levels of the cis-trans isomerization reaction of butadiene?

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11.6: Benzene and Aromaticity

Learning Objectives

- Apply Hückel theory to describing the pi bonding in cyclical conjugated system
- Identify the origin of aromaticity within Hückel theory to describe extra stabilization in certain cyclical conjugated systems

The previous sections addressed the π orbitals of linear conjugated system. Here we address conjugated systems of **cyclic conjugated hydrocarbons** with the general formula of $\mathrm{C}_n\mathrm{H}_n$ where n is the number of carbon atoms in the ring. The molecule from this important class of organic molecule that you are most familiar with is benzene ($\mathrm{C}_6\mathrm{H}_6$) with $n = 6$, although many other molecules exist like cyclobutadiene ($\mathrm{C}_4\mathrm{H}_4$) with $n = 4$ (Figure 10.7.1).

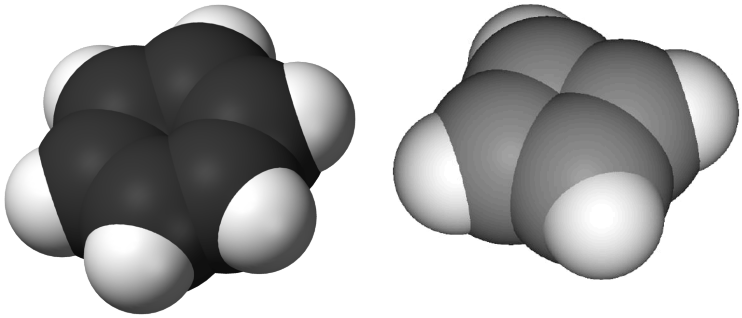


Figure 10.7.1 : Space-filling model of benzene (left) and cyclobutadiene (right). Carbon atoms are indicated in black, while hydrogen atoms are indicated in white. (Public domain; Benjah-bmm27 and Edgar181, respectively).

Structure of Benzene

The structure of benzene is an interesting historical topic. In 1865, the German chemist Friedrich August Kekulé published a paper suggesting that the structure of benzene contained a ring of six carbon atoms with alternating single and double bonds. Within this argument, two resonance structures can be formulated.

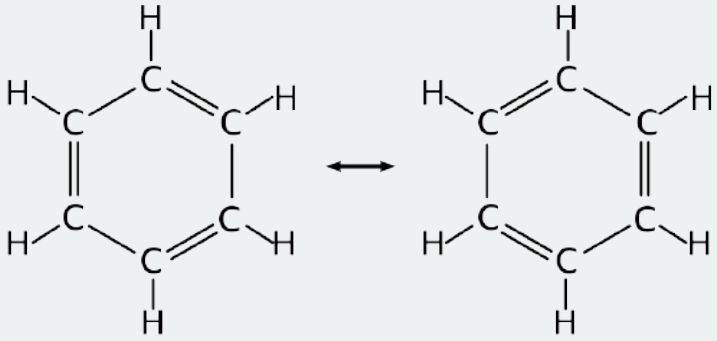


Figure 10.7.2 : Resonance structures of benzene.

However, X-ray diffraction shows that all six carbon-carbon bonds in benzene are of the same length, at 140 pm. The C–C bond lengths are greater than a double bond (135 pm), but shorter than a typical single bond (147 pm). This means that neither of the structures in Figure 10.7.2 are correct and the true 'structure' of benzene is a mixture of the two. As discussed previously, that such a valence bond perspective results in a **delocalization energy** within a molecular orbital approach.

Aromatic systems provide the most significant applications of Hückel theory. For benzene, we find the secular determinant

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{11.6.1}$$

with the six roots $x = \pm 2, \pm 1, \pm 1$. This corresponds to the following energies (ordered from most stable to least since $\beta < 0$):

- $E_1 = \alpha + 2\beta$
- $E_2 = \alpha + \beta$
- $E_3 = \alpha + \beta$
- $E_4 = \alpha - \beta$
- $E_5 = \alpha - \beta$
- $E_6 = \alpha - 2\beta$

The two pairs of $E = \alpha \pm \beta$ energy levels are two-fold degenerate (Figure 10.7.3).

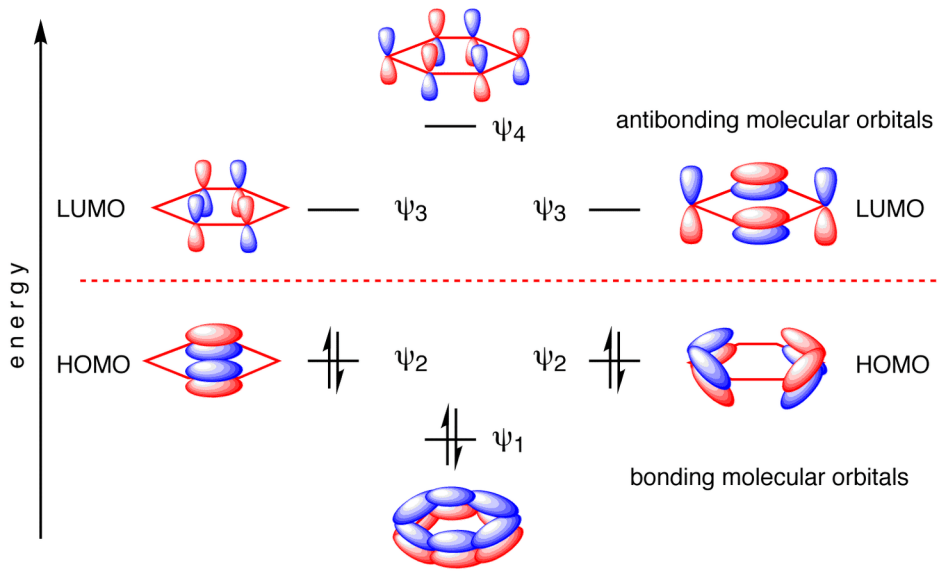


Figure 10.7.3 : The π molecular orbitals for benzene. The dashed lines represent the energy of an isolated p orbitals and all orbitals below this line are bonding. All orbitals above it are antibonding. (CC BY-NC-SA 4.0; Nick Greeves via ChemTube3D)

The resulting wavefunctions are below (expanded in terms of carbon $|2p\rangle$ atomic orbitals).

$$
\begin{aligned}
|\psi_1\rangle &= \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle\right] \\
|\psi_2\rangle &= \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle\right] \\
|\psi_3\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle + \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle - |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle + \frac{1}{2}|2p_{z6}\rangle\right] \\
|\psi_4\rangle &= \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle\right] \\
|\psi_5\rangle &= \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle - \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle + |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle - \frac{1}{2}|2p_{z6}\rangle\right] \\
|\psi_6\rangle &= \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle\right]
\end{aligned}
$$

Each of the carbons in benzene contributes one electron to the π-bonding framework (Figure 10.7.3). This means that all bonding molecular orbitals are fully occupied and benzene then has an electron configuration of $\pi_1^2\pi_2^2\pi_3^2$. With the three lowest molecular orbitals occupied, the total π-bonding energy is

$$
\begin{aligned}
E_{tot}(\text{benzene}) &= 2(\alpha + 2\beta) + 4(\alpha + \beta) \\
&= 6\alpha + 8\beta
\end{aligned} \tag{11.6.2}
$$

Since the energy of a localized double bond is $2(\alpha + \beta)$, as determined from the analysis of ethylene, the delocalization energy of benzene is

$$
\begin{aligned}
\Delta E &= E_{tot}(\text{benzene}) - 3E_{tot}(\text{ethylene}) \\
&= (6\alpha + 8\beta) - 3 \times 2(\alpha + \beta) \\
&= 2\beta
\end{aligned}
$$

The experimental thermochemical value is -152 kJ mol^{-1}.

Aromaticity

In general, cyclic polyenes are only closed shell (i.e., each electron paired up) and extra stable for with $(4n + 2)\pi$ electrons (n=0,1,2...). These special molecules have the highest delocalization energies and are said to be “aromatic”. For benzene this is 2β (Equation 11.6.2), which is the energy by which the delocalized π electrons in benzene are more stable than those in three isolated double bonds.

Hückel's Rule

A stable, closed-shell conjugated cyclic structure is obtained for molecules with $(4n + 2)\pi$ electrons with n=2, 6, 10, ... electrons.

Evidence for the enhanced thermodynamic stability of benzene was obtained from measurements of the heat released when double bonds in a six-carbon ring are hydrogenated (hydrogen is added catalytically) to give cyclohexane as a common product.

$$\mathrm{C_6H_6 + 3\,H_2 \longrightarrow C_6H_{12}}$$

In the following diagram cyclohexane represents a low-energy reference point. Addition of hydrogen to cyclohexene produces cyclohexane and releases heat amounting to 11.9 kJ mol^{-1}. If we take this value to represent the energy cost of introducing one double bond into a six-carbon ring, we would expect a cyclohexadiene to release 23.9 kJ mol^{-1} on complete hydrogenation, and 1,3,5-cyclohexatriene to release 35.9 kJ mol^{-1}. These heats of hydrogenation ΔH_{hyd} reflect the relative thermodynamic stability of the compounds (Figure 10.7.4).

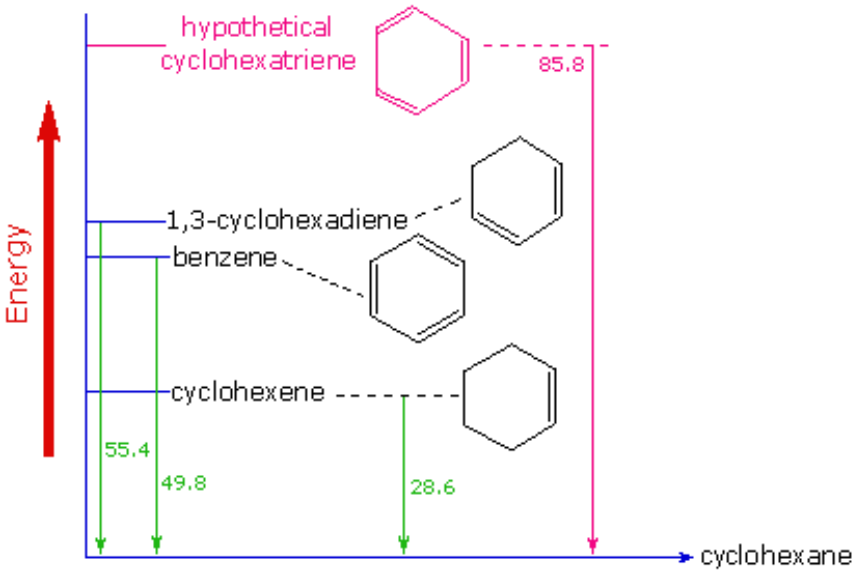


Figure 10.7.4 : Experimental evidence for aromatic stabilization energy in benzene from the heat of hydrogenation. Energies are in kcal/mol. (CC BY-NC-SA 4.0; William Resuch);

In practice, 1,3-cyclohexadiene is slightly more stable than expected, by about 8.1 kJ mol^{-1}, presumably due to conjugation of the double bonds. Benzene, however, is an extraordinary 15 kJ mol-1 more stable than expected. This additional stability is a characteristic of all aromatic compounds.

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11.E: Bonding in Polyatomic Molecules (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook
Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 10 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q10.8

Show that the four sp^3 orbitals are orthonormal.

S10.8

This means showing that each pair of $|sp^3\rangle$ hybrid orbitals meets the criteria: $\langle sp_i^3|sp_j^3\rangle = \delta_{ij}$

Designating the four sp^3 orbitals as:

$$|1\rangle = \frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)$$

$$|2\rangle = \frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle)$$

$$|3\rangle = \frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle)$$

$$|4\rangle = \frac{1}{2}(|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle)$$

Normality:

$$\langle 1|1\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| + \langle p_y| + \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{11.E.1}$$

$$= \frac{1}{4}\left(\langle s|s\rangle + \langle s|p_x\rangle + \langle s|p_y\rangle + \langle s|p_z\rangle + \langle p_x|s\rangle + \langle p_x|p_x\rangle + \langle p_x|p_y\rangle + \langle p_x|p_z\rangle + \langle p_y|s\rangle + \langle p_y|p_x\rangle + \langle p_y|p_y\rangle + \langle p_y|p_z\rangle + \langle p_z|s\rangle + \langle p_z\right.$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{11.E.3}$$

$$\langle 2|2\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| - \langle p_y| + \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle)\right) \tag{11.E.4}$$

$$= \frac{1}{4}\left(\langle s|s\rangle - \langle s|p_x\rangle - \langle s|p_y\rangle + \langle s|p_z\rangle - \langle p_x|s\rangle + \langle p_x|p_x\rangle + \langle p_x|p_y\rangle - \langle p_x|p_z\rangle - \langle p_y|s\rangle + \langle p_y|p_x\rangle + \langle p_y|p_y\rangle - \langle p_y|p_z\rangle + \langle p_z|s\rangle - \langle p_z\right.$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{11.E.6}$$

$$\langle 3|3\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| - \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle)\right) \tag{11.E.7}$$

$$= \frac{1}{4}\left(\langle s|s\rangle + \langle s|p_x\rangle - \langle s|p_y\rangle - \langle s|p_z\rangle + \langle p_x|s\rangle + \langle p_x|p_x\rangle - \langle p_x|p_y\rangle - \langle p_x|p_z\rangle - \langle p_y|s\rangle - \langle p_y|p_x\rangle + \langle p_y|p_y\rangle + \langle p_y|p_z\rangle - \langle p_z|s\rangle - \langle p_z\right.$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{11.E.9}$$

$$\langle 4|4\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| + \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle)\right) \tag{11.E.10}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle s|p_x\rangle + \langle s|p_y\rangle - \langle s|p_z\rangle - \langle p_x|s\rangle + \langle p_x|p_x\rangle - \langle p_x|p_y\rangle + \langle p_x|p_z\rangle + \langle p_y|s\rangle - \langle p_y|p_x\rangle + \langle p_y|p_y\rangle - \langle p_y|p_z\rangle - \langle p_z|s\rangle + \langle p$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{11.E.12}$$

Orthogonality:

For the longer wavefunctions, only surviving terms in the dot product are included:

$$\langle 1|2\rangle = \langle 2|1\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| - \langle p_y| + \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{11.E.13}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle - \langle p_y|p_y\rangle + \langle p_z|p_z\rangle) = \frac{1}{4}(1-1-1+1) = 0 \tag{11.E.14}$$

$$\langle 1|3\rangle = \langle 3|1\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| - \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{11.E.15}$$

$$= \frac{1}{4}(\langle s|s\rangle + \langle p_x|p_x\rangle - \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1+1-1-1) = 0 \tag{11.E.16}$$

$$\langle 1|4\rangle = \langle 4|1\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| + \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{11.E.17}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle + \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1-1+1-1) = 0 \tag{11.E.18}$$

$$\langle 2|3\rangle = \langle 3|2\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| - \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle)\right) \tag{11.E.19}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle + \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1-1+1-1) = 0 \tag{11.E.20}$$

$$\langle 2|4\rangle = \langle 4|2\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| + \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle)\right) \tag{11.E.21}$$

$$= \frac{1}{4}(\langle s|s\rangle + \langle p_x|p_x\rangle - \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1+1-1-1) = 0 \tag{11.E.22}$$

$$\langle 3|4\rangle = \langle 4|3\rangle = (\frac{1}{2}(\langle s| - \langle p_x| + \langle p_y| - \langle p_z|))(\frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle)) \tag{11.E.23}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle - \langle p_y|p_y\rangle + \langle p_z|p_z\rangle) = \frac{1}{4}(1-1-1+1) = 0 \tag{11.E.24}$$

Q10.9

The sp^3d^2 hybrid orbitals are given by:

$$\chi_1(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) - \frac{1}{\sqrt{2}}\psi_{3p_x}(r) - \frac{1}{\sqrt{12}}\psi_{3d_{z^2}} + \frac{1}{\sqrt{4}}\psi_{3d_{x^2-y^2}}$$

$$\chi_2(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) + \frac{1}{\sqrt{2}}\psi_{3p_x}(r) - \frac{1}{\sqrt{12}}\psi_{3d_{z^2}} + \frac{1}{\sqrt{4}}\psi_{3d_{x^2-y^2}}$$

$$\chi_3(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) - \frac{1}{\sqrt{2}}\psi_{3p_y}(r) - \frac{1}{\sqrt{12}}\psi_{3d_{z^2}} - \frac{1}{\sqrt{4}}\psi_{3d_{x^2-y^2}}$$

$$\chi_4(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) + \frac{1}{\sqrt{2}}\psi_{3p_y}(r) - \frac{1}{\sqrt{12}}\psi_{3d_{z^2}} - \frac{1}{\sqrt{4}}\psi_{3d_{x^2-y^2}}$$

$$\chi_5(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) - \frac{1}{\sqrt{2}}\psi_{3p_z}(r) + \frac{1}{\sqrt{12}}\psi_{3d_{z^2}}$$

$$\chi_6(r) = \frac{1}{\sqrt{6}}\psi_{3s}(r) + \frac{1}{\sqrt{2}}\psi_{3p_z}(r) + \frac{1}{\sqrt{12}}\psi_{3d_{z^2}}$$

Determine the angles of SF_6 using the vector approach (dot product formula).

S10.9

The s orbitals are spherical and therefor do not contribute to the directional vectors for this problem. The d_{z^2} orbital only has z directionality and the $d_{x^2-y^2}$ orbital has equal parts x and y directionality. The equations can be rewritten:

$$\psi_1 = \left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{4}}\right)\mathbf{i} + \frac{1}{\sqrt{4}}\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k} \qquad \psi_2 = \left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{4}}\right)\mathbf{i} + \frac{1}{\sqrt{4}}\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k} \tag{11.E.25}$$

$$\psi_3 = -\frac{1}{\sqrt{4}}\mathbf{i} + \left(-\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{4}}\right)\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k} \qquad \psi_4 = -\frac{1}{\sqrt{4}}\mathbf{i} + \left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{4}}\right)\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k} \tag{11.E.26}$$

$$\psi_5 = \left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\mathbf{k} \qquad \psi_6 = \left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\mathbf{k} \tag{11.E.27}$$

For any two ψ the angel can be calculated using:

$$\left(\sqrt{A_x^2 + A_y^2 + A_z^2}\right)\left(\sqrt{B_x^2 + B_y^2 + B_z^2}\right) cos\theta = A_xB_x + A_yB_y + A_zB_z \tag{11.E.28}$$

So, choosing ψ_5 and ψ_6 we get:

$$\left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right) cos\theta = \left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right) \tag{11.E.29}$$

$$-\frac{5}{12}cos\theta = -\frac{5}{12} \tag{11.E.30}$$

$$cos\theta = 0 \tag{11.E.31}$$

$$\theta = 90^\circ \tag{11.E.32}$$

Q10.10

Given

$$\xi_1 = \frac{1}{\sqrt{4}}2s + \sqrt{\frac{3}{4}}2p_z \tag{11.E.33}$$

$$\xi_2 = \frac{1}{\sqrt{4}}2s + \sqrt{\frac{2}{3}}2p_x - \frac{1}{\sqrt{12}}2p_z \tag{11.E.34}$$

what is the angle between ξ_1 and ξ_2?

What is the purpose of the square root constants before the orbitals?

S10.10

Since we know that

$$(\sqrt{A_x^2 + A_y^2 + A_z^2})(\sqrt{B_x^2 + B_y^2 + B_z^2})\cos\theta = A_xB_x + A_yB_y + A_zB_z \tag{11.E.35}$$

When we plug in our constants in the x, y, and z directions for the two equations we get

$$(\sqrt{\frac{2}{3}+\frac{1}{12}})(\sqrt{\frac{3}{4}})\cos\theta = -\sqrt{\frac{1}{12}}\sqrt{\frac{3}{4}} \tag{11.E.36}$$

isolating the theta term we get

$$\theta = \arccos(-\sqrt{\frac{1}{12}}/\sqrt{\frac{12}{9}} \tag{11.E.37}$$

yielding

$$\theta = 109.47^{\circ} \tag{11.E.38}$$

The square root constants are the necessary normalization constants.

Q10.11

Given that

$$\psi_1 = 0.71j + 0.55k \tag{11.E.39}$$

and

$$\psi_2 = -0.71j + 0.55k \tag{11.E.40}$$

Find the bond angle between ψ_1 and ψ_2 using the vector approach.

S10.11

Using this equation below:

$$\left(\sqrt{A_x^2+A_y^2+A_z^2}\right)\left(\sqrt{B_x^2+B_y^2+B_z^2}\right)cos\theta = A_xB_x + A_yB_y + A_zB_z \tag{11.E.41}$$

use to find the angle between the orbitals,

$$(0.71^2+0.55^2)^{0.5}(0.71^2+0.55^2)^{0.5}cos\theta = -0.71^2+0.55^2 \tag{11.E.42}$$

$$cos\theta = -0.25 \tag{11.E.43}$$

$$\theta = 104.5^{\circ} \tag{11.E.44}$$

Q10.12

Assuming a water molecule sits in the yz-plane, show that two bonding hybrid atomic orbitals on the oxygen atom can be expressed as

$$\psi_1 = N[\gamma 2s + (sin[\theta]2p_y + cos[\theta]2p_z] \tag{11.E.45}$$

and

$$\psi_2 = N[\gamma 2s - (sin[\theta]2p_y + cos[\theta]2p_z]. \tag{11.E.46}$$

Additionally, find γ assuming the bond angles to be 104.5 °.

S10.12

Because the molecules are in the yz plane, the p_x orbital can be neglected because it is completely orthogonal. The hybrid orbitals are a linear combination of the $2s,\ 2p_y,$ and $2p_z$ orbitals.

$$\psi_{bonding} = N[\gamma 2_s + c_1 2p_y + c_2 2p_z] \tag{11.E.47}$$

c_1 and c_2 can be found by thinking about how the bonds are oriented. The two bonds both have $cos[\theta]$ character in the z-direction and have $\pm sin[\theta]$ in the y-direction. The two functions can therefore be written as

$$\psi_1 = N[\gamma 2s + (sin[\theta]2p_y + cos[\theta]2p_z) \tag{11.E.48}$$

and

$$\psi_2 = N[\gamma 2s - (sin[\theta]2p_y + cos[\theta]2p_z) \tag{11.E.49}$$

when c_1 and c_2 are replaced with the sin and cos functions above.

The two functions when integrated will equal zero due to orthogonality.

$$\langle \psi_1 | \psi_2 \rangle = 0 \tag{11.E.50}$$

$$N^2(\gamma^2 + cos^2[\theta] - sin^2[\theta]) \tag{11.E.51}$$

$$\gamma^2 = sin^2[\theta] - cos^2[\theta] \tag{11.E.52}$$

The bond angles in water are 104.5° which can be substituted into θ.

$$\gamma = 0.5 \tag{11.E.53}$$

Q10.13

The lone pair wave functions of H2O can be described as:

$$\psi_{l1} = 0.54(2s) - 0.44(2pz) + 0.72(2px) \tag{11.E.54}$$

$$\psi_{l2} = 0.54(2s) - 0.44(2pz) - 0.72(2px) \tag{11.E.55}$$

Confirm the orthonormality of these wave functions.

S10.13

The two wave functions must be normalized and orthogonal to each other.

$$\int d\tau \psi_{l1}^* \psi_{l1} = 1 \tag{11.E.56}$$

$$= (0.54)^2(2s) + (-0.44)^2(2pz) + (0.72)^2(2px) = 1 \tag{11.E.57}$$

$$\int d\tau \psi_{l2}^* \psi_{l2} = 1 \tag{11.E.58}$$

$$= (0.54)^2(2s) + (-0.44)^2(2pz) + (-0.72)^2(2px) = 1 \tag{11.E.59}$$

$$\int d\tau \psi_{l1}^* \psi_{l2} = 0 \tag{11.E.60}$$

$$= (0.54)^2(2s) + (-0.44)^2(2pz) - (0.72)^2(2px) = 0 \tag{11.E.61}$$

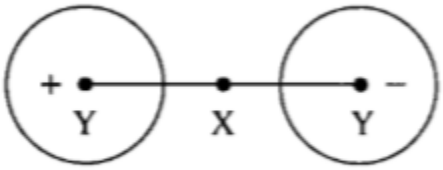
The atomic orbitals within the linear combination of the lone pair wave functions are normalized and orthogonal, zeroing out cross products and leaving only the squares of the coefficients.

10.14

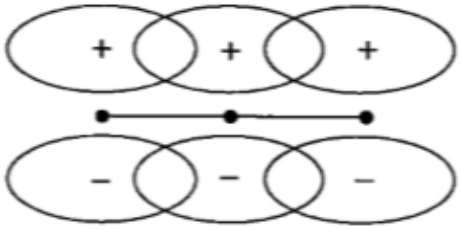
Molecular orbitals for a linear

$$XY_2 \tag{11.E.62}$$

molecule can be represented as



$2\sigma_u$



$1\pi_g$

Draw a schematic representation for the

$$3\sigma_g, 4\sigma_g, 1\pi_g, 2\sigma_g \tag{11.E.63}$$

orbitals

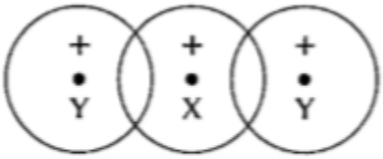
Which has the highest energy?

S10.14

$$3\sigma_g \tag{11.E.64}$$

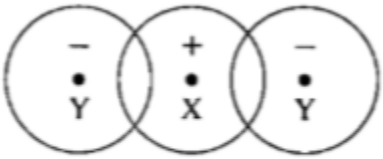
NOTE:

$$3\sigma_g \tag{11.E.65}$$



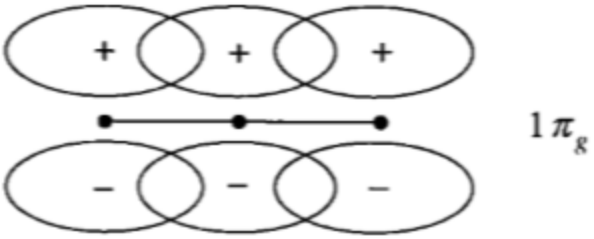
$3\sigma_g$

$$4\sigma_g \tag{11.E.66}$$



$4\sigma_g$

$$1\pi_g \tag{11.E.67}$$



$$2\sigma_g \tag{11.E.68}$$

$$4\sigma_g \tag{11.E.69}$$

has the highest energy

The

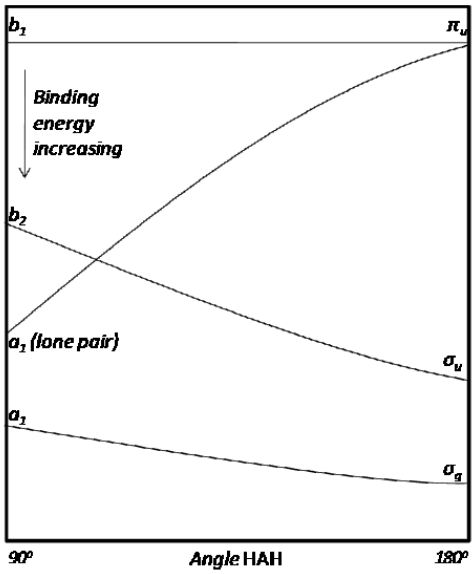
$$4\sigma_g \tag{11.E.70}$$

moleclar orbital has the highest energy; as expected since it more nodes.

Q10.18

Use the given Walsh diagram to predict the geometry of the following molecules:

a. H_2O
b. H_2S
c. H_2Be



Walsh Diagram of an HAH molecule.Public Domain

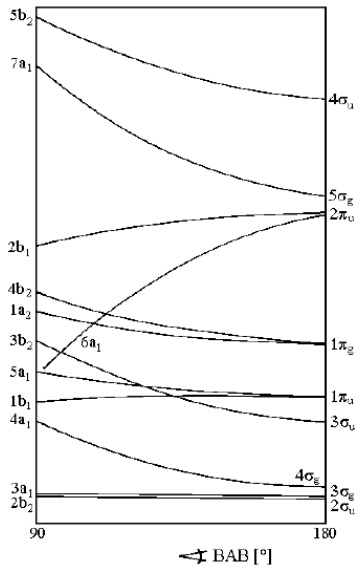
S10.18

The Walsh Diagram predicts the geometry of a molecule by assigning its valence electrons to the appropriate energy levels. In general, the lowest energy configuration is preferred.

a. H_2O has 8 valence electrons, which corresponds to the 4th highest orbital on the diagram. The **bent configuration** (90°) is lower in energy in this case.
b. H_2S has 8 valence electrons as well, because sulfur and oxygen are in the same periodic group. Therefore, the **bent configuration** will be favored.
c. H_2Be has 4 valence electrons, which corresponds to the 2nd highest orbital on the diagram. The **linear configuration** (180°) is lower in energy in this case.

Q10.19

Use the Walsh diagram for the valence electrons of a XY_2 molecule to predict whether the following molecules are linear or bent:



a. (CO_2) **b.** (CO_2^+) **c.** (CO_2^-) **d.** (SO_2^-) **b.** (CF_2^+)

S10.19

Valence Electrons	Geometry
2-16	linear
17-20	bent
21-24	linear

a. CO_2 16 valence electrons **Linear**
b. CO_2^+ 15 valence electrons **Linear**
c. CO_2^- 17 valence electrons **Bent**
d. SO_2^- 19 valence electrons **Bent**
e. CF_2^+ 18 valence electrons **Bent**

Q10.20

Walsh correlation diagrams can be used to predict the shapes of polyatomic molecules that contain more than three atoms. In this and the following three problems we consider molecules that have the general formula XH_3. We will restrict our discussion to XH_3 molecules, where all the H—X—H bond angles are the

same. If the molecule is planar, then the H—X—H bond angle is 120°. A nonplanar XH_3 molecule, then, has an H—X—H bond angle that is less than 120°. Figure 10.26 shows the Walsh correlation diagram that describes how the energies of the molecular orbitals for an XH3 molecule change as a function of the H—X—H bond angle. Note that because XH_3 is not linear, the labels used to describe the orbitals on the two sides of the correlation diagram do not have designations such as and . We see that the lowest-energy molecular orbital is insensitive to the H—X—H bond angle. Which atomic orbital(s) contribute to the lowest-energy molecular orbital? Explain why the energy of this molecular orbital is insensitive to changes in the H—X—H bond angle.

S10.20

The lowest energy molecular orbital is the 1s orbital, which is a core atomic orbital instead of a bonding atomic orbital.

Q10.21

Consider the BH2 where the general Walsh diagram for a XH2 is shown below. What is the geometric preference of the molecule in ground and excited state?

S10.21

The BH2 molecule has the same geometric shape as water, it is bent where the HOMO is \({\pi_u}\). The first excited state relies on the degree of bending, and the $2a_1$ is unoccupied, and the next $1b_2$ is the highest occupied where the preferred geometry is linear, so at the first excited state will be linear.

BH_2 is a linear molecule. It has 4 valance electrons which fill 2 of the lines in the Walsh diagram. This second line has lower energy towards linear conformation and $1\sigma_u$.

Q10.24

Solve for ψ_π corresponding to the energy $E = \alpha + \beta$ for ethene.

S10.24

The bonding Huckel molecular orbitals is

$$\psi_\pi = c_1 2p_{z1} + c_2 2p_{z2} \tag{11.E.71}$$

the relationship of the coefficients can be defined as the following from the secular determinate:

$$c_1(\alpha - E) + c_2\beta = 0 \tag{11.E.72}$$

$$c_1\beta + c_2(\alpha - E) = 0 \tag{11.E.73}$$

Substituting $E = \alpha + \beta$ into these expressions and solving gives

$$-c_1\beta + c_2\beta = 0 \tag{11.E.74}$$

$$c_1 = c_2 \tag{11.E.75}$$

Then plugging back into the original equation gives

$$\psi_\pi = c_1(2p_{zA} + 2p_{zB}) \tag{11.E.76}$$

Now we can solve for c_1 by normalizing the wavefunction

$$c_1^2(1+2S+1)=1 \tag{11.E.77}$$

where S = 0 so solving yields

$$c_1=\frac{1}{\sqrt{2}} \tag{11.E.78}$$

.

The final wave function can be written as

$$\psi_\pi=\frac{1}{\sqrt{2}}(2p_{z1}+2p_{z2}) \tag{11.E.79}$$

Q10.25

Generalize the molecular orbital treatment of propene allyl cation. Find the energies and wave function of this molecule.

S10.25

The Huckel secular determinant for propene is

$$\begin{vmatrix}\alpha-E & \beta & 0\\ \beta & \alpha-E & \beta\\ 0 & \beta & \alpha-E\end{vmatrix}=0 \tag{11.E.80}$$

making a substitution for $x=\frac{\alpha-E}{\beta}$ the secular determinant becomes

$$\begin{vmatrix}x & 1 & 0\\ 1 & x & 1\\ 0 & 1 & x\end{vmatrix}=0 \tag{11.E.81}$$

Solving the determinant yields a cubic polynomial $x^3-2x=0$ the roots of this polynomial are $x=0,\pm\sqrt{2}$

Replacing x with the previous substitution made it is found that

$$E=\alpha\pm\sqrt{2}\beta \tag{11.E.82}$$

and

$$E=0 \tag{11.E.83}$$

To find the wave function of propene you must find the constants

$$\begin{vmatrix}c_1(x) & c_2 & 0\\ c_1 & c_2(x) & c_3\\ 0 & c_2 & c_3(x)\end{vmatrix}=0 \tag{11.E.84}$$

solving the determinant yields

$$c_1=c_3=\frac{1}{2} \tag{11.E.85}$$

$$c_2=\frac{1}{\sqrt{2}} \tag{11.E.86}$$

therefore the wave function is

$$\psi=\frac{1}{2}1s+\frac{1}{\sqrt{2}}2s+\frac{1}{2}2p_z \tag{11.E.87}$$

Q10.26

Show that the six molecular orbitals for Benzene consturcted from the $2Pp_x$ atomic orbital on each of the six carbon atoms:

$$\psi_i = \sum_{j=1}^{6} c_{ij} 2p_{xj} \tag{11.E.88}$$

leads to a secular determinant.

S10.26

The above equation for benzene is :

$$\psi_i = c_{i1}2p_{z1} + c_{i2}2p_{z2} + c_{i3}2p_{z3} + c_{i4}2p_{z4} + c_{i5}2p_{z5} + c_{i6}2p_{z6} \tag{11.E.89}$$

The secular determinant for the benzene is :

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES_{14} & H_{15} - ES_{15} & H_{16} - ES_{16} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & H_{23} - ES_{23} & H_{24} - ES_{24} & H_{25} - ES_{25} & H_{26} - ES_{26} \\ H_{13} - ES_{13} & H_{23} - ES_{23} & H_{33} - ES_{33} & H_{34} - ES_{34} & H_{35} - ES_{35} & H_{36} - ES_{36} \\ H_{14} - ES_{14} & H_{24} - ES_{24} & H_{34} - ES_{34} & H_{44} - ES_{44} & H_{45} - ES_{45} & H_{46} - ES_{46} \\ H_{15} - ES_{15} & H_{25} - ES_{25} & H_{35} - ES_{35} & H_{45} - ES_{45} & H_{55} - ES_{55} & H_{56} - ES_{56} \\ H_{16} - ES_{16} & H_{26} - ES_{26} & H_{36} - ES_{36} & H_{46} - ES_{46} & H_{56} - ES_{56} & H_{66} - ES_{66} \end{vmatrix} = 0 \tag{11.E.90}$$

$H_{11} = H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = \alpha$

$H_{12} = H_{23} = H_{34} = H_{45} = H_{56} = \beta$ The $H_{ij} = H_{ji}$ is a hermitian operator when i and j are neighbors

$H_{ij} = 0$ when i and j are not neighbors

$S_{11} = S_{22} = S_{33} = S_{44} = S_{55} = S_{66} = 1$

$S_{ij} = 0$

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12: MOLECULAR SPECTROSCOPY

Spectroscopy generally is defined as the area of science concerned with the absorption, emission, and scattering of electromagnetic radiation by atoms and molecules, which may be in the gas, liquid, or solid phase. Visible electromagnetic radiation is called light, although the terms light, radiation, and electromagnetic radiation can be used interchangeably. Spectroscopy played a key role in the development of quantum mechanics and is essential to understanding molecular properties and the results of spectroscopic experiments. It is used as a “stepping stone” to take us to the concepts of quantum mechanics and the quantum mechanical description of molecular properties in order to make the discussion more concrete and less abstract and mathematical.

12.1: The Electromagnetic Spectrum

12.2: Rotations Accompany Vibrational Transitions

12.3: Unequal Spacings in Vibration-Rotation Spectra

12.4: Unequal Spacings in Pure Rotational Spectra

12.5: Vibrational Overtones

12.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information

12.7: The Franck-Condon Principle

12.8: Rotational Spectra of Polyatomic Molecules

12.9: Normal Modes in Polyatomic Molecules

12.10: Time-Dependent Perturbation Theory

12.11: The Selection Rule for the Rigid Rotor

12.12: The Harmonic Oscillator Selection Rule

12.13: Group Theory Determines Infrared Activity

12.E: Molecular Spectroscopy (Exercises)

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12.1: The Electromagnetic Spectrum

An important aspect of studying Physical Chemistry is to be able to recognize the interaction of molecules to the surroundings. Molecular Spectroscopy provides a clear image of how diatomic and polyatomic molecules interact by looking at the Frequency, Wavelength, Wave number, Energy, and molecular process. We will also be able to see the absorption properties of molecules in various regions from the electromagnetic spectrum.

Electromagnetic Radiation

Electromagnetic radiation—light—is a form of energy whose behavior is described by the properties of both waves and particles. Some properties of electromagnetic radiation, such as its refraction when it passes from one medium to another are explained best by describing light as a wave. Other properties, such as absorption and emission, are better described by treating light as a particle. The exact nature of electromagnetic radiation remains unclear, as it has since the development of quantum mechanics in the first quarter of the 20th century. Nevertheless, the dual models of wave and particle behavior provide a useful description for electromagnetic radiation.

Electromagnetic radiation consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity. In a vacuum electromagnetic radiation travels at the speed of light, c, which is $2.99792 \times 10^8\ m/s$. When electromagnetic radiation moves through a medium other than a vacuum its velocity, v, is less than the speed of light in a vacuum. The difference between v and c is sufficiently small (<0.1%) that the speed of light to three significant figures, $3.00 \times 10^8\ m/s$, is accurate enough for most purposes.

The oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave's propagation. Figure 13.1.1 shows an example of plane-polarized electromagnetic radiation, consisting of a single oscillating electric field and a single oscillating magnetic field.

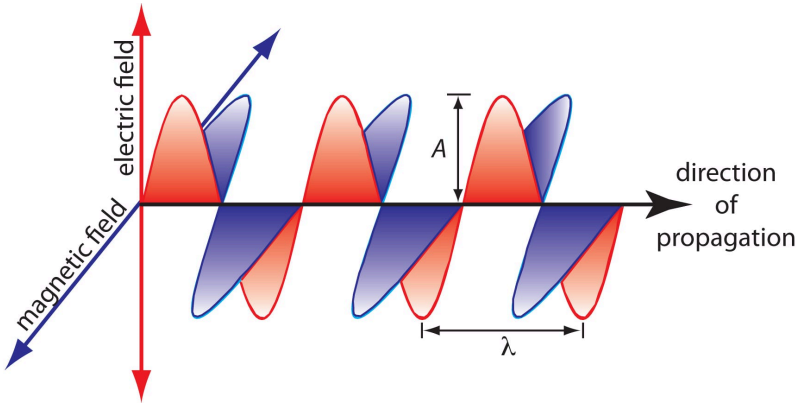


Figure 13.1.1 : Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, A, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation.[2] For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_\mathrm{t} = A_\mathrm{e} \sin(2\pi\nu t + \phi)$$

where A_t is the magnitude of the electric field at time t, A_e is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and ϕ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at $t = 0$. The identical equation for the magnetic field is

$$A_\mathrm{t} = A_\mathrm{m} \sin(2\pi\nu t + \phi)$$

where A_m is the magnetic field's maximum amplitude.

The frequency and wavelength of electromagnetic radiation vary over many orders of magnitude. For convenience, we divide electromagnetic radiation into different regions—the **electromagnetic spectrum**—based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons (Figure 13.1.2). The boundaries between the regions of the electromagnetic spectrum are not rigid, and overlap between spectral regions is possible.

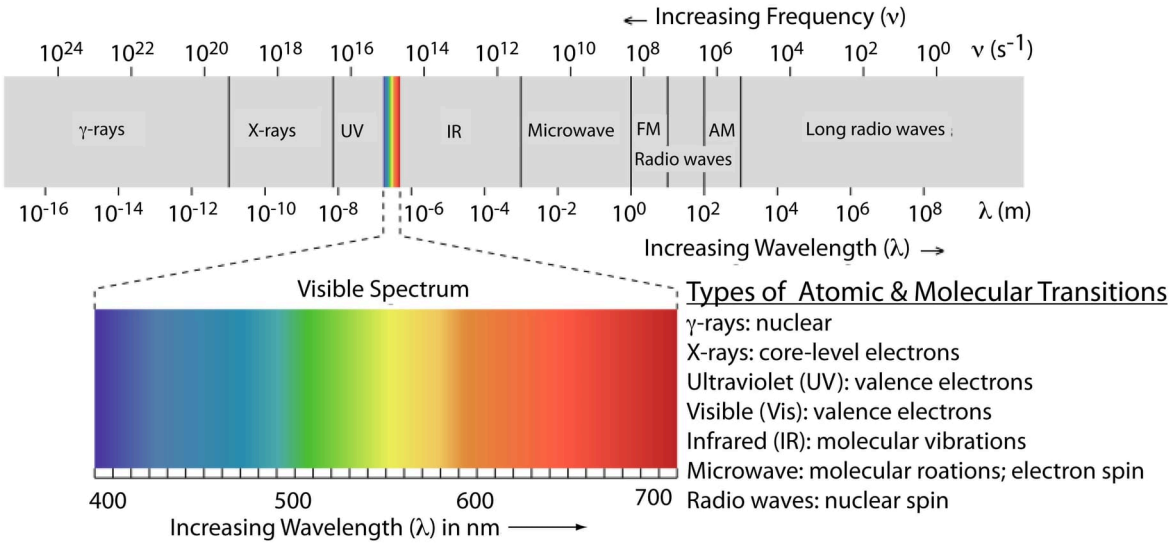


Figure 13.1.2 : The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.Wikipedia.org).

Other Units

Other properties also are useful for characterizing the wave behavior of electromagnetic radiation. The **wavelength**, λ, is defined as the distance between successive maxima (Figure 13.1.1). For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (1 nm = 10^{-9} m), and for infrared radiation it is given in microns (1 μm = 10^{-6} m). The relationship between wavelength and frequency is

$$\lambda = \frac{c}{\nu}$$

Another unit useful unit is the **wavenumber**, $\tilde{\nu}$, which is the reciprocal of wavelength

$$\tilde{\nu} = \frac{1}{\lambda}$$

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

Example 13.1.1

In 1817, Josef Fraunhofer studied the spectrum of solar radiation, observing a continuous spectrum with numerous dark lines. Fraunhofer labeled the most prominent of the dark lines with letters. In 1859, Gustav Kirchhoff showed that the D line in the sun's spectrum was due to the absorption of solar radiation by sodium atoms. The wavelength of the sodium D line is 589 nm. What are the frequency and the wavenumber for this line?

Solution

The frequency and wavenumber of the sodium D line are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{589 \times 10^{-9}\ \text{m}} = 5.09 \times 10^{14}\ \text{s}^{-1}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{589 \times 10^{-9}\ \text{m}} \times \frac{1\ \text{m}}{100\ \text{cm}} = 1.70 \times 10^{4}\ \text{cm}^{-1}$$

Exercise 13.1.1

Another historically important series of spectral lines is the Balmer series of emission lines form hydrogen. One of the lines has a wavelength of 656.3 nm. What are the frequency and the wavenumber for this line?

Above, we defined several characteristic properties of electromagnetic radiation, including its energy, velocity, amplitude, frequency, phase angle, polarization, and direction of propagation. A spectroscopic measurement is possible only if the photon's interaction with the sample leads to a change in one or more of these characteristic properties. We can divide spectroscopy into two broad classes of techniques. In one class of techniques there is a transfer of energy between the photon and the sample. Table 13.1.1 provides a list of several representative examples.

Table 13.1.1 : Examples of Spectroscopic Techniques Involving an Exchange of Energy Between a Photon and the Sample

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Technique
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis	UV/Vis spectroscopy atomic absorption spectroscopy
	IR	infrared spectroscopy raman spectroscopy
	Microwave	microwave spectroscopy
	Radio wave	electron spin resonance spectroscopy nuclear magnetic resonance spectroscopy
emission (thermal excitation)	UV/Vis	atomic emission spectroscopy
photoluminescence	X-ray	X-ray fluorescence
	UV/Vis	fluorescence spectroscopy phosphorescence spectroscopy atomic fluorescence spectroscopy
chemiluminescence	UV/Vis	chemiluminescence spectroscopy

Electromagnetic spectrum provides clearly information of molecules if they are rotational transitions, vibrational transitions, or electronic transitions. A molecule or a set of molecules can be read by the absorption of microwave radiation which provides transitions between rotational energy levels. In addition, if the molecules absorbs infrared radiation provides the transitions

between vibrational levels follows by transitions between rotational energy levels. Finally, when molecules absorbs visible and ultraviolet radiation gives transitions between electronic energy levels follows by simultaneous transitions between vibrational and rotational levels.

When given the energy level of the molecules along with wavelength, we can easily figure the frequency of the molecules where they fall in the electromagnetic spectrum regions:

$$\Delta E = E_u - E_l = h\nu$$

The above equation describes the energy change between upper state and lower state of energy.

- Frequency falls between 10^9 - 10^{11} which is in the microwave range correlates to the rotation of polyatomic molecules.
- Frequency falls between 10^{11} - 10^{13} which is in the far infrared range correlates to the rotation of small molecules.
- Frequency falls between 10^{13} - 10^{14} which is in the infrared range correlates to the vibrations of flexible bonds.
- Frequency falls between 10^{14} - 10^{16} which is in the visible and ultraviolet range correlates to the electronic transitions.

The powerful technique of figuring out the the frequency of the molecules can help us determine the bond length, temperature, probability distribution as you will learn later on from the degree of freedoms and how the process is undergo in specific a reaction.

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12.2: Rotations Accompany Vibrational Transitions

Each of the modes of vibration of diatomic molecules in the gas phase also contains closely-spaced (1-10 cm^{-1} difference) energy states attributable to rotational transitions that accompany the vibrational transitions. A molecule's rotation can be affected by its vibrational transition because there is a change in bond length, so these rotational transitions are expected to occur. Since vibrational energy states are on the order of 1000 cm^{-1}, the rotational energy states can be superimposed upon the vibrational energy states.

Selection Rules

Rotational and Vibration transitions (also known as rigid rotor and harmonic oscillator) of molecules help us identify how molecules interact with each other, their bond length as mentioned in previous section. In order to know each transitions, we have to consider other terms like wavenumber, force constant, quantum number, etc. There are rotational energy levels associated with all vibrational levels. From this, vibrational transitions can couple with rotational transitions to give **rovibrational spectra**. Rovibrational spectra can be analyzed to determine average bond length.

We treat the molecule's **vibrations** as those of a harmonic oscillator (ignoring anharmonicity). The energy of a vibration is quantized in discrete levels and given by

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$

Where v is the vibrational quantum number and can have integer values 0, 1, 2..., and ν is the frequency of the vibration given by:

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

where k is the force constant and μ is the reduced mass of a diatomic molecule with atom masses m_1 and m_2, given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{12.2.1}$$

We treat the molecule's **rotations** as those of a rigid rotor (ignoring centrifugal distortion from non-rigid rotor aspects). The energy of a rotation is also quantized in discrete levels given by

$$E_r = \frac{h^2}{8\pi^2 I}J(J+1)$$

In which I is the moment of inertia, given by

$$I = \mu r^2$$

where μ is the reduced mass (Equation 12.2.1) and r is the equilibrium bond length.

Experimentally, frequencies or wavenumbers are measured rather than energies, and dividing by h or hc gives more commonly seen term symbols, $F(J)$ using the rotational quantum number J and the rotational constant B in either frequency

$$F(J) = \frac{E_r}{h} = \frac{h}{8\pi^2 I}J(J+1) = BJ(J+1)$$

or wavenumbers

$$\tilde{F}(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 cI}J(J+1) = \tilde{B}J(J+1)$$

It is important to note in which units one is working since the rotational constant is always represented as B, whether in frequency or wavenumbers.

- **Vibrational Transition Selection Rules**: At room temperature, typically only the lowest energy vibrational state v= 0 is populated, so typically v_0 = 0 and Δv = +1. The full selection rule is technically that Δv = ±1, however here we assume energy can only go upwards because of the lack of population in the upper vibrational states.
- **Rotational Transition Selection Rules**: At room temperature, states with J≠0 can be populated since they represent the fine structure of vibrational states and have smaller energy differences than successive vibrational levels. Additionally, ΔJ = ±1 since a photon contains one quantum **of angular momentum** and we abide by the principle of **conservation of energy**. This is also the selection rule for rotational transitions.

These two selection rules mean that the transition ΔJ = 0 (i.e. J" = 0 and J' = 0, but $\nu_0 \neq 0$ is forbidden and the pure vibrational transition is not observed in most cases. The rotational selection rule gives rise to an R-branch (when ΔJ = +1) and a P-branch (when ΔJ = -1). Each line of the branch is labeled R(J) or P(J), where J represents the value of the lower state Figure 13.2.1).

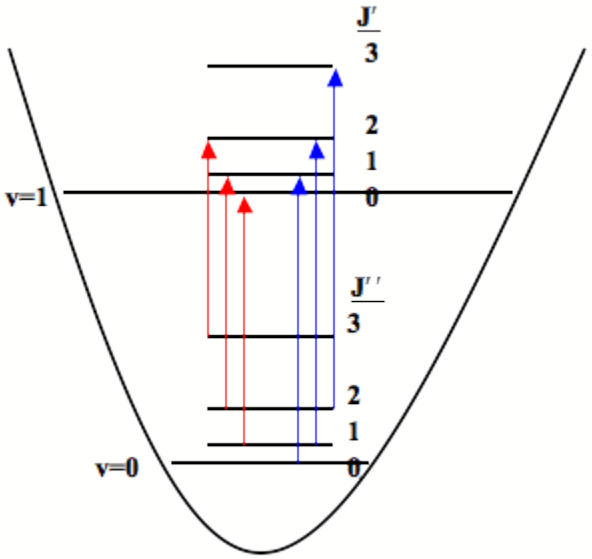


Figure 13.2.1 : Rotation-Vibration Transitions. Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels.

R-branch

When ΔJ = +1, i.e. the rotational quantum number in the ground state is one more than the rotational quantum number in the excited state – R branch (in French, *riche* or rich). To find the energy of a line of the R-branch:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{12.2.2}$$
$$= h\nu_0 + hB\left[(J+1)(J+2) - J(J+1)\right] \tag{12.2.3}$$
$$= h\nu_0 + 2hB(J+1) \tag{12.2.4}$$

P-branch

When ΔJ = -1, i.e. the rotational quantum number in the ground state is one less than the rotational quantum number in the excited state – P branch (in French, *pauvre* or poor). To find the energy of a line of the P-branch:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{12.2.5}$$
$$= h\nu_0 + hB\left[J(J-1) - J(J+1)\right] \tag{12.2.6}$$
$$= h\nu_0 - 2hBJ \tag{12.2.7}$$

Q-branch

When ΔJ = 0, i.e. the rotational quantum number in the ground state is the same as the rotational quantum number in the excited state – Q branch (simple, the letter between P and R). To find the energy of a line of the Q-branch:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \tag{12.2.8}$$

$$= h\nu_0 \tag{12.2.9}$$

The Q-branch can be observed in polyatomic molecules and diatomic molecules with electronic angular momentum in the ground electronic state, e.g. nitric oxide, NO. Most diatomics, such as O_2, have a small moment of inertia and thus very small angular momentum and yield no Q-branch.

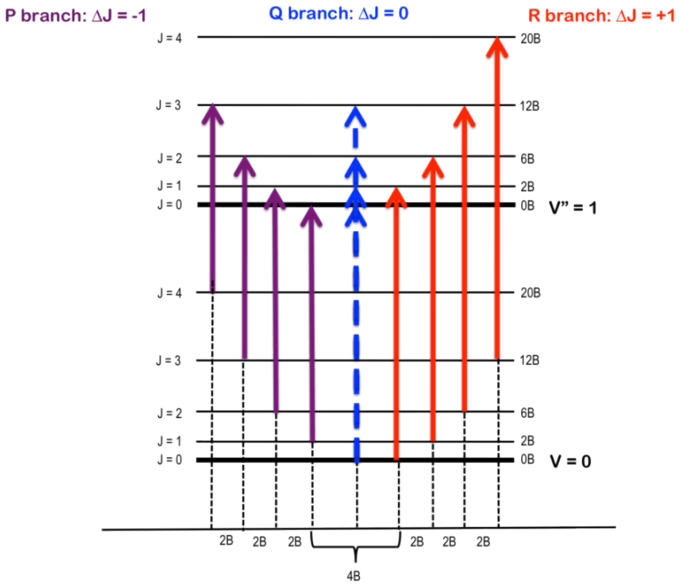


Figure 13.2.3 : Cartoon depiction of rotational energy levels, J, imposed on vibrational energy levels, v. The transitions between levels that would result in the P- and R-branches are depicted in purple and red, respectively, in addition to the theoretical Q-branch line in blue.

As seen in Figure 13.2.2 , the lines of the P-branch (represented by purple arrows) and R-branch (represented by red arrows) are separated by specific multiples of B (i.e, $2B$), thus the bond length can be deduced without the need for pure rotational spectroscopy.

The total nuclear energy of the combined rotation-vibration terms, $S(v, J)$, can be written as the sum of the vibrational energy and the rotational energy

$$S(v, J) = G(v) + F(J)$$

where $G(v)$ represents the energy of the harmonic oscillator, ignoring anharmonic components and $S(J)$ represents the energy of a rigid rotor, ignoring centrifugal distortion.

From this, we can derive

$$S(v, J) = \nu_0 \left(v + \frac{1}{2}\right) + BJ(J+1)$$

The spectrum we expect, based on the conditions described above, consists of lines equidistant in energy from one another, separated by a value of $2B$. The *relative* intensity of the lines is a function of the rotational populations of the ground states, i.e. the intensity is proportional to the number of molecules that have made the transition. The *overall* intensity of the lines depends on the vibrational transition dipole moment.

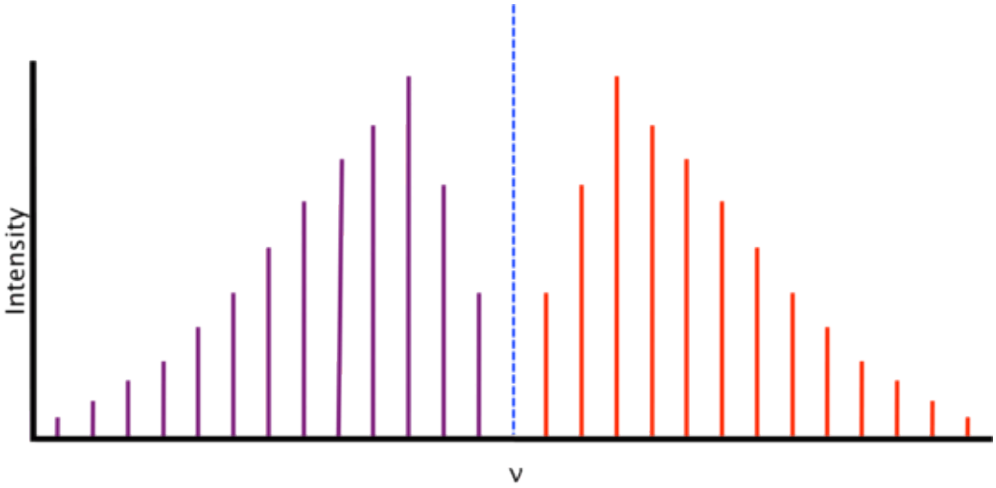


Figure 13.2.3 : A cartoon depiction of an ideal rovibrational spectrum.

