QUANTUM CHEMISTRY



Pacific Union College

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Quantum Chemistry

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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 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 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: Chemical Bonding in Diatomic Molecules

- 9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules
- 9.2: The H_2^+ Prototypical Species
- 9.3: The Overlap Integral

- 9.4: Chemical Bond Stability
- 9.5: Bonding and Antibonding Orbitals
- 9.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital
- 9.7: Molecular Orbitals Can Be Ordered According to Their Energies
- 9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule
- 9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle
- 9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic
- 9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals
- 9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules
- 9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently
- 9.14: Molecular Term Symbols Describe Electronic States of Molecules
- 9.15: Molecular Term Symbols Designate Symmetry
- 9.16: Most Molecules Have Excited Electronic States
- 9.E: Chemical Bond in Diatomic Molecules (Exercises)

10: Bonding in Polyatomic Molecules

- 10.1: Hybrid Orbitals Account for Molecular Shape
- 10.2: Hybrid Orbitals in Water
- 10.3: Why is BeH_2 Linear and H_2O Bent?
- 10.4: Photoelectron Spectroscopy
- 10.5: The \(\pi\)-Electron Approximation of Conjugation
- 10.6: Butadiene is Stabilized by a Delocalization Energy
- 10.7: Benzene and Aromaticity
- 10.E: Bonding in Polyatomic Molecules (Exercises)

11: Computational Quantum Chemistry

- 11.1: Overview of Quantum Calculations
- 11.2: Gaussian Basis Sets
- 11.3: Extended Basis Sets
- 11.4: Orbital Polarization Terms in Basis Sets
- 11.5: The Ground-State Energy of H_2
- 11.6: Quantum Calculations
- 11.E: Computational Quantum Chemistry (Exercises)

12: Group Theory - The Exploitation of Symmetry

- 12.1: The Exploitation of Symmetry
- 12.2: Symmetry Elements
- 12.3: Symmetry Operations Define Groups
- 12.4: Symmetry Operations as Matrices
- 12.5: The \(C_{3V}\) Point Group
- 12.6: Character Tables
- 12.7: Characters of Irreducible Representations
- 12.8: Using Symmetry to Solve Secular Determinants
- 12.9: Generating Operators
- 12.E: Group Theory - The Exploitation of Symmetry (Exercises)

13: Molecular Spectroscopy

- 13.1: The Electromagnetic Spectrum
- 13.2: Rotations Accompany Vibrational Transitions
- 13.3: Unequal Spacings in Vibration-Rotation Spectra
- 13.4: Unequal Spacings in Pure Rotational Spectra
- 13.5: Vibrational Overtones
- 13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
- 13.7: The Franck-Condon Principle
- 13.8: Rotational Spectra of Polyatomic Molecules
- 13.9: Normal Modes in Polyatomic Molecules
- 13.10: Irreducible Representation of Point Groups
- 13.11: Time-Dependent Perturbation Theory
- 13.12: The Selection Rule for the Rigid Rotor
- 13.13: The Harmonic Oscillator Selection Rule
- 13.14: Group Theory Determines Infrared Activity
- 13.E: Molecular Spectroscopy (Exercises)

14: Nuclear Magnetic Resonance Spectroscopy

- 14.1: Nuclei Have Intrinsic Spin Angular Momenta
- 14.2: Magnetic Moments Interact with Magnetic Fields
- 14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz
- 14.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded
- 14.5: Chemical Shifts Depend upon the Chemical Environment of the Nucleus
- 14.6: Spin-Spin Coupling Can Lead to Multiplets in NMR Spectra
- 14.7: Spin-Spin Coupling Between Chemically Equivalent Protons is Not Observed
- 14.8: The n+1 Rule Applies Only to First-Order Spectra
- 14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method
- 14.E: Nuclear Magnetic Resonance Spectroscopy (Exercises)

15: Lasers, Laser Spectroscopy, and Photochemistry

- 15.1: Electronically Excited Molecules can Relax by a Number of Processes
- 15.2: The Dynamics of Transitions can be Modeled by Rate Equations
- 15.3: A Two-Level System Cannot Achieve a Population Inversion
- 15.4: Population Inversion can be Achieved in a Three-Level System
- 15.5: What is Inside a Laser?
- 15.6: The Helium-Neon Laser
- 15.7: High-Resolution Laser Spectroscopy
- 15.8: Pulsed Lasers Can by Used to Measure the Dynamics of Photochemical Processes
- 15.E: Lasers, Laser Spectroscopy, and Photochemistry (Exercises)

Index

Glossary

Detailed Licensing

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CHAPTER OVERVIEW

1: The Dawn of the Quantum Theory

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

"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-Boltmann'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**).

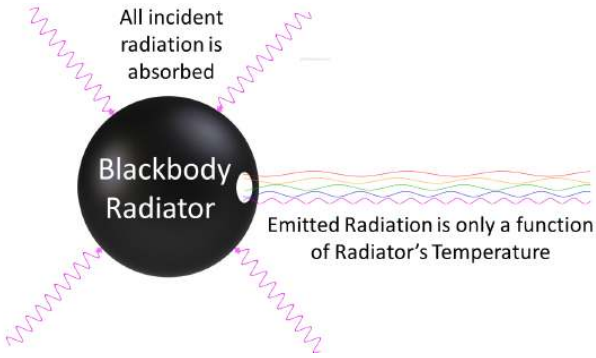


Figure **1.1.2**: Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation.

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**.

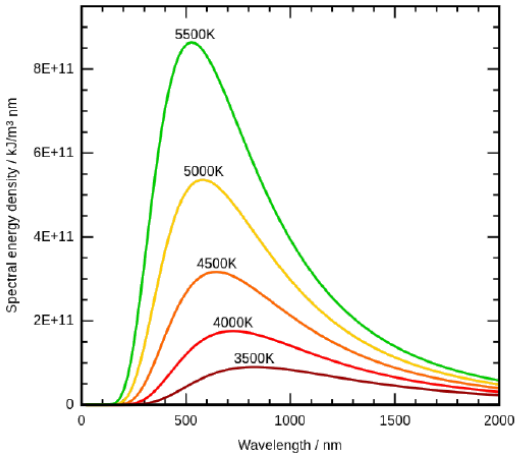
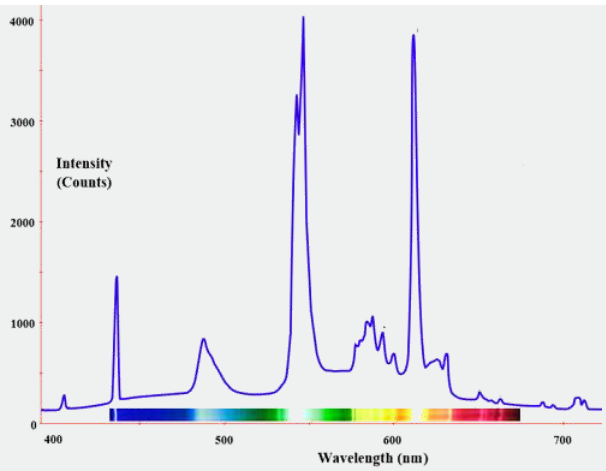


Figure **1.1.3**: Graphic representation of spectral distribution of blackbody radiation at different temperatures. (CC-SA-BY 3.0; 4C). The Stefan-Boltmann's Law is observed as the increase in the emission amplitude with increasing temperature and the Wien's Displacement Law is observed as the shift to smaller wavelength with increasing temperature.

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-Boltmann'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-SA 2.5; Deglr6328 and H Padleckas).

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.

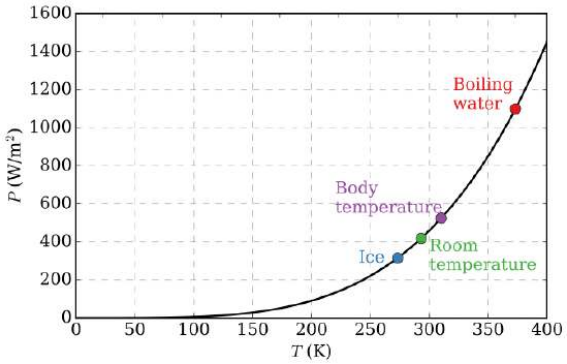


Figure **1.1.4**: Graph of a function of total emitted energy of a blackbody proportional to the fourth power of its thermodynamic temperature T according to the Stefan–Boltzmann law. (CC -SA-BY 4.0; Nicoguaro).

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 $A = 4\pi R^2$.

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

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

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

This value is per square meter.

(b) To calculate the total power radiated by the sun is thus:

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

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 $P = \sigma T^4$.

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

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

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

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

500 nm

Answer b

10.0 microns

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

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

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

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. The charge e of the oscillator does not appear: the result is independent of the coupling strength between the oscillator and the radiation, the coupling only has to be strong enough to ensure thermal equilibrium. The derivation of the law can be found here.

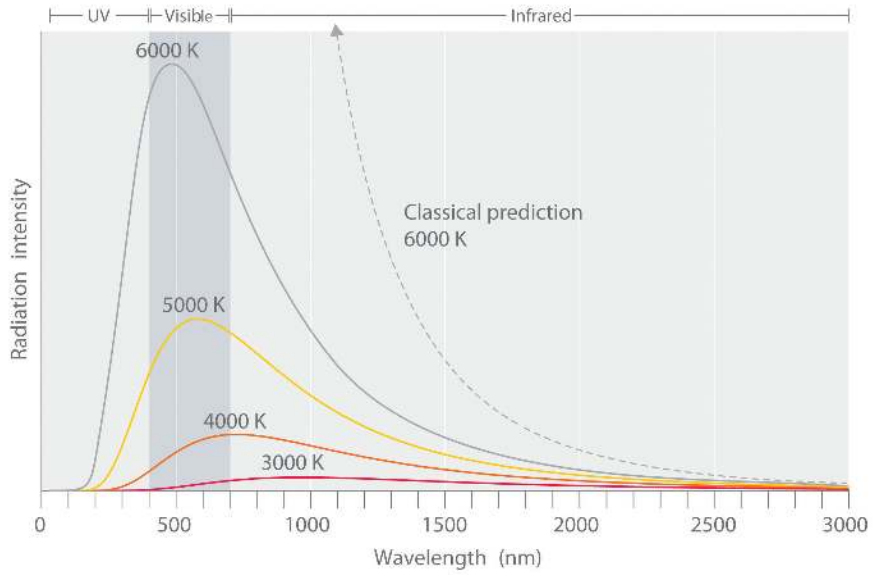


Figure 1.1.5: Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the hot metalwork in Figure 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).

Differential vs. Integral representation of the distribution

Radiation is understand as a continuous distribution of amplitude vs. wavelength or, equivalently, vs. frequency (Figure **1.1.5**). At an specific frequency ν, according to Rayleigh-Jeans law, radiation is

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

In practice, it is hard to measure a single frequency and 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:

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

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).

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

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 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

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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. 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." There was no agreement between theory and experiment in the ultraviolet region of the blackbody spectrum.

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.

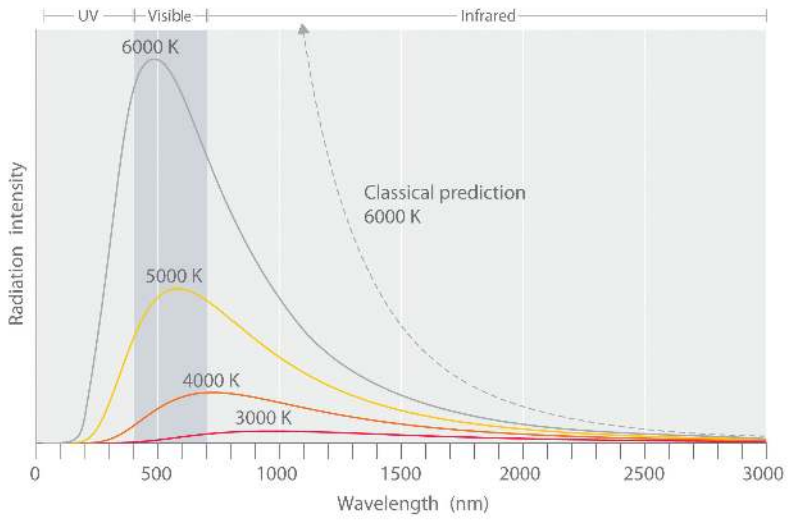


Figure **1.2.1**: Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases, 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 by request).

Quantization

Although quantization may seem to be an unfamiliar concept, we encounter it frequently. 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. Even electrical charge is quantized: an ion may have a charge of −1 or −2, but *not* −1.33 electron charges.

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

$$h = 6.626070040(81) \times 10^{-34}\, J \cdot s \tag{1.2.2}$$

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

$$h = 6.626 \times 10^{-34}\, J \cdot s \tag{1.2.3}$$

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*ν, Planck devised an equation that fit the experimental data shown in Figure **1.2.2**. 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 **1.2.2**, 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:

$$d\rho(\nu, T) = \rho_\nu(T)d\nu \tag{1.2.4}$$

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

with

- $\pi = 3.14159$
- $h = 6.626 \times 10^{-34} J \cdot s$
- $c = 3.00 \times 10^{8}\ \frac{m}{s}$
- $\nu = \frac{1}{s}$
- $k_B = 1.38 \times 10^{-23}\ \frac{J}{K}$
- T is absolute temperature (in Kelvin)

Planck's radiation energy density (Equation 1.2.5) can also be expressed in terms of wavelength λ.

$$\rho(\lambda, T)d\lambda = \frac{2hc^2}{\lambda^5}\frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1}d\lambda \tag{1.2.6}$$

Planck's equation (Equation 1.2.6) gave an excellent agreement with the experimental observations for all temperatures.

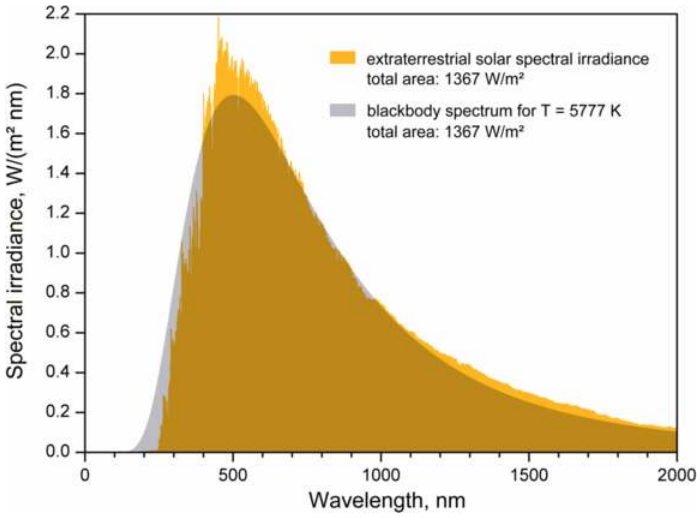
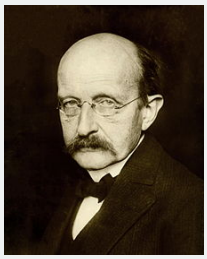


Figure **1.2.3**: The Sun is an excellent approximation of a blackbody. Its effective temperature is ~5777 K. (CC-SA-BY 3.0; Sch).

Max Planck (1858–1947)

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.



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. (credit: Library of Congress, Prints and Photographs Division via Wikimedia Commons)

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 1.2.6 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

$$E = nh\nu \tag{1.2.7}$$

where n is an integer (now called a quantum number), 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

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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 this result? 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 (also called photoelectrons) leaving the metal's surface by J.J. Thomson (Figure **1.3.1**).

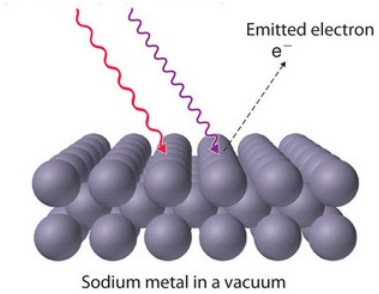


Figure **1.3.1**: The Photoelectric Effect involves the irradiating a metal surface with photons of sufficiently high energy to causes electrons to be ejected from the metal.

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.

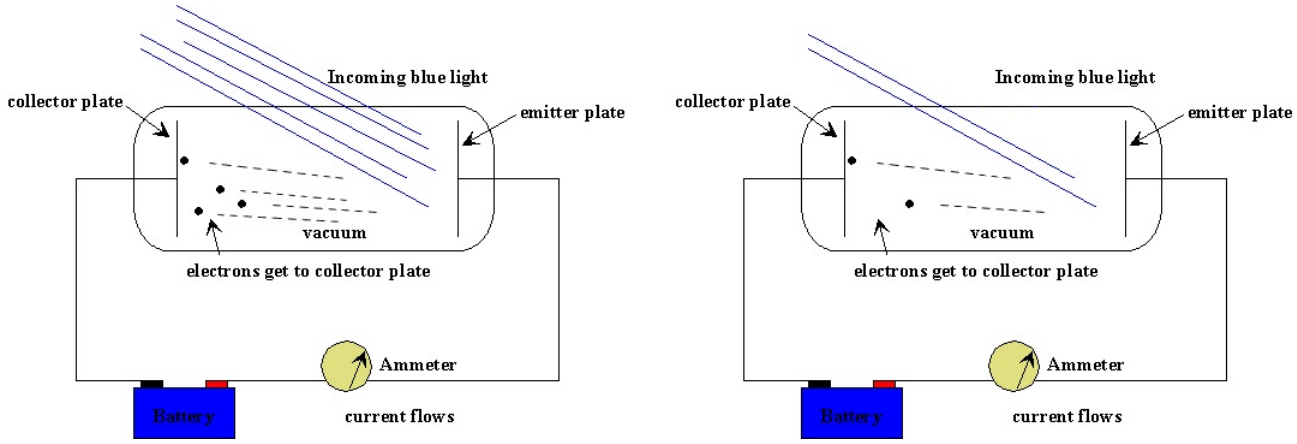


Figure **1.3.2**: Millikan's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (Michael Fowler).

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.

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 caused electrons to be ejected with more energy (Figures **1.3.3**).

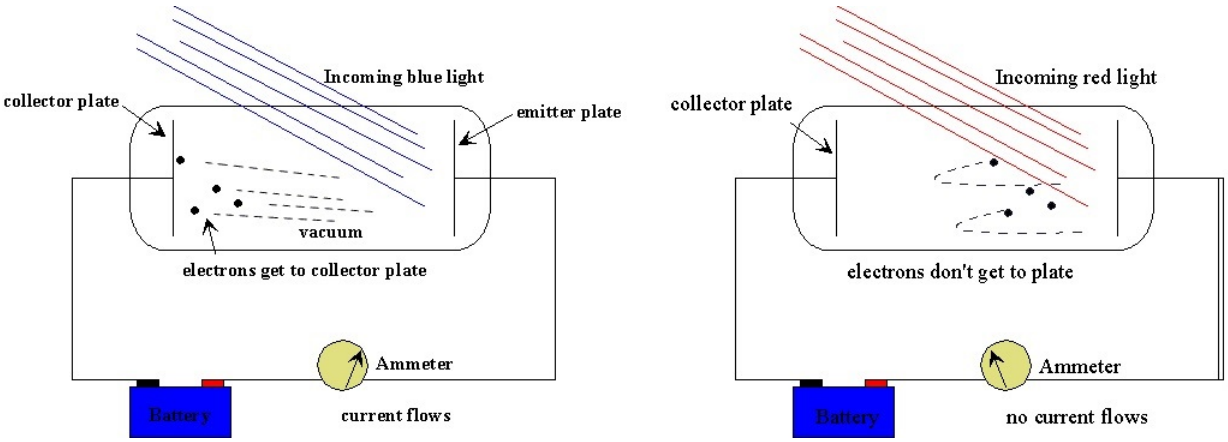


Figure **1.3.3**: Millikan's photoelectric experiment (left) High-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector plate, the potential supplied by the battery is less than V_{stop}, for blue light. (right) 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. (Michael Fowler).

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).

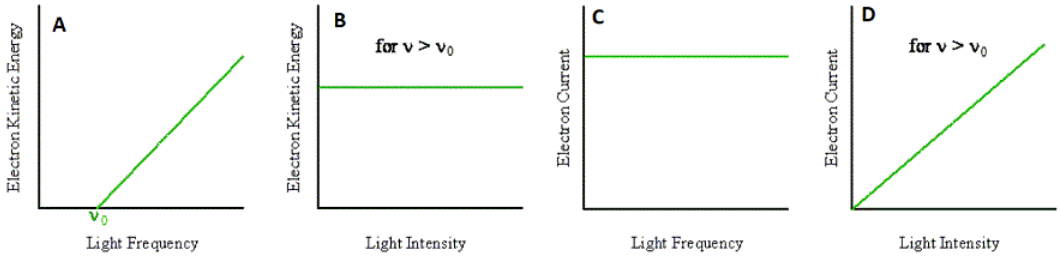


Figure **1.3.4**: Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the light intensity. (C) The number of electrons emitted per second (i.e. the electric current) is independent of frequency. (D) The number of electrons increases linearly with the light intensity. (Michael Fowler).

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.

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, this is usually called 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 **1.3.4***A*). 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.

$$\mathrm{M(s) + E \ \rightarrow M^{+}(s) + e^{-}(free)} \tag{1.3.3}$$

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

$$\mathrm{M(g) + E \ \rightarrow M^{+}(g) + e^{-}(free)} \tag{1.3.4}$$

These two energies are generally different (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 (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)
Copper (Cu)	4.7	7.7
Silver (Ag)	4.72	7.57
Aluminum (Al)	4.20	5.98
Gold (Au)	5.17	9.22
Boron (B)	4.45	8.298
Beryllium (Be)	4.98	9.32
Bismuth (Bi)	4.34	7.29
Carbon (C)	5.0	11.26
Cesium (Ce)	1.95	3.89
Iron (Fe)	4.67	7.87
Gallium (Ga)	4.32	5.99
(Hg) liquid	4.47	10.43
Sodium (Na)	2.36	5.13
Lithium (Li)	2.93	5.39
Potassium	2.3	4.34
Selenium (Se)	5.9	9.75
Silicon (Si)	4.85	8.15
Tin (Sn)	4.42	7.34
Germanium (Ge)	5.0	7.89
Arsenic (As)	3.75	9.81

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

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

Answer

Given that the workfunction is 4.73 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.

? Exercise 1.3.2

Why is the workfunction generally lower than the ionization energy?

Answer

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 an particle is, the lower its energy.

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 $KE_e = h\nu - \Phi$, 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 BE 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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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).

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.

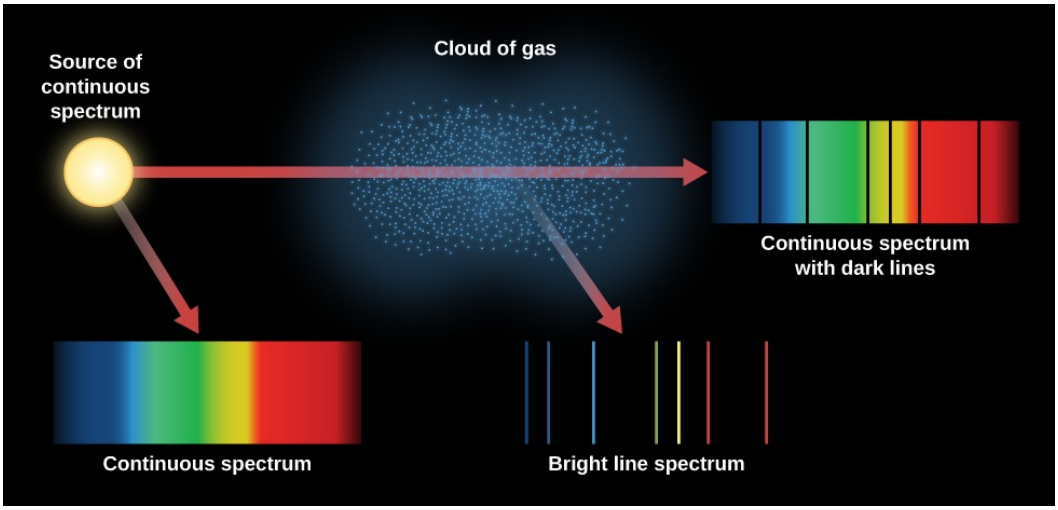


Figure **1.4.1**: Three Kinds of Spectra. When we see a lightbulb or other source of continuous radiation, all the colors are present. When the continuous spectrum is seen through a thinner gas cloud, the cloud's atoms produce absorption lines in the continuous spectrum. When the excited cloud is seen 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; OpenStax).

In 1802, William Wollaston in England had discovered (perhaps by using a thinner slit or a better prism) that in fact the solar spectrum itself 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

Fraunhofer Lines

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.

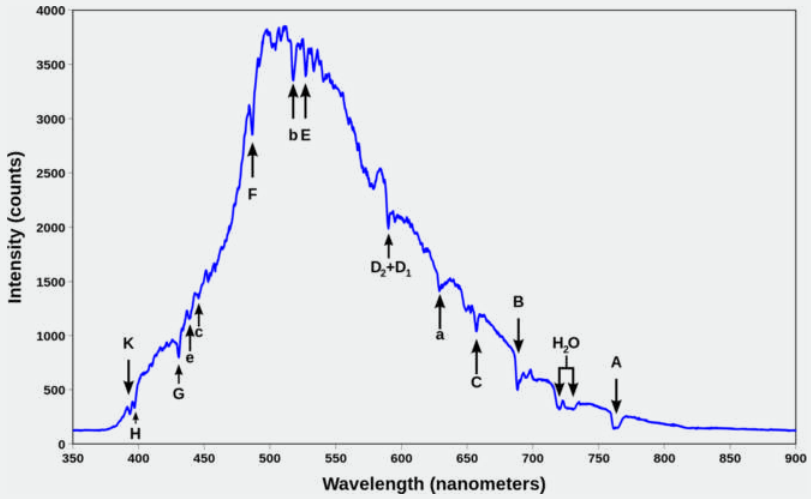


Figure **1.4.2**: Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. (CC BY-SA 4.0; Eric Bajart via Wikipedia).

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**.

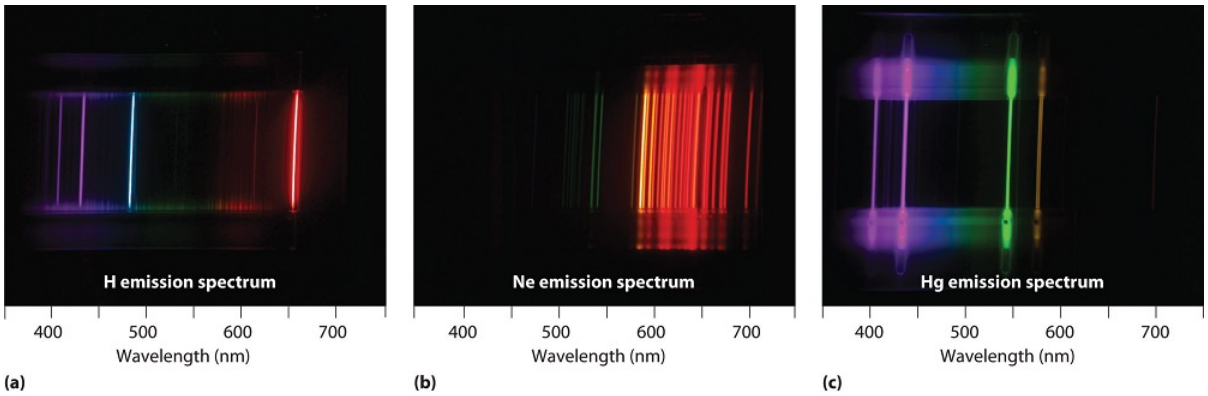


Figure **1.4.3**: The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. 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.

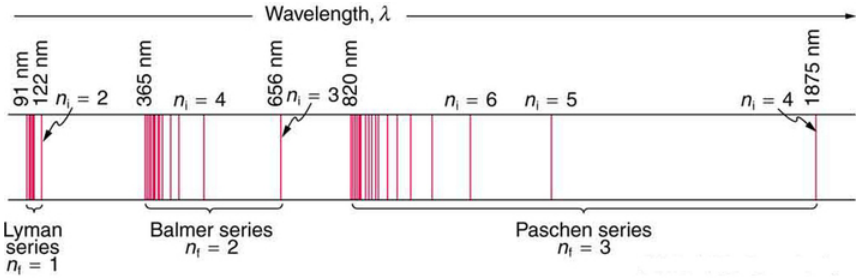


Figure **1.4.4**: A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of n_f and 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. Angstrom 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 Angstrom (Table **1.4.2**). Balmer predicted that other lines exist in the infrared that correspond to \(n_2 >= 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 resents 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.

$$E = \frac{hc}{\lambda}$$
$$= hc \times \frac{1}{\lambda}$$
$$= hc\tilde{\nu} \tag{1.4.4}$$
$$\propto \tilde{\nu}$$

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

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

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

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:

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

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} 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., $n_1 = 1$)?

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

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	...