In Figure 13.2.2 , between $P(1)$ and $R(0)$ lies the zero gap, where the the first lines of both the P- and R-branch are separated by $4B$, assuming that the rotational constant B is equal for both energy levels. The zero gap is also where we would expect the Q-branch, depicted as the dotted line, if it is allowed.

Advanced Concept: Occupations (Peak Intensities)

The relative intensity of the P- and R-branch lines depends on the thermal distribution of electrons; more specifically, they depend on the population of the lower J state. If we represent the population of the Jth upper level as N_J and the population of the lower state as N_0, we can find the population of the upper state relative to the lower state using the Boltzmann distribution:

$$\frac{N_J}{N_0} = (2J+1)e^{\left(-\frac{E_r}{kT}\right)}$$

(2J+1) gives the degeneracy of the Jth upper level arising from the allowed values of M_J (+J to –J). As J increases, the degeneracy factor increases and the exponential factor decreases until at high J, the exponential factor wins out and N_J/N_0 approaches zero at a certain level, J_{max}. Thus, when

$$\frac{d}{dJ}\left(\frac{N_J}{N_0}\right) = 0$$

by differentiation, we obtain

$$J_{max} = \left(\frac{kT}{2hB}\right)^{\frac{1}{2}} - \frac{1}{2}$$

This is the reason that rovibrational spectral lines increase in energy to a maximum as J increases, then decrease to zero as J continues to increase, as seen in Figure 13.2.2 .

From this relationship, we can also deduce that in heavier molecules, B will decrease because the moment of inertia will increase, and the decrease in the exponential factor is less pronounced. This results in the population distribution shifting to higher values of J. Similarly, as temperature increases, the population distribution will shift towards higher values of J.

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12.3: Unequal Spacings in Vibration-Rotation Spectra

We find that real rovibrational spectra do not exhibit the equal spacing expectations from the treatment in the previous section and look more like the idealized spectrum in Figure 13.3.1 . As energy increases, the R-branch lines become increasingly similar in energy (i.e., the lines move closer together) and as energy decreases, the P-branch lines become increasingly dissimilar in energy (i.e. the lines move farther apart). This is attributable to two phenomena: *rotational-vibrational coupling* and *centrifugal distortion*.

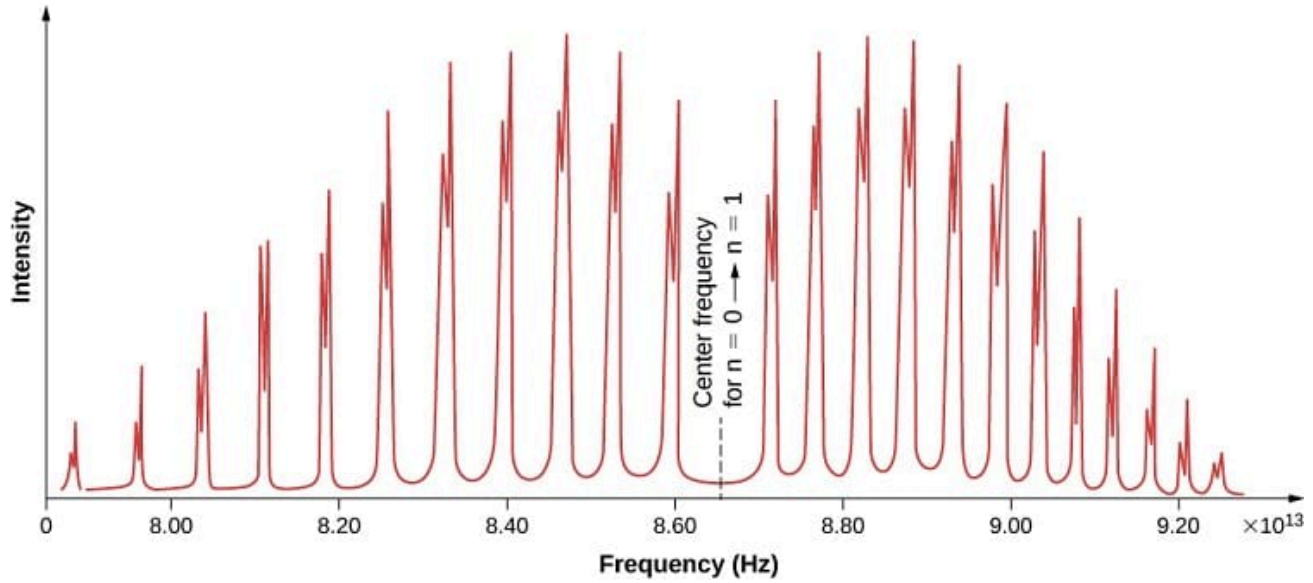


Figure 13.3.1 : Absorption spectrum of hydrogen chloride (HCl) from the $n = 0$ to $n = 1$ vibrational levels. The discrete peaks indicate a quantization of the angular momentum of the molecule. The bands to the left indicate a decrease in angular momentum, whereas those to the right indicate an increase in angular momentum. (CC-SA; OpenStax).

Experimental data shows that the P branch has closer spaces between the lines as the frequencies decrease while R branch has further spaces between the lines as the frequencies increase. On the spectrum, R region is on the left and P region is on the right separated by a large gap in between. There are other graphs show differently, but the regions can be labeled using their spacing characteristic discussed below.

Vibration-Rotation Interaction

Consider the rotational constant for a rigid rotator $\tilde{B} = h/8\pi^2 c\mu R_e^2$ where $\tilde{B}$ is the rotational constant, and R_e^2 is the bond length. It is clear from the equation that $\tilde{B}$ depends on R_e^2 in a inverse manner, so $\tilde{B}$ will decrease as R_e^2 increase, and vice versa.

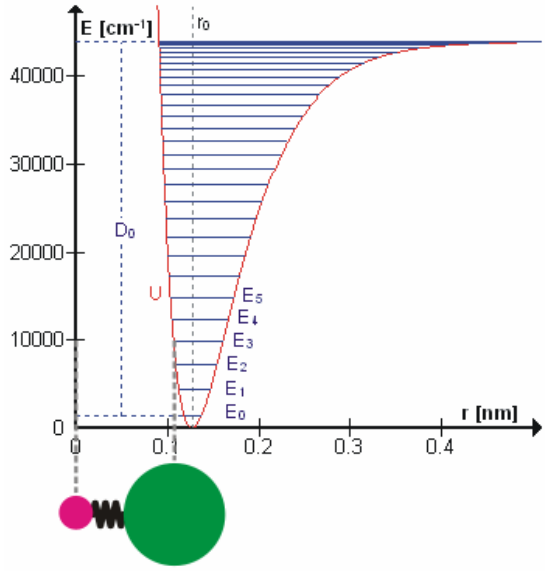


Figure 13.3.2 : Anharmonic Oscillator and Bond Length. Figure used with permission from Wikipedia.

Vibrational state and the bond length also possess a relationship, and that is bond length, R_e^2, will increase as the vibrational state, v increases. High vibrational states have large vibrational amplitudes (the amplitude can be visualized as the distance from one side to the other on the harmonic-oscillator parabola, and higher states has greater distance). On a potential graph, imagine a diatomic molecule with one of the atom fixed at the origin, the bond is along the x-axis, and the molecule vibrate toward and away from the origin along x-axis. The range at how much the bond can stretch or squeeze depend on the vibrational amplitude. So, at high vibrational state (thus high amplitude), the bond can squeeze in and stretch out more (just a little more) on the regular harmonic-oscillator potential, but it can stretch out greatly on an anharmonic oscillator. That's why bond length increase with vibrational state.

Note

The two relationship established above

- $\tilde{B} \propto R_e^2$ (inversely proportional)

and

- $R_e^2 \propto v$ (directly proportional)

Therefore,

- $\tilde{B} \propto v$ (inversely proportional)

The rotational constant dependent on the vibrational state is denoted as $\tilde{B}_v$, and the dependence of $\tilde{B}$ on v is the vibrational-rotational interaction.

Let's calculate the frequencies of R and P Branches with vibrational dependent rotational constants. The energies of the rigid rotator-harmonic oscillator is

$$\tilde{E}_{v,J} = G(v) + F(J) = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}J(J+1)$$

or in term of $\tilde{B}_v$

$$\tilde{E}_{v,J} = \tilde{\nu}\left(v + \frac{1}{2}\right) + \tilde{B}_v J(J+1)$$

According to the vibration-rotation interaction, $\tilde{B}_1 < \tilde{B}_0$ because $R_e^2(v=1) > R_e^2(v=0)$. Hence, the frequencies of rovibrational transitions from $v = 0 \rightarrow 1$ can be calculated as the following:

For R branch, allowed $J = 0, 1, 2, ...$

$$\tilde{\nu}_R(\Delta J = +1) = \tilde{E}_{1,J+1} - \tilde{E}_{0,J}$$

$$= \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1)$$

$$= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

For P branch, allowed $J = 1, 2, 3, ...$

$$\tilde{\nu}_P(\Delta J = -1) = \tilde{E}_{1,J-1} - \tilde{E}_{0,J}$$

$$= \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

Decrease in Spacing of Lines in the R Branch with Increasing J

A closer look at

$$\tilde{\nu}_R = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value for increasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$ +(smaller and smaller value) as J increase. Because the rotational frequencies keep getting smaller, the spacing between lines in R branch decreases as J increases.

Increasing in Spacing of Lines in the P Branch with Decreasing J

Using the same analysis as above,

$$\tilde{\nu}_P = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value even for decreasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$ −(smaller and smaller value) as J decreases. Because the rotational frequencies keep getting larger, the spacing between lines in P branch increase as J decreases.

References

1. McQuarrie, Donald A. Quantum Chemistry. New York: University Science Books, 2007.
2. Hollas, M. J. *Modern spectroscopy*. (3rd ed.). Chichester: John Wiley & Sons, 1996.
3. Hollas, M. J. *Basic atomic and molecular spectroscopy*. Cambridge: The Royal Society of Chemistry, 2002.
4. Herzberg, G. *Molecular spectra and molecular structure*. (2nd ed.). New York: Prentice-Hall, 1950.
5. Fetterolf, Monty L. Enhanced Intensity Distribution Analysis of the Rotational–Vibrational Spectrum of HCl. J. Chem. Ed. **2007**, *84*, 1064. DOI: 10.1021/ed084p1062

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12.4: Unequal Spacings in Pure Rotational Spectra

Vibrational energy which is a consequence of the oscillations/ vibrations of the nuclei along inter nuclear axis, is possible only when the distance between the nuclei is not fixed/ rigid; that means the separation between the two nuclei is flexible/ elastic (non-rigid rotator). Consequently, centrifugal force, when the molecule is rotating, tends to fly the reduced mass μ away from the axis of rotation. To keep the mass rotating about the axis, there must be some restoring force to counter balance the centrifugal force. The work done to supply this force is stored as potential energy. Therefore, unlike the case of rigid rotator, total energy of rotation in a molecule comprises of kinetic and the potential energy corresponding to centrifugal force of rotation.

Let r_e is the distance between the nuclei when the separation is taken to be rigid and r_c under the action of the centrifugal force. According to Hook's law, restoring force is proportional to change in internuclear distance $(r_c - r_e)$, or $= k(r_c - r_e)$ which in turn, will be equal to the centrifugal force.

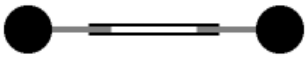


Figure 12.4.1: This animation can serve as an illustration of one of the aspects of the conservation of angular momentum. The animation is a schematic representation of two weights that are connected to each other. The two weights are circling around their common center of mass, the center of mass is stationary. The connection between the weight consists of pistons. When the connecting pistons contract, the rotation rate goes up. When the inward force exerted by the pistons relaxes the weight slide outwards, and the rotation rate goes down. (Public domain; Cleonis).

Centrifugal force,

$$F_c = \mu r_c \omega^2 = L^2/\mu {r_c}^3 \tag{12.4.1}$$

Equating the restoring force to the centrifugal force, one gets

$$k(r_c - r_e) = \frac{L^2}{\mu {r_c}^3} \tag{12.4.2}$$

$$r_c - r_e = \frac{L^2}{k\mu {r_c}^3} \cong \frac{L^2}{k\mu {r_e}^3} \tag{12.4.3}$$

Total energy, on adding kinetic energy, as expressed in Equation 12.4.3 to the potential energy,

$$\frac{1}{2}k(r_c - r_e)^2 \tag{12.4.4}$$

is given by

$$E_r = \frac{L^2}{2\mu {r_c}^2} + \frac{1}{2}k\,(r_c - r_e)^2 \tag{12.4.5}$$

Using $(r_c - r_e) = \Delta r$ and eliminating r_c from equation 12.4.5, one gets

$$E_r = \frac{L^2}{2\mu\ {r_e}^2(1+\Delta r/r_e)^2} + \frac{1}{2}k\Delta r^2 \tag{12.4.6}$$

$$= \frac{L^2(1-2\Delta r/r_e)}{2\mu\ {r_e}^2} + \frac{1}{2}k\Delta r^2 \tag{12.4.7}$$

using

$$(1+\Delta r/r_e)^{-2} \approx (1-2\Delta r/r_e) \tag{12.4.8}$$

$$E_r = \frac{L^2}{2\mu\, {r_e}^2} - \frac{L^4}{k\mu^2\, {r_e}^6} + \frac{1}{2}k\frac{L^4}{k^{2\mu 2}{r_e}^6} \tag{12.4.9}$$

$$= \frac{L^2}{2\mu\, {r_e}^2} - \frac{1}{2}\frac{L^4}{k\mu^2\, {r_e}^6} \tag{12.4.10}$$

$$= \frac{\hbar^2\ J(J+1)}{2\mu\, {r_e}^2} - \frac{\hbar^4\ J^2(J+1)^2}{2k\mu^2\, {r_e}^6} \tag{12.4.11}$$

Use of Equation 12.4.3 and of the relation regarding angular momentum of a rotor

$$L = \hbar\ \sqrt{J(J+1)} \tag{12.4.12}$$

has been made to obtain relation in Equation 12.4.11, which may be expressed in cm^{-1} as

$$F(J) = \underbrace{\tilde{B}J(J+1)}_{\text{rigid rotator term}} - \underbrace{\tilde{D}J^2(J+1)^2 cm^{-1}}_{\text{centrifugal stretching}} \tag{12.4.13}$$

where

$$\tilde{B} = \frac{\hbar}{4\pi\,\mu\, {r_e}^2 c}\ (\text{in cm}^{-1}) \tag{12.4.14}$$

and

$$\tilde{D} = \frac{\hbar^3}{4\pi k\,\mu^2\, {r_e}^6\, c}\ (\text{in cm}^{-1}) \tag{12.4.15}$$

First term in the Equation 12.4.13 is same as for the rigid rotator; second term is the consequence of the centrifugal stretching. Recall Equation 12.4.3 wherein k is the spring constant that, as we will see in the following section, plays the same role as in the vibrational motion. In other words, centrifugal stretching constant $\tilde{D}$ is not only measures the influence of centrifugal force, but also hints upon the interaction between the rotational and vibrational motions.

Since $\tilde{D}$ is positive, it is clear from Equation 12.4.13 that the energy levels for the non-rigid rotator are slightly lower on energy scale than those of rigid rotator for the corresponding J values; the magnitude of decrease in energy of the non-rigid rotator states increases with J as shown in the Figure 12.4.2.

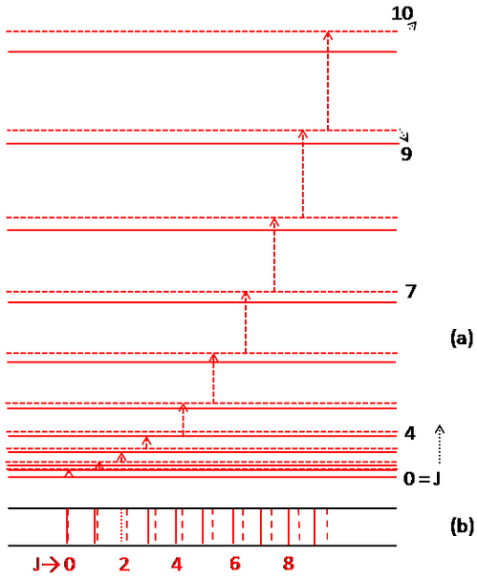


Figure 12.4.2: Energy levels and the transitions of rigid rotator (broken red lines) & of non-rigid rotator (solid red lines). (b) resulting spectra from both the models

Consequently, on applying the selection rule $\Delta J = \pm 1$, rotational spectrum of a non-rigid rotator consists of a series of lines (red lines) wherein separation, unlike the case of spectral series (broken red lines) of a rigid rotator, between the consecutive rotational lines decreases with increase in J , as shown in the Figure 12.4.2. It may be noted that value of D is very small compared to B with the result that the influence of D is significant only for very large J values.

For example, for HCl the values are $B \sim 10.4 \quad cm^{-1}$ and $D \sim 0.0004 \ cm^{-1}$. Usually, D is ignored in the calculations. Figure 12.4.2 exaggerates the decrease in energy to visualize its effect. Nevertheless, non-rigid rotator is the model that describes the rotational motion more accurately and hence explains the spectral experimental observations not only in the microwave region but also the rotation-vibration spectra and the rotational structure of the electronic bands discussed in the later sections.

Contributors and Attributions

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12.5: Vibrational Overtones

Although the harmonic oscillator proves useful for modeling lower energy levels, like $v = 0, 1$, it fails at higher numbers of v. It not only fails to properly model atomic bonds and dissociations, but also is unable to match spectra showing additional lines that are not accounted for in the harmonic oscillator model.

Anharmonicity

Until this point, we have been using the harmonic oscillator to describe the internuclear potential energy of the vibrational motion. Fundamental vibrational frequencies of a molecule corresponds to a transition of $\Delta v = \pm 1$. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator approximation (Figure $12.5.1$). For example, the parabolic potential of the Harmonic Oscillator approximation means that the vibrations can hold any amount of energy and bonds can stretch to any length, while in real molecules if the atoms are too far apart the bond will dissociate.

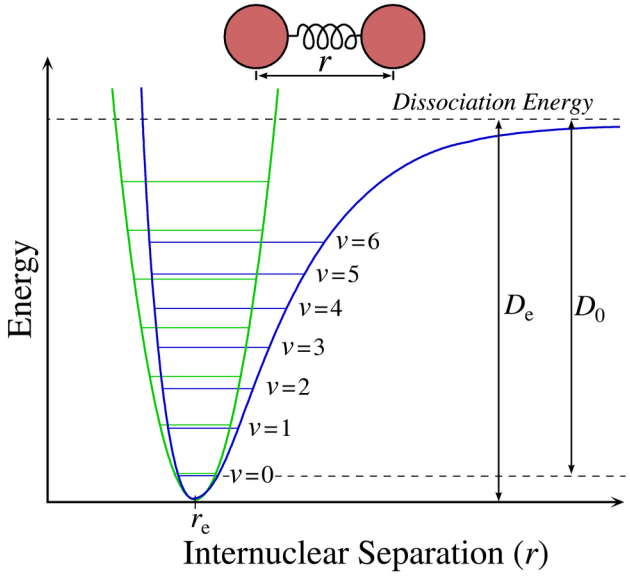


Figure $12.5.1$: Pictured above is the Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left is compression of the bond, towards the right is extension. (CC BY-SA 3.0; Created by Mark Somoza March 26 2006).

As you can see in Figure $12.5.1$, the harmonic oscillator potential well (in green) only roughly fits over the more accurate anharmonic oscillator well (in blue). The blue curve accounts for dissociation at large R values, which the green curve does not even remotely cover. However, this is just one important difference between the harmonic and anharmonic (real) oscillators.

The real potential energy can be expanded in the Taylor series.

$$V(R) = V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}(R-R_e)^4 + \ldots \tag{12.5.1}$$

This expansion was discussed in detail previously. The first term in the expansion is ignored since the derivative of the potential at R_e is zero (i.e., at the bottom of the well). The Harmonic Oscillator approximation only uses the next term, the quadratic term, in the series

$$V_{HO}(R) \approx V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2$$

or in terms of a spring constant, ignoring the absolute energy term($V(R_e)$) and defining r to equal the displacement from equilibrium ($r = R - R_e$), then we get the "standard" harmonic oscillator potential:

$$V_{HO}(R) = \frac{1}{2}kr^2$$

Alternatively, the expansion in Equation 12.5.1 can be shortened to the cubic term

$$V(x) = \frac{1}{2}kr^2 + \frac{1}{6}\gamma r^3 \tag{12.5.2}$$

where

- $V(x_0) = 0$, and $r = R - R_0$.
- k is the harmonic force constant, and
- γ is the first (i.e., cubic) *anharmonic* term

It is important to note that this approximation is only good for R near R_0.

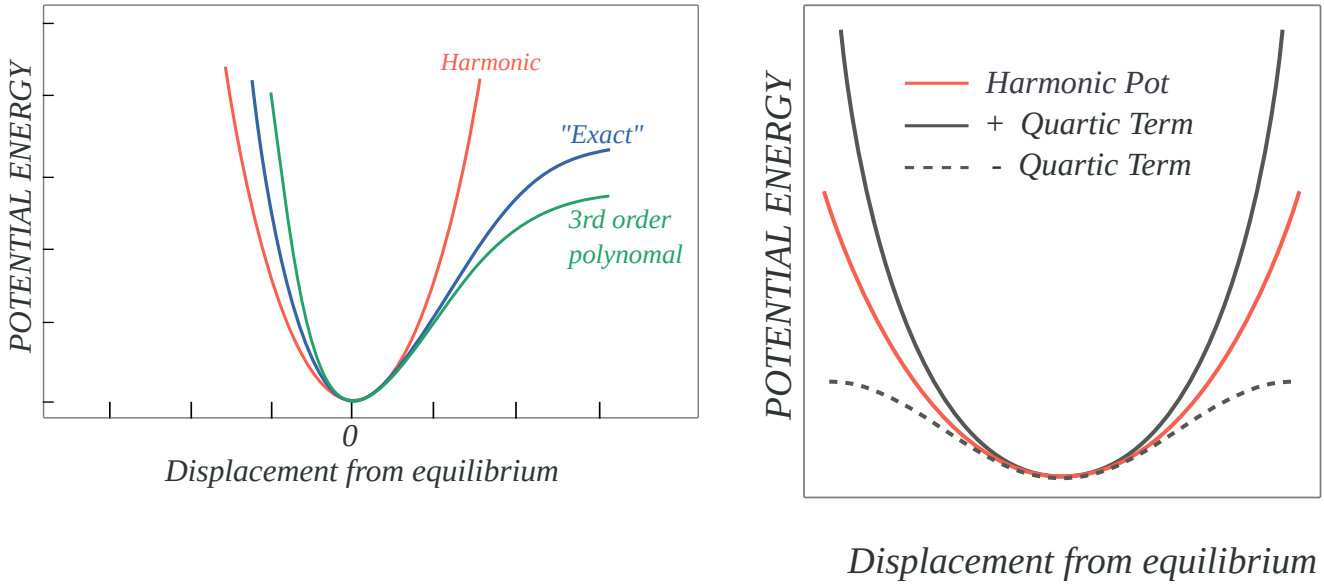


Figure 12.5.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

The harmonic oscillator approximation gives by the following energies:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right)$$

When the cubic term in the expansion (Equation 12.5.2) is included, and the Schrödinger equation is solved using perturbation theory this gives:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right) - \tilde{\chi_e}\tilde{\nu}\left(v + \frac{1}{2}\right)^2$$

where $\tilde{\chi_e}$ is the **anharmonicity constant**. It is much smaller than 1, which makes sense because the terms in the Taylor series approach zero. This is why, although E_v technically includes all of the Taylor series, we only concern ourselves with the first and second terms. The rest are so small and barely add to the total and thus can be ignored. To get a more accurate approximation, more terms can be included, but otherwise, can be ignored. Almost all diatomics have experimentally determined $\frac{d^2V}{dx^2}$ for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 have had terms up to $n < 10$ determined of Equation 12.5.1.

Overtones

The Harmonic Oscillator approximation predicts that there will be only one line in the spectrum of a diatomic molecule, while experimental data shows there is in fact one dominant line--**the fundamental**--and other weaker lines. How can we account for

these extra lines?

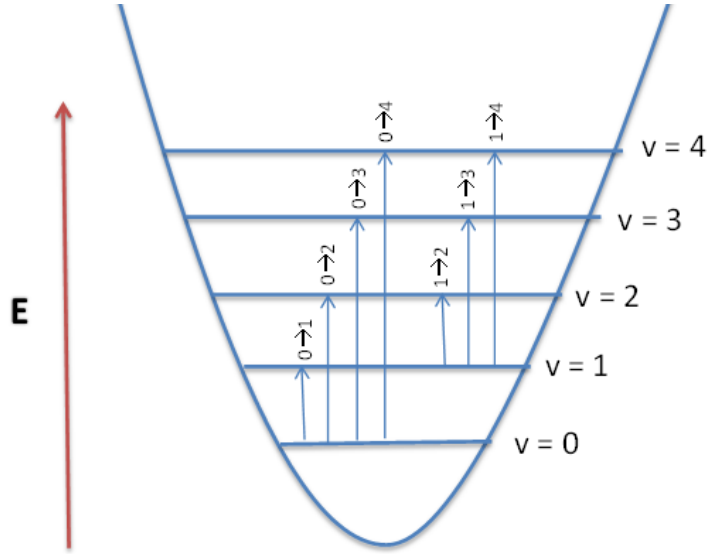


Figure $12.5.3$: A diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potential energy for the harmonic (quadratic) oscillator. The transition $0 \rightarrow 1$ is the fundamental, transitions $0 \rightarrow n$ (n>1) are called overtones, and transitions $1 \rightarrow n$ (n > 1) are called hot transitions (hot bands).

Any resonant frequency above the fundamental frequency is referred to as an *overtone*. In the IR spectrum, overtone bands are multiples of the fundamental absorption frequency. As you can recall, the energy levels in the Harmonic Oscillator approximation are evenly spaced apart. Energy is proportional to the frequency absorbed, which in turn is proportional to the wavenumber, the first overtone that appears in the spectrum will be twice the wavenumber of the fundamental. That is, first overtone $v = 0 \rightarrow 2$ is (approximately) twice the energy of the fundamental, $v = 0 \rightarrow 1$.

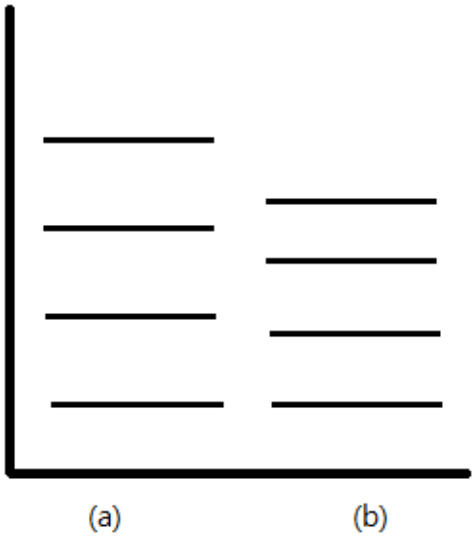


Figure $12.5.4$: An exaggerated view of the energy levels. (a) would be the harmonic oscillator, with the evenly spaced out energy levels. (b) would be the anharmonic, with the energy levels compressing until they converge.

The levels are not equally spaced, like in the harmonic oscillator, but decrease as v increases, until it ultimately converges, as implied by Figure $12.5.4$. Also as a result of anharmonicity, the $\Delta v = \pm 1$ selection rule is no longer valid and v can be any number. This leads to the observation of higher order transitions, or **overtones**, which result from the transition of the ground state to higher energy levels.

Anharmonic Oscillator Selection Rules

For the anharmonic oscillator, the selection rule is $\Delta V = \text{any number}$. That is, there are no selection rules (for state to state transitions)

Overtones occur when a vibrational mode is excited from $v = 0$ to $v = 2$ (the first overtone) or $v = 0$ to $v = 3$ (the second overtone). The fundamental transitions, $v = \pm 1$, are the most commonly occurring, and the probability of overtones rapidly decreases as $\Delta v > \pm 1$ gets bigger. Based on the harmonic oscillator approximation, the energy of the overtone transition will be approximately v times the fundamental associated with that particular transition. The anharmonic oscillator calculations show that the overtones are usually less than a multiple of the fundamental frequency. Overtones are generally not detected in larger molecules.

This is demonstrated with the vibrations of the diatomic HCl in the gas phase:

Table $12.5.1$ *: HCl vibrational spectrum.*

Transition	$\tilde{\nu}_{obs}$ [cm^{-1}]	$\tilde{\nu}_{obs}$ Harmonic [cm^{-1}]	$\tilde{\nu}_{obs}$ Anharmonic [cm^{-1}]
$0 \rightarrow 1$ (fundamental)	2885.9	2885.9	2,885.3
$0 \rightarrow 2$ (first overtone)	5668.0	5771.8	5,665.0
$0 \rightarrow 3$ (second overtone)	8347.0	8657.7	8,339.0
$0 \rightarrow 4$ (third overtone)	10 923.1	11 543.6	10,907.4
$0 \rightarrow 5$ (fourth overtone)	13 396.5	14 429.5	13,370

We can see from Table $12.5.1$ that the anharmonic frequencies correspond much better with the observed frequencies, especially as the vibrational levels increase. Because the energy levels and overtones are closer together in the anharmonic model, they are also more easily reached. This means that there is a higher chance of that level possibly being occupied, meaning it can show up as additional, albeit weaker intensity lines (the weaker intensity indicates a smaller probability of the transition occuring).

Exercise 13.5.1

HCl has a fundamental band at 2885.9 cm^{-1} and an overtone at 5668.1 cm^{-1} Calculate $\tilde{\nu}$ and $\tilde{\chi}_e$.

Exercise 13.5.2

Write out the Taylor series, and comment on the trend in the increasing terms. Using a test number x, please add terms 3, 4, and 5, then compare this to term 2. How do they compare? We have seen that the anharmonic terms increase the accuracy of our oscillator approximation. Why don't we care so much about terms past the second?

References

1. Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry; Part B: Application in Coordination, Organometallic, and Bioinorganic Chemistry, 5th Edition (Nakamoto, Kazuo)
2. Lyle McAfee Journal of Chemical Education 2000 77 (9), 1122
3. Stuart, Barbara. *Infrared Spectroscopy: Fundamentals and Applications*. Wiley, 2004. Print.

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12.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information

Molecules can also undergo changes in electronic transitions during microwave and infrared absorptions. The energy level differences are usually high enough that it falls into the visible to UV range; in fact, most emissions in this range can be attributed to electronic transitions.

Electron Transitions are not Purely Electronic

We have thus far studied *rovibrational transitions*--that is, transitions involving both the vibrational and rotational states. Similarly, electronic transitions tend to accompany both rotational and vibrational transitions. These are often portrayed as an electronic potential energy cure with the vibrational level drawn on each curve. Additionally, each vibrational level has a set of rotational levels associated with it.

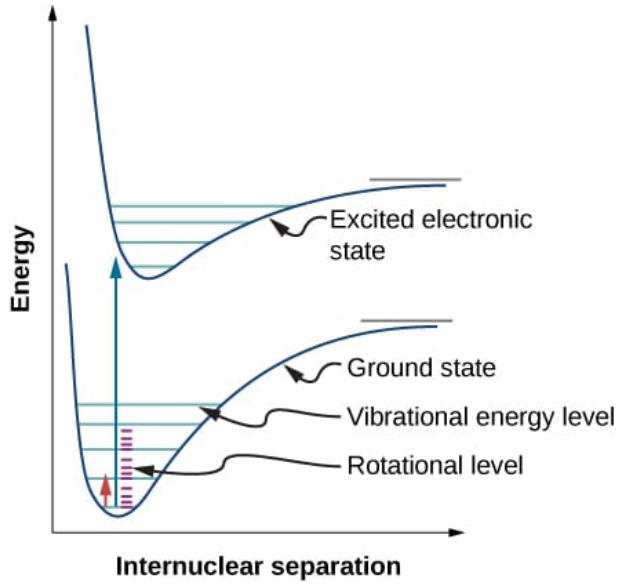


Figure 12.6.1: Three types of energy levels in a diatomic molecule: electronic, vibrational, and rotational. If the vibrational quantum number (n) changes by one unit, then the rotational quantum number (l) changes by one unit. (CC BY 3.0; OpenStax).

Recall that in the Born-Oppenheimer approximation, nuclear kinetic energies can be ignored (e.g., fixed) to solve for electronic wavefunctions and energies, which are much faster than rotation or vibration. As such, it is important to note that unlike rovibrational transitions, electronic transitions aren't dependent on rotational or transitional terms and are assumed to be separate. Therefore, when using an anharmonic oscillator-nonrigid rotator approximation (and excluding translation energy), the total energy of a diatomic is:

$$\tilde{E}_{total} = \tilde{\nu}_{el} + G(v) + F(J) \tag{12.6.1}$$

where $\tilde{\nu}_{el}$ is the electronic transition energy change in wavenumbers, $G(n)$ is the vibrational energy with energy level v (assuming anharmonic oscillator), and $F(J)$ is the rotational energy, assuming a nonrigid rotor. Equation 12.6.1 can be expanded accordingly:

$$\tilde{E}_{total} = \underbrace{\tilde{\nu}_{el}}_{\text{electronic}} + \underbrace{\tilde{\nu}_e\left(v+\frac{1}{2}\right) - \tilde{\chi}_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^2}_{\text{vibrational}} + \underbrace{\tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2}_{\text{rotational}} \tag{12.6.2}$$

Notice that both the vibration constant ($\tilde{\nu}_e$) and anharmonic constant ($\tilde{\chi}_e$) are electronic state dependent (and hence the rotational constants would be too, but are ignored here). Since rotational energies tend to be so small compared to electronic, their effects are minimal and are typically ignored when we do calculations and are referred to as *vibronic* transitions.

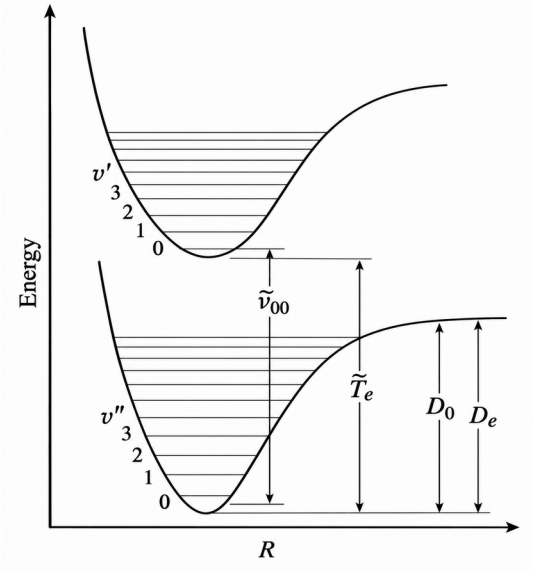


Figure 12.6.2: As you can see, electronic transitions involve two energy potential wells! The vibrational levels are included, but rotational levels are excluded. (CC BY 4.0; LibreTexts)

The eigenstate-to-eigenstate transitions (e.g., $1 \rightarrow 2$) possible are numerous and have absorption lines at

$$\tilde{\nu}_{obs} = \tilde{E}_2 - \tilde{E}_1 \tag{12.6.3}$$

and for simplification, we refer to constants associated with these states as $|'\rangle$ and $|''\rangle$, respectively. So Equation 12.6.3 is

$$\tilde{\nu}_{obs} = E''\tilde{(}v'') - E'\tilde{(}v')$$

Also important to note that typically vibronic transitions are usually the result of the vibrational $v' = 0$ vibratonal state. Within this assumption and excluding the rotational contributions (due to their low energies), Equation 12.6.2 can be used with Equation 12.6.3 to get

$$\tilde{\nu}_{obs} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right) + \tilde{\nu}'_e v'' - \tilde{\chi}'_e\tilde{\nu}'_e v''(v''+1) \tag{12.6.4}$$

A common transition of importance is the $\tilde{\nu}_{00}$, which is the $0 \rightarrow 0$ transition and include no vibrational change. For this case, equation 12.6.4 is then

$$\tilde{\nu}_{00} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right)$$

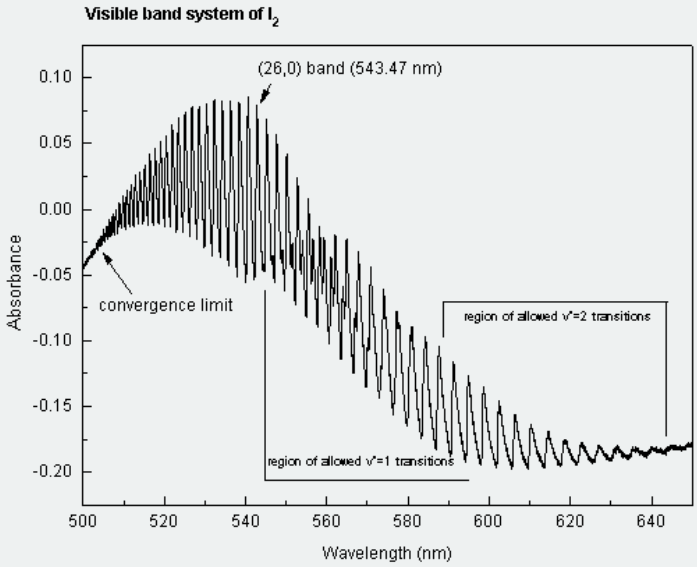
This is the lowest energy possible to observe in an electronic transition although it may be of low intensity as discussed in the following section.

Iodine

The absorption spectrum of iodine yields information about the excited state well rather than the ground state well (notice that equation 12.6.4 depends primarily on excited state parameters). In this experiment you will characterize the excited state well by extracting values for the following excited state parameters.

Recall that as v' increases, the vibrational energy spacing decreases. At the upper edge of the well, the vibrational energy spacing decreases to 0, which means that the energies form a continuum rather than being quantized. It is at this limit that **bond dissociation occurs**. The energy required to dissociate the bond is actually D'_o rather than D'_e because the molecule cannot have less than **the zero point energy**.

The vibrational-electronic spectrum of I_2 in the region from 500-650 nm displays a large number of well-defined bands which, for the most part, correspond to v'<-- 0 transitions connecting the v" = 0 vibrational level of the ground electronic state (denoted as $X^1\Sigma^+$) to many different vibrational levels v' of the excited $B^3\Pi$ electronic state. Under the conditions of this experiment (i.e., low resolution), the rotational lines within each band are not resolved. However, the peaks may be identified as R-branch band heads (1). For a molecule as heavy as I_2, the position of each band head is within a few tenths of one cm^{-1} of the band origin (2), and for the purposes of this experiment, the distinction between the two may be ignored. The general features of the absorption spectrum are shown below:



Each small bump, or peak, such as the (26,0) band labelled on the spectrum, corresponds to a transition between two vibrational levels and is called a *band*. Each band is comprised of several hundred *lines*, each of which involves different upper and lower rotational quantum numbers; as mentioned, these lines are not resolved in the present experiment. The region of maximum absorption in each band is caused by many of these lines falling together; it is called the *band head*. The set of all of these bands is referred to as the *visible band system* of I_2.

If the sample is hot, then excited vibrational levels of the ground state may be populated, and these also will absorb light. The *hot bands* arising from absorption from v"=1 and v"=2 are shown very approximately on the absorption spectrum above.

At a point called the *convergence limit*, the spacing between bands decreases to zero. Beyond this convergence limit, the spectrum is continuous because the excited state of the I_2 molecule is not bound. One of the purposes of this experiment is to identify this convergence limit accurately.

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12.7: The Franck-Condon Principle

Learning Objectives

- To explain the vibrational fine structure in electronic spectroscopy for bound excited states in terms of the Franck-Condon approximation
- To calculate the vibrational progressions (Franck-Condon factors) in a single displaced harmonic oscillator vibronic system.

The **Franck-Condon Principle** describes the intensities of vibronic transitions, or the absorption or emission of a photon. It states that when a molecule is undergoing an electronic transition, such as ionization, the nuclear configuration of the molecule experiences no significant change. This is due in fact that nuclei are much more massive than electrons and the electronic transition takes place faster than the nuclei can respond. When the nucleus realigns itself with the new electronic configuration, the theory states that it must undergo a vibration.

If we picture the vertical transition from ground to excited electronic state as occurring from a vibrational wavefunction that gives a probability distribution of finding the nuclei in a give region of space we can determine the probability of a given vibrational level from the overlap integral $S_{v',v}$ which gives the overlap of the vibrational wavefunction in the ground and excited state. The v' quantum numbers refer to the ground state and the v quantum numbers refer to the excited state. The transition probability can be separated into electronic and nuclear parts using the Condon approximation.

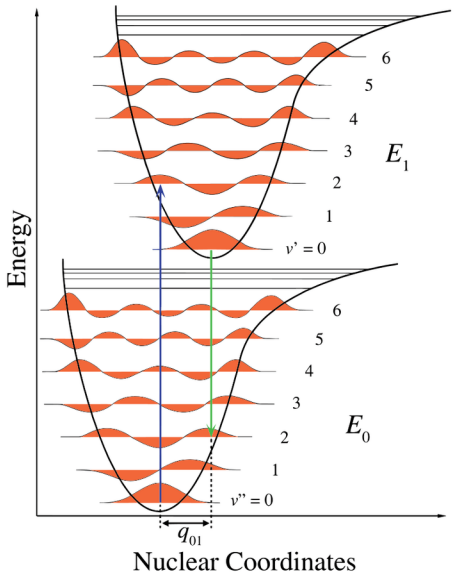


Figure 12.7.1 : Franck–Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v' = 2$. (CC-SA-BY-3.0; Samoza).

In Figure 12.7.1 , the nuclear axis shows a consequence of the internuclear separation and the vibronic transition is indicated by the blue and green vertical arrows. This figure demonstrates three things:

1. An absorption leads to a higher energy state,
2. fluorescence leads to a lower energy state, and
3. the shift in nuclear coordinates between the ground and excited state is indicative of a new equilibrium position for nuclear interaction potential. The fact that the fluorescence arrow is shorter than the absorption indicates that it has less energy, or that its wavelength is longer.

The Classical Condon approximation

Condon approximation is the assumption that the electronic transition occurs on a time scale short compared to nuclear motion so that the transition probability can be calculated at a fixed nuclear position.

This change in vibration is maintained during a state termed the **rapid electronic excitation**. The resulting Coulombic forces produce an equilibrium as shown in the figure for the nuclei termed a turning point. The turning point can be mapped by drawing a vertical line from the minimum of the lower curve to the intersection of the higher electronic state. This procedure is termed a **vertical transition** and was discussed before in the context of photoelectron spectroscopy (another electronic spectroscoy).

The Franck-Condon Principle explains the relative intensities of vibronic transitions by relating the probability of a vibrational transition to the overlap of the vibrational wavefunctions. It states that the probability of a vibrational transition occurring is weighted by the Franck-Condon overlap integral:

$$\begin{aligned} {}_{i\rightarrow f} &= |\langle \psi^*_{final}|\boldsymbol{\mu}|\psi_{initial}\rangle|^2 \\ &= \left|\int \psi^*_{final}\boldsymbol{\mu}\psi_{initial}d\tau\right|^2 \end{aligned}$$

Within the Franck-Condon approximation, the nuclei are considered "fixed" during electronic transitions. Thus, electronic transitions can be considered vertical transitions on electronic potential energy curves (vierical transitions in Figure $12.7.1$).

The Quantum Franck-Condon Principle

The Franck-Condon Principle has both a Classical and Quantum application. Classically, the Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

The Franck-Condon principle is based on the Born-Oppenheimer approximation, which allows separation of the electronic q and nuclear Q wavefunctions given the total wavefunction.

$$|\psi_{total}(Q,q) = |\psi_{nuc}(Q)\rangle\psi_{el}(Q;q)\rangle$$

Since the transition operator, $\hat{\mu}(q)$, is dependent only on the electronic component, the nuclear components can be separated from the transition moment integral that dictates the probability of the transition occurring:

$$\langle\psi^*_{total,f}|\hat{\mu}|\psi_{total,i}\rangle = \langle\psi^*_{nuc,f}|\langle\psi^*_{el,f}|\boldsymbol{\mu}|\psi_{el,i}\rangle|\psi_{nuc,i}\rangle \tag{12.7.1}$$

$$= \underbrace{\langle\psi^*_{nuc,f}|\psi_{nuc,i}\rangle}_{\text{nuclear overlap}}\langle\psi^*_{el,f}|\boldsymbol{\mu}|\psi_{el,i}\rangle \tag{12.7.2}$$

If the nuclear overlap integral is zero for this transition, then the transition will not be observed, irrespective of the magnitude of the electronic factor.

S_{00} Transition Evaluated within Harmonic Oscillator Model

The nuclear overlap for the zero-zero transition S_{00} can be calculated quite simply using the definition of the Gaussian form of the harmonic oscillator wavefunctions.

The zero-point wavefunction in the ground electronic state is

$$|\psi(R)\rangle = |\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2}\rangle$$

The zero-point wavefunction in the excited electronic state is

$$|\psi(R)\rangle = \Big| \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-Q_e)^2/2} \Big\rangle$$

where

- $\alpha = \dfrac{\sqrt{mk}}{\hbar}$
- R_e is the equilibrium bond length in the ground electronic state
- Q_e is the equilibrium bond length in the excited electronic state

The nuclear overlap integral is

$$S_{00} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} e^{-\alpha(R-Q_e)^2/2} dR \tag{12.7.3}$$

The exponent in Equation 12.7.3 can be expanded as

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(2R^2 - RR_e - 2RQ_e + R_e^2 + Q_e^2)/2} dR \tag{12.7.4}$$

and we use

$$(R_e + Q_e)^2 = R_e^2 + Q_e^2 + 2R_eQ_e$$

and

$$(R_e - Q_e)^2 = R_e^2 + Q_e^2 - 2R_eQ_e$$

to substitute and complete the square inside the integral. We can express

$$R_e^2 + Q_e^2 = \frac{1}{2}[(R_e + Q_e)^2 + (R_e - Q_e)^2].$$

Thus, the integral in Equation 12.7.4 is

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \int_{-\infty}^{\infty} e^{-\alpha\{R - 1/2(R_e + Q_e)\}^2} dR$$

The integral is a **Gaussian integral**. You can show that if we let $z = \sqrt{\alpha}\{R - 1/2(R_e + Q_e)\}$ then $dz = \sqrt{\alpha} dR$ and the integral becomes

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \frac{1}{\sqrt{\alpha}} \int_{-\infty}^{\infty} e^{z^2} dz \tag{12.7.5}$$

this integral has been solved already, from a table of integrals, Equation 12.7.5 becomes

$$S_{00} = e^{-\alpha(R_e - Q_e)^2/4}$$

We would follow the same procedure to calculate that overlap of the zeroth level vibration in the ground to the first excited vibrational level of the excited state: S_{01}.

S_{01} Transition Evaluated within Harmonic Oscillator Model

To calculate the overlap of zeroth ground state level ($v = 0$) with the first excited state level ($v' = 1$) we use the Hermite polynomial $H_1(x) = 2x$ for describing the excited state wavefunction (see here for a review on harmonic oscillator wavefunctions). Here $x = \sqrt{\alpha}(R - Q_e)$.

$$S_{01} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle \tag{12.7.6}$$

with the zero-point wavefunction in the ground electronic state is

$$|\psi(R)\rangle = \Big| \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2} \Big\rangle$$

The first excited-state wavefunction in the excited electronic state is

$$|\psi(R)\rangle = \Big| \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{\alpha} 2(R-Q_e) e^{-\alpha(R-Q_e)^2/2} \Big\rangle$$

The overlap of zeroth ground state level with the first excited state level (Equation 12.7.6) is then

$$S_{01} = \frac{1}{\sqrt{2}} \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} \sqrt{\alpha} 2(R-Q_e) e^{-\alpha(R-Q_e)^2/2}$$

and

$$S_{01} = \sqrt{\frac{2\alpha^2}{\pi}} e^{-\alpha(R_e-Q_e)^2/4} \int_{-\infty}^{\infty} (R-Q_e) e^{-\alpha\{R-1/2(R_e+Q_e)^2\}}$$

The same substitutions can be made as above so that the integral can be written as (not shown and to be demonstrated in a homework exercises) and the final result is

$$S_{01} = \sqrt{\frac{\alpha^2}{2}} (R_e - Q_e) e^{-\alpha(R_e-Q_e)^2/4}$$

We could continue and calculate that overlap of the zeroth level in the ground state with all the higher light vibrational levels: S_{02} , S_{03}, etc. Each term corresponds to a transition with a different energy since the vibrational levels have different energies. The absorption band then has the appearance of a progression (a Franck-Condon progression) of transitions between different levels each with its own probability.

Franck-Condon Progressions

To understand the significance of the above formula for the FC factor, let us examine a ground and excited state potential energy surface at $T = 0$ Kelvin. Shown below are two states separated by 8,000 cm^{-1} in energy. This is energy separation between the bottoms of their potential wells, but also between the respective zero-point energy levels. Let us assume that the wavenumber of the vibrational mode is 1,000 cm^{-1} and that the bond length is increased due to the fact that an electron is removed from a bonding orbital and placed in an anti-bonding orbital upon electronic excitation.

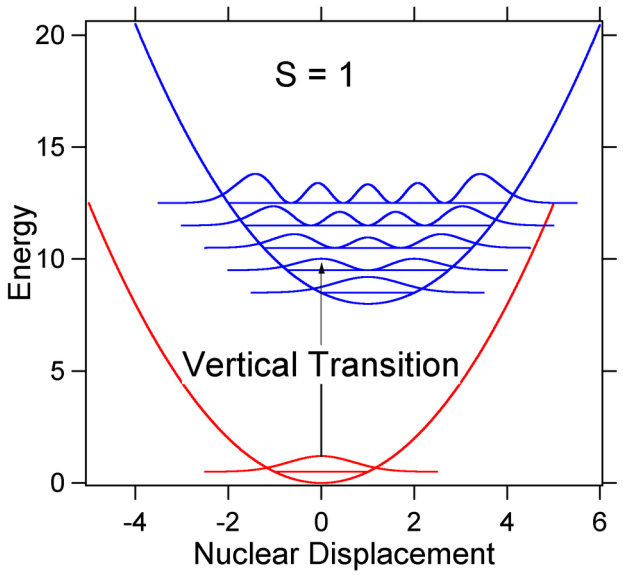


Figure 12.7.2 : Wavefunctions transitions for a harmonic oscillator model system with moderate displacement (S=1).

According to the above model for the Franck-Condon factor we would generate a "stick" spectrum (Figure 12.7.3) where each vibrational transition is infinitely narrow and transition can only occur when $E = h\nu$ exactly. For example, the potential energy surfaces were given for S = 1 and the transition probability at each level is given by the sticks (black) in the figure below.

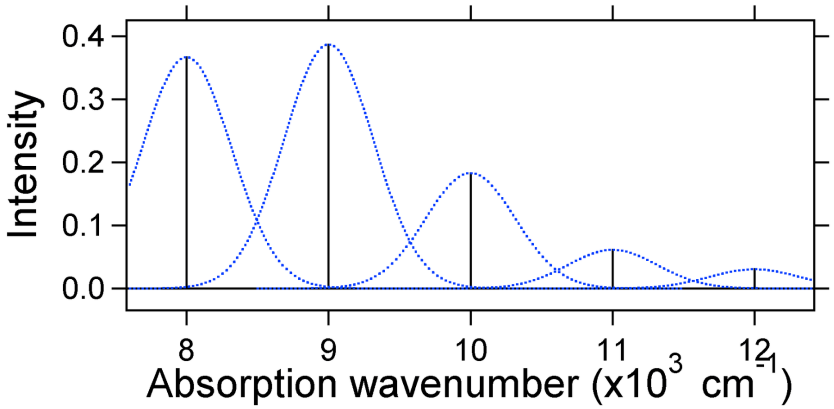


Figure 12.7.3 : Stick spectrum, dressed with Gaussians, for the moderate displacement (S=1) harmonic oscillator system from Figure 12.7.2 .

The dotted Gaussians that surround each stick give a more realistic picture of what the absorption spectrum should look like. In this first place each energy level (stick) will be given some width by the fact that the state has a finite lifetime. Such broadening is called homogeneous broadening since it affects all of the molecules in the ensemble in a similar fashion. There is also broadening due to small differences in the environment of each molecule. This type of broadening is called inhomogeneous broadening. Regardless of origin the model above was created using a Gaussian broadening

The nuclear displacement between the ground and excited state determines the shape of the absorption spectrum. Let us examine both a smaller and a large excited state displacement. If $S = ½$ and the potential energy surfaces in this case are:

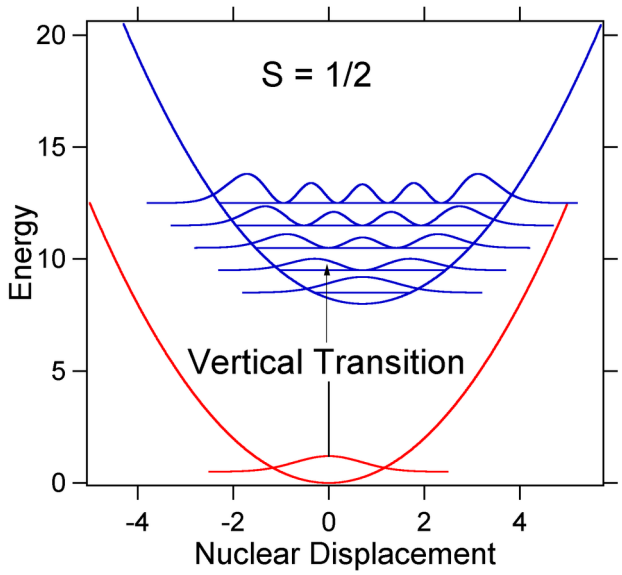


Figure 12.7.4 : Wavefunctions transitions for a harmonic oscillator model system with small displacement (S=1/2).

For this case the "stick" spectrum has the appearance in Figure 12.7.5

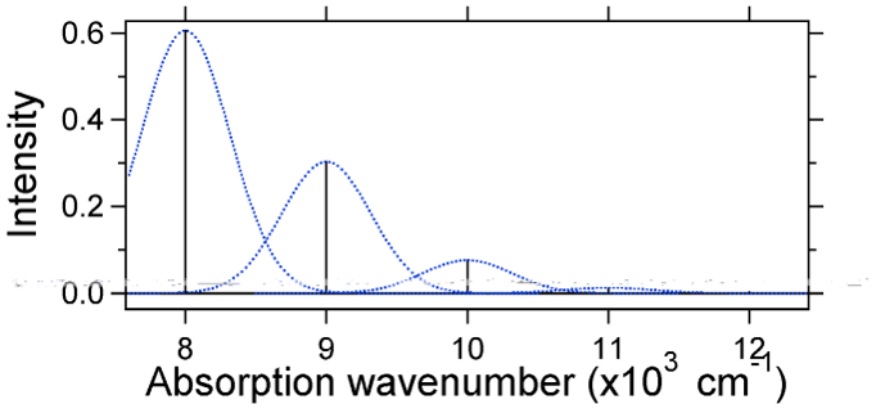


Figure 12.7.5 : Stick spectrum, dressed with Gaussians, for the small displacement (S=1/2) harmonic oscillator system from Figure 12.7.4.

Note that the zero-zero or $S_{0,0}$ vibrational transition is much large in the case where the displacement is small.

> As a general rule of thumb the S constant gives the ratio of the intensity of the $v = 2$ transition to the $v = 1$ transition. In this case since $S = 0.5$, the $v = 2$ transition is 0.5 the intensity of $v = 1$ transition.

As an example of a larger displacement the disposition of the potential energy surfaces for S = 2 is shown below.

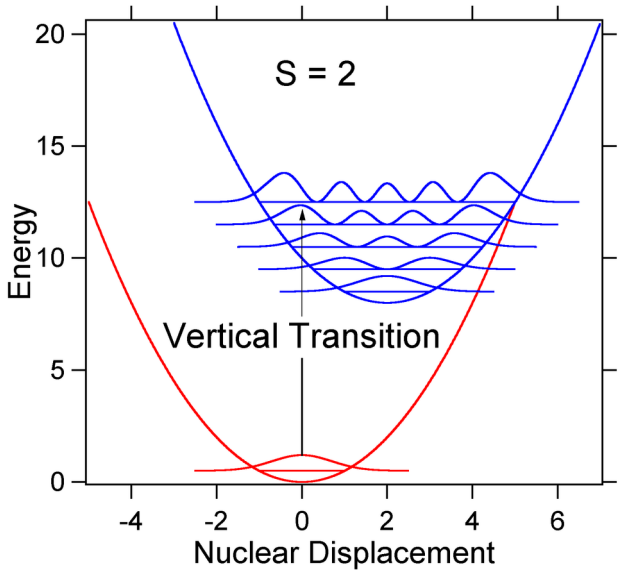


Figure 12.7.6 : Wavefunctions transitions for a harmonic oscillator model system with strong displacement (S=2).

The larger displacement results in decreased overlap of the ground state level with the v = 0 level of the excited state. The maximum intensity will be achieved in higher vibrational levels as shown in the stick spectrum.

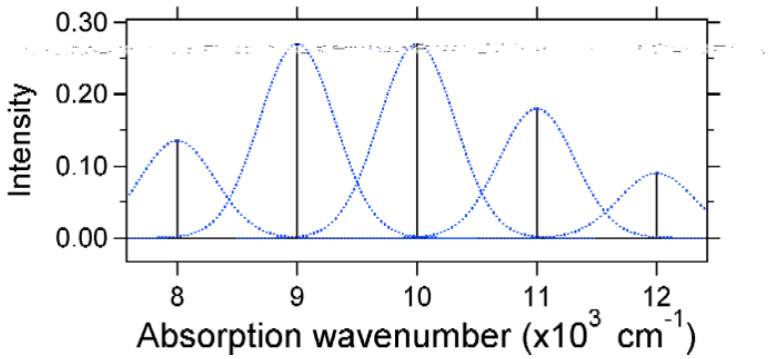


Figure 12.7.7 : Stick spectrum, dressed with Gaussians, for the large displacement (S=2) harmonic oscillator system from Figure 12.7.6.

The absorption spectra plotted below all have the same integrated intensity, however their shapes are altered because of the differing extent of displacement of the excited state potential energy surface.

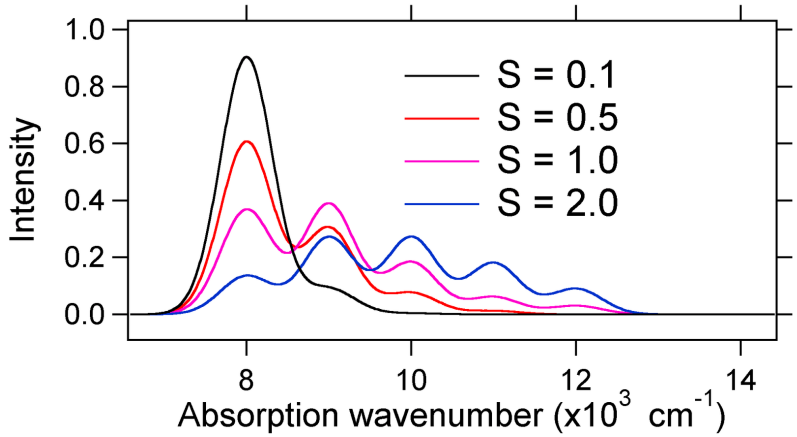


Figure 12.7.8 : Stick spectra, dressed with Gaussians, for the small to large displacements in harmonic oscillator system described above.

So the nature of the relative vibronic band intensities can tell us whether there is a displacement of the equilibrium nuclear coordinate that accompanied a transition. When will there be an increase in bond length (i.e., $Q_e > R_e$)? This occurs when an electron is promoted from a bonding molecular orbital to a non-bonding or anti-bonding molecular orbitals (i.e., when the bond order is less in the excited state than the ground state).

- Non-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ non-bonding molecular orbital

In short, when the bond order is lower in the excited state than in the ground state, then $Q_e > R_e$; an increase in bond length will occur when this happens.

References

1. J.M. Luis, D.M. Bishop, B. Kirtman. *A different approach for calculating Franck–Condon factors including anharmonicity*. J. Chem. Phys., 120 (2004), pp. 813–822.
2. Atkins, Peter and Julio de Paula. Physical Chemistry for the Life Sciences. 2006. New York, NY: W.H. Freeman and Company. p. 563-564
3. Franck-Condon Principle. 1996, 68, 2243. IUPAC Compendium of Chemical Terminology 2nd Edition (1997). www.iupac.org/goldbook/F02510.pdf
4. E.Rabinowitch and Govindjee. Light Absorption and Fate of Excitation of Energy. 1969. Franck-Condon Principle. http://www.life.uiuc.edu/govindjee/b...em494/Abs.html

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12.8: Rotational Spectra of Polyatomic Molecules

Quick Review of Diatomic Rotation

As discussed previously, the Schrödinger equation for the angular motion of a rigid (i.e., having fixed bond length R) diatomic molecule is

$$\frac{\hbar^2}{2\mu}\left[\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{R^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\psi\rangle = E|\psi\rangle$$

or

$$\frac{L^2}{2\mu R^2}|\psi\rangle = E|\psi\rangle$$

The Hamiltonian in this problem contains only the kinetic energy of rotation; no potential energy is present because the molecule is undergoing unhindered "free rotation". The angles θ and φ describe the orientation of the diatomic molecule's axis relative to a laboratory-fixed coordinate system, and μ is the reduced mass of the diatomic molecule

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The eigenvalues corresponding to each eigenfunction are straightforward to find because H_{rot} is proportional to the L^2 operator whose eigenvalues have already been determined. The resultant rotational energies are given as:

$$E_J = \frac{\hbar^2 J(J+1)}{2\mu R^2} = BJ(J+1) \tag{12.8.1}$$

and are independent of M. B is the rotational constant. Thus each energy level is labeled by J and is $2J+1$-fold degenerate (because M ranges from $-J$ to J). The rotational energy in Equation 12.8.1 can be expressed in terms of the moment of inertia I

$$I = \sum_i m_i R_i^2 \tag{12.8.2}$$

where m_i is the mass of the ith atom and R is its distance from the center of mass of the molecule. This moment of inertia replaces μR^2 in the denominator of Equation 12.8.1:

$$E_J = \frac{\hbar^2 J(J+1)}{2I} = BJ(J+1) \tag{12.8.3}$$

Rotation of Polyatomic Molecules

In contrast to diatomic molecules (Equation 12.8.2), the rotational motions of polyatomic molecules in three dimensions are characterized by multiple moments of inertia. typically reflected in an 3×3 inertia tensor. It is common in rigid body mechanics to express in these moments of inertia in *lab-based Cartesian coordinates* via a notation that explicitly identifies the x, y, and z axes such as I_{xx} and I_{xy}, for the components of the inertia tensor.

$$I = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix} \tag{12.8.4}$$

The components of this tensor can be assembled into a matrix given by

$$I_{xx} = \sum_{k=1}^{N} m_k (y_k^2 + z_k^2)$$

$$I_{yy} = \sum_{k=1}^{N} m_k (x_k^2 + z_k^2)$$

$$I_{zz} = \sum_{k=1}^{N} m_k (x_k^2 + y_k^2)$$

$$I_{yx} = I_{xy} = -\sum_{k=1}^{N} m_k x_k y_k$$

$$I_{zx} = I_{xz} = -\sum_{k=1}^{N} m_k x_k z_k$$

$$I_{zy} = I_{yz} = -\sum_{k=1}^{N} m_k y_k z_k.$$

The rotational motions of polyatomic molecules are characterized by moments of inertia that are defined in a *molecule based coordinates* with axes that are labeled a, b, and c. Measured in the body frame the inertia matrix (Equation 12.8.4) is a constant real symmetric matrix, which can be decomposed into a diagonal matrix, given by

$$I = \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix}$$

These labels are assigned so that I_c is the **largest** principal moment of inertia with an order of the three moments set as

$$I_a < I_b < I_c$$

The rotational kinetic energy operator for a rigid non-linear polyatomic molecule is then expressed as

$$H_{rot} = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} \tag{12.8.5}$$

The components of the quantum mechanical angular momentum operators along the three principal axes are:

$$J_a = -i\hbar \cos\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \sin\chi \frac{\partial}{\partial\theta} \tag{12.8.6}$$

$$J_b = i\hbar \sin\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \cos\chi \frac{\partial}{\partial\theta} \tag{12.8.7}$$

$$J_c = -\frac{ih\partial}{\partial\chi} \tag{12.8.8}$$

The angles θ, φ, and χ are the **Euler angles** needed to specify the orientation of the rigid molecule relative to a laboratory-fixed coordinate system. The corresponding square of the total angular momentum operator J^2 can be obtained as

$$J^2 = J_a^2 + J_b^2 + J_c^2 \tag{12.8.9}$$

$$= -\frac{\partial^2}{\partial\theta^2} - \cot\theta \frac{\partial}{\partial\theta} - \left(\frac{1}{\sin\theta} \right) \left(\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial\chi^2} - 2\cos\theta \frac{\partial^2}{\partial\varphi\partial\chi} \right) \tag{12.8.10}$$

and the component along the lab-fixed Z axis is

$$J_Z = -ih \frac{\partial}{\partial\varphi}.$$

Spherical Tops

When the three principal moment of inertia values are identical, the molecule is termed a spherical top. In this case, the total rotational energy Equation 12.8.5 can be expressed in terms of the total angular momentum operator J^2

$$H_{rot} = \frac{J^2}{2I}$$

As a result, the eigenfunctions of H_{rot} are those of J^2 (and J_a as well as J_Z both of which commute with J_2 and with one another; J_Z is the component of J along the lab-fixed Z-axis and commutes with J_a because

$$J_Z = -ih\frac{\partial}{\partial\varphi}$$

and

$$J_a = -ih\frac{\partial}{\partial\chi}$$

act on different angles. The energies associated with such eigenfunctions are

$$E(J,K,M) = \frac{\hbar^2 J(J+1)}{2I^2}$$

for all K (i.e., J a quantum numbers) ranging from -J to J in unit steps and for all M (i.e., J Z quantum numbers) ranging from -J to J. Each energy level is therefore $(2J+1)^2$ degenarate because there are $2J+1$ possible K values and $2J+1$ possible M values for each J. The eigenfunctions of J^2, J_Z and J_a, $|J,M,K>$ are given in terms of the set of rotation matrices $D_{J,M,K}$:

$$|J,M,K\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D^*_{J,M,K}(\theta,\varphi,\chi)$$

which obey

$$J^2|J,M,K\rangle = \hbar^2 J(J+1)|J,M,K\rangle$$

$$J_a|J,M,K\rangle = \hbar K|J,M,K\rangle$$

$$J_Z|J,M,K\rangle = \hbar M|J,M,K\rangle$$

Symmetric Tops

Symmetrical tops are molecules with two rotational axes that have the same inertia and one unique rotational axis with a different inertia. Symmetrical tops can be divided into two categories based on the relationship between the inertia of the unique axis and the inertia of the two axes with equivalent inertia. If the unique rotational axis has a greater inertia than the degenerate axes the molecule is called an **oblate symmetrical top** (Figure 13.8.1). If the unique rotational axis has a lower inertia than the degenerate axes the molecule is called a **prolate symmetrical top**. For simplification think of these two categories as either frisbees for oblate tops or footballs for prolate tops.

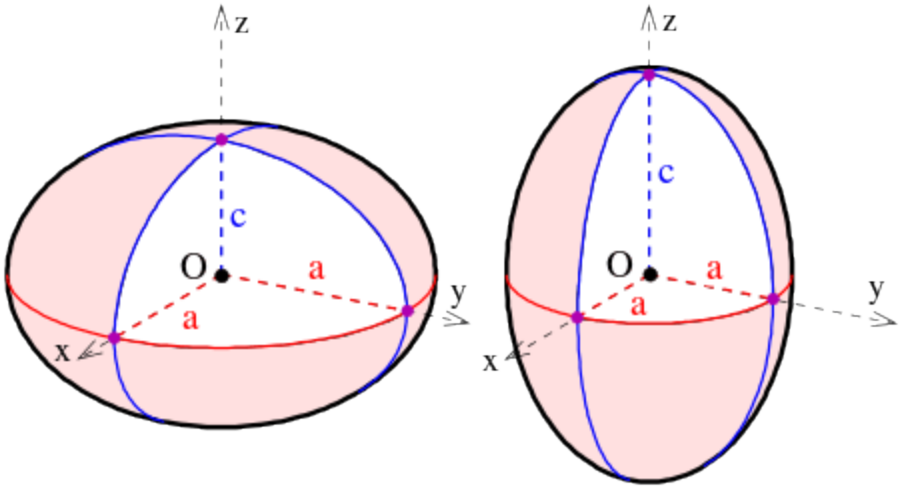


Figure 13.8.1 : The assignment of semi-axes on a spheroid. It is oblate if $c < a$ (left) and prolate if $c > a$ (right). (CC BY-SA 4.0; Ag2gaeh)

Again, the rotational kinetic energy, which is the full rotational Hamiltonian, can be written in terms of the total rotational angular momentum operator J^2 and the component of angular momentum along the axis with the unique principal moment of inertia.

For prolate tops, Equation 12.8.5 becomes

$$H_{rot} = \frac{J^2}{2I} + J_a^2 \left(\frac{1}{2I_a} - \frac{1}{2I} \right)$$

For oblate tops, Equation 12.8.5 becomes

$$H_{rot} = \frac{J^2}{2I} + J_c^2 \left(\frac{1}{2I_c} - \frac{1}{2I} \right)$$

As a result, the eigenfunctions of H_{rot} are those of J^2 and J_a or J_c (and of J_Z), and the corresponding energy levels.

The energies for prolate tops are

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I^2} + h^2 K^2 \left(\frac{1}{2I_a} - \frac{1}{2I} \right)$$

and the energies for oblate tops are

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I2} + h^2 K^2 \left(\frac{1}{2I_c} - \frac{1}{2I} \right)$$

again for K and M (i.e., J_a or J_c and J_Z quantum numbers, respectively) ranging from $-J$ to J in unit steps. Since the energy now depends on K, these levels are only $2J+1$ degenerate due to the $2J+1$ different M values that arise for each J value. The eigenfunctions $|J,M,K>$ are the same rotation matrix functions as arise for the spherical-top case.

Asymmetric Tops

The rotational eigenfunctions and energy levels of a molecule for which all three principal moments of inertia are distinct (a **asymmetric top**) can not easily be expressed in terms of the angular momentum eigenstates and the J, M, and K quantum numbers. However, given the three principal moments of inertia I_a, I_b, and I_c, a matrix representation of each of the three contributions to the general rotational Hamiltonian in Equation 12.8.5 can be formed within a basis set of the $\{|J,M,K\rangle\}$ rotation matrix functions. This matrix will **not** be diagonal because the $|J,M,K\rangle$ functions are not eigenfunctions of the asymmetric top H_{rot}. However, the matrix can be formed in this basis and subsequently brought to diagonal form by finding its eigenvectors {C n, J,M,K } and its eigenvalues $\{E_n\}$. The vector coefficients express the asymmetric top eigenstates as

$$\psi_n(\theta,\varphi,\chi) = \sum_{J,M,K} C_{n,J,M,K} |J,M,K\rangle$$

Because the total angular momentum J^2 still commutes with H_{rot}, each such eigenstate will contain only one J-value, and hence Ψ_n can also be labeled by a J quantum number:

$$\psi_{n,J}(\theta,\varphi,\chi) = \sum_{M,K} C_{n,J,M,K}|J,M,K\rangle$$

To form the only non-zero matrix elements of H_{rot} within the $|J,M,K\rangle$ basis, one can use the following properties of the rotation-matrix functions:

$$\langle j,\rangle = \langle j,\rangle = 1/2 < j,\rangle = h2[J(J+1) - K2],$$

$$\langle j,\rangle = h^2K^2$$

$$\langle j\rangle = -\langle j\rangle = h^2[J(J+1) - K(K\pm1)]1/2[J(J+1) - (K\pm1)(K\pm2)]1/2\langle j\rangle = 0$$

Each of the elements of J_c^2, J_a^2, and J_b^2 must, of course, be multiplied, respectively, by $1/2I_c$, $1/2I_a$, and $1/2I_b$ and summed together to form the matrix representation of H_{rot}. The diagonalization of this matrix then provides the asymmetric top energies and wavefunctions.

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12.9: Normal Modes in Polyatomic Molecules

Normal modes are used to describe the different vibrational motions in molecules. Each mode can be characterized by a different type of motion and each mode has a certain symmetry associated with it. Group theory is a useful tool in order to determine what symmetries the normal modes contain and predict if these modes are IR and/or Raman active. Consequently, IR and Raman spectroscopy is often used for vibrational spectra.

Degrees of Freedom

In general, a normal mode is an independent motion of atoms in a molecule that occurs without causing movement to any of the other modes. Normal modes, as implied by their name, are orthogonal to each other. In order to discuss the quantum-mechanical equations that govern molecular vibrations it is convenient to convert Cartesian coordinates into so called normal coordinates. Vibrations in polyatomic molecules are represented by these normal coordinates.

A molecule can have three types of degrees of freedom and a total of 3N degrees of freedom, where N equals the number of atoms in the molecule. These degrees of freedom can be broken down into three categories.

- **Translational**: These are the simplest of the degrees of freedom. These entail the movement of the entire molecule's center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.
- **Rotational**: These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational**: These are any other types of movement not assigned to rotational or translational movement and thus there are 3N – 6 degrees of vibrational freedom for a nonlinear molecule and 3N – 5 for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Table 13.9.1 : Overview of degrees of freedom

	Total Degrees of Freedom	Translational degrees of freedom	Rotational degrees of freedom	Vibrational degrees of freedom
Nonlinear Molecules	3N	3	3	3N -**6**
Linear Molecules	3N	3	2	3N - 5

Each of these degrees of freedom is able to store energy. However, In the case of rotational and vibrational degrees of freedom, energy can only be stored in discrete amounts. This is due to the quantized break down of energy levels in a molecule described by quantum mechanics. In the case of rotations the energy stored is dependent on the rotational inertia of the gas along with the corresponding quantum number describing the energy level.

Example 13.9.1 : Ethane vs. Carbon Dioxide

Ethane, C_2H_6 has eight atoms ($N = 8$) and is a nonlinear molecule so of the $3N = 24$ degrees of freedom, three are translational and three are rotational. The remaining 18 degrees of freedom are internal (vibrational). This is consistent with:

$$3N - 6 = 3(8) - 6 = 18$$

Carbon Dioxide, CO_2 has three atoms ($N = 3$ and is a linear molecule so of the $3N = 9$ degrees of freedom, three are translational and two are rotational. The remaining 4 degrees of freedom are vibrational. This is consistent with:

$$3N - 5 = 3(3) - 5 = 4$$

The normal modes of vibration are: asymmetric, symmetric, wagging, twisting, scissoring, and rocking for polyatomic molecules.

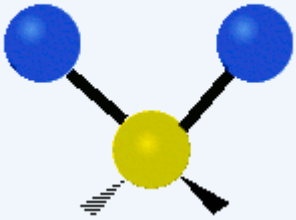
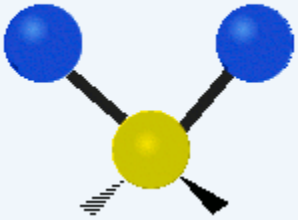
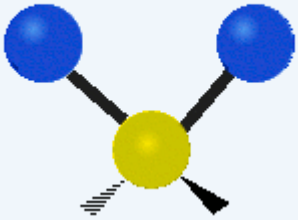
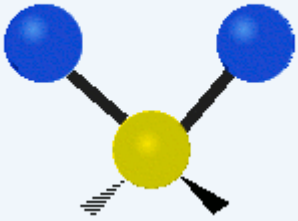
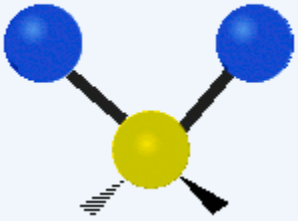
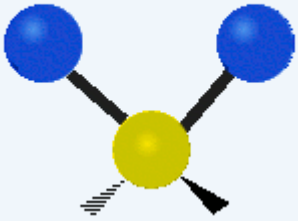
Symmetricical Stretching	Asymmetrical Stretching	Wagging
		
Twisting	**Scissoring**	**Rocking**
		

Figure 13.9.1 : *Six types of Vibrational Modes. Taken from publisher en.Wikipedia.org/wiki/Infrared_spectroscopy with permission from copyright holder.*

Normal Modes

If there is no external field present, the energy of a molecule does not depend on its orientation in space (its translational degrees of freedom) nor its center of mass (its rotational degrees of freedom). The potential energy of the molecule is therefore made up of its vibrational degrees of freedom only of $3N - 6$ (or $3N - 5$ for linear molecules). The difference in potential energy is given by:

$$\Delta V = V(q_1, q_2, q_3, ..., q_n) - V(0, 0, 0, ..., 0) \tag{12.9.1}$$

$$= \frac{1}{2} \sum_{i=1}^{N_{vib}} \sum_{j=1}^{N_{vib}} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right) q_i q_j \tag{12.9.2}$$

$$= \frac{1}{2} \sum_{i=1}^{N_{vib}} \sum_{j=1}^{N_{vib}} f_{ij} q_i q_j \tag{12.9.3}$$

where q represents the equilibrium displacement and N_{vib} the number of vibrational degrees of freedom.

For simplicity, the *anharmonic* terms are neglected in this equation (i.e., higher order terms are ignore). A theorem of classical mechanics states that the cross terms can be eliminated from the above equation (the details of the theorem are very complex and will not be discussed in detail). By using matrix algebra a new set of coordinates {Qj} can be found such that

$$\Delta V = \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{12.9.4}$$

Note that there are no cross terms in this new expression. These new coordinates are called **normal coordinates** or **normal**

modes. With these new normal coordinates in hand, the Hamiltonian operator for vibrations can be written as follows:

$$\hat{H}_{vib} = -\sum_{j=1}^{N_{vib}} \frac{\hbar^2}{2\mu_i} \frac{d^2}{dQ_j^2} + \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{12.9.5}$$

The total wavefunction is a product of the individual wavefunctions and the energy is the sum of independent energies. This leads to:

$$\hat{H}_{vib} = \sum_{j=1}^{N_{vib}} \hat{H}_{vib,j} = \sum_{j=1}^{N_{vib}} \left(\frac{-\hbar^2}{2\mu_j} \frac{d^2}{dQ_i^2} + \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \right) \tag{12.9.6}$$

and the wavefunction is then

$$\begin{aligned} \psi_{vib} &= Q_1, Q_2, Q_3 ..., Q_{vib} \\ &= \psi_{vib,1}(Q_1)\psi_{vib,2}(Q_2)\psi_{vib,3}(Q_3), ..., \psi_{vib,N_{vib}}(Q_{N_{vib}}) \end{aligned}$$

and the total vibrational energy of the molecule is

$$E_{vib} = \sum_{j=1}^{N_{vin}} h\nu_j \left(v_j + \frac{1}{2} \right) \tag{12.9.7}$$

where $v_j = 0, 1, 2, 3....$

The consequence of the result stated in the above equations is that each vibrational mode can be treated as a harmonic oscillator approximation. There are N_{vib} harmonic oscillators corresponding to the total number of vibrational modes present in the molecule.

Pictorial description of normal coordinates using CO

The normal coordinate q is used to follow the path of a normal mode of vibration. As shown in Figure 13.9.2 the displacement of the C atom, denoted by $\Delta r_o(\mathrm{C})$, and the displacement of the O atom, denoted by $\Delta r_o(\mathrm{O})$, occur at the same frequency. The displacement of atoms is measured from the equilibrium distance in ground vibrational state, r_o.

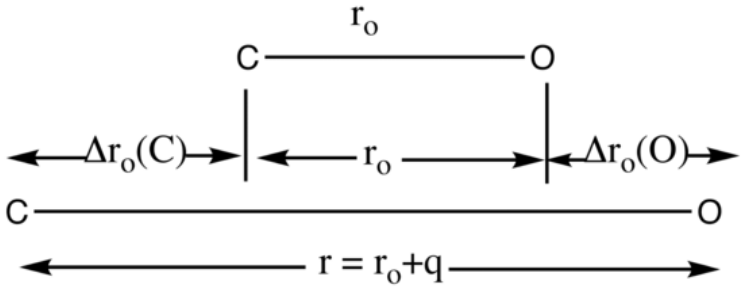


Figure 13.9.2 : The Normal coordinate for CO is equation to $\Delta r(C) + \Delta r(O)$

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12.10: Time-Dependent Perturbation Theory

Time-independent perturbation theory was presented by Erwin Schrödinger in a 1926 paper, shortly after he produced his theories in wave mechanics. In time-independent perturbation theory, the perturbation Hamiltonian is **static** (i.e., possesses no time dependence). Time-dependent perturbation theory, developed by Paul Dirac, studies the effect of a time-dependent perturbation $V(t)$ applied to a **time-independent Hamiltonian** H_0. Since the perturbed Hamiltonian is time-dependent, so are its energy levels and eigenstates. Thus, the goals of time-dependent perturbation theory are slightly different from time-independent perturbation theory, where one may be interested in the following quantities:

- The time-dependent expectation value of some observable A, for a given initial state.
- The time-dependent amplitudes of those quantum states that are energy eigenkets (eigenvectors) in the unperturbed system.

The first quantity is important because it gives rise to the classical result of a measurement performed on a macroscopic number of copies of the perturbed system. The second quantity looks at the time-dependent probability of occupation for each eigenstate. This is particularly useful in laser physics, where one is interested in the populations of different atomic states in a gas when a time-dependent electric field is applied. We will briefly examine the method behind Dirac's formulation of time-dependent perturbation theory. Choose an energy basis $|n\rangle$ for the unperturbed system. (We drop the (0) superscripts for the eigenstates, because it is not useful to speak of energy levels and eigenstates for the perturbed system.)

If the unperturbed system is in eigenstate $|j\rangle$ at time $t = 0$, its state at subsequent times varies only by a phase (this is the Schrödinger picture, where state vectors evolve in time and operators are constant)

$$|j(t)\rangle = e^{-iE_j t/\hbar}|j\rangle$$

Now, introduce a time-dependent perturbing Hamiltonian $H_1(t)$. The Hamiltonian of the perturbed system is

$$H = H_0 + H_1(t)$$

Let $|\psi(t)\rangle$ denote the quantum state of the perturbed system at time t and obeys the time-dependent Schrödinger equation,

$$H|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$

The quantum state at each instant can be expressed as a linear combination of the complete eigenbasis of $|n\rangle$:

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}|n\rangle$$

where the $c_n(t)$ coefficients are to be determined complex functions of *t* which we will refer to as **amplitudes**

We have explicitly extracted the exponential phase factors $\exp(-iE_n t/\hbar)$ on the right hand side. This is only a matter of convention, and may be done without loss of generality. The reason we go to this trouble is that when the system starts in the state $|j\rangle$ and no perturbation is present, the amplitudes have the convenient property that, for all t, $c_j(t) = 1$ and $c_n(t) = 0$ if $n \neq j$.

The square of the absolute amplitude $c_n(t)$ is the probability that the system is in state n at time t, since

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}|n\rangle$$

Plugging into the Schrödinger equation and using the fact that $\partial/\partial t$ acts by a chain rule, one obtains

$$\sum_n \left(i\hbar\frac{\partial c_n}{\partial t} - c_n(t)V(t)\right)e^{-iE_n t/\hbar}|n\rangle = 0\ .$$

By resolving the identity in front of *V*, this can be reduced to a set of partial differential equations for the amplitudes,

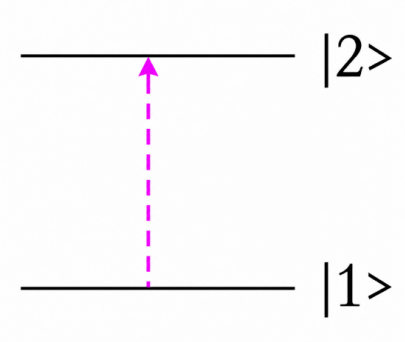
$$\frac{\partial c_n}{\partial t} = \frac{-i}{\hbar}\sum_k \langle n|H_1(t)|k\rangle\, c_k(t)\, e^{-i(E_k - E_n)t/\hbar}\ .$$

The matrix elements of H_1 play a similar role as in time-independent perturbation theory, being proportional to the rate at which amplitudes are shifted between states. Note, however, that the direction of the shift is modified by the exponential phase factor. Over times much longer than the energy difference $E_k - E_n$, the phase winds around 0 several times. If the time-dependence of H_1 is sufficiently slow, this may cause the state amplitudes to oscillate (e.g., such oscillations are useful for managing radiative transitions in a laser).

Two-Level System

Consider the two level system (i.e. $n = 1, 2$)

$$|\psi\rangle = \sum_{n=1,2} c_n(t)|n\rangle_o$$



Solution of time-dependent perturbation for two level system:

$$i\hbar\frac{\partial c_1(t)}{\partial t} = c_1(t)H_{11}(t) + c_2 e^{-i\omega_o t}H_{12}(t)$$

$$i\hbar\frac{\partial c_2(t)}{\partial t} = c_2(t)H_{22}(t) + c_1 e^{+i\omega_o t}H_{21}(t)$$

where the matrix elements of the permutation (in terms of the eigenstates of $H(0)$) are

$$\langle m|H_1(t)|n\rangle = H_{mn}(t)$$

Assume initial state is $n = 1$, and $H_{11} = H_{22} = 0$

$$|\psi(t = 0)\rangle = |1\rangle$$

Probability of particle at $n = 2$ at time t after the perturbation is turned on (i.e., incident light):

$$c_2(t) = \frac{-i}{\hbar}\int_o^t e^{i\omega_o t}dt' H_{21}(t') \tag{12.10.1}$$

where

$$H_1(t) = \cos(\omega t)V(r)$$

$V(r)$ is an amplitude of polarization vector, which we can ignore for now.

If we assume incident frequency of incident light ω is comparable to the natural frequency of oscillation from ω_o

$$\omega \approx \omega_o$$

then Equation 12.10.1 can be simplified to

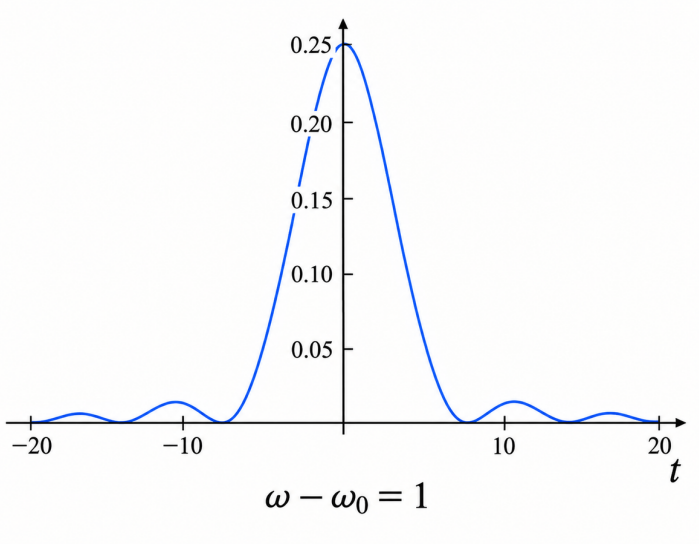
$$c_2(t) = -\frac{2i}{\hbar}\frac{\sin(\omega - \omega_o)t/2}{(\omega - \omega_o)t}e^{i(\omega_0 - \omega)t/2}H_{21}$$

Transition Probability

Assume initial state is $n = 1$, and probability of transition from $n = 1$ state to $n = 2$ state is:

$$P_{12}(t) = |c_2(t)|^2 = \frac{4}{\hbar^2} \left| \frac{\sin(\omega - \omega_o)t/2}{(\omega - \omega_o)t} \right|^2 |H_{21}|^2$$

What does this mean? Strangely, it means that the probability of making a transition is actually oscillating sinusoidally (squared)! If you want to cause a transition, should turn off perturbation after time $\pi/|\omega - \omega_o|$or some odd multiple, when the system is in upper state with maximum probability.



$P_{12}(t)$ is peaked at $\omega - \omega_o = 0$. The height of $|H_{12}t/2\hbar|^2$ and width of $4\pi/t$ gets higher and narrower as time goes on. Recall this is perturbative treatment, however, and $P_{12}(t)$ cannot get bigger than 1, so perturbation theory breaks down eventually.

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12.11: The Selection Rule for the Rigid Rotor

A **selection rule** describes how the probability of transitioning from one level to another cannot be **zero**. It has two sub-pieces: a **gross selection rule** and a **specific selection rule**. A gross selection rule illustrates characteristic requirements for atoms or molecules to display a spectrum of a given kind, such as an IR spectroscopy or a microwave spectroscopy. Once the atom or molecules follow the gross selection rule, the specific selection rule must be applied to the atom or molecules to determine whether a certain transition in quantum number may happen or not.

Selection rules specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation. Incident electromagnetic radiation presents an oscillating electric field $E_0 \cos(\omega t)$ that interacts with a transition dipole. The dipole operator is $\mu = e \cdot r$ where r is a vector pointing in a direction of space.

A dipole moment of a given state is

$$\mu_z = \int \Psi_1{}^* \mu_z \Psi_1 \, d\tau$$

A transition dipole moment is a transient dipolar polarization created by an interaction of electromagnetic radiation with a molecule

$$(\mu_z)_{12} = \int \Psi_1{}^* \mu_z \Psi_2 \, d\tau$$

In an experiment we present an electric field along the z axis (in the laboratory frame) and we may consider specifically the interaction between the transition dipole along the x, y, or z axis of the molecule with this radiation. If μ_z is zero then a transition is forbidden. The selection rule is a statement of when μ_z is non-zero.

> The selection rule is a statement of when μ_z is non-zero.

Rotational transitions

We can use the definition of the transition moment and the spherical harmonics to derive selection rules for a rigid rotator. Once again we assume that radiation is along the z axis.

$$(\mu_z)_{J,M,J',M'} = \int_0^{2\pi} \int_0^{\pi} Y_{J'}^{M'}(\theta,\phi) \mu_z Y_J^M(\theta,\phi) \sin\theta \, d\phi, d\theta$$

Notice that m must be non-zero in order for the transition moment to be non-zero. This proves that a molecule must have a permanent dipole moment in order to have a rotational spectrum. The spherical harmonics can be written as

$$Y_J^M(\theta,\phi) = N_{JM} P_J^{|M|}(\cos\theta) e^{iM\phi}$$

where N_{JM} is a normalization constant. Using the standard substitution of $x = \cos q$ we can express the rotational transition moment as

$$(\mu_z)_{J,M,J',M'} = \mu N_{JM} N_{J'M'} \int_0^{2\pi} e^{I(M-M')\phi} \, d\phi \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

The integral over f is zero unless M = M' so $\Delta M = 0$ is part of the rigid rotator selection rule. Integration over ϕ for $M = M'$ gives 2π so we have

$$(\mu_z)_{J,M,J',M'} = 2\pi\mu N_{JM} N_{J'M'} \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

We can evaluate this integral using the identity

$$(2J+1)x \, P_J^{|M|}(x) = (J - |M| + 1) P_{J+1}^{|M|}(x) + (J - |M|) P_{J-1}^{|M|}(x)$$

Substituting into the integral one obtains an integral which will vanish unless $J' = J + 1$ or $J' = J - 1$.

$$\int_{-1}^{1} P_{J'}^{|M'|}(x)\left(\frac{(J-|M|+1)}{(2J+1)}P_{J+1}^{|M|}(x)+\frac{(J-|M|)}{(2J+1)}P_{J-1}^{|M|}(x)\right)dx$$

This leads to the selection rule $\Delta J = \pm 1$ for absorptive rotational transitions. Keep in mind the physical interpretation of the quantum numbers J and M as the total angular momentum and z-component of angular momentum, respectively. As stated above in the section on electronic transitions, these selection rules also apply to the orbital angular momentum ($\Delta l = \pm 1$, $\Delta m = 0$).

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12.12: The Harmonic Oscillator Selection Rule

Selection rules are a very important concept in spectroscopy and physical chemistry, as they directly complement the concept that systems on the atomic level are quantized. Quantization tells us how electrons, neutrons, and protons are set up, and selection rules tell us how, energetically speaking, they may move about. For example, the principal quantum number, n, determines the energy state of particles in the Particle in a Box model. With respect to real systems, the quantum number n describes electronic transitions, such as the excitation of an electron. There are other transitions, such as the rotational transition, which applies to the rigid rotator model and occurs where there are spherical harmonics. Vibrational transitions occur where there is a system that can be visualized as two masses connected by a spring, such as a diatomic molecule.

Selection rules can be very useful in spectroscopy for obtaining information about an unknown substance; any given substance has properties and behaviors that operate within the selection rules and determine the wavelengths of electromagnetic radiation (light) that cause transitions. By tracking these properties, chemists can use techniques like IR spectroscopy to determine the chemical structure of a molecule. For example, a selection rule might govern how a quantum number changes during a transition. That quantum number appears in equations that determine the energy transition based on the mass and other structural properties of a molecule. Thus, if one knows the selection rules and the energy transition, he or she can determine other properties about the molecule, such as its mass or its bond strength.

Example: Evaluating vibrational transitions using a transition moment integral.

Vibrational systems are described by the harmonic oscillator wavefunctions, which look like

$$\Psi_v(x) = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

A transition dipole moment can be written to describe a transition along the z-axis.

$$\mu_z = \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}\mu_z(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

μ is the dipole moment, so we pull it out of the integral.

$$\mu_z = \mu_z \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

Using the idea that the transition moment μ_z changes on x, we express it as a derivative.

$$\mu_z = \frac{d\mu}{dx} \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

To evaluate the integral, we take advantage of a special Hermite relationship: $\sqrt{\alpha}xH_v(\sqrt{\alpha}x) = vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)$

$$\mu_z = \frac{N_v N_{v+1}}{\sqrt{\alpha}}\left(\frac{d\mu}{dx}\right) \int_{-\infty}^{\infty} H_{v+1}(\sqrt{\alpha}x)e^{(}-\alpha x^2/2)[vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)]dx$$

By inspection, it is clear that the integral only allows transitions of $\Delta v = \pm 1$, because for any other value, the integral will be zero.

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12.13: Group Theory Determines Infrared Activity

Determining if a Normal Modes is IR or Raman Active

A transition from $v \rightarrow v'$ is IR active if the **transition moment integral** contains the totally symmetric irreducible representation of the point group the molecule belongs to. The transition moment integral is derived from the one-dimensional harmonic oscillator. Using the definition of electric dipole moment μ, the integral is:

$$M(v \rightarrow v') = \langle \text{final wavefunction} | \vec{\mu} | \text{initial wavefunction} \rangle$$

or in terms of vibrational wavefunctions for a specific normal mode $|\phi(v)\rangle$

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) | \vec{\mu} | \phi(v = 0) \rangle \tag{12.13.1}$$

assuming the transition from the $v = 0$ wavefunction to the $v' \neq 0$ wavefunction.

Now, consider the case that $\vec{\mu}$, is a constant and therefore independent of the vibration (i.e., the electric dipole moment does not change during the vibration). This it could be taken outside the integral in Equation 12.13.1 becomes

$$M(v \rightarrow v') = \vec{\mu} \langle \phi(v' \neq 0) | \phi(v = 0) \rangle \tag{12.13.2}$$

Since $|\phi(v = 0)\rangle$ and $|\phi(v =\neq 0)\rangle$ are mutually orthogonal to each other, the integral in Equation 12.13.1 will equal zero and the transition will **not** be allowed (i.e., it is forbidden). For the M to be nonzero, $\vec{\mu}$ must change during a vibration. This selection rule explains why homonuclear diatomic molecules do not produce an IR spectrum. There is no change in dipole moment resulting in a transition moment integral of zero and a transition that is forbidden.

For a transition to be Raman active, the same rules apply. The transition moment integral must contain the totally symmetric irreducible representation of the point group. The integral contains the polarizability tensor α (usually represented by a square matrix):

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) | \alpha | \phi(v = 0) \rangle \tag{12.13.3}$$

Following a similar argument as above, α must be nonzero for the transition to be allowed and exhibits Raman scattering.

Character Table

For a molecule to be IR active the dipole moment has to change during the vibration. For a molecule to be Raman active the polarizability of the molecule has to change during the vibration. The reducible representation $\mathbf{\Gamma_{vib}}$ can also be found by determining the reducible representation of the 3N degrees of freedom of H_2O, $\mathbf{\Gamma}_{tot}$. By applying Group Theory it is straightforward to find $\mathbf{\Gamma_{x,y,z}}$ as well as UMA (number of unmoved atoms). Again, using water as an example with C_{2v} symmetry where 3N = 9, $\mathbf{\Gamma_{tot}}$ can be determined:

C_{2v}	E	C_2	σ (xz)	σ (yz)	
$\mathbf{T_{x,y,z}}$	3	-1	1	1	
UMA	3	1	1	3	
$\mathbf{\Gamma_{tot}}$	**9**	**-1**	**1**	**3**	$\mathbf{=3a_1 + a_2 + 2b_1 + 3b_2}$
Note that $\mathbf{\Gamma}_{tot}$ contains nine degrees of freedom consistent with 3N = 9.					

$\mathbf{\Gamma}_{tot}$ contains $\mathbf{\Gamma}_{translational}$, $\mathbf{\Gamma}_{rotational}$ as well as $\mathbf{\Gamma}_{vibrational}$. $\mathbf{\Gamma}_{trans}$ can be obtained by finding the irreducible representations corresponding to x,y and z in the right side of the character table, $\mathbf{\Gamma}_{rot}$ by finding the ones corresponding to R_x, R_y and R_z. $\mathbf{\Gamma}_{vib}$ can be obtained by $\mathbf{\Gamma}_{tot}$ - $\mathbf{\Gamma}_{trans}$ - $\mathbf{\Gamma}_{rot}$.

$$\Gamma_{vib}(H_2O) = (3a_1 + a_2 + 2b_1 + 3b_2) - (a_1 + b_1 + b_2) - (a_2 + b_1 + b_2) = 2a_1 + b_2$$

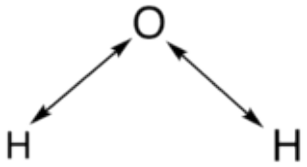
In order to determine which modes are IR active, a simple check of the irreducible representation that corresponds to x,y and z and a cross check with the reducible representation Γ_{vib} is necessary. If they contain the same irreducible representation, the mode is IR active.

For H_2O, z transforms as a_1, x as b_1 and y as b_2. The modes a1 and b2 are IR active since Γvib contains $2a_1 + b_2$.

In order to determine which modes are Raman active, the irreducible representation that corresponds to z^2, x^2-y^2, xy, xz and yz is used and again cross checked with Γvib. For H_2O, z^2 and x^2-y^2 transform as a_1, xy as a_2, xz as b_1 and yz as b_2.The modes a_1 and b_2 are also Raman active since Γ_{vib} contains both these modes.

The IR spectrum of H2O does indeed have three bands as predicted by Group Theory. The two symmetric stretches v1 and v2 occur at 3756 and 3657 cm-1 whereas the bending v3 motion occurs at 1595 cm-1.

In order to determine which normal modes are stretching vibrations and which one are bending vibrations, a stretching analysis can be performed. Then the stretching vibrations can be deducted from the total vibrations in order to obtain the bending vibrations. A double-headed arrow is drawn between the atom as depicted below:



Then a determination of how the arrows transform under each symmetry operation in C2v symmetry will yield the following results:

C_{2v}	E	C_2	σ (xz)	σ (yz)	
$\Gamma_{stretch}$	2	0	0	2	**= $a_1 + b_2$**

$$\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch} = 2a_1 + b_2 - a_1 - b_2 = a_1$$

H_2O has two stretching vibrations as well as one bending vibration. This concept can be expanded to complex molecules such as $PtCl4^-$. Four double headed arrows can be drawn between the atoms of the molecule and determine how these transform in D_{4h} symmetry. Once the irreducible representation for $\Gamma_{stretch}$ has been worked out, Γ_{bend} can be determined by $\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch}$.

Most molecules are in their zero point energy at room temperature. Therefore, most transitions do originate from the v=0 state. Some molecules do have a significant population of the v=1 state at room temperature and transitions from this thermally excited state are called **hot** bands.

References

1. Merlin, J.C., Cornard, J.P., *J. Chem. Educ.*, **2006**, 83 (9), p 1383. **DOI:** 10.1021/ed083p1393
2. McGuinn, C.J., *J. Chem. Educ.*, **1982**, 59 (10), p 813. **DOI:** 10.1021/ed059p813
3. Harris, D.C., Bertolucci, M.D., *Symmetry and Spectroscopy: An introduction to Vibrational and Electronic Spectroscopy*. Dover Publocations, Inc., New York, **1989**.
4. McQuarrie, D. A., Simon, J.D., *Physical Chemistry: A Molecular Approach*, University Science Books, Sausalito, California, **1997**; 518-521.
5. Housecroft, C.E., Sharpe, A.G., **Inorganic Chemistry.** Pearson Education Limited, England, **2008**, 107.
6. Atkins, P., dePaula, J., *Physical Chemistry*, W.H. Freeman and Company, New York, **2002**, 520-523.
7. Bishop, D.M., *Group Theory and Chemistry*, Dover Publications, Inc, New York, **1973**, 166.

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12.E: Molecular Spectroscopy (Exercises)

These are homework exercises to accompany Chapter 13 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q13.1

1. Calculate the energy difference for radiation wavenumber of, $\nu = 1.00 cm^{-1}$ including the type of molecular process that absorbs of this radiation corresponding to.
2. Given the wavelength of 3.4 x 10^{-4}, which molecular process does it fall into?
3. What are other advantages of knowing the spectroscopy of molecules?
4. Do you think the spectroscopy and molecular processes of the molecules have relationship to temperature? Explain.
5. What is other form that you can express in above equation?

Q13.20

The vibrational term of a diatomic molecule is

$$G(v) = (v + \frac{1}{2})\nu_e - (v + \frac{1}{2})^2 \chi_e \nu_e \tag{12.E.1}$$

Show that the spacing between adjacent levels is given by

$$\Delta G = G(v+1) - G(v) = \nu_e - 2\chi_e \nu_e (v+1)$$

Show that the maximum vibrational quantum number, v_{max} is given by

$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{12.E.2}$$

Use this result to show that the dissociation energy of the diatomic molecule can be written as

$$D_e = \frac{\nu_e - \nu_e \chi_e^2}{4\chi_e} \approx \frac{\nu_e}{4\chi_e} \tag{12.E.3}$$

Explain how the constants ν_e and χ_e can be evaluated from a plot of ΔG versus $v + 1$, called a Birge-Sponer plot. After finding these constants, determine the dissociation energy of the molecule. Use the following experimental data of H_2 to determine the dissociation energy of the molecule.

v	G(v) / cm^{-1}
0	4161.12
1	8087.11
2	11782.35
3	15250.36
4	18497.92
5	21505.65
6	24287.83
7	26830.97
8	29123.93
9	31150.19

v	G(v) / cm^{-1}
10	32886.65
11	34301.83
12	35351.01
13	35972.97

Explain why your plot is not linear for high values of v. How does this dissocation energy differ with the experimental value of $38269.48cm^{-1}$.

S13.20

$$\Delta G = G(v+1) - G(v) = \left(v+\frac{3}{2}\right)\nu_e - \left(v+\frac{3}{2}\right)^2 \chi_e\nu_e - \left(v+\frac{1}{2}\right)\nu_e + \left(v+\frac{1}{2}\right)^2 \chi_e\nu_e = \nu_e - \chi_e\nu_e(2v+2) = \nu_e - 2\chi_e\nu_e(v+1)$$

In the limit that $\Delta G \to 0, v \to v_{max}$, solving for v_{max} gives

$$0 = \nu_e - 2\chi_e\nu_e(v_{max}+1) \tag{12.E.4}$$

$$2\chi_e(v_{max}+1) = 1 \tag{12.E.5}$$

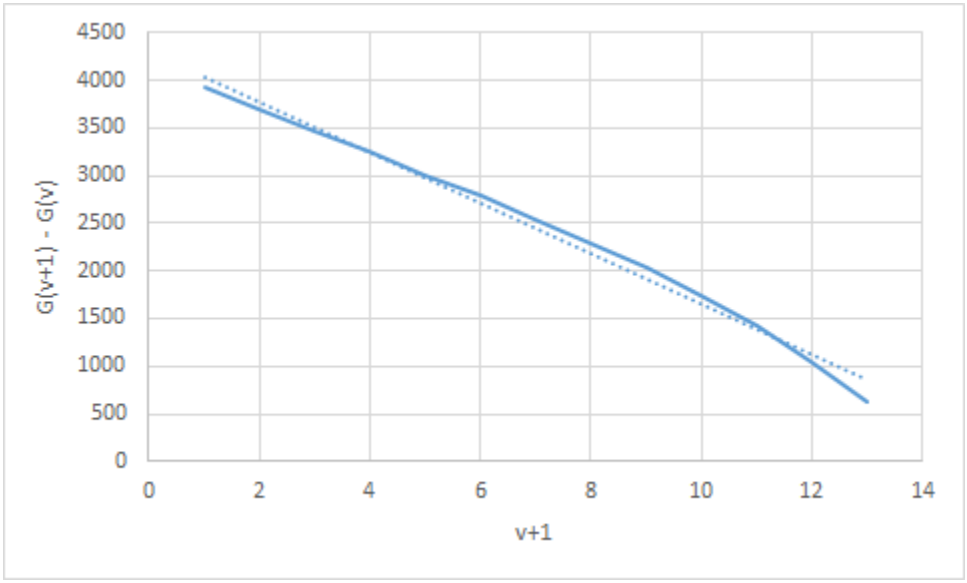
$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{12.E.6}$$

The molecule dissociates in the limit $\Delta G \to 0$, so the dissociation energy is given by

$$D_e = G(v_{max}) = (\frac{1}{2\chi_e} - \frac{1}{2})\nu_e - (\frac{1}{2\chi_e} - \frac{1}{2})^2\chi_e\nu_e = \frac{\nu_e}{2\chi_e}(1-\chi_e) - \frac{\nu_e}{4\chi_e}(1-\chi_e)^2 = \frac{\nu_e}{4\chi_e}(2-2\chi_e-1+2\chi_e-\chi_e^2) = \frac{\nu_e}{4\chi_e}(1$$

The final step can be made if we assume χ_e to be very small.

Looking at the equation for ΔG, we conclude that a plot of ΔG versus $v+1$ will have an intercept of ν_e and a slope of $-2\chi_e\nu_e$. The experimental data points for H_2 can be plotted as such:



If we use a best linear fit, we determine that the intercept is $\nu_e = 4164.4cm^{-1}$ and the slope is $-2\chi_e\nu_e = -232.01cm^{-1}$. Thus, $\chi_e = 0.0279$. Then, the dissociation energy is

$$D_e = \frac{\nu_e}{4\chi_e} = 37400cm^{-1} \tag{12.E.8}$$

The plot is not linear for large values of v because the potential curve is not well described by the anharmonic potential energy function.

Q13.21

An analysis of the vibrational spectrum of the ground-state homonuclear diatomic molecule Na_2 gives $\tilde{\nu}_e = 159.125\ \ cm^{-1}$ and $\tilde{\nu}_e\tilde{x}_e = 0.7255\ \ cm^{-1}$. Suggest an experimental method that can be used to determine there spectroscopic parameters. Use $\nu_{max} = \dfrac{1}{2\tilde{x}_e} - 1$ to determine the number of bound vibrational levels for ground state of Na_2.

S13.21

First solve for $\tilde{x}$:

$$\tilde{x} = \frac{0.7255\ cm^{-1}}{159.125\ cm^{-1}} = 4.5593 \times 10^{-3}\ cm^{-1} \tag{12.E.9}$$

Then plug it in to the equation:

$$\nu_{max} = \frac{1}{2 \times 4.5593 \times 10^{-3}\ cm^{-1}} - 1 = 109.67\ cm^{-1} \tag{12.E.10}$$

There are 109 bound vibrational levels for the ground state of Ne_2.

Q13.22

A Morse potential is a decent representation of internuclear potential and is modeled by

$$U(q) = D_e(1 - e^{-/betaq})^2 \tag{12.E.11}$$

where $q = R - R_e$. Prove the force constant for the Morse Potential is evaluated

$$k = 2D_e\beta^2 \tag{12.E.12}$$

If $D_e = 6.23 \times 10^{-19} J \cdot Molecule^{-1}$ and $\beta = 1.37 \times 10^{10} m^{-1}$ for a given compound, calculate the force constant for that compound.

S13.22

Using a Maclaurin series expansion of the Morse potential, the formula can be rewritten

$$U(q) = D_e(1 - e^{-\beta q})^2 = D_e(1 - (1 - \beta q + \frac{\beta^2 q^2}{2} O(q)^3))^2 = D_e(\beta^2 q^2 + O(q)^3) \tag{12.E.13}$$

We know that

$$U(q) = \frac{kq^2}{2} \tag{12.E.14}$$

assuming that $O(q)^3$ approaches zero, we get

$$\frac{kq^2}{2} = D_e(\beta^2 q^2 + O(q)^3) \implies k = 2D_e\beta^2 \tag{12.E.15}$$

Plugging in our given values, we get

$$l = 2(6.23 \times 10^{-19} J \cdot Molecule^{-1})(1.37 \times 10^{10})^2 = 234N \cdot m^{-1} \tag{12.E.16}$$

Q13.23

Given that $D_e = 7.33 \times 10^{-19} J \cdot molecule^{-1}, \tilde{v}_e = 1580.0 cm^{-1}, and R_e = 121 pm$, find k and β for $^{16}O_2$.

S13.23

Assuming a a harmonic oscillator model, we can use the equation:

$$\tilde{v}_e = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{12.E.17}$$

We can find k from the parameters given in the problem. Solving for k gives

$$k = (2\pi c \tilde{v}_e)^2 \mu \tag{12.E.18}$$

$$= [2\pi(3 \times 10^{10} cm \cdot s^{-1})(1580.0 cm^{-1})]^2 (7.9975 amu)(1.661 x 10^{-27} kg \cdot amu^{-1}) \tag{12.E.19}$$

$$= 1176.3 N \cdot m^{-1} \tag{12.E.20}$$

Using the equation:

$$\beta = \left(\frac{k}{2D_e}\right)^{1/2} \tag{12.E.21}$$

We can solve for β using the information above

$$\beta = \left[\frac{1176.3 N \cdot m^{-1}}{2(7.33 \times 10^{-19} J)}\right]^{1/2} \tag{12.E.22}$$

$$= 2.84 \times 10^{10} m^{-1} \tag{12.E.23}$$

Q13.24

The fundamental line in the IR spectrum of $^{12}C^{16}O\ cm^{-1}$, and the first overtone occurs at 4260.0 cm^{-1}. Find $\tilde{v}_e$ and $\tilde{x}_e\tilde{v}_e$ for $^{12}C^{16}O$.

S13.24

The equations for the fundamental frequency and the overtone are

$$\tilde{v} = \tilde{v}_e - 2\tilde{x}_e\tilde{v}_e \tag{12.E.24}$$

and

$$\tilde{v} = 2\tilde{v}_e - 6\tilde{x}_e\tilde{v}_e, \tag{12.E.25}$$

respectively.

We can set the fundamental frequency equal to $2143.0\ cm^{-1}$ and the first overtone equal to $4260.0\ cm^{-1}$ which is given from the problem statement. Then, we want to solve for $\tilde{x}_e\tilde{v}_e$.

Multiply the fundamental frequency by 3 and subtract the overtone.

$$\tilde{v}_e = [3(2143.0) - 4260.0] cm^{-1} = 2169.0 cm^{-1} \tag{12.E.26}$$

Then multiply the fundamental frequency by 2 and subtract from the overtone.

$$\tilde{x}_e\tilde{v}_e = 13.0 cm^{-1} \tag{12.E.27}$$

Q13.24

Which of the following molecules exhibit a microwave rotational absorption spectrum: BF_2,SO_2,C_2F_2,NO_3^-

S13.24

SO_2

notes: microwave rotational absorption correlates to the rotation of polyatomic molecules. Would BF_2 and NO_3^- also fall in this range?

Q13-25 Slightly Incorrect

Calculate the fundamental and the first two overtones of

$$H^{35}Cl \tag{12.E.28}$$

given

$$\tilde{v_e} = 2990.946 cm^{-1} \tag{12.E.29}$$

$$\tilde{x_e}\tilde{v_e} = 52.819 cm^{-1} \tag{12.E.30}$$

S13-25

Use equation,

$$\tilde{v_{obs}} = \tilde{v_e}\nu - \tilde{x_e}\tilde{v_e}\nu(\nu+1) \tag{12.E.31}$$

with v =1,2...