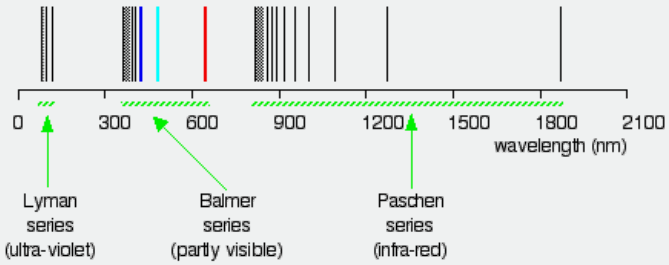
Do you know in what region of the electromagnetic radiation these lines are? Of course, these lines are in the UV region, and they are not visible, but they are detected by instruments; these lines form a **Lyman series**. The existences of the Lyman series and Balmer's series suggest the existence of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

Mulitple 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 $n_1 = 6$



The spectral series of hydrogen based of the Rydberg Equation (on a logarithmic scale). (Jim Clark).

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:

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

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}.

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

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

B This 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

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

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.

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1.6: Matter Has Wavelike Properties

Learning Objectives

- To introduce the wave-particle duality of light extends to matter

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 *particle-wave 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

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

Solving for the wavelength λ gives Equation 1.6.1:

$$\lambda = \frac{h}{p} = \frac{h}{mv} \tag{1.6.3}$$

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 1.6.3 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 1.6.3), 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:

$$KE = \frac{mv^2}{2}$$
$$= \frac{p^2}{2m} = 1000\ eV$$

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

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

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

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

For perspective, the hydrogen atom is about 120 pm across.

? 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

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:

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

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.

Contributors

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

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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.

Light Diffraction (Young's Double Slit Experiment)

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**).

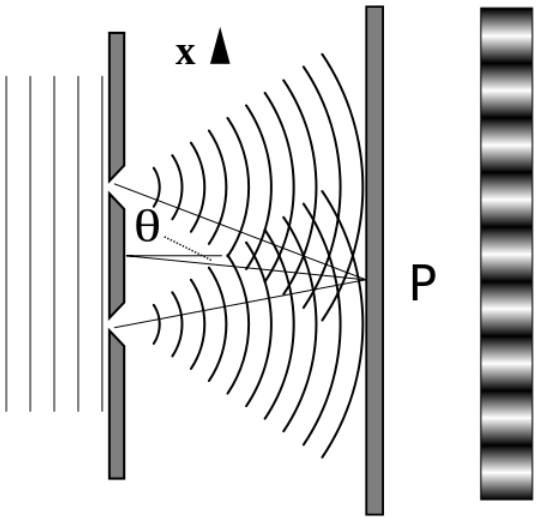


Figure **1.7.1**: Young double slit experiment. Two slits are illuminated by a plane light waves. from Wikipedia.

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

Here, we use water waves (pictured as waves in a plane parallel to the double slit apparatus) and observe what happens when they impinge on the 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 **1.7.2**).

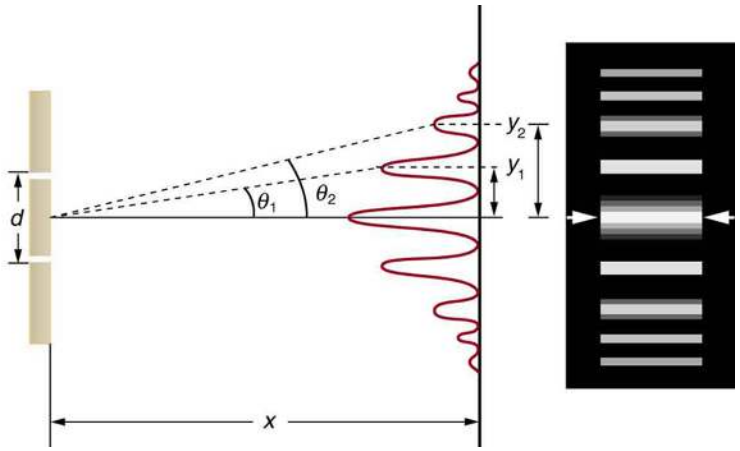


Figure **1.7.2**: Interference through a double slit. (CC SA-BY; OpenSTAX).

Electron Diffraction (Davisson–Germer Experiment)

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).

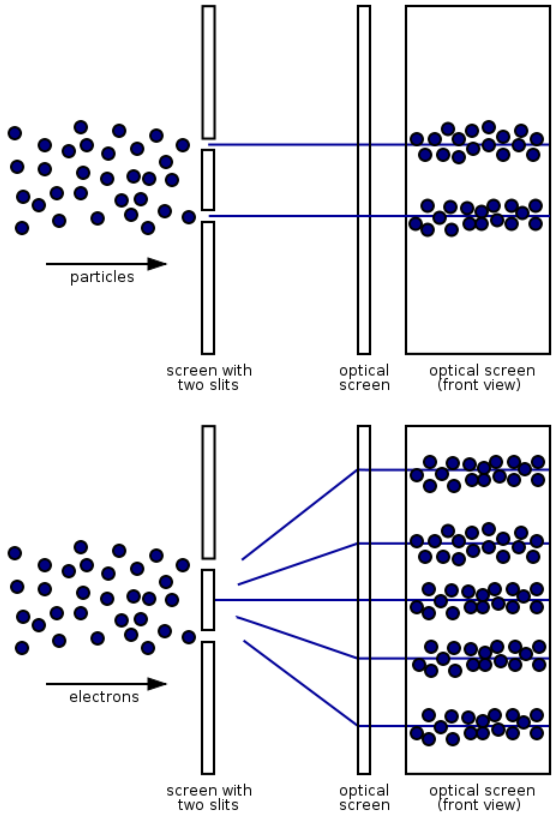


Figure **1.7.3**: (left) classical model of electrons. (right) wave property of electrons.

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. 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. 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.(public domain; United States Geological Survey, an agency of the United States Department of the Interior)

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

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):

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

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

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

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 appreciable.

Contributors

- Michael Fowler (Beams Professor, Department of Physics, University of Virginia)
- Mark Tuckerman (New York University)
- Wikipedia
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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.

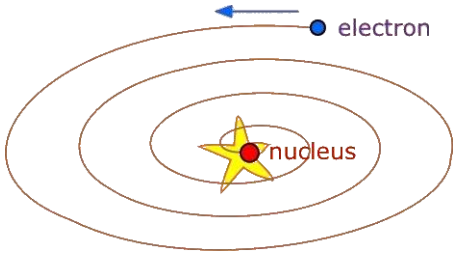


Figure 1.8.1: The classical death spiral of an electron around a nucleus. (Stephen Lower).

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:

$$F = -\frac{dV}{dx} \tag{1.8.3}$$

or as gradients in 3-D forces

$$F = -\nabla V \tag{1.8.4}$$

where ∇ is the vector of partial derivatives

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \tag{1.8.5}$$

The most familiar conservative forces are gravity and Coloumbic forces.

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

$$V(r) = \frac{kQ_1Q_2}{r} \tag{1.8.6}$$

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

$$F(r) = -\frac{dV}{dr} \tag{1.8.7}$$

As r is varied, the energy will change, so that we have an example of a potential energy curve $V(r)$. If Q_1 and Q_2 are the same sign, then the curve appears roughly as follows:

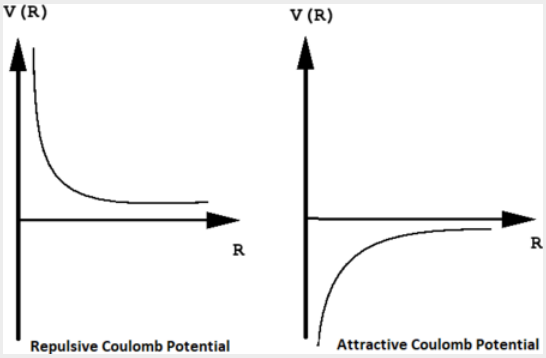


Figure 1.8.2: Potential energy curve for the Coulomb interactions between two charges of same sign (left) and opposite signs (right).

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. If the charges are of opposite sign, then the curve appears roughly Figure 1.8.2 (right). 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.

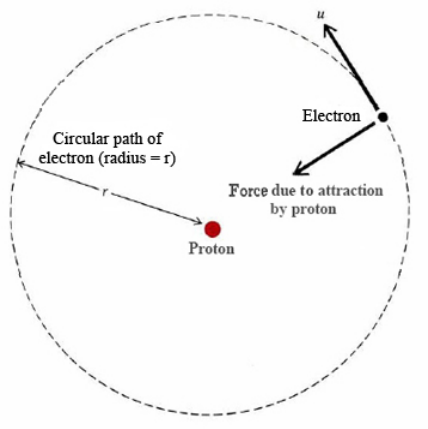


Figure **1.8.3**: Bohr atom with an electron revolving around a fixed nucleus.

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 1.8.6), which is more commonly represented in the form:

$$k = \frac{1}{4\pi\epsilon_0} \tag{1.8.8}$$

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:

$$E_{total} = \underbrace{\frac{p^2}{2m_e}}_{\text{kinetic energy}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r}}_{\text{potential energy}} \tag{1.8.9}$$

The force on the electron is

$$\vec{F} = -\frac{Ze^2}{4\pi\epsilon_0 r^3} r \tag{1.8.10}$$

and its magnitude is

$$\vec{F} = \left|\vec{F}\right| = \frac{Ze^2}{4\pi\epsilon_0 r^3}|r| = \frac{Ze^2}{4\pi\epsilon_0 r^2} \tag{1.8.11}$$

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

$$|a| = \frac{v^2}{r} \tag{1.8.12}$$

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

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = m_e\frac{v^2}{r} \tag{1.8.13}$$

or

$$\frac{Ze^2}{4\pi\epsilon_0} = m_e v^2 r \tag{1.8.14}$$

or

$$\frac{Ze^2m_er}{4\pi\epsilon_0} = (m_ev r)^2 \tag{1.8.15}$$

The reason for writing the equation this way is that the quantity $m_ev r$ 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 radation and positing that the orbital angular momentum $m_ev r$ of the electron could only take on specific values

$$m_ev r = n\hbar \tag{1.8.16}$$

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

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

Substituting Equation 1.8.16 into the Equation 1.8.15, we find

$$\frac{Ze^2m_er}{4\pi\epsilon_0} = n^2(\hbar)^2 \tag{1.8.17}$$

Equation 1.8.17 implies that orbits could only have certain allowed radii

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{Ze^2m_e}n^2 \tag{1.8.18}$$

$$= \frac{a_0}{Z}n^2 \tag{1.8.19}$$

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

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2m_e} \tag{1.8.20}$$

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

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

$$p_nr_n = n\hbar \tag{1.8.21}$$

$$p_n = \frac{n\hbar}{r_n} \tag{1.8.22}$$

$$= \frac{\hbar Z}{a_0n} \tag{1.8.23}$$

$$= \frac{Ze^2m_e}{4\pi\epsilon_0\hbar n} \tag{1.8.24}$$

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

$$E_n = \frac{p_n^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0r_n} \tag{1.8.25}$$

Substituting in the expressions for p_n and r_n and simplifying gives

$$E_n = -\frac{Z^2e^4m_e}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} = -\frac{e^4m_e}{8\epsilon_0^2h^2}\frac{Z^2}{n^2} \tag{1.8.26}$$

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

$$1\ Ry = \frac{e^4m_e}{8\epsilon_0^2h^2} = 2.18 \times 10^{-18}\ J. \tag{1.8.27}$$

and this simplifies the allowed energies predicted by the Bohr model (Equation 1.8.26) as

$$E_n = -(2.18 \times 10^{-18}) \frac{Z^2}{n^2} \; J = -\frac{Z^2}{n^2} \; R_y \tag{1.8.28}$$

Hence, the energy of the electron in an atom also is quantized. Equation 1.8.28 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).

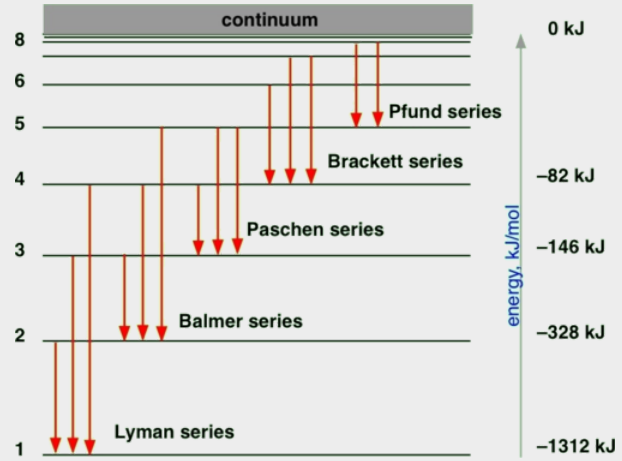


Figure 1.8.4: Energy levels predicted by the Bohr model. (Stephan Lower).

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 1.8.17 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

Starting from Equation 1.8.17 and solving for r:

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

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

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 permitivity of free space: $\epsilon_o = 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$
- $\hbar$ is the reduced planks constant: $\hbar = 1.0546 \times 10^{-34} m^2 kg/s$

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

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

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

$$
\begin{aligned}
r &= \frac{4\hbar^2\pi\epsilon_0}{3e^2m_e} \\
&= \frac{4(1.0546\times10^{-34}m^2kg/s)^2\times\pi\times8.854\times10^{-12}C^2N^{-1}m^{-2}}{3(1.60217662\times10^{-19}C^2)(9.10938356\times10^{-31}kg)} \\
&= 1.76\times10^{-11}m = 17.6\,pm
\end{aligned}
$$

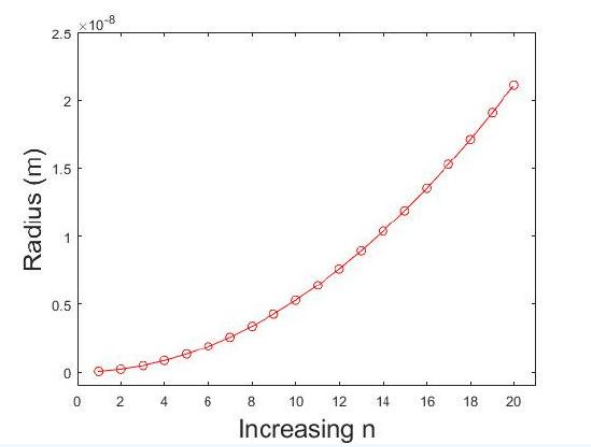
As expected, the $\mathbf{Li^{2+}}$ has a smaller radius than the $\mathbf{H}$ atoms because of the inreased nuclear charge.

? 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

This is a straightforward application of Equation of 1.8.19. 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.

$4\pi\epsilon_0 = 1.113\times10^{-10}\mathrm{C^2J^{-1}m^{-1}}$ and $\hbar = 1.054\times10^{-34}\mathrm{Js}$, also knowing

$$
\begin{aligned}
e &= 1.602\times10^{-19}\mathrm{C\ with} \\
m_e &= 9.109\times10^{-31}\mathrm{kg}
\end{aligned}
\tag{1.8.29}
$$

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

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

resulting in

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

where $a_0 = 5.292\times10^{-11}\mathrm{m}$ which is the Bohr Radius.

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

$$
\begin{aligned}
r_n &= \frac{(5.292\times10^{-11})}{(1)}(40000) \\
&= 2.117\times10^{-6}m
\end{aligned}
$$

for the radius of a hydrogen atom with an electron excited to the $\mathbf{n = 200}$ state. The diameter is then $4.234\times10^{-6}\mathrm{m}$.

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 1.8.16) 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

$$\lambda = \frac{h}{p} \tag{1.8.30}$$

Hence, a larger momentum p implies a shorter wavelength. That means as n increases (Equation 1.8.28), 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 1.8.1*A*). If not, then the waves will overlap imperfectly and cancel out (i.e., the electron will cease to exist) as demonstrated in Figure 1.8.1*B*.

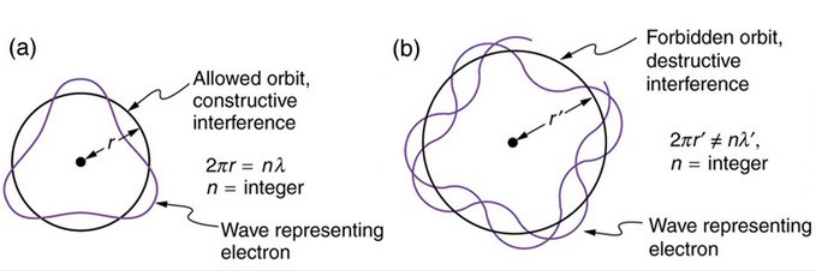


Figure 1.8.5: Waves on a string have a wavelength related to the length of the string, allowing them to interfere constructively. (A) If we imagine the string bent into a closed circle, we get a rough idea of how electrons in circular orbits can interfere constructively. (B) If the wavelength does not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

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).

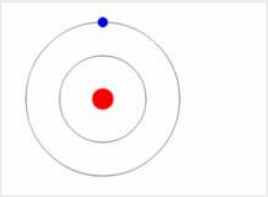


Figure 1.8.6: A simple illustration of Bohr's model of the atom, with an electron making quantum leaps. (CC BY-SA 3.0 unported; Kurzon via Wikipedia)

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 as long as $n_f < n_i$)

$$E_{nf} = E_{ni} - h\nu \tag{1.8.31}$$

or

$$\nu = \frac{E_{nf} - E_{ni}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{1.8.32}$$

We can now identify the Rydberg constant R_H with the ratio of constants on the right hand side of Equation 1.8.32

$$R_H = \frac{me^4}{8\epsilon_0^2 h^3} \tag{1.8.33}$$

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.

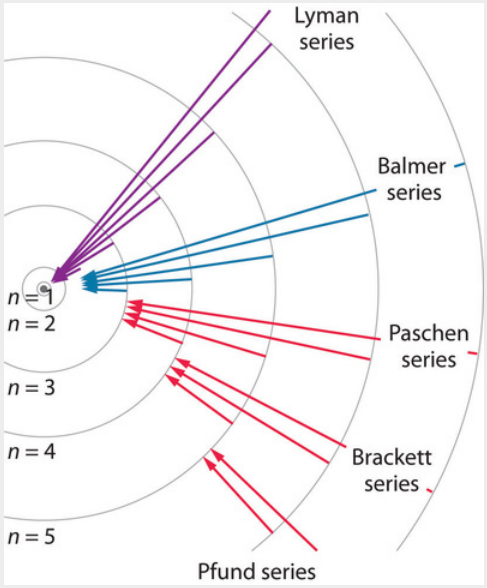


Figure 1.8.7: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to 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.)

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

$$E_{nf} = E_{ni} + h\nu \tag{1.8.34}$$

or

$$\nu = \frac{E_{nf} - E_{ni}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \tag{1.8.35}$$

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 and orbit with $n = 1$.

b. What happens to the energy of the photon as the initial value of n approaches infinity?

Answer

a:

$$
\begin{aligned}
E_{\text{nf}} &= E_{ni} - h\nu \\
E_{photon} = h\nu &= E_{nf} - E_{ni} \\
&= \frac{Z^2 e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \\
&= \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{1^2} - \frac{1}{4^2}\right) \\
&= 2.18 \times 10^{-18}\left(1 - \frac{1}{16}\right) \\
&= 2.05 \times 10^{-18} J
\end{aligned}
$$

b:

As $n_i \to \infty$

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

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 can't 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

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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).

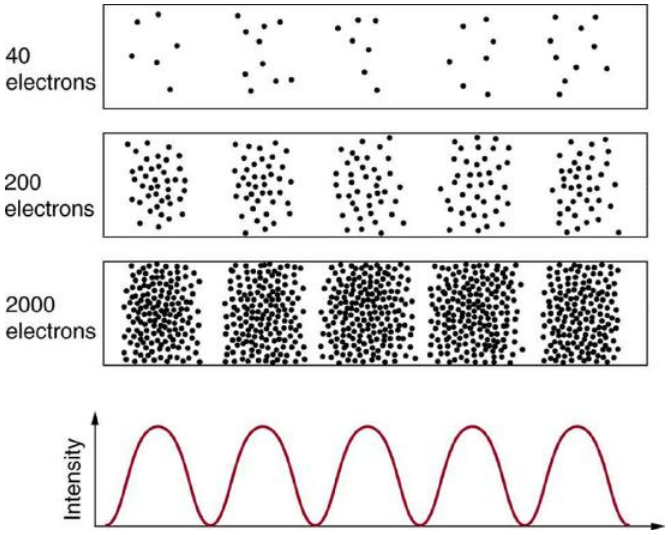


Figure 1.9.1: The building up of the diffraction pattern of electrons scattered from a crystal surface. Each electron arrives at a definite location, which cannot be precisely predicted. The overall distribution shown at the bottom can be predicted as the diffraction of waves having the de Broglie wavelength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

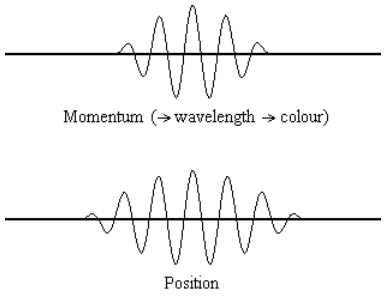


Figure 1.9.2: The animation shows the relevant spreads in the uncertainty for position and momentum of light/photons (light wave's corresponding photon particle). From the result of de Broglie, we know that for a particle with known momentum, p will have a precise value for its de Broglie wavelength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

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

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.



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 $10^{-6}\ m/s$. Calculate the *minimum* uncertainty in its position. What is the *maximum* uncertainty of its position?

Solution

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

$$\begin{aligned}\Delta x &= \frac{\hbar}{2m\Delta v} \\ &= \frac{1.0545718 \times 10^{-34}\ m^2 \cdot kg/s}{(2)(1.0\ g)(10^{-6}\ m/s)} \\ &= 5.3 \times 10^{-29}\ m\end{aligned}$$

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

? 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

$$\Delta v = 1.1 \times^{6} km/s$$

Notice that the uncertainty is 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.

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!"

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

(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 $\mathbf{1.30\ kW/m^2}$ (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 $\boldsymbol{KE_e = h\nu - \Phi}$ 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?

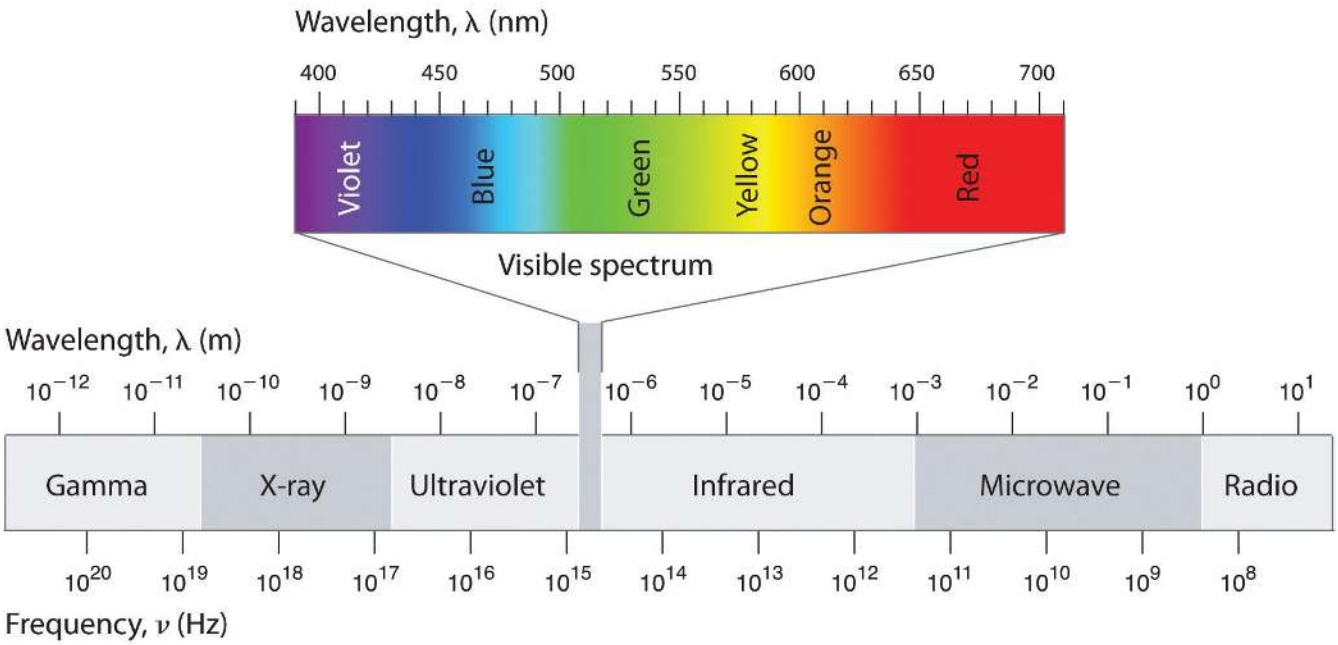
1.2B

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 2.0×10^4 **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

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

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:

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

Given: T = 7500K

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

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

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

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

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

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

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.

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

$$50eV\left(\frac{1.602 \times 10^{-19} J}{1eV}\right) = \frac{(v^2)(9.109 \times 10^{-31} kg)}{2}$$

$$v = 4.19 \times 10^{6}\, m \cdot s^{-1}$$

So

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

b. Replace m_e with m_p in (a) to find $\lambda = 2.86 \times 10^{-3} nm$.

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

$$v = \frac{(1.602 \times 10^{-19} C)^2}{2(2)(6.626 \times 10^{-34} J \cdot s)(8.854 \times 10^{-12} C^2 J^{-1} m^{-1})}$$
$$= 1.09 \times 10^{6} m \cdot s^{-1}$$

So

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

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.

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

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

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

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

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

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

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

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

$$T = 293.5K$$
$$= 20.35°C$$

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 $\mathbf{He^{+}}$ or $\mathbf{Li^{2+}}$.

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.

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

Simplifying this expression we find that

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

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

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

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 $\frac{Ze^2}{4r^2\pi\epsilon_o} = \frac{m_e\nu^2}{r}$ We find that

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

Now solving for the total energy of the system

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

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

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

Substituting r from above we quantize the energy such that

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

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

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

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

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

1.32

The series in the $\mathbf{He^+}$ 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 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 nth 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 $\Delta t \leq h/(mc^2)$. 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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CHAPTER OVERVIEW

2: The Classical Wave Equation

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

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 wave function 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).

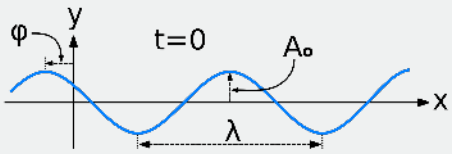
Wave Fundamentals

The simplest wave is the (spatially) one-dimensional sine wave (or *harmonic wave* or *sinusoid*) with an amplitude u described by the equation:

$$u(x,t) = A\sin(kx - \omega t + \phi) \tag{2.1.1}$$

where

- A 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 the illustration to the right, 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*. These two wavelike extreme also apply to particles.

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:

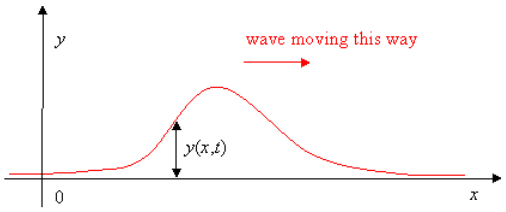


Figure **2.1.1**: A one-dimensional traveling wave at one instance of time t.

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 **2.1.1** 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 **2.1.2**). 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.

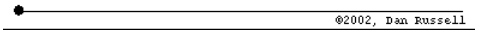


Figure **2.1.2**: A one-dimensional traveling wave at as a function of time. Traveling waves propagate energy from one spot to another with a fixed velocity v. (CC BY-NC-ND; Daniel A. Russell).

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

$$y(x,t) = f(x - vt) \tag{2.1.2}$$

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 **2.1.3**) 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 *nodes*. The places of maximum oscillation are *antinodes*.

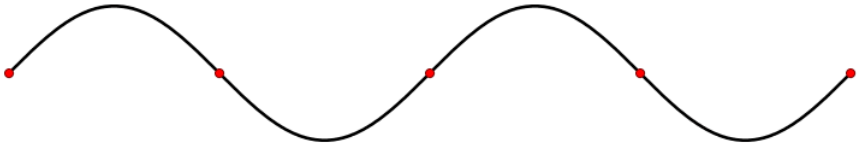


Figure **2.1.3**: Animation of standing wave in the stationary medium with marked wave nodes (red circles). (public domain; LucasVB).

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

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2} \tag{2.1.3}$$

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 2.1.3 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 2.1.3 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

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

and

$$u(L,t) = 0 \tag{2.1.5}$$

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 2.1.3 subject to the boundary conditions in Equations 2.1.4 and 2.1.5 (discussed in detail later) results in the wave in Figure **2.1.4**. 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 **2.1.4**: 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 2.1.3) 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.