The fundamental frequency is given by v=1 and the first two overtones are given by v=2 and v=3.

Fundamental:

$$\tilde{v_{obs}} = \tilde{v_e} - 2\tilde{x_e}\tilde{v_e} = 2990.946 cm^{-1} - 2(52.819 cm^{-1}) = 2885.308 cm^{-1} \tag{12.E.32}$$

First overtone:

$$\tilde{v_{obs}} = 2\tilde{v_e} - 6\tilde{x_e}\tilde{v_e} = 2990.946 cm^{-1} - 6(52.819 cm^{-1}) = 5664.978 cm^{-1} \tag{12.E.33}$$

Second overtone:

$$\tilde{v_{obs}} = 3\tilde{v_e} - 12\tilde{x_e}\tilde{v_e} = 3(2990.946 cm^{-1}) - 12(52.819 cm^{-1}) = 8339.01 cm^{-1} \tag{12.E.34}$$

Q13.26

Plot the

$$\frac{\nu_{obs}}{\nu} \tag{12.E.35}$$

versus

$$(\nu+1) \tag{12.E.36}$$

for the anharmonic oscillator approximation and use it to determine the values of

$$\nu_e \tag{12.E.37}$$

and

$$x_e\nu_e \tag{12.E.38}$$

for

$$H^{3}5Cl \tag{12.E.39}$$

. Use the information in Table13.4.

S13.26

$$\nu_{obs} = \nu_{obs}\nu - x_e\nu_e\nu(\nu+1) \tag{12.E.40}$$

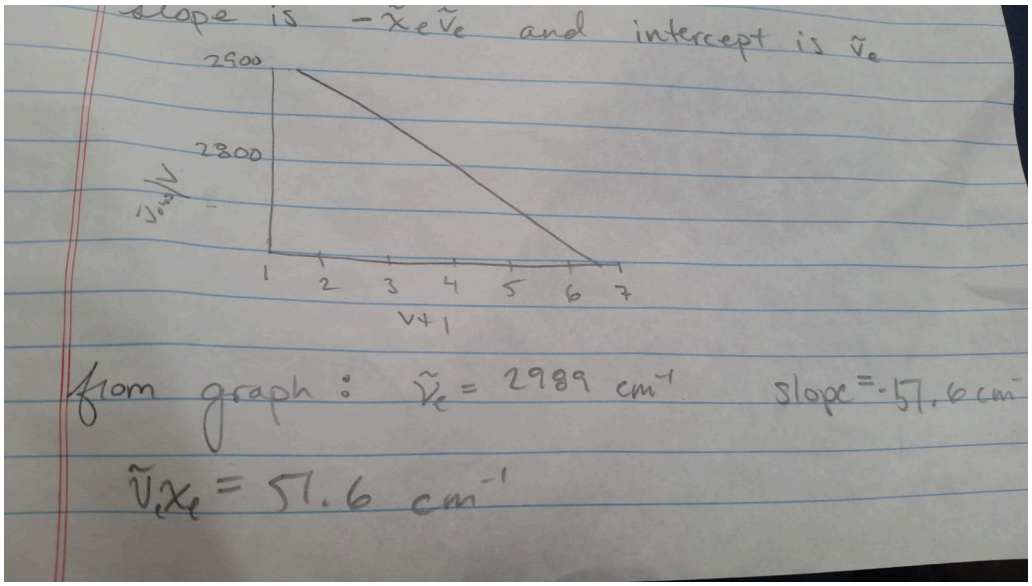
$$\frac{\nu_{obs}}{\nu} = \nu_e - x_e\nu_e(\nu+1) \tag{12.E.41}$$

The slope is

$$-x_e\nu_e \tag{12.E.42}$$

and the intercept is

$$\nu_e \tag{12.E.43}$$



The problem is nice and straight forward. It would be great for an explanation of why the slope is negative for an insight of the graph

Q13.31

Phosphorus nitride (PN) is a heteronuclear diatomic molecule that is a similar to N_2 with a triple bond, although is substantially weaker because P is a larger atomic radius than N. Using the following data, calculate $\tilde{\nu_e}'$ and $\tilde{\chi_e}'\ \tilde{\nu_e}'$ for PN.

IR Transition	$\nu_{\tilde{abs}}$ [cm^{-1}]
$0 \rightarrow 0$	39,699.10
$0 \rightarrow 1$	40,786.80
$0 \rightarrow 2$	41,858.90

S13.31

We will use the following equation:

$$\nu_{\tilde{abs}} = \nu_{\tilde{0,0}}' + \tilde{\nu_e}'\tilde{\nu}' - \tilde{\chi_e}'\tilde{\nu_e}'\tilde{\nu}'(\nu'+1) \tag{12.E.44}$$

Plugging in the appropriate values of ν', we get:

According to your table $\tilde{\nu_{0,0}}'$ should be 39,699.10 not 29,699.10.

- $\nu' = 0$:

$$\tilde{\nu_{0,0}}' = 29,699.10\ cm^{-1} \tag{1}$$

- $\nu' = 1$:

$$\tilde{\nu_{0,0}}' + \tilde{\nu_e}' - 2\tilde{\chi_e}'\tilde{\nu_e}' = 40,786.80\ cm^{-1} \tag{2}$$

- $\nu' = 2$:

$$\tilde{\nu_{0,0}}' + 2\tilde{\nu_e}' - 6\tilde{\chi_e}'\tilde{\nu_e}' = 41,858.90\ cm^{-1} \tag{3}$$

Solving as a system of equations, we subtract:

(2) - (1) = (4), (3) - (1) = (5), and finally (5) - 2x(4) = (6)

Equation (6) can be solved for $\tilde{\chi_e}'\tilde{\nu_e}'$, and then plugged back in to equation (4) or equation (5) to solve for $\tilde{\nu_e}'$. The answer is:

$$\tilde{\chi_e}'\tilde{\nu_e}' = 1103.3\ cm^{-1} \tag{12.E.45}$$

and

$$\tilde{\nu_e}' = 7.80\ cm^{-1} \tag{12.E.46}$$

from my calculations $\tilde{\nu_e}' = 1103.3$ and $\tilde{\chi_e}'\tilde{\nu_e}' = 7.80$ it looks like you had them switched

Q13.32

The frequencies of the first few vibronic transitions to an excited state of NaCl* are as follows:

Vibronic Transitions	$0 \rightarrow 0$	$0 \rightarrow 1$	$0 \rightarrow 2$
$\tilde{v}_{obs}/cm^{-}1$	12376	89706	15219

*not accurate values for NaCl

Use these data to calculate the values of $\tilde{v}_e$ and $\tilde{v}_e\tilde{x}_e$ for the excited state of NaCl

S13.32

$A = \tilde{v}'_e, B = \tilde{v}'_e\tilde{x}'_e$

$12376 = \tilde{v}_0, 0$

$89706 = \tilde{v}_0, 0 + \tilde{v}'_e - 2\tilde{v}'_e\tilde{x}'_e - 12376 = \tilde{v}_0, 0 = 77330 = +\tilde{v}'_e - 2\tilde{v}'_e\tilde{x}'_e$ (1)

$15219 = \tilde{v}_0, 0 + 2\tilde{v}'_e - 6\tilde{v}'_e\tilde{x}'_e - 12376 = \tilde{v}_0, 0 = 2843 = 2\tilde{v}'_e - 6\tilde{v}'_e\tilde{x}'_e$ (2)

77330 + 2B = A (1a)

2843 = 2A - 6B (2a)

77330+2B = A

2843 - 154660 = -2B

B = 75908.5 cm^{-1} = $\tilde{v}'_e$

A = 229147 cm^{-1} = $\tilde{v}'_e\tilde{x}'_e$

Q13.33

Determine the number of translational, rotational, and vibrational degrees of freedom in

a. Xe
b. HCl
c. CS_2
d. hemoglobin containing 9272 molecules

The total number of degrees of freedom is 3N, where N is the number of atoms in the molecule. All molecules have three translational degrees of freedom. A nonlinear molecule has three rotational degrees of freedom and a linear molecule has two rotational degrees of freedom. A linear molecule has $3N-5$ vibrational degrees of freedom and a nonlinear molecule has 3N — 6 vibrational degrees of freedom.

S13.33

The number of translational degrees of freedom is 3, the number of rotational degrees of freedom is 2 for linear molecules and 3 for non-linear molecules. Therefore, the remaining degrees of freedom, which is equal to 3N-5 for linear molecules or 3N-6 for non-linear molecules, is equal to the number of vibrational degrees of freedom.

	Translation	Rotation	Vibration	Total
Xe	3	0	0	3
HCl	3	2	1	6
CS_2	3	2	4	9
hemoglobin	3	3	27810	27816

Q13.36

Classify each of the following molecules as either a prolate or an oblate symmetric top: XeF_4, $ClCH_3$, NH_3, and C_6H_6.

S13.36

- XeF_4 :oblate
- $ClCH_3$:prolate
- NH_3:prolate
- C_6H_6:oblate

Q13.37

Solve for the components of the moment of inertia of a trigonal planar molecule if all the masses are m, the bond lengths are unit length, and all bond angles are 120°.

S13.37

$$I_{xx} = \sum m_j y_j^2 = m(1)^2 + 2m(sin^2 30^\circ) = \frac{3}{2}m \tag{12.E.47}$$

$$I_{yy} = \sum m_j x_j^2 = m(0)^2 + 2m(cos^2 30^\circ) = \frac{3}{2}m \tag{12.E.48}$$

$$I_{zz} = \sum m_j x_j^2 + \sum m_j y_j^2 = 3m \tag{12.E.49}$$

Q13.38

This problem illustrates how the principal moments of inertia can be obtained as an eigenvalue problem. Consider a molecule where all the masses are unit masses and the long and short bond lengths are 2 and 1, respectively.

Show that

$$I_{xx} = 2\cos^2\theta + 8\sin^2\theta \tag{12.E.50}$$

$$I_{yy} = 8\cos^2\theta + 2\sin^2\theta \tag{12.E.51}$$

$$I_{xy} = -6\cos\theta\sin\theta \tag{12.E.52}$$

Solve the secular determinant equation for λ

$$\begin{vmatrix} I_{xx} - \lambda & I_{xy} \\ I_{xy} & I_{yy} - \lambda \end{vmatrix} = 0 \tag{12.E.53}$$

and compare the result with the values of I_{xx} and I_{yy} that you would obtain if you align the "molecule" and coordinate system such that $\theta = 180^\circ$. What does this comparison tell you? What are the values of I_{xx} and I_{yy} if $\theta = 90$?

S13.38

We use trigonometric functions to find the x and y components

$$I_{xx} = \sum m_i y_i^2 = 2(1)(2\sin\theta)^2 + 2(1)\left[\sin\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\sin^2\theta + 2\cos^2\theta \tag{12.E.54}$$

$$I_{yy} = \sum m_i x_i^2 = 2(1)(2\cos\theta)^2 + 2(1)\left[\cos\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\cos^2\theta + 2\sin^2\theta \tag{12.E.55}$$

$$I_{xy} = -\sum m_i x_i y_i = -(2\cos\theta)(2\sin\theta) - 2\left[\cos(\pi) + \theta\right]\left[\sin(\pi) + \theta\right] - \left[\sin\left(\frac{\pi}{2}\right) - \theta\right]\left[\cos\left(\frac{\pi}{2}\right) - \theta\right] - \left[\cos\left(\frac{\pi}{2}\right) + \theta\right]\left[\sin\left(\frac{\pi}{2}\right.\right.$$

$$= -6\cos\theta\sin\theta$$

The secular determinantal equation becomes

$$\begin{vmatrix} 8\sin^2\theta + 2\cos^2\theta - \lambda & -6\cos\theta\sin\theta \\ -6\cos\theta\sin\theta & 8\cos^2\theta + 2\sin^2\theta - \lambda \end{vmatrix} = 0 \tag{12.E.57}$$

Expanding the determinant gives

$$0 = \lambda^2 - \lambda(10)(\sin\theta^2 + \cos\theta^2) + 16(\sin\theta^2 + \cos\theta^2)^2 \tag{12.E.58}$$

$$0 = \lambda^2 - 10\lambda + 16 \tag{12.E.59}$$

$$\lambda = 5 \pm 3 \tag{12.E.60}$$

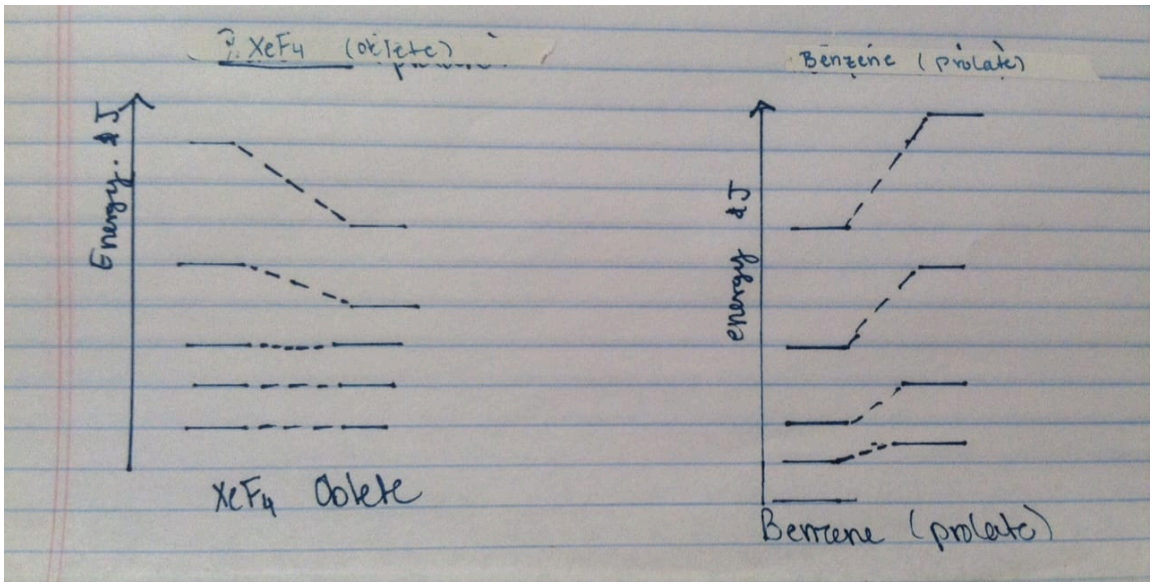
If $\theta = 180^\circ$ then $I_{xx} = 2, I_{yy} = 8, and I_{xy} = 0$. If $\theta = 90^\circ$ then $I_{xx} = 8, I_{yy} = 2, and I_{xy} = 0$. This tells us that the coordinate system does not affect the values of the principal momentum of inertia.

Q13.39

Sketch the energy level diagram of NH_3 (a prolate symmetric top molecule) and XeF_4 (an oblate symmetric top). How do they differ?

S13.39

The energies increase as the J levels increases for the prolate symmetry and the energies decrease as J increases for the oblate symmetry



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13: LASERS, LASER SPECTROSCOPY, AND PHOTOCHEMISTRY

The word 'laser' is an acronym for "light amplification by stimulated emission of radiation." The use of lasers in science and in society has rapidly expanded since their development in the early 1960s. Lasers provides chemists with a powerful and versatile tool for probing the nature of and dynamics of species and chemical reactions. This chapter will discuss the foundations of lasers and the interaction of their output toward understanding atomic and molecular properties. We will describe the generation of laser light from electronically excited atoms using the rate-equation model developed by Einstein. Modern laser designs and applications will then be discussed.

13.1: Electronically Excited Molecules can Relax by a Number of Processes

13.2: The Dynamics of Transitions can be Modeled by Rate Equations

13.3: A Two-Level System Cannot Achieve a Population Inversion

13.4: Population Inversion can be Achieved in a Three-Level System

13.5: What is Inside a Laser?

13.6: The Helium-Neon Laser

13.7: Modern Applications of Laser Spectroscopy

13.E: Lasers, Laser Spectroscopy, and Photochemistry (Exercises)

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13.1: Electronically Excited Molecules can Relax by a Number of Processes

To understand how lasers work we must first describe how a molecule in an excited state can relax back to the ground state because the light emitted by a laser is influenced by these relaxation processes. The two radiative decay pathways for an excited molecule are fluorescence and phosphorescence. Fluorescence differs from phosphorescence in that the energy transition that is responsible for fluorescence does not involve a change in electron spin multiplicity. Thus fluorescence lifetimes are short (10^{-9} - 10^{-6} s). In phosphorescence, there is a change in electron spin multiplicity, resulting in a longer lifetime of the excited state (second to minutes). A description of electron spin and the differences between singlet and triplet states will clarify the difference between fluorescence and phosphorescence.

Spin Multiplicity - Singlet and Triplet Excited States

The Pauli Exclusion principle states that two electrons in an atom cannot have the same four quantum numbers (n, l, m_l, m_s). Therefore, because two electrons can occupy each orbital, these two electrons must have opposite spin states. These opposite spin states are called spin pairing. Because of this spin pairing, most molecules are diamagnetic, and are not attracted or repelled by an external magnetic or electric field. Molecules that contain unpaired electrons (free radicals) do have magnetic moments that are attracted to an external magnetic or electric field.

A molecule is said to be in a singlet state when all the electron spins are paired in the molecular electronic state, and the electronic energy levels do not split when the molecule is exposed to a magnetic field. A doublet state occurs when there is an unpaired electron that gives two possible orientations when exposed to a magnetic field and imparts different energies to the system. A singlet or a triplet state can form when one electron is excited to a higher energy level. In an excited singlet state, the promoted electron retains the spin orientation it had in the ground state (i.e., paired). In a triplet excited state, the promoted electron undergoes a change in spin, and so has the same spin orientation (parallel) to the unpaired electron that remains in the ground state orbital. The difference between the spins of ground singlet, excited singlet, and excited triplet is shown in Figure 13.1.1. The terms singlet, doublet and triplet are derived using the equation for multiplicity, 2S+1, where S is the total spin angular momentum (sum of all the electron spins). Individual spins are denoted as spin up (s = +1/2) or spin down (s = -1/2). If we were to calculate the multiplicity for the singlet ground state or the singlet excited state, the equation would be

$$2(+1/2 + -1/2) + 1 = 2(0) + 1 = 1$$

In a similar fashion, the spin multiplicity for the triplet excited state can be calculated as

$$2(+1/2 + +1/2) + 1 = 2(1) + 1 = 3$$

which gives a triplet state as expected.

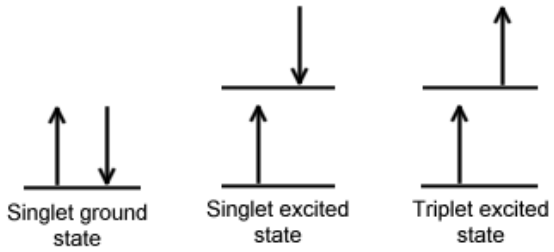


Figure 13.1.1: Spin in the ground and excited states (Tyler Matthews - Paint Shop Pro, Public Domain, https://commons.wikimedia.org/w/inde...curid=64926546)

The difference between a molecule in the ground and the triplet excited state is that the molecule is diamagnetic in the ground state and paramagnetic in the triplet excited state. This difference in spin state makes the transition from singlet to triplet (or triplet to singlet) less likely than the singlet-to-singlet transitions. For this reason, the lifetime of the triplet state is longer than

the lifetime of the singlet state by a factor of roughly 10^4 seconds. The transition from ground to excited triplet state has a low probability of occurring, thus these absorption bands are less intense than singlet-singlet state absorption bands. However, an excited triplet state can be populated from an excited singlet state of certain molecules. Jablonski diagrams can be used to explain transitions such as this that occur in photoluminescence molecules.

Jablonski Diagrams

Aleksander Jablonski was a Polish academic who devoted his life to the study of molecular absorbance and emission of light. He developed a graphic representation that shows the possible consequences of applying photons from the visible spectrum of light to a particular molecule. These schematics are referred to as Jablonski diagrams.

A Jablonski diagram is an energy diagram, arranged with energy on a vertical axis. The energy levels can be quantitatively denoted, but most of these diagrams use energy levels schematically. The rest of the diagram is arranged into columns. Every column usually represents a specific spin multiplicity for a particular species. However, some diagrams divide energy levels within the same spin multiplicity into different columns. Within each column, horizontal lines represent eigenstates for that particular molecule. Bold horizontal lines are representations of the limits of electronic energy states. Within each electronic energy state are multiple vibrational energy states that may be coupled with the electronic state. Usually only a portion of these vibrational eigenstates are represented due to the massive number of possible vibrations in a molecule. Each of these vibrational energy states can be subdivided even further into rotational energy levels; however, typical Jablonski diagrams omit such intense levels of detail.

Through the use of straight and wavy lines, these figures show transitions between eigenstates that occur from the exposure of a molecule to a particular wavelength of light. Straight lines show the conversion between a photon of light and the energy of an electron. Wavy lines show nonradiative transitions of electrons. Within a Jablonski diagram several different pathways show how an electron may accept and then dissipate the energy from a photon. Thus, most diagrams start with arrows originating from the ground electronic state and finish with arrows returning to the ground electronic state.

The Jablonski diagram that drawn below is a partial energy diagram that represents the energy of a photoluminescent molecule in its different energy states. The lowest and darkest horizontal line represents the ground-state electronic energy of the molecule which is the singlet state labeled as S_o. At room temperature, a majority of the molecules are in this state. The thicker lines on the left labeled S_1, S_2 , and S_3 represent the excited electronic states for the molecule in the singlet state. The thicker lines on the right labeled T_1, T_2, and T_3 represent excited triplet states.

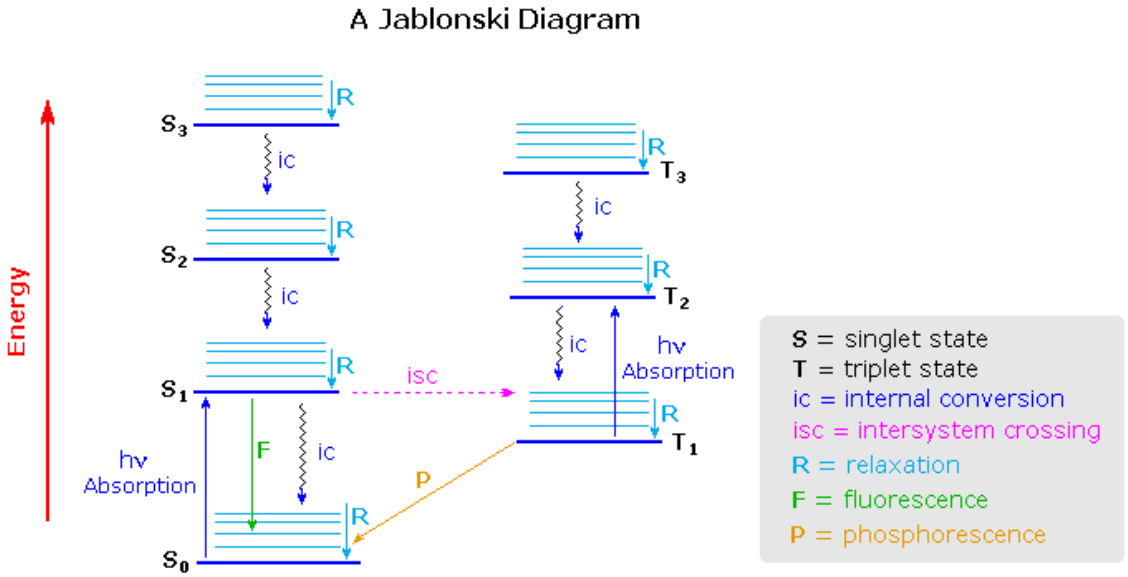


Figure 13.1.2: Partial Jablonski Diagram for Absorption, Fluorescence, and Phosphorescence. (Bill Reusch, Michigan State University).

Deactivation Processes

A molecule that is excited can return to the ground state by several combinations of mechanical steps that will be described

below and shown in Figure 13.1.2.The deactivation process of fluorescence and phosphorescence involve an emission of a photon radiation as shown by the straight arrow in Figure 13.1.2. The wiggly arrows in Figure 13.1.2 are deactivation processes without the use of radiation. The favored deactivation process is the route that is most rapid and spends the least time in the excited state. If the rate constant for relaxation is more favorable in the radiationless path, the fluorescence will be less intense or absent.

Relaxation and Fluorescence

Often, when an excited state species relaxes, giving off a photon, the wavelength of the photon is different from the one that initially led to excitation. When this happens, the photon is invariably red-shifted; its wavelength is longer than the initial one. This situation is called "fluorescence" (Figure 13.1.3).

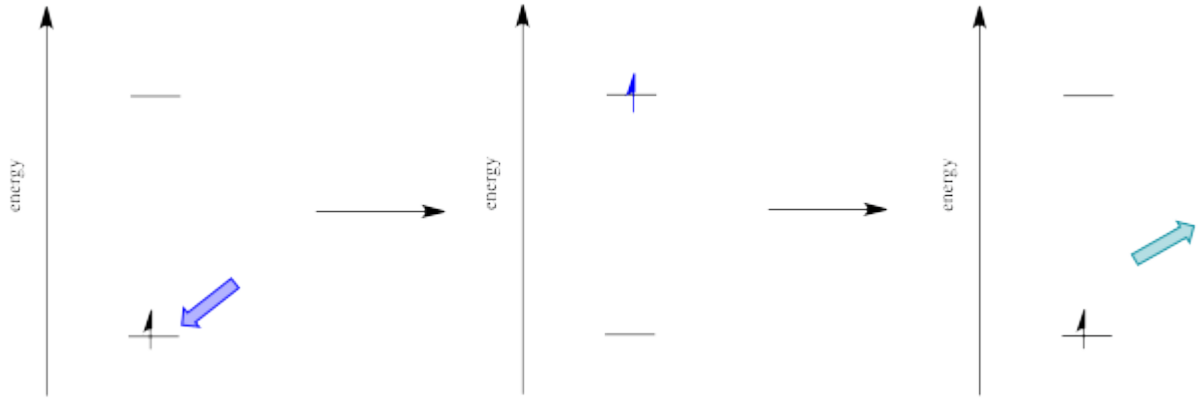


Figure 13.1.3: The absorption of purple light by a ground state particle, leading to the creation of an excited state particle. This excited state particle then emits blue light as it returns to the ground state.

How can that be? Isn't energy quantized? How is the molecule suddenly losing some of the energy that the original photon brought with it? This energy discrepancy is related to the Franck-Condon principle from the previous page. When an electron is promoted to an electronic excited state, it often ends up in an excited vibrational state as well (Figure 13.1.4). Vibrational energy, however, is not exchanged exclusively by means of photons. It can be gained or lost through molecular collisions and heat transfer.

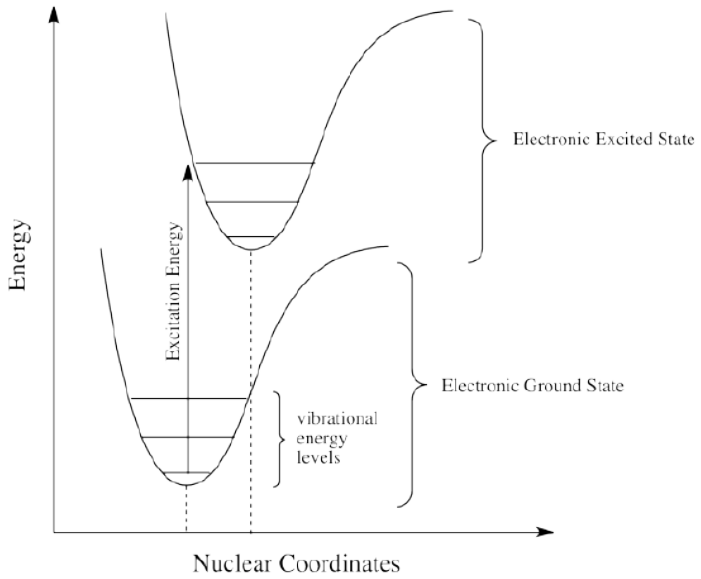


Figure 13.1.4: Transition from the ground state to an excited vibrational state within the excited electronic state.

Thus, an excited state molecule with an electron in a high-energy vibrational level within an excited electronic state might simply re-emit a photon of exactly the same wavelength as the one that was absorbed. But the excited electron is much more likely to relax into the lowest vibrational state within the excited electronic state, losing some of that initial excitation energy as heat. When the electron relaxes to this lower vibrational state, the energy gap between this excited state and the ground state is a little

smaller. The photon that is emitted upon fluorescence will have lower energy and longer wavelength than a photon emitted from the original, higher vibrational level, excited state. See Figure 13.1.5.

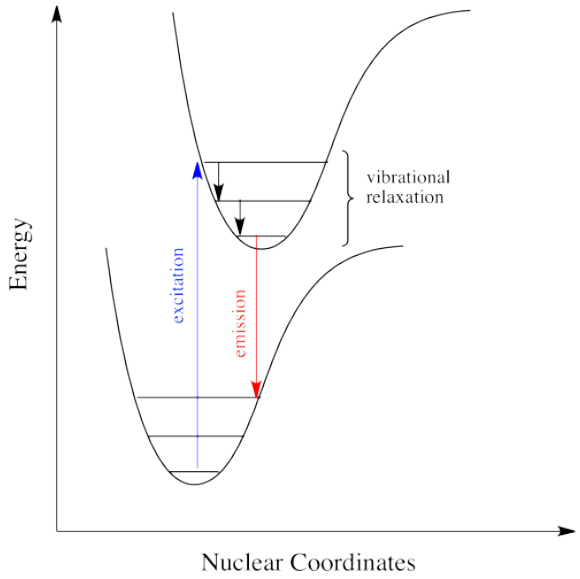


Figure 13.1.5: Excitation, followed by vibrational relaxation, and then emission.

Figure 13.1.6 shows the fluorescence transitions of a hypothetical diatomic molecule in which the equilibrium bond length of the ground state and the first singlet excited state are identical. In this molecule all absorptions involve transitions from the lowest vibrational level of the electronic ground state ($v'' = 0$) to various vibrational levels in the excited electronic state. Because vibrational relaxation occurs more rapidly than fluorescence, the fluorescence spectrum is composed of lines showing transitions from the lowest vibrational level of the excited state ($v' = 0$) to various vibrational levels in the electronic ground state.

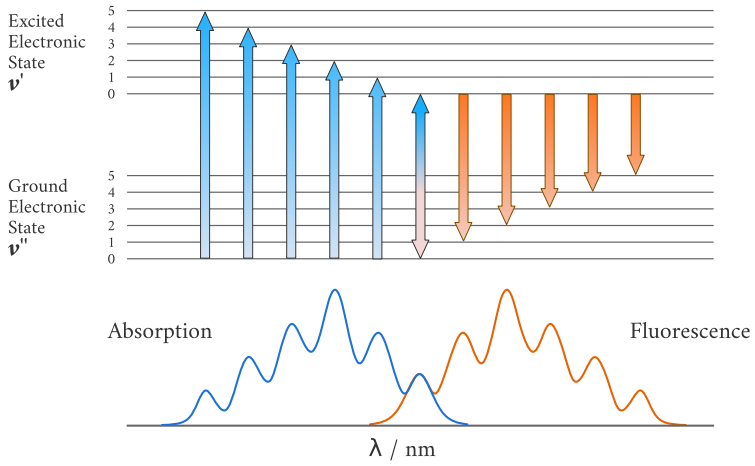


Figure 13.1.6: Absorption and fluorescence transitions in a hypothetical diatomic molecule in which the equilibrium bond length of the ground state is equal to the equilibrium bond length of the excited state. (CC BY-NC; Ümit Kaya, via LibreTexts)

Just how does a molecule undergo vibrational relaxation? Vibrational energy is the energy used to lengthen or shorten bonds, or to widen or squeeze bond angles. Given a big enough molecule, some of this vibrational energy could be transferred into bond lengths and angles further away from the electronic transition. Otherwise, if the molecule is small, it may transfer some of its energy in collisions with other molecules. In molecules, as one molecule drops to a lower vibrational state, the other will hop up to a higher vibrational state with the energy it gains. In Figure 13.1.7 below, the red molecule is in an electronic excited and vibrational state. In a collision, it transfers some of its vibrational energy to the blue molecule.

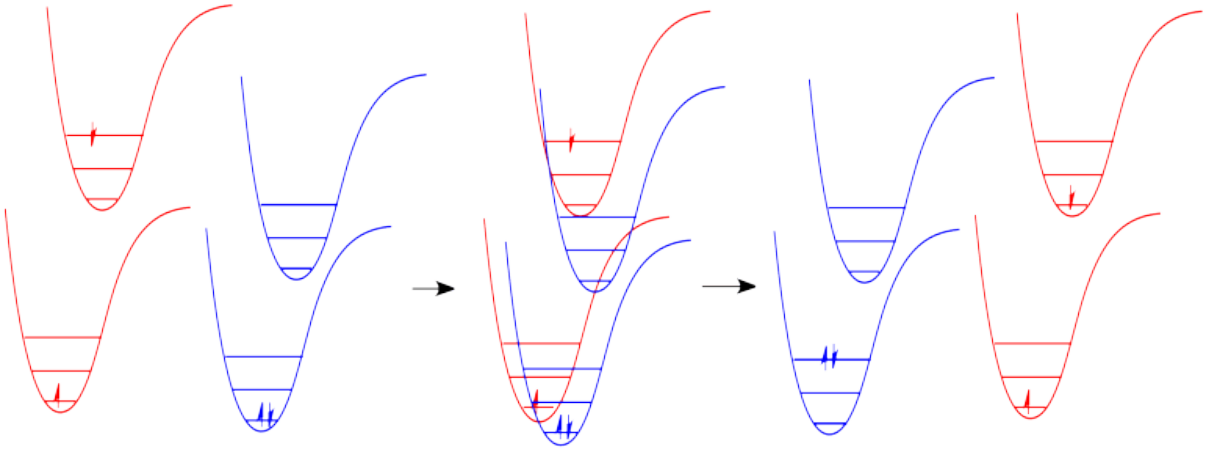


Figure 13.1.7: The transfer of vibrational energy (heat) through a collision.

Note

There are many examples of energy being transferred this way in everyday life. In a game of pool, one billiard ball can transfer its energy to another, sending it toward the pocket. Barry Bonds can transfer a considerable amount of energy through his bat into a baseball, sending it out of the park, just as Serena Williams can send a whole lot of energy whizzing back at her sister.

Exercise 13.1.1

How does the energy of an electronic absorption compare to other processes? To find out, you might consider the excitation of an entire mole of molecules, rather than a single molecule absorbing a single photon. Calculate the energy in kJ/mol for the following transitions.

a. absorbance at 180 nm (ultraviolet)
b. absorbance at 476 nm (blue)
c. absorbance at 645 nm (red)

Answer available at the end of this section.

Exercise 13.1.2

How does the energy of an excitation between vibrational states compare to that of an electronic excitation? Typically, infrared absorptions are reported in cm^{-1}, which is simply what it looks like: the reciprocal of the wavelength in cm. Because wavelength and frequency are inversely related, wavenumbers are considered a frequency unit. Calculate the energy in kJ/mol for the following transitions.

a. absorbance at 3105 cm^{-1}
b. absorbance at 1695 cm^{-1}
c. absorbance at 963 cm^{-1}

Answer available at the end of this section.

Internal Conversion

If electrons can get to a lower energy state, and give off a little energy at a time, relaxing to lower and lower vibrational levels, do they need to give off a photon at all? Maybe they can relax all the way down to the ground state via vibrational relaxation.

That is certainly the case. Given many vibrational energy levels, and an excited state that is low enough in energy so that some of its lower vibrational levels overlap with some of the higher vibrational levels of the ground state, an electron can relax from an excited electronic state back to the ground state without releasing a photon (Figure \({13{.}1{.}\eatSpaces{8} \endSpaces}).

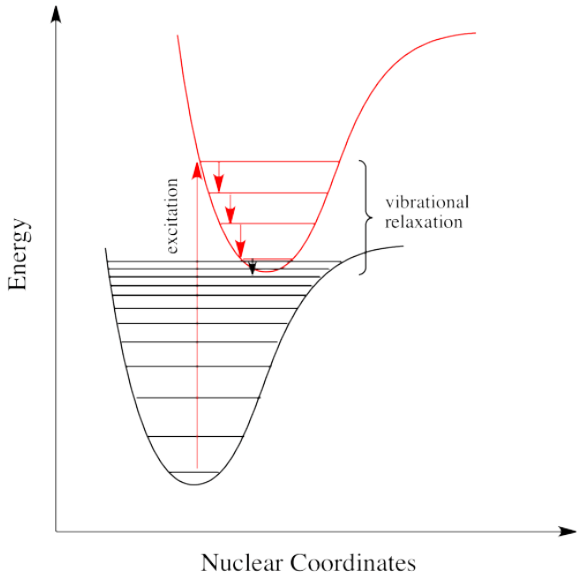


Figure 13.1.8: Relaxation of an excited state particle to the ground state through the nonradiative process of internal conversion.

This event is called a "radiationless transition", because it occurs without release of a photon. The electron simply slides over from a low vibrational state of the excited electronic state to a high vibrational state of the electronic ground state. If the electron simply keeps dropping a vibrational level at a time back to the ground state, the process is called **"internal conversion"**.

Internal conversion has an important consequence. Because the absorption of UV and visible light can result in energy transfer into vibrational states, much of the energy that is absorbed from these sources is converted into heat. That can be a good thing if you happen to be a marine iguana trying to warm up in the sun after a plunge in the icy Pacific. It can also be a tricky thing if you are a process chemist trying to scale up a photochemical reaction for commercial production of a pharmaceutical, because you have to make sure the system has adequate cooling available.

Intersystem Crossing

Intersystem crossing is a process that leads to the electron getting caught between the excited state and the ground state. Just as, little by little, vibrational relaxation can lead the electron back onto the ground state energy surface, it can also lead the electron into states that are intermediate in energy in which the spin multiplicity has changed.

For example, suppose an organic molecule undergoes electronic excitation. Generally, organic molecules have no unpaired electrons. Their ground states are singlet states. According to one of the selection rules for electronic excitation, the excited state must also have no unpaired electrons. In other words, the spin on the electron that gets excited is the same after excitation as it was before excitation.

However, that's not the lowest possible energy state for that electron. When we think about atomic orbital filling, there is a rule that governs the spin on the electrons in degenerate orbitals: in the lowest energy state, **spin is maximized** (Hund's rule). In other words, when we draw a picture of the valence electron configuration of nitrogen, we show nitrogen's three p electrons each in its own orbital, with their spins parallel.



Figure 13.1.9: The diagram on the left shows the energetically stable quartet spin state. The diagram on the right shows the less stable doublet spin state.

In Figure 13.1.9, the diagram on the left, with three unpaired electrons, all with parallel spins, shows a nitrogen in the quartet spin state. This is the most stable state. Having one of those spins point the other way would result in a different, higher energy spin state. The diagram on the right shows a different a different spin state, in which one pair of electrons in the p level is spin-paired, one up and one down, even though they are in different p orbitals. That would leave one electron without an opposite partner, so the nitrogen would be in a doublet spin state. The spin state on the left is **lower** in energy than the state on the right. That's just one of the rules of quantum mechanics (**Hund's rule**): maximize spin when degenerate orbitals are singly occupied.

A similar argument can be made for a molecule with the triplet state lower in energy than the singlet state, as shown in Figure 13.1.10. Why didn't the electron get excited to the triplet state in the first place? That is a forbidden (unlikely) electronic transition. But sliding down vibrationally onto the triplet state from the singlet excited state is not, because it doesn't involve absorption or emission of a photon.

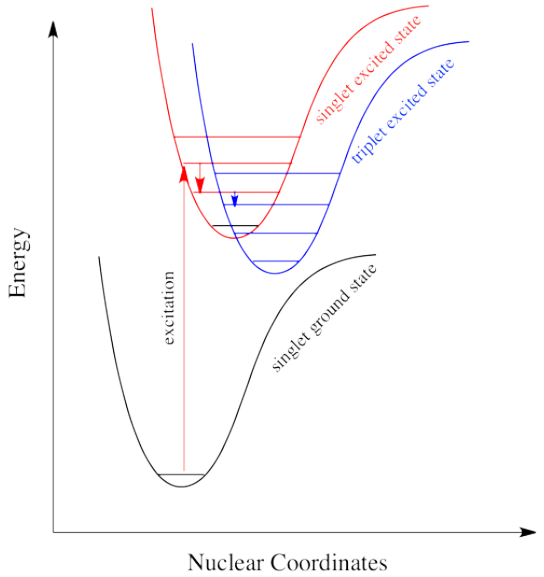


Figure 13.1.10: Intersystem crossing from a singlet excited state to a triplet excited state.

Intersystem crossing can have important consequences in reaction chemistry because it allows access to triplet states that are not normally available in many molecules. Because triplet states feature unpaired electrons, their reactivity is often typified by radical processes. That means an added suite of reactions can be accessed via this process.

Phosphorescence: A Radiationless Transition Followed by Emission

Intersystem crossing is one way a system can end up in a triplet excited state. Even though this state is lower in energy than a singlet excited state, it cannot be accessed directly via electronic excitation because that would violate the spin selection rule (\Delta S=0\). Once intersystem crossing has occurred, the process of reattaining the ground state slows down dramatically. The quick way back to ground state is to emit a photon. But because that would involve a change in spin state, it is not allowed. Realistically speaking, that means it takes a long time. By "a long time", we might mean a few seconds, several minutes, or possibly even hours. Eventually, the electron can drop back down, accompanied by the emission of a photon. This situation is called "phosphorescence" (Figure \({13{.}1{.}\eatSpaces{11} \endSpaces}).

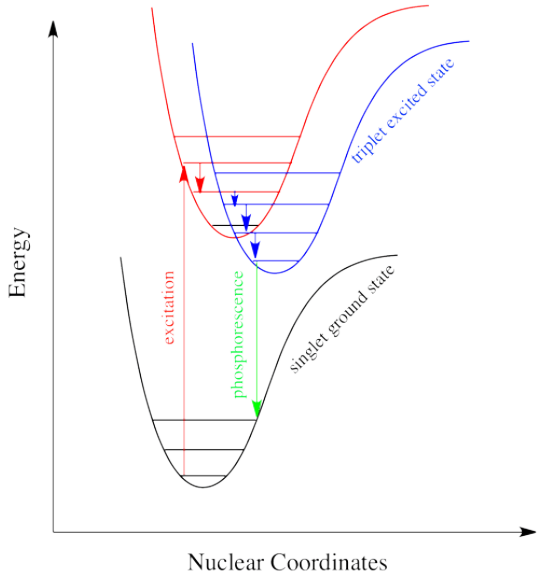


Figure 13.1.11: The process of phosphorescence - excitation, followed by vibrational relaxation, intersystem crossing, and phosphorescence.

Many plants and animals use phosphorescence as a means of signaling. Molecules that display phosphorescence are also often incorporated into toys and shirts so that they will glow in the dark.

External Conversion

Deactivation of the excited electronic state may also involve the interaction and energy transfer between the excited state and the solvent or solute in a process called **external conversion.** Low temperature and high viscosity lead to enhanced fluorescence because they reduce the number of collision between molecules, thus slowing down this type of deactivation process.

Absorption and Emission Rates

The table below compares the absorption and emission rates of fluorescence and phosphorescence. The rate of photon absorption is very rapid. Fluorescence emission occurs at a slower rate. Since the triplet to singlet (or reverse) is a forbidden transition, meaning it is less likely to occur than the singlet-to-singlet transition, the rate of triplet to singlet is typically slower. Therefore, phosphorescence emission requires more time than fluorescence.

Table 15.1.1 : Rates of Absorption and Emission comparison.

Process	Radiative Process?	Transition	Timescale (sec)
Light Absorption (Excitation)	yes	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	no	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	no	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	no	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	yes	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	yes	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay to Ground State (Internal Conversion)	no	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

References

1. D. A. Skoog, et al. "Principles of Instrumental Analysis" 6th Edition, Thomson Brooks/Cole. 2007
2. D. C. Harris and M.D. Bertolucci "Symmetry and Spectroscopy, An Introduction to Vibrational and Electronic Spectroscopy" Dover Publications, Inc., New York. 1989.

Contributors and Attributions

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- Tom Neils (Grand Rapids Community College)

Answers

Exercise 13.1.1

One method to carry out this calculation: $\frac{1}{x\text{nm}} \times \frac{1\,\text{nm}}{1x10^{-9}\,\text{m}} \times 6.626x10^{-34}\text{Js} \times \frac{3.000x10^{8}\text{m}}{\text{s}} \times \frac{6.022x10^{23}\text{photons}}{1.000\text{mole}} \times \frac{1\text{kJ}}{1000\text{J}}$

a. 665.0 kJ/mol
b. 251.5 kJ/mol
c. 185.6 kJ/mol

Exercise 13.1.2

One method to carry out this calculation: $x\text{cm}^{-1} \times \frac{100\,\text{cm}}{1\,\text{m}} \times 6.626x10^{-34}\text{Js} \times \frac{3.000x10^{8}\text{m}}{\text{s}} \times \frac{6.022x10^{23}\text{photons}}{1.000\text{mole}} \times \frac{1\text{kJ}}{1000\text{J}}$

a. 37.14 kJ/mol
b. 20.27 kJ/mol
c. 11.52 kJ/mol

By comparing these answers with those from Exercise 13.1.1, we can see that the energy difference between vibrational states is an order of magnitude less than the energy difference between electronic states.

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13.2: The Dynamics of Transitions can be Modeled by Rate Equations

The Interaction of Light with Atoms

In 1916, Albert Einstein proposed that there are three processes occurring in the formation of an atomic spectral line. The three processes are referred to as spontaneous emission, stimulated emission, and absorption (figure 13.2.1).

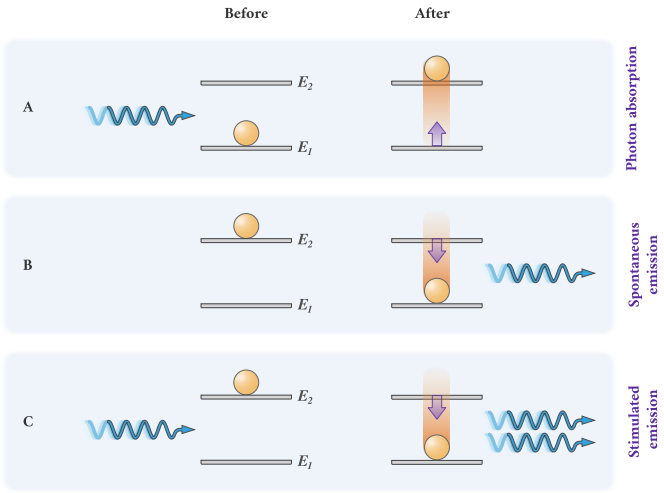


Figure 13.2.1: The three processes that can occur during the formation of a spectral line. A) Absorption of a photon, leading to the promotion of an electron to a higher electronic energy level. B) The spontaneous emission of a photon created by the relaxation of an electron back to the ground state. C) The stimulated emission of a photon created by the influence of a passing photon, accompanied by the relaxation of an electron back to the ground state. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

For now, let's make our discussion as simple as possible, by assuming we are talking about the interaction of light with an atom that has only two energy levels. There is a collection of these atoms present, and they are in an assortment of states, some in the ground state, and some in "the" excited state. Our discussion of photon emission to this point has generally centered around *spontaneous emission*, the triggering of which we attributed to a perturbation in the hamiltonian that comes from (if nothing else) vacuum fluctuations.

Suppose some of these atoms spontaneously emit photons, and now the collection of atoms is not sitting in a total vacuum, but is in the presence of many photons as well. We now consider what effects these present photons can have on the atoms. The answer depends upon which state the atom is in when it encounters the photon. If the atom is in the ground state, then it can absorb the photon and go to the excited state. If the atom is in its excited state, it can't absorb the photon, but the time-varying EM fields of the photon present a nice perturbation to the electron's hamiltonian (at just the right frequency!) to induce the emission of a photon. This is called *stimulated emission*. The photon that induces the emission is unaffected by the interaction, and continues on its merry way. The emitted photon naturally has the same frequency as the passing photon (the energy gap assured this), but it also emerges moving in the same direction as, *and in phase with* the stimulating photon. This completes the acronym - **L**ight **A**mplification by the **S**timulated **E**mission of **R**adiation.

It turns out that if a photon happens by two of these atoms, the first in the ground state and the second in the excited state, the probability that it will be absorbed by the first is equal to the probability that it will stimulate emission in the other – neither of these results is preferred over the other. Now consider a collection of these atoms in a state of some fixed total energy. This total energy comes from the number of atoms in the ground state multiplied by the energy of that state, plus the number of atoms in the excited state multiplied by the number of atoms in that state. As we will discuss in a future chapter, the populations of these two states subject to the constraint of the total energy can be shown to be a function that depends upon the energy difference of

the two states and the temperature of the collection of atoms. Specifically, if N_1 is the number of atoms in the ground state, N_2 is the number of atoms in the excited state, and the energy difference is ΔE, then the following relation holds:

$$N_1 = N_2\, e^{\frac{\Delta E}{k_B T}}$$

where T is the temperature and k_B is Boltzmann's constant. Clearly N_1 is greater than N_2, but how much greater? We can do a very quick calculation of this using an approximation that at room temperature, the constant $k_B T$ is about 1/40 eV. Let's assume that the energy difference between two energy states of an atom is on the order of 1eV. Then the number of ground state atoms would exceed the number of excited state atoms by a factor of $e^{40} = 2.4\times10^{17}$!

Thus, a photon passing through this collection has an equal probability of being absorbed or stimulating emission if it happens by an atom prepared for one of those actions. But there are so many more atoms available to absorb the photon, that this has a much greater chance of happening. While waiting for a photon to stimulate emission, an atom in an excited state will impatiently emit a photon spontaneously, which will then be much more likely to be absorbed than stimulate emission, and things continue like this, with some atoms spontaneously sending out photons while others absorb them... no laser.

Einstein Coefficients

Einstein proposed a separate rate equation for each of the three processes described above. The rate of each process is proportional to the number of particles in either the ground state (absorption) or the excited state (emission). Each rate is also proportional to the spectral radiant energy density, ρ_ν, which is a measure of the radiant energy density (ρ) per unit frequency of the light associated with the transition. Thus, $\rho_\nu = \frac{d\rho}{d\nu}$, and has units of $\frac{J \cdot s}{m^3}$. With each process there is also an associated Einstein coefficient, which is a proportionality constant.

Photon absorption

Absorption is the process by which a photon is absorbed by the atom, causing an electron to jump from a lower energy level to a higher one (figure $13.2.1a$). The process is described by the Einstein coefficient $B_{12}\left(\frac{m^3}{J \cdot s^2}\right)$, which gives the probability per unit time per unit spectral radiance of the radiation field that an electron in state 1 with energy E_1 will absorb a photon with an energy $E_2 - E_1 = h\nu_{12}$ and jump to state 2 with energy E_2. If $N_1(t)$ is the number density of atoms in state 1, then the change in the number density of atoms in state 1 per unit time due to absorption will be

$$-\frac{dN_1(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t)$$

If only absorption occurred, the increase of the excited state population as a function of time is equal to the decrease of the ground state population as a function of time.

Spontaneous emission

Spontaneous emission is the process by which an electron "spontaneously" (i.e. without any outside influence) decays from a higher energy level to a lower one (figure $13.2.1b$). The process is described by the Einstein coefficient $A_{21}(s^{-1})$, which gives the probability per unit time that an electron in state 2 with energy E_2 will decay spontaneously to state 1 with energy E_1, emitting a photon with an energy $E_2 - E_1 = h\nu_{21}$. Due to the energy-time uncertainty principle, the transition actually produces photons within a narrow range of frequencies called the spectral linewidth. If $N_2(t)$ is the number density of atoms in state 2, then the change in the number density of atoms in state 2 per unit time due to spontaneous emission will be

$$-\frac{dN_2(t)}{dt} = A_{21}N_2(t)$$

The same process results in increasing of the population of the state 1:

$$\frac{dN_1(t)}{dt} = A_{21}N_2(t)$$

Stimulated emission

Stimulated emission (also known as induced emission) is the process by which an electron is induced to jump from a higher energy level to a lower one by the presence of electromagnetic radiation at (or near) the frequency of the transition (figure 13.2.1c). From the thermodynamic viewpoint, this process must be regarded as negative absorption. The process is described by the Einstein coefficient $B_{21}\left(\frac{m^3}{J\cdot s^2}\right)$, which gives the probability per unit time per unit spectral radiance of the radiation field that an electron in state 2 with energy E_2will decay to state 1 with energy E_1, emitting a photon with an energy $E_2 - E_1 = h\nu_{21}$. The change in the number density of atoms in state 1 per unit time due to induced emission will be

$$\frac{dN_1(t)}{dt} = B_{21}\rho_\nu(\nu_{21})N_2(t)$$

The Relationship between A_{21}, B_{12}, and B_{21}

In 1900, Max Planck derived a formula for the energy density per unit bandwidth of a blackbody radiator by making the assumption that only discrete energies are allowed. His work agreed with known experimental data, and it is one of the fundamental ideas of quantum mechanics. More specifically, the spectral energy density per unit bandwidth, $\rho_\nu(\nu_{12})$ in units $\frac{J\cdot s}{m^3}$, is given by

$$\rho_\nu(\nu_{12}) = \frac{8\pi h}{c^3}\frac{\nu_{12}^3}{e^{(h\nu_{12})/(k_BT)}-1} \tag{13.2.1}$$

In a given sample of atoms exposed to radiation of the correct frequency all three processes will be occurring simultaneously. Thus the rate of change of the populations of the two states will be

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) - A_{21}N_2(t) - B_{21}\rho_\nu(\nu_{21})N_2(t) \tag{13.2.2}$$

If we assume that the two energy states are in thermal equilibrium, then N_1 and N_2 are constant, and thus

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) - A_{21}N_2(t) - B_{21}\rho_\nu(\nu_{21})N_2(t) = 0 \tag{13.2.3}$$

Upon solving for $\rho_\nu(\nu_{12})$, we get

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{(N_1(t)/N_2(t))B_{12} - B_{21}} \tag{13.2.4}$$

Recall that in this equation N_1/N_2 represents the electron density in the lower energy state divided by the electron density in the upper state at equilibrium. This quantity is a function of temperature. Assuming many allowed energy states, the number of occupied states decreases exponentially with temperature, as per Boltzmann statistics.

$$N_2/N_1 = \frac{g_2}{g_1}e^{(-h\nu_{12})/(k_BT)} \tag{13.2.5}$$

The quantity $\frac{g_2}{g_1}$ represents the degeneracy level, which is the number of allowed electrons in the upper state over the number of allowed electrons in the lower state. In this expression, g_1 and $g2$ are unitless measures of the number of ways electrons can occupy an energy states. Upon rearrangement, equation 13.2.5 becomes

$$N_1/N_2 = \frac{g_1}{g_2}e^{(h\nu_{12})/(k_BT)} \tag{13.2.6}$$

Equations 13.2.6 and 13.2.4 can be combined to get

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{\left(\frac{g_1}{g_2}e^{(h\nu_{12})/(k_BT)}\right)B_{12} - B_{21}} \tag{13.2.7}$$

which can be rearranged to

$$\rho_\nu(\nu_{12}) = \frac{\frac{A_{21}}{B_{21}}}{\left(\frac{g_1 B_{12}}{g_2 B_{21}} e^{(h\nu_{12})/(k_B T)}\right) - 1} \tag{13.2.8}$$

One expression for the energy density per unit bandwidth of this system is given by Equation 13.2.1. Equation 13.2.8 gives a second expression for the energy density per unit bandwidth, and it was found by considering the relative rates of absorption, spontaneous emission, and stimulated emission. These equations can be combined to relate the rates of the different processes.

$$\frac{8\pi h}{c^3} \frac{\nu_{12}^3}{e^{(h\nu_{12})/(k_B T)} - 1} = \frac{\frac{A_{21}}{B_{21}}}{\left(\frac{g_1 B_{12}}{g_2 B_{21}} e^{(h\nu_{12})/(k_B T)}\right) - 1} \tag{13.2.9}$$

The above equation is true for the conditions

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h \nu_{12}^3}{c^3} \tag{13.2.10}$$

and

$$\frac{g_1 B_{12}}{g_2 B_{21}} = 1 \tag{13.2.11}$$

If we know one of the Einstein coefficients, we can quickly calculate the other two Einstein coefficients using equations 13.2.10 and 13.2.11.