Contributors

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2.2: The Method of Separation of Variables

Learning Objectives

- To be introduced to the Separation of Variables 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

   $$u(x,t) = X(x)T(t) \tag{2.2.2}$$

   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*,

   $$u(x,t) = \sum_i c_i X_i(x) T_i(t) \tag{2.2.3}$$

   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 2.2.3 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.

$$u(x,t) = X(x)T(t) \tag{2.2.4}$$

Substitute Equation 2.2.4 into the one-dimensional wave equation (Equation 2.2.1) gives

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

Since X is not a function of t and T is not a function of x, Equation 2.2.5 can be simplified

$$T(t)\frac{\partial^2 X(x)}{\partial x^2} = \frac{1}{v^2}X(x)\frac{\partial^2 T(t)}{\partial t^2} \tag{2.2.6}$$

Collecting the expressions that depend on x on the left side of Equation 2.2.6 and of t on the right side results in

$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2} = \frac{1}{v^2}\frac{1}{T(t)}\frac{\partial^2 T(t)}{\partial t^2} \tag{2.2.7}$$

Equation 2.2.7 is an interesting equation since the 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:*

$$\frac{d^2 T(t)}{dt^2} - Kv^2 T(t) = 0 \tag{2.2.8}$$

$$\frac{d^2 X(x)}{dx^2} - KX(x) = 0 \tag{2.2.9}$$

Hence, by substituting the new product solution form (Equation 2.2.4) 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 2.2.9 is

$$X(x) = Ae^{\sqrt{K}x} + Be^{-\sqrt{K}x} \tag{2.2.10}$$

At this stage, Equation 2.2.10 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

$$u(0, t) = X(x)T(t) = 0 \tag{2.2.11}$$

$$u(L, t) = X(x)T(t) = 0 \tag{2.2.12}$$

for all times t.

Applying the two boundary conditions in Equations 2.2.11 and 2.2.12 into the general solution in Equation 2.2.10 results into relationships between A and B:

$$X(0) = A + B = 0 \ @ \ x = 0 \tag{2.2.13}$$

and

$$X(L) = Ae^{\sqrt{K}L} + Be^{-\sqrt{K}L} = 0 \ @ \ x = L \tag{2.2.14}$$

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 2.2.8 and 2.2.9 can be generalized into the following equations

$$\frac{d^2 y(x)}{dx^2} - k^2 y(x) = 0 \tag{2.2.15}$$

where k is a real constant (i.e., not complex). Equation 2.2.15 is a *homogeneous* second order linear differential equation. The general solution to these types of differential equations has the form

$$y(x) = e^{\alpha x} \tag{2.2.16}$$

where α is a constant to be determined by the constraints of system. Substituting Equation 2.2.16 into Equation 2.2.15 results in

$$\left(\alpha^2 - k^2\right) y(x) = 0 \tag{2.2.17}$$

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

$$\alpha^2 - k^2 = 0 \tag{2.2.18}$$

so

$$\alpha = \pm k \tag{2.2.19}$$

Hence, there are two solutions to the general Equation 2.2.15, 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 2.2.19 into Equation 2.2.16

$$y(x) = e^{k x} \tag{2.2.20}$$

$$y(x) = e^{-k x} \tag{2.2.21}$$

The general solution can then be any linear combination of these two equations

$$y(x) = c_1 e^{k x} + c_2 e^{-k x} \tag{2.2.22}$$

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

$$\begin{aligned} \alpha^2 e^{\alpha t} + 3(\alpha e^{\alpha t}) - 4(e^{\alpha t}) &= (\alpha^2 + 3\alpha - 4) e^{\alpha t} \\ &= 0 \end{aligned}$$

Now divide by $e^{\alpha t}$ to get

$$\begin{aligned} \alpha^2 + 3\alpha - 4 &= 0 \\ (\alpha - 1)(\alpha + 4) &= 0 \\ \alpha &= 1 \end{aligned}$$

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

$$\begin{aligned} r^2 e^{rt} + (re^{rt}) - 6(e^{rt}) &= (r^2 - r - 6)e^{rt} \\ &= 0 \end{aligned}$$

Now divide by e^{rt} to get

$$\begin{aligned} r^2 - r - 6 &= 0 \\ (r-3)(r+2) &= 0 \end{aligned}$$

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

$$y' = 3C_1e^{3t} - 2C_2e^{-2t}$$

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 2.2.8 and 2.2.9 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

$$X(x) = Ae^{ix} + Be^{-ix} \tag{2.3.3}$$

Exercise 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

$$X(x) = Ae^{ipx} + Be^{-ipx} \tag{2.3.4}$$

Expand the complex exponentials into trigonometric functions via Euler formula ($e^{i\theta} = \cos\theta + i\sin\theta$)

$$X(x) = A\left[\cos(px) + i\sin(px)\right] + B\left[\cos(px) - i\sin(px)\right] \tag{2.3.5}$$

collecting like terms

$$X(x) = (A+B)\cos(px) + i(A-B)\sin(px) \tag{2.3.6}$$

Introduce new *complex* constants $c_1 = A + B$ and $c_2 = i(A - B)$ so that the general solution in Equation **2.3.6** can be expressed as oscillatory functions

$$X(x) = c_1 \cos(px) + c_2 \sin(px) \tag{2.3.7}$$

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 2.3.7 results in

$$X(x=0) = c_1 \cos(0) + c_2 \sin(0) = 0 \;\; at \; x = 0 \tag{2.3.8}$$

$$c_1 + 0 = 0 \tag{2.3.9}$$

$$c_1 = 0 \tag{2.3.10}$$

and substituting the second boundary condition ($X(x=L)=0$) into the general solutions of Equation 2.3.7 results in

$$X(x=L) = c_1 \cos(pL) + c_2 \sin(pL) = 0 \;\; at \; x = L \tag{2.3.11}$$

we already know that $c_1 = 0$ from the first boundary condition so Equation 2.3.11 simplifies to

$$c_2 \sin(pL) = 0 \tag{2.3.12}$$

Given the properties of sines, Equation 2.3.11 simplifies to

$$pL = n\pi \tag{2.3.13}$$

with $n = 0$ is the *trivial solution* that we ignore so $n = 1, 2, 3....$

$$p = \frac{n\pi}{L} \tag{2.3.14}$$

Substituting Equations 2.3.14 and 2.3.10 into Equation 2.3.7 results in

$$X(x) = c_2 \sin\left(\frac{n\pi x}{L}\right) \tag{2.3.15}$$

which can simplify to

$$X(x) = c_2 \sin(\omega x) \tag{2.3.16}$$

with

$$\omega = \frac{n\pi}{L} \tag{2.3.17}$$

A similar argument applies to the other half of the *ansatz* ($T(t)$).

Exercise 2.3.1

Given two traveling waves:

$$\psi_1 = \sin(c_1 x + c_2 t) \;\; \text{and} \;\; \psi_2 = \sin(c_1 x - c_2 t) \tag{2.3.18}$$

a. Find the wavelength and the wave velocity of ψ_1 and ψ_2
b. Find the following and identify nodes:

$$\psi_+ = \psi_1 + \psi_2 \;\; \text{and} \;\; \psi_- = \psi_1 - \psi_2 \tag{2.3.19}$$

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 $\psi_+ = \psi_1 + \psi_2$ and $\psi_- = \psi_1 - \psi_2$.

$$\begin{aligned}\psi_+ &= \sin(c_1 x + c_2 t) + \sin(c_1 x - c_2 t) \\ &= \sin(c_1 x)\cos(c_2 t) + \cancel{\cos(c_1 x)\sin(c_1 t)} + \sin(c_1 x)\cos(c_2 t) - \cancel{\cos(c_1 x)\sin(c_1 t)} \\ &= 2\sin(c_1 x)\cos(c_2 t)\end{aligned}$$

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.

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.

$$u(x,t) = X(x)T(t) \tag{2.4.1}$$

By substituting the new product solution form into the original wave equation, one can obtain a 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 end 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 2.2.5. So we can rewrite K:

$$K = -p^2 \tag{2.4.2}$$

and Equation 2.2.4b can be

$$\frac{d^2X(x)}{dx^2} + p^2X(x) = 0 \tag{2.4.3}$$

The general solution to differential equations of the form of Equation 2.4.3 is Equation 2.2.5

$$X(x) = Ae^{\sqrt{K}x} + Be^{-\sqrt{K}x} \tag{2.4.4}$$

that when substituted with Equation 2.4.2 give

$$X(x) = Ae^{ipx} + Be^{-ipx} \tag{2.4.5}$$

The complex exponentials can be expressed as trigonometric functions via Euler formula ($e^{i\theta} = \cos\theta + i\sin\theta$

$$X(x) = A\left[\cos(px) + i\sin(px)\right] + B\left[\cos(px) - i\sin(px)\right] \tag{2.4.6}$$

collecting like terms

$$X(x) = (A+B)\cos(px) + i(A-B)\sin(px) \tag{2.4.7}$$

Introduce new *complex* constants $C = A + B$ and $D = i(A - B)$ so that the general solution in Equation 2.4.7 can be expressed as oscillatory functions

$$X(x) = C\cos(px) + D\sin(px) \tag{2.4.8}$$

? Exercise 2.4.1

Verify that Equation 2.4.4 is the general form for differential equations of the form of Equation 2.4.3.

Answer

In order to show that

$$X(x) = Ae^{\sqrt{\alpha}x} + Be^{-\sqrt{\alpha}x}$$

is a general solution to the differential equation

$$\frac{d^2X(x)}{dx^2} + p^2X(x) = 0$$

we have to take the second derivative of Equation 2.4.5, and the plug both it and the original function into the appropriate locations in Equation 2.4.4 and verify that it does in fact equal 0.

First we have to take the first and then second derivative of Equation 2.4.5

$$\frac{d}{dx}\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) = \sqrt{k}Ae^{\sqrt{k}x} - \sqrt{k}Be^{-\sqrt{k}x}$$
$$\frac{d^2}{dx^2}\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) = kAe^{\sqrt{k}x} + kBe^{-\sqrt{k}x}$$

Now that we have the second derivative of Equation 2.4.5 we plug the relevant values into Equation 2.4.3

$$\frac{d^2X(x)}{dx^2} + p^2X(x) = 0$$
$$kAe^{\sqrt{k}x} + kBe^{-\sqrt{k}x} + p^2\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) =^2 0$$

We are given in Equation 2.4.3 that

$$k = -p^2$$

So

$$p^2 = -k$$

Now we can plug that into our differential equation to simplify

$$kAe^{\sqrt{k}x} + kBe^{-\sqrt{k}x} + k\left(Ae^{\sqrt{k}x} + Be^{-\sqrt{k}x}\right) =^7 0$$
$$kAe^{\sqrt{k}x} + kBe^{-\sqrt{k}x} - kAe^{\sqrt{k}x} - kBe^{-\sqrt{k}x} = 0$$

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.

Now let's apply the boundary conditions from Equation 2.2.7 to determine the constants C and D. Substituting the first boundary condition ($X(x=0)=0$) into the general solutions of Equation 2.4.8 results in

$$X(x=0) = C\cos(0) + D\sin(0) = 0 \;\; at\; x = 0 \tag{2.4.9}$$

$$C + 0 = 0 \tag{2.4.10}$$

$$C = 0 \tag{2.4.11}$$

and substituting the second boundary condition ($X(x=L)=0$) into the general solutions of Equation 2.4.8 results in

$$X(x=L) = C\cos(pL) + D\sin(pL) = 0 \;\; at\; x = L \tag{2.4.12}$$

we already know that $C=0$ from the first boundary condition so Equation 2.4.12 simplifies to

$$D\sin(pL) = 0 \tag{2.4.13}$$

Given the properties of sines, Equations 2.4.12 simplifies to

$$pL = n\pi \tag{2.4.14}$$

with $n=0$ is the *trivial solution* that we ignore so $n = 1, 2, 3...$.

$$p = \frac{n\pi}{L} \tag{2.4.15}$$

Substituting Equations 2.4.15 and 2.4.11 into Equation 2.4.8 results in

$$X(x) = D\sin\left(\frac{n\pi x}{L}\right) \tag{2.4.16}$$

Equation 2.4.16 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.

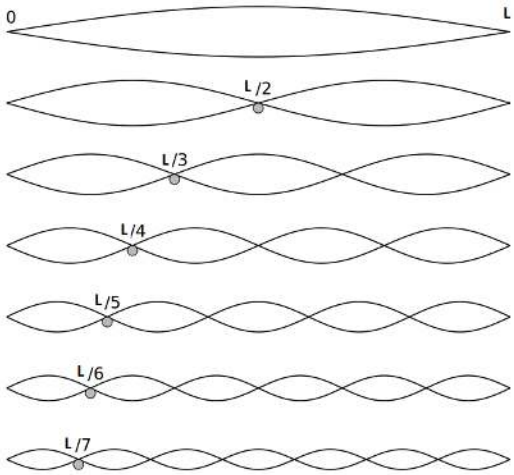


Figure 2.4.1: The first seven $X(x)$ solutions of a vibrating string of length L at two times of maximum displacement. (Public Domain; Qef via Wikipedia).

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 2.2.4a, which qualitatively resembles the original spatial differential equation solved above (Equation 2.2.4b).

$$\frac{d^2T(t)}{dt^2} - Kv^2T(t) = 0 \tag{2.4.17}$$

However, the constraints extracted from solving spatial dependence apply to the time dependence. When Equations 2.4.2 and 2.4.15 are substituted into Equation 2.2.4a, a more simplified expression is obtained

$$\frac{d^2T(t)}{dt^2} + p^2v^2T(t) = \frac{d^2T(t)}{dt^2} + \left(\frac{nv\pi}{L}\right)^2 T(t) = 0 \tag{2.4.18}$$

Define a new constant: ω_n

$$\omega_n = \left(\frac{nv\pi}{L}\right) \tag{2.4.19}$$

and substitute into Equation 2.4.18

$$\frac{d^2T(t)}{dt^2} + \omega_n^2T(t) = 0 \tag{2.4.20}$$

This is the same functional form of Equation 2.4.3

$$T(t) = E\cos(\omega_n t) + F\sin(\omega_n t) \tag{2.4.21}$$

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 2.2.1), which can be substituted with Equations 2.4.16 and 2.4.21

$$u(x,t) = X(x)T(t) \tag{2.4.22}$$

$$= \left[D\sin\left(\frac{n\pi x}{L}\right)\right](E\cos(\omega_n t) + F\sin(\omega_n t)) \tag{2.4.23}$$

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.

$$u_n(x,t) = [G_n \cos(\omega_n t) + H_n \sin(\omega_n t)] \sin\left(\frac{n\pi x}{L}\right) \tag{2.4.24}$$

The functions represented in Equation 2.4.24 are set of solutions including both spatial and temporal features that solve the wave equation of a string held tight on two ends.

> 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:
>
> $$\frac{\partial^2(f+g)}{\partial x^2} = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 g}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 f}{\partial t^2} + \frac{1}{v^2}\frac{\partial^2 g}{\partial t^2} = \frac{1}{v^2}\frac{\partial^2(f+g)}{\partial t^2} \tag{2.4.25}$$
>
> 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.

This important 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. This simple addition of the displacements is termed "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***.

> *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 2.4.24.

$$u(x,t) = \sum_{n=1}^{\infty} u_n(x,t) \tag{2.4.26}$$

$$= \sum_{n=1}^{\infty} (G_n \cos(\omega_n t) + H_n \sin(\omega_n t)) \sin\left(\frac{n\pi x}{L}\right) \tag{2.4.27}$$

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

$$\nu_n = \frac{\omega_n}{2\pi} = \frac{nv}{2L} \tag{2.4.28}$$

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 mechanic problems and is a direct consequence of the starting wave equation (Equation 2.1.1).

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2.5: A Vibrating Membrane

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's 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:

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2}, \frac{\partial^2}{\partial y^2}, \frac{\partial^2}{\partial z^2}\right) \tag{2.5.3}$$

so Equation 2.5.2 can be more easily written as

$$\nabla^2 u(x,y,z,t) = \frac{1}{v^2}\frac{\partial^2 u(x,y,z,t)}{\partial t^2} \tag{2.5.4}$$

Just as we found in one dimension traveling harmonic waves (no boundary conditions)

$$u(x,t) = A\sin(kx - \omega t) \tag{2.5.5}$$

with $\omega = \nu k$, you can verify that the *three*-dimensional equation has harmonic solutions

$$u(x,y,z,t) = A\sin(k_x x + k_x + k_z z - \omega t) \tag{2.5.6}$$

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

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

$$u(x,y,t) = A_{nm}\cos(\omega_{nm}t + \phi_{nm})\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right) \tag{2.5.7}$$

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).

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).

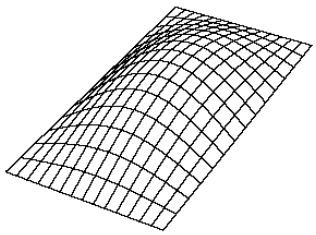
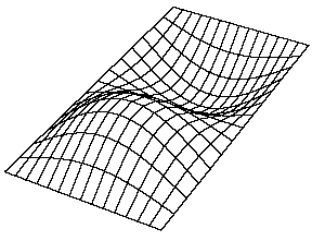
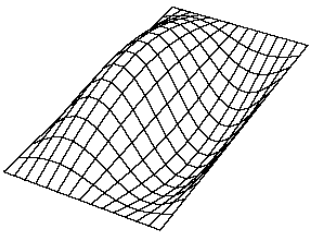
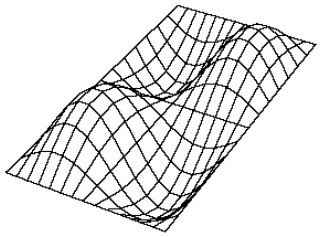
The ($n_x = 1$, $n_y = 1$) Solution	The ($n_x = 1$, $n_y = 2$) Solution	The ($n_x = 2$, $n_y = 1$) Solution	The ($n_x = 2$, $n_y = 2$) Solution
			

Figure **2.5.1**: Select Vibrational Modes of a Rectangular Membrane. from Daniel A. Russell.

Vibrational Modes of a Circular Membrane

The basic principles of a vibrating rectangular membrane applies to other 2-D members including a circular membrane. As with the 1D wave equations, a **node** is a point (or line) on a structure that does not move while the rest of the structure is vibrating. On the animations below, 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.

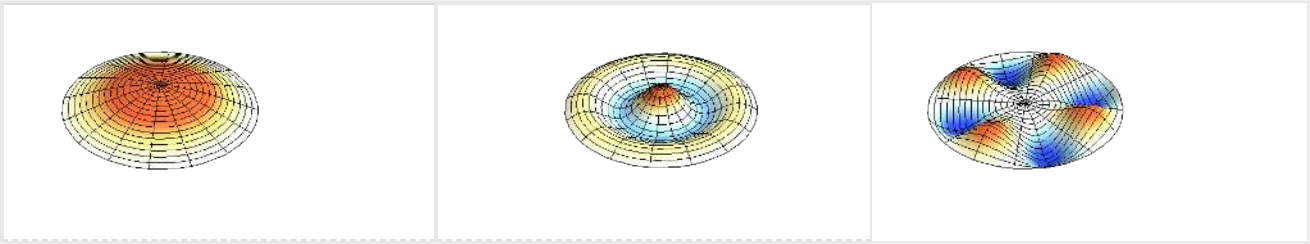


Figure **2.5.2**: Select Vibrational Modes of a Circular Membrane. from Daniel A. Russell.

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.

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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.

2.E: The Classical Wave Equation (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

3: The Schrödinger Equation and a Particle in a Box

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

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, a theorist in Zurich, 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 Quantum 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 $\frac{\partial^2}{\partial x^2}$ 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,

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{3.1.18}$$

with the del operator,

$$\nabla = \left(\vec{x}\frac{\partial}{\partial x} + \vec{y}\frac{\partial}{\partial y} + \vec{z}\frac{\partial}{\partial z}\right) \tag{3.1.19}$$

also is used in Quantum Mechanics. The symbols with arrows over them 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. Let's go back to Equation 3.1.20:

$$\Psi(\vec{r},t) = \psi(\vec{r})e^{-iEt/\hbar} \tag{3.1.22}$$

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

$$\Psi(\vec{r},t) = \psi(\vec{r})\left(\cos\frac{Et}{\hbar} - i\,\sin\frac{Et}{\hbar}\right) \tag{3.1.23}$$

This means the total wavefunction has a complex behavior with a real part and an imaginary part. Moreover, using the Trigonometry identity $\sin(\theta) = \cos(\theta - \pi/2)$ this can further simplified to

$$\Psi(\vec{r},t) = \psi(\vec{r})\cos\left(\frac{Et}{\hbar}\right) - i\psi(\vec{r})\cos\left(\frac{Et}{\hbar} - \frac{\pi}{2}\right) \tag{3.1.24}$$

Hence, the imaginary part of the total wavefunction oscillates out of phase by $\frac{\pi}{2}$ with respect to the real part. While all wavefunctions have a time-dependence, that dependence may not be manifested in simple quantum problems as the next sections discuss.

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.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{3.2.2}$$

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

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \tag{3.2.3}$$

Equation 3.2.3 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.

The sum and difference of two operators $\hat{A}$ and $\hat{B}$ are given by

$$(\hat{A} \pm \hat{B})f = \hat{A}f \pm \hat{B}f \tag{3.2.4}$$

The product of two operators is defined by

$$\hat{A}\hat{B}f \equiv \hat{A}[\hat{B}f] \tag{3.2.5}$$

Two operators are equal if

$$\hat{A}f = \hat{B}f \tag{3.2.6}$$

for **all** functions f.

The identity operator $\hat{1}$ does nothing (or multiplies by 1)

$$\hat{1}f = f \tag{3.2.7}$$

The n-th power of an operator $\hat{A}^n$ is defined as n successive applications of the operator, e.g.

$$\hat{A}^2 f = \hat{A}\hat{A}f \tag{3.2.8}$$

The *associative law* holds for operators

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C} \tag{3.2.9}$$

The *commutative law* does **not** generally hold for operators. In general,but not always,

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}. \tag{3.2.10}$$

To help identify if the inequality in Equation 3.2.10 holds for any two specific operators, we define the commutator.

Definition: The Commutator

It is convenient to define the **commutator** of $\hat{A}$ and $\hat{B}$

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \tag{3.2.11}$$

If $\hat{A}$ and $\hat{B}$ commute, then

$$[\hat{A}, \hat{B}] = 0. \tag{3.2.12}$$

If the commutator is not zero, the order of operating matters and the operators are said to "not commute." Moreover, this property applies

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]. \tag{3.2.13}$$

Linear Operators

The action of an operator that turns the function $f(x)$ into the function $g(x)$ is represented by

$$\hat{A}f(x) = g(x) \tag{3.2.14}$$

The most common kind of operator encountered are *linear operators* which satisfies the following two conditions:

$$\underset{\text{Condition A}}{\hat{O}(f(x) + g(x)) = \hat{O}f(x) + \hat{O}g(x)} \tag{3.2.15}$$

and

$$\underset{\text{Condition B}}{\hat{O}cf(x) = c\hat{O}f(x)} \tag{3.2.16}$$

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 3.2.15 or 3.2.16 then it is not a linear operator.

Example 3.2.1

Is this operator $\hat{O} = -i\hbar\frac{d}{dx}$ linear?

Solution

To confirm is an operator is linear, both conditions in Equation 3.2.16 must be demonstrated.

Condition A (Equation 3.2.15):

$$\hat{O}(f(x) + g(x)) = -i\hbar\frac{d}{dx}(f(x) + g(x))$$

From basic calculus, we know that we can use the **sum rule for differentiation**

$$\hat{O}(f(x) + g(x)) = -i\hbar\frac{d}{dx}f(x) - i\hbar\frac{d}{dx}g(x)$$
$$= \hat{O}f(x) + \hat{O}g(x) \quad \checkmark$$

Condition A is confirmed. Does Condition B (Equation 3.2.16) hold?

$$\hat{O}cf(x) = -i\hbar\frac{d}{dx}cf(x)$$

Also from basic calculus, this can be factored out of the derivative

$$\hat{O}cf(x) = -ci\hbar\frac{d}{dx}f(x)$$
$$= c\hat{O}f(x) \quad \checkmark$$

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

To confirm is an operator is linear, both conditions in Equations 3.2.15 and 3.2.16 must be demonstrated. Let's look first at Condition B.

Does Condition B (Equation 3.2.16) 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.

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:

$$\hat{H} = -\frac{h^2}{2m}\frac{d^2}{dx^2} \tag{3.2.17}$$

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

$$\int_0^a f(x)\,\hat{H}\,g(x)\,dx = -\frac{\hbar^2}{2m}\int_0^a f(x)\,g''(x)\,dx \tag{3.2.18}$$

Now, using integration by parts,

$$\int_0^a f(x)\,g''(x)\,dx = -\int_0^a f'(x)\,g'(x)\,dx + f(x)\,g'(x)\Big|_0^a \tag{3.2.19}$$

The boundary terms vanish by the assumed conditions on f and g. A second integration by parts transforms Equation 3.2.19 to

$$\int_0^a f''(x)\,g(x)\,dx - f'(x)\,g(x)\Big|_0^a \tag{3.2.20}$$

It follows therefore that

$$\int_0^a f(x)\,\hat{H}\,g(x)\,dx = \int_0^a g(x)\,\hat{H}\,f(x)\,dx \tag{3.2.21}$$

An obvious generalization for complex functions will read

$$\int_0^a f^*(x)\,\hat{H}\,g(x)\,dx = \left(\int_0^a g^*(x)\,\hat{H}\,f(x)\,dx\right)^* \tag{3.2.22}$$

In mathematical terminology, an operator $\hat{A}$ for which

$$\int f^* \hat{A} g \, d\tau = \left(\int g^* \hat{A} f \, d\tau \right)^* \tag{3.2.23}$$

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.*

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3.3: The Schrödinger Equation is an Eigenvalue Problem

Learning Objectives

- The Schrödinger Equation gives the solutions to the problem and is an eigenvalue problem.
- Define key operators that correlate to measurables.

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 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.

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.

$$\psi = \sum_i c_i\phi_i \tag{3.3.21}$$

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. $\psi = Ne^{-ix/\hbar}$
c. $\psi = Me^{-bx}$

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:

$$\hat{p}_x\psi = p_x\psi \tag{3.3.22}$$

$$\hat{KE}\psi = KE\psi \tag{3.3.23}$$

where p_x and KE are the measurables (eigenvalues) for these operators.

Solution

a.

Let's look at the left side of Equation 3.3.22 for linear momentum

$$-i\hbar\frac{\partial}{\partial x}A\sin(ax) = -i\hbar Aa\cos(ax)$$

and the right side of Equation 3.3.22

$$p_x A\sin(ax)$$

These are **not** the same so this wavefunction is not an eigenstate of momentum.

Let's look at the left side of Equation 3.3.23 for kinetic energy

$$\begin{aligned}-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}A\sin(ax) &= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}Aa\cos(ax)\\ &= +\frac{\hbar^2}{2m}Aa^2\sin(ax)\end{aligned}$$

and the right side

$$KEA\sin(ax)$$

These are same so this wavefunction is an eigenstate of kinetic energy. And the measured kinetic energy will be

$$KE = +\frac{\hbar^2}{2m}a^2$$

b.

Let's look at the left side of Equation 3.3.22 for linear momentum

$$-i\hbar\frac{\partial}{\partial x}Ne^{-ix/\hbar} = -Ne^{-ix/\hbar}$$

and the right side of Equation 3.3.22

$$p_x Ne^{-ix/\hbar}$$

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 3.3.23 for kinetic energy

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}Ne^{-ix/\hbar} = +i\frac{\hbar}{2m}\frac{\partial}{\partial x}Ne^{-ix/\hbar}$$
$$= +\frac{1}{2m}Ne^{-ix/\hbar}$$

and the right side

$$KEe^{-ix/\hbar}$$

These are same so this wavefunction is an eigenstate of kinetic energy. And the measured kinetic energy will be

$$KE = \frac{1}{2m}N$$

This wavefunction is an eigenstate of both momentum and kinetic energy.

c.

TBA

Contributors

- Seymour Blinder (Professor Emeritus of Chemistry and Physics at the University of Michigan, Ann Arbor)
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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3.4: Wavefunctions Have a Probabilistic Interpretation

Learning Objectives

- To understand that wavefunctions can have probabilistic interpretations.

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:

$$d\tau = dx\,dy\,dz \tag{3.4.5}$$

- Spherical:

$$d\tau = r^2 \sin\phi\, dr\, d\theta\, d\phi \tag{3.4.6}$$

- Cylindrical:

$$d\tau = r\, dr\, d\phi\, dz. \tag{3.4.7}$$

For rectilinear Cartesian space, Equation 3.4.4 can be is expanded with dimension explicitly indicated

$$P(x \in [a,b]) = \int_{a_x}^{b_x}\int_{a_y}^{b_y}\int_{a_z}^{b_z} |\psi(x,y,z)|^2 dx\,dy\,dz \tag{3.4.8}$$

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 $e\psi^*(r_0)(r_0)d\tau$?

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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3.5: The Energy of a Particle in a Box is Quantized

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

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x) \tag{3.5.1}$$

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

$$V(x) = \begin{cases} 0 & 0 \le x \le L \\ \infty & x < 0 \; and \; x > L \end{cases} \tag{3.5.2}$$

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.

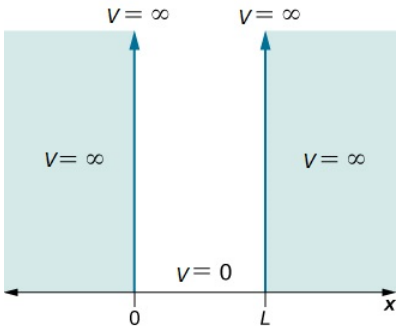


Figure **3.5.1**: The barriers outside a one-dimensional box have infinitely large potential, while the interior of the box has a constant, zero potential. (CC-BY 4.0; OpenStax).

The particle is thus bound to a *"potential well"* since the particle cannot penetrate beyond $x = 0$ or $x = L$

$$\psi(x) = 0 \quad for \;\; x < 0 \;\; and \;\; x > L \tag{3.5.3}$$

By the requirement that the wavefunction be continuous, it must be true as well that

$$\psi(0) = 0 \quad and \quad \psi(L) = 0 \tag{3.5.4}$$

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:

$$-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x) \tag{3.5.5}$$

with $0 \le x \le L$.

We again have the differential equation

$$\psi''(x) + k^2\psi(x) = 0 \tag{3.5.6}$$

with

$$k^2 = 2mE/\hbar^2 \tag{3.5.7}$$

The general solution can be written

$$\psi(x) = A \sin kx + B \cos kx \tag{3.5.8}$$

where A and B are constants to be determined by the boundary conditions in Equation 3.5.4. By the first condition, we find

$$\psi(0) = A \sin 0 + B \cos 0 = B = 0 \tag{3.5.9}$$

The second boundary condition at $x = L$ then implies

$$\psi(a) = A \sin kL = 0 \tag{3.5.10}$$

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

$$kL = n\pi \tag{3.5.11}$$

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 3.5.6 and 3.5.11, we obtain

$$E_n = \frac{\hbar^2\pi^2}{2mL^2} n^2 = \frac{h^2}{8mL^2} n^2 \tag{3.5.12}$$

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

These are the only values of the energy which allows solutions of the Schrödinger Equation 3.5.5 consistent with the boundary conditions in Equation 3.5.4. 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 3.5.12 depends on n^2.

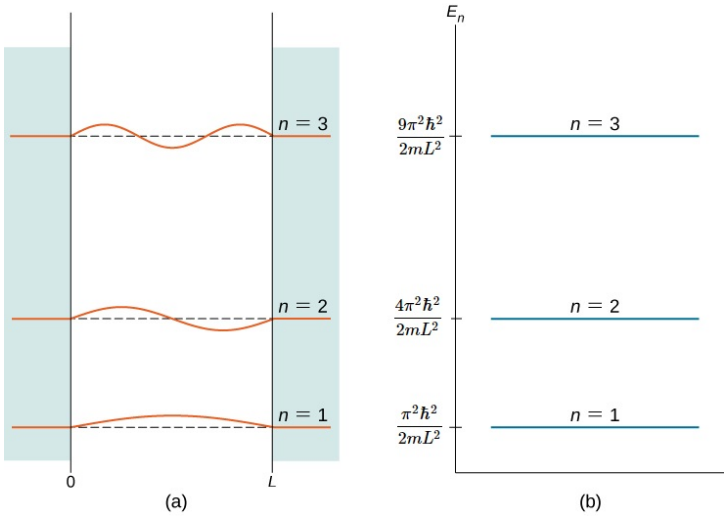


Figure 3.5.2: A plot of $\psi_n(x)$ for the first four wavefunctions. (CC-BY 4.0; OpenStax).

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

$$E_1 = \frac{h^2}{8mL^2} \tag{3.5.13}$$

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

$$\Delta x \Delta p \approx h \tag{3.5.14}$$

This is in accord with the *Heisenberg uncertainty principle*.

The particle-in-a-box eigenfunctions are given by Equation 3.5.15, with $B = 0$ and $k = n\pi/L = a$, in accordance with Equation 3.5.11

$$\psi_n(x) = A \sin \frac{n\pi x}{L} \tag{3.5.15}$$

with

$$n = 1, 2, 3... \tag{3.5.16}$$

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,

$$\int_0^a [\psi_n(x)]^2 \, dx = 1 \tag{3.5.17}$$

the integration running over the domain of the particle $0 \leq x \leq a$. Substituting Equation 3.5.15 into Equation 3.5.17,

$$A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = A^2 \frac{L}{n\pi} \int_0^{n\pi} \sin^2 \theta \, d\theta \tag{3.5.18}$$

$$= A^2 \frac{L}{2} = 1 \tag{3.5.19}$$

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 3.5.19, we can identify the general normalization constant

$$A = \sqrt{\frac{2}{L}} \tag{3.5.20}$$

for all values of n. Finally we can write the normalized eigenfunctions:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \tag{3.5.21}$$

with

$$n = 1, 2, 3... \tag{3.5.22}$$

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 3.5.21.

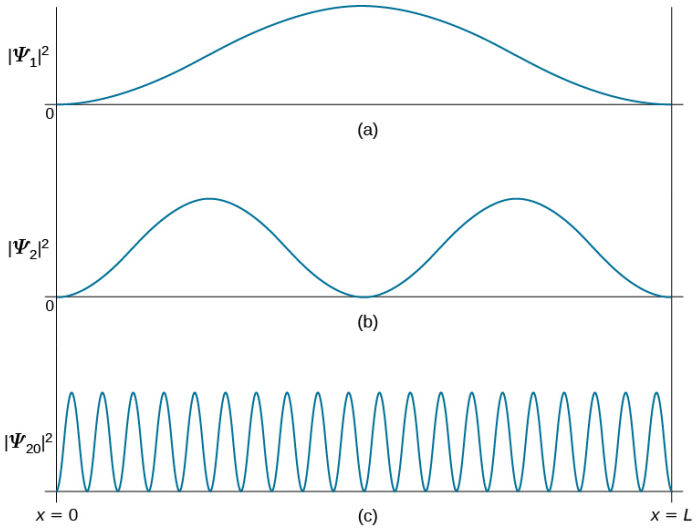


Figure **3.5.3**: The probability density distribution $|\psi_n(x)|^2$ for a quantum particle in a box for: (a) the ground state, $n = 1$; (b) the first excited state, $n = 2$; and, (c) the nineteenth excited state, $n = 20$. (CC-BY 4.0; OpenStax).

Nodes and Curvature

A significant feature of the particle-in-a-box quantum states is the occurrence of *nodes*. 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?

Solution

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,

$$P(a,b) = \frac{2}{L}\int_a^b \sin^2\frac{3\pi x}{L}\,dx$$
$$= \frac{2}{L}\left(\frac{x}{2} - \frac{L\sin\left(\frac{6\pi x}{L}\right)}{12\pi}\right)\Bigg|_a^b$$
$$= \frac{b-a}{L} - \frac{1}{6\pi}\left[\sin\left(\frac{6\pi b}{L}\right) - \sin\left(\frac{6\pi a}{L}\right)\right]$$

(a) The probability that the particle is in the left half of the box is

$$P\left(0,\frac{L}{2}\right) = \frac{\frac{L}{2}-0}{L} - \frac{1}{6\pi}\left[\sin\left(\frac{6\pi\left(\frac{L}{2}\right)}{L}\right) - \sin\left(\frac{6\pi(0)}{L}\right)\right]$$
$$= \frac{1}{2}$$

(b) The probability that the particle is in the middle third of the box

$$P\left(\frac{L}{3},\frac{2L}{3}\right) = \frac{\frac{2L}{3}-\frac{L}{3}}{L} - \frac{1}{6\pi}\left[\sin\frac{6\pi\left(\frac{2L}{3}\right)}{L} - \sin\frac{6\pi\left(\frac{L}{3}\right)}{L}\right]$$
$$= \frac{1}{3}$$

Exercise 3.5.1: ground State Probability

For a particle in a one-dimensional box, the ground state wave function 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

$$P\left(0,\frac{L}{2}\right) = \frac{2}{L}\int_0^{\frac{L}{2}} \sin^2\frac{x\pi}{L}dx$$
$$= \frac{2}{L}\frac{\frac{L\pi}{L} + \sin 0 + \sin\frac{L\pi}{L}}{\frac{4\pi}{L}}$$
$$= \frac{1}{2}$$

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).

Time dependence and Complex Behavior of wavefunctions

Recall that the time-dependence of the wavefunction with time-independent potential was discussed in Section 3.1 and is expressed as

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \tag{3.5.23}$$

so for the particle in a box, these are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} e^{-iE_n t/\hbar} \tag{3.5.24}$$

with E_n given by Equation 3.5.12.

The phase part of Equation 3.5.24 can be expanded into a real part and a complex components. So the total wavefunction for a particle in a box is

$$\Psi(x,t) = \underbrace{\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\cos\frac{E_n t}{\hbar}\right)}_{\text{real part}} - i\underbrace{\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\sin\frac{E_n t}{\hbar}\right)}_{\text{imaginary part}} \tag{3.5.25}$$

which can be simplified (slightly) to

$$\Psi(x,t) = \underbrace{\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\cos\frac{E_n t}{\hbar}\right)}_{\text{real part}} - i\underbrace{\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)\left(\cos\frac{E_n t}{\hbar} - \frac{\pi}{2}\right)}_{\text{imaginary part}} \tag{3.5.26}$$

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.

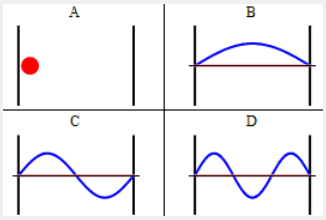


Figure 3.5.5: Some trajectories of a particle in a box according to Newton's laws of classical mechanics (A), and according to the Schrödinger equation of quantum mechanics (B-F). In (B-D), the horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the 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 3.5.12) 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

Another important property of the eigenfunctions in Equation 3.5.21 applies to the integral over a product of two *different* eigenfunctions. It is easy to see from Figure 3.5.5 that the integral

$$\int_0^a \psi_2(x)\psi_1(x)dx = 0 \tag{3.5.27}$$

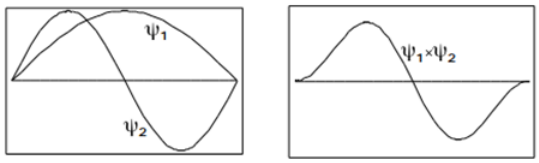


Figure 3.5.5: Product of $n = 1$ and $n = 2$ eigenfunctions.

To prove this result in general, use the trigonometric identity

$$\sin\alpha \sin\beta = \frac{1}{2}\left[\cos(\alpha-\beta) - \cos(\alpha+\beta)\right] \tag{3.5.28}$$

to show that

$$\int_0^L \psi_m(x)\psi_n(x)dx = 0 \quad if \quad m \neq n \tag{3.5.29}$$

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 3.5.27) together with the orthogonality (Equation 3.5.29) can be combined into a single relationship

$$\int_0^L \psi_m(x)\psi_n(x)dx = \delta_{mn} \tag{3.5.30}$$

In terms of the *Kronecker delta*

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \tag{3.5.31}$$

A set of functions $\{\psi_n\}$ which obeys Equation 3.5.30 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. $\langle\psi_4|\psi_4\rangle$

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 3.5.31) to evaluate.

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 3.5.28 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 3.5.31).

Therefore $\langle\psi_3|\psi_3\rangle = 1$.

b.

$$\langle \psi_4 | \psi_4 \rangle = \int_{-\infty}^{+\infty} \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) dx$$
$$= \frac{2}{L} \int_{-\infty}^{+\infty} \sin^2 \frac{4\pi x}{L} \, dx$$

We can expand and solve, but again there is no need. The wavefunctions are normalized therefore $\langle \psi_4 | \psi_4 \rangle = 1$.

c.

$$\langle \psi_3 | \psi_4 \rangle = \int_{-\infty}^{+\infty} \left(\sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) dx$$
$$= \frac{2}{L} \int_{-\infty}^{+\infty} \sin^2 \frac{4\pi x}{L} \, dx$$

We can expand this integral and evaluate, but since the integrand is odd, this integral is zero. Alternatively, we can use the orgonality criteria into the greater orthonormal criteria (Equation 3.5.31).

d.

$$\langle \psi_4 | \psi_3 \rangle = \int_{-\infty}^{+\infty} \left(\sqrt{\frac{2}{L}} \sin \frac{4\pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} \right) dx$$
$$= \frac{2}{L} \int_{-\infty}^{+\infty} \sin^2 \frac{4\pi x}{L} \, dx$$

We can expand this integral and evaluate, but since the integrand is odd, this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.5.31).

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.

Contributors

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3.6: Wavefunctions Must Be Normalized

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.

$$\Psi^*(r,t)\psi(r,t) = |\Psi(r,t)|^2 \tag{3.6.1}$$

where 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. 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 dτ 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.

? Example 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

$$\begin{aligned}\Psi(r,t)^*\Psi(r,t) &= \psi(r)\,\cancel{e^{+i\omega t}}\,\psi(r)\,\cancel{e^{-i\omega t}} \\ &= \psi(r)^2\end{aligned}$$

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.

Normalization 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

$$P_{x\in-\infty:\infty}(t) = \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx. \tag{3.6.2}$$

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

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 1, \tag{3.6.3}$$

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:

$$\psi(x) = \psi_0 e^{-(x-x_0)^2/(4\sigma^2)}. \tag{3.6.4}$$

Solution

To determine the normalization constant ψ_0, we simply substitute Equation 3.6.4 into Equation 3.6.3, to obtain

$$|\psi_0|^2 \int_{-\infty}^{\infty} e^{-(x-x_0)^2/(2\sigma^2)} dx = 1.$$

Changing the variable of integration to $y = (x - x_0)/(\sqrt{2}\sigma)$, we get

$$|\psi_0|^2 \sqrt{2}\sigma \int_{-\infty}^{\infty} e^{-y^2} dy = 1.$$

However, from an integral table we know

$$\int_{-\infty}^{\infty} e^{-y^2} dy = \sqrt{\pi},$$

which implies that

$$|\psi_0|^2 = \frac{1}{(2\pi\sigma^2)^{1/2}}.$$

Hence, a general normalized Gaussian wavefunction takes the form

$$\psi(x) = \frac{e^{i\phi}}{(2\pi\sigma^2)^{1/4}} e^{-(x-x_0)^2/(4\sigma^2)}$$

where ϕ is an arbitrary real phase-angle.

? Exercise 3.6.2: 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 integrating.

Solution

The $n = 1$ state

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

For $n = 1$, $\psi_{n=1} = \sqrt{\frac{2}{2}} \sin\left(\frac{\pi x}{2}\right)$

$$|\psi_{n=1}|^2 = \frac{2}{L} \int_{\frac{99L}{200}}^{\frac{101L}{200}} \sin^2\left(\frac{\pi x}{L}\right) dx \tag{3.6.5}$$

We can solve this, but we can also recognize that Equation 3.6.5 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 ($\Delta x = L/100$):

$$\begin{aligned} |\psi_{n=1}|^2 &\approx \frac{2}{L} \sin^2\left(\frac{\pi(L/2)}{L}\right)^{1} \Delta x \\ &\approx \left(\frac{2}{L}\right)(L/100) \\ &\approx 1/50 = 0.02 \end{aligned}$$

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.

The $n = 2$ state

For the $n = 2$ state, $\psi_{n=2} = \sqrt{\frac{2}{2}} \sin\left(\frac{2\pi x}{2}\right)$

$$|\psi_{n=2}|^2 = \frac{2}{L} \int_{\frac{99L}{200}}^{\frac{101L}{200}} \sin^2\left(\frac{2\pi x}{L}\right) dx \tag{3.6.6}$$

We can use the same approximation as above

$$|\psi_{n=1}|^2 \approx \frac{2}{L}\sin^2\left(\frac{2\pi(L/2)}{L}\right)^{0}\Delta x$$
$$\approx 0$$

The probability of finding an electron in a box at $\frac{L}{2}$ for $n = 2$ is approximately zero.

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

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi(x,t)|^2 dx = 0 \tag{3.6.7}$$

for wavefunctions satisfying the time-dependent Schrödinger's equation (this results from the time-dependent Schrödinger's equation and Equation 3.6.3). The above equation gives

$$\frac{d}{dt}\int_{-\infty}^{\infty}\psi^*\psi dx = \int_{-\infty}^{\infty}\left(\frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t}\right)dx = 0. \tag{3.6.8}$$

Now, multiplying Schrödinger's equation by $\psi^*/(\mathrm{i}\hbar)$, we obtain

$$\psi^*\frac{\partial\psi}{\partial t} = \frac{\mathrm{i}}{2m}\psi^*\frac{\partial^2\psi}{\partial x^2} - \frac{\mathrm{i}}{\hbar}V|\psi|^2 \tag{3.6.9}$$

The complex conjugate of this expression yields

$$\psi\frac{\partial\psi^*}{\partial t} = -\frac{\mathrm{i}}{2m}\psi\frac{\partial^2\psi^*}{\partial x^2} + \frac{\mathrm{i}}{\hbar}V|\psi|^2 \tag{3.6.10}$$

since

- $(AB)^* = A^*B^*$,
- $A^{**} = A$, and
- $i^* = -i$.

Summing Equation 3.6.9 and 3.6.10 results in

$$\frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t} = \frac{\mathrm{i}}{2m}\left(\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2}\right) = \frac{\mathrm{i}}{2m}\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right). \tag{3.6.11}$$

Equations 3.6.8 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 3.6.3 to converge. Hence, we conclude that all wavefunctions which are *square-integrable* [i.e., are such that the integral in Equation 3.6.3 converges] have the property that if the normalization condition Equation 3.6.3 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 3.6.3. 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.

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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3.7: The Average Momentum of a Particle in a Box is Zero

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).

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 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 wights:

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:

$$\frac{1}{8}+\frac{3}{8}+\frac{2}{8}+\frac{1}{8}+\frac{1}{8}=\frac{8}{8}=1 \tag{3.7.3}$$

This 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.

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

$$\langle o \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{O} \psi \, dx \tag{3.7.4}$$

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 3.7.4. In the equation below, the symbol $\langle H \rangle$ is used to denote the average value for the total energy.

$$\langle H \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{H} \psi(x) dx \tag{3.7.5}$$

$$= \int_{-\infty}^{\infty} \psi^*(x) \hat{KE} \psi(x) dx + \int_{-\infty}^{\infty} \psi^*(x) \hat{V} \psi(x) dx \tag{3.7.6}$$

$$= \underbrace{\int_{-\infty}^{\infty} \psi^*(x) \left(\frac{-\hbar^2}{2m} \right) \frac{\partial^2}{\partial x^2} \psi(x) dx}_{\text{average kinetic energy}} + \underbrace{\int_{-\infty}^{\infty} \psi^*(x) \hat{V}(x) \psi(x) dx}_{\text{average potential energy}} \tag{3.7.7}$$

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 3.7.7.

Equation 3.7.7 can be simplified

$$\langle H \rangle = \langle KE \rangle + \langle V \rangle \tag{3.7.8}$$

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

$$\langle V \rangle = \int_{-\infty}^{\infty} V(x) \psi^*(x) \psi(x) dx \tag{3.7.9}$$

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 3.7.7 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

$$\langle KE \rangle = \int_0^L \left(\sqrt{\frac{2}{L}}\right)\sin(kx)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\left(\sqrt{\frac{2}{L}}\right)\sin(kx)dx$$

$$= \left(\frac{2}{L}\right)\int_0^L \sin(kx)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial}{\partial x}\cos(kx)(k)dx$$

$$= \left(\frac{2}{L}\right)\int_0^L \sin(kx)\left(\frac{-\hbar^2}{2m}\right)\sin(kx)(k)(-k)dx$$

$$= \left(\frac{2}{L}\right)\left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \sin^2(kx)dx$$

We can solve this intragral using the standard half-angle represention from an integral table. Or we can recognize that we already did this integral when we normalized the PIB wavefunction by rewriting this integral:

$$\langle KE \rangle = \left(\frac{2}{L}\right)\left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \sin^2(kx)dx$$

$$= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \left(\frac{2}{L}\right)\sin^2(kx)dx$$

$$= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \psi^*(x)\psi(x)dx \quad (\int_0^L \psi^*(x)\psi(x)dx = 1)$$

$$= \frac{k^2\hbar^2}{2m}$$

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 3.7.8 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

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 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 3.7.1*a*)

$$\psi_{n=1} = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \tag{3.7.10}$$

This state has the following probability distribution (Figure 3.7.1*b*):

$$\psi^*_{n=1}\psi_{n=1} = \frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right) \tag{3.7.11}$$

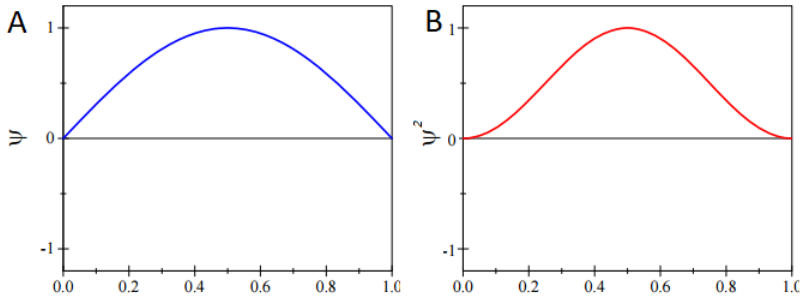


Figure 3.7.1: (left) The ground-state (n=1) wavefunction for a particle in a box. (right) The ground-state (n=1) probability for a particle in a box.

The expectation value for position with the $\hat{x} = x$ operation for any wavefunction (Equation 3.7.4) is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^* x \psi \, dx \tag{3.7.12}$$

which for the ground-state wavefunction (Equation 3.7.10) shown in Figure 3.7.1 is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) x \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \tag{3.7.13}$$

$$= \frac{2}{L} \int_{-\infty}^{+\infty} x \sin^2\left(\frac{\pi x}{L}\right) \tag{3.7.14}$$

Solution by Inspection

Without even having to evaluate Equation 3.7.14, we can get the expectation value from simply inspecting $\psi^*_{n=1}\psi_{n=1}$ in (Figure 3.7.1;). 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) and more specifcally at any point away from the mean, i.e.

$$\psi^*_{n=1}\psi_{n=1}(L/2 + \Delta x) = \psi^*_{n=1}\psi_{n=1}(L/2 - \Delta x)$$

Therefor, 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 3.7.4 and use the momentum operator

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \tag{3.7.15}$$

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 3.7.4 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 3.7.4) with the momentum operator. Then insert the expression for the wavefunction and evaluate the integral as shown here.

Answer

$$\begin{aligned}\langle p\rangle &= \int_0^L \psi_n^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi_n(x)dx \\ &= \int_0^L \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)\left(-i\hbar\frac{d}{dx}\right)\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)dx \\ &= -i\hbar\left(\frac{2}{L}\right)\int_0^L \sin\left(\frac{n\pi x}{L}\right)\left(\frac{d}{dx}\right)\sin\left(\frac{n\pi x}{L}\right)dx \\ &= -i\hbar\left(\frac{2}{L}\right)\left(\frac{n\pi}{L}\right)\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx \\ &= 0\end{aligned}$$

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 3.7.15).

Answer

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

$$\psi_n = \sqrt{2/L}\sin\left(\frac{n\pi x}{L}\right)$$

and

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}$$

and p is a real scalar (since it is a measurable).

$$\begin{aligned}\hat{p}_x\psi_n &= -i\hbar\frac{\partial}{\partial x}\left[\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\right] \\ &= -i\hbar\sqrt{\frac{2}{L}}\cos\left(\frac{n\pi x}{L}\right)\left(\frac{n\pi}{L}\right) \\ &\neq p\psi_n\end{aligned}$$

Hence, the PIB wavefunctions are NOT eigenfunctions of the momentum operator.

Dec 25, 2019, 5:17 PM

An alternative approach is to recognize that the uncertainty of p must be zero is the wavefunction is an eigenstate of mometnum. Hence

$$\sqrt{\langle^2> - < P >^2} = 0 \tag{3.7.16}$$

$\langle P\rangle >= \int_0^L \Psi^*[-i\hbar\delta/\delta x]\Psi dx$

$= -i\hbar \int_0^L 2/L \sin(n\pi x/L)\partial/\partial x \sin(n\pi x/L)dx$
$= -i\mathrm{h}2/L \int_0^L \sin(n\pi x/L)\cos(n\pi x/L)dx \rightarrow u \sin g$ orthonormality this integral is 0

$\langle P >= 0$

$\langle P^2\rangle = \int_0^L \Psi^*[-i\hbar\delta/\delta x]^2\psi dx$
$= \mathrm{n}2/L \int_0^L \sin(n\pi x/L)\delta^2/\delta x^2 \sin(n\pi x/L)dx$
$= -\mathrm{h}2/L \int_0^L \sin(n\pi x/L)\sin(n\pi x/L)dx \rightarrow$

using orthonormality this integral is 1

$\langle \mathrm{P}^2\rangle = -\mathrm{h}2/L$
$\sqrt{< P^2\rangle - \langle < P\rangle^2} = \sqrt{-\mathrm{h}2/L - 0^2} = \sqrt{-\mathrm{h}2/L} \neq 0 \rightarrow$

This is not 0 so 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**).

? 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**).

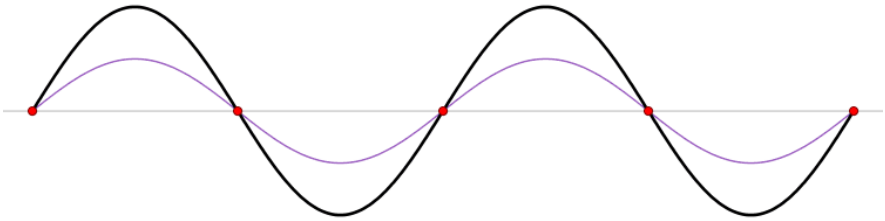


Figure **3.7.2**: Two waves traveling in opposite directions across the same medium combine linearly. In this animation, both waves have the same wavelength and the sum of amplitudes results in a standing wave. (Public Domain; LucasVB).

> *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 oethogonality extends to functions (wavefunctions or otherwise) too. Two functions ψ_A and ψ_B are said to be orthogonal if

$$\int_{allspace} \psi_A^* \psi_B d\tau = 0 \tag{3.7.17}$$

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.

Contributors

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

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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

$$\begin{aligned} \langle x \rangle &= \langle \Psi(t) \left| \hat{x} \right| \Psi(t) \rangle \\ &= \int \Psi^*(x,t) x \Psi(x,t)\, dx \end{aligned} \tag{3.8.4}$$

and

$$\begin{aligned} \langle x^2 \rangle &= \langle \Psi(t) \left| \hat{x}^2 \right| \Psi(t) \rangle \\ &= \int \Psi^*(x,t) x^2 \Psi(x,t)\, dx \end{aligned} \tag{3.8.5}$$

The middle terms in both Equations 3.8.4 and 3.8.5 are the integrals expressed in Dirac's Bra-ket notation. Similarly using the definition of the linear momentum operator:

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}. \tag{3.8.6}$$

So

$$\begin{aligned} \langle p \rangle &= \langle \Psi(t) \left| \hat{p} \right| \Psi(t) \rangle \\ &= \int \Psi^*(x,t) - i\hbar \frac{\partial}{\partial x} \Psi(x,t)\, dx \end{aligned} \tag{3.8.7}$$

and

$$\begin{aligned} \langle p^2 \rangle &= \langle \Psi(t) \left| \hat{p}^2 \right| \Psi(t) \rangle \\ &= \int \Psi^*(x,t) \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) \Psi(x,t)\, dx \end{aligned} \tag{3.8.8}$$

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 suing the general formula for a stationary wavefunction

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \tag{3.8.9}$$

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:

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{3.8.10}$$

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

$$\psi(x) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-ax^2} \tag{3.8.11}$$

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 3.8.10).

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:

$$\begin{aligned}\langle p^2\rangle &= \int_{-\infty}^{\infty}\psi^* p^2\psi dx \\ &= -\hbar^2\left(\frac{2a}{\pi}\right)^{1/2}\int_{-\infty}^{\infty}2a(ax^2-1)e^{-2ax^2}dx \\ &= -4\hbar^2a^2\left(\frac{2a}{\pi}\right)^{1/2}\int_0^{\infty}x^2e^{-2ax^2}dx + 4\hbar^2a\left(\frac{2a}{\pi}\right)^{1/2}\int_0^{\infty}e^{-2ax^2}dx \\ &= a\hbar^2\end{aligned}$$

We use Equation 3.8.1 to check on the uncertainty

$$\Delta x^2 = \langle x^2\rangle - \langle x\rangle^2 = \frac{1}{4a} - 0$$

$$\Delta x = \sqrt{\Delta x^2} = \frac{1}{2\sqrt{a}}$$

$$\Delta p^2 = \langle p^2\rangle - \langle p\rangle^2 = a\hbar^2 - 0$$

$$\Delta p = \sqrt{\Delta p^2} = \hbar\sqrt{a}$$

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 3.8.10), but the equality is established for this wavefunction. This is because the Gaussian wavefunction (Equation 3.8.11) 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

$$\psi = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{\pi x}{L}\right) \tag{3.8.12}$$

where L is the length of the box and $0 \le x \le L$. Verify that the value of the product $\Delta p\Delta x$ is consistent with the predictions from the uncertainty principle (Equation 3.8.10).

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.

Contributors

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3.9: A Particle in a Three-Dimensional Box

Learning Objectives

- To see the particle in 1-D box can easily extrapolate to boxes of higher dimensions.
- 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).

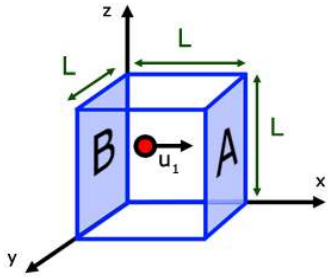


Figure 3.9.1: A particle in a 3-D box scheme with equal lengths on all three dimensions. (CC BY-SA-ND 3.0; www.a-levelphysicstutor.com).