These equations also provide further insight into the operation of lasers and other devices based on stimulated emission. The overall nonequilibrium upper state population rate is given by

$$\frac{dN_2(t)}{dt} = -A_{21} N_2 - B_{21} \rho_\nu(\nu_{21}) N_2 + B_{21} \frac{g_2}{g_1} \rho_\nu(\nu_{12}) N_1 \tag{13.2.12}$$

which can be simplified with some algebra.

$$\frac{dN_2(t)}{dt} = -A_{21} N_2 - B_{21} \rho_\nu(\nu_{12}) \left(N_2 - \frac{g_2}{g_1} N_1\right) \tag{13.2.13}$$

The term in parenthesis is the net upper state population. Optical amplification and lasing can only occur when the term in parenthesis is positive. The condition

$$N_2 - \frac{g_2}{g_1} N_1 > 0 \tag{13.2.14}$$

is called a population inversion. It only occurs when enough energy is being supplied to the system, by optical, electrical, or thermal means, so that there are more electrons in the upper energy level than the lower energy level. This situation cannot be achieved for a two-level system, as will be shown in the next section. However, in section 15.4, it will be shown that this situation can be achieved if the system has more than two levels.

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13.3: A Two-Level System Cannot Achieve a Population Inversion

Lasing in Two-Level Systems

For the sake of our studies, let's first consider a laser medium whose atoms have only two energy states: a ground state and one excited state. In such an idealized atom the only possible transitions are excitation from the ground state to the excited state and de-excitation from the excited state back into ground state. Could such an atom be used to make a laser?

There are several important conditions that our laser must satisfy. First of all, the light that it produces must be coherent. That is to say, it must emit photons that are in-phase with one another. Secondly, it should emit monochromatic light, i.e. photons of the same frequency (or wavelength). Thirdly, it would be desirable if our laser's output were collimated, producing a sharply defined "pencil-like" beam of light (this is not crucial, but clearly a desirable condition). Lastly, it would also be desirable for our laser to be efficient, i.e. the higher the ratio of output energy - to - input energy, the better.

Let us begin by examining the requirements for our first condition for lasing, coherence. This condition is satisfied only when the lasing transition occurs through stimulated emission. As we have already seen, stimulated emission produces identical photons that are of equal energy and phase and travel in the same direction. But for stimulated emission to take place a "passer-by" photon whose energy is just equal to the de-excitation energy must approach the excited atom before it de-excites via spontaneous emission. Typically, a photon emitted by the spontaneous emission serves as the seed to trigger a collection of stimulated emissions. Still, if the lifetime of the excited state is too short, then there will not be enough excited atoms around to undergo stimulated emission. So, the first criteria that we need to satisfy is that the upper lasing state must have a relatively long lifetime, otherwise known as a meta-stable state, with typical lifetimes in the milliseconds range. In addition to the requirement of a long lifetime, we need to ensure that the likelihood of absorption of the "passer-by" photons is minimized. This likelihood is directly related to the ratio of the atoms in their ground state versus those in the excited state. The smaller this ratio, the more likely that the "passer-by" photon will cause a stimulated emission rather than get absorbed. So, to satisfy this requirement, we need to produce a **population inversion**: create more atoms in the excited state than those in the ground state.

Another way of stating the above set of conditions is that the rate of absorption must be less than the rate of stimulated emission

$$\underbrace{B_{21}\rho_\nu(\nu_{21})N_2}_{\text{rate of stimulated emission}} > \underbrace{B_{12}\rho_\nu(\nu_{12})N_1}_{\text{rate of absorption}} \tag{13.3.1}$$

As shown in the previous section, $B_{21} = B_{12}$ and $\rho_\nu(\nu_{12}) = \rho_\nu(\nu_{21})$, thus Equation 13.3.1 becomes

$$N_2 > N_1.$$

Hence, if $N_2 > N_1$ then there is a population inversion.

Achieving population inversion in a two-level atom is not very practical. Such a task would require a very strong pumping transition that would send any decaying atom back into its excited state. This would be similar to reversing the flow of water in a waterfall. It can be done but is very energy costly and inefficient. In a sense, the pumping transition would have to work against the lasing transition.

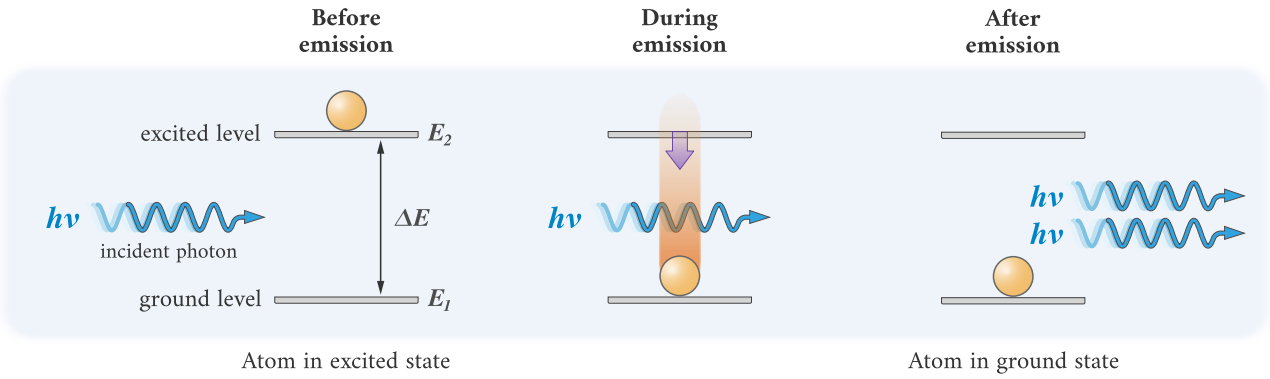


Figure 13.3.1: A two-level lasing system. (CC BY-NC; Ümit Kaya via LibreTexts)

It is clear, from figure 13.3.1, that in the two-level atom the pump is, in a way, the laser itself! Such a two-level laser would work only in jolts. That is to say, once the population inversion is achieved the laser would lase. But immediately it would end up with more atoms in the lower level. Such two-level lasers involve a more complicated process. We will see, in later material, examples of these in the context of excimer lasers, which are pulsed lasers. For continuous lasing action, we need to consider other possibilities, such as a three-level atom.

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13.4: Population Inversion can be Achieved in a Three-Level System

Optical pumping will at most achieve only an equal population in a two-level system. This is because the probabilities for raising an electron to the upper level and inducing the decay of an electron to the lower level (stimulated emission) are exactly the same! In other words, when both levels are equally populated, the numbers of electrons "going up" and "down" will be the same, so you cannot achieve population inversion which is required for lasers. The solution is to involve a third, metastable level of intermediate energy. The pumping will occur between the two levels with the greatest energy difference, creating a highly populated upper energy level. Two lasing processes are possible once this situation has been obtained. Lasing occurs between the upper level and the intermediate level if the electrons in the upper energy level decay slowly to the intermediate, metastable level, and if the electrons in the intermediate level decay rapidly to the ground state. However, if the electrons in the upper energy level quickly decay into the intermediate level, and the transition from the intermediate level to the ground level is slow, then lasing occurs between the intermediate level and the ground state. In both cases, the lasing frequency has a frequency different than that of the pumping frequency between the ground level and the upper level, so the pumping is off-resonant to the laser transition and will not trigger stimulated emission.

Lasing in Three-Level Systems

The first laser that was demonstrated to operate was a three-level laser, known as **Maiman's ruby laser**.

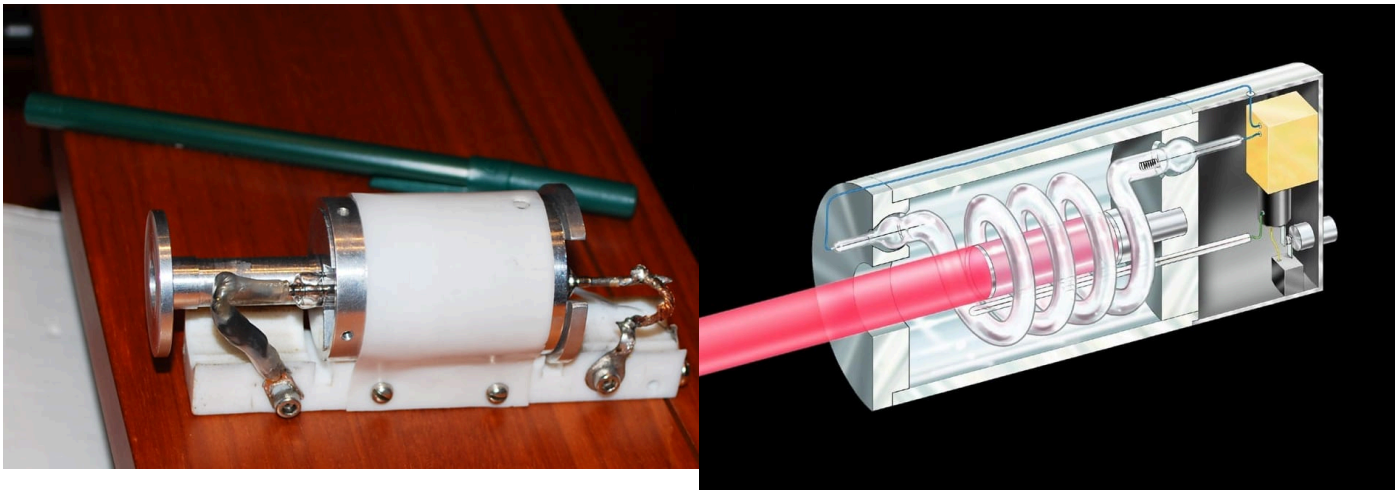


Figure 13.4.1: (left) A copy of a Maiman laser (CC 0; Guy Immega) (right) Internal view of a Maiman laser (https://commons.wikimedia.org/w/inde...ldid=42317741)

Figure 13.4.1 shows the outside and inside of a three-level laser. A pump causes an excitation from the ground state to the second excited state. This state is a rather short-lived state so that the atom quickly decays into the first excited level. (Atoms in the second excited state may also decay directly back to the ground state, but these atoms can be pumped back to the second excited state again.) The first excited state is a long-lived (i.e. metastable) state which allows the atom to "wait" for the "passer-by" photon while building up a large population of atoms in this state. The lasing transition, in this laser, is due to the decay of the atom from this first excited metastable state to the ground state. If the number of atoms in the ground state exceeds the number of atoms that are pumped into the excited state, then there is a high likelihood that the "lasing photon" will be absorbed and we will not get sustained laser light. The fact that the lower lasing transition is the ground state makes it rather difficult to achieve efficient population inversion. In a ruby laser, this task is accomplished by providing the ruby crystal with a very strong pulsating light source, called a flash lamp. The flash lamp produces a very strong pulse of light that is designed to excite the atoms from their ground state into a short-lived upper level. In this way, the ground state is depopulated and population inversion is achieved until a pulse of laser light is emitted. In the ruby laser, the flash lamp light lasts for about 1/1000 of a second (1 ms) and can be repeated about every second. The duration of the laser pulse is shorter than this, typically 0.1 ms. In some pulsed lasers, the pulse duration can be tailored using special methods to be much shorter than this, down to about 10 fs (where 1 fs = 10^{-15} s or

one thousandth of a millionth of a millionth of a second). So, the output of a three-level laser is not continuous but consists of pulses of laser light.

Transition Rates in Three-level Systems

In a three-level system, there are nine (9) events that can occur (Figure 13.4.2):

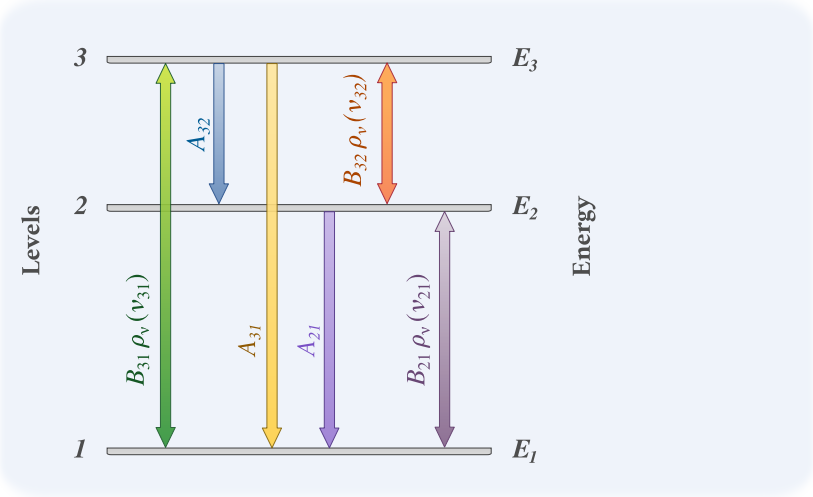


Figure 13.4.2: The nine possible events in a three-level system. (CC BY-NC; Ümit Kaya via LibreTexts)

a. absorption from level 1 to level 3, as described by $\rho_\nu(\nu_{13})B_{13}N_1$
b. spontaneous emission from level 3 to level 1, as described by $A_{31}N_3$
c. stimulated emission from level 3 to level 1, as described by $\rho_\nu(\nu_{31})B_{31}N_3$
d. spontaneous emission from level 3 to level 2, as described by $A_{32}N_3$
e. stimulated emission from level 3 to level 2 (possible lasing), as described by $\rho_\nu(\nu_{32})B_{32}N_3$
f. absorption from level 2 to level 3, as described by $\rho_\nu(\nu_{23})B_{23}N_2$
g. absorption from level 1 to level 2, as described by $\rho_\nu(\nu_{12})B_{12}N_1$
h. spontaneous emission from level 2 to level 1, as described by $A_{21}N_2$
i. stimulated emission from level 2 to level 1 (possible lasing), as described by $\rho_\nu(\nu_{21})B_{21}N_2$

In most three-level lasers, neither the spontaneous emission from level 3 to level 1, nor the stimulated emission from level 3 to level 1 occur to any significant extent, and so these events are ignored in terms of the kinetics of the lasing process. It is also true that there is no excitation source to cause absorption from level 1 to level 2 other than the possible reabsorption of light emitted from a level 2 to level 1 transition, but this event is unlikely because most atoms in the ground state are pumped up to level 3. Because the pump will be used to drive the absorption from level 1 to level 3, this event is essentially under the control of the experimenter. This leaves a maximum of five events that we need to take into consideration when studying the lasing process.

A Ruby Laser

In a three-level system ruby laser such as that described above, the flash lamp will serve as the pump to repeatedly excite most of the atoms from the ground state to the second excited state. In this laser, lasing occurs due to the stimulated emission from level 2 to level 1 (Figure 13.4.3.)

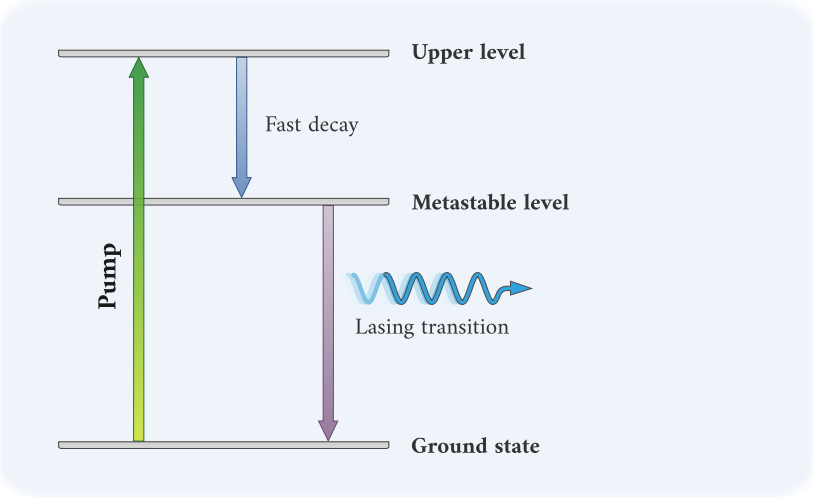


Figure 13.4.3: Lasing from level 2 to level 1 in a three-level laser. (CC BY-NC; Ümit Kaya via LibreTexts)

Because the lasing will occur from the intermediate, metastable energy level 2, we will focus on the five events that affect its population:

a. absorption from level 2 to level 3, as described by $\rho_\nu(\nu_{32})B_{32}N_2$
b. spontaneous emission from level 3 to level 2, as described by $A_{32}N_3$
c. stimulated emission from level 3 to level 2, as described by $\rho_\nu(\nu_{32})B_{32}N_3$
d. spontaneous emission from level 2 to level 1, as described by $A_{21}N_2$
e. stimulated emission from level 2 to level 1 (lasing), as described by $\rho_\nu(\nu_{21})B_{21}N_2$

In this system, the rate of spontaneous emission from level 3 to level 2 is much more rapid than the rate of absorption from level 2 to level 3, and also much more rapid than the rate of stimulated emission from level 3 to level 2. Thus, any electrons pumped into the upper level are most likely to transition between level 2 and level 3 by spontaneous emission. This means that N_2 is greater than N_1 and thus, population inversion between states 2 and 1 can be achieved. A system of atoms that are able to attain such a population inversion is called a gain medium, and can lase.

A Copper Vapor Laser

In this three-level system, the flash lamp will again, serve as the pump to repeatedly excite most of the atoms from the ground state to the second excited state. However, in this laser, lasing occurs due to the stimulated emission from level 3 to level 2 (Figure 13.4.4).

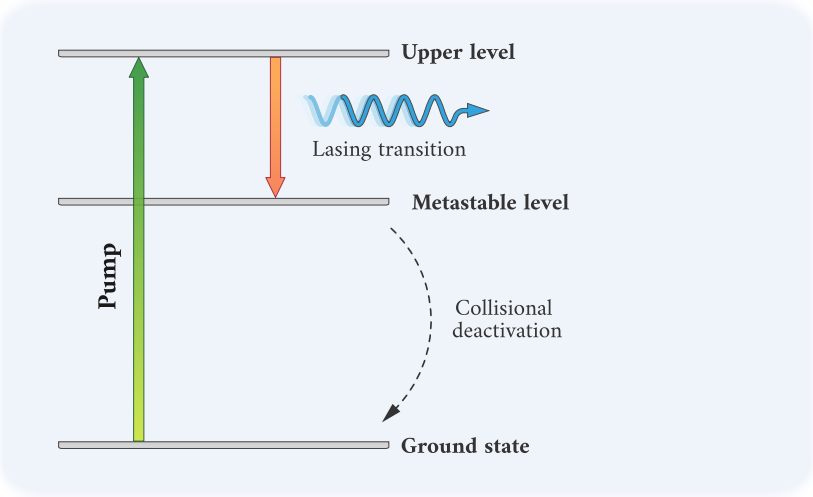


Figure 13.4.4: Lasing from level 3 to level 2 in a three-level laser. (CC BY-NC; Ümit Kaya via LibreTexts)

Because the lasing will occur from the higher energy excited state, we focus on the four events that affect the population ratio between level 3 and level 2:

a. absorption from level 2 to level 3, as described by $\rho_\nu(\nu_{32})B_{32}N_2$
b. spontaneous emission from level 3 to level 2, as described by $A_{32}N_3$
c. stimulated emission from level 3 to level 2 (lasing), as described by $\rho_\nu(\nu_{32})B_{32}N_3$
d. spontaneous emission from level 2 to level 1, as described by $A_{21}N_2$

If we assume that the atoms in the total population will be distributed between the three energy levels, then

$$N_1(t) + N_2(t) + N_3(t) = N_{total}$$

At equilibrium, the population of each level will remain constant, and so

$$0 = \frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = \frac{dN_3(t)}{dt}.$$

Thus,

$$\frac{N_2(t)}{dt} = -\rho_\nu(\nu_{32})B_{32}N_2 + A_{32}N_3 - A_{21}N_2 + \rho_\nu(\nu_{32})B_{32}N_3 = 0 \tag{13.4.1}$$

Rearranging Equation 13.4.1 gives

$$N_2(A_{21} + \rho_\nu(\nu_{32})B_{32}) = N_3(A_{32} + \rho_\nu(\nu_{32})B_{32}) \tag{13.4.2}$$

which rearranges to

$$\frac{N_3}{N_2} = \frac{A_{21} + \rho_\nu(\nu_{32})B_{32}}{A_{32} + \rho_\nu(\nu_{32})B_{32}} \tag{13.4.3}$$

From Equation 13.4.3 we can see that if A_{21} is greater than A_{32}, then N_3 can be greater than N_2. If N_3 is greater than N_2, then population inversion between states 3 and 2 can be achieved. In other words, if atoms in state 2 decay to the ground state more rapidly than atoms in state 3 decay to state 2, there will be a population inversion between states 3 and 2, and the system can lase.

Four-Level Lasers

There are also lasers based on transitions between four energy levels. These lasers can be more efficiently pumped, because the

lower level of the lasing transition is not the ground state. Only four-level lasers can provide a continuous lasing output. He-Ne and Nd:YAG lasers are common four-level lasers and will be described in section 15.6.

References

D.W. Coutts, in Encyclopedia of Modern Optics, 2005, page 460, https://doi.org/10.1016/B0-12-369395-0/00847-2

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13.5: What is Inside a Laser?

Most lasers consist of three basic components:

1. the gain medium from which light of a specific frequency is emitted
2. the pump source which provides energy to the gain medium to create the light
3. the laser optical cavity in which the light is amplified by repeatedly passing through the gain medium

The Gain Medium

The gain medium, or active medium, is a collection of atoms or molecules that can undergo stimulated emission. The active medium can be in a gaseous, liquid, or solid form. It can be a pure substance or a solution. Because the emitted light of a laser is created by the transition between two quantized states of the gain medium, laser light is always monochromatic. Laser light is also always coherent, meaning that the light waves emitted by the laser are all in phase.

Solids

The first laser, Maiman's ruby laser, described in section 15.4, used a solid rod of synthetic ruby as the gain medium (Figure 13.5.1).

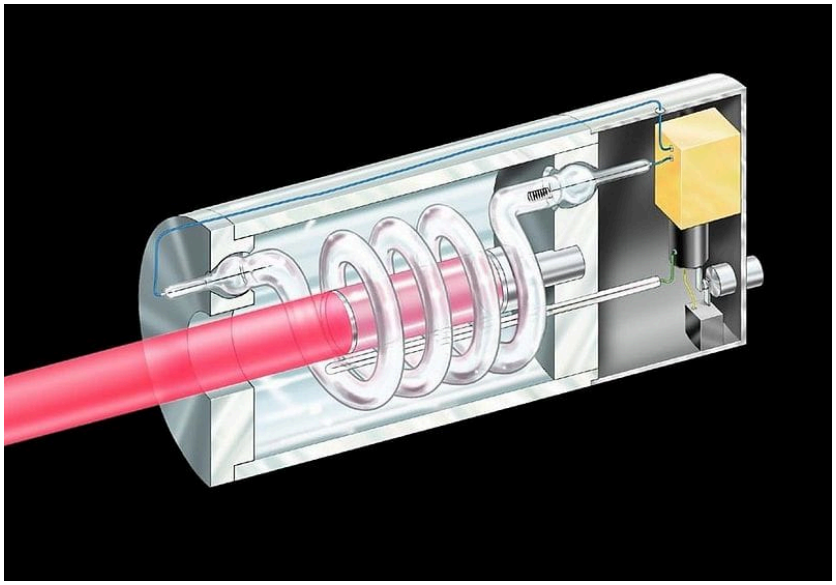


Figure 13.5.1: Internal view of a Maiman laser (Public Domain; United States Department of Energy via Wikipedia)

Ruby is a gem variety of the mineral corundum, Al_2O_3, in which Cr^{3+} ions replace roughly 0.05% (by mass) of the Al^{3+} ions. The electronic structure of the Cr^{3+} impurities enables to ruby to act as a gain medium. However, synthetic ruby must be used because natural rubies have too many crystal defects. Other solid-state gain media are shown in Table 13.5.1.

Table 13.5.1: Solid-phase gain media

Solid-state Host	Active Ion	Wavelength (nm)	Output	Lifetime
Al_2O_3	Ti^{3+}	780	continuous and pulsed	10 fs - 5 ps
Al_2O_3	Cr^{3+}	694.3	pulsed	10 ps
Glass (SiO_2)	Nd^{3+}	1059	pulsed	1 ps

Solid-state Host	Active Ion	Wavelength (nm)	Output	Lifetime
YAG $Y_3Al_5O_{15}$	Nd^{3+}	1064.1	continuous and pulsed	10-150 ps
YLF Y_3LixFy	Nd^{3+}	1054.3	continuous and pulsed	10-100 ps

Gases

A basic He-Ne laser is shown in figure 13.5.2. The gain medium is the gas mixture through which the laser beam passes.

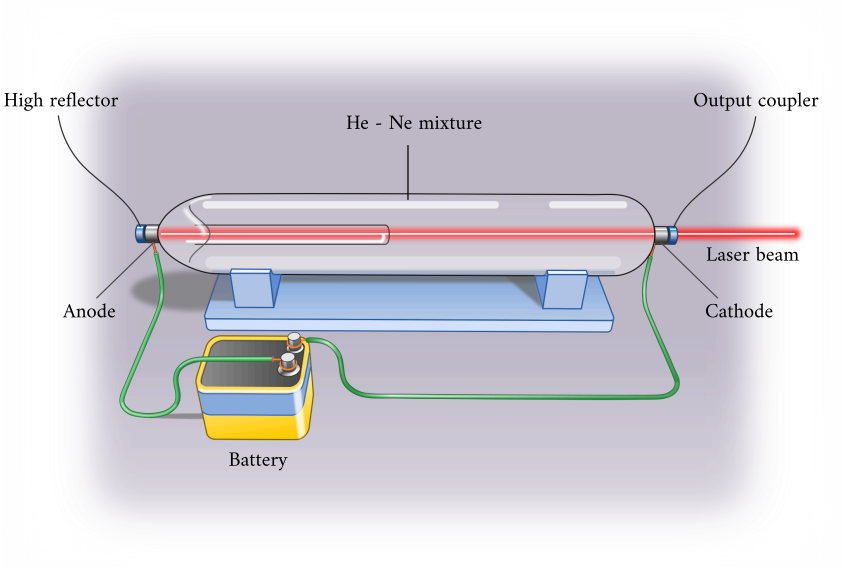


Figure 13.5.2: Internal view of a He-Ne laser. (CC BY-NC; Ümit Kaya via LibreTexts)

Other common gas-phase media include noble gases and molecules, but also metal cations, and metal atoms as shown in Table 13.5.2.

Table 13.5.2: Gas-phase gain media

Gaseous Gain Medium	Wavelength (nm)	Output	Pulse Duration
N_2	337	pulsed	1 ns
Cu	510	pulsed	30 ns
CO_2, He, N_2	tunable near 10,000	pulsed	> 100 ns
He, Ne	3391, 1152, 632, 544	continuous	continuous
He, Cd	441, 325	continuous	continuous
Ar^+	488, 515	continuous	continuous
K^+	647	continuous	continuous.

Exciplex Lasers

Exciplex lasers involve the formation of an exciplex, a gaseous species that forms and exists only in an excited state. Because only the upper, excited state can exist, there is no population in the lower, dissociated state, thus a population inversion is obtained. The lasing transition occurs as the excited state exciplex emits its excitation energy and simultaneously falls apart. Two common exciplex lasers are XeCl* (308 nm) and KrF* ((249 nm). These lasers are often referred to as excimer laser, but the term "excimer" refers to an excited dimer, AA*, and so should not be used to describe an exciplex, AB*.

Liquid Solutions

Many dye lasers use an organic dye, usually dissolved in a solution, as the gain medium. One advantage of using a dye solution as the gain medium is that it can create a tunable laser, which allows for continuous tuning over a wide range of wavelengths. For example, rhodamine 6G is a dye that can be tuned from 635 nm to 560 nm. The dye solution enters the laser cavity by passing through a cell or by streaming through the air using a dye jet. (Figure 13.5.3).

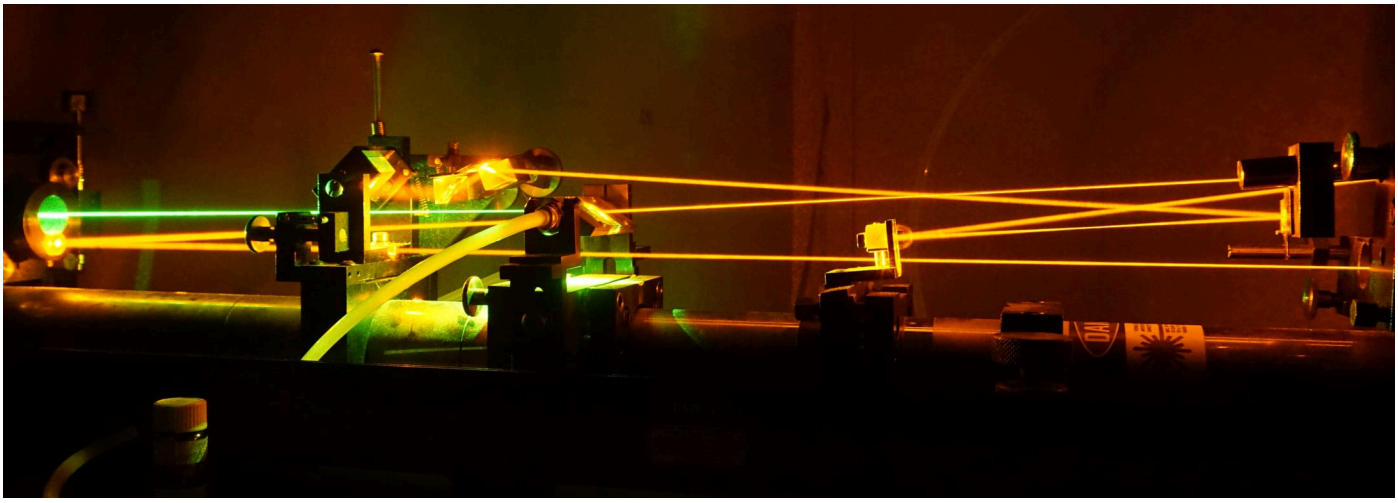


Figure 13.5.3: A dye laser in use. The dye is entering the dye cell through the yellow tube in the left foreground. (CC BY-SA 4.0, By Zaereth - Own work, https://commons.wikimedia.org/w/inde...curid=55762750)

Some common laser dyes other than rhodamine 6G and the rhodamines, include various coumarins, stilbenes, and fluorescein. There are solid state dye lasers (SSDL), in which the dye is dispersed uniformly within a solid polymer matrix.

The Pump Source

For lasing to take place, the gain medium must be pumped into an *excited state* capable of undergoing stimulated emission. The energy required for excitation is often supplied by an electric current or an intense light source, such as a flashlamp or an excitation laser. Diode lasers, excimer lasers, and YAG lasers have all been used as pump sources.

Lasers are categorized as having either a continuous beam or a pulsed beam. In theory, any laser could be run as a pulsed beam laser if the pump source is set to deliver the excitation energy in regularly repeated bursts. Not all lasers can operate as continuous-wave (CW) lasers, though, because there are gain media in which it is not possible to maintain a continuous population inversion. The ruby laser is an example of a laser that cannot produce a continuous wave.

The Laser Optical Cavity

Figure 13.5.4 shows the main components of a generic laser optical (or resonator) cavity. The optical cavity is formed by a pair of mirrors that surround the gain medium and enable feedback of light into the medium. This feedback is critical to the operation of a laser because it is where the amplification of the signal occurs. The gain medium is excited by an external pump source, such as a flash lamp, electric current, or another laser. The output coupler is a partially reflective mirror that allows a portion of the laser radiation to leave the cavity but reflects a majority of the light back through the gain medium. The light trapped between the mirrors forms standing wave structures called modes. Although beyond the scope of this discussion, the reader interested in cavity modes can consult the “Laser Radiation Properties” module.

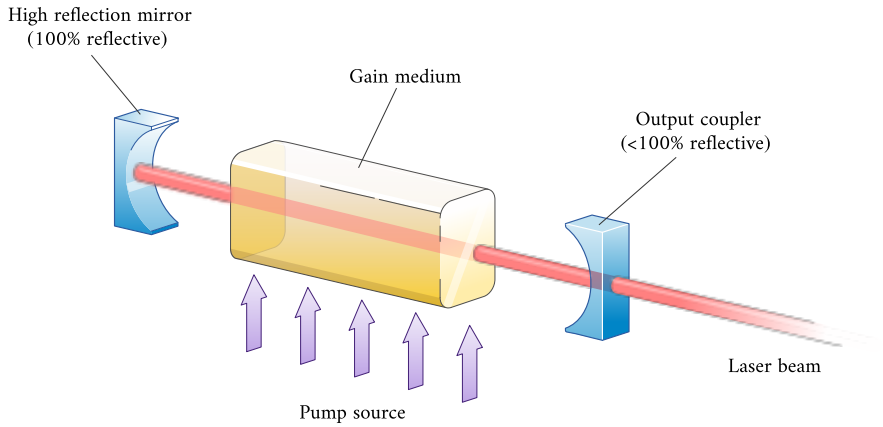


Figure 13.5.4: A schematic of a generic laser cavity. (CC BY-NC; Ümit Kaya via LibreTexts)

Figure 13.5.5 shows the laser cavity of a tunable dye laser. The laser is tunable because the pump source provides several excitation energies, which result in the creation of several possible energies for the lasing beam. The user chooses the desired lasing energy by means of a tuning element, which is often a movable diffraction grating.

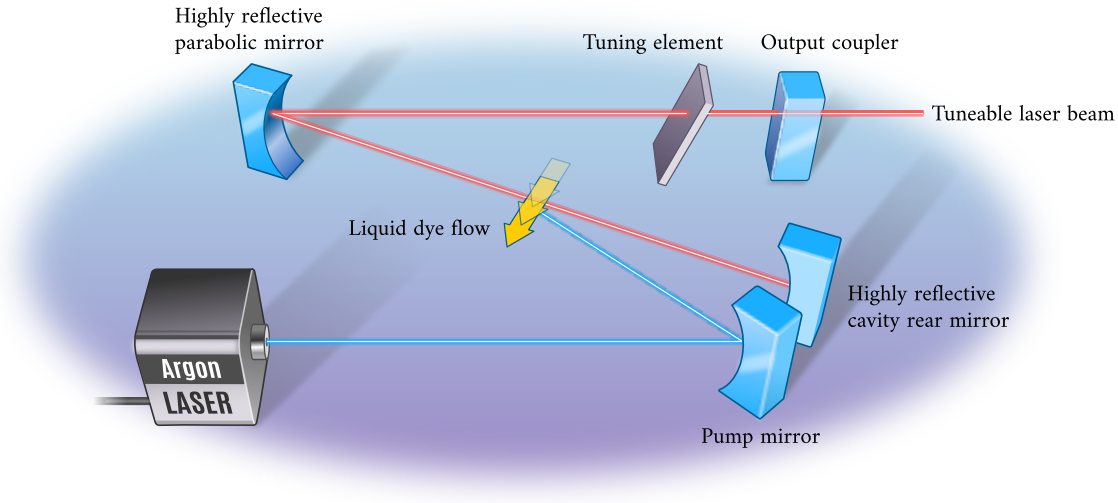


Figure 13.5.5: A schematic of a dye laser cavity with a dye jet. (CC BY-NC; Ümit Kaya via LibreTexts)

Diode Lasers

Diode lasers do not lase in the same manner as the lasers described above. There is no laser optical cavity, and thus there is no stimulated emission. Diodes made of materials such as GaAs emit light when the recombination of an electron and a hole in a semiconductor releases energy in the form of photons. A population inversion is maintained by rapidly removing the electrons that are falling into the holes of the p-type semiconductor. A pseudo-optical cavity is formed because the semiconductor materials generally have a very high refractive index, causing the photons to be trapped in the crystal of the semiconductor due to the large and abrupt difference in the refractive indices at the surfaces of the crystal. GaAs emits infrared light, but it can be doped to create a material that emits at another wavelength. For example, $GaAs_{0.6}P_{0.4}$ emits red light.

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13.6: The Helium-Neon Laser

The He-Ne laser was the first continuous-wave (cw) laser invented. A few months after Maiman announced his invention of the pulsed ruby laser, Ali Javan and his associates W. R. Bennet and D. R. Herriott announced their creation of a cw He-Ne laser. This gas laser is a four-level laser that uses helium atoms to excite neon atoms. The atomic transitions in the neon produce the laser light. The most commonly used neon transition in these lasers produces red light at 632.8 nm. These lasers can also produce green and yellow light in the visible region, as well as several UV and IR wavelengths (Javan's first He-Ne operated in the IR at 1152.3 nm). By using highly reflective mirrors designed for one of these many possible lasing transitions, a given He-Ne's output is made to operate at a single wavelength.

He-Ne lasers are not sources of high-power laser light, typically producing a few to tens of mW (milli-Watt, or 10^{-3} W) of power. Probably one of the most important features of these lasers is that they are highly stable, both in terms of their wavelength (mode stability) and intensity of their output light (low jitter in power level). For these reasons, He-Ne lasers are often used to stabilize other lasers. They are also used in applications, such as holography, where mode stability is important. Until the mid-1990's, He-Ne lasers were the dominant type of lasers produced for low-power applications - from range finding to scanning to optical transmission, to laser pointers, etc. Recently, however, other types of lasers, most notably the semiconductor lasers, seem to have won the competition because of reduced costs.

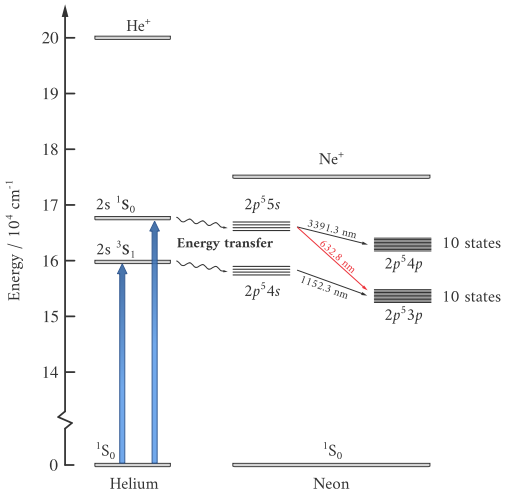


Figure 13.6.1: An energy level diagram for He and Ne in a He-Ne laser. The pumping creates helium atoms in two excited states. These excited states have energies similar to two sets of four excited states in the Ne atoms. Thus, collisions between the excited He atoms and Ne atoms can lead to nonradiative energy transfer. The excited state Ne atoms have lifetimes that enable a population inversion and lasing. (CC BY-NC; Ümit Kaya via LibreTexts)

The energy level diagram in figure 13.6.1 shows the two excited states of a helium atom, the 2 ^{3}S and 2 ^{1}S, that get populated as a result of electromagnetic pumping. Both of these states are metastable and do not allow de-excitations via radiative transitions. Instead, the helium atoms give off their energy to neon atoms through collisional excitation. In this way, the 4s and 5s levels in neon get populated.

$$He^*(2s^3\ S_1) + Ne(g) \rightarrow He(g) + Ne^*(2p^5 4s)$$

$$He^*(2s^1\ S_0) + Ne(g) \rightarrow He(g) + Ne^*(2p^5 5s)$$

These are the two upper lasing levels, each for a separate set of lasing transitions. Each of these upper lasing levels contains 4 states ($^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$). Radiative decay from the 5s to the 4s levels is forbidden. So, ten states associated with the 4p and 3p levels serve as the lower lasing levels and rapidly decay into the metastable 3s level. In this way, population inversion is easily achieved in the He-Ne mixture. The 632.8 nm laser transition, for example, involves the 5s and 3p levels, as shown above. Table 13.6.1 lists parameters of several of the Ne transitions.

Table 13.6.1: Several Lasing Transitions for an Excited State Ne Atom

Transition	λ (nm)	Einstein Coefficient A (s^{-1})	Relative Intensity
$5s^1\ P_1 \rightarrow 3p^3\ P_1$	640.1	0.60×10^6	100
$5s^1\ P_1 \rightarrow 3p^3\ P0$	635.2	0.70×10^6	100
$5s^1\ P_1 \rightarrow 3p^3\ P2$	632.8	6.56×10^6	300
$5s^1\ P_1 \rightarrow 3p^1\ P_1$	629.4	1.35×10^6	100
$5s^1\ P_1 \rightarrow 3p^1\ D_2$	611.8	1.28×10^6	100

In most He-Ne lasers the gas, a mixture of 5 parts helium to 1 part neon, is contained in a sealed glass tube with a narrow (2 to 3 mm diameter) bore as shown above in figure 13.6.2. Typically the laser's optical cavity mirrors, the high reflector and the output coupler form the two sealing caps for the narrow bore tube. High voltage electrodes create a narrow electric discharge along the length of this tube, which then leads to the narrow beam of laser light.

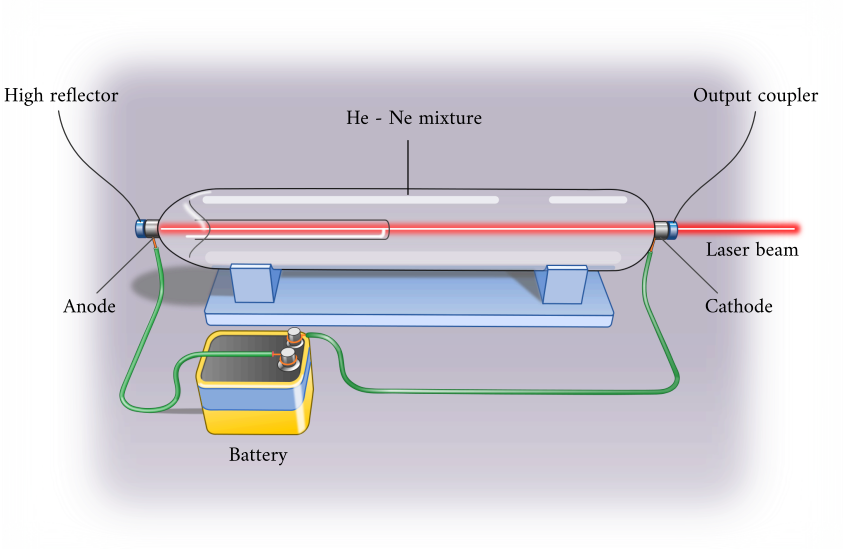


Figure 13.6.2: A He-Ne laser cavity. (CC BY-NC; Ümit Kaya via LibreTexts)

Many He-Ne lasers also contain a ballast which serves to maintain the desired gas mixture. Since some of the atoms may get embedded in the glass and/or the electrodes as they accelerate within the discharge, in the absence of a ballast the lasing mixture would not last very long. To further prolong the useable life of the laser, some of these lasers also use "getters", often metals such as titanium, that absorb impurities in the gas. Figure 13.6.3 below shows a He-Ne laser with a ballast.

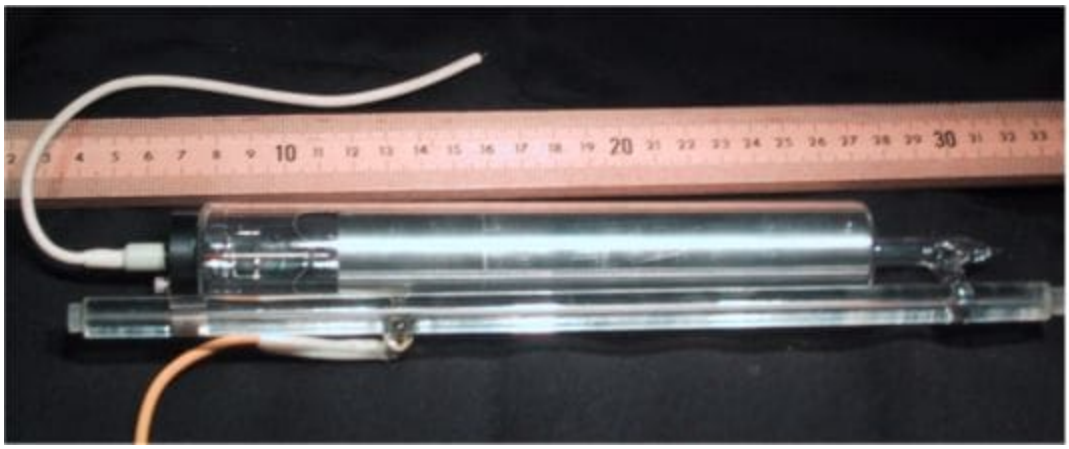


Figure 13.6.3: A commercial He-Ne tube. The thicker cylinder closest to the meter-stick (shown for scale) is the ballast. The thinner tube houses the resonant cavity where the lasing occurs. Notice the two mirrors that seal the two ends of the bore. For mode stability reasons, these mirrors are concave; they serve as the output coupler and the high reflector. (Copyright; author via source)

A typical commercially available He-Ne produces about a few mW of 632.8 nm light with a beam width of a few millimeters at an overall efficiency of near 0.1%. This means that for every 1 Watt of input power from the power supply, 1 mW of laser light is produced. Still, because of their long operating lifetime of 20,000 hours or more and their relatively low manufacturing cost, He-Ne lasers are among the most popular gas lasers.

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13.7: Modern Applications of Laser Spectroscopy

A Quick Overview

Laser light offers valuable tools to researchers who wish to use the interaction of light with matter to interrogate atomic and molecular systems. Most laser light is characterized by its near monochromaticity (relative to light from other sources), directionality, and coherence [1]. Those characteristics are used in modern laser spectroscopy. The monochromaticity of laser light allows it to be used to probe specific energy changes in atoms and molecules. This ability to select specific wavelengths allows scientists to focus on chosen components in mixtures, including complex reaction mixtures. For example, Park et. al. tracked the dynamics of the reaction of ground state oxygen with ethyl radical by using a 355 nm laser beam to track one of the products of this reaction [2]. Parsons et. al. used near monochromatic laser light sources to achieve state-selective ionization for the study of the products of a photodissociation reaction of atmospheric relevance [3]. Laser monochromaticity can be used to quantify the amount of greenhouse gases in the atmosphere [4]. Even when the samples are not mixtures, monochromaticity allows researchers to gather detailed information about atomic and/or molecular structure. Applications of this type are extremely numerous, including detailed studies of atomic systems [5], semiconductor materials [6], single molecules [7], and biological molecules [8]. Lasers find research applications in art and archeology, where the property of monochromaticity allows specific energies to be probed and laser beam directionality and small spot size curtail destruction of samples [9,10].

Other laser applications focus on the ability of pulsed lasers to provide short pulses. Short-pulsed lasers offer myriad tools for exploring chemical kinetics at a range of timescales, including very short ones. Short-pulse lasers open the opportunity for time-resolved studies of molecular processes such as reaction processes [2,11] and biological processes [12 - 15], and the properties of excited states [16]. Some research applications take advantage of the ability of certain lasers to produce high intensity light. One such application is laser-induced break down spectroscopy (LIBS), in which the high intensity of the laser creates a plasma from solid or liquid samples; that plasma can subsequently be probed [17]. Other techniques that exploit high laser intensities are the nonlinear spectroscopies, where the high intensities of some lasers can produce behaviors in samples that lower-power sources cannot sufficiently stimulate [18,19]. Although most lasers are monochromatic and coherent, some researchers have modified laser light to obtain information from broadband, incoherent laser light [20 – 22], which allows them to probe the response of samples to light that more resembles sunlight (incoherent) than do traditional laser sources [22, 23]. Another possibility is to probe multiple wavelengths with broadband laser sources that are coherent [24].

Conclusion

This brief overview has only skimmed the surface of the vast field of laser spectroscopy. The examples given here are a very small, somewhat arbitrary, and significantly biased subset of the enormous library of published laser-based experiments. References have been chosen to give examples of the topics covered here and have not been extensively reviewed by the author.

Overall, lasers are especially useful as light sources when one or more of the following properties are desired for light in an experiment:

1. A high degree of monochromaticity
2. A well-known central wavelength for a light source
3. A tunable light source
4. Spatial coherence
5. Phase coherence
6. Directionality
7. High intensity
8. Tight focus
9. Short pulses

A particular laser type will not necessarily have all the properties in the list above; however, the menu of available laser types allows a researcher to choose a laser system or systems with the characteristics needed for a particular experiment. New applications of laser spectroscopy and new spectroscopic techniques employing laser light continue to be invented.

References

[1] https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Analytical_Sciences_Digital_Library/JASDL/Courseware/Introduction_to_Lasers/03_Basic_Principles/01_Laser_Radiation_Properties

[2] *J. Phys. Chem. A* 2010, 114, 14, 4891–4895; Publication Date: February 19, 2010; https://doi.org/10.1021/jp910615y

[3] *J. Phys. Chem. A* 2022, 126, 34, 5729–5737; Publication Date: August 22, 2022; https://doi.org/10.1021/acs.jpca.2c04265

[4] https://www.nist.gov/news-events/news/2021/06/nist-laser-comb-systems-now-measure-all-primary-greenhouse-gases-air

[5] R. C. Thompson, 1985 *Rep. Prog. Phys.* **48** 531; https://iopscience.iop.org/article/10.1088/0034-4885/48/4/003

[6] *J. Phys. Chem. A* 2020, 124, 15, 2972–2981; Publication Date: March 23, 2020; https://doi.org/10.1021/acs.jpca.0c00370

[7] *J. Phys. Chem. A* 1997, 101, 45, 8435–8440; Publication Date: November 6, 1997; https://doi.org/10.1021/jp9719063

[8] Jörg Standfuss, Membrane protein dynamics studied by X-ray lasers – or why only time will tell, *Current Opinion in Structural Biology,* Volume 57, 2019, Pages 63-71, ISSN 0959-440X, https://doi.org/10.1016/j.sbi.2019.02.001

[9] https://www.getty.edu/conservation/about/science/laser_mass.html

[10] https://www.laserfocusworld.com/test-measurement/spectroscopy/article/14183101/spectroscopy-uncovers-the-hidden-in-art-and-archaeology

[11] *J. Phys. Chem.* 1996, 100, 31, 12701–12724; Publication Date: August 1, 1996; https://doi.org/10.1021/jp960658s

[12] Hideki Hashimoto, Mitsuru Sugisaki, Masayuki Yoshizawa,

Ultrafast time-resolved vibrational spectroscopies of carotenoids in photosynthesis, *Biochimica et Biophysica Acta - Bioenergetics*, Volume 1847, Issue 1, 2015, Pages 69-78,

ISSN 0005-2728, https://doi.org/10.1016/j.bbabio.2014.09.001.

[13] *J Phys Chem A*. 2003 Oct 9; 107(40): 8208–8214.; Publication Date: June 12, 2003 ; https://doi.org/10.1021/jp030147n

[14] *Biochemistry* 2003, 42, 34, 10054-10059; Publication Date: August 5, 2003; https://doi.org/10.1021/bi034878p

[15] Holzwarth, A. (1989). Applications of ultrafast laser spectroscopy for the study of biological systems. *Quarterly Reviews of Biophysics, 22*(3), 239-326.

https://doi.org/10.1017/S0033583500002985

[16] *J. Phys. Chem. B* 2015, 119, 29, 9335–9344; Publication Date:November 4, 2014; https://doi.org/10.1021/jp509959n

[17] *Anal. Chem.* 2013, 85, 2, 640–669; Publication Date:November 8, 2012; https://doi.org/10.1021/ac303220r

[18]https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Book%3A_Nonlinear_and_Two-Dimensional_Spectroscopy_(Tokmakoff)/00%3A_Front_Matter/05%3A_What_is_Nonlinear_Spectroscopy

[19] Marc Levenson and Satoru Kano, *Introduction to Nonlinear Laser Spectroscopy*, revised edition, 2012, Academic Press, ISBN-13: 978-0124447226, ISBN-10: 0124447228

[20] *J. Phys. Chem. A* 2013, 117, 29, 5926–5954; Publication Date: November 26, 2012; https://doi.org/10.1021/jp310477y

[21] Turner, D., Arpin, P., McClure, S. *et al.* Coherent multidimensional optical spectra measured using incoherent light. *Nat Commun* **4**, 2298 (2013). https://doi.org/10.1038/ncomms3298

[22] *J. Phys. Chem. Lett.* 2012, 3, 21, 3136–3142; Publication Date: October 9, 2012; https://doi.org/10.1021/jz3010317

[23] *J. Phys. Chem. Lett.* 2018, 9, 11, 2946–2955; Publication Date: May 15, 2018; https://doi.org/10.1021/acs.jpclett.8b00874

[24] Muraviev, A.V., Konnov, D. & Vodopyanov, K.L. Broadband high-resolution molecular spectroscopy with interleaved mid-infrared frequency combs. *Sci Rep* **10**, 18700 (2020). https://doi.org/10.1038/s41598-020-75704-3

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13.E: Lasers, Laser Spectroscopy, and Photochemistry (Exercises)

These are homework exercises to accompany Chapter 15 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q15.9

The Einstein coefficient of a ground and excited state with a degeneracy of g_1 and g_2 is given by

$$A = \frac{16\pi^3 v^3 g_1}{3\epsilon_0 h c^3 g_2} |\mu|^2$$

where $|\mu|$ is the transition dipole moment. Consider the 1s --> 2p absorption of H(g), which is observed at 121.8 nm. The radiative lifetime of the triply degenerate excited 2p state of H(g) is 1.6 x 10^{-9} s. Determine the value of the transition dipole moment of this transition.

S15.9

Using the expression given in the problem, we can isolate $|\mu|$ to be given as

$$|\mu| = \sqrt{\frac{3A\epsilon_0 h c^3 g_2}{16\pi^3 v^3 g_1}} \tag{13.E.1}$$

Since we know the wavelength and the radiative lifetime, we can find frequency (v) and amplitude (A) with the following equations, respectively.

$$v = \frac{c}{\lambda} = 2.46 \times 10^{15} s^{-1} \tag{13.E.2}$$

$$A = \frac{1}{\tau} = 6.25 \times 10^{8} s^{-1} \tag{13.E.3}$$

where τ represents radiative lifetime.

The 2p orbital is threefold degenerate $g_2 = 3$ and the 1s orbital is signly degenerate $g_1 = 1$. Therefore, we can plug the corresponding numbers into the equation below in order to yield the transition dipole moment, which would be

$$|\mu| = \sqrt{\frac{3A\epsilon_0 h c^3 g_2}{16\pi^3 v^3 g_1}} \tag{13.E.4}$$

$$|\mu| = 1.1 \times 10^{-29} C * m \tag{13.E.5}$$

Q15.10

$$A = \frac{16\pi^3 \nu^3 g_1}{3\varepsilon_0 h c^3 g_2} |\mu|^2 \tag{13.E.6}$$

$$A_{21} = \frac{8h\pi\nu_{12}^3}{c^3} B_{21} \tag{13.E.7}$$

Use the equations above to derive the quantum mechanical expression for the Einstein B coefficient. Consider the $5s^1P_1 \rightarrow 3p^1S_0$ transition of neon at $730.0\ nm$. Einstein A coefficient is $0.48 \times 10^6 s^{-1}$. Determine the values of the Einstein B coefficient and the transition moment dipole for this transition.

S15.10

$$\mu = \frac{h\nu}{4\pi} n_2 A_{21} \tag{13.E.8}$$

$$A = \frac{32h\pi^3\nu^7}{c^3\varepsilon_0} n_2 B_{21} \tag{13.E.9}$$

$$B_{21} = \frac{c^3\varepsilon_0}{n_2 A 32h\pi^3\nu^7} \tag{13.E.10}$$

$$730nm = 7.3 * 10^{-7}m \tag{13.E.11}$$

$\lambda = 7.3 * 10^{-7}m$ and thus $\nu = c\lambda = 2.189 * 10^{16}s^{-1}$

$$B_{21} = \frac{c^3\varepsilon_0}{n_2 A 32h\pi^3\nu^7} \tag{13.E.12}$$

$$B_{21} = \frac{c^3 A}{8h\pi\nu^3} \tag{13.E.13}$$

$$B_{21} = \frac{(2.998 * 10^8 m * s^{-1})^3 * (0.48 * 10^6 s^{-1})}{8h\pi(2.189 * 10^{16})^3} \tag{13.E.14}$$

$$B_{21} = 7.420 * 10^{13} kg^{-1} m \tag{13.E.15}$$

Q15.11

Given

$$N_{total} = N_1(t) + N_2(t) + N_3(t) \tag{13.E.16}$$

find the rate equation for each N_i.