The potential for the particle inside the box

$$V(\vec{r}) = 0 \tag{3.9.1}$$

- $0 \leq x \leq L_x$
- $0 \leq y \leq L_y$
- $0 \leq z \leq L_z$
- $L_x < x < 0$
- $L_y < y < 0$
- $L_z < z < 0$

$\vec{r}$ 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

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r) \tag{3.9.2}$$

Since we are dealing with a 3-dimensional figure, we need to add the 3 different axes into the Schrondinger equation:

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2}\right) = E\psi(r) \tag{3.9.3}$$

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):

$$\psi(x,y,z) = X(x)Y(y)Z(z) \tag{3.9.4}$$

Now each function has its own variable:

- $X(x)$ is a function for variable x only
- $Y(y)$ function of variable y only
- $Z(z)$ function of variable z only

Now substitute Equation 3.9.4 into Equation 3.9.3 and divide it by the product: xyz:

$$\frac{d^2\psi}{dx^2} = YZ\frac{d^2X}{dx^2} \Rightarrow \frac{1}{X}\frac{d^2X}{dx^2} \tag{3.9.5}$$

$$\frac{d^2\psi}{dy^2} = XZ\frac{d^2Y}{dy^2} \Rightarrow \frac{1}{Y}\frac{d^2Y}{dy^2} \tag{3.9.6}$$

$$\frac{d^2\psi}{dz^2} = XY\frac{d^2Z}{dz^2} \Rightarrow \frac{1}{Z}\frac{d^2Z}{dz^2} \tag{3.9.7}$$

$$\left(-\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2}\right) + \left(-\frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2}\right) + \left(-\frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2}\right) = E \tag{3.9.8}$$

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,

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0 \tag{3.9.9}$$

Now separate each term in Equation 3.9.8 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:

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E \tag{3.9.10}$$

Do these equations look familiar? They should because we have now reduced the 3D box into three particle in a 1D box problems!

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}E_x X = 0 \approx \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \tag{3.9.11}$$

Now the equations are very similar to a 1-D box and the boundary conditions are identical, i.e.,

$$n = 1, 2, ..\infty \tag{3.9.12}$$

Use the normalization wavefunction equation for each variable:

$$\psi(x) = \begin{cases} \sqrt{\frac{2}{L_x}}\sin\frac{n\pi x}{L_x} & \text{if } 0 \le x \le L \\ 0 & \text{if } L < x < 0 \end{cases} \tag{3.9.13}$$

Normalization wavefunction equation for each variable

$$X(x) = \sqrt{\frac{2}{L_x}}\sin\left(\frac{n_x\pi x}{L_x}\right) \tag{3.9.14}$$

$$Y(y) = \sqrt{\frac{2}{L_y}}\sin\left(\frac{n_y\pi y}{L_y}\right) \tag{3.9.15}$$

$$Z(z) = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n_z\pi z}{L_z}\right) \tag{3.9.16}$$

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:

$$\varepsilon_x = \frac{n_x^2 h^2}{8mL_x^2} \tag{3.9.17}$$

with $n_x = 1...\infty$

Do the same for variables n_y and n_z. Combine Equation 3.9.4 with Equations 3.9.14-3.9.16 to find the wavefunctions inside a 3D box.

$$\psi(r) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \tag{3.9.18}$$

with

$$V = \underbrace{L_x \times L_y \times L_z}_{\text{volume of box}} \tag{3.9.19}$$

To find the Total Energy, add Equation 3.9.17 and Equation 3.9.10.

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{3.9.20}$$

Notice the similarity between the energies a particle in a 3D box (Equation 3.9.20) and a 1D box.

Degeneracy in a 3D Cube

The energy of the particle in a 3-D cube (i.e., $a = L$, $b = L$, and $c = L$) in the *ground state* is given by Equation 3.9.20 with $n_x = 1$, $n_y = 1$, and $n_z = 1$. This energy ($E_{1,1,1}$) is hence

$$E_{1,1,1} = \frac{3h^2}{8mL^2} \tag{3.9.21}$$

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 3.9.18). 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:

$$E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = \frac{6h^2}{8mL^2} \tag{3.9.22}$$

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

$$n^2 = n_x^2 + n_y^2 + n_z^2 \tag{3.9.23}$$

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 $a = L$, $b = L$, and $c = L$.

$n_x^2+n_y^2+n_z^2$	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 3.9.20 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

$$\frac{17h^2}{8mL^2}$$

Answer b

three-fold (i.e., there are three wavefunctions that share the same energy.

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4. Riggs. N. V. Quantum Chemistry. Toronto, Ontario. The Macmillan Company. 1969
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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

$$\begin{aligned}\hat{A}[c_1 f(x) + c_2 f_2(x)] &= [c_1 f_1(x) + c_2 f_2(x)]^2 \\ &= c_1^2 f_1(x)^2 + 2c_1 f_1(x) c_2 f_2(x) + c_2^2 f_2(x)^2\end{aligned}$$

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

$$c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x) = \frac{c_1}{f_1(x)} + \frac{c_2}{f_2(x)}$$

$$\neq \hat{A}[c_1f_1(x) + c_2f_2(x)]$$

This operator is nonlinear

e)

Evaluate the left side

$$\hat{A}[c_1f_1(x) + c_2f_2(x)] = c_1f_1(0) + c_2f_2(0)$$

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

$$\hat{A}[c_1f_1(x) + c_2f_2(x)] = \ln[c_1f_1(x) + c_2f_2(x)]$$

Evaluate the right side

$$c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x) = c1\ln f_1(x) + c_2\ln f_2(x)$$

$$\neq \hat{A}[c_1f_1(x) + c_2f_2(x)]$$

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

$$\frac{3px}{a} = \frac{2m+1}{2}p \qquad m = 0, 1, 2, \ldots$$

$$x = \frac{(2m+1)\,a}{6}$$

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 $\phi_n = \sqrt{\frac{2}{L}} \sin(\frac{n\pi x}{L})$ 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,

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

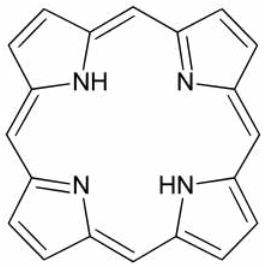
We can see that even if $a \neq b$, the energy levels will not necessarily be degenerate.

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 $n = 1$

$$\nu = \frac{(6.626 \times 10^{-34})(1)}{2 \times (1.67 \times 10^{-27})(10^{-14})}$$
$$= 19.8 \times 10^{6} m/s$$

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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CHAPTER OVERVIEW

4: Postulates and Principles of Quantum Mechanics

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

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

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 $r=(x_1,y_1,z_1,x_2,y_2,z_2,\ldots x_n,y_n,z_n)$. 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.

$$\int_{-\infty}^{\infty}\psi^*(x)\psi(x)\,dx=1 \tag{4.1.3}$$

this means is that the chance to find a particle is 100% over all space.

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.

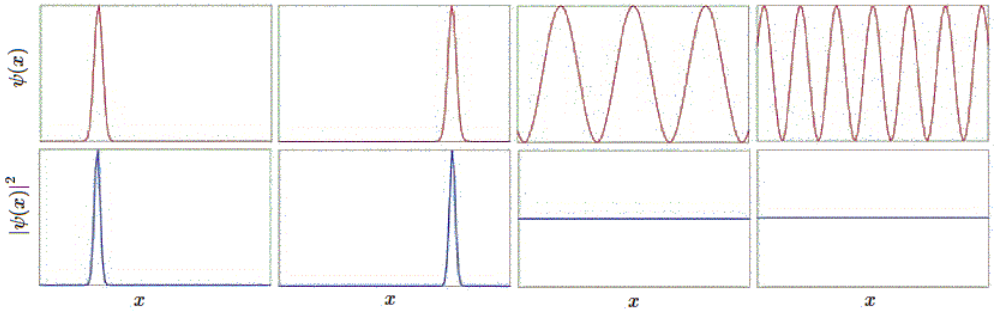


Figure 4.1.1: Examples of good wavefunctions, $\psi(x)$, (red, top) and corresponding probability densities, $P(x)$, (blue, bottom).

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

$$\psi(x)=Ne^{ikx} \tag{4.1.4}$$

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,

$$P(x) = \psi^*(x)\psi(x) = \left|e^{ikx}\right|^2 = N^2 e^{-ikx} \times e^{ikx} = N^2 \tag{4.1.5}$$

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.

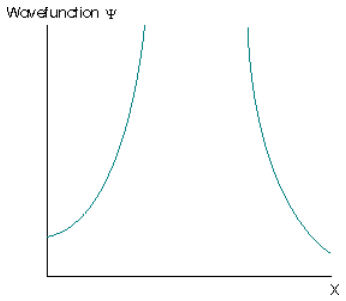


Figure 4.1.2: A invalid wavefunction since the amplitude is going to infinity over a region (the middle in this case).

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 wavefunction in Figure 4.1.3 violates this requirement. The grey lines indicate the region where the wavefunction is multivalued.

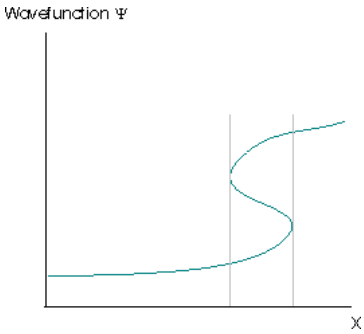


Figure 4.1.3: A invalid wavefunction since the wavefunction is not a function (i.e., not one-to-one).

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 wavefunctions in Figure **4.1.4** are also not acceptable for these reasons.

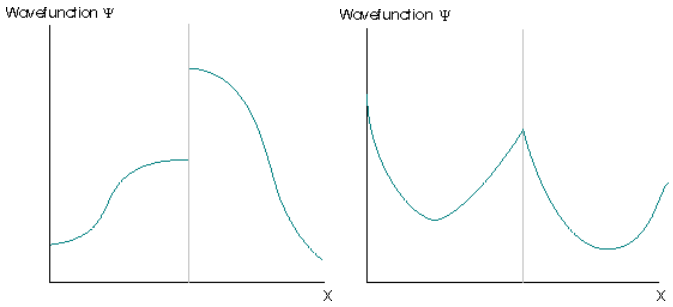


Figure **4.1.4**: Invalid wavefunctions. (left) The first derivative of a function gives its gradient at a given point, and it thus exists as long as the function is continuous - only if there is a break in the function is there a point at which its first derivative does not exist. (right) The second 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.

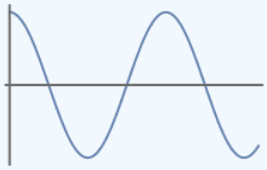
? Exercise 4.1.1

Determine if each of the following functions is acceptable or not 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 $[0, 2\theta]$

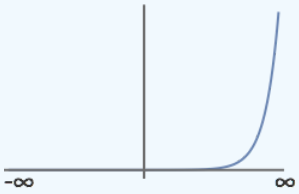
Solution a

This is not an acceptable wavefunction. It is **single-valued** across the entire range. There is only 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. $\int_0^{\infty} |\cos(x)|^2 dx \not< \infty$



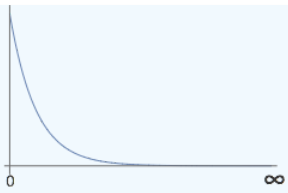
Solution b

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 ∞.



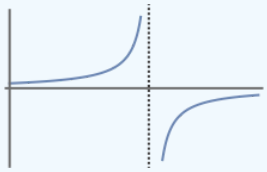
Solution c

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 $\int_0^{\infty} |\Psi(x)|^2 dx = \frac{1}{2}$.



Solution d

This is not an acceptable wavefunction. It is discontinuous over the limits of integration.



Contributors

- Prof. Allan Adams, Prof. Matthew Evans, Prof. Barton Zwiebach (used with permission, MIT OpenCourseWare)

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4.2: Quantum Operators Represent Classical Variables

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

For every observable property of a system there is a corresponding quantum mechanical operator.

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 term Hamiltonian, named after the Irish mathematician Hamilton, 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	$\hat{P}_x$	$-i\hbar\frac{d}{dx}$
Momentum (in 3D)	$\vec{p}$	$\hat{P}$	$-i\hbar\left[\hat{i}\ \frac{d}{dx}+\hat{j}\frac{d}{dy}+\hat{k}\frac{d}{dz}\right]$
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 $\frac{-\hbar^2}{2m}\nabla^2$
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	$\hat{L_x}$	$-i\hbar\left[y\frac{d}{dz}-z\frac{d}{dy}\right]$
Angular Momentum (y axis component)	L_y	$\hat{L_y}$	$-i\hbar\left[z\frac{d}{dx}-x\frac{d}{dz}\right]$
Angular Momentum (z axis component)	L_z	$\hat{L_z}$	$-i\hbar\left[x\frac{d}{dy}-y\frac{d}{dx}\right]$

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4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

The Laplacian operator ∇ is called an operator because it does something to the function that follows: namely, it produces or generates the sum of the three second-derivatives of the function. Of course, this is not done automatically; you must do the work, or remember to use this operator properly in algebraic manipulations. Symbols for operators are often (although not always) denoted by a hat ^ over the symbol, unless the symbol is used exclusively for an operator, e.g. ∇ (del/nabla), or does not involve differentiation, e.g.r for position.

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

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

$$\langle A\rangle = \int_{-\infty}^{\infty} \psi_a^* A \psi_a dx \tag{4.3.5}$$

$$= a\int_{-\infty}^{\infty} \psi_a^* \psi_a dx \tag{4.3.6}$$

$$= a \tag{4.3.7}$$

where use has been made of Equation 4.3.4 and the normalization condition. Moreover,

$$\langle A^2\rangle = \int_{-\infty}^{\infty} \psi_a^* A^2 \psi_a dx \tag{4.3.8}$$

$$= a \int_{-\infty}^{\infty} \psi_a^* A \psi_a dx \tag{4.3.9}$$

$$= a^2 \int_{-\infty}^{\infty} \psi_a^* \psi_a dx \tag{4.3.10}$$

$$= a^2, \tag{4.3.11}$$

so the variance of A is

$$\sigma_A^2 = \langle A^2\rangle - \langle A\rangle^2 = a^2 - a^2 \tag{4.3.12}$$

$$= 0. \tag{4.3.13}$$

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

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi|^2 dx \tag{4.3.14}$$

Here, $\langle x\rangle$ is called the *expectation value* of x. Similarly the expectation value of any function of x is

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)|\psi|^2 dx. \tag{4.3.15}$$

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 $\langle a\rangle$:

$$\langle a\rangle = \langle \psi\,|a|\,\psi\rangle \tag{4.3.16}$$

$$= \int_{-\infty}^{\infty} \psi^* \hat{A} \psi dx \tag{4.3.17}$$

If an unormalized wavefunction is used, then Equation 4.3.17 changes to

$$\langle a\rangle = \frac{\langle \psi\,|a|\,\psi\rangle}{\langle \psi|\psi\rangle} \tag{4.3.18}$$

$$= \frac{\int_{-\infty}^{\infty} \psi^* \hat{A} \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx} \tag{4.3.19}$$

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

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x - \langle x\rangle)^2 |\psi|^2 dx \tag{4.3.20}$$

$$\equiv \langle x^2\rangle - \langle x\rangle^2, \tag{4.3.21}$$

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**).

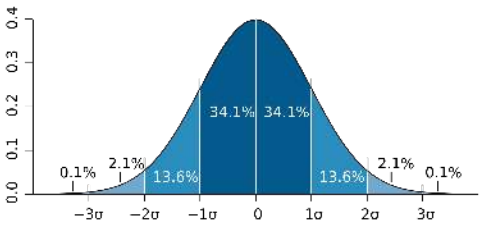


Figure **4.3.1**: A plot of a normal distribution (or bell-shaped curve) where each band has a width of 1 standard deviation. image usd with permission from Wikipedia.

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 4.3.17 is the relevant equation to use.

The expectation value of the **position** is:

$$\begin{aligned} \langle x \rangle &= \int \psi^* x \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} x \sin\left(\frac{\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2}{L} \int_0^L x \sin^2\left(\frac{\pi x}{L}\right) dx \\ &= \frac{L}{2} \end{aligned}$$

The expectation value of the **momentum** is:

$$\begin{aligned} \langle p \rangle &= \int \psi^* \hat{p} \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \left(-i\hbar \frac{d}{dx}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \\ &= \frac{2i\hbar\pi}{L^2} \int_0^L \sin\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right) dx \\ &= 0 \end{aligned}$$

The expectation value of the **kinetic energy** is:

$$\langle T \rangle = \int \psi^* \hat{K} \psi \, d\tau = \frac{2}{L} \int_0^L \sin\left(\frac{\pi x}{L}\right) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\right) \sin\left(\frac{\pi x}{L}\right) dx$$
$$= \frac{\hbar^2 \pi^2}{2mL^2} \frac{2}{L} \int_0^L \sin^2\left(\frac{\pi x}{L}\right) dx$$
$$= \frac{\hbar^2 \pi^2}{2mL^2}$$

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. 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

$$\psi = \sum_i c_i \psi_i \tag{4.3.22}$$

where the c_i are complex weights, and the $\psi(x)$ are the properly normalized (and mutually orthogonal) eigenstates of $\hat{A}$: i.e.,

$$A\psi_i = a_i \psi_i \tag{4.3.23}$$

where a_i is the eigenvalue corresponding to the eigenstate ψ_i, and

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = \delta_{ij}. \tag{4.3.24}$$

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 4.3.19 and 4.3.24 that

$$c_i = \int_{-\infty}^{\infty} \psi_i^* \psi dx. \tag{4.3.25}$$

Thus, the expansion coefficients in Equation 4.3.25 are easily determined, given the wavefunction ψ and the eigenstates ψ_i. Moreover, if ψ is a properly normalized wavefunction then Equations 4.3.19 and 4.3.24 yield

$$\sum_i |c_i|^2 = 1. \tag{4.3.26}$$

Collapsing the Wavefunction

Wave function collapse is said to occur when a wave function—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. Mathematically, an operator $\hat{A}$ is associated with this measurement process, which you suppose has a *complete orthonormal set* of eigenvalues:

$$\{\psi_i\} \tag{4.3.27}$$

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 $\{c_n'\}$.

Sep 10, 2018, 7:01 PM

https://farside.ph.utexas.edu/teachi..es/node93.html

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4.4: The Time-Dependent Schrödinger Equation

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 4.4.1).

Stationary States

Suppose that we are lucky enough to choose

$$\Psi(x, 0) = \psi_n(x) \tag{4.4.5}$$

with corresponding probability density

$$p(x, 0) = |\psi_n(x)|^2 \tag{4.4.6}$$

We will show that

$$\Psi(x, t) = \psi_n(x)e^{-iE_nt/\hbar} \tag{4.4.7}$$

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 equation.

Consider the probability density $p(x,t) = |\Psi(x,t)|^2$:

$$\begin{aligned}p(x,t) &= \left[\psi_n(x)e^{iE_nt/\hbar}\right]\left[\psi_n(x)e^{-iE_nt/\hbar}\right]\\ &= \psi_n^2(x)e^{iE_nt/\hbar}e^{-iE_nt/\hbar}\\ &= |\psi_n(x)|^2 = p(x,0)\end{aligned}$$

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 combination of the two lowest energy states:

$$\Psi(x,0) = a\psi_1(x) + b\psi_2(x) \tag{4.4.8}$$

for example

$$\Psi(x,0) = \frac{1}{\sqrt{2}}[\psi_1(x) + \psi_2(x)] \tag{4.4.9}$$

as in the previous example. Then, the probability density at time t

$$p(x,t) = |\Psi(x,t)|^2 \neq p(x,0) \tag{4.4.10}$$

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

$$\Psi(x,0) = \frac{1}{\sqrt{2}}[\psi_1(x) + \psi_2(x)] \tag{4.4.11}$$

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 completely 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

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 Â can operate on ψ^* to produce the same result after integration as Â 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,

$$\hat{A}^* \int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau_* \tag{4.5.7}$$

produces a new function. Since functions commute, Equation 4.5.6 can be rewritten as

$$\int \psi^* \hat{A} \psi d\tau = \int (\hat{A}^* \psi^*) \psi d\tau \tag{4.5.8}$$

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 $a_2^* = a_2$.

$$\hat{A}\psi = a_1\psi \tag{4.5.9}$$

$$\hat{A}^*\psi^* = a_2\psi^* \tag{4.5.10}$$

Multiply the first equation by φ^* and the second by ψ and integrate.

$$\int \psi^* \hat{A}\psi \, d\tau = a_1 \int \psi^*\psi \, d\tau \tag{4.5.11}$$

$$\int \psi \hat{A}^*\psi^* \, d\tau = a_2 \int \psi\psi^* \, d\tau \tag{4.5.12}$$

Subtract the two equations in Equation 4.5.12 to obtain

$$\int \psi^* \hat{A}\psi \, d\tau - \int \psi \hat{A}^*\psi^* \, d\tau = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{4.5.13}$$

The left-hand side of Equation 4.5.13 is zero because $\hat{A}$ is Hermitian yielding

$$0 = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{4.5.14}$$

If a_1 and a_2 in Equation 4.5.14 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

$$\int_{-\infty}^{\infty} \psi_1^*\psi_2 \, dx = 0. \tag{4.5.15}$$

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,

$$A\psi_a = a\psi_a \tag{4.5.16}$$

$$A\psi_a' = a'\psi_a' \tag{4.5.17}$$

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

$$\int_{-\infty}^{\infty} (A\psi_a)^*\psi_{a'} dx = a\int_{-\infty}^{\infty} \psi_a^*\psi_{a'} dx, \tag{4.5.18}$$

$$\int_{-\infty}^{\infty} \psi_a^*(A\psi_{a'}) dx = a'\int_{-\infty}^{\infty} \psi_a^*\psi_{a'} dx. \tag{4.5.19}$$

However, from Equation 4.5.13, the left-hand sides of the above two equations are equal. Hence, we can write

$$(a - a')\int_{-\infty}^{\infty} \psi_a^*\psi_{a'} dx = 0. \tag{4.5.20}$$

By assumption, $a \neq a'$, yielding

$$\int_{-\infty}^{\infty} \psi_a^*\psi_{a'} dx = 0. \tag{4.5.21}$$

In other words, eigenstates of an Hermitian operator corresponding to *different* eigenvalues are automatically *orthogonal*.

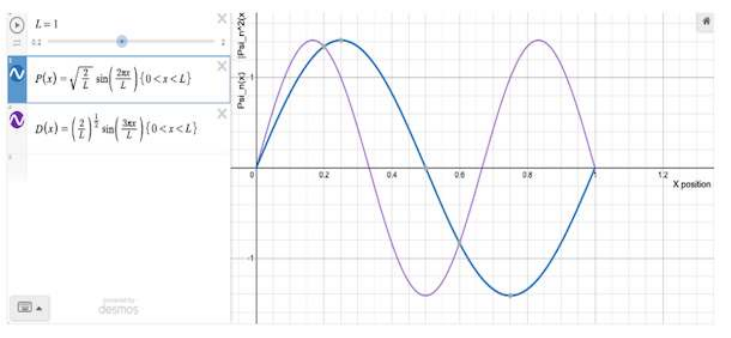
The eigenvalues of operators associated with experimental measurements are all *real*.

Example 4.5.1

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

$$\int_{-\infty}^{\infty} \psi(n=2)\psi(n=3) = 0$$

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, and

$$\int_{-\infty}^{\infty} \psi_a^* \psi'_a dx = S, \tag{4.5.22}$$

then it is easily demonstrated that

$$\psi''_a = \frac{|S|}{\sqrt{1-|S|^2}} \left(\psi_a - S^{-1}\psi'_a\right) \tag{4.5.23}$$

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 an Hermitian

operator are, or can be chosen to be, *mutually orthogonal.*

Theorem: Gram-Schmidt Orthogonalization

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.

Degenerate eigenfunctions are **not** automatically orthogonal, but can be made so mathematically via the Gram-Schmidt Orthogonalization. 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.

$$\begin{aligned} \langle \psi_a | \psi''_a \rangle &= \langle \psi_a | \psi'_a - S\psi_a \rangle \\ &= \cancelto{S}{\langle \psi_a | \psi'_a \rangle} - S \cancelto{1}{\langle \psi_a | \psi_a \rangle} \\ &= S - S = 0 \end{aligned}$$

Oct 19, 2019, 9:08 AM

Double exponent: use braces to clarify

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

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

$$N = \frac{1}{\sqrt{1 - S^2}} \tag{4.5.24}$$

We conclude that the eigenstates of a operator are, or can be chosen to be, **mutually orthogonal**.

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4.6: Commuting Operators Allow Infinite Precision

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:

$$\hat{A}\hat{E}f(x) \neq \hat{E}\hat{A}f(x) \tag{4.6.1}$$

unless the two operators *commute*. Two operators commute if the following equation is true:

$$\left[\hat{A}, \hat{E}\right] = \hat{A}\hat{E} - \hat{E}\hat{A} = 0 \tag{4.6.2}$$

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.

$$\hat{A}\hat{B} = \hat{B}\hat{A}. \tag{4.6.3}$$

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

$$\hat{B}\hat{A}\psi = \hat{A}\hat{B}\psi = \hat{A}b\psi = b\hat{A}\psi \tag{4.6.4}$$

Equation 4.6.4 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.

$$\hat{A}\psi = a\psi \tag{4.6.5}$$

$$\hat{B}(\hat{A}\psi) = \hat{B}(a\psi) = a\hat{B}\psi = ab\psi = b(a\psi) \tag{4.6.6}$$

Equation 4.6.6 shows that Equation 4.6.5 is consistent with Equation 4.6.4. Consequently ψ also is an eigenfunction of $\hat{A}$ with eigenvalue a.

Example 4.6.1

Consider the following operators:

- $\hat{A} = \dfrac{d}{dx}$
- $\hat{E} = x^2$
- $\hat{B} = \dfrac{h}{x}$
- $\hat{C}\{f(x)\} = f(x) + 3$
- $\hat{J} = 3x$
- $\hat{O} = x^{-1}$

a. Do $\hat{A}$ and $\hat{E}$ commute?
b. Do $\hat{B}$ and $\hat{C}$ commute?
c. Do $\hat{J}$ and $\hat{O}$ commute ?

Solution

Solution a

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.

Solution b

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.

Solution c

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.

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

$$\sigma_A \sigma_B \geq \left| \int \psi^* [\hat{A}\hat{B} - \hat{B}\hat{A}] \psi \, d\tau \right| \tag{4.6.7}$$

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 4.6.7 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 4.6.7 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.

Exercise 4.6.1

Show that the commutator for position and momentum in one dimension equals $-i\hbar$ and that the right-hand-side of Equation 4.6.7 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 wave function using the Schrödinger Equation.

$$\hat{H}\psi = E\psi \tag{4.6.8}$$

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.

$$\left[\hat{L}^2, \hat{L}_x^2\right] = \left[\hat{L}^2, \hat{L}_y^2\right] = \left[\hat{L}^2, \hat{L}_z^2\right] = 0 \tag{4.6.9}$$

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.*

Example 4.6.2A

Determine whether the following two operators commute:

$$\hat{K} = \alpha \int [1]^{[\infty]} d[x]$$

and

$$\hat{H} = d/dx$$

Solution

Evaluate

$$\left[\hat{K}, \hat{H}\right]$$

Example 4.6.2B

Determine whether the following two operators commute:

$$\hat{I} = 5$$

and

$$\hat{L} = \int_{[1]}^{[\infty]} d[x]$$

Solution

The identity operator, $\hat{I}$, is a real number. It commutes with everything. Thus, these two operators commute. We can also evaluate the commutator:

$$\left[\hat{I}, \hat{L}\right]$$

$$\left[\hat{I},\hat{L}\right] f(x) = 5\int_1^\infty f(x)d(x) - \int_1^\infty 5f(x)d(x) = 0$$

Exercise 4.6.2

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

Evaluate

$$\left[\hat{L}_z,\hat{L}_x\right] = i\hbar\hat{L}_y$$

$$\left[\hat{L}_x,\hat{L}_y\right] = i\hbar\hat{L}_z$$

$$\left[\hat{L}_y,\hat{L}_z\right] = i\hbar\hat{L}_x$$

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Contributors

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

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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. $\psi = N\cos\frac{n\pi x}{L}$

b. $\psi = \frac{N}{\sin\frac{n\pi x}{a}}$

c. $\psi = N\tan\frac{n\pi x}{a}$

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 $x = \frac{a}{2}$

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 $n = m$

$$\int_0^L \psi^*\psi dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx$$
$$= \frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx$$
$$\frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx = 1$$

Letting $n \neq m$

$$\int_0^L \psi^*\psi dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{m\pi x}{L}\right)dx$$
$$= \frac{2}{L}\frac{1}{2}\int_0^L \left[\cos\left(\frac{(n-m)\pi x}{L}\right) - \cos\left(\frac{(n+m)\pi x}{L}\right)\right]dx$$
$$= \frac{1}{L}\left[\frac{L}{(n-m)\pi}\left[\sin\left(\frac{(n-m)\pi L}{L}\right) - \sin\left(\frac{(n-m)\pi 0}{L}\right)\right] - \frac{L}{(n+m)\pi}\left[\sin\left(\frac{(n+m)\pi L}{L}\right) - \sin\left(\frac{(n+m)\pi 0}{L}\right)\right]\right] = 0$$

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.

$$[\mathbf{L}_z, \mathbf{L}_x] = (xp_y - yp_x)(yp_z - zp_y)\Psi - (yp_z - zp_y)(xp_y - yp_x)\Psi$$

$$= (yp_zxp_y - y^2p_zp_x - zxp_yp_y - zyp_zp_y)\Psi - (xp_yyp_z - xzp_yp_y + y^2p_zp_z + yzp_yp_z)\Psi$$

$$[\mathbf{L}_z, \mathbf{L}_x] = i\hbar\mathbf{L}_y,$$

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

$$[\hat{K}_x, \hat{L}_x] = \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, -i\hbar\left(y\frac{d}{dz} - z\frac{d}{dy}\right)\right]$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\left(-i\hbar\left(y\frac{d}{dz} - z\frac{d}{dy}\right)\right) - -i\hbar\left(y\frac{d}{dz} - z\frac{d}{dy}\right)\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\frac{i\hbar^3}{2m}\left(y\frac{d^3}{dx^2dz} - z\frac{d^3}{dx^2dy}\right) - \frac{i\hbar^3}{2m}\left(y\frac{d^3}{dx^2dz} - z\frac{d^3}{dx^2dy}\right) = 0$$

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

$$\hat{H}\Psi(x,t) = i\hbar\,\partial\Psi(x,y)/\partial t$$

Plug Ψ(x,t) into the time-dependent equation.

$$\hat{H}c_n\Psi_n(x)e^{-iE_nt/\hbar} + c_m\Psi_m(x)e^{-iE_mt/\hbar} = i\hbar\,\partial/\partial t c_n\Psi_n(x)e^{-iE_nt/\hbar} + c_m\Psi_m(x)e^{-iE_mt/\hbar}$$

$$\hat{H}c_n\Psi_n(x)e^{-iE_nt/\hbar} + c_m\Psi_m(x)e^{-iE_mt/\hbar} = E_nc_n\Psi_n(x)e^{-iE_nt/\hbar} + E_mc_m\Psi_m(x)e^{-iE_mt/\hbar}$$

$$\partial/\partial t c_n\Psi_n(x)e^{-iE_nt/\hbar} + c_m\Psi_m(x)e^{-iE_mt/\hbar} = -[(iE_mc_me^{-iE_mt/\hbar}\Psi_m(x))/\hbar] - [(iE_nc_ne^{-iE_nt/\hbar}\Psi_n(x))/\hbar]$$

combine all the constants (except for E) into c_n and c_m

$$i\hbar\,[-[(ic_me^{-iE_mt/\hbar}\Psi_m(x))/\hbar] - [(ic_ne^{-iE_nt/\hbar}\Psi_n(x))/\hbar]] = E_nc_n\Psi_n(x)e^{-iE_nt/\hbar} + E_mc_m\Psi_m(x)e^{-iE_mt/\hbar}$$

Since $\hat{H}\Psi(x,t)$ and $i\hbar\,\partial\Psi(x,y)/\partial t$ are equal, they satisfy the time-dependent equation.

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

$$\int vdu = uv + \int udv$$

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

$$\psi_1(x) = A\sin(k_1x) + B\cos(k_1x) \tag{4.E.1}$$

and

$$\psi_2(x) = C\sin(k_2x) + D\cos(k_2x)$$

Given the boundary conditions are:

$$\psi(0) = 0$$

and

$$\frac{d\psi_1}{dx} = \frac{d\psi_2}{dx} \quad atx = 0$$

$$A + B = C, k_1(A - B) = k_2C$$

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

$$A + B = C, k_1(A - B) = k_2C \tag{4.E.3}$$

,

$$k_1(A - B) = k_2(A + B) \tag{4.E.4}$$

$$k_1A - k_1B = k_2A + k_2B \tag{4.E.5}$$

$$(k_1 - k_2)A = (k_1 + k_2)B \tag{4.E.6}$$

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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CHAPTER OVERVIEW

5: The Harmonic Oscillator and the Rigid Rotor

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

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 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.

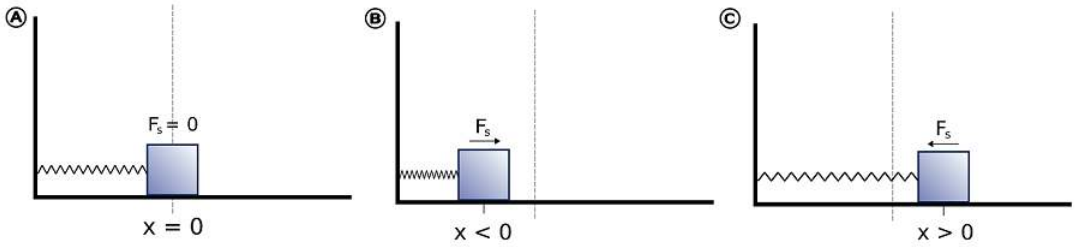


Figure **5.1.2**: A mass connected to a spring that follows Hooke's law is a system that, when displaced from its equilibrium position ($x_o = 0$), experiences a restoring force, F that is proportional to the displacement, x from the equilibrium length (x_o). (Public Domain; LucasVB).

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.

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 flaw in the model in describing real vibrating diatomics.

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.

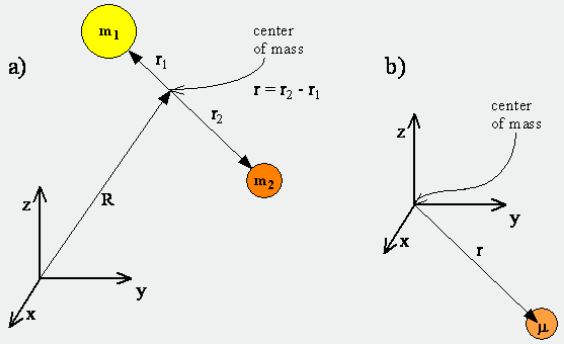


Figure **5.1.3**: Diagrams of the coordinate systems and relevant vectors for a) a diatomic molecule with atoms of mass m_1 and m_2 and b) the equivalent reduced particle of reduced mass μ.

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.
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.

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.

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.

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 written in the standard wave equation form:

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0 \tag{5.1.4}$$

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

$$p = mv \tag{5.1.7}$$

$$= mx_o\omega \cos(\omega t + \phi) \tag{5.1.8}$$

Figure 5.1.4 show the displacement of the bond from its equilibrium length as a function of time. Such motion is called **harmonic**.

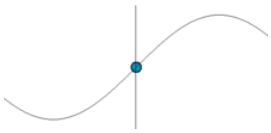


Figure 5.1.4: Solution to the Harmonic Oscillator. Displacement (y-axis) is plotted as a function of time.

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.

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$
$$\frac{d^2}{dt^2}\left(x_o e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$
$$x_o\frac{d^2}{dt^2}\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$
$$x_o i^2\omega^2\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$
$$x_o i^2\omega^2 e^{-i\omega t} + \frac{k}{m}x_o e^{-i\omega t} = 0$$
$$x_o i^2\omega^2 + \frac{k}{m}x_o = 0$$
$$-x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \quad \text{with} \quad \omega = \sqrt{\frac{k}{m}}$$

Example 5.1.3

Show that sine and cosine functions also are solutions to Equation 5.1.4.

Answer

Using Equation 5.1.4

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$
$$w = (\frac{k}{m})^{1/2}$$

For

$$x(t) = x_o sin(wt + \phi)$$

Take the second derivative of $x(t)$

$$\frac{d^2x(t)}{dt} = -w^2 x_o sin(wt + phi)$$
$$-w^2 x_o sin(wt + phi) = -\frac{k}{m}x_o sin((\frac{k}{m})^{1/2}t + phi)$$

Plug in $x(t)$ and the second derivative of $x(t)$ into Equation 5.1.4

$$-\frac{k}{m}x_o sin((\frac{k}{m})^{1/2}t + phi) + \frac{k}{m}x_o sin((\frac{k}{m})^{1/2}t + phi) = 0$$

The sine equation is a solution to eEquation 5.1.4

For

$x(t) = x_o \cos(wt + \phi)$

Take the second derivative of $x(t)$

$$\frac{d^2x(t)}{dt} = -w^2 x_o cos(wt + phi)$$
$$-w^2 x_o cos(wt + phi) = -\frac{k}{m}x_o cos((\frac{k}{m})^{1/2}t + phi)$$

Plug in x(t) and the second derivative of x(t) into Equation 5.1.4

$$-\frac{k}{m}x_o cos((\frac{k}{m})^{1/2}t + phi) + \frac{k}{m}x_o cos((\frac{k}{m})^{1/2}t + phi) = 0$$

The cosine equation is a solution to Equation 5.1.4

Example 5.1.4

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

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.

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

$$p = m\frac{dx}{dt} \tag{5.1.9}$$

so combining Equations 5.1.9 and 5.1.2, the total energy can be written as

$$E = T + V \tag{5.1.10}$$

$$= \frac{p^2}{2m} + \frac{k}{2}x^2 \tag{5.1.11}$$

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 5.1.11) is continuously being shifted between potential energy stored in the spring and kinetic energy of the mass.

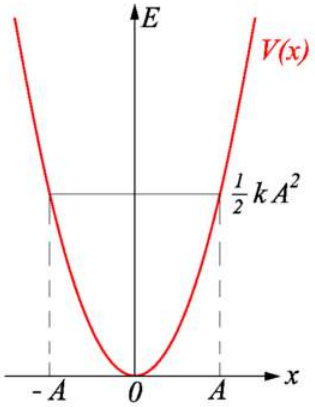


Figure **5.1.5**: The potential $V(x)$ for a harmonic oscillator. Vertical axis energy; horizontal axis displacement x. The potential energy $V(x) = ½kx^2$ is shown in red. (Paul Wormer Wikipedia).

The motion of a classical oscillator is confined to the region where its kinetic energy is nonnegative, which is what the energy relation Equation 5.1.11 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.)

Example 5.1.5

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

Dec 25, 2019, 7:48 PM

a. Frequency

The energy of the harmonic oscillator can be written as

$$E_v = h\nu\left(v + \frac{1}{2}\right) \tag{5.1.12}$$

We can see from the formula of energy that frequency is proportional to energy, so an increase in energy would mean higher frequency.

b. Amplitude

The kinetic and potential terms for energy of the harmonic oscillator can be written as

$$\begin{aligned} E = K + V &= \frac{1}{2}m\omega^2 A^2 \sin^2 \omega t + \frac{1}{2}kA^2 \cos^2 \omega t \\ \omega &= \sqrt{\frac{k}{m}} \\ E &= \frac{1}{2}kA^2\left(\sin^2 \omega t + \cos^2 \omega t\right) = \frac{1}{2}kA^2 \end{aligned} \tag{5.1.13}$$

The maximum amplitude of the vibration will **increase** as the energy **increases.**

Here, amplitude increases both with energy and with frequency, giving both frequency and amplitude a direct relationship with energy of vibration.

Example 5.1.6

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

The equation that defines the energy of a molecular vibration can be approximated is:

$$E_{hit} = T + V = \frac{p^2}{2m} + \frac{k}{2}x \tag{5.1.14}$$

The maximum amplitude of a harmonic oscillator is equal to x when the kinetic energy term of total energy equals zero

$$E_{hit} = \frac{k}{2}x \tag{5.1.15}$$

Solving for x gives the maximum amplitude:

$$x = \sqrt{\frac{2}{k}E_{hit}} \tag{5.1.16}$$

The constraint for the energy that can be introduced cannot be greater than the energy required to break the bond between atoms.

Contributors

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

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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.

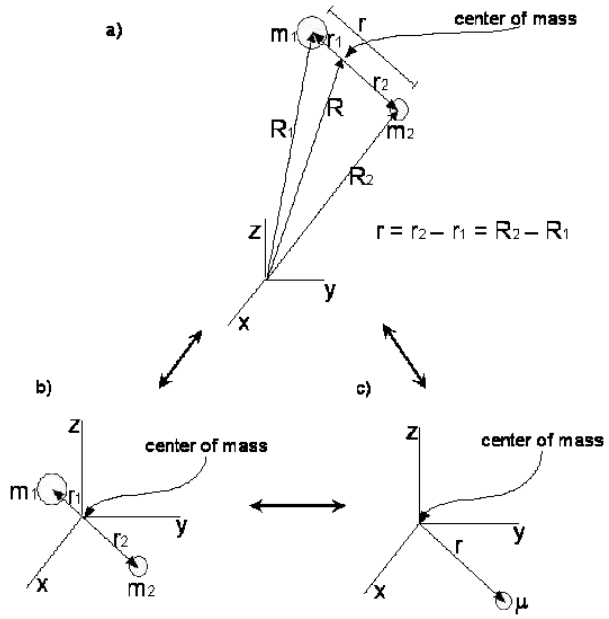


Figure **5.2.1**: a) the individual vectors to the particles m_1 and m_2 in the coordinate space and the resultant vector. b) center of mass. c) reduced mass.

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

$$\mu_{pe} = \frac{(1.6727 \times 10^{-27})(9.110 \times 10^{-31})}{1.6727 \times 10^{-27} + 9.110 \times 10^{-31}}$$
$$= 9.105 \times 10^{-31} kg$$

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.

$$\hat{H}\left|\psi\right\rangle = \left[\frac{-\hbar}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]\left|\psi\right\rangle = E|\psi\rangle \tag{5.2.3}$$

Solving this quantum harmonic oscillator is appreciably harder than the simplier Schrödinger Equation for the particle in the box mode 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 the quantum number v

$$E_v = \hbar\left(\sqrt{\frac{k}{\mu}}\right)\left(v + \frac{1}{2}\right) \tag{5.2.4}$$

$$= h\nu\left(v + \frac{1}{2}\right) \tag{5.2.5}$$

with the natural vibrational frequency of the system given as

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{5.2.6}$$

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).

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5.3: The Harmonic Oscillator Approximates Vibrations

The quantum harmonic oscillator is the quantum analog of the classical harmonic oscillator and 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).

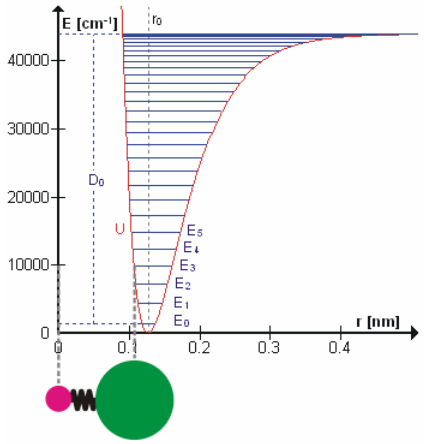


Figure 5.3.1: The HCl molecule is really an anharmonic oscillator. Here HCl is vibrating at energy level E_3. D_0 is dissociation energy here, r_0 bond length, V potential energy. Energy is expressed in wavenumbers. The hydrogen chloride molecule is attached to the coordinate system to show bond length changes on the curve. from Wikipedia.

A general potential energy ($V(x)$) curve for a molecular vibration can be expanded as a Taylor series (Figure 5.3.2)

$$V(x) = V(x_0) + \left.\frac{dV(x)}{dx}\right|_{x_0}^{x} (x - x_0) + \frac{1}{2!}\left.\frac{d^2V(x)}{dx^2}\right|_{x_0}^{x} (x - x_0)^2 + \ldots + \frac{1}{n!}\left.\frac{d^nV(x)}{dx^n}\right|_{x_0}^{x} (x - x_0)^n \tag{5.3.1}$$

$V(x)$ 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 (i.e., cubic) *anharmonic term.* 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.

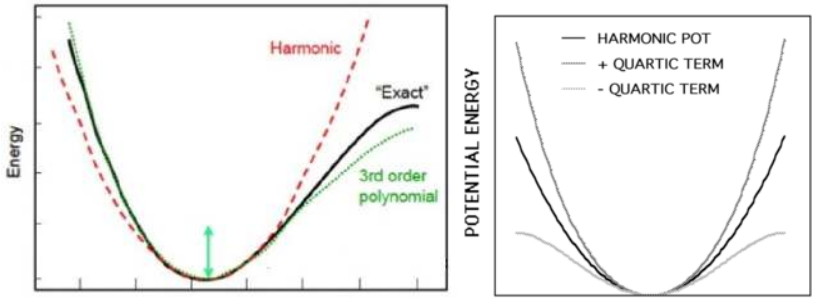


Figure 5.3.2: (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (black curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. Images used with permission from Heather Kulik (MIT) via OpenCourseWare.

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 5.3.1.

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. 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

$$E_v = \left(v + \frac{1}{2}\right) v_e - \left(v + \frac{1}{2}\right)^2 v_e x_e + \left(v + \frac{1}{2}\right)^3 v_e y_e + \text{higher terms} \tag{5.3.3}$$

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).

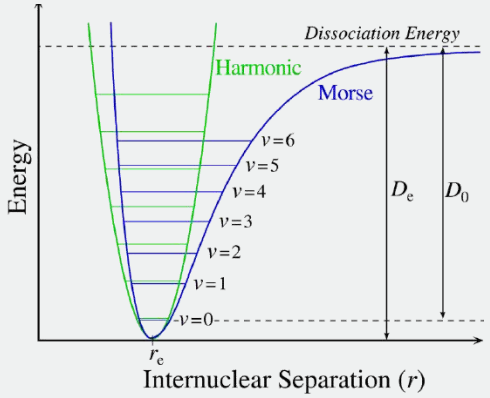


Figure 5.3.4: The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by ħω, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e is 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:

$$V(x) = D(1 - e^{-\beta(x - x_0)})^2 \tag{5.3.4}$$

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 5.3.4) is not trivial, but can be done analytically.

$$\hat{H}|\psi\rangle = E_n|\psi\rangle \tag{5.3.5}$$

with

$$\hat{H} = \hat{T} + \hat{V} \tag{5.3.6}$$

$$= \frac{-\hbar^2 d^2}{2m\, dx^2} + D(1 - e^{-\beta(x-x_0)})^2 \tag{5.3.7}$$

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.

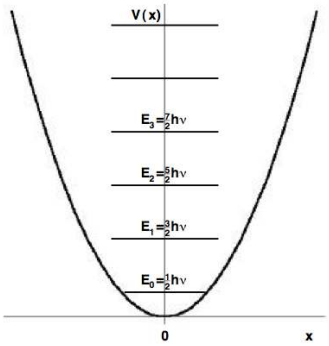


Figure 5.4.1: Potential energy function and first few energy levels for harmonic oscillator.

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

$$v = 0, 1, 2, 3, \cdots \infty \tag{5.4.2}$$

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

$$P_{Q \to Q+dQ} = \int_{Q}^{Q+dQ} \psi_v^*(Q)\psi_v(Q)dQ \tag{5.4.3}$$

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

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.

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

$$\int_{-\infty}^{\infty} \psi_v^*(x)\psi_v(x)dx = 1 \tag{5.4.4}$$

and are orthogonal to each other.

$$\int_{-\infty}^{\infty} \psi_{v'}^*(x)\psi_v(x)dx = 0 \text{ for } v' \neq v \tag{5.4.5}$$

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

$$\frac{\hbar\omega}{2} = \frac{kQ_0^2}{2} \tag{5.4.6}$$

> *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

$$\omega = \sqrt{\frac{k}{\mu}} \tag{5.4.7}$$

? Example 5.4.2: Hydrogen Chloride

The HCl 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 HCl in its lowest state. Compute the classical limit for the stretching of the HCl bond from its equilibrium length in this state. What percent of the equilibrium bond length is this extension?

Solution

H-Cl bond length = 0.127nm = 1.27 * 10^-10m

Transition observed at 2886 cm^-1 => 2886 cm^-1 * (3*10^10 cm/s) = 8.646*10^13 s^-1 or 8.656*10^13 Hz

E_v = (v + 1/2)(hbar)(w), or, at v=0 (ground state), E_0 = (1/2)(hbar)(w)

The term w (omega) is equal to sqrt(k/u) where k is the force constant of the molecular bond and u is the reduced mass of the molecule.

Reduced mass = m1m2/(m1+m2) or ~ (17)(1)/(17+1) amu

or when converted into kg, is 1.568*10^-27kg

The term w is also equal to 2(pi)(f), so we can solve for k by the equality 2(pi)(f) = sqrt(k/u) or

2(pi)(8.656*10^-13 Hz) = sqrt(k/(1.57*10^-27 kg)) where we obtain k = 481 N/m

and w = sqrt((481 N/m)/1.57*10^27 kg)) = 5.54*10^14 rad/s

We can then acquire the ground state vibrational energy from

E_0 = (1/2)(hbar)(w) = (1/2)(hbar)(5/54*10^14 rad/s) = **2.916*10^-20 J**

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 force equation, Q_0 is calculated as V = (1/2)(k)(Q_0^2)

As described above, we can relate the two as (1/2)(hbar)(w) = (1/2)(k)(Q_0^2)

or, 2.916*10^-20 J = (1/2)(481)(Q_0^2) where Q_0 = **1.10*10^-11 m or 0.0110 nm**

Lastly, this classical limit to length can be compared to the equilibrium bond length by a simple relation of

(Q_0/x_{eq})*100 = Percent bond length => (0.110nm)/(0.127nm)*100 = **8.66%**

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

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.

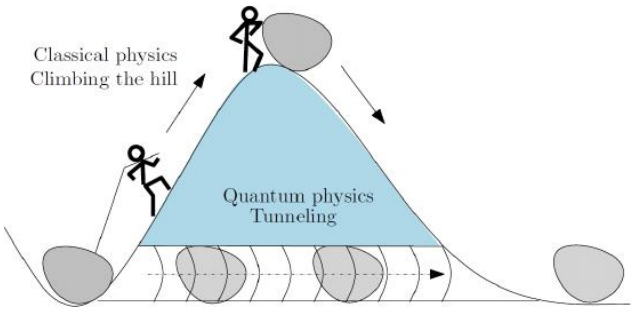


Figure 5.4.2: In classical mechanics a particle can only pass through a barrier if it has enough kinetic energy to get over the barrier in potential energy. A quantum particle can sometimes sneak through a barrier even when its energy would seem to trap it on one side. This effect, called quantum tunneling, explains how trapped nuclear particles can sometimes escape their nuclei, leading to radioactive decay. Tunneling also allows photons of visible light to escape the interior of the sun and electrical currents to function.

? Exercise 5.4.3

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.

The fact that a quantum mechanical oscillator has a finite probability to enter the classically forbidden region of space is a consequence of the wave property of matter and the Heisenberg Uncertainty Principle. A wave changes gradually, and the wavefunction approaches zero gradually as the potential energy approaches infinity.

To understand quantum tunneling, think about a particle moving on a line. Now imagine placing a wall on each side of the particle. In classical physics, the particle bounces back and forth between the walls and eventually stops, trapped. The particle has enough energy to be outside the walls, but it does not have enough energy to get there.

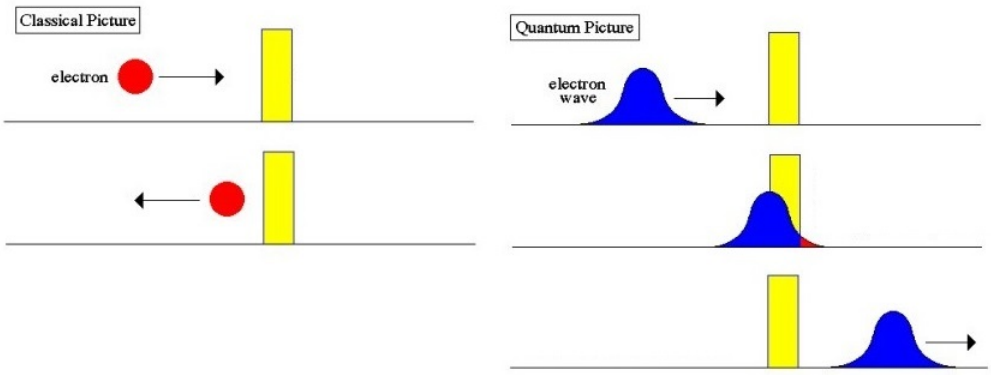


Figure 5.4.2: (left) Classical behavior of a particle colliding with a barrier of finite thickness and height. (right) Corresponding quantum behavior. This chance to be found beyond the barrier is called the tunneling probability.

In quantum mechanics, the particle behaves like a wave. The wave is most intense between the walls, so the particle is probably there. At the walls, the quantum wave diminishes but does not become zero; it extends slightly into the walls. A very low-intensity wave extends outside the walls. There is thus a tiny probability that the particle will be found outside the walls.

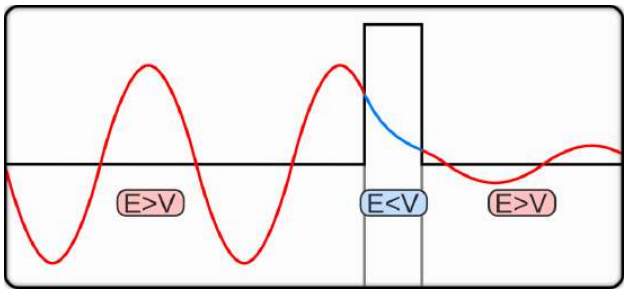


Figure **5.4.3**: Quantum tunnelling through a barrier. The energy of the tunneled particle is the same but the probability amplitude is decreased. (CC-SA-BY 3.0; Felix Kling).

Tunneling in Harmonic Oscillators

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 **5.4.3**. The area of this shaded region gives the probability that the bond oscillation will extend into the forbidden region (Figure **5.4.3**). To calculate this probability, we use

$$P[\text{forbidden}] = 1 - P[\text{allowed}] \tag{5.4.8}$$

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[allowed], to evaluate is

$$P[\text{allowed}] = 2\int_0^{Q_0} \Psi_0^*(Q)\Psi_0(Q)dQ \tag{5.4.9}$$

The factor 2 appears in Equation 5.4.9 from the symmetry of the wavefunction, which extends from $-Q_0$ to $+Q_0$. To evaluate the integral in Equation 5.4.9, 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 5.4.9 produces

$$P[\text{allowed}] = \frac{2}{\sqrt{\pi}}\int_0^1 exp(-x^2)dx \tag{5.4.10}$$

The integral in Equation 5.4.10 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 5.4.4

Numerically Verify that Pr[allowed] in Equation 5.4.10 equals 0.843. To obtain a value for the integral do not use symbolic integration or symbolic equals.

Contributors

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

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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.

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

$$\begin{aligned} h\nu_{photon} &= \Delta E_{vv'} \\ &= E_{v'} - E_v \\ &= \left(v' + \frac{1}{2}\right) h\nu_m - \left(v + \frac{1}{2}\right) h\nu_m \qquad (5.5.3) \\ &= (v' - v)\, h\nu_m \qquad (5.5.4) \end{aligned}$$

Let's consider only transitions between adjacent eigenstates so

$$v' - v = \pm 1 \tag{5.5.5}$$

which is positive if an IR photon is absorbed and negative if it is emitted. For the absorption of a IR photon, Equation 5.5.4 simplifies to

$$\begin{aligned} h\nu_{photon} &= h\nu_m \\ &= \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (5.5.6) \end{aligned}$$

The frequency of radiation ν_{photon} that will bring about this change is **identical** to the classical vibrational frequency of the bond ν and can be expressed as

The Wavenumber unit

The cm^{-1} is the wavenumber scale and it can also be defined as 1/wavelength in cm. A linear 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:

$$\bar{\nu}(cm^{-1}) = \frac{1}{\lambda(\mu m)} \times 10^4 \left(\frac{\mu m}{cm}\right) \tag{5.5.7}$$

$$= \frac{v(Hz)}{c(cm/s)} \tag{5.5.8}$$

Equation 5.5.4 can be modified so that the radiation can be expressed in wavenumbers

$$\tilde{\nu}_m = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{5.5.9}$$

where c is the velocity of light (cm s^{-1}) and $\tilde{\nu}$ is the wavenumber of an absorption maximum (cm^{-1})

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 5.5.1

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 ($rad \cdot s^{-1}$)
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

$$\omega = 5.45 \times 10^{14} \text{rad} \cdot s^{-1}$$

b. natural frequency:

$$\nu = \frac{\omega}{2pi} = 8.68 \times^{13}$$

c. period (s):

$$T = \frac{1}{\nu} = 1.15 \times 10^{-14}$$

d. separation between energy levels:

$$\Delta E = E_{v=1} - E_{v=0} = \hbar\omega = 5.75 \times 10^{-21}\ J$$

e. wavelength λ of the electromagnetic radiation absorbed in the transition $v = 0 \rightarrow v = 1$:

$$3.46 \times 10^{-5}\ m$$

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.

Selection Rules for IR Transitions

Photons can be absorbed or emitted, and the harmonic oscillator can go from one vibrational energy state to another. Which transitions between vibrational states are allowed? 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 wave. 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.