S15.11

For each one we must look at the excitation energy, and the stimulated and spontaneous emissions energies.

For example, the excitation from 1 to 3, stimulated emission from 3 to 1 and the spontaneous emission from 3 to 1 and 2 to 1.

$$\frac{dN_1}{dt} = -B_{31}\rho_v\nu_{31}N_1 + B_{31}\rho_v\nu_{31}N_3 + A_{31}N_3 + A_21N_2 \tag{13.E.17}$$

the others follow as

$$\frac{dN_2}{dt} = -B_{32}\rho_v\nu_{32}N_2 + B_{32}\rho_v\nu_{32}N_3 + A_{32}N_3 - A_21N_2 \tag{13.E.18}$$

and

$$\frac{dN_3}{dt} = -B_{31}\rho_v\nu_{31}N_1 + -B_{31}\rho_v\nu_{31}N_3 - A_{32}N_3 - A_31N_3 - B_{32}\rho_v\nu_{32}N_3 + B_{32}\rho_v\nu_{32}N_2 \tag{13.E.19}$$

where we estimate the emission from level 3 to level 2.

Q15.12

Consider a nondegenerate 3-level system. Suppose that an incident light beam of energy $h\nu = E_3 - E_1$ is turned on for a while and then turned off. Show that the subsequent decay of the E_3 is given by

$$N_3(t) = N_3^0 e^{-(A_{32}+A_{31})t} \tag{13.E.20}$$

Where N_3^0 is the number of atoms in state 3 at the instant the light source is turned off. What will be the observed radiative lifetime of this excited state?

S15.12

After the light is turned off, no stimulated processes will occur and the rate equation of N_3 becomes:

$$N_3 = Ce^{-(A_{32}+A_{31})t} \tag{13.E.21}$$

At t = 0 (when the light is turned off), $N_3(t) = N_3^0 = C$, so

$$N_3(t) = N_3^0 e^{-(A_{32}+A_{31})t} \tag{13.E.22}$$

The observed radiative lifetime will be $(A_{32} + A_{31})^{-1}$. (The radiative lifetime is the reciprocal of the coefficient of the t in the exponential term.)

Q15-14

An excited state of Lithium has the electron configuration,

$$1s^2 2p^1 \tag{13.E.23}$$

Define the lowest energy term symbol.

S15-14

Construct a micro state table with spin (M(S)) across the top and angular momentum (M(L)) down the left side.

	-1/2	1/2
-1	-1(-)	-1(+)
0	0(-)	0(+)
1	1(-)	1(+)

The highest spin value is +1/2, while the highest angular momentum value is 1. As a result, J can range from 3/2 (L+S) to 1/2 (L-S). Because the p-orbital is less than half-full, the term symbol with the lowest J value will be lower in energy.

Term symbol:

$$^2P_{1/2} \tag{13.E.24}$$

Q15.15

The ground state energy of the He atom is -2.904 hartrees. Use this value to determine the energy of He^+

S15.15

(good job however you could have shown more steps as it us unclear how you made the jumps from energy to He^+ and then that the energy was 0.904, it took me some time to fiddle with what you gave me as a solution to arrive to that number so more in between steps are need --RM)

$$E = \frac{-Z^2}{2n^2} \tag{13.E.25}$$

$$He^+ = -2E_h \tag{13.E.26}$$

Therefore the energy of He+ is 0.904 hartrees above that of He.

There isn't too many steps in solving the problem. It would have been great to compare it to another method or the actual energy of an H+ hydrogen, such as, using the Rydberg formula to evaluate the energy....

Q15.19

A laser operating at 640 nm produces pulses at a rate of 85 MHz. Calculate the radiant power of each pulse if the pulses last 15 fs each and the average radiant power of the laser is 2.6 W. How many photons are produced by the laser per second?

S15.19

We can first calculate the amount of energy per pulse:

$$\frac{2.6W}{85\frac{pulses}{MHz}} = \frac{2.6\frac{J}{s}}{85\cdot 10^{6}\frac{pulses}{s}} = 3.059\cdot 10^{-8}\frac{J}{pulse} \tag{13.E.27}$$

Using this, we can then calculate the radiant energy of each laser pulse:

$$\frac{3.059\cdot 10^{-8}\frac{J}{pulse}}{15\cdot 10^{-15}s} = 2039.216\frac{kW}{pulse} \tag{13.E.28}$$

Finally, we can calculate the radiant energy of a single photon:

$$E_{photon} = \frac{hc}{\lambda} = \frac{(6.626\cdot 10^{-34}J\cdot s)(2.988\cdot 10^{8}\frac{m}{s})}{640\cdot 10^{-9}m} = 3.094\cdot 10^{-19}J \tag{13.E.29}$$

Using this energy, we can calculate the the number of photons produced per second by the laser:

$$\frac{E_{laser}}{E_{photon}} = \frac{2.6\frac{J}{s}}{3.094\cdot 10^{-19}\frac{J}{photon}} = 8.40\cdot 10^{18}\frac{photons}{second} \tag{13.E.30}$$

Q15.21

Which laser pulse contains more photons, a 945 ns, 9.45 mJ pulse at 945 nm or a 23 ns, 2.30 mJ at 230 nm? Does the speed of the pulse effect the number of photons?

S15.21

- $\mathbf{E}$ = energy per photon
- $\mathbf{h}$ = plancks constant = $6.626 * 10^{-34} J\cdot s$
- $\mathbf{c}$ = speed of light = $3.00 * 10^{8}\frac{m}{s}$
- λ = wavelength = 945 nm or 230 nm = $540 * 10^{-9}m \ or \ 230 * 10^{-9}m$

$$E_{photon} = \frac{(6.626 * 10^{-34} J\cdot s) * (3.00 * 10^{8}\ \frac{m}{s})}{945 * 10^{-9}\, m} = 2.104x10^{-19}\ J/photon$$

$$E_{pulse} = 9.45\ mJ = 9.45 * 10^{-3} J$$

$$\#_{photon} = \frac{E_{pulse}}{E_{photon}} = \frac{9.45 * 10^{-3} J}{2.104 * 10^{-19}\, J/photon} = \mathbf{4.493 * 10^{16}\ photons}$$

$$E_{photon} = \frac{(6.626 * 10^{-34} J \cdot s) * (3.00 * 10^{8} \frac{m}{s})}{230 * 10^{-9} m} = 8.64 * 10^{-19} J$$

$$E_{pulse} = 2.30\ mJ = 2.30 * 10^{-3} J$$

$$\#_{photon} = \frac{E_{pulse}}{E_{photon}} = \frac{2.30 * 10^{-3} J}{8.64 * 10^{-19}\ J/photon} = \mathbf{2.66 * 10^{15}\ photons}$$

First and foremost, the speed of the laser DOES NOT effect the number of photons! The 9.45 mJ at 945 nm laser pulse has more photons than the 2.30 mJ at 230 nm pulse.

The pulse duration does not affect the number of photons a laser pulse contains. Energies of both laser pulses are equivalent. Energy per pulse is propotional to the number of photons and inversely proportional to the wavelength of the emitted photons. Therefore, the 945 pulse contains more photons.

Q15.22

Given the following laser pulses: a $10 \times 10^{-9} s$, $1.6 \times 10^{6} J$ pulse at $76 \times 10^{-10} m$ or a $5 \times 10^{8} s$, $1.6 \times 10^{6} J$ pulse at 5.32×10^{-11}, which one has the most photons?

S15.22

For 10-ns, 1.60-mJ pulse at 760 nm:

$$Q_p = \frac{hc}{\lambda} \tag{13.E.31}$$

$$= \frac{(6.626 \times 10^{-34})(3 \times 10^{8})}{760 \times 10^{-9}} \tag{13.E.32}$$

$$= 2.62 \times 10^{-19} \tag{13.E.33}$$

Number of photon in 1.6 mJ pulse is:

$$N_1 = \frac{Q}{Q_p} = 6.12 \times 10^{15} \tag{13.E.34}$$

For 500-ms, 1.60-mJ pulse at 5320 nm:

$$Q_p = 3.75 \times 10^{-18} \tag{13.E.35}$$

Number of photon in 1.6 mJ pulse is:

$$N_2 = \frac{Q}{Q_p} = 0.4 \times 10^{15} \tag{13.E.36}$$

Thus, 10-ns, 1.60-mJ pulse at 760 nm contain more photon.

Q15.24

A CO_2 laser operating at 9.0 μm uses an electrical power of 5.20 kW. If this laser produces 100-ns pulses at a repetition rate of 20Hz and has an efficiency of 29%, how many photons are in each laser pulses?

S15.24

The pump energy per pulse is:

$$\frac{5200J * s^{-1}}{20s^{-1}} = 260J * pulse^{-1}$$

Given that the laser is 29% effcient, the radiant per pulse is $(260J)(0.29) = 67.6J$.

The number of photons per pulse, n is

$$n = \frac{E\lambda}{hc},$$

by plugging in the values into this equation, we have

$$n = \frac{(260J)(0.29)(9.0 * 10^{-6}m)}{(6.626 * 10^{-34}J * s)(2.998 * 10^{8}m * s^{-1})}$$

$= 3.42 * 10^{37}$ photons

My calculation reveals the final answer to be 3.42×10^{21} photons (Aaron Choi)/ I believe you accidentally calculated using the speed of light as $2.998 \times 10^{-8}\frac{m}{s}$

Q15.25

Figure 15.10 displays the energy levels of the CO_2 laser. Given the following spectroscopic data for $CO_2(g)$, calculate the spacing between the $J' = 3 \rightarrow 2$ laser lines for the $001 \rightarrow 100$ vibrational transition.

$$Fundamental frequency (J' = 0 \rightarrow 0) 100 \rightarrow 001 = 960.80cm^{-1} \tag{13.E.37}$$

$$\tilde{B}(001) = 0.3871cm^{-1} \tilde{B}(100) = 0.3902cm^{-1} \tag{13.E.38}$$

The fundamental frequency is \(960.80cm^{-1}

S15.25

Using the following equation F(J) for J = 2 and J = 3 can calculated:

$$F(J) = \tilde{B}J(J+1) \tag{13.E.39}$$

$$F_{001}(3) = (0.3871cm^{-1})(3)(3+1) = 4.645cm^{-1} \tag{13.E.40}$$

$$F_{100}(2) = (0.3902cm^{-1})(2)(2+1) = 2.341cm^{-1} \tag{13.E.41}$$

Therefore the spacing is

$$960.80cm^{-1} + 4.645cm^{-1} - 2.341cm^{-1} = 963.10cm^{-1} \tag{13.E.42}$$

Q15.26

The upper level of the $H_2(g)$ laser is the lowest excited state of the molecule, the $B^1 \sum_u^+$ state, and the lower level is the $X^1 \sum_g^+$ ground state.The lasting occurs between the $v^{'} = 6$ level of the excited state and the $v^{''} = 13$ level of the ground state. Use the following spectroscopic data to determine the wavelength of the laser light from $H_2(g)$ laser.

State	$\tilde{T}_e/cm^{-1}$	$\tilde{\nu}_e/cm^{-1}$	$\tilde{\nu}_e\tilde{x}_e/cm^{-1}$
$B^1 \sum_u^+$	91,689.9	1356.9	19.93
$X^1 \sum_g^+$	0	4401.2	121.34

A 3.0 ns pulse can be generated with a pulse radiant power of 200kW. Calculate the radiant energy of such a laser pulse. How

many photons are there in this pulse?

S15.26

To calculate the energy of the upper and lower lasing levels the following equation is used:

$$G(v) = \tilde{\nu}_e \left(v + \frac{1}{2}\right) - \tilde{x}_e \tilde{\nu}_e \left(v + \frac{1}{2}\right)^2 \tag{13.E.43}$$

$$G^{''}(13) = (4401.2cm^{-1})(13.5) - (121.34cm^{-1})(13.5)^2 = 37,301.98cm^{-1} \tag{13.E.44}$$

$$G^{''}(6) = (1356.9cm^{-1})(6.5) - (19.93cm^{-1})(6.5)^2 = 7,977.81cm^{-1} \tag{13.E.45}$$

the transition is as follows

$$\tilde{\nu} = \tilde{T}_e + G^{''}(6) - G^{''}(13) \tag{13.E.46}$$

$$= 91,689.9cm^{-1} + 7,977.81cm^{-1} - 37,301.98cm^{-1} = 62,365.73cm^{-1} \tag{13.E.47}$$

therefore

$$\lambda = 160.34nm \tag{13.E.48}$$

The radiant energy of the laser pulse is found using dimensional analysis

$$\left(200\frac{kJ}{s}\right)\left(2 \times 10^{-9}s\right) = 1x10^{-4}J \tag{13.E.49}$$

the number of photons per pulse is determined using $E = nhv = 8.06 \times 10^{13}$ photons.

Q15.27

Determine the excited-state rotational quantum number for $X \rightarrow A$ adsorption bands of H_2(g). The transition is from the $v'' = 0$of the X state to the excited vibrational level of the A state $v^{'} = 3$. To accurately calculate the vibrational term $G(v)$ for the excited state A, a second-order anharmonic correction is made to account for the shape of the potential curve, while first-order corrections are sufficient for the ground level electron state.

$$G(v) = \tilde{v}_e(v + \frac{1}{2}) - \tilde{v}_e\tilde{x}_e(v + \frac{1}{2})^2 + \tilde{v}_e\tilde{y}_e(v + \frac{1}{2})^3$$

The need spectroscopic constants are tabulated below for the ground state X and the excited state A of H_2(g).

State	$\tilde{T}_e/cm^{-1}$	$\tilde{v}_e/cm^{-1}$	$\tilde{v}_e\tilde{x}_e/cm^{-1}$	$\tilde{v}_e\tilde{y}_e/cm^{-1}$	$\tilde{B}_e/cm^{-1}$	$\tilde{\alpha}_e/cm^{-1}$
A	120952	2321.4	62.8	0	29.9	1.24
X	0	2291.7	62.4			

These values are from the NIST website for the H_2

Determine the value of $\tilde{v}$ corresponding to the transition $X(v'' = 0, j'' = 0) \rightarrow A(v^{'} = 3, j^{'} = 0)$. Given that the ground state levels are $v'' = 0, j'' = 1$ of the X state and that the rotational term for this level is $F(1) = 1.057cm^{-1}$, determine the closest value of $J^{'}$, the rotational number of the $v'' = 3$ level of the excited A state.

S15.27

For the ground state, the $G(v)$ value is :

$$G''(0) = (\frac{1}{2})(2291cm^{-1}) - (\frac{1}{2})^2 62.4cm^{-1}$$

$$G''(0) = 1129.9cm^{-1}$$

For the excited state $G(v)$ value is :

$$G''(3) = (2321.4cm^{-1})(3+\frac{1}{2}) - (62.8cm^{-1})(3+\frac{1}{2})^2$$

$$G''(32) = 7354cm^{-1}$$

$\tilde{T}_e$is the difference in the minima of the electronic potential energy curve in wave numbers, so the transition will have the energy

$$\tilde{v}_e = \tilde{T}_e + G^{'}(32) - G''(0)$$

$$\tilde{v}_e = 120952cm^{-1} + 7354cm^{-1} - 1129.9cm{-}1$$

$$\tilde{v}_e = 127176.1cm^{-1}$$

$\tilde{B}_v$ can be found for A state, $v = 3$ with this equation:

$$\tilde{B}_{32} = \tilde{B}_e - \tilde{\alpha}_e(v+\frac{1}{2})$$

$$\tilde{B}_{32} = 29.9cm^{-1} - (1.24cm^{-1})(3+\frac{1}{2}) = 25.56cm{-}1.$$

the observed lines are in between 35714.29 cm^{-1} and 3448.28 cm_{-1} recalling that $\tilde{E}_{v,j} = G(v) - F(j)$;

$$35717.29cm^{-1} = 127176.1cm^{-1} - 1.057cm{-}1 + F^{'}(j)$$

$$35717.29cm^{-1} = 127175.043cm^{-1} + F^{'}(j)$$

Therefore 91461 $\approx F^{'}(j)$ so j would be around 10 or higher.

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14: MATH CHAPTERS

14.1: Complex Numbers

14.2: Probability and Statistics

14.3: Determinants

14.3.1: The Solutions of Simultaneous Linear Equations

14.3.2: Calculation of a 3 × 3 determinant

14.3.3: The Determinant as a Volume

14.3.4: Properties of Determinants

14.3.5: Problems

14.4: Vectors

14.5: Spherical Coordinates

14.6: Matrices

14.7: Numerical Methods

14.8: Partial Differentiation

14.9: Series and Limits

14.10: Fourier Analysis

14.10.1: Fourier Analysis in Matlab

14.10.2: Fourier Synthesis of Periodic Waveforms

14.11: The Binomial Distribution and Stirling's Appromixation

14.12: Formula Sheets

14.12.1: Some Important Numbers

14.12.2: Quadratic Equation

14.12.3: Logarithms and Exponentials

14.12.4: Trigonometric Identities

14.12.5: Complex Numbers

14.12.6: Operators

14.12.7: Taylor Series

14.12.8: Fourier Series

14.12.9: Derivatives and Primitives (Indefinite Integrals)

14.12.10: Definite integrals

14.12.11: Differentiation Rules

14.12.12: Partial Derivatives

14.12.13: Coordinate Systems

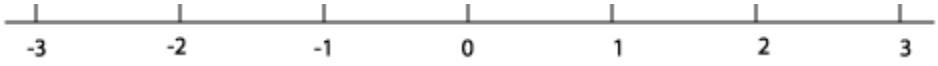
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14.1: Complex Numbers

Real Numbers

Let us think of the ordinary numbers as set out on a line which goes to infinity in both positive and negative directions. We could start by taking a stretch of the line near the origin (that is, the point representing the number zero) and putting in the integers as follows:



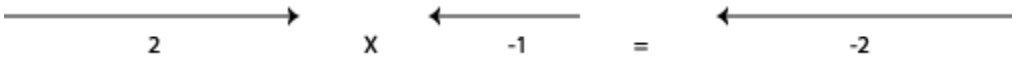
Next, we could add in rational numbers, such as ½, 23/11, etc., then the irrationals like $\sqrt{2}$, then numbers like π, and so on, so any number you can think of has its place on this line. Now let's take a slightly different point of view, and think of the numbers as represented by a *vector* from the origin to that number, so 1 is



and, for example, –2 is represented by:



Note that if a number is multiplied by –1, the corresponding vector is turned through 180 degrees. In pictures,



The "vector" 2 is turned through π, or 180 degrees, when you multiply it by –1.

Example A.1

What are the square roots of 4?

Solution

Well, 2, obviously, but also –2, because multiplying the backwards pointing vector –2 by –2 not only doubles its length, but also turns it through 180 degrees, so it is now pointing in the positive direction. We seem to have invented a hard way of stating that multiplying two negatives gives a positive, but thinking in terms of turning vectors through 180 degrees will pay off soon.

Solving Quadratic Equations

In solving the standard quadratic equation

$$ax^2 + bx + c = 0 \tag{14.1.1}$$

we find the solution to be:

$$x = \frac{-b \pm \sqrt{b^2 - ac}}{2a} \tag{14.1.2}$$

The problem with this is that sometimes the expression inside the square root is negative. What does that signify? For some

problems in physics, it means there is no solution. For example, if I throw a ball directly upwards at 10 meters per sec, and ask when will it reach a height of 20 meters, taking g = 10 m per sec^2, the solution of the quadratic equation for the time t has a negative number inside the square root, and that means that the ball doesn't get to 20 meters, so the question didn't really make sense.

We shall find, however, that there are other problems, in wide areas of physics, where negative numbers inside square roots have an important physical significance. For that reason, we need to come up with a scheme for interpreting them.

The simplest quadratic equation that gives trouble is:

$$x^2 + 1 = 0 \tag{14.1.3}$$

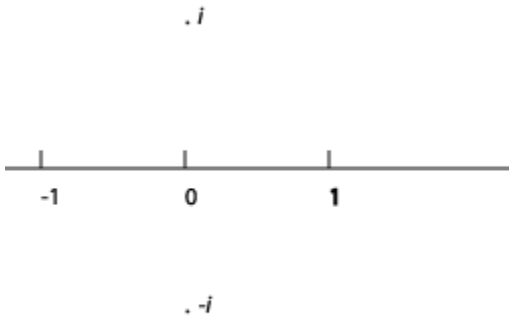
the solutions being

$$x = \pm\sqrt{-1} \tag{14.1.4}$$

What does that mean? We've just seen that the square of a positive number is positive, and the square of a negative number is also positive, since multiplying one negative number, which points backwards, by another, which turns any vector through 180 degrees, gives a positive vector. Another way of saying the same thing is to regard the minus sign itself, -, as an operator which turns the number it is applied to through 180 degrees. Now $(-2) \times (-2)$ has two such rotations in it, giving the full 360 degrees back to the positive axis.

To make sense of the square root of a negative number, we need to find something which when multiplied by itself gives a negative number. Let's concentrate for the moment on the square root of –1, from the quadratic equation above. Think of –1 as the operator – acting on the vector 1, so the – turns the vector through 180 degrees. We need to find the square root of this operator, the operator which applied *twice* gives the rotation through 180 degrees. Put like that, it is pretty obvious that the operator we want rotates the vector 1 through 90 degrees.

But if we take a positive number, such as 1, and rotate its vector through 90 degrees only, it isn't a number at all, at least in our original sense, since we put all known numbers on one line, and we've now rotated 1 away from that line. The new number created in this way is called a pure imaginary number, and is denoted by i.



Once we've found the square root of –1, we can use it to write the square root of any other negative number—for example, $2i$ is the square root of -4. Putting together a real number from the original line with an imaginary number (a multiple of *i*) gives a *complex number*. Evidently, complex numbers fill the entire two-dimensional plane. Taking ordinary Cartesian coordinates, any point P in the plane can be written as (x, y) where the point is reached from the origin by going x units in the direction of the positive real axis, then y units in the direction defined by i, in other words, the y axis.

Thus the point *P* with coordinates (*x*, *y*) can be identified with the complex number *z*, where

$$z = x + iy. \tag{14.1.5}$$

The plane is often called the *complex plane*, and representing complex numbers in this way is sometimes referred to as an Argand Diagram.

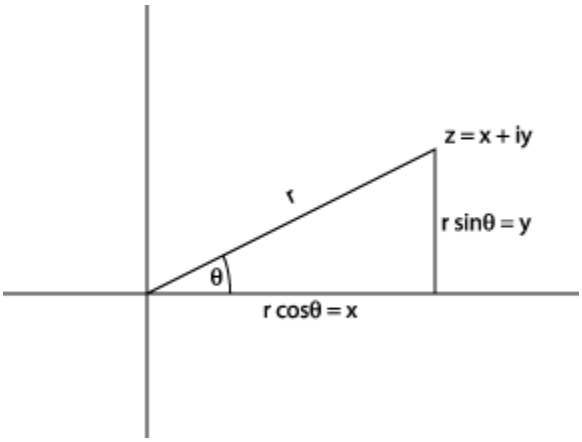
Visualizing the complex numbers as two-dimensional vectors, it is clear how to *add* two of them together. If $z_1 = x_1 + iy_1$, and $z_2 = x_2 + iy_2$, then $z_1 + z_2 = (x_1 + x_2) + i(y_1 + y_2)$. The real parts and imaginary parts are added separately, just like vector components.

Multiplying two complex numbers together does not have quite such a simple interpretation. It is, however, quite straightforward—ordinary algebraic rules apply, with i^2 replaced where it appears by -1. So for example, to multiply $z_1 = x_1 + iy_1$ by $z_2 = x_2 + iy_2$,

$$z_1 z_2 = (x_1 + iy_1)(x_2 + iy_2) = (x_1 x_2 - y_1 y_2) + i(x_1 y_2 + x_2 y_1). \tag{14.1.6}$$

Polar Coordinates

Some properties of complex numbers are most easily understood if they are represented by using the polar coordinates r, θ instead of (x, y) to locate z in the complex plane.



Note that $z = x + iy$ can be written $r(\cos\theta + i\sin\theta)$ from the diagram above. In fact, this representation leads to a clearer picture of multiplication of two complex numbers:

$$z_1 z_2 = r_2(\cos(\theta_1 + i\sin\theta_1) r_2(\cos(\theta_2 + i\sin\theta_2) \tag{14.1.7}$$

$$= r_1 r_2 \left[(\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2) + i(\sin\theta_1 \cos\theta_2 + \cos\theta_1 \sin\theta_2)\right] \tag{14.1.8}$$

$$= r_1 r_2 \left[\cos(\theta_1 + \theta_2) + i\sin(\theta_1 + \theta_2)\right] \tag{14.1.9}$$

So, if

$$z = r(cos\theta + i\sin\theta) = z_1 z_2 \tag{14.1.10}$$

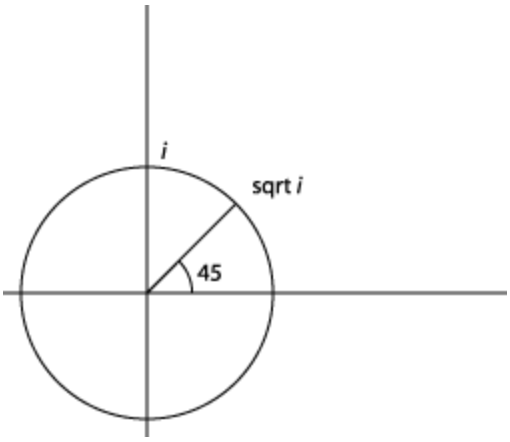
then

$$r = r_1 r_2 \tag{14.1.11}$$

and

$$\theta = \theta_1 \theta_2 \tag{14.1.12}$$

That is to say, to multiply together two complex numbers, we *multiply* the *r*'s – called the *moduli* – and *add* the phases, the θ 's. The modulus r is often denoted by \(|z|\), and called **mod *z***, the phase θ is sometimes referred to as **arg *z***. For example, $|i| = 1$, $\arg\ i = \pi/2$.

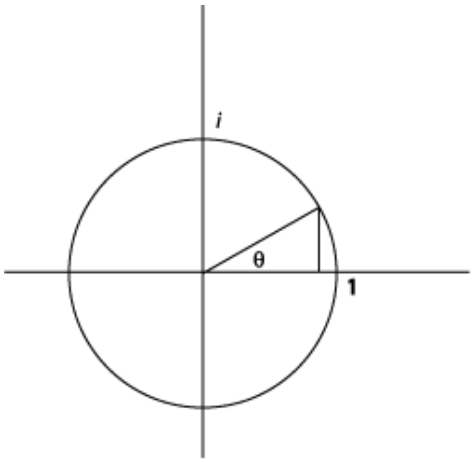


We can now see that, although we had to introduce these complex numbers to have a $\sqrt{-1}$, we do not need to bring in new types of numbers to get $\sqrt{-1}$, or $\sqrt{i}$. Clearly, $|\sqrt{i}| = 1$, $arg\sqrt{i} = 45\ °$. It is on the circle of unit radius centered at the origin, at 45°, and squaring it just doubles the angle.

The Unit Circle

In fact this circle—called the *unit circle*—plays an important part in the theory of complex numbers and every point on the circle has the form

$$z = \cos\theta + i\sin\theta = Cis(\theta) \tag{14.1.13}$$



Since all points on the unit circle have $|z| = 1$, by definition, multiplying any two of them together just amounts to adding the angles, so our new function $Cis(\theta)$ satisfies

$$Cis(\theta_1)Cis(\theta_2) = Cis(\theta_1 + \theta_2). \tag{14.1.14}$$

But that is just how multiplication works for exponents! That is,

$$a^{\theta_1}a^{\theta_2} = a^{\theta_1+\theta_2} \tag{14.1.15}$$

for a any constant, which strongly suggests that maybe our function $Cis(\theta$ is nothing but some constant a raised to the power θ, that is,

$$Cis(\theta) = a^{\theta} \tag{14.1.16}$$

It turns out to be convenient to write $a^\theta = e^{(\ln a)\theta} = e^{A\theta}$, where $A = \ln a$. This line of reasoning leads us to write

$$\cos\theta + i\sin\theta = e^{A\theta} \tag{14.1.17}$$

Now, for the above "addition formula" to work for multiplication, A must be a constant, *independent* of θ. Therefore, we can find the value of *A* by choosing θ for which things are simple. We take θ to be very small—in this limit:

$$\cos\theta = 1$$

$$\sin\theta = \theta$$

$$e^{A\theta} = 1 + A\theta$$

with we drop terms of order θ^2 and higher.

Substituting these values into Equation 14.1.17 gives θ

So we find:

$$(\cos\theta + i\sin\theta)e^{i\theta} \tag{14.1.18}$$

To test this result, we expand $e^{i\theta}$:

$$e^{i\theta} = 1 + i\theta + \frac{(i\theta)^2}{2!} + \frac{(i\theta)^3}{3!} + \frac{(i\theta)^4}{4!} + \frac{(i\theta)^5}{5!}... \tag{14.1.19}$$

$$= 1 + i\theta - \frac{\theta^2}{2!} - \frac{i\theta^3}{3!} + \frac{\theta^4}{4!} + \frac{i\theta^5}{5!}... \tag{14.1.20}$$

$$= \left(1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!}\right) + i\left(\theta - \frac{i\theta^3}{3!} + \frac{i\theta^5}{5!}\right) \tag{14.1.21}$$

$$= \cos\theta + i\sin\theta \tag{14.1.22}$$

We write $= \cos\theta + i\sin\theta$ in Equation 14.1.22 because the series in the brackets are precisely the Taylor series for $\cos\theta$ and $\sin\theta$ confirming our equation for $e^{i\theta}$. Changing the sign of θ it is easy to see that

$$e^{-i\theta} = \cos\theta - i\sin\theta \tag{14.1.23}$$

so the two trigonometric functions can be expressed in terms of exponentials of complex numbers:

$$\cos(\theta) = \frac{1}{2}\left(e^{i\theta} + e^{-i\theta}\right)$$

$$\sin(\theta) = \frac{1}{2i}\left(e^{i\theta} - e^{-i\theta}\right)$$

Euler Formula

The Euler formula states that any complex number can be written:

$$e^{i\theta} = \cos\theta + i\sin\theta$$

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14.2: Probability and Statistics

A random variable X can have more than one value x as an outcome. Which value the variable has in a particular case is a matter of *chance* and cannot be predicted other than that we associate a probability to the outcome. **Probability** p is a number between 0 and 1 that indicates the likelihood that the variable X has a particular outcome x. The set of outcomes and their probabilities form a ***probability distribution***. There are two kinds of distributions:

1. discrete ones
2. continuous ones

Total probability should always add up to unity.

Discrete Distributions

A good example of a discrete distribution is a *true coin*. The random variable X can have two values:

1. heads (0)
2. tails (1)

Both have equal probability and as the sum must equal unity, the probability must be ½ for each. 'The probability that X=heads' is written formally as:

$$Pr(X = heads) = Pr(X = 0) = 0.5$$

The random function is written as a combination of three statements.

- Pr(X=0) = ½
- Pr(X=1) = ½
- elsewhere Pr = 0

Continuous Distributions

Now consider a spherical die. One could say it has an infinite number of facets that it can land on. Thus the number of outcomes $n = \infty$, this make each probability

$$p = 1/\infty = 0.$$

This creates a bit of a mathematical problem, because how can we get a total probability of unity by adding up zeros? Also, if we divide the sphere in a northern and a southern hemisphere clearly the probability that it lands on a point in say, the north should be ½. Still, p = 0 for all points. We introduce a new concept: **probability density** over which we *integrate* rather than *sum*. We assign an equal density to each point of the sphere and make sure that if we integrate over a hemisphere we get ½. (This involves two angles θ and φ and an integration over them and I won't go into that).

A bit simpler example of a continuous distribution than the spherical die is the 1D ***uniform*** distribution. It is the one that the Excel function =RAND() produces to good approximation. Its probability density is defined as

- f(x) = 1 for 0<1>
- f(x) = 0 elsewhere

The figure shows a (bivariate) uniform distribution.

The probability that the outcome is smaller than 0.5 is written as Pr(X<0.5) and is found by integrating from 0 to 0.5 over f(x).

$$\Pr(X<0.5) = \int \mathbf{f(x)}.dx \text{ from } 0 \text{ to } 0.5 = \int \mathbf{1}.dx \text{ from } 0 \text{ to } 0.5 = [x]^{0.5}\text{-}[x]_0 = 0.5$$

Notice that in each individual outcome b the probability is indeed zero because an integral from b to b is always zero, even if the probability density f(b) is not zero. Clearly the probability and the probability density are not the same. Unfortunately the distinction between probability and probability density is often not properly made in the physical sciences. Moments can also be computed for continuous distributions by integrating over the probability densityalt

Another well-known continuous distribution is the ***normal*** (or ***Gaussian***) distribution, defined as:

\[f(x) = 1/[√(2π)σ] * exp(-½[(x-μ)/σ]^2) \nonumber \]

(Notice the normalization factor 1/[√(2π)σ])

We can also compute moments of continuous distribution. Instead of using a summation we now have to evaluate an integral:

$$\langle X \rangle = \int [f(x)^* x] dx$$

$$\langle X^2 \rangle = \int [f(x)^* x^2] dx$$

For the normal distribution $\langle X \rangle = \mu$

Exercise

Compute ^{2}> and ^{3}> for the uniform distribution. answer>

Indistinguishable Outcomes

When flipping two coins we could get four outcomes: two heads (0), heads plus tails (1), tails plus heads (1), two tails (2)

Each outcome is equally likely, this implies a probability of ¼ for each:

X_{tot} = X1 + X2 = 0 + 0 = 0 p=¼

X_{tot} = X1 + X2 = 0 + 1 = 1 p=¼

X_{tot} = X1 + X2 = 1 + 0 = 1 p=¼

X_{tot} = X1 + X2 = 1 + 1 = 2 p=¼

The probability of a particular outcome is often abbreviated simply to p. The two middle outcomes collapse into one with p=¼+¼= ½ if the coins are **indistinguishable**. We will see that this concept has very important consequences in statistical thermodynamics.

If we cannot distinguish the two outcomes leading to X_{tot}=1 we get the following random function:

- Pr(X_{tot}=0) = ¼
- Pr(X_{tot}=1) = ½
- Pr(X_{tot}=2) = ¼
- elsewhere Pr = 0

Notice that it is quite possible to have a distribution where the probabilities differ from outcome to outcome. Often the p values are given as f(x), a function of x. An example:

X3 defined as:

- f(x) = (x+1)/6 for x=0,1,2;
- f(x) =0 elsewhere;

The factor 1/6 makes sure the probabilities add up to unity. Such a factor is known as a **normalization factor**. Again this concept is of prime importance in statistical thermodynamics.

Another example of a discrete distribution is a die. If it has 6 sides (the most common die) there are six outcomes, each with p= 1/6. There are also dice with n=4, 12 or 20 sides. Each outcome will then have p= 1/n.

Moments of Distributions

In important aspect of probability distributions are the **moments** of the distribution. They are values computed by summing over the whole distribution.

The **zero** order moment is simply the sum of all p and that is unity:

$$^0> = \Sigma X^0 * p = \Sigma 1 * p = 1$$

The **first** moment multiplies each outcome with its probability and sums over all outcomes:

$$= \Sigma X * p$$

This moment is known as the ***average*** or ***mean***. (It is what we have done to your grades for years...)

For one coin is ½, for two coins is 1. (Exercise: verify this)

The **second** moment is computed by summing the product of the square of X and p:

$$^2> = \Sigma X^2 * p$$

For one coin we have $^2>$ = ½,

For two coins $^2>$= [0*¼ + 1*½ + 4*¼] = 1.5

What is $^2>$ for X3? answer

The notation is used a lot in quantum mechanics, often in the form <ψ*ψ> or <ψ*|h|ψ>. The <.. part is known as the ***bra***, the ..> part as the ***ket***. (Together ***bra***(c)***ket***)

Intermezzo: The strange employer

You have a summer job but your employer likes games of chance. At the end of every day he rolls a die and pays you the square of the outcome in dollars per hour. So on a lucky day you'd make $36.- per hour, but on a bad day $1.-. Is this a bad deal? What would you make on the average over a longer period?

To answer this we must compute the second moment $^2>$ of the distribution:

Answer available at the end of this section.

(I have taken p=1/6 out of brackets because the value is the same for all six outcomes)

As you see in the intermezzo, the value of the second moment is in this case what you ***expect*** to be making on the long term. Moments are examples of what is know as **expectation values**. Another term you may run into that of a **functional**. A functional is a *number* computed by some operation (such as summation or integration) over a whole function. Moments are clearly an example of that too.

Answers

^{2}> = 1/6 *[1+4+9+16+25+36] = 91/6 = $15.17 per hour.

^{2}> = 1/6 *[1+4+9+16+25+36] = 91/6 = $15.17 per hour.

^{2}> = 1/6 *[1+4+9+16+25+36] = 91/6 = $15.17 per hour.

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14.3: DETERMINANTS

Chapter Objectives

- Learn how to calculate the determinant of a square matrix.
- Understand how to solve systems of simultaneous linear equations using determinants.
- Learn the properties of determinants.

14.3.1: The Solutions of Simultaneous Linear Equations

14.3.2: Calculation of a 3 × 3 determinant

14.3.3: The Determinant as a Volume

14.3.4: Properties of Determinants

14.3.5: Problems

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14.3.1: The Solutions of Simultaneous Linear Equations

The concept of determinants has its origin in the solution of simultaneous linear equations. In physical chemistry, they are an important tool in quantum mechanics

Suppose you want to solve the following system of two equations with two unknowns (x and y):

$$a_1x + b_1y = c_1$$

$$a_2x + b_2y = c_2$$

In order to find y, we could use the following general procedure: we multiply the first equation by a_2 and the second by a_1, and subtract one line from the other to cancel the term in x:

$$a_1x + b_1y = c_1 \overset{\times a_2}{\rightarrow} a_1a_2x + b_1a_2y = c_1a_2$$

$$a_2x + b_2y = c_2 \overset{\times a_1}{\rightarrow} a_1a_2x + b_2a_1y = c_2a_1$$

$$\left.\begin{aligned} a_1a_2x + b_1a_2y = c_1a_2 \\ a_1a_2x + b_2a_1y = c_2a_1 \end{aligned}\right\} \rightarrow (b_2a_1 - b_1a_2)y = a_1c_2 - a_2c_1 \rightarrow y = \frac{a_1c_2 - a_2c_1}{b_2a_1 - b_1a_2}$$

We can follow the same strategy to find x: we multiply the first equation by b_2 and the second by b_1, and subtract one line from the other to cancel the term in y:

$$a_1x + b_1y = c_1 \overset{\times b_2}{\rightarrow} a_1b_2x + b_1b_2y = c_1b_2$$

$$a_2x + b_2y = c_2 \overset{\times b_1}{\rightarrow} b_1a_2x + b_2b_1y = c_2b_1$$

$$\left.\begin{aligned} a_1b_2x + b_1b_2y = c_1b_2 \\ b_1a_2x + b_2b_1y = c_2b_1 \end{aligned}\right\} \rightarrow (b_2a_1 - b_1a_2)x = b_2c_1 - b_1c_2 \rightarrow x = \frac{b_2c_1 - b_1c_2}{b_2a_1 - b_1a_2}$$

We define a 2×2 determinant as:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - cb$$

The determinant, which is denoted with two parallel bars, is a number. For example,

$$\begin{vmatrix} 3 & -1 \\ 1/2 & 2 \end{vmatrix} = 3 \times 2 - (-1) \times 1/2 = 13/2$$

Let's look at the expressions we obtained for x and y, and write them in terms of determinants:

$$x = \frac{b_2c_1 - b_1c_2}{b_2a_1 - b_1a_2} = \frac{\begin{vmatrix} c_1 & b_1 \\ c_2 & b_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}$$

$$y = \frac{a_1c_2 - a_2c_1}{b_2a_1 - b_1a_2} = \frac{\begin{vmatrix} a_1 & c_1 \\ a_2 & c_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}$$

Let's look at our equations, and see how these determinants are constructed from the coefficients.

$$a_1x + b_1y = c_1$$

$$a_2x + b_2y = c_2$$

The determinant in the denominator of both x and y is the determinant of the coefficients on the left-side of the equal sign:

$$\left.\begin{aligned} a_1x + b_1y &= c_1 \\ a_2x + b_2y &= c_2 \end{aligned}\right\} \begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}$$

The numerator in the expression of y is built by replacing the coefficients in the y-column with the coefficients on the right side of the equation:

$$\left.\begin{aligned} a_1x + b_1y &= c_1 \\ a_2x + b_2y &= c_2 \end{aligned}\right\} \begin{vmatrix} a_1 & c_1 \\ a_2 & c_2 \end{vmatrix}$$

The numerator in the expression of x is built by replacing the coefficients in the x-column with the coefficients on the right side of the equation:

$$\left.\begin{aligned} a_1x + b_1y &= c_1 \\ a_2x + b_2y &= c_2 \end{aligned}\right\} \begin{vmatrix} c_1 & b_1 \\ c_2 & b_2 \end{vmatrix}$$

We can extend this idea to n equations with n unknowns $(x_1, x_2, x_3, ..., x_n)$.

$$\begin{array}{ccccccc} a_{11}x_1 & + & a_{12}x_2 & + & \cdots & + & a_{1n}x_n & = b_1 \\ a_{21}x_1 & + & a_{22}c_2 & + & \cdots & + & a_{2n}x_n & = b_2 \\ \vdots & & \vdots & & \ddots & & \vdots & \vdots \\ a_{n1}x_1 & + & a_{n2}c_2 & + & \cdots & + & a_{nn}x_n & = b_n \end{array}$$

Note that we use two subscripts to identify the coefficients. The first refers to the row, and the second to the column. Let's define the determinant D as the determinant of the coefficients of the equation (the ones on the left side of the equal sign):

$$D = \begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{vmatrix}$$

and let's define the determinant D_k as the one obtained from D by replacement of the kth column of D by the column with elements $b_1, b_2...b_n$. For example, D_2 is

$$D_2 = \begin{vmatrix} a_{11} & b_1 & \cdots & a_{1n} \\ a_{21} & b_2 & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & b_n & \cdots & a_{nn} \end{vmatrix}$$

The unknowns of the system of equations are calculated as:

$$x_1 = \frac{D_1}{D}, x_2 = \frac{D_2}{D}, ..., x_n = \frac{D_n}{D}$$

For example, let's say we want to find x, y and z in the following system of equations:

$$2x + 3y + 8z = 0$$

$$x - \frac{1}{2}y - 3z = \frac{1}{2}$$

$$-x - y - z = \frac{1}{2}$$

We can calculate the unknowns as;

$$x = \frac{D_1}{D}, y = \frac{D_2}{D}, z = \frac{D_3}{D}$$

where

$$D = \begin{vmatrix} 2 & 3 & 8 \\ 1 & -1/2 & -3 \\ -1 & -1 & -1 \end{vmatrix}$$

$$D_1 = \begin{vmatrix} 0 & 3 & 8 \\ 1/2 & -1/2 & -3 \\ 1/2 & -1 & -1 \end{vmatrix}$$

$$D_2 = \begin{vmatrix} 2 & 0 & 8 \\ 1 & 1/2 & -3 \\ -1 & 1/2 & -1 \end{vmatrix}$$

$$D_3 = \begin{vmatrix} 2 & 3 & 0 \\ 1 & -1/2 & 1/2 \\ -1 & -1 & 1/2 \end{vmatrix}$$

In order to do this, we need to learn how to solve 3×3 determinants, or in general, $n \times n$ determinants.

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14.3.2: Calculation of a 3 × 3 determinant

There are several techniques to calculate determinants, but if this topic is new to you, expanding along the first row is the easiest (although maybe not the most computationally efficient) way of doing it.

A 3 × 3 matrix is calculated as:

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11} \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13} \begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix} \tag{14.3.2.1}$$

Notice that we multiply each entry in the first row by the determinant formed by what is left after deleting the corresponding row and column. In addition, notice that we alternate signs. Formally, the sign that corresponds to a particular entry a_{ij} is $(-1)^{i+j}$, but if we use the first raw we will always start with a "+" and alternate signs afterwards. A schematics of the procedure is shown in Figure 14.3.2.1.

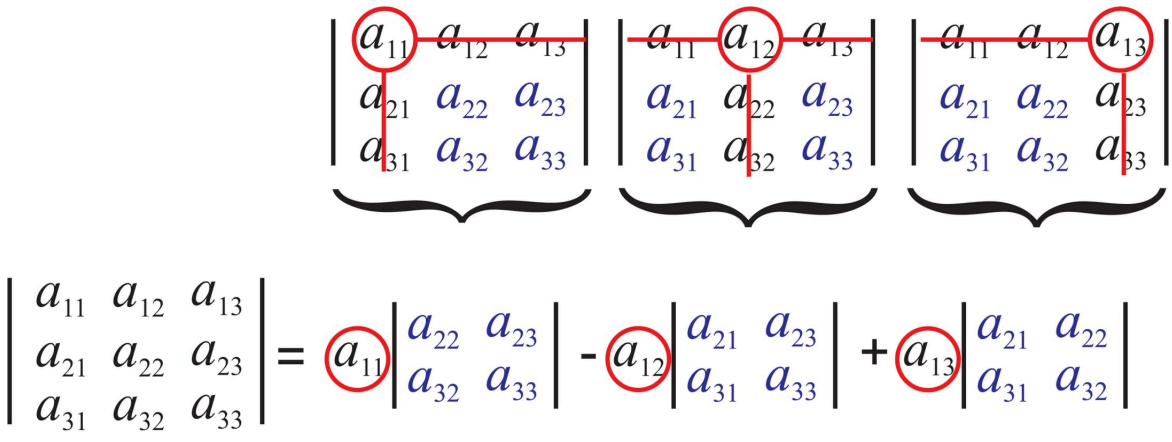


Figure 14.3.2.1: A 3×3 determinant (CC BY-NC-SA; Marcia Levitus)

We can use the same idea to calculate a determinant of any size. For example, for a 4×4 determinant:

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{vmatrix} = a_{11} \begin{vmatrix} a_{22} & a_{23} & a_{24} \\ a_{32} & a_{33} & a_{34} \\ a_{42} & a_{43} & a_{44} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} & a_{23} & a_{24} \\ a_{31} & a_{33} & a_{34} \\ a_{41} & a_{43} & a_{44} \end{vmatrix} + a_{13} \begin{vmatrix} a_{21} & a_{22} & a_{24} \\ a_{31} & a_{32} & a_{34} \\ a_{41} & a_{42} & a_{44} \end{vmatrix} - a_{14} \begin{vmatrix} a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \\ a_{41} & a_{42} & a_{43} \end{vmatrix} \tag{14.3.2.2}$$

The 3×3 determinants are then calculated using Equation 14.3.2.1.

Example 14.3.2.1

Find x in the following system of equations:

$$\begin{aligned} 2x + 3y + 8z &= 0 \\ x - \frac{1}{2}y - 3z &= \frac{1}{2} \\ -x - y - z &= \frac{1}{2} \end{aligned}$$

Solution

We can calculate the x as;

$$x = \frac{D_1}{D}$$

where

$$D = \begin{vmatrix} 2 & 3 & 8 \\ 1 & -1/2 & -3 \\ -1 & -1 & -1 \end{vmatrix}$$

and

$$D_1 = \begin{vmatrix} 0 & 3 & 8 \\ 1/2 & -1/2 & -3 \\ 1/2 & -1 & -1 \end{vmatrix}$$

D is a 3x3 determinant D and can be expanded using quation 14.3.2.1:

$$\begin{aligned} D &= 2\begin{vmatrix} -1/2 & -3 \\ -1 & -1 \end{vmatrix} - 3\begin{vmatrix} 1 & -3 \\ -1 & -1 \end{vmatrix} + 8\begin{vmatrix} 1 & -1/2 \\ -1 & -1 \end{vmatrix} \\ &= 2 \times (-5/2) - (3) \times (-4) + 8 \times (-3/2) = -5 \end{aligned}$$

The determinant D_1 is similarly expanded:

$$\begin{aligned} D_1 &= 0\begin{vmatrix} -1/2 & -3 \\ -1 & -1 \end{vmatrix} - 3\begin{vmatrix} 1/2 & -3 \\ 1/2 & -1 \end{vmatrix} + 8\begin{vmatrix} 1/2 & -1/2 \\ 1/2 & -1 \end{vmatrix} \\ &= 0 \times (-5/2) - (3) \times (1) + 8 \times (-1/4) = -5 \end{aligned}$$

So,

$$x = \frac{D_1}{D} = 1$$

To practice, finish this problem and obtain y and z (Problem 13.1).

Example 14.3.2.2

Show that a 3×3 determinant that contains zeros below the principal diagonal (top left to bottom right) is the product of the diagonal elements.

Solution

We are asked to prove that

$$D = \begin{vmatrix} a & b & c \\ 0 & d & e \\ 0 & 0 & f \end{vmatrix} = adf$$

Because we have two zeros in the first column, it makes more sense to calculate the determinant by expanding along the first column instead of the first row. Yet, if you feel uncomfortable doing this at this point we can expand along the first row as we just learned:

$$D = a \times \begin{vmatrix} d & e \\ 0 & f \end{vmatrix} - b \times \begin{vmatrix} 0 & e \\ 0 & f \end{vmatrix} + c \times \begin{vmatrix} 0 & d \\ 0 & 0 \end{vmatrix} = a \times d \times f$$

The conclusion is true in any dimension.

Need help? The links below contain solved examples. The determinant of a 3x3 matrix: http://tinyurl.com/n2a3uxw

External links:

- Finding the determinant of a 3x3 matrix: http://patrickjmt.com/finding-the-determinant-of-a-3-x-3-matrix/
- Solving a system of 3 linear equations: http://patrickjmt.com/cramers-rule-to-solve-a-system-of-3-linear-equations-example-1/

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14.3.3: The Determinant as a Volume

Before discussing the properties of determinants, it will be useful to note that a determinant represents the volume of a box.

In two dimensions, the absolute value of a 2×2 determinant represents the area of the parallelogram whose sides are the two columns (or rows) of the determinant. Suppose you have two vectors: $\vec{v}_1 = (b, d)$ and $\vec{v}_2 = (a, c)$ (see Figure 14.3.3.2). The area of the parallelogram constructed with these two vectors as sides is the absolute value of the determinant whose columns are $\vec{v}_1$ and $\vec{v}_2$:

$$A = \begin{vmatrix} b & a \\ d & c \end{vmatrix}$$

A geometrical proof of this statement is shown in Figure 14.3.3.1. The sign of the determinant is related to the orientation of the parallelogram. If you extend your right hand, and use your thumb and index finger to represent the two vectors, the determinant will be positive if the vector along your thumb is in the first column and the vector and your index finger is in the second column, and will be negative if it is the other way around (Figure 14.3.3.2).

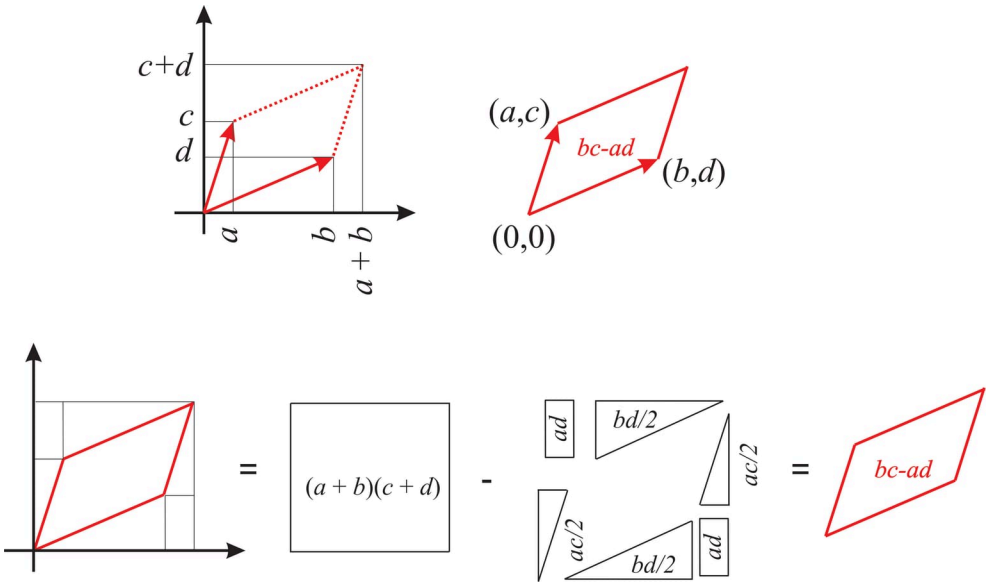


Figure 14.3.3.1: A 2× 2 determinant as the area of a parallelogram. The area of the parallelogram is calculated as the area of the rectangle of sides $(a + b)$ and $(c + d)$ minus the areas of the triangles and rectangles shown in the figure (CC BY-NC-SA; Marcia Levitus)

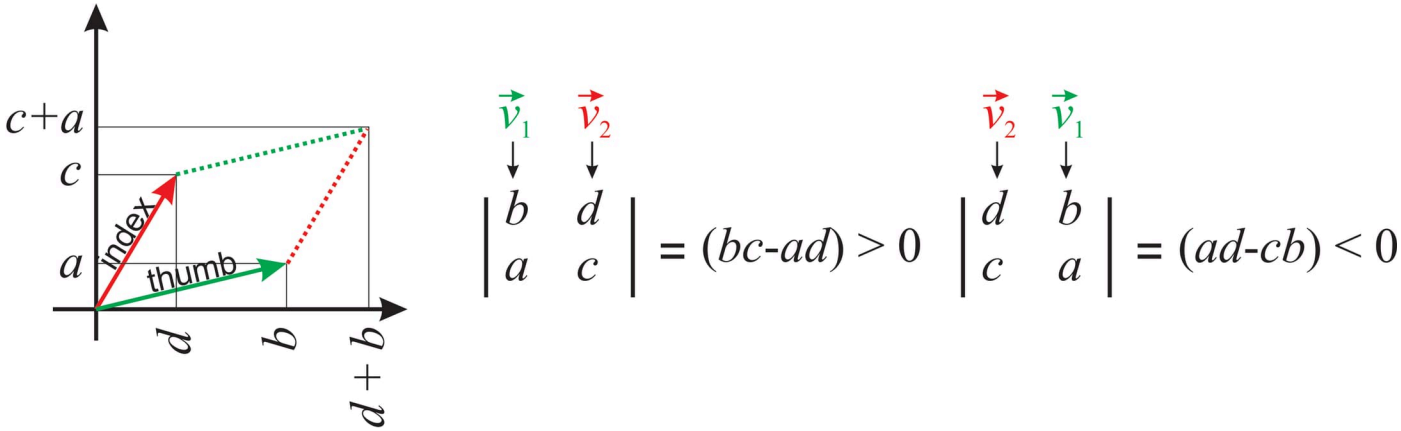


Figure 14.3.3.2: The order of the vectors in the determinant determines the sign. (CC BY-NC-SA; Marcia Levitus)

For a 3×3 determinant, its absolute value represents the volume of the parallelepiped ("the box") whose edges are the vectors that are the columns of the determinant (Figure 14.3.3.3)

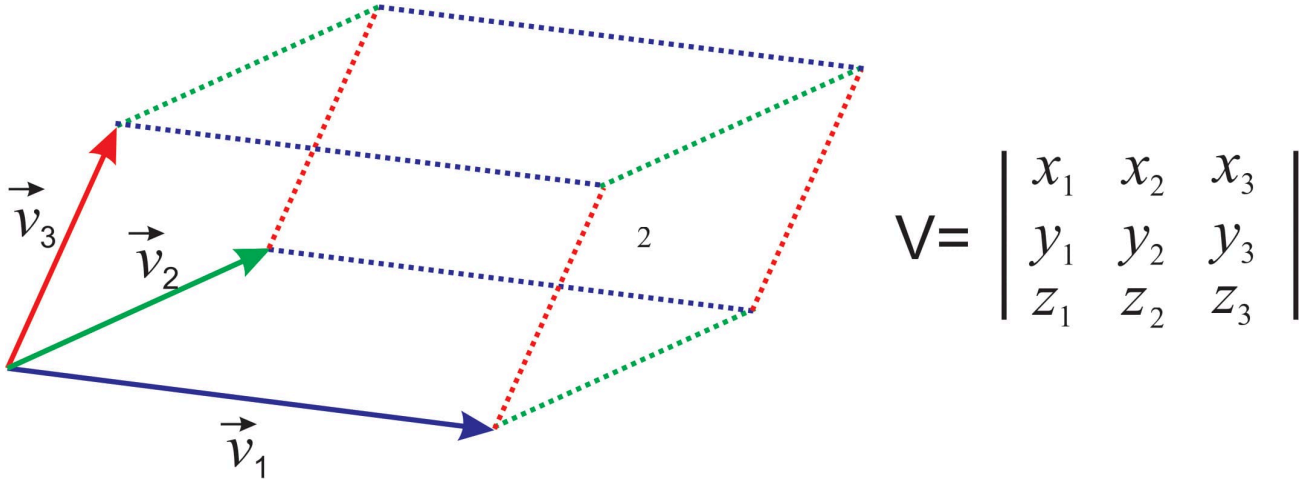


Figure 14.3.3.3: A 3× 3 determinant as the volume of a parallelepiped. (CC BY-NC-SA; Marcia Levitus)

This notion will help us understand and remember some useful properties of determinants. For example, we can readily conclude that a determinant that contains non-zero entries only in the main diagonal (top left to bottom right) is the product of the diagonal entries:

$$\begin{vmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{vmatrix} = abc$$

This is true because the columns represent vectors that are aligned with the x, y and z axes respectively, so the volume of the resulting box is the product of the dimensions along x, y and z (Figure 14.3.3.4):

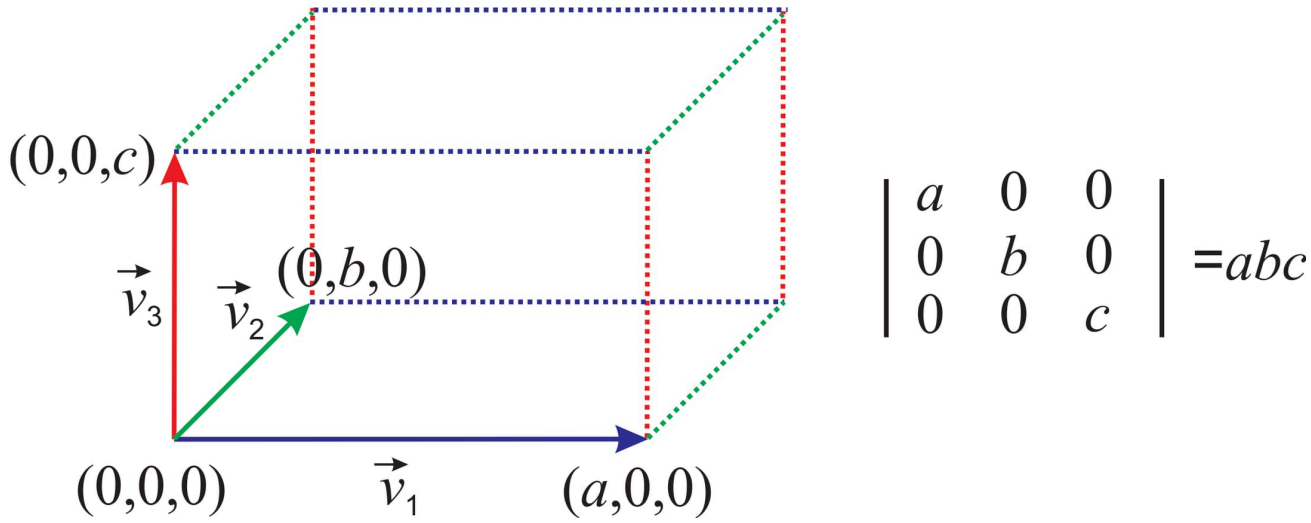


Figure 14.3.3.4: The determinant of a 3× 3 diagonal matrix (CC BY-NC-SA; Marcia Levitus)

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14.3.4: Properties of Determinants

1-

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} = 1 \tag{14.3.4.1}$$

This is true in any dimension, and can be understood easily from geometrical arguments. In two dimensions, the columns represent unitary vectors along the x and y axis, and the parallelogram is therefore a square of unit area. In three dimensions, the columns represent unitary vectors along the x, y and z axis, and the box is therefore a cube of unit volume.