Furthermore, there are **selection rules** that describes whether particular transitions is allow. These results from evaluating the following *transition moment integral* that expresses the probability of a transition from the v to the v' eigenstates:

$$\mu_T = \langle \psi_{v'} \left| \hat{\mu}(x) \right| \psi_v \rangle \tag{5.5.10}$$

$$= \int_{-\infty}^{\infty} \psi^*_{v'}(x) \hat{\mu}(x) \psi_v(x) dx \tag{5.5.11}$$

To evaluate this integral 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

$$\hat{\mu} = \sum_{electrons} e\vec{r} + \sum_{nuclei} q\vec{R} \tag{5.5.12}$$

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 .

$$\mu(x) = \mu_{x=0} + \left(\frac{d\mu(x)}{dx} \right)_{x=0} x + \left(\frac{d^2\mu(x)}{dx^2} \right)_{x=0} x^2 + \cdots \tag{5.5.13}$$

Retaining only the first two terms and substituting into Equation 5.5.11 produces

$$\mu_T = \mu_{x=0} \int_{-\infty}^{\infty} \psi_{v'}(x) \psi_v(x) dx + \left(\frac{d\mu(x)}{dx} \right)_{x=0} \int_{-\infty}^{\infty} x \psi^*_{v'}(x) \psi_v(x) dx \tag{5.5.14}$$

where

$$\mu_{x=0} = 0 \tag{5.5.15}$$

is the dipole moment of the molecule when the nuclei are at their equilibrium positions, and

$$\left(\frac{d\mu(x)}{dx}\right)_{x=0} \tag{5.5.16}$$

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 5.5.13. Both μ and

$$\left(\frac{d\mu(x)}{dx}\right)_{x=0} \tag{5.5.17}$$

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 5.5.14 is 0 because any two harmonic oscillator wavefunctions are *orthogonal*. The integral in the second term of Equation 5.5.14 is zero except when $v' = v \pm 1$ as demonstrated in Exercise 5.5.1. Also note that the second term is zero if

$$\left(\frac{d\mu(x)}{dx}\right)_{x=0} = 0 \tag{5.5.18}$$

? Exercise 5.5.1

Use one of the Hermite polynomial recursion relations to verify that the second integral in Equation 5.5.14 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 5.5.18 **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

$$\underbrace{\Delta v = \pm 1}_{\text{For allowed transitions}} \tag{5.5.19}$$

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

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 1 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

$\mu_T = \langle \psi_{v'} \left| \hat{\mu}(x) \right| \psi_v \rangle$

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.

The case $v' = v + 1$ corresponds to going from one vibrational state to a higher energy one by absorbing a photon with energy hν. The case $v' = v - 1$ corresponds to a transition that emits a photon with energy hν. 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 5.5.6. 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.

$$\Delta E = E_{final} - E_{initial} = h\nu_{photon} = \hbar\omega_{oscillator} \tag{5.5.20}$$

In a perfect harmonic oscillator, the only possibilities are $\Delta = \pm 1$; all others are forbidden. This conclusion predicts that the vibrational absorption spectrum of a diatomic molecule consists of only one strong line since the energy levels are equally spaced in the harmonic oscillator model. If the levels were not equally spaced, then transitions from v = 0 to 1 and from v = 1 to 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 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, Δv = 2, generally appears at a frequency slightly less than twice that of the fundamental, i.e. the frequency due to the $\Delta v = 1$ transition.

? Exercise 5.5.3

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}.

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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.

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 wavefunction must approach zero. The function that has this property and satisfies the differential equation for large values of x is the exponential function

$$\lim_{x\to\infty} \psi(x) \exp\left(\frac{-x^2}{2}\right) \tag{5.6.10}$$

The general expression for a power series is

$$\sum_{n=0}^{\infty} c_n x^n \tag{5.6.11}$$

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 5.6.10 to create a family of valid solutions to the differential equation.

$$\psi_v(x) = \sum_{n=0}^{v} c_n x^n exp\left(\frac{-x^2}{2}\right) \tag{5.6.13}$$

? 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.

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 Hermite polynomials like those in Table 5.6.1 can be produced by using the following generating function

$$H_v(x) = (-1)^v \exp(x^2)\frac{d^v}{dx^v}\exp(-x^2) \tag{5.6.14}$$

Generating functions provide a more economical way to obtain sets of functions compared to purchasing books of tables, and they are often more convenient to use in mathematical derivations.

Exercise 5.6.3

Use the generating formula, Equation 5.6.14, to verify H_3 in Table 5.6.1. Use the generating formula to produce H_8.

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.

$$N_v = \frac{1}{(2^v v! \sqrt{\pi})^{1/2}} \tag{5.6.15}$$

The final form of the harmonic oscillator wavefunctions is thus

$$\psi_v(x) = N_v H_v(x) e^{-x^2/2} \tag{5.6.16}$$

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:

$$\alpha = 1/\sqrt{\beta} = \sqrt{\frac{k\mu}{\hbar^2}} \tag{5.6.17}$$

so Equation 5.6.16 becomes

$$\psi_v(x) = N_v'' H_v(\sqrt{\alpha} Q) e^{-\alpha Q^2/2} \tag{5.6.18}$$

with a slightly different normalization constant

$$N_v'' = \sqrt{\frac{1}{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4} \tag{5.6.19}$$

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

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \tag{5.6.20}$$

with $v = 0, 1, 2, 3, \cdots$.

The energies depend both on the quantum number, v, and the oscillator frequency

$$\omega = \sqrt{\frac{k}{\mu}} \tag{5.6.21}$$

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 5.6.20, 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 **5.6.1**, and the corresponding probability densities are shown in Figure **5.6.2**. 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.

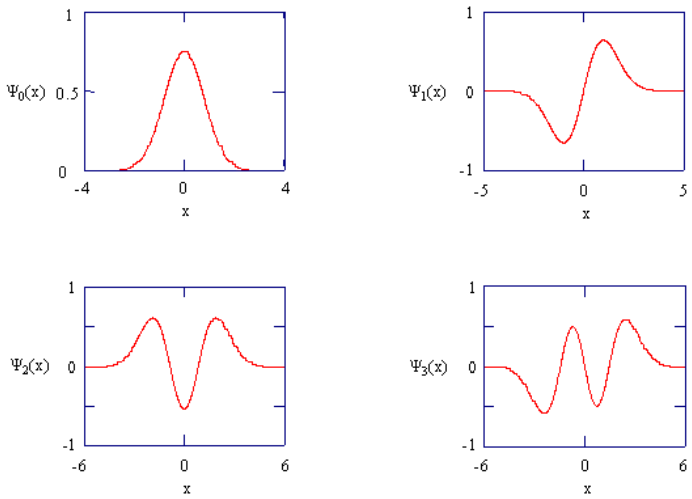


Figure **5.6.1**: The harmonic oscillator wavefunctions describing the four lowest energy states.

? Exercise 5.6.7

Write a few sentences describing and comparing the plots in Figure **5.6.1**.

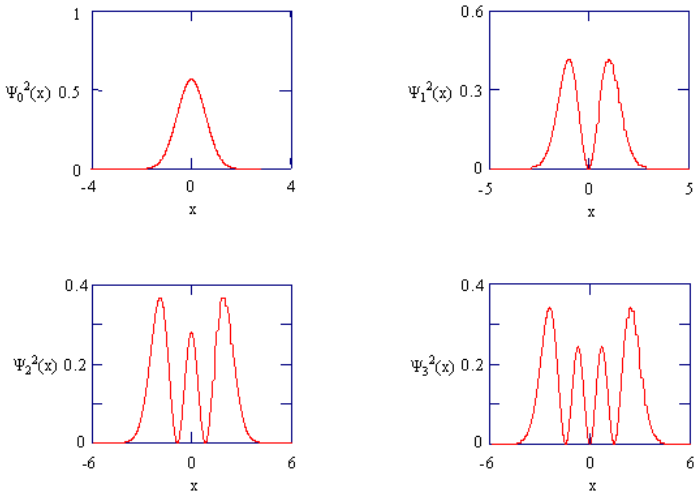


Figure **5.6.2**: The probability densities for the four lowest energy states of the harmonic oscillator.

? Exercise 5.6.8

Explain how Figure **5.6.2** is related to Figure **5.6.1**. Explain the physical significance of the plots in Figure **5.6.2** 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

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).

? 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?

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

5.6: The Harmonic-Oscillator Wavefunctions involve Hermite Polynomials is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

5.7: Hermite Polynomials are either Even or Odd Functions

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**.

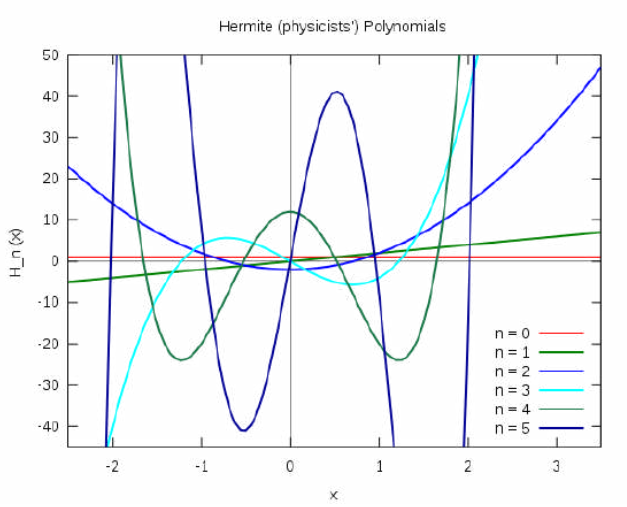


Figure **5.7.1**: The first six Hermite polynomials $H_n(x)$. from Wikipedia.

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 form an orthogonal set of functions for the weight weight function $e^{-x^2/2}$. The exact relation is:

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 0 \tag{5.7.2}$$

if $m \neq n$ and

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 2^n n!\sqrt{\pi} \tag{5.7.3}$$

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. $H_n(x)$ are *n*th-degree polynomials for *n* = 0, 1, 2, 3. and are orthogonal, with weight function (e^{-x^2})

Example 5.7.1: Hermite Polynomials are Orthogonal

Demonstrate that $H_2(x)$ and $H_3(x)$ are orthogonal.

Solution

We need to confirm

$$\int_{-\infty}^{\infty} (4x^2 - 2)(8x^3 - 12x)dx = 0$$

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.

$$\int_L^L (4x^2-2)(8x^3-12x)dx = 8\left(\frac{2x^6}{3}-2x^4+\frac{3x^2}{2}\right)\Big|_{-L}^{L}$$
$$= 8\left(\frac{2L^6}{3}-2L^4+\frac{3L^2}{2}\right)-8\left(\frac{2(-L)^6}{3}-2(-L)^4+\frac{3(-L)^2}{2}\right)$$
$$= 0.$$

Oct 19, 2016, 9:24 PM

http://math.stackexchange.com/questi...are-orthogonal

Even/Odd Functions

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

$$f(x) = f(-x) \tag{5.7.4}$$

- Then f is **odd** if the following equation holds for all x and -x in the domain of f

$$-f(x) = f(-x) \tag{5.7.5}$$

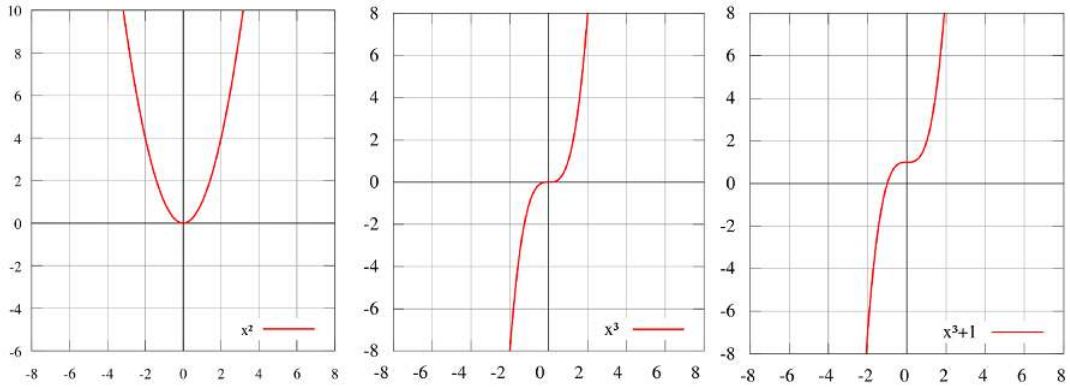


Figure 5.7.2: (left) $f(x) = x^2$ is an example of an even function. (middle) $f(x) = x^3$ is an example of an odd function. (right) I$f(x) = x^3 + 1$ is an example of a function that is neither even nor odd. (CC -BY-SA; Qualc1).

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

$$f(-x) = f(x) \tag{5.7.6}$$

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 if $f(x)$ is odd if, for all x and $-x$ in the domain of f, we have

$$f(-x) = -f(x) \tag{5.7.7}$$

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 nor even)
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 odd nor even)	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

$$H_n(-x) = (-1)^n H_n(x) \tag{5.7.8}$$

- $H_n(x)$ is an even function, when n is even.
- $H_n(x)$ is an odd function, when n is odd.

Integration over Odd/Even Functions

You often consider integrals of the form

$$I = \int_{-a}^{a} f(x)\,\mathrm{d}x \tag{5.7.9}$$

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:

$$\begin{aligned} I = \int_{-a}^{a} f(x)\,\mathrm{d}x &= \int_{-a}^{0} f(x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \\ &= \int_{0}^{a} f(-x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \end{aligned}$$

For an even function, we have $f(-x) = f(x)$, whence

$$I = 2\int_{0}^{a} f(x)\,\mathrm{d}x \tag{5.7.10}$$

For an odd function, we have $f(-x) = -f(x)$, whence

$$I = 2\int_{0}^{a} f(x)\,\mathrm{d}x \tag{5.7.11}$$

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 5.7.2

Technically, evaluating the orthogonality of Hermite polynomials requires integrating over the $\exp(-x^2)$ weight function (Equations 5.7.2 and 5.7.3).

Solution

For the Hermite polynomials $H_n(x)$, the relevant inner product (using Dirac Notation)

$$\langle f, g \rangle = \int_{-\infty}^{\infty} f(x) g(x) \exp(-x^2)\, dx$$

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:

$$\int_{-\infty}^{\infty} f(x)\, dx = 0 \tag{5.7.12}$$

This simplifies calculations greatly as demonstrated in the following chapters.

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

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.

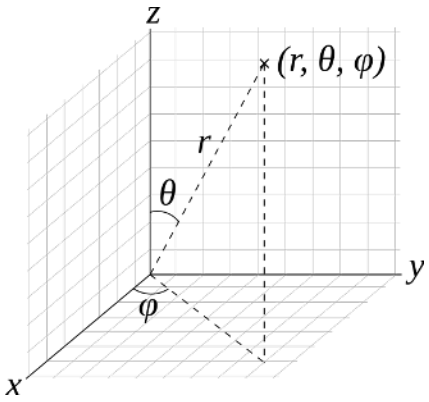


Figure 5.8.1: The spherical coordinate system in terms of the Cartesian system. (Public Domain; Andeggs via Wikipedia).

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

Substitute

$$\Phi_m(\varphi) = \mathrm{N}e^{\pm \mathrm{i}m_J\varphi}$$

into

$$\frac{d^2}{d\varphi^2}\Phi(\varphi) + m_J^2\Phi(\varphi) = 0$$

$$\begin{aligned}\frac{d^2}{d\varphi^2}\Phi_\mathrm{m}(\varphi) + m_J^2\Phi_\mathrm{m}(\varphi) &= \frac{d}{d\varphi}\left(\mathrm{N}\left(\pm \mathrm{i}m_J\right)e^{\pm \mathrm{i}m_J\varphi}\right) + m_J^2\Phi_\mathrm{m}(\varphi) \\ &= \mathrm{N}\left(\pm \mathrm{i}m_J\right)^2 e^{\pm \mathrm{i}m_J\varphi}\Big) + m_J^2\left(\mathrm{N}e^{\pm \mathrm{i}m_J\varphi}\right) \\ &= -\mathrm{N}m_J^2 e^{\pm \mathrm{i}m_J\varphi} + \mathrm{N}m_J^2 e^{\pm \mathrm{i}m_J\varphi} = 0\end{aligned} \tag{5.8.19}$$

The normalization condition, Equation 5.8.20 is used to find a value for N that satisfies Equation 5.8.18.

$$\int_0^{2\pi} \Phi^*(\varphi)\Phi(\varphi)d\varphi = 1 \tag{5.8.20}$$

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 5.8.20 to demonstrate that $N = 1/\sqrt{2\pi}$.

Answer

$$\int_0^{2\pi} \psi^*(\varphi)\psi(\varphi)d\varphi = 1 \tag{5.8.21}$$

$$\psi(\varphi) = Ne^{\pm imJ\varphi} \tag{5.8.22}$$

$$\begin{aligned} \psi^*(\varphi)\psi(\varphi) &= Ne^{+imJ\varphi}Ne^{-imJ\varphi} = N^2 \\ 1 = \int_0^{2\pi} N * N d\varphi &= 1 \\ N^2(2\pi) &= 1 \\ N &= \sqrt{1/2\pi} \end{aligned} \tag{5.8.23}$$

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.

$$e^{im_J\varphi} = e^{im_J(\varphi+2\pi)} \tag{5.8.24}$$

$$= e^{im_J\varphi}e^{im_J2\pi} \tag{5.8.25}$$

For the equality in Equation 5.8.25 to hold, $e^{im_J2\pi}$ must equal 1, which is true only when

$$m_J = \cdots, -3, -2, -1, 0, 1, 2, 3, \cdots \tag{5.8.26}$$

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

$$\Phi_{m_J}(\varphi) = \sqrt{\frac{1}{2\pi}}e^{\pm im_J\varphi} \tag{5.8.27}$$

with

$$m_J = 0, \pm1, \pm2, \cdots \tag{5.8.28}$$

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

$$\lambda = J(J+1) \tag{5.8.29}$$

where

$$J \geq |m_J| \tag{5.8.30}$$

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 5.8.30 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 5.8.29 reveals that the energy of this system is quantized.

$$E = \frac{\hbar^2\lambda}{2I} = J(J+1)\frac{\hbar^2}{2I} \tag{5.8.31}$$

Using Equation 5.8.31, you can construct a rotational energy level diagram. For simplicity, use energy units of $\frac{\hbar^2}{2I}$.

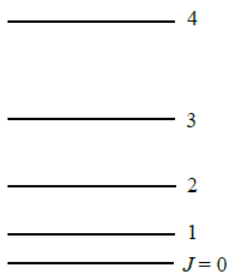


Figure 5.8.2: Energy spacing for a rigid rotor (in 3D). Notice the energy depends only on J and not depend on m_J. That is, the energy of the rotor is not affected by its orientation.

- $J = 0$: 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.

> *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

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 5.8.31):

$$E = J(J + 1)(\hbar^2/2I)$$

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, $E = (5)(6)(\hbar^2/2I) = 30(\hbar^2/2I)$

? 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.

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 5.8.31), which measures the length of the vector, not its direction given mb m_J.

Example 5.8.1: 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.

$$Y_J^{m_J}(\theta, \varphi) = \Theta_J^{|m_J|}(\theta)\Phi_{m_J}(\varphi) \tag{5.8.32}$$

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.

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.

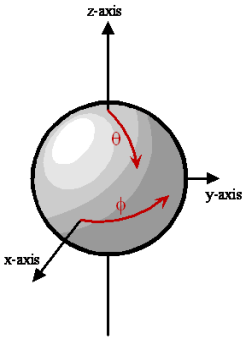


Figure 5.8.4: Space for a rigid rotor is restricted to the surface of a sphere of radius r_0. The only degrees of freedom are motions along θ or φ on the surface of the sphere.

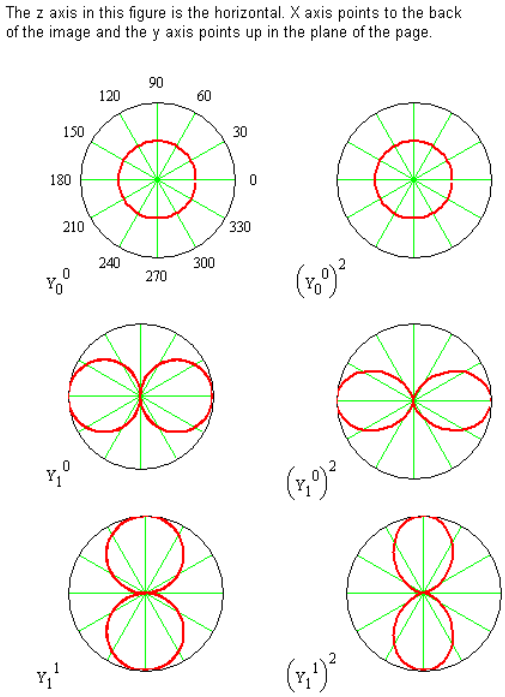


Figure 5.8.3: Polar plots in which the distance from the center gives the value of the function Y for the indicated angle θ.

The 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

$$Pr\,[\theta_0, \varphi_0] = Y_J^{m_J*}(\theta_0, \varphi_0)Y_J^{m_J}(\theta_0, \varphi_0)ds \tag{5.8.33}$$

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

$$ds = \sin\theta\, d\theta\, d\varphi \tag{5.8.34}$$

? 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 5.8.1.

Consider the significance of the probability density function by examining the $J = 1$, $m_J = 0$ wavefunction. The Spherical Harmonic for this case is

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta \tag{5.8.35}$$

The polar plot of $(Y_1^0)^2$ is shown in Figure 5.8.1. 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 for the rigid rotor in 3D: J is the total angular momentum quantum number and m_J is the z-component of the angular momentum. The spherical harmonics called $J_J^{m_J}$ 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.

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- 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)

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5.9: The Rigid Rotator is a Model for a Rotating 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.

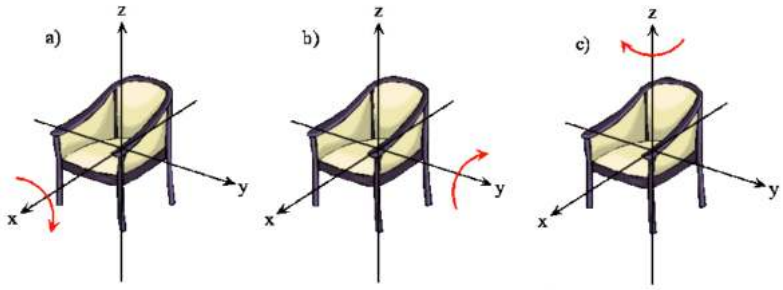


Figure **5.9.1**: Cartesian rotations of a chair. Rotations about the (a) x axis, (b) y axis, and (c) z axis.

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?

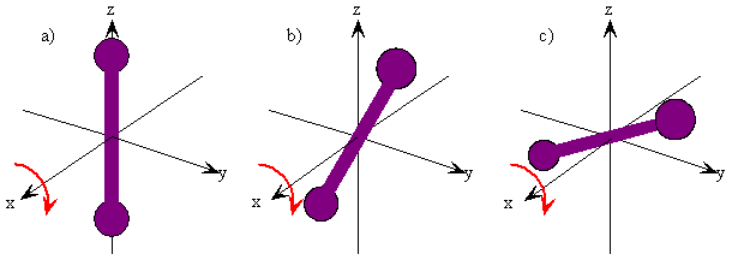


Figure **5.9.2**: Rotation of a diatomic molecule about the x axis.

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.

Degeneracy of the Rotational Eigenstates

Each energy level of a rigid rotor has a degeneracy of $2J+1$ due to the different m_J values.

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 5.9.10 results in

$$h\nu = hc\bar{\nu} = J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \tag{5.9.11}$$

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 included in Equation 5.9.11. When we add in the constraints imposed by the selection rules, J_f can be replaced by J_i+1, because 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 5.9.11) then can be written in terms of the only the quantum number J_i of the initial state.

$$E_{photon} = h\nu \tag{5.9.12}$$
$$= hc\bar{\nu} \tag{5.9.13}$$
$$= 2(J_i+1)\frac{\hbar^2}{2I} \tag{5.9.14}$$

Equation 5.9.14 can be rewritten as

$$E_{photon} = 2B(J_i + 1) \tag{5.9.15}$$

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 5.9.11 to Equation 5.9.16 and identify the units of B at the end.

Answer

$$\begin{aligned}
\Delta E_{photon} &= E_f - Ei \\
E_{r.rotor} &= J(J+1)\frac{\hbar^2}{2I} \\
E_{photon} = h_\nu = hc\tilde{\nu} &= J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \\
J_f - J_i &= 1 \\
J_f &= 1 + J_i \\
E_{photon} = h_\nu = hc\tilde{\nu} &= (1+J_i)(2+J_i)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \\
&= \frac{\hbar^2}{2I}[2 + 3J_i + J_i^2 - J_i^2 - J_i] \\
&= \frac{\hbar^2}{2I}2(J_i+1) \\
&= 2B(J_i+1) \\
B = \frac{\hbar^2}{2I} &\equiv \left[\frac{kgm^2}{s^2}\right] = [J] \\
\frac{B}{h} = B(infreq.) &= \frac{h}{8\pi^2\mu r_o^2} \equiv \left[\frac{1}{s}\right] \\
\frac{B}{hc} = \widetilde{B} &= \frac{h}{8\pi^2\mu c r_o^2} \equiv \left[\frac{s}{m}\right]
\end{aligned}$$

? Exercise 5.9.4

Infrared spectroscopists use units of wavenumbers. Rewrite the steps going from Equation 5.9.11 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.

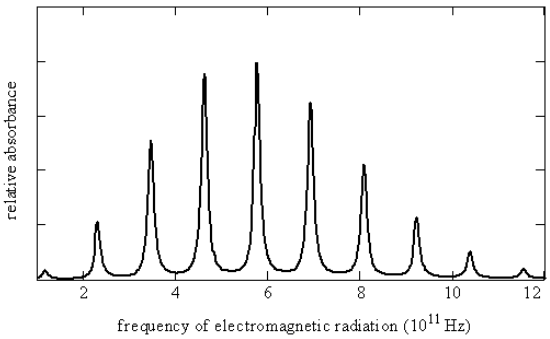


Figure 5.9.3: The rotation spectrum of $^{12}C^{16}O$ at 40 K. The peaks are tabulated in Table 5.9.1.

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
$4 \rightarrow 5$	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%.

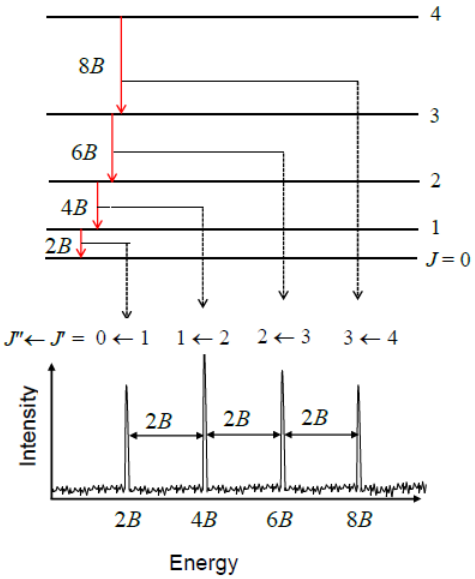


Figure 5.9.4: Energy levels and line positions calculated in the rigid rotor approximation. (CC BY-SA 3.0; Nrrw via Wikipedia)

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

To prove the relationship, evaluate the LHS. First, define the terms:

$$\upsilon_{J_i} = 2B(J_i + 1), \upsilon_{J_i+1} = 2B((J_i + 1) + 1) \tag{5.9.20}$$

Substitute into the equation and evaluate:

$$2B((J_i + 1) + 1) - 2B(J_i + 1) = 2B \tag{5.9.21}$$

$$2B(J_i + 1) + 2B - 2B(J_i + 1) = 2B \tag{5.9.22}$$

$$2B = 2B \tag{5.9.23}$$

LHS equals RHS.Therefore, the spacing between any two lines is equal to 2B.

Example 5.9.1

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

$$\mu = \frac{m_{Na} m_H}{m_{Na} + m_H} = \frac{(22.989)(1.0078)}{22.989 + 1.0078} = 0.9655$$

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

$$R_e = \sqrt{\frac{(1.055 \times 10^{-34}\ J \cdot s)}{2\pi(1.603 \times 10^{-27}\ kg)(2.94 \times 10^{11}\ Hz)}} = 1.899 \times 10^{-10}\ m = 1.89\ \mathring{A}$$

? 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 $^{12}C^{16}O$.

Dec 25, 2019, 10:01 PM

Solution

- J=0: $v_0 = 115271.21\ MHz$
- J=1: $v_1 = 230538.01\ MHz$

$$\Delta v = 230538.01 MHz - 115271.21 MHz = 115266.8 MHz = 1.153 \times 10^{11} Hz = \frac{\hbar}{2\pi\mu R_e} \tag{5.9.24}$$

The reduced mass is

$$\mu = \frac{m_C m_O}{m_C + m_O} = \frac{12.01 \times 16.00}{12.01 + 16.00} = 6.86\, amu \tag{5.9.25}$$

Convert to kg

$$6.86 amu \frac{1.661 \times 10^{-27} kg}{12 mu} = 1.139 \times 10^{-26} kg \tag{5.9.26}$$

\[

$$R_e = \sqrt{\frac{\hbar}{2\pi\mu\Delta v}} = \sqrt{\frac{1.055 \times 10^{-34} J \cdot s}{2\pi \cdot 1.139 \times 10^{-26} kg \cdot 1.153 \times 10^{11} Hz}} = 1.131 \times 10^{-10} \mathrm{m} = 1.131 A \tag{5.9.27}$$

\)

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).

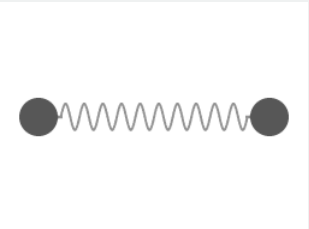


Figure 5.9.5: Two atoms connected by a vibrating bond. There is a rotation around the common center of mass, and oscillation in bond distance. (CC SA-BY 3.0; www.cleonis.nl).