2-

Antisymmetry: If two rows (or two columns) of a determinant are interchanged, the value of the determinant is multiplied by -1. This property is extremely useful in quantum mechanics, so it is worth remembering!

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = - \begin{vmatrix} b & a & c \\ e & d & f \\ h & g & i \end{vmatrix} = - \begin{vmatrix} d & e & f \\ a & b & c \\ g & h & i \end{vmatrix} \tag{14.3.4.2}$$

We already discussed this property in two dimensions (see Figure 13.3.3).

3-

Scalars can be factored out from rows and columns.

$$\begin{vmatrix} a & b & c \\ \lambda d & \lambda e & \lambda f \\ g & h & i \end{vmatrix} = \lambda \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} \tag{14.3.4.3}$$

Geometrically speaking, if you multiply the length of one of the edges of the parallelepiped by λ, the volume is also multiplied by λ.

4-

Addition rule: If all the elements of any row (or column) are written as the sum of two terms, then the determinant can be written as the sum of two determinants

$$\begin{vmatrix} a+b & c & d \\ e+f & g & h \\ i+j & k & l \end{vmatrix} = \begin{vmatrix} a & c & d \\ e & g & h \\ i & k & l \end{vmatrix} + \begin{vmatrix} b & c & d \\ f & g & h \\ j & k & l \end{vmatrix} \tag{14.3.4.4}$$

$$\begin{vmatrix} a+b & c+d & e+f \\ g & h & i \\ j & k & l \end{vmatrix} = \begin{vmatrix} a & c & e \\ g & h & i \\ j & k & l \end{vmatrix} + \begin{vmatrix} b & d & f \\ g & h & i \\ j & k & l \end{vmatrix} \tag{14.3.4.5}$$

5-

The value of a determinant is zero if two rows or two columns are equal. This is a consequence of property 2. Exchanging the two identical rows is supposed to change the sign of the determinant, but we know that exchanging two identical rows does nothing to the determinant. Therefore, the determinant has to be zero.

Geometrically, two edges of the box would be the same, rendering a flat box with no volume.

$$\begin{vmatrix} a & a & b \\ c & c & d \\ e & e & f \end{vmatrix} = 0 \tag{14.3.4.6}$$

6-

The value of a determinant is unchanged if one row or column is added or subtracted to another. This property is a consequence of properties 4 and 5:

$$\begin{vmatrix} a+b & b & c \\ d+e & e & f \\ g+h & h & i \end{vmatrix} = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} + \begin{vmatrix} b & b & c \\ e & e & f \\ h & h & i \end{vmatrix} \tag{14.3.4.7}$$

7-

A special case of property 3 is that if all the elements of a row or column are zero, the value of the determinant is zero. In geometrical terms, if one of the edges is a point, the volume is zero.

$$\begin{vmatrix} a & b & c \\ 0 & 0 & 0 \\ d & e & f \end{vmatrix} = 0 \tag{14.3.4.8}$$

8-

The value of a determinant is zero if one row (or column) is a multiple of another row (or column). Geometrically, this means that two edges of the parallelepiped lie on the same line, and therefore the volume is zero. This is a consequence of properties 3 and 5:

$$\begin{vmatrix} a & b & c \\ \lambda a & \lambda b & \lambda c \\ d & e & f \end{vmatrix} = \lambda \begin{vmatrix} a & b & c \\ a & b & c \\ d & e & f \end{vmatrix} = 0 \tag{14.3.4.9}$$

9-

Transposition: the value of the determinant is unchanged if its rows and columns are interchanged. This property can be derived from the previous properties, although it is a little complicated for the level of this course.

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = \begin{vmatrix} a & d & g \\ b & e & h \\ c & f & i \end{vmatrix} \tag{14.3.4.10}$$

Geometrically, interchanging rows by columns rotates the parallelogram (or the box in 3D) without changing the area (or volume). Figure 14.3.4.1 shows that

$$\begin{vmatrix} b & a \\ d & c \end{vmatrix} = \begin{vmatrix} b & d \\ a & c \end{vmatrix}$$

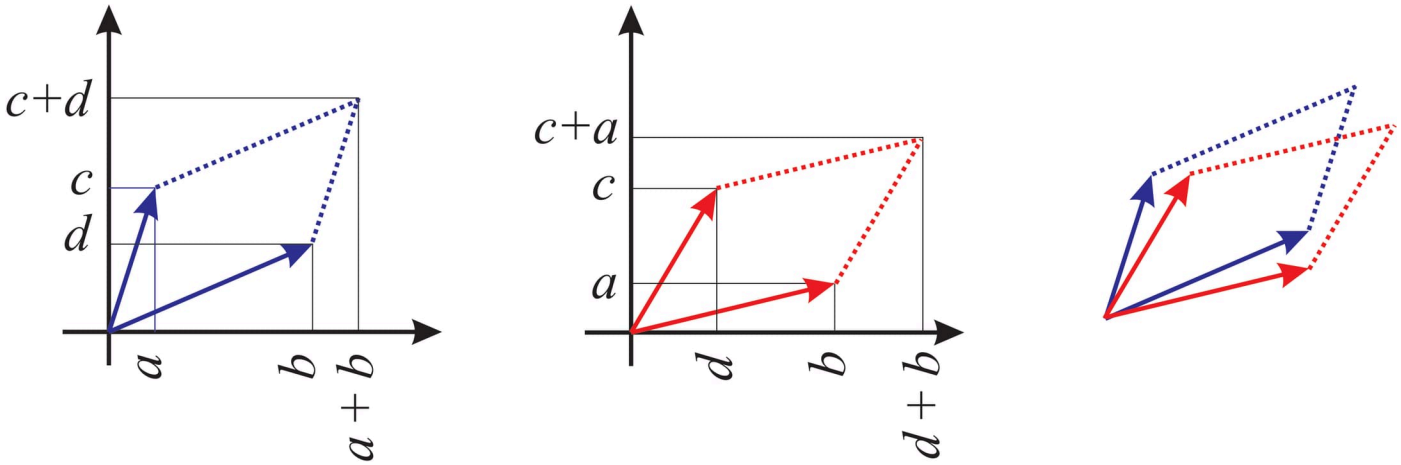


Figure 14.3.4.1: Transposing rows and columns rotates the parallelogram (CC BY-NC-SA; Marcia Levitus)

Example 14.3.4.1

Determine the value of the following determinant by inspection.

$$\begin{vmatrix} 2 & 6 & 1 \\ -4 & 4 & -2 \\ 2 & -3 & 1 \end{vmatrix}$$

Solution

We notice that the third column is a multiple of the first:

$$\begin{vmatrix} 2 & 6 & 1 \\ -4 & 4 & -2 \\ 2 & -3 & 1 \end{vmatrix} = \begin{vmatrix} 1 \times 2 & 6 & 1 \\ -2 \times 2 & 4 & -2 \\ 1 \times 2 & -3 & 1 \end{vmatrix}$$

$$= 2 \times \begin{vmatrix} 1 & 6 & 1 \\ -2 & 4 & -2 \\ 1 & -3 & 1 \end{vmatrix}$$

$$= 0$$

The determinant is zero because two of its columns are the same.

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14.3.5: Problems

Problem 14.3.5.1

Finish the problem of Example 13.1.1 and obtain y and z.

Problem 14.3.5.2

Use determinants to solve the equations:

A)

$$\begin{aligned} x+y+z &= 6 \\ x+2y+3z &= 14 \\ x+4y+9z &= 36 \end{aligned}$$

B)

$$\begin{aligned} x+iy-z &= 0 \\ ix+y+z &= 0 \\ x+2y-iz &= 1 \end{aligned}$$

Problem 14.3.5.3

Show that a 3×3 determinant that contains zeros above the principal diagonal is the product of the diagonal elements.

$$D = \begin{vmatrix} a & 0 & 0 \\ b & c & 0 \\ d & e & f \end{vmatrix} = acf$$

Problem 14.3.5.4

Prove that

$$D = \begin{vmatrix} 1 & 2 & 3 \\ 2 & 3 & 3 \\ 3 & 4 & 3 \end{vmatrix} = 0$$

using the properties of determinants (that is, without calculating the determinant!). Clearly state the properties you use in each step.

Exercise 14.3.5.5

In previous lectures, we discussed how to perform double and triple integrals in different coordinate systems. For instance, we learned that the area elements and volume elements are:

2D:

Cartesian: $dA = dx.dy$
Polar: $dA = r.dr.d\theta$

3D:

Cartesian: $dV = dx.dy.dz$
Spherical: $dV = r^2.\sin\theta dr.d\theta d\phi$

In general, for any coordinate system, we can express the area (or volume) element in a new coordinate system using the Jacobian (J). For example, in polar coordinates in two dimensions:

$$dA = dx.dy = J.dr.d\theta$$

where the Jacobian is defined as:

$$J = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} \\ \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} \end{vmatrix}$$

a) Calculate the Jacobian in two-dimensional polar coordinates and show that $dA = r.dr.d\theta$.

In spherical coordinates,

$$dV = dx.dy.dz = J.dr.d\theta.d\phi$$

where

$$J = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{vmatrix}$$

b) Calculate the Jacobian in three-dimensional spherical coordinates and show that

$$dV = r^2.\sin\theta dr.d\theta d\phi$$

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14.4: Vectors

32.03: Vectors

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14.5: Spherical Coordinates

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14.6: Matrices

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14.7: Numerical Methods

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14.8: Partial Differentiation

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14.9: Series and Limits

Maclaurin Series

A function $f(x)$ can be expressed as a series in powers of x as long as $f(x)$ and all its derivatives are finite at $x = 0$. For example, we will prove shortly that the function $f(x) = \frac{1}{1-x}$ can be expressed as the following infinite sum:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + ... \tag{14.9.1}$$

We can write this statement in this more elegant way:

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n \tag{14.9.2}$$

If you are not familiar with this notation, the right side of the equation reads "sum from $n = 0$ to $n = \infty$ of x^n." When $n = 0$, $x^n = 1$, when $n = 1$, $x^n = x$, when $n = 2$, $x^n = x^2$, etc (compare with Equation 14.9.1). The term "series in powers of x" means a sum in which each summand is a power of the variable x. Note that the number 1 is a power of x as well ($x^0 = 1$). Also, note that both Equations 14.9.1 and 14.9.2 are exact, they are not approximations.

Similarly, we will see shortly that the function e^x can be expressed as another infinite sum in powers of x (i.e. a Maclaurin series) as:

$$e^x = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \frac{1}{24}x^4 + ... \tag{14.9.3}$$

Or, more elegantly:

$$e^x = \sum_{n=0}^{\infty} \frac{1}{n!}x^n \tag{14.9.4}$$

where $n!$ is read "n factorial" and represents the product $1 \times 2 \times 3... \times n$. If you are not familiar with factorials, be sure you understand why $4! = 24$. Also, remember that by definition $0! = 1$, not zero.

At this point you should have two questions: 1) how do I construct the Maclaurin series of a given function, and 2) why on earth would I want to do this if $\frac{1}{1-x}$ and e^x are fine-looking functions as they are. The answer to the first question is easy, and although you should know this from your calculus classes we will review it again in a moment. The answer to the second question is trickier, and it is what most students find confusing about this topic. We will discuss different examples that aim to show a variety of situations in which expressing functions in this way is helpful.

How to obtain the Maclaurin Series of a Function

In general, a well-behaved function ($f(x)$ and all its derivatives are finite at $x = 0$) will be expressed as an infinite sum of powers of x like this:

$$f(x) = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + ... + a_n x^n \tag{14.9.5}$$

Be sure you understand why the two expressions in Equation 14.9.5 are identical ways of expressing an infinite sum. The terms a_n are called the **coefficients**, and are constants (that is, they are NOT functions of x). If you end up with the variable x in one of your coefficients go back and check what you did wrong! For example, in the case of e^x (Equation 14.9.3), $a_0 = 1, a_1 = 1, a_2 = 1/2, a_3 = 1/6, etc$. In the example of Equation 14.9.1, all the coefficients equal 1. We just saw that two very different functions can be expressed using the same set of functions (the powers of x). What makes $\frac{1}{1-x}$ different from e^x are the coefficients a_n.

As we will see shortly, the coefficients can be negative, positive, or zero.

How do we calculate the coefficients? Each coefficient is calculated as:

$$a_n = \frac{1}{n!}\left(\frac{d^n f(x)}{dx^n}\right)_0 \tag{14.9.6}$$

That is, the n-th coefficient equals one over the factorial of n multiplied by the n-th derivative of the function $f(x)$ evaluated at zero. For example, if we want to calculate a_2 for the function $f(x) = \frac{1}{1-x}$, we need to get the second derivative of $f(x)$, evaluate it at $x = 0$, and divide the result by $2!$. Do it yourself and verify that $a_2 = 1$. In the case of a_0 we need the zeroth-order derivative, which equals the function itself (that is, $a_0 = f(0)$, because $\frac{1}{0!} = 1$). It is important to stress that although the derivatives are usually functions of x, the coefficients are constants because they are expressed in terms of the derivatives evaluated at $x = 0$.

Note that in order to obtain a Maclaurin series we evaluate the function and its derivatives at $x = 0$. This procedure is also called the expansion of the function around (or about) zero. We can expand functions around other numbers, and these series are called Taylor series (see Section 3).

Example 14.9.1

Obtain the Maclaurin series of $sin(x)$.

Solution

We need to obtain all the coefficients ($a_0, a_1 ... etc$). Because there are infinitely many coefficients, we will calculate a few and we will find a general pattern to express the rest. We will need several derivatives of $sin(x)$, so let's make a table:

n	$\frac{d^n f(x)}{dx^n}$	$\left(\frac{d^n f(x)}{dx^n}\right)_0$
0	$\sin(x)$	0
1	$\cos(x)$	1
2	$-\sin(x)$	0
3	$-\cos(x)$	-1
4	$\sin(x)$	0
5	$\cos(x)$	1

Remember that each coefficient equals $\left(\frac{d^n f(x)}{dx^n}\right)_0$ divided by $n!$, therefore:

n	$n!$	a_n
0	1	0
1	1	1
2	2	0
3	6	$-\frac{1}{6}$
4	24	0
5	120	$\frac{1}{120}$

This is enough information to see the pattern (you can go to higher values of n if you don't see it yet):

1. the coefficients for even values of n equal zero.
2. the coefficients for $n = 1, 5, 9, 13, ...$ equal $1/n!$
3. the coefficients for $n = 3, 7, 11, 15, ...$ equal $-1/n!$.

Recall that the general expression for a Maclaurin series is $a_0 + a_1x + a_2x^2...a_nx^n$, and replace $a_0...a_n$ by the coefficients we just found:

$$\sin(x) = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7...$$

This is a correct way of writing the series, but in the next example we will see how to write it more elegantly as a sum.

Example 14.9.2

Express the Maclaurin series of $\sin(x)$ as a sum.

Solution

In the previous example we found that:

$$\sin(x) = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7... \tag{14.9.7}$$

We want to express this as a sum:

$$\sum_{n=0}^{\infty} a_n x^n$$

The key here is to express the coefficients a_n in terms of n. We just concluded that 1) the coefficients for even values of n equal zero, 2) the coefficients for $n = 1, 5, 9, 13, ...$ equal $1/n!$ and 3) the coefficients for $n = 3, 7, 11, ...$ equal $-1/n!$. How do we put all this information together in a unique expression? Here are three possible (and equally good) answers:

- $\sin(x) = \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n+1)!} x^{2n+1}$
- $\sin(x) = \sum_{n=1}^{\infty} (-1)^{(n+1)} \frac{1}{(2n-1)!} x^{2n-1}$
- $\sin(x) = \sum_{n=0}^{\infty} cos(n\pi) \frac{1}{(2n+1)!} x^{2n+1}$

This may look impossibly hard to figure out, but let me share a few tricks with you. First, we notice that the sign in Equation 14.9.7 alternates, starting with a "+". A mathematical way of doing this is with a term $(-1)^n$ if your sum starts with $n = 0$, or $(-1)^{(n+1)}$ if you sum starts with $n = 1$. Note that $\cos(n\pi)$ does the same trick.

n	$(-1)^n$	$(-1)^{n+1}$	$\cos(n\pi)$
0	1	-1	1
1	-1	1	-1
2	1	-1	1
3	-1	1	-1

We have the correct sign for each term, but we need to generate the numbers $1, \frac{1}{3!}, \frac{1}{5!}, \frac{1}{7!}, \ldots$ Notice that the number "1" can be expressed as $\frac{1}{1!}$. To do this, we introduce the second trick of the day: we will use the expression $2n+1$ to generate odd numbers (if you start your sum with $n=0$) or $2n-1$ (if you start at $n=1$). Therefore, the expression $\frac{1}{(2n+1)!}$ gives $1, \frac{1}{3!}, \frac{1}{5!}, \frac{1}{7!}, \ldots$, which is what we need in the first and third examples (when the sum starts at zero).

Lastly, we need to use only odd powers of x. The expression $x^{(2n+1)}$ generates the terms $x, x^3, x^5 \ldots$ when you start at $n=0$, and $x^{(2n-1)}$ achieves the same when you start your series at $n=1$.

Confused about writing sums using the sum operator $(\sum)$? This video will help: http://tinyurl.com/lvwd36q

Need help? The links below contain solved examples.

External links:

Finding the maclaurin series of a function I: http://patrickjmt.com/taylor-and-maclaurin-series-example-1/

Finding the maclaurin series of a function II: http://www.youtube.com/watch?v= dp2ovDuWhro

Finding the maclaurin series of a function III: http://www.youtube.com/watch?v= WWe7pZjc4s8

Graphical Representation

From Equation 14.9.5 and the examples we discussed above, it should be clear at this point that any function whose derivatives are finite at $x=0$ can be expressed by using the same set of functions: the powers of x. We will call these functions the **basis set**. A basis set is a collection of linearly independent functions that can represent other functions when used in a linear combination.

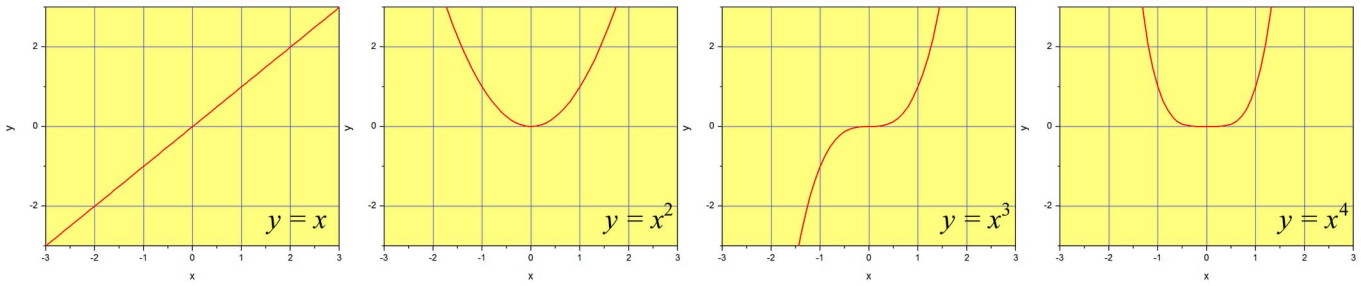


Figure 14.9.1: Some of the functions of the basis set for a Maclaurin expansion (CC BY-NC-SA; Marcia Levitus)

Figure 14.9.1 is a graphic representation of the first four functions of this basis set. To be fair, the first function of the set is $x^0 = 1$, so these would be the second, third, fourth and fifth. The full basis set is of course infinite in length. If we mix all the functions of the set with equal weights (we put the same amount of x^2 than we put x^{245} or x^0), we obtain $(1-x)^{-1}$ (Equation 14.9.1. If we use only the odd terms, alternate the sign starting with a '+', and weigh each term less and less using the expression $1/(2n-1)!$ for the $n-th$ term, we obtain $\sin x$ (Equation 14.9.7). This is illustrated in Figure 14.9.2, where we multiply the even powers of x by zero, and use different weights for the rest. Note that the 'etcetera' is crucial, as we would need to include an infinite number of functions to obtain the function $\sin x$ exactly.

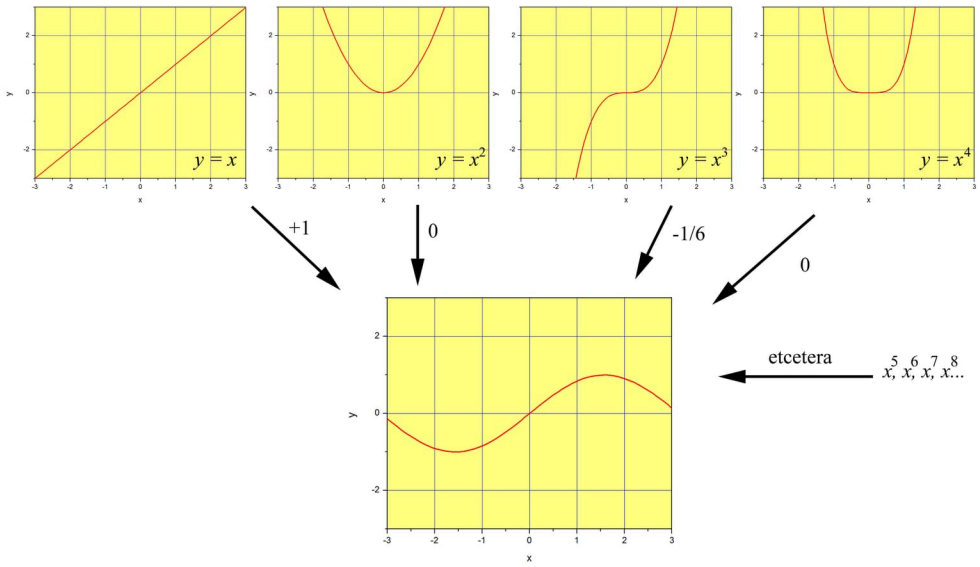


Figure 14.9.2: Construction of $\sin x$ using the powers of x as the basis set. (CC BY-NC-SA; Marcia Levitus)

Although we need an infinite number of terms to express a function exactly (unless the function is a polynomial, of course), in many cases we will observe that the weight (the coefficient) of each power of x gets smaller and smaller as we increase the power. For example, in the case of $\sin x$, the contribution of x^3 is $1/6th$ of the contribution of x (in absolute terms), and the contribution of x^5 is $1/120th$. This tells you that the first terms are much more important than the rest, although all are needed if we want the sum to represent $\sin x$ exactly. What if we are happy with a 'pretty good' approximation of $\sin x$? Let's see what happens if we use up to x^3 and drop the higher terms. The result is plotted in blue in Figure 14.9.3 together with $\sin x$ in red. We can see that the function $x - 1/6x^3$ is a very good approximation of $\sin x$ as long as we stay close to $x = 0$. As we move further away from the origin the approximation gets worse and worse, and we would need to include higher powers of x to get it better. This should be clear from eq. [series:sin], since the terms x^n get smaller and smaller with increasing n if x is a small number. Therefore, if x is small, we could write $\sin(x) \approx x - \frac{1}{3!}x^3$, where the symbol $\approx$ means approximately equal.

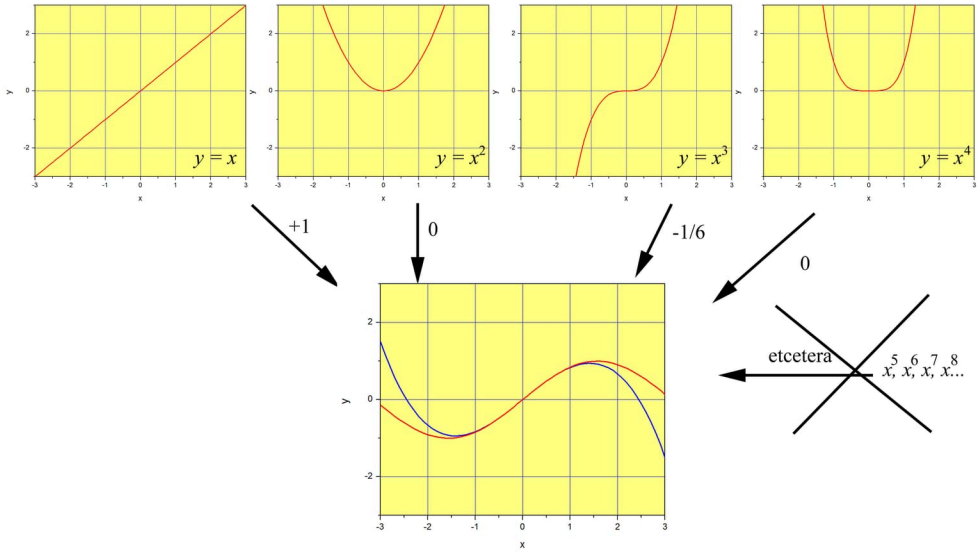


Figure 14.9.3: Approximation of $\sin x$ up to the third power of x. The curve in blue is the function $x - 1/6x^3$, and the curve in red is $\sin x$ (CC BY-NC-SA; Marcia Levitus)

But why stopping at $n = 3$ and not $n = 1$ or 5? The above argument suggests that the function x might be a good approximation of $\sin x$ around $x = 0$, when the term x^3 is much smaller than the term x. This is in fact this is the case, as shown in Figure 14.9.4.

We have seen that we can get good approximations of a function by **truncating** the series (i.e. not using the infinite terms).

Students usually get frustrated and want to know how many terms are 'correct'. It takes a little bit of practice to realize there is no universal answer to this question. We would need some context to analyze how good of an approximation we are happy with. For example, are we satisfied with the small error we see at $x = 0.5$ in Figure $14.9.4$? It all depends on the context. Maybe we are performing experiments where we have other sources of error that are much worse than this, so using an extra term will not improve the overall situation anyway. Maybe we are performing very precise experiments where this difference is significant. As you see, discussing how many terms are needed in an approximation out of context is not very useful. We will discuss this particular approximation when we learn about second order differential equations and analyze the problem of the pendulum, so hopefully things will make more sense then.

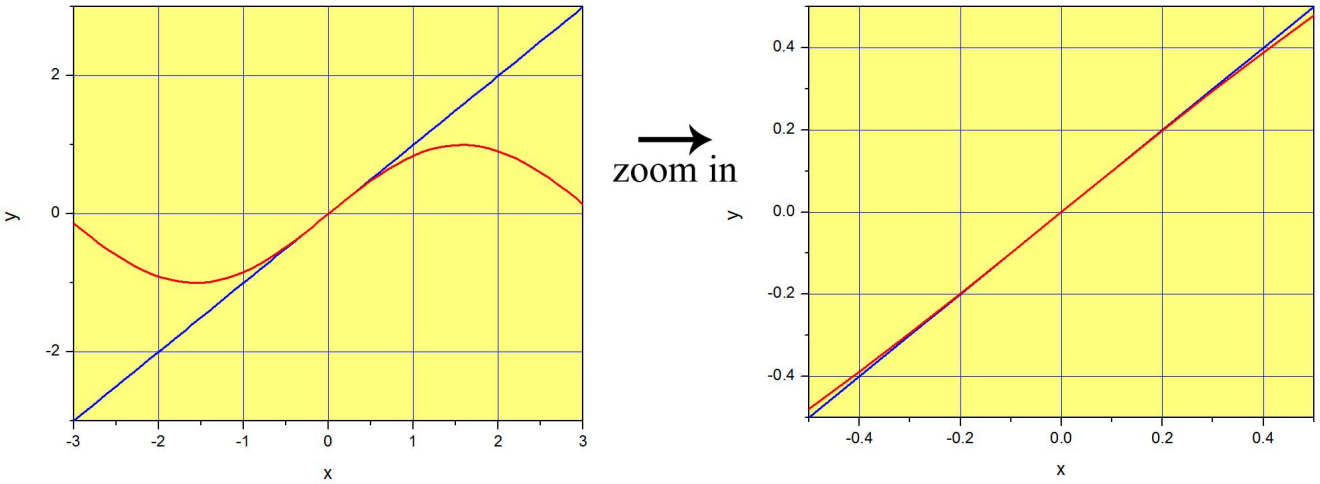


Figure $14.9.4$: Approximation of $\sin x$ up to the first power of x. The curve in blue is the function x, and the curve in red is $\sin x$ (CC BY-NC-SA; Marcia Levitus)

Linear Approximations

If you take a look at Equation $3.1.5$ you will see that we can always approximate a function as $a_0 + a_1 x$ as long as x is small. When we say 'any function' we of course imply that the function and all its derivatives need to be finite at $x = 0$. Looking at the definitions of the coefficients, we can write:

Label 'eq1' multiply defined

We call this a linear approximation because Equation $14.9.1$ is the equation of a straight line. The slope of this line is $f'(0)$ and the y-intercept is $f(0)$.

A fair question at this point is 'why are we even talking about approximations?' What is so complicated about the functions $\sin x$, e^x or $\ln(x+1)$ that we need to look for an approximation? Are we getting too lazy? To illustrate this issue, let's consider the problem of the pendulum, which we will solve in detail in the chapter devoted to differential equations. The problem is illustrated in Figure $14.9.1$, and those of you who took a physics course will recognize the equation below, which represents the law of motion of a simple pendulum. The second derivative refers to the acceleration, and the $\sin\theta$ term is due to the component of the net force along the direction of motion. We will discuss this in more detail later in this semester, so for now just accept the fact that, for this system, Newton's law can be written as:

$$\frac{d^2\theta(t)}{dt^2} + \frac{g}{l}\sin\theta(t) = 0$$

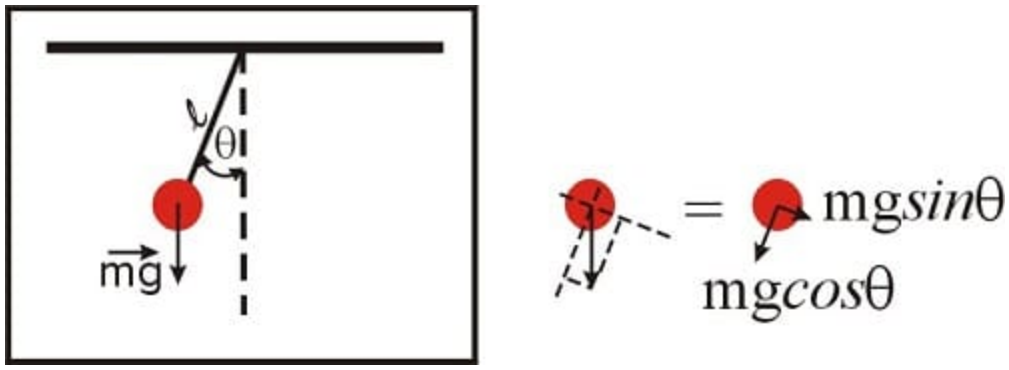


Figure 14.9.1: A rigid pendulum with massless and inextensible cord of length l. The motion is assumed to occur in two dimensions, and the friction is assumed to be negligible. The mass of the object is m, and g is the acceleration due to gravity. (CC BY-NC-SA; Marcia Levitus)

This equation should be easy to solve, right? It has only a few terms, nothing too fancy other than an innocent sine function...How difficult can it be to obtain $\theta(t)$? Unfortunately, this differential equation does not have an analytical solution! An analytical solution means that the solution can be expressed in terms of a finite number of elementary functions (such as sine, cosine, exponentials, etc). Differential equations are sometimes deceiving in this way: they look simple, but they might be incredibly hard to solve, or even impossible! The fact that we cannot write down an analytical solution does not mean there is no solution to the problem. You can swing a pendulum and measure $\theta(t)$ and create a table of numbers, and in principle you can be as precise as you want to be. Yet, you will not be able to create a function that reflects your numeric results. We will see that we can solve equations like this numerically, but not analytically. Disappointing, isn't it? Well... don't be. A lot of what we know about molecules and chemical reactions came from the work of physical chemists, who know how to solve problems using numerical methods. The fact that we cannot obtain an analytical expression that describes a particular physical or chemical system does not mean we cannot solve the problem numerically and learn a lot anyway!

But what if we are interested in small displacements only (that is, the pendulum swings close to the vertical axis at all times)? In this case, $\theta << 1$, and as we saw $\sin\theta \approx \theta$ (see Figure 3.1.4). If this is the case, we have now:

$$\frac{d^2\theta(t)}{dt^2} + \frac{g}{l}\theta(t) = 0$$

As it turns out, and as we will see in Chapter 2, in this case it is very easy to obtain the solution we are looking for:

$$\theta(t) = \theta(t=0)\cos\left((\frac{g}{l})^{1/2}t\right)$$

This solution is the familiar 'back and forth' oscillatory motion of the pendulum you are familiar with. What you might have not known until today is that this solution assumes $\sin\theta \approx \theta$ and is therefore valid only if $\theta << 1$!

There are lots of 'hidden' linear approximations in the equations you have learned in your physics and chemistry courses. You may recall your teachers telling you that a give equation is valid only at low concentrations, or low pressures, or low... you hopefully get the point. A pendulum is of course not particularly interesting when it comes to chemistry, but as we will see through many examples during the semester, oscillations, generally speaking, are. The example below illustrates the use of series to a problem involving diatomic molecules, but before discussing it we need to provide some background.

The vibrations of a diatomic molecule are often modeled in terms of the so-called *Morse potential*. This equation does not provide an exact description of the vibrations of the molecule under any condition, but it does a pretty good job for many purposes.

$$V(R) = D_e\left(1 - e^{-k(R-R_e)}\right)^2 \tag{14.9.8}$$

Here, R is the distance between the nuclei of the two atoms, R_e is the distance at equilibrium (i.e. the equilibrium bond length), D_e is the dissociation energy of the molecule, k is a constant that measures the strength of the bond, and V is the potential energy. Note that R_e is the distance at which the potential energy is a minimum, and that is why we call this the equilibrium distance. We would need to apply energy to separate the atoms even more, or to push them closer (Figure 14.9.2).

At room temperature, there is enough thermal energy to induce small vibrations that displace the atoms from their equilibrium positions, but for stable molecules, the displacement is very small: $R - R_e \to 0$. In the next example we will prove that under these conditions, the potential looks like a parabola, or in mathematical terms, $V(R)$ is proportional to the square of the displacement.

This type of potential is called a 'harmonic potential'. A vibration is said to be simple harmonic if the potential is proportional to the square of the displacement (as in the simple spring problems you may have studied in physics).

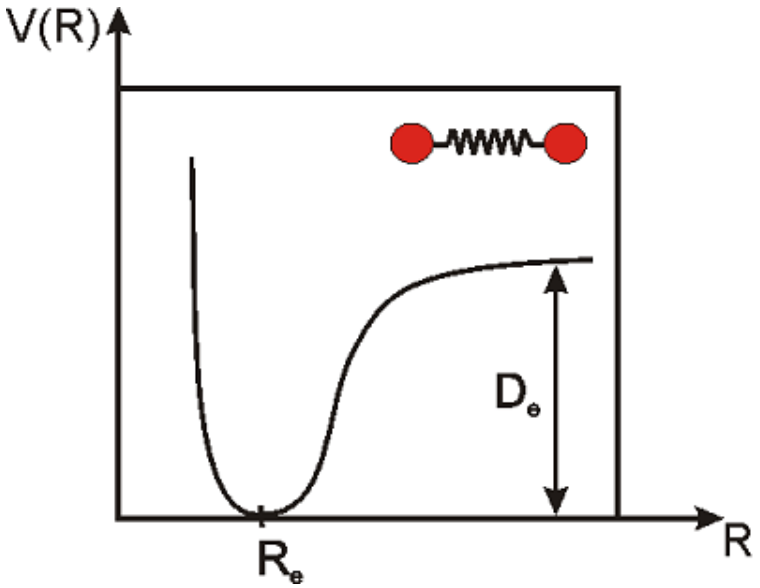


Figure 14.9.2: The Morse potential (CC BY-NC-SA; Marcia Levitus)

Example 14.9.1

Expand the Morse potential as a power series and prove that the vibrations of the molecule are approximately simple harmonic if the displacement $R - R_e$ is small.

Solution

The relevant variable in this problem is the displacement $R - R_e$, not the actual distance R. Let's call the displacement $R - R_e = x$, and let's rewrite Equation 14.9.8 as

$$V(R) = D_e \left(1 - e^{-kx}\right)^2 \tag{14.9.9}$$

The goal is to prove that $V(R) = cx^2$ (i.e. the potential is proportional to the square of the displacement) when $x \to 0$. The constant c is the proportionality constant. We can approach this in two different ways. One option is to expand the function shown in Equation 14.9.9 around zero. This would be correct, but it but involve some unnecessary work. The variable x appears only in the exponential term, so a simpler option is to expand the exponential function, and plug the result of this expansion back in Equation 14.9.9. Let's see how this works:

We want to expand e^{-kx} as $a_0 + a_1x + a_2x^2 ... a_nx^n$, and we know that the coefficients are $a_n = \frac{1}{n!}\left(\frac{d^n f(x)}{dx^n}\right)_0$.
The coefficient a_0 is $f(0) = 1$. The first three derivatives of $f(x) = e^{-kx}$ are

- $f'(x) = -ke^{-kx}$
- $f''(x) = k^2e^{-kx}$
- $f'''(x) = -k^3e^{-kx}$

When evaluated at $x = 0$ we obtain, $-k, k^2, -k^3 ...$

and therefore $a_n = \frac{(-1)^n k^n}{n!}$ for $n = 0, 1, 2....$

Therefore,

$$e^{-kx} = 1 - kx + k^2x^2/2! - k^3x^3/3! + k^4x^4/4! ...$$

and

$$1-e^{-kx}=+kx-k^2x^2/2!+k^3x^3/3!-k^4x^4/4!...$$

From the last result, when $x<<1$, we know that the terms in $x^2, x^3...$ will be increasingly smaller, so $1-e^{-kx}\approx kx$ and $(1-e^{-kx})^2\approx k^2x^2$.

Plugging this result in Equation 14.9.9 we obtain $V(R)\approx D_e k^2x^2$, so we demonstrated that the potential is proportional to the square of the displacement when the displacement is small (the proportionality constant is $D_e k^2$). Therefore, stable diatomic molecules at room temperatures behave pretty much like a spring! (Don't take this too literally. As we will discuss later, microscopic springs do not behave like macroscopic springs at all).

Taylor Series

Before discussing more applications of Maclaurin series, let's expand our discussion to the more general case where we expand a function around values different from zero. Let's say that we want to expand a function around the number h. If $h=0$, we call the series a Maclaurin series, and if $h\neq 0$ we call the series a Taylor series. Because Maclaurin series are a special case of the more general case, we can call all the series Taylor series and omit the distinction. The following is true for a function $f(x)$ as long as the function and all its derivatives are finite at h:

$$f(x)=a_0+a_1(x-h)+a_2(x-h)^2+...+a_n(x-h)^n=\sum_{n=0}^{\infty}a_n(x-h)^n \tag{14.9.10}$$

The coefficients are calculated as

$$a_n=\frac{1}{n!}\left(\frac{d^nf}{dx^n}\right)_h \tag{14.9.11}$$

Notice that instead of evaluating the function and its derivatives at $x=0$ we now evaluate them at $x=h$, and that the basis set is now $1,(x-h),(x-h)^2,...,(x-h)^n$ instead of $1,x,x^2,...,x^n$. A Taylor series will be a good approximation of the function at values of x close to h, in the same way Maclaurin series provide good approximations close to zero.

To see how this works let's go back to the exponential function. Recall that the Maclaurin expansion of e^x is shown in Equation 3.1.3. We know what happens if we expand around zero, so to practice, let's expand around $h=1$. The coefficient a_0 is $f(1)=e^1=e$. All the derivatives are e^x, so $f'(1)=f''(1)=f'''(1)...=e$. Therefore, $a_n=\frac{e}{n!}$ and the series is therefore

$$e\left[1+(x-1)+\frac{1}{2}(x-1)^2+\frac{1}{6}(x-1)^3+...\right]=\sum_{n=0}^{\infty}\frac{e}{n!}(x-1)^n \tag{14.9.12}$$

We can use the same arguments we used before to conclude that $e^x\approx ex$ if $x\approx 1$. If $x\approx 1$, $(x-1)\approx 0$, and the terms $(x-1)^2,(x-1)^3$ will be smaller and smaller and will contribute less and less to the sum. Therefore,

$$e^x\approx e\left[1+(x-1)\right]=ex.$$

This is the equation of a straight line with slope e and y-intercept 0. In fact, from Equation 3.1.7 we can see that all functions will look linear at values close to h. This is illustrated in Figure 14.9.1, which shows the exponential function (red) together with the functions $1+x$ (magenta) and ex (blue). Not surprisingly, the function $1+x$ provides a good approximation of e^x at values close to zero (see Equation 3.1.3) and the function ex provides a good approximation around $x=1$ (Equation 14.9.12).

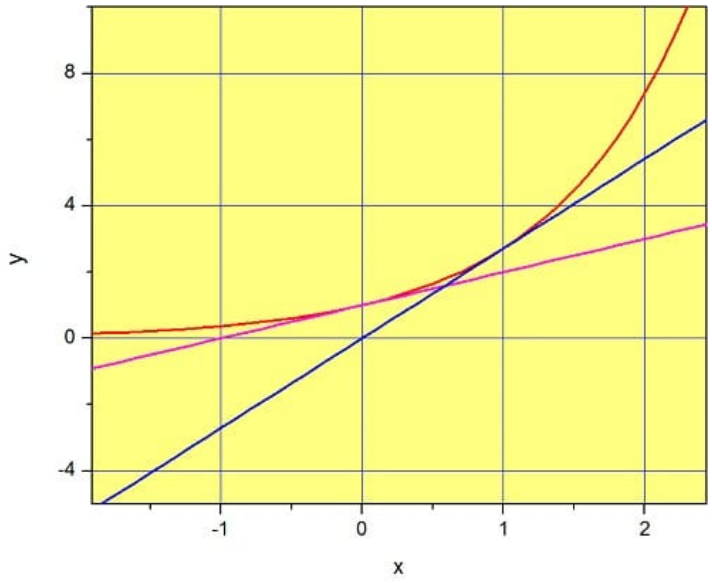


Figure 14.9.1: Two linear approximations of the exponential function. The function e^x is plotted in red together with the function $y = 1 + x$ (magenta) and $y = ex$ (blue). (CC BY-NC-SA; Marcia Levitus)

Example 14.9.1:

Expand $f(x) = \ln x$ about $x = 1$

Solution

$$f(x) = a_0 + a_1(x-h) + a_2(x-h)^2 + \ldots + a_n(x-h)^n, a_n = \frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_h$$

$$a_0 = f(1) = \ln(1) = 0$$

The derivatives of $\ln x$ are:

$$f'(x) = 1/x, f''(x) = -1/x^2, f'''(x) = 2/x^3, f^{(4)}(x) = -6/x^4, f^{(5)}(x) = 24/x^5 \ldots$$

and therefore,

$$f'(1) = 1, f''(1) = -1, f'''(1) = 2, f^{(4)}(1) = -6, f^{(5)}(1) = 24 \ldots.$$

To calculate the coefficients, we need to divide by $n!$:

- $a_1 = f'(1)/1! = 1$
- $a_2 = f''(1)/2! = -1/2$
- $a_3 = f'''(1)/3! = 2/3! = 1/3$
- $a_4 = f^{(4)}(1)/4! = -6/4! = -1/4$
- $a_n = (-1)^{n+1}/n$

The series is therefore:

$$f(x) = 0 + 1(x-1) - 1/2(x-1)^2 + 1/3(x-1)^3 \ldots = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n}(x-1)^n$$

Note that we start the sum at $n = 1$ because $a_0 = 0$, so the term for $n = 0$ does not have any contribution.

Need help? The links below contain solved examples.

External links:

Finding the Taylor series of a function I: http://patrickjmt.com/taylor-and-maclaurin-series-example-2/

Other Applications of Mclaurin and Taylor series

So far we have discussed how we can use power series to approximate more complex functions around a particular value. This is very common in physical chemistry, and you will apply it frequently in future courses. There are other useful applications of Taylor series in the physical sciences. Sometimes, we may use relationships to derive equations or prove relationships. Example $14.9.1$ illustrates this last point.

Example $14.9.1$

Calculate the following sum (λ is a positive constant)

$$\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!}$$

Solution

Let's 'spell out' the sum:

$$\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!} = e^{-\lambda}\left[1 + \frac{\lambda^1}{1!} + \frac{\lambda^2}{2!} + \frac{\lambda^3}{3!}...\right]$$

The sum within the brackets is exactly e^{λ}. This is exact, and not an approximation, because we have all infinite terms.

Therefore,

$$\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!} = e^{-\lambda}e^{\lambda} = 1$$

This would require that you recognize the term within brackets as the Maclaurin series of the exponential function. One simpler version of the problem would be to ask you to prove that the sum equals 1.

There are more ways we can use Taylor series in the physical sciences. We will see another type of application when we study differential equations. In fact, power series are extremely important in finding the solutions of a large number of equations that arise in quantum mechanics. The description of atomic orbitals, for example, require that we solve differential equations that involve expressing functions as power series.

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14.10: FOURIER ANALYSIS

The Fourier transform converts a function vs. continuous (or descrete) time and maps it into a function vs. continuous (or descrete) frequencies. Hence, the transform converts *time-domain* data into *frequency-domain* data (and vice versa). This decomposion of a function into sinusoids of different frequencies is a powerful approach to many experimental and theoretical problems. **Fourier transform spectroscopy** is an approach whereby spectra are collected based on measurements using time-domain or space-domain measurements of the electromagnetic radiation or other type of radiation. It can be applied to a variety of types of spectroscopy including optical spectroscopy, infrared spectroscopy (FT IR, FT-NIRS), Fourier transform nuclear magnetic resonance (NMR), mass spectrometry and electron spin resonance spectroscopy.

Introduction

Fourier analysis is a subject area which grew out of the study of Fourier series. The subject began with trying to understand when it was possible to represent general functions by sums of simpler trigonometric functions. The attempt to understand functions (or other objects) by breaking them into basic pieces that are easier to understand is one of the central themes in Fourier analysis. Fourier analysis is named after Joseph Fourier who showed that representing a function by a trigonometric series greatly simplified the study of heat propagation. Today the subject of Fourier analysis encompasses a vast spectrum of mathematics with parts that, at first glance, may appear quite different. In the sciences and engineering the process of decomposing a function into simpler pieces is often called an **analysis**. In Fourier analysis, the term Fourier transform often refers to the process that decomposes a given function into the basic pieces. This process results in another function that describes how much of each basic piece are in the original function. However, the transform is often given a more specific name depending upon the domain and other properties of the function being transformed, as elaborated below. Moreover, the original concept of Fourier analysis has been extended over time to apply to more and more abstract and general situations, and the general field is often known as harmonic analysis.

Fourier Series

When the function f is a function of time and represents a physical signal, the transform has a standard interpretation as the frequency spectrum of the signal. The magnitude of the resulting complex-valued function F at frequency ω represents the amplitude of a frequency component whose initial phase is given by the phase of F. However, it is important to realize that Fourier transforms are not limited to functions of time, and temporal frequencies. They can equally be applied to analyze *spatial* frequencies, and indeed for nearly any function domain.

Properties

http://www.math.ubc.ca/~feldman/demos/demo3.html

Continuous Fourier Trasnform (CFT)

Most often, the unqualified term **Fourier transform** refers to the transform of functions of a continuous real argument, such as time (t). In this case the Fourier transform describes a function $f(t)$ in terms of basic complex exponentials of various frequencies. In terms of ordinary frequency ν, the Fourier transform is given by the complex number**:**

$$F(\nu) = \int_{-\infty}^{\infty} f(t) \cdot e^{-2\pi \cdot i \cdot \nu \cdot t} dt.$$

Evaluating this quantity for all values of ν produces the *frequency-domain* function.

Discrete Fourier Transform (DFT)

Experimentally, we collect data that is not continuous, but samples a measurements at specific point. Hence we have to deal with

the discrete version of the Fourier Transform.

Fast Fourier Transfer (FFT)

The discrete version of the Fourier transform (see below) can be evaluated quickly on computers using fast Fourier transform (FFT) algorithms. This algortihm sympically requires a 2^n number of measurements to operate. Hence you will notice data sets often with such dimensions. (Conte & de Boor 1980)

References

1. Arfken, G. "Fourier Series." Ch. 14 in *Mathematical Methods for Physicists, 3rd ed.* Orlando, FL: Academic Press, pp. 760-793, 1985.
2. Askey, R. and Haimo, D. T. "Similarities between Fourier and Power Series." *Amer. Math. Monthly* **103**, 297-304, 1996.
3. Beyer, W. H. (Ed.). *CRC Standard Mathematical Tables, 28th ed.* Boca Raton, FL: CRC Press, 1987.
4. Brown, J. W. and Churchill, R. V. *Fourier Series and Boundary Value Problems, 5th ed.* New York: McGraw-Hill, 1993.
5. Byerly, W. E. *An Elementary Treatise on Fourier's Series, and Spherical, Cylindrical, and Ellipsoidal Harmonics, with Applications to Problems in Mathematical Physics.* New York: Dover, 1959.
6. Carslaw, H. S. *Introduction to the Theory of Fourier's Series and Integrals, 3rd ed., rev. and enl.* New York: Dover, 1950.
7. Davis, H. F. *Fourier Series and Orthogonal Functions.* New York: Dover, 1963.
8. Dym, H. and McKean, H. P. *Fourier Series and Integrals.* New York: Academic Press, 1972.
9. Folland, G. B. *Fourier Analysis and Its Applications.* Pacific Grove, CA: Brooks/Cole, 1992.
10. Groemer, H. *Geometric Applications of Fourier Series and Spherical Harmonics.* New York: Cambridge University Press, 1996.
11. Körner, T. W. *Fourier Analysis.* Cambridge, England: Cambridge University Press, 1988.
12. Körner, T. W. *Exercises for Fourier Analysis.* New York: Cambridge University Press, 1993.
13. Krantz, S. G. "Fourier Series." §15.1 in *Handbook of Complex Variables.* Boston, MA: Birkhäuser, pp. 195-202, 1999.
14. Lighthill, M. J. *Introduction to Fourier Analysis and Generalised Functions.* Cambridge, England: Cambridge University Press, 1958.
15. Morrison, N. *Introduction to Fourier Analysis.* New York: Wiley, 1994.
16. Sansone, G. "Expansions in Fourier Series." Ch. 2 in *Orthogonal Functions, rev. English ed.* New York: Dover, pp. 39-168, 1991.
17. Weisstein, E. W. "Books about Fourier Transforms." http://www.ericweisstein.com/encyclopedias/books/FourierTransforms.html.
18. Whittaker, E. T. and Robinson, G. "Practical Fourier Analysis." Ch. 10 in *The Calculus of Observations: A Treatise on Numerical Mathematics, 4th ed.* New York: Dover, pp. 260-284, 1967.
19. R. R. Williams Spectroscopy and the Fourier Transform Wiley: New York, 1995
20. Bettis, Cliff; Lyons, Edward J.; Brooks, David W. J. Chem. Educ. 1996, 73, 839
21. Graff, Daria K. J. Chem. Educ. 1995, 72, 304.
22. Chesick, John P. J. Chem. Educ. 1989, 66, 128.
23. Glasser, L. J. Chem. Educ. 1987, 64, A228.
24. Glasser, L. J.Chem. Educ. 1987, 64, A255.
25. Glasser, L. J. Chem. Educ. 1987, 64, A306.

Contributors and Attributions

- Wikipedia entry (to begin with)
- mmrc.caltech.edu/FTIR/FTIRintro.pdf

14.10.1: Fourier Analysis in Matlab

14.10.2: Fourier Synthesis of Periodic Waveforms

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14.10.1: Fourier Analysis in Matlab

Fourier analysis encompasses a vast spectrum of mathematics with parts that, at first glance, may appear quite different. In the sciences and engineering the process of decomposing a function into simpler pieces is often called an analysis. The corresponding operation of rebuilding the function from these pieces is known as synthesis. In this context the term Fourier synthesis describes the act of rebuilding and the term Fourier analysis describes the process of breaking the function into a sum of simpler pieces. In mathematics, the term Fourier analysis often refers to the study of both operations.

Introduction

In Fourier analysis, the term Fourier transform often refers to the process that decomposes a given function into the basic pieces. This process results in another function that describes how much of each basic piece are in the original function. It is common practice to also use the term Fourier transform to refer to this function. However, the transform is often given a more specific name depending upon the domain and other properties of the function being transformed, as elaborated below. Moreover, the original concept of Fourier analysis has been extended over time to apply to more and more abstract and general situations and the general field is often known as harmonic analysis.

(Continuous) Fourier transform

Most often, the unqualified term Fourier transform refers to the transform of functions of a continuous real argument, such as time (t). In this case the Fourier transform describes a function ƒ(t) in terms of basic complex exponentials of various frequencies. In terms of ordinary frequency ν, the Fourier transform is given by the complex number.

Evaluating this quantity for all values of ν produces the frequency-domain function.

Matlab and the FFT

Matlab's FFT function is an effective tool for computing the discrete Fourier transform of a signal.The following code examples will help you to understand the details of using the FFT function.

Example 1

The typical syntax for computing the FFT of a signal is FFT(x,N) where x is the signal, x[n], you wish to transform, and N is the number of points in the FFT. N must be at least

as large as the number of samples in x[n]. To demonstrate the effect of changing the value of N,

synthesize a cosine with 30 samples at 10 samples per period.

- n = [0:29];
- x = cos(2*pi*n/10);

Define 3 different values for N. Then take the transform of x[n] for each of the 3 values that were

defined. The abs function find the magnitude of the transform, as we are not concerned with distinguishing between real and imaginary components.

- N1 = 64;
- N2 = 128;
- N3 = 256;
- X1 = abs(fft(x,N1));
- X2 = abs(fft(x,N2));
- X3 = abs(fft(x,N3));

The frequency scale begins at 0 and extends to N - 1 for an N-point FFT. We then normalize the scale so that it extends from 0 to 1 - 1/N

- F1 = [0 : N1 - 1]/N1;
- F2 = [0 : N2 - 1]/N2;
- F3 = [0 : N3 - 1]/N3;

Plot each of the transforms one above the other

- subplot(3,1,1)
- plot(F1,X1,'-x'),title('N = 64'),axis([0 1 0 20])
- subplot(3,1,2)
- plot(F2,X2,'-x'),title('N = 128'),axis([0 1 0 20])
- subplot(3,1,3)
- plot(F3,X3,'-x'),title('N = 256'),axis([0 1 0 20])

Upon examining the plot one can see that each of the transforms adheres to the same shape, differing only in the number of samples used to approximate that shape. What happens if N is the same as the number of samples in x[n]? To find out, set N1 = 30. What does the resulting plot look like? Why does it look like this?

Example 2

In the last example the length of x[n] was limited to 3 periods in length. Now, let's choose a large value for N (for a transform with many points), and vary the number of repetitions of the fundamental period.

- n = [0:29];
- x1 = cos(2*pi*n/10); % 3 periods
- x2 = [x1 x1]; % 6 periods
- x3 = [x1 x1 x1]; % 9 periods

- N = 2048;
- X1 = abs(fft(x1,N));
- X2 = abs(fft(x2,N));
- X3 = abs(fft(x3,N));
- F = [0:N-1]/N;

- subplot(3,1,1)
- plot(F,X1),title('3 periods'),axis([0 1 0 50])
- subplot(3,1,2)
- plot(F,X2),title('6 periods'),axis([0 1 0 50])
- subplot(3,1,3)
- plot(F,X3),title('9 periods'),axis([0 1 0 50])

The previous code will produce three plots. The first plot, the transform of 3 periods of a cosine, looks like the magnitude of 2 sincs with the center of the first sinc at 0.1fs and the second at 0.9fs.

The second plot also has a sinc-like appearance, but its frequency is higher and it has a larger magnitude at 0:1fs and 0:9fs. Similarly, the third plot has a larger sinc frequency and magnitude.

As x[n] is extended to a large number of periods, the sincs will begin to look more and more like impulses.

But I thought a sinusoid transformed to an impulse, why do we have sincs in the frequency domain? When the FFT is computed with an N larger than the number of samples in x[n], it fills in the samples after x[n] with zeros. Example 2 had an x[n] that was 30 samples long, but the FFT had an N = 2048. When Matlab computes the FFT, it automatically fills the spaces from n = 30 to n = 2047 with zeros. This is like taking a sinusoid and multiplying it with a rectangular box of length 30. A multiplication of a box and a sinusoid in the time domain should result in the convolution of a sinc with impulses in the frequency domain. Furthermore, increasing the width of the box in the time domain should increase the frequency of the sinc in the frequency domain. The previous Matlab experiment supports this conclusion.

Identifying Signals in noise with FFT

A common use of Fourier transforms is to find the frequency components of a signal buried in a noisy time domain signal. Consider data sampled at 1000 Hz. Form a signal containing a 50 Hz sinusoid of amplitude 0.7 and 120 Hz sinusoid of amplitude 1 and corrupt it with some zero-mean random noise:

- Fs = 1000; % Sampling frequency
- T = 1/Fs; % Sample time
- L = 1000; % Length of signal
- t = (0:L-1)*T; % Time vector
- x = 0.7*sin(2*pi*50*t) + sin(2*pi*120*t);
  % Sum of a 50 Hz sinusoid and a 120 Hz sinusoid
- y = x + 2*randn(size(t)); % Sinusoids plus noise
- plot(Fs*t(1:50),y(1:50))
- title('Signal Corrupted with Zero-Mean Random Noise')
- xlabel('time (milliseconds)')

It is difficult to identify the frequency components by looking at the original signal. Converting to the frequency domain, the discrete Fourier transform of the noisy signal y is found by taking the fast Fourier transform (FFT):

- NFFT = 2^nextpow2(L); % Next power of 2 from length of y
- Y = fft(y,NFFT)/L;
- f = Fs/2*linspace(0,1,NFFT/2+1); % Plot single-sided amplitude spectrum.
- plot(f,2*abs(Y(1:NFFT/2+1)))
- title('Single-Sided Amplitude Spectrum of y(t)')
- xlabel('Frequency (Hz)')
- ylabel('|Y(f)|')

The main reason the amplitudes are not exactly at 0.7 and 1 is because of the noise. Several executions of this code (including recomputation of y) will produce different approximations to 0.7 and 1. The other reason is that you have a finite length signal. Increasing L from 1000 to 10000 in the example above will produce much better approximations on average.

Outside Links

- http://www.chem.uoa.gr/applets/Apple...FourAnal2.html

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14.10.2: Fourier Synthesis of Periodic Waveforms

Java Developed by Dr. Constantinos E. Efstathiou, Laboratory of Analytical Chemistry, National and Kapodistrian University of Athens

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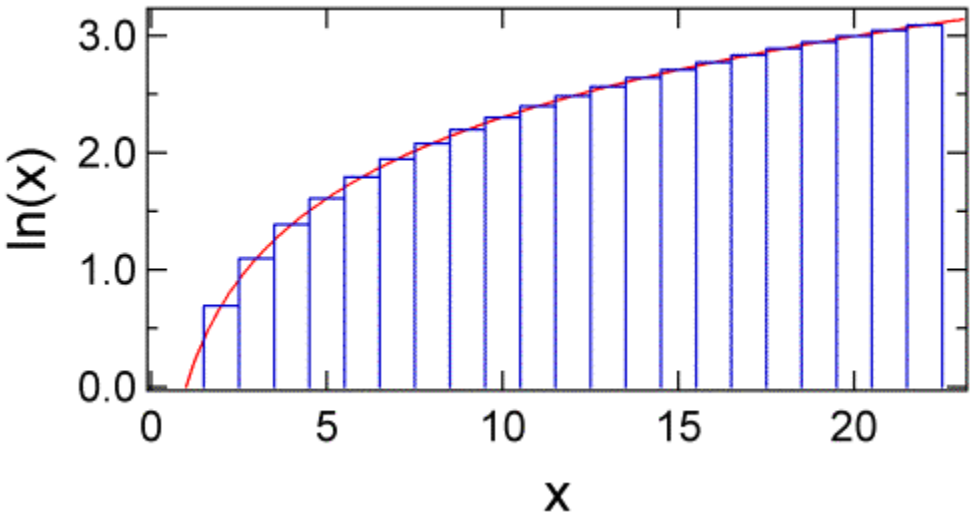
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14.11: The Binomial Distribution and Stirling's Appromixation

Stirling's approximation is named after the Scottish mathematician James Stirling (1692-1770). In confronting statistical problems we often encounter factorials of very large numbers. The factorial $N!$ is a product $N(N-1)(N-2)...(2)(1)$. Therefore, $\ln\ N!$ is a sum

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + ... + \ln N = \sum_{k=1}^{N} \ln k. \tag{14.11.1}$$

where we have used the property of logarithms that $\log(abc) = \log(a) + \log(b) + \log(c)$. The sum is shown in figure below.



Using **Euler-MacLaurin** formula one has

$$\sum_{k=1}^{N} \ln k = \int_{1}^{N} \ln x\, dx + \sum_{k=1}^{p} \frac{B_{2k}}{2k(2k-1)} \left(\frac{1}{n^{2k-1}} - 1 \right) + R, \tag{14.11.2}$$

where B_1 = –1/2, B_2 = 1/6, B_3 = 0, B_4 = –1/30, B_5 = 0, B_6 = 1/42, B_7 = 0, B_8 = –1/30, ... are the **Bernoulli numbers**, and \(R\) is an error term which is normally small for suitable values of \(p\).

Then, for large N,

$$\ln N! \sim \int_{1}^{N} \ln x\, dx \approx N \ln N - N. \tag{14.11.3}$$

after some further manipulation one arrives at (apparently Stirling's contribution was the prefactor of $\sqrt{2\pi}$)

$$N! = \sqrt{2\pi N}\ N^N e^{-N} e^{\lambda_N} \tag{14.11.4}$$

where

$$\frac{1}{12N+1} < \lambda_N < \frac{1}{12N}. \tag{14.11.5}$$

The sum of the area under the blue rectangles shown below up to N is $\ln N!$. As you can see the rectangles begin to closely approximate the red curve as m gets larger. The area under the curve is given the integral of $\ln x$.

$$\ln N! = \sum_{m=1}^{N} \ln m \approx \int_{1}^{N} \ln x \, dx \tag{14.11.6}$$

To solve the integral use integration by parts

$$\int u \, dv = uv - \int v \, dy \tag{14.11.7}$$

Here we let $u = \ln x$ and $dv = dx$. Then $v = x$ and $du = \frac{dx}{x}$.

$$\int_{0}^{N} \ln x \, dx = x \ln x|_{0}^{N} - \int_{0}^{N} x \frac{dx}{x} \tag{14.11.8}$$

Notice that $x/x = 1$ in the last integral and $x \ln x$ is 0 when evaluated at zero, so we have

$$\int_{0}^{N} \ln x \, dx = N \ln N - \int_{0}^{N} dx \tag{14.11.9}$$

Which gives us Stirling's approximation: $\ln N! = N \ln N – N$. As is clear from the figure above Stirling's approximation gets better as the number N gets larger (Table 14.11.1).

Table 14.11.1: Evaluation of Approximation with absolute values

N	N!	ln N!	N ln N – N	Error
10	3.63×10^{6}	15.1	13.02	13.8%
50	3.04×10^{64}	148.4	145.6	1.88%
100	9.33×10^{157}	363.7	360.5	0.88%
150	5.71×10^{262}	605.0	601.6	0.56%

Calculators often overheat at 200!, which is all right since clearly result are converging. In thermodynamics, we are often dealing very large N (i.e., of the order of Avagadro's number) and for these values Stirling's approximation is excellent.

References

1. J. Stirling "Methodus differentialis, sive tractatus de summation et interpolation serierum infinitarium", London (1730). English translation by J. Holliday "The Differential Method: A Treatise of the Summation and Interpolation of Infinite Series" (1749)

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14.12: FORMULA SHEETS

14.12.1: Some Important Numbers

14.12.2: Quadratic Equation

14.12.3: Logarithms and Exponentials

14.12.4: Trigonometric Identities

14.12.5: Complex Numbers

14.12.6: Operators

14.12.7: Taylor Series

14.12.8: Fourier Series

14.12.9: Derivatives and Primitives (Indefinite Integrals)

14.12.10: Definite integrals

14.12.11: Differentiation Rules

14.12.12: Partial Derivatives

14.12.13: Coordinate Systems

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14.12.1: Some Important Numbers

$$\ln 2 \approx 0.69$$
$$e \approx 2.72$$
$$e^{-1} \approx 0.37$$

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14.12.2: Quadratic Equation

$$ax^2 + bx + c = 0 \rightarrow x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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14.12.3: Logarithms and Exponentials

- $\log_b xy = \log_b x + \log_b y$
- $\log_b x^y = y \log_b x$
- $\log_b 1 = 0$
- $\log_b (1/x) = -\log_b x$
- $e^{x+y} = e^x e^y$
- $e^{x-y} = e^x / e^y$

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14.12.4: Trigonometric Identities

- $\sin^2 u + \cos^2 u = 1$
- $\tan u = \frac{\sin u}{\cos u}$
- $\sin\left(\frac{\pi}{2} - u\right) = \cos u$
- $\cos\left(\frac{\pi}{2} - u\right) = \sin u$
- $\sin(u \pm v) = \sin u \cos v \pm \cos u \sin v$
- $\cos(u \pm v) = \cos u \cos v \mp \sin u \sin v$
- $\sin(-u) = -\sin u$
- $\cos(-u) = \cos u$
- $\tan(-u) = -\tan u$
- $\sin u \cos v = \frac{1}{2}\left[\sin(u+v) + \sin(u-v)\right]$
- $\sin u \sin v = \frac{1}{2}\left[\cos(u-v) - \cos(u+v)\right]$
- $\cos u \cos v = \frac{1}{2}\left[\cos(u-v) + \cos(u+v)\right]$

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14.12.5: Complex Numbers

$$re^{\pm i\phi} = r\cos\phi \pm ir\sin\phi = x \pm iy$$

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14.12.6: Operators

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

$[\hat{A}, \hat{B}] = 0$ if the operators $\hat{A}$ and $\hat{B}$ commute.

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14.12.7: Taylor Series

$$f(x) = a_0 + a_1(x-h) + a_2(x-h)^2 + a_3(x-h)^3 + \ldots$$
$$a_n = \frac{1}{n!}\left(\frac{d^n f(x)}{dx^n}\right)_h, n = 1, 2, 3\ldots$$

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14.12.8: Fourier Series

For a periodic function of period $2L$:

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right)$$

$$a_0 = \frac{1}{L} \int_{-L}^{L} f(x)dx$$

$$a_n = \frac{1}{L} \int_{-L}^{L} f(x) \cos\left(\frac{n\pi x}{L}\right)dx$$

$$b_n = \frac{1}{L} \int_{-L}^{L} f(x) \sin\left(\frac{n\pi x}{L}\right)dx$$

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14.12.9: Derivatives and Primitives (Indefinite Integrals)

$f(x)$	$f'(x)$	$\int f(x)dx(\pm c)$
k	0	kx
x^n	nx^{n-1}, $n \neq 0$	$\frac{x^{n+1}}{n+1}$, $n \neq -1$
$\frac{1}{x}$	$-\frac{1}{x^2}$	$ln\|x\|$
a^x	$a^x \ln a$	$\frac{a^x}{\ln a}$
e^x	e^x	e^x
$\log_a x$	$\frac{1}{x \ln a}$	$\frac{x \ln x - x}{\ln a}$
$\ln x$	$\frac{1}{x}$	$x \ln x - x$
$\sin x$	$\cos x$	$-\cos x$
$\cos x$	$-\sin x$	$\sin x$
$\tan x$	$\frac{1}{\cos^2 x}$	$-\ln(\cos x)$
$\arcsin x$	$\frac{1}{\sqrt{1-x^2}}$	$x \arcsin x + \sqrt{1-x^2}$
$\arccos x$	$-\frac{1}{\sqrt{1-x^2}}$	$x \arccos x - \sqrt{1-x^2}$
$\arctan x$	$\frac{1}{1+x^2}$	$x \arctan x - \frac{1}{2}\ln(1+x^2)$
$\frac{1}{a^2+x^2}$	$\frac{-2x}{(a^2+x^2)^2}$	$\frac{1}{a}\arctan\left(\frac{x}{a}\right)$
$\frac{1}{\sqrt{a^2-x^2}}$	$\frac{x}{(a^2-x^2)^{\frac{3}{2}}}$	$\arcsin\left(\frac{x}{a}\right)$

- $\int \sin^2(ax)dx = \frac{x}{2} - \frac{\sin(2ax)}{4a} + c$
- $\int \cos^2(ax)dx = \frac{x}{2} + \frac{\sin(2ax)}{4a} + c$
- $\int \sin^3(ax)dx = \frac{1}{12a}\cos(3ax) - \frac{3}{4a}\cos(ax) + c$
- $\int \cos^3(ax)dx = \frac{1}{12a}\sin(3ax) + \frac{3}{4a}\sin(ax) + c$
- $\int x\cos(ax)dx = \frac{\cos(ax)}{a^2} + \frac{\sin(ax)}{a}x + c$
- $\int x\sin(ax)dx = \frac{\sin(ax)}{a^2} - \frac{\cos(ax)}{a}x + c$
- $\int x\sin^2(ax)dx = \frac{x^2}{4} - \frac{x\sin(2ax)}{4a} - \frac{\cos(2ax)}{8a^2} + c$
- $\int xe^{x^2}dx = e^{x^2}/2 + c$
- $\int xe^{ax} = \frac{e^{ax}(ax-1)}{a^2} + c$
- $\int \frac{x}{x^2+1}dx = \frac{1}{2}\ln(1+x^2) + c$

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14.12.10: Definite integrals

- $\int_0^\infty xe^{-x^2}dx = \frac{1}{2}$
- $\int_0^\infty e^{-ax}dx = \frac{1}{a}, a > 0$
- $\int_0^\infty \sqrt{x}e^{-ax}dx = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$
- $\int_0^\infty x^{2n+1}e^{-ax^2}dx = \frac{n!}{2a^{n+1}}, a > 0$
- $\int_0^\infty x^{2n}e^{-ax^2}dx = \frac{1.3.5...(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}$
- $\int_0^\infty x^n e^{-ax}dx = \frac{n!}{a^{n+1}}$, $a > 0$, n positive integer

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14.12.11: Differentiation Rules

- $\frac{d[f(x)+g(x)]}{dx} = \frac{df(x)}{dx} + \frac{dg(x)}{dx}$
- $\frac{d[f(x)g(x)]}{dx} = f(x)\frac{dg(x)}{dx} + g(x)\frac{df(x)}{dx}$
- $\frac{d[af(x)]}{dx} = a\frac{df(x)}{dx}$
- $\frac{df(g(x))}{dx} = \frac{df(g)}{dg}\frac{dg(x)}{dx}$

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14.12.12: Partial Derivatives

- $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$
- $\left(\frac{\partial y}{\partial x}\right)_{z,u} = \frac{1}{(\partial x/\partial y)_{z,u}}$
- $\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1$
- $du = \left(\frac{\partial u}{\partial x_1}\right)_{x_2,x_3\ldots} dx_1 + \left(\frac{\partial u}{\partial x_2}\right)_{x_1,x_3\ldots} dx_2 + \left(\frac{\partial u}{\partial x_3}\right)_{x_1,x_2\ldots} dx_3$
- Given $u = u(x, y)$, $x = x(\theta, r)$ and $y = y(\theta, r)$

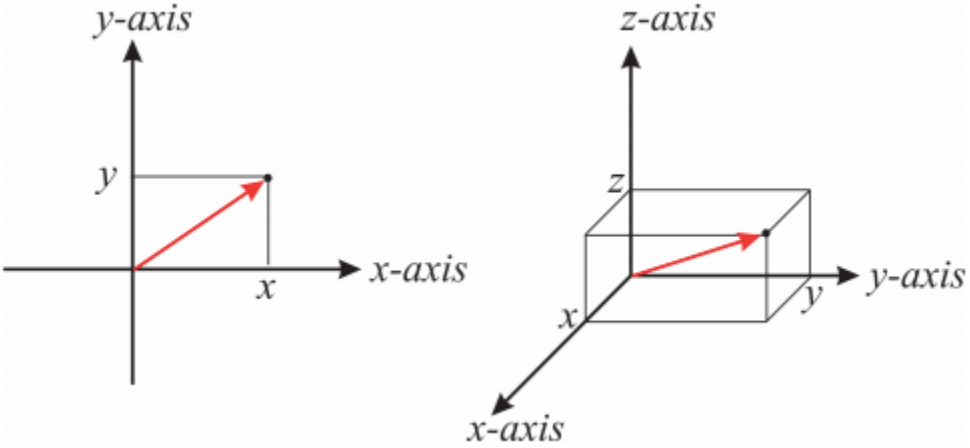
$$\left(\frac{\partial u}{\partial r}\right)_\theta = \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial r}\right)_\theta + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial r}\right)_\theta$$
$$\left(\frac{\partial u}{\partial \theta}\right)_r = \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial \theta}\right)_r + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial \theta}\right)_r$$

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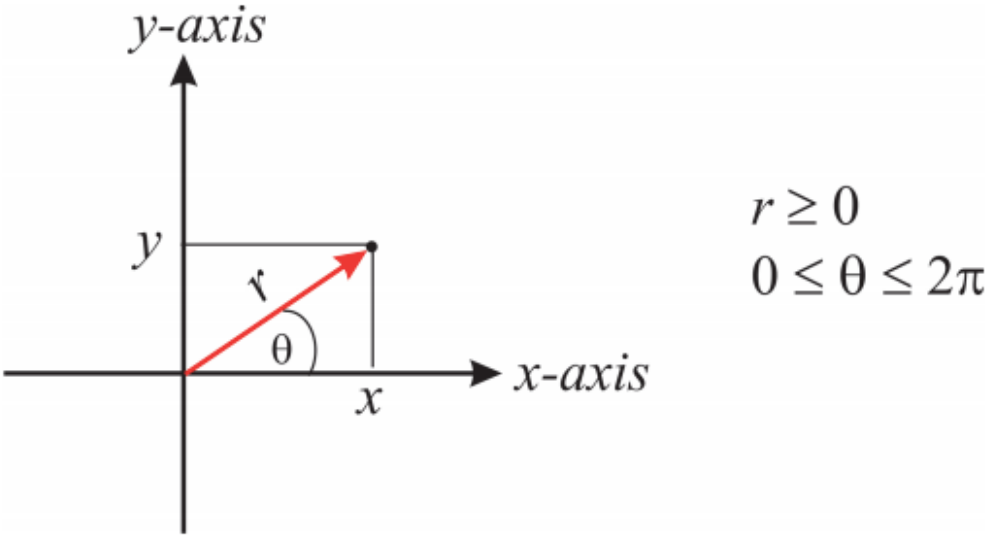
14.12.13: Coordinate Systems

Cartesian coordinates



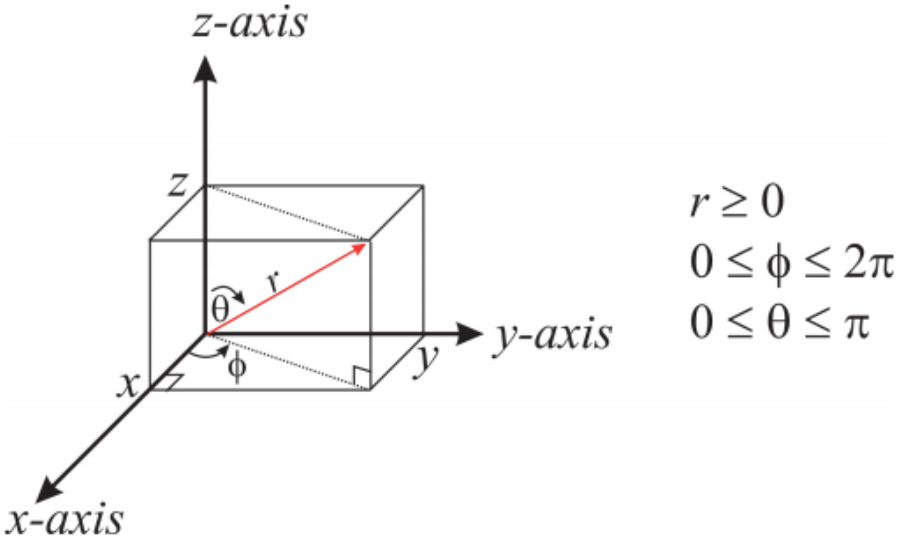
2 dimensions: area element: $dA = dx.dy$.
3 dimensions: volume element: $dV = dx.dy.dz$.

Polar coordinates



- $x = r\cos\theta$
- $y = r\sin\theta$
- $r^2 = x^2 + y^2$
- $tan\theta = y/x$
- $dA = r.dr.d\theta$

Spherical coordinates



- $x = r \sin\theta \cos\phi$
- $y = r \sin\theta \sin\phi$
- $z = r \cos\theta$
- $r^2 = x^2 + y^2 + z^2$
- $\theta = \cos^{-1}\left[\frac{z}{\sqrt{x^2+y^2+z^2}}\right]$
- $\phi = \tan^{-1}\left(\frac{y}{x}\right)$
- $dV = r^2 \sin\theta dr.d\phi.d\theta$

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INDEX

A

anharmonicity
- *12.5: Vibrational Overtones*
- *5.3: The Harmonic Oscillator Approximates Molecular Vibrations*

anharmonicity constant
- *12.5: Vibrational Overtones*

antibonding molecular orbital
- *10.2: The H_2^+ Prototypical Species*
- *10.5: Bonding and Antibonding Orbitals*

Argand diagram
- *14.1: Complex Numbers*

aromaticity
- *11.6: Benzene and Aromaticity*

Asymmetric Tops
- *12.8: Rotational Spectra of Polyatomic Molecules*

atomic term symbols
- *8.11: Using Atomic Term Symbols to Interpret Atomic Spectra*
- *8.8: Term Symbols Gives a Detailed Description of an Electron Configuration*

Atomic units
- *8.1: Atomic and Molecular Calculations are Expressed in Atomic Units*

autonumheader:yes2

1: The Dawn of the Quantum Theory
1.1: Blackbody Radiation Cannot Be Explained Classically
1.2: Quantum Hypothesis Used for Blackbody Radiation Law
1.3: Photoelectric Effect Explained with Quantum Hypothesis
1.4: The Hydrogen Atomic Spectrum
1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum
1.6: Matter Has Wavelike Properties
1.7: de Broglie Waves can be Experimentally Observed
1.8: The Bohr Theory of the Hydrogen Atom
1.9: The Heisenberg Uncertainty Principle
10: Chemical Bonding in Diatomic Molecules
10.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules
10.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic
10.11: Photoelectron Spectroscopy
10.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules
10.13: Molecular Term Symbols Describe Electronic States of Molecules
10.14: Molecular Term Symbols Designate Symmetry
10.2: The H_2^+ Prototypical Species
10.3: The Overlap Integral
10.4: Chemical Bond Stability
10.5: Bonding and Antibonding Orbitals
10.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital
10.7: Molecular Orbitals Can Be Ordered According to Their Energies
10.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule
10.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle
10.E: Chemical Bond in Diatomic Molecules (Exercises)
11: Bonding in Polyatomic Molecules
11.1: Hybrid Orbitals Account for Molecular Shape
11.2: Hybrid Orbitals in Water
11.3: BeH_2 is Linear and H_2O is Bent
11.4: The pi-Electron Approximation of Conjugation
11.5: Butadiene is Stabilized by a Delocalization Energy
11.6: Benzene and Aromaticity
11.E: Bonding in Polyatomic Molecules (Exercises)
12: Molecular Spectroscopy
12.1: The Electromagnetic Spectrum
12.10: Time-Dependent Perturbation Theory
12.11: The Selection Rule for the Rigid Rotor
12.12: The Harmonic Oscillator Selection Rule
12.13: Group Theory Determines Infrared Activity
12.2: Rotations Accompany Vibrational Transitions
12.3: Unequal Spacings in Vibration-Rotation Spectra
12.4: Unequal Spacings in Pure Rotational Spectra
12.5: Vibrational Overtones
12.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
12.7: The Franck-Condon Principle
12.8: Rotational Spectra of Polyatomic Molecules
12.9: Normal Modes in Polyatomic Molecules
13: Lasers, Laser Spectroscopy, and Photochemistry
13.1: Electronically Excited Molecules can Relax by a Number of Processes
13.2: The Dynamics of Transitions can be Modeled by Rate Equations
13.3: A Two-Level System Cannot Achieve a Population Inversion
13.4: Population Inversion can be Achieved in a Three-Level System
13.5: What is Inside a Laser?
13.6: The Helium-Neon Laser
13.7: Modern Applications of Laser Spectroscopy
14: Math Chapters
14.1: Complex Numbers
14.10: Fourier Analysis
14.10.1: Fourier Analysis in Matlab
14.10.2: Fourier Synthesis of Periodic Waveforms
14.11: The Binomial Distribution and Stirling's Appromixation
14.2: Probability and Statistics
14.4: Vectors
14.5: Spherical Coordinates
14.6: Matrices
14.7: Numerical Methods
14.8: Partial Differentiation
14.9: Series and Limits
2: The Classical Wave Equation
2.1: The One-Dimensional Wave Equation
2.2: The Method of Separation of Variables
2.3: Oscillatory Solutions to Differential Equations
2.4: The General Solution is a Superposition of Normal Modes
2.5: A Vibrating Membrane
3: The Schrödinger Equation and a Particle in a Box
3.1: The Schrödinger Equation
3.2: Linear Operators in Quantum Mechanics
3.3: The Schrödinger Equation is an Eigenvalue Problem
3.4: Wavefunctions Have a Probabilistic Interpretation
3.5: The Energy of a Particle in a Box is Quantized
3.6: Wavefunctions Must Be Normalized
3.7: The Average Momentum of a Particle in a Box is Zero
3.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions
3.9: A Particle in a Three-Dimensional Box
4: Postulates and Principles of Quantum Mechanics
4.1: The Wavefunction Specifies the State of a System
4.2: Quantum Operators Represent Classical Variables
4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators
4.4: The Time-Dependent Schrödinger Equation
4.5: Eigenfunctions of Operators are Orthogonal
4.6: Commuting Operators Allow Infinite Precision
5: The Harmonic Oscillator and the Rigid Rotor
5.1: A Harmonic Oscillator Obeys Hooke's Law
5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule
5.3: The Harmonic Oscillator Approximates Molecular Vibrations
5.4: The Harmonic Oscillator Energy Levels
5.5: The Harmonic Oscillator and Infrared Spectra
5.6: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials
5.7: Hermite Polynomials are either Even or Odd Functions
5.8: The Energy Levels of a Rigid Rotor
5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
6: The Hydrogen Atom
6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly
6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics
6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision
6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers
6.5: s-orbitals are Spherically Symmetric
6.6: Orbital Angular Momentum and the p-Orbitals
6.8: The Helium Atom Cannot Be Solved Exactly
7: Approximation Methods
7.1: The Variational Method Approximation
7.2: Linear Variational Method and the Secular Determinant
7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters
7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems
7.E: Approximation Methods (Exercises)
8: Multielectron Atoms
8.1: Atomic and Molecular Calculations are Expressed in Atomic Units
8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States
8.11: Using Atomic Term Symbols to Interpret Atomic Spectra
8.2: Perturbation Theory and the Variational Method for Helium
8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method
8.4: An Electron has an Intrinsic Spin Angular Momentum
8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants
8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data
8.8: Term Symbols Gives a Detailed Description of an Electron Configuration
8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number
9: Computational Quantum Chemistry
9.1: Overview of Quantum Calculations
9.2: Gaussian Basis Sets
9.3: Extended Basis Sets
9.4: Orbital Polarization Terms in Basis Sets
9.E: Computational Quantum Chemistry (Exercises)

B

Balmer series
1.4: The Hydrogen Atomic Spectrum
benzene ring
11.6: Benzene and Aromaticity
blackbody radiation
1.1: Blackbody Radiation Cannot Be Explained Classically
1.2: Quantum Hypothesis Used for Blackbody Radiation Law
Bohr Atom
1.8: The Bohr Theory of the Hydrogen Atom
Bohr magneton
8.4: An Electron has an Intrinsic Spin Angular Momentum
Bohr model
1.8: The Bohr Theory of the Hydrogen Atom
Bohr radius
1.8: The Bohr Theory of the Hydrogen Atom
bond order
10.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

bonding molecular orbital
10.2: The H_2^+ Prototypical Species
10.5: Bonding and Antibonding Orbitals

bosons
8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

boundary conditions
2.2: The Method of Separation of Variables

bracketing theorem
7.2: Linear Variational Method and the Secular Determinant

C

centrifugal distortion
12.3: Unequal Spacings in Vibration-Rotation Spectra

Chandrasakar wavefunction
8.2: Perturbation Theory and the Variational Method for Helium

Classical Harmonic Oscillator
5.1: A Harmonic Oscillator Obeys Hooke's Law

Classical Wave Equation
2: The Classical Wave Equation

commutator
3.2: Linear Operators in Quantum Mechanics
4.6: Commuting Operators Allow Infinite Precision

Commuting Operators
4.6: Commuting Operators Allow Infinite Precision

complex numbers
14.1: Complex Numbers

conservative forces
1.8: The Bohr Theory of the Hydrogen Atom

correspondence principle
3.3: The Schrödinger Equation is an Eigenvalue Problem
4.2: Quantum Operators Represent Classical Variables

Coulomb integral
10.4: Chemical Bond Stability
11.4: The pi-Electron Approximation of Conjugation

Coulombic force
1.8: The Bohr Theory of the Hydrogen Atom

cyclic boundary condition
5.8: The Energy Levels of a Rigid Rotor

cyclic permutations (angular momenta)
6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

D

Davisson–Germer Eexperiment
1.7: de Broglie Waves can be Experimentally Observed

de Broglie wavelength
1.6: Matter Has Wavelike Properties

degeneracy
3.9: A Particle in a Three-Dimensional Box

delocalization energy
11.5: Butadiene is Stabilized by a Delocalization Energy

determinants
14.3.1: The Solutions of Simultaneous Linear Equations
14.3.2: Calculation of a 3 × 3 determinant

Diatomic Vibration
5.5: The Harmonic Oscillator and Infrared Spectra

dipole moment operator
5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

E

effective nuclear charge
7.1: The Variational Method Approximation

Eigenfunction
3.3: The Schrödinger Equation is an Eigenvalue Problem
4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

eigenvalue
4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

eigenvalue equation
3.2: Linear Operators in Quantum Mechanics

eigenvalue problem
3.3: The Schrödinger Equation is an Eigenvalue Problem
4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

electron diffraction
1.7: de Broglie Waves can be Experimentally Observed

Euler Equation
14.1: Complex Numbers

exact differential
14.8: Partial Differentiation

exchange integral
10.4: Chemical Bond Stability

exchange operator
8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

exchange term
8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

expectation value
3.7: The Average Momentum of a Particle in a Box is Zero

F

fermions
8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

fine structure
8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

Fourier analysis
14.10: Fourier Analysis
14.10.1: Fourier Analysis in Matlab

frozen orbital approximation
8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

G

Gaussian type orbitals
9.3: Extended Basis Sets

H

Hamiltonian operator
4.2: Quantum Operators Represent Classical Variables

harmonic oscillator
5.3: The Harmonic Oscillator Approximates Molecular Vibrations
5.4: The Harmonic Oscillator Energy Levels
5.5: The Harmonic Oscillator and Infrared Spectra

hartree (unit)
8.2: Perturbation Theory and the Variational Method for Helium

Hartree equations
8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

Heisenberg uncertainty principle
1.9: The Heisenberg Uncertainty Principle
3.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

Hermite polynomials
5.6: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials
5.7: Hermite Polynomials are either Even or Odd Functions

Hermitian operators
3.2: Linear Operators in Quantum Mechanics
4.5: Eigenfunctions of Operators are Orthogonal
7.2: Linear Variational Method and the Secular Determinant

Hooke's Law
5.1: A Harmonic Oscillator Obeys Hooke's Law

Hückel theory
11.4: The pi-Electron Approximation of Conjugation

Hückel's rule
11.6: Benzene and Aromaticity

Hund's Rules
8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States

hybridization
11.1: Hybrid Orbitals Account for Molecular Shape

Hylleraas Wavefunction
8.2: Perturbation Theory and the Variational Method for Helium

I

inexact differential
14.8: Partial Differentiation

infrared spectroscopy
5.5: The Harmonic Oscillator and Infrared Spectra

intrinsic spin
8.4: An Electron has an Intrinsic Spin Angular Momentum

IR spectra
5.5: The Harmonic Oscillator and Infrared Spectra

K

Koopmans' Theorem
10.11: Photoelectron Spectroscopy

L

laplacian
4.2: Quantum Operators Represent Classical Variables

Laplacian operator
3.1: The Schrödinger Equation

LCAO
10.4: Chemical Bond Stability

legendre polynomials
6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics
lenard
1.3: Photoelectric Effect Explained with Quantum Hypothesis
Linear Combination of Atomic Orbitals (LCAO)
10.2: The H_2^+ Prototypical Species
7.2: Linear Variational Method and the Secular Determinant
lone pairs
11.2: Hybrid Orbitals in Water
Lyman series
1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum

M

microscopic reversibility
13.2: The Dynamics of Transitions can be Modeled by Rate Equations
microwave spectroscopy
5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
millikan
1.3: Photoelectric Effect Explained with Quantum Hypothesis
molecular spectroscopy
12: Molecular Spectroscopy
molecular term symbols
10.13: Molecular Term Symbols Describe Electronic States of Molecules
10.14: Molecular Term Symbols Designate Symmetry
moment of inertia tensor
12.8: Rotational Spectra of Polyatomic Molecules
Morse potential
5.3: The Harmonic Oscillator Approximates Molecular Vibrations
5.5: The Harmonic Oscillator and Infrared Spectra
multiplicity
8.8: Term Symbols Gives a Detailed Description of an Electron Configuration

N

neglect of differential overlap (NDO)
11.4: The pi-Electron Approximation of Conjugation
node
2.5: A Vibrating Membrane
nodes
2.1: The One-Dimensional Wave Equation
3.7: The Average Momentum of a Particle in a Box is Zero
Nonstationary States
4.4: The Time-Dependent Schrödinger Equation
normal modes
12.9: Normal Modes in Polyatomic Molecules

O

oblate top
12.8: Rotational Spectra of Polyatomic Molecules
operators
3.2: Linear Operators in Quantum Mechanics
3.3: The Schrödinger Equation is an Eigenvalue Problem
4.2: Quantum Operators Represent Classical Variables
orbital angular momentum
6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision
orbital approximation
6.8: The Helium Atom Cannot Be Solved Exactly
7.1: The Variational Method Approximation
orthogonality
3.5: The Energy of a Particle in a Box is Quantized
4.5: Eigenfunctions of Operators are Orthogonal
Orthonormality
3.5: The Energy of a Particle in a Box is Quantized
overlap
10.3: The Overlap Integral
Overlap integral
10.3: The Overlap Integral
overtones
12.5: Vibrational Overtones

P

Paschen series
1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum
Pauli's exclusion principle
8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
penetration
7.1: The Variational Method Approximation
permutation operator
8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
Pertubation Theory for Helium
8.2: Perturbation Theory and the Variational Method for Helium
perturbation theory
7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems
Pfund series
1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum
photoelectric effect
1.3: Photoelectric Effect Explained with Quantum Hypothesis
photoelectron spectroscopy
10.11: Photoelectron Spectroscopy
photons
1.3: Photoelectric Effect Explained with Quantum Hypothesis
physical
12.1: The Electromagnetic Spectrum
12.E: Molecular Spectroscopy (Exercises)
Planck's constant
1.2: Quantum Hypothesis Used for Blackbody Radiation Law
population inversion
13.3: A Two-Level System Cannot Achieve a Population Inversion
13.4: Population Inversion can be Achieved in a Three-Level System
Probabilistic Interpretation
3.4: Wavefunctions Have a Probabilistic Interpretation
probability
14.2: Probability and Statistics
probability density
14.2: Probability and Statistics
3.4: Wavefunctions Have a Probabilistic Interpretation
probability distribution
1.9: The Heisenberg Uncertainty Principle
14.2: Probability and Statistics
prolate top
12.8: Rotational Spectra of Polyatomic Molecules

Q

quanta
1.2: Quantum Hypothesis Used for Blackbody Radiation Law
quantum number
2.4: The General Solution is a Superposition of Normal Modes
3.5: The Energy of a Particle in a Box is Quantized

R

radial probability density
6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics
Redox in Acid Solution
5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule
reduced mass
5.1: A Harmonic Oscillator Obeys Hooke's Law
reducing agent
5.5: The Harmonic Oscillator and Infrared Spectra
resonance integral
11.4: The pi-Electron Approximation of Conjugation
rigid rotor
12.11: The Selection Rule for the Rigid Rotor
5.8: The Energy Levels of a Rigid Rotor
5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
rotational constant
5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
Rotational of Polyatomic Molecules
12.8: Rotational Spectra of Polyatomic Molecules
rovibrational spectroscopy
12.2: Rotations Accompany Vibrational Transitions
Rydberg constant
1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum
Rydberg states
1.8: The Bohr Theory of the Hydrogen Atom

S

Schmidt orthogonalization theorem
4.5: Eigenfunctions of Operators are Orthogonal
Schrödinger equation
3.1: The Schrödinger Equation

Secular Determinant
7.2: Linear Variational Method and the Secular Determinant
secular equations
10.5: Bonding and Antibonding Orbitals
7.2: Linear Variational Method and the Secular Determinant
selection rules
12.11: The Selection Rule for the Rigid Rotor
5.5: The Harmonic Oscillator and Infrared Spectra
separation of variables
2.2: The Method of Separation of Variables
shielding
7.1: The Variational Method Approximation
Slater determinant wavefunction
8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants
spherical coordinates
14.5: Spherical Coordinates
spherical harmonics
5.8: The Energy Levels of a Rigid Rotor
6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics
Spherical Tops
12.8: Rotational Spectra of Polyatomic Molecules
Spin Multiplicity
13.1: Electronically Excited Molecules can Relax by a Number of Processes
standing wave
2.1: The One-Dimensional Wave Equation
stationary state
4.4: The Time-Dependent Schrödinger Equation
STO
7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters
Stokes shift
13.1: Electronically Excited Molecules can Relax by a Number of Processes
superposition principle
2.4: The General Solution is a Superposition of Normal Modes
Symmetric Tops
12.8: Rotational Spectra of Polyatomic Molecules

T

total angular momentum
8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number
Total Angular Momentum Quantum Number (J)
8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number
Total Differentials
14.8: Partial Differentiation
total orbital angular momenta
8.8: Term Symbols Gives a Detailed Description of an Electron Configuration
transition energies
5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
traveling wave
2.1: The One-Dimensional Wave Equation
trial wavefunction
7.2: Linear Variational Method and the Secular Determinant
turning points
5.1: A Harmonic Oscillator Obeys Hooke's Law

U

Ultraviolet Catastrophe
1.1: Blackbody Radiation Cannot Be Explained Classically
Ultraviolet Photoelectron Spectroscopy (UPS)
10.11: Photoelectron Spectroscopy
uncertainty
3.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions

V

Variational Method
7.1: The Variational Method Approximation
7.2: Linear Variational Method and the Secular Determinant
Variational Method for Helium
8.2: Perturbation Theory and the Variational Method for Helium
vertical ionization energy
10.11: Photoelectron Spectroscopy
vertical transition
12.7: The Franck-Condon Principle

W

Walsh diagrams
11.3: BeH_2 is Linear and H_2O is Bent
Wave equations
2.1: The One-Dimensional Wave Equation
Wavefunction
3.1: The Schrödinger Equation
Wavefunction Normalization
3.6: Wavefunctions Must Be Normalized
wavenumbers (units)
5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
Wien's Displacement Law
1.1: Blackbody Radiation Cannot Be Explained Classically

Y

Young double slit
1.7: de Broglie Waves can be Experimentally Observed

Z

Zeeman effect
8.4: An Electron has an Intrinsic Spin Angular Momentum
zero point energy
3.5: The Energy of a Particle in a Box is Quantized

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S

Sample Word 1 | Sample Definition 1

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By Page

- CHM 364: Physical Chemistry 2 (Grinnell College) - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: The Dawn of the Quantum Theory - *Undeclared*
    - 1.1: Blackbody Radiation Cannot Be Explained Classically - *CC BY 4.0*
    - 1.2: Quantum Hypothesis Used for Blackbody Radiation Law - *Undeclared*
    - 1.3: Photoelectric Effect Explained with Quantum Hypothesis - *CC BY-NC-SA 4.0*
    - 1.4: The Hydrogen Atomic Spectrum - *Undeclared*
    - 1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum - *CC BY-NC-SA 4.0*
    - 1.6: Matter Has Wavelike Properties - *CC BY-NC-SA 4.0*
    - 1.7: de Broglie Waves can be Experimentally Observed - *Undeclared*
    - 1.8: The Bohr Theory of the Hydrogen Atom - *CC BY-NC-SA 4.0*
    - 1.9: The Heisenberg Uncertainty Principle - *CC BY 4.0*
    - 1.E: The Dawn of the Quantum Theory (Exercises) - *Undeclared*
  - 2: The Classical Wave Equation - *Undeclared*
    - 2.1: The One-Dimensional Wave Equation - *Undeclared*
    - 2.2: The Method of Separation of Variables - *CC BY-NC-SA 4.0*
    - 2.3: Oscillatory Solutions to Differential Equations - *Undeclared*
    - 2.4: The General Solution is a Superposition of Normal Modes - *Undeclared*
    - 2.5: A Vibrating Membrane - *Undeclared*
    - 2.E: The Classical Wave Equation (Exercises) - *Undeclared*
  - 3: The Schrödinger Equation and a Particle in a Box - *Undeclared*
    - 3.1: The Schrödinger Equation - *Undeclared*
    - 3.2: Linear Operators in Quantum Mechanics - *Undeclared*
    - 3.3: The Schrödinger Equation is an Eigenvalue Problem - *Undeclared*
    - 3.4: Wavefunctions Have a Probabilistic Interpretation - *Undeclared*
    - 3.5: The Energy of a Particle in a Box is Quantized - *Undeclared*
    - 3.6: Wavefunctions Must Be Normalized - *CC BY-NC-SA 4.0*
    - 3.7: The Average Momentum of a Particle in a Box is Zero - *Undeclared*
    - 3.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions - *Undeclared*
    - 3.9: A Particle in a Three-Dimensional Box - *Undeclared*
    - 3.E: The Schrödinger Equation and a Particle in a Box (Exercises) - *Undeclared*
  - 4: Postulates and Principles of Quantum Mechanics - *Undeclared*
    - 4.1: The Wavefunction Specifies the State of a System - *CC BY-NC-SA 4.0*
    - 4.2: Quantum Operators Represent Classical Variables - *Undeclared*
    - 4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators - *Undeclared*

- 4.4: The Time-Dependent Schrödinger Equation - *Undeclared*
- 4.5: Eigenfunctions of Operators are Orthogonal - *Undeclared*
- 4.6: Commuting Operators Allow Infinite Precision - *CC BY-NC-SA 3.0*
- 4.E: Postulates and Principles of Quantum Mechanics (Exercises) - *Undeclared*

◦ 5: The Harmonic Oscillator and the Rigid Rotor - *Undeclared*
- 5.1: A Harmonic Oscillator Obeys Hooke's Law - *Undeclared*
- 5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule - *CC BY-NC-SA 4.0*
- 5.3: The Harmonic Oscillator Approximates Molecular Vibrations - *CC BY 4.0*
- 5.4: The Harmonic Oscillator Energy Levels - *CC BY-NC-SA 4.0*
- 5.5: The Harmonic Oscillator and Infrared Spectra - *Undeclared*
- 5.6: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials - *Undeclared*
- 5.7: Hermite Polynomials are either Even or Odd Functions - *CC BY-SA 4.0*
- 5.8: The Energy Levels of a Rigid Rotor - *CC BY-NC-SA 4.0*
- 5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule - *Undeclared*
- 5.E: The Harmonic Oscillator and the Rigid Rotor (Exercises) - *Undeclared*

◦ 6: The Hydrogen Atom - *Undeclared*
- 6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly - *Undeclared*
- 6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics - *CC BY-NC-SA 4.0*
- 6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision - *Undeclared*
- 6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers - *Undeclared*
- 6.5: s-orbitals are Spherically Symmetric - *Undeclared*
- 6.6: Orbital Angular Momentum and the p-Orbitals - *Undeclared*
- 6.7: The Schrödinger Wave Equation for the Hydrogen Atom - *Undeclared*
- 6.8: The Helium Atom Cannot Be Solved Exactly - *Undeclared*
- 6.E: The Hydrogen Atom (Exercises) - *Undeclared*

◦ 7: Approximation Methods - *Undeclared*
- 7.1: The Variational Method Approximation - *CC BY-NC-SA 3.0*
- 7.2: Linear Variational Method and the Secular Determinant - *Undeclared*
- 7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters - *CC BY-NC-SA 3.0*
- 7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems - *CC BY-NC-SA 4.0*
- 7.E: Approximation Methods (Exercises) - *Undeclared*

◦ 8: Multielectron Atoms - *CC BY 4.0*
- 8.1: Atomic and Molecular Calculations are Expressed in Atomic Units - *CC BY-SA 4.0*
- 8.2: Perturbation Theory and the Variational Method for Helium - *CC BY 4.0*
- 8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method - *CC BY-NC-SA 4.0*
- 8.4: An Electron has an Intrinsic Spin Angular Momentum - *CC BY-NC-SA 3.0*
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons - *Undeclared*
- 8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants - *CC BY-NC-SA 4.0*
- 8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data - *Undeclared*
- 8.8: Term Symbols Gives a Detailed Description of an Electron Configuration - *CC BY 4.0*
- 8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number - *Undeclared*
- 8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States - *Undeclared*
- 8.11: Using Atomic Term Symbols to Interpret Atomic Spectra - *Undeclared*
- 8.E: Multielectron Atoms (Exercises) - *Undeclared*

◦ 9: Computational Quantum Chemistry - *Undeclared*
- 9.1: Overview of Quantum Calculations - *Undeclared*
- 9.2: Gaussian Basis Sets - *Undeclared*
- 9.3: Extended Basis Sets - *Undeclared*
- 9.4: Orbital Polarization Terms in Basis Sets - *Undeclared*
- 9.E: Computational Quantum Chemistry (Exercises) - *Undeclared*

◦ 10: Chemical Bonding in Diatomic Molecules - *Undeclared*
- 10.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules - *Undeclared*
- 10.2: The H_2^+ Prototypical Species - *Undeclared*
- 10.3: The Overlap Integral - *Undeclared*
- 10.4: Chemical Bond Stability - *Undeclared*
- 10.5: Bonding and Antibonding Orbitals - *Undeclared*
- 10.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital -

Undeclared
- 10.7: Molecular Orbitals Can Be Ordered According to Their Energies - *Undeclared*
- 10.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule - *Undeclared*
- 10.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle - *Undeclared*
- 10.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic - *Undeclared*
- 10.11: Photoelectron Spectroscopy - *CC BY 4.0*
- 10.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules - *CC BY-NC-SA 3.0*
- 10.13: Molecular Term Symbols Describe Electronic States of Molecules - *CC BY 4.0*
- 10.14: Molecular Term Symbols Designate Symmetry - *CC BY-NC-SA 4.0*
- 10.E: Chemical Bond in Diatomic Molecules (Exercises) - *Undeclared*

◦ 11: Bonding in Polyatomic Molecules - *Undeclared*
- 11.1: Hybrid Orbitals Account for Molecular Shape - *CC BY-NC-SA 4.0*
- 11.2: Hybrid Orbitals in Water - *Undeclared*
- 11.3: BeH_2 is Linear and H_2O is Bent - *Undeclared*
- 11.4: The pi-Electron Approximation of Conjugation - *Undeclared*
- 11.5: Butadiene is Stabilized by a Delocalization Energy - *CC BY-SA 4.0*
- 11.6: Benzene and Aromaticity - *Undeclared*
- 11.E: Bonding in Polyatomic Molecules (Exercises) - *Undeclared*

◦ 12: Molecular Spectroscopy - *Undeclared*
- 12.1: The Electromagnetic Spectrum - *CC BY 4.0*
- 12.2: Rotations Accompany Vibrational Transitions - *CC BY 4.0*
- 12.3: Unequal Spacings in Vibration-Rotation Spectra - *Undeclared*
- 12.4: Unequal Spacings in Pure Rotational Spectra - *Undeclared*
- 12.5: Vibrational Overtones - *CC BY 4.0*
- 12.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information - *CC BY-SA 4.0*
- 12.7: The Franck-Condon Principle - *CC BY-NC-SA 4.0*
- 12.8: Rotational Spectra of Polyatomic Molecules - *CC BY-NC-SA 4.0*
- 12.9: Normal Modes in Polyatomic Molecules - *CC BY-NC-SA 4.0*
- 12.10: Time-Dependent Perturbation Theory - *CC BY-SA 4.0*
- 12.11: The Selection Rule for the Rigid Rotor - *CC BY-SA 4.0*
- 12.12: The Harmonic Oscillator Selection Rule - *CC BY-NC-SA 4.0*
- 12.13: Group Theory Determines Infrared Activity - *CC BY-NC-SA 4.0*
- 12.E: Molecular Spectroscopy (Exercises) - *Undeclared*

◦ 13: Lasers, Laser Spectroscopy, and Photochemistry - *CC BY 4.0*
- 13.1: Electronically Excited Molecules can Relax by a Number of Processes - *Undeclared*
- 13.2: The Dynamics of Transitions can be Modeled by Rate Equations - *Undeclared*
- 13.3: A Two-Level System Cannot Achieve a Population Inversion - *Undeclared*
- 13.4: Population Inversion can be Achieved in a Three-Level System - *Undeclared*
- 13.5: What is Inside a Laser? - *Undeclared*
- 13.6: The Helium-Neon Laser - *CC BY 4.0*
- 13.7: Modern Applications of Laser Spectroscopy - *Undeclared*
- 13.E: Lasers, Laser Spectroscopy, and Photochemistry (Exercises) - *Undeclared*

◦ 14: Math Chapters - *Undeclared*
- 14.1: Complex Numbers - *Undeclared*
- 14.2: Probability and Statistics - *Undeclared*
- 14.3: Determinants - *CC BY-NC-SA 4.0*
  - 14.3.1: The Solutions of Simultaneous Linear Equations - *CC BY-NC-SA 4.0*
  - 14.3.2: Calculation of a 3 × 3 determinant - *CC BY-NC-SA 4.0*
  - 14.3.3: The Determinant as a Volume - *CC BY-NC-SA 4.0*
  - 14.3.4: Properties of Determinants - *CC BY-NC-SA 4.0*
  - 14.3.5: Problems - *CC BY-NC-SA 4.0*
- 14.4: Vectors - *Undeclared*
- 14.5: Spherical Coordinates - *Undeclared*
- 14.6: Matrices - *Undeclared*
- 14.7: Numerical Methods - *Undeclared*
- 14.8: Partial Differentiation - *Undeclared*
- 14.9: Series and Limits - *Undeclared*
- 14.10: Fourier Analysis - *Undeclared*
  - 14.10.1: Fourier Analysis in Matlab - *Undeclared*
  - 14.10.2: Fourier Synthesis of Periodic Waveforms - *Undeclared*
- 14.11: The Binomial Distribution and Stirling's Appromixation - *Undeclared*
- 14.12: Formula Sheets - *CC BY-NC-SA 4.0*
  - 14.12.1: Some Important Numbers - *CC BY-NC-SA 4.0*
  - 14.12.2: Quadratic Equation - *CC BY-NC-SA 4.0*
  - 14.12.3: Logarithms and Exponentials - *CC BY-NC-SA 4.0*
  - 14.12.4: Trigonometric Identities - *CC BY-NC-SA 4.0*
  - 14.12.5: Complex Numbers - *CC BY-NC-SA 4.0*

- 14.12.6: Operators - *CC BY-NC-SA 4.0*
- 14.12.7: Taylor Series - *CC BY-NC-SA 4.0*
- 14.12.8: Fourier Series - *CC BY-NC-SA 4.0*
- 14.12.9: Derivatives and Primitives (Indefinite Integrals) - *CC BY-NC-SA 4.0*
- 14.12.10: Definite integrals - *CC BY-NC-SA 4.0*
- 14.12.11: Differentiation Rules - *CC BY-NC-SA 4.0*
- 14.12.12: Partial Derivatives - *CC BY-NC-SA 4.0*
- 14.12.13: Coordinate Systems - *CC BY-NC-SA 4.0*

◦ Back Matter - *Undeclared*
- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*

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