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. The maximum absorption coefficient for each line, γ_{max}, is proportional to the magnitude of the transition moment, μ_T which is given by Equation 5.9.3, and to the **population difference** between the initial and final states, Δn. Since Δn is the difference in the number of molecules present in the two states per unit volume, it is actually a difference in number density. This will be discussed in more detail in the following chapters

Contributors

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

5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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

$$\mu = \frac{(79\ amu)^2}{79\ amu + 79\ amu} = 39.5 amu$$

and convert to Kg:

$1.66e^{-27}$ kg•amu^{-1}

substitute the given values

$$\nu = \frac{1}{2\pi}\sqrt{\frac{240 kg\ m\ s^{-2}\ s}{39.5 amu \times 1.66 \times 10^{-27} kg\ amu^{-1}}} = 9.63 \times 10^{12} s^{-1}$$

It can also be convert to wavenumber (inverse centimeter cm^{-1}):

$$\nu_{cm^{-1}} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{9.63 \times 10^{12} s^{-1}}{3.0 \times 10^{10} cm\ s^{-1}} = 321 cm^{-1}$$

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

$$\mu_{deuterium} = \frac{(9.109390 \times 10^{-31}kg)(3.343586 \times 10^{-27}kg)}{(9.109390 \times 10^{-31}kg + 3.343586 \times 10^{-27}kg)}$$

$$\mu_{deuterium} = 9.106909 \times 10^{-31}kg = 0.9997277m_e$$

R_H = Rydberg constant

$$R_H = (109,737.2cm^{-1})(0.9997277m_e) = 109,707.3cm^{-1}$$

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 $\mathbf{9.106909 \times 10^{-31} kg}$ and the reduced mass of hydrogen is $\mathbf{9.104431 \times 10^{-31} kg}$. Compare both of these answers with the experimental result ($\mathbf{109677.6 cm^{-1}}$). 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 $\mathbf{2.7 \times 10^{-2}\%}$.

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 $\mathbf{9.1 \times 10^{-5}\%}$.

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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CHAPTER OVERVIEW

6: The Hydrogen Atom

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

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 ℓ = 0, 1, 2, ... determines the magnitude of the angular momentum. The magnetic quantum number m = $-\ell$, ..., $+\ell$ 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 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.

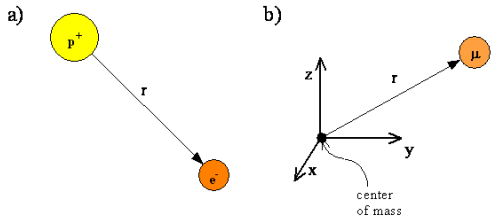


Figure 6.1.1: a) The proton (p^+) and electron (e^-) of the hydrogen atom. b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

? 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 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 used. 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

$$\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right) + 2\mu r^2\left[E + \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(r,\theta,\varphi) = \tag{6.1.5}$$

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\varphi) \tag{6.1.6}$$

Manipulating the Schrödinger equation in this way helps us recognize the square of the angular momentum operator in Equation 6.1.6. The square of the angular momentum operator in Equation 6.1.7.

$$\hat{M}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{6.1.7}$$

Substituting Equation 6.1.7 into Equation 6.1.6 produces

$$\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right) + 2\mu r^2[E - \hat{V}]\psi(r,\theta,\varphi) = \hat{M}^2\psi(r,\theta,\varphi) \tag{6.1.8}$$

? Exercise 6.1.2

Show the algebraic steps going from Equation 6.1.4 to 6.1.6 and finally to 6.1.8. Justify the statement that the rotational and radial motion are separated in Equation 6.1.8.

Since the angular momentum operator does not involve the radial variable, r, we can separate variables in Equation 6.1.8 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

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi) \tag{6.1.9}$$

> *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 6.1.9 into Equation 6.1.8, 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.

$$\frac{\hbar^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \frac{2\mu r^2}{R(r)}[E - V]R(r) = \lambda \tag{6.1.10}$$

$$\frac{1}{Y(\theta,\varphi)}\hat{M}^2 Y(\theta,\varphi) = \lambda \tag{6.1.11}$$

Equations 6.1.10 and 6.1.11 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 6.1.8 to 6.1.10 and 6.1.11.

Rearranging Equation 6.1.11 yields

$$\hat{M}^2 Y_l^{m_l}(\theta,\varphi) = \lambda Y_l^{m_l}(\theta,\varphi) \tag{6.1.12}$$

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. Further, the electronic angular momentum is designated by L and the corresponding operator is called $\hat{L}$. In complete electronic notation, Equation 6.1.12 is

$$\hat{L}^2 Y_l^{m_l}(\theta,\varphi) = \lambda Y_l^{m_l}(\theta,\varphi) \tag{6.1.13}$$

Equation 6.1.13 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 6.1.13 becomes

$$\hat{L}^2 Y_l^{m_l}(\theta,\varphi) = l(l+1)\hbar^2 Y_l^{m_l}(\theta,\varphi) \tag{6.1.14}$$

Using this value for λ and rearranging Equation 6.1.10, we obtain

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) - E\right]R(r) = 0 \tag{6.1.15}$$

? Exercise 6.1.4

Write the steps leading from Equation 6.1.10 to Equation 6.1.15.

The details for solving Equation 6.1.15 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

- 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 functions 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 proton 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

$$\int_{allspace} |\psi(r,\theta,\phi)|^2 d\tau$$

or in braket notation

$$\langle\psi(r,\theta,\phi)|\psi(r,\theta,\phi)\rangle \ ?$$

The quantum numbers have names:

- n is called the principle 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 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.

The Φ function is found to have the quantum number m, where

$$\Phi_m(\phi) = A_m e^{im\phi} \tag{6.2.2}$$

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 $Y_J^m(\theta,\phi)$.

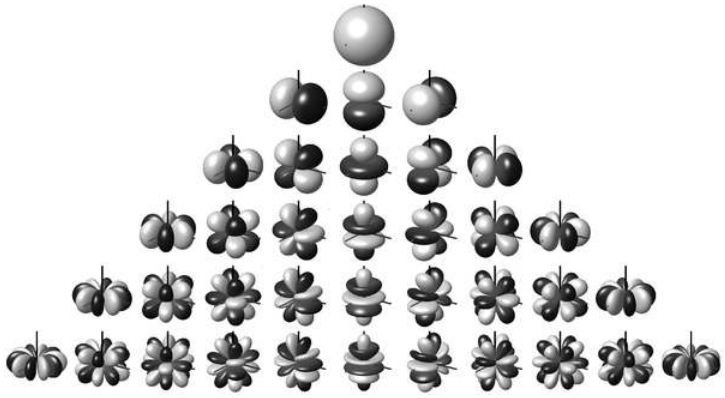


Figure **6.2.1**: Spherical Harmonics as commonly displayed, sorted by increasing energies and aligned for symmetry.

Figure **6.2.1** shows the spherical harmonics Y_J^M, which are solutions of the angular Schrödinger equation of a 3D rigid rotor. 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. 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?

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\), ($m_e ll = 0$ 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.

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**.

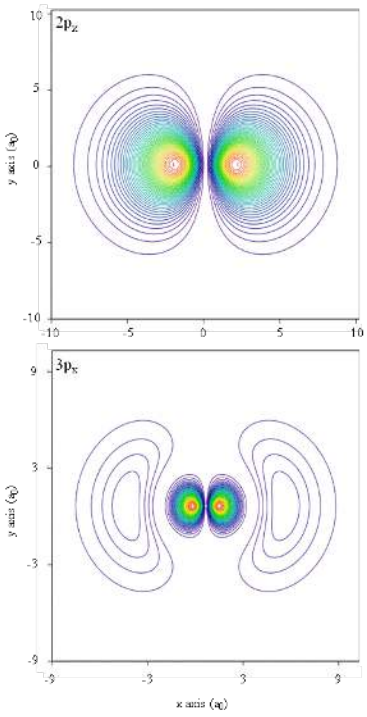


Figure **6.2.2**: Contour plots in the x-y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low $R(r)^2$. The angular function used to create the figure was a linear combination of two 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**.

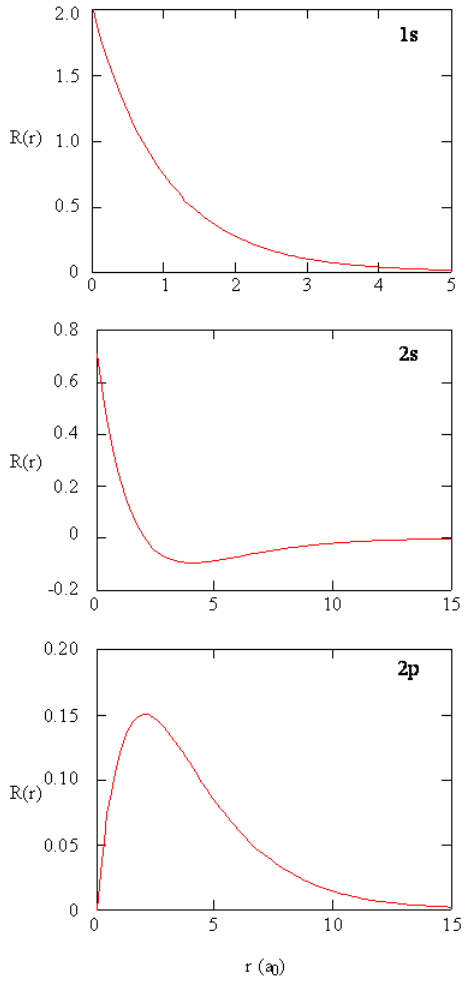


Figure **6.2.3**: Radial function, $R(r)$, for the 1s, 2s, and 2p orbitals.

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

The Laguerre polynomial controls the radial nodes with the number of roots for the Laguerre polynomial is the number of radial nodes.

Exercise 6.2.7

At what value of r does the 2s radial node occur?

Answer

A node exists when the radial portion of the wavefunction equals 0. The radial portion of the 2s wavefunction is:

$$\left(\frac{1}{2\sqrt{2}}\right)\left(\frac{Z}{\alpha_0}\right)^{\frac{3}{2}}(2-\rho)e^{\frac{-\rho}{2}} \tag{6.2.3}$$

where

$$\rho = \frac{Zr}{\alpha_0} \tag{6.2.4}$$

*Z=1\(for the hydrogen atom

and $\alpha_0 = \$$ is the Bohr radius

Therefore:

$$\left(\frac{1}{2\sqrt{2}}\right)\left(\frac{1}{\alpha_0}\right)^{\frac{3}{2}}\left(2-\frac{r}{\alpha_0}\right)e^{\frac{-2r}{\alpha_0}} \tag{6.2.5}$$

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

$$r = 2\alpha_0 \tag{6.2.6}$$

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

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

$$E = \frac{Z^2 E_h}{2n^2} \tag{6.2.7}$$

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.

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**.

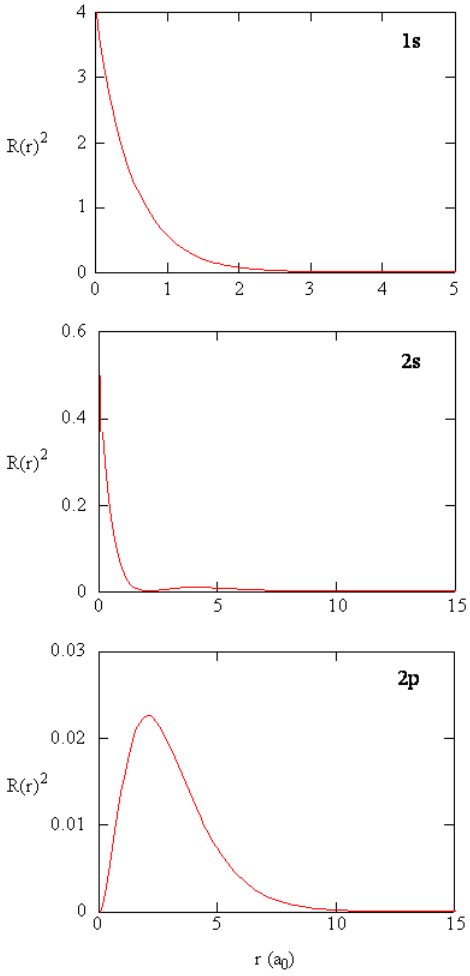


Figure **6.2.4**: Radial probability densities for the 1s, 2s, and 2p orbitals.

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

$$\underbrace{4\pi r^2 R(r)^* R(r)}_{radial probability density} \tag{6.2.8}$$

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.

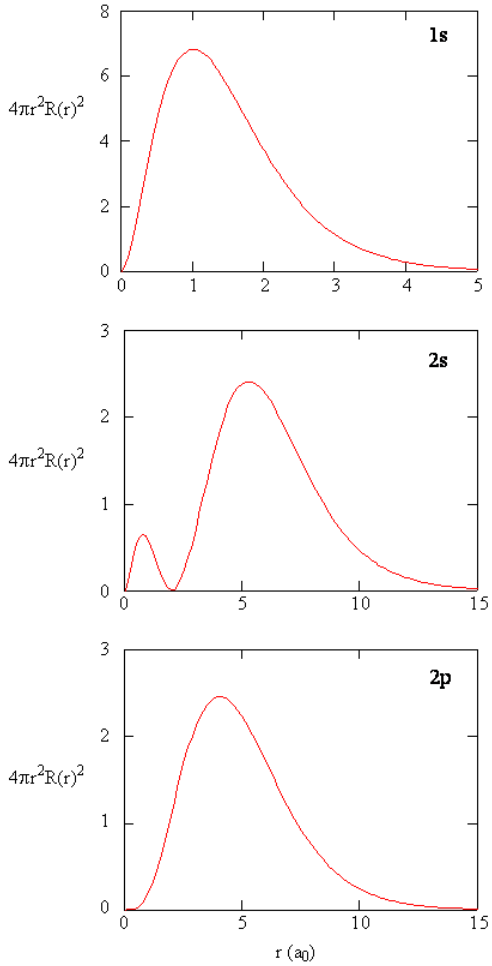


Figure **6.2.5**: The radial distribution function for the 1s, 2s, and 2p orbitals.

? 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

$\4piR(r)^2R(r)^2$ gives the radial probability density of the distance of electron at distance r from the nucleus.

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.

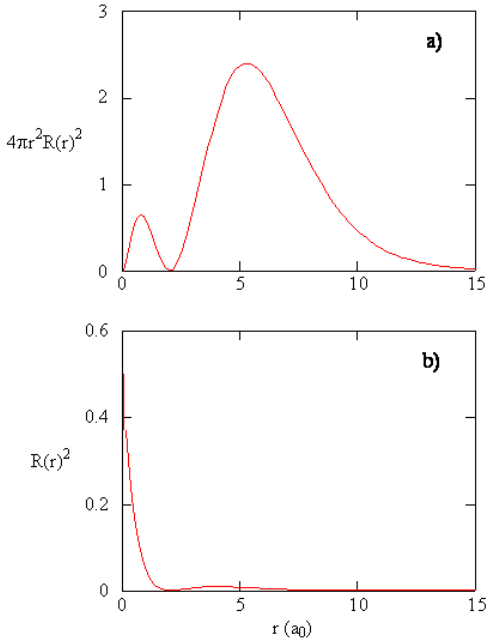


Figure **6.2.6**: Comparison of a) the radial distribution function and b) the radial probability density for the 2s orbital.

Contributors

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6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

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 cross product):

$$\vec{L} = \vec{r} \times \vec{p} \tag{6.3.1}$$

which can be separated into projections into each of the primary axes :

$$L_x = y p_z - z p_y, \tag{6.3.2}$$
$$L_y = z p_x - x p_z \tag{6.3.3}$$
$$L_z = x p_y - y p_x \tag{6.3.4}$$

Extending this discussion to the quantum mechanics, we can us assume that the operators $(\hat{L}_x, \hat{L}_y, \hat{L}_z) \equiv \vec{L}$ which 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

$$\hat{L}_x = -\mathrm{i}\,\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \tag{6.3.5}$$

$$\hat{L}_y = -\mathrm{i}\,\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \tag{6.3.6}$$

$$\hat{L}_z = -\mathrm{i}\,\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \tag{6.3.7}$$

These can be transforming to operators in standard spherical polar coordinates,

$$x = r \sin\theta \cos\varphi \tag{6.3.8}$$
$$y = r \sin\theta \sin\varphi \tag{6.3.9}$$
$$z = r \cos\theta \tag{6.3.10}$$

we obtain

Multiple \label

We can introduce a new operator $\hat{L}^2$:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{6.3.11}$$
$$= -\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right) \tag{6.3.12}$$

The eigenvalue problem for $\hat{L}^2$ takes the form

$$\hat{L}^2 |\psi\rangle = \lambda \hbar^2 |\psi\rangle \tag{6.3.13}$$

where $\psi(r, \theta, \varphi)$ is the wavefunction, and λ is a number. Let us write

$$\psi(r, \theta, \varphi) = R(r)\, Y(\theta, \varphi) \tag{6.3.14}$$

By definition,

$$L^2 Y_l^{m_l} = l(l+1) \hbar^2 Y_l^{m_l} \tag{6.3.15}$$

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 6.3.15). From this, the

amplitude of angular momentum can be expressed

$$|\vec{L}| = \sqrt{L^2} = \sqrt{l(l+1)}\hbar \tag{6.3.16}$$

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

$$L_z Y_l^{m_l} = m\hbar Y_l^{m_l} \tag{6.3.17}$$

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:

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\hbar\hat{L}_z \tag{6.3.18}$$

$$[\hat{L}_y, \hat{L}_z] = \mathrm{i}\hbar\hat{L}_x \tag{6.3.19}$$

$$[\hat{L}_z, \hat{L}_x] = \mathrm{i}\hbar\hat{L}_y \tag{6.3.20}$$

The three commutation relations (Equations 6.3.18 - 6.3.20) 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 6.3.18 - 6.3.20) represent the components of some sort of angular momentum.

> *In fact, we shall assume that any three operators that satisfy the commutation relations (Equations 6.3.18 - 6.3.20) 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 6.3.11 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

$$[\hat{L^2}, \hat{L}_y] = [\hat{L^2}, \hat{L}_z] = 0$$

The fact that L_z is known with certainty, but L_x and L_y are **unknown**; therefore every classical vector with the appropriate length and z-component can drawn, forming 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).

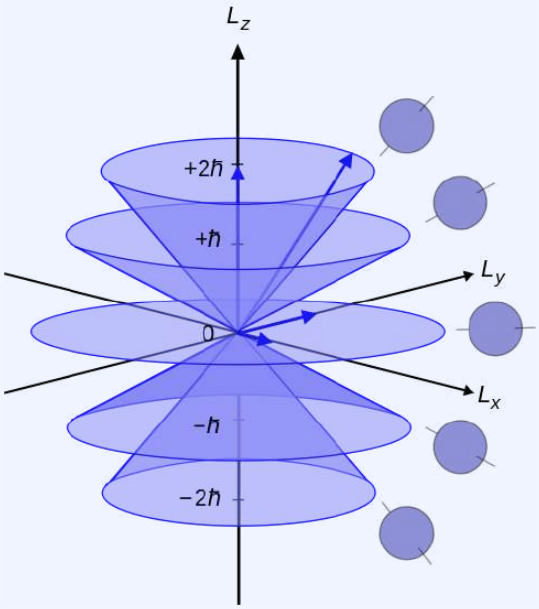


Figure **6.3.1**: Illustration of the vector model of orbital angular momentum. A set of states with quantum numbers $l = 2$, and $m_l = -2, -1, 0, +1, +2$. (Public Domain; Maschen via Wikipedia)

The Physical 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

$$\hat{A}\hat{B} - \hat{B}\hat{A} = 0, \tag{6.3.21}$$

which can be rearranged to

$$\hat{A}\hat{B} = \hat{B}\hat{A}. \tag{6.3.22}$$

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.,

$$\hat{A}\hat{B}\left|\psi\right\rangle = \hat{B}\hat{A}\left|\psi\right\rangle. \tag{6.3.23}$$

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:

$$\hat{L^2}\left|\psi\right\rangle = \lambda\left|\psi\right\rangle \tag{6.3.24}$$

and

$$\hat{L}_x\left|\psi\right\rangle = \beta\left|\psi\right\rangle \tag{6.3.25}$$

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

$$l(l+1)\hbar^2$$

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

$$L_z = m\hbar$$

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

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6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

6.4: Hydrogen Atomic Orbitals Depend upon Three 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**.

$$\psi_{n,l,m_\ell}(r,\theta,\varphi) = \underbrace{R_{n,\ell}(r)}_{radial}\underbrace{Y_l^{m_\ell}(\theta,\varphi)}_{angular} \tag{6.4.1}$$

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. $\langle\psi_{n,l,m}(r,\theta,\varphi)|\psi_{n,l,m}(r,\theta,\varphi)\rangle$
b. $\langle\psi_{n,l,m}(r,\theta,\varphi)|\psi_{n',l',m'}(r,\theta,\varphi)\rangle$

Answer

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

$$\begin{aligned}
\langle\psi(r,\theta,\varphi)|\psi_{n',l',m'}(r,\theta,\varphi)\rangle &= \int_{allspace}\psi^*(r,\theta,\varphi)\psi_{n',l',m'}(r,\theta,\varphi)d\tau \\
&= \int_0^\infty dr\int_0^\pi d\theta\int_0^{2\pi} d\varphi(r^2\sin(\theta))\overbrace{\psi*(r,\theta,\varphi)}^{R_{n,l}(r)Y_l^{m_l}(\theta,\varphi)}\overbrace{\psi_{n',l',m'}(r,\theta,\varphi)}^{R_{n',l'}(r)Y_{l'}^{m_l'}(\theta,\varphi)} \\
&= \int_0^\infty dr\int_0^\pi d\theta\int_0^{2\pi} d\varphi(r^2\sin(\theta))[R_{n,l}(r)Y_l^{m_l}(\theta,\varphi)][R_{n',l'}(r)Y_{l'}^{m_l'}(\theta,\varphi)] \\
&= \left[\int_0^\infty r^2[R_{n,l}(r)R_{n',l'}(r)]dr\right]\left[\int_0^{2\pi}\int_0^\pi \sin(\theta)[Y_l^{m_l}(\theta,\varphi)Y_{l'}^{m_l'}(\theta,\varphi)]d\theta d\varphi\right] \\
&= \langle R_{n,l}(r)|R_{n',l'}(r)\rangle\langle Y_l^{m_l}(\theta,\varphi)|Y_{l'}^{m_l'}(\theta,\varphi)\rangle \\
&= (\delta_{nn'}\delta_{ll'})(\delta_{ll'}\delta_{mm'}) = \delta_{nn'}\delta_{ll'}\delta_{mm'}
\end{aligned}$$

While part a demonstrates normality of the eigenstates, part b demonstrates the orthogonality of the eigenstate (and normality too).

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 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.

Radial Part of the Wavefunction

The asymptotic behavior (i.e., far away from the nucleus) to the radial part of the wavefunction is

$$R_{asymptotic}(r) \sim \exp\left(-\frac{r}{n}a_0\right) \tag{6.4.2}$$

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 $R_{asymptotic}(r)$ as the distance r from the proton approaches infinity? Sketch a graph of the function, $R_{asymptotic}(r)$. Why might this behavior be expected for an electron in a hydrogen atom?

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 ($N_{n,\ell}$) and $\left(\frac{r}{a_0}\right)^l$.

$$R(r) = N_{n,\ell}\left(\frac{r}{a_0}\right)^l L_{n,\ell}(r) e^{-\frac{r}{na_0}} \tag{6.4.4}$$

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 6.4.1: 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	$R_{n,\ell}(\rho)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}$
2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/2}$
3	0	$\frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18\rho+2\rho^2)e^{-\rho/3}$
3	1	$\frac{1}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6\rho+\rho^2)e^{-\rho/3}$
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.

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2} \tag{6.4.5}$$

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.

The Three Quantum Numbers

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 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?

Contributors

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

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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 wave function 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.)

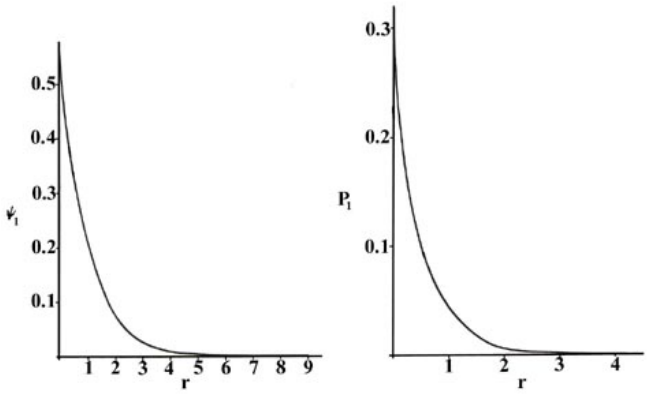


Figure **6.5.1**: The wave function and probability distribution as functions of r for the $n = 1$ level of the H atom. The functions and the radius r are in atomic units in this and succeeding figures.

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.

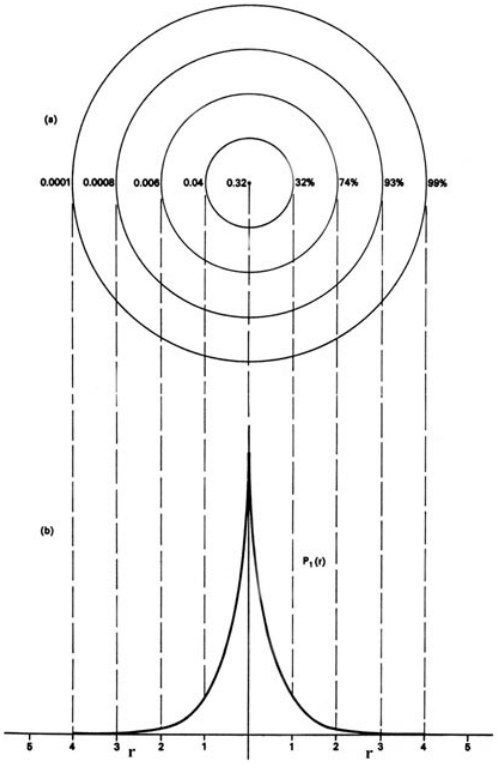


Figure **6.5.2**: (a) A contour map of the electron density distribution in a plane containing the nucleus for the $n = 1$ level of the H atom. The distance between adjacent contours is 1 au. The numbers on the left-hand side on each contour give the electron density in au. The numbers on the right-hand 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 = 4.2×10^{-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 0.52917×10^{-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; 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.

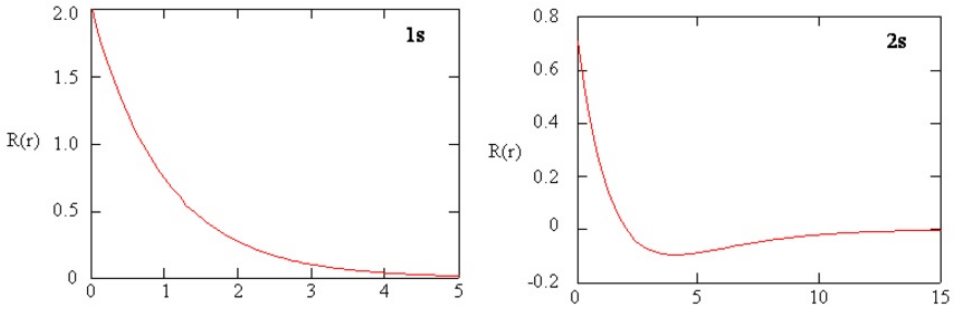


Figure 6.5.3: Radial function, $R(r)$, for the 1s and 2s orbitals. For an interactive graph click here.

Next notice how the radial function for the 2s orbital, Figure 6.5.3;, 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.

Radial probability densities for the 1s and 2s atomic orbitals are plotted in Figure 6.5.4.

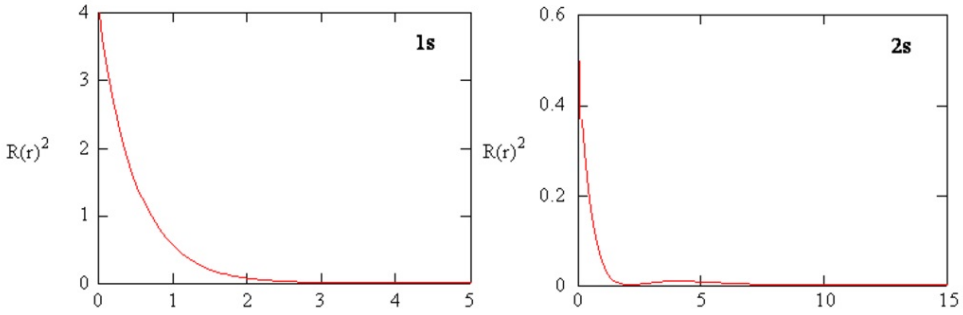


Figure 6.5.4: Radial densities ($R(r)^*R(r)$) for the 1s and 2s orbitals.

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 $r + Dr$. The area of the inner sphere is $4pr^2$ and the thickness of the shell is D*r*. 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 $r + Dr$. 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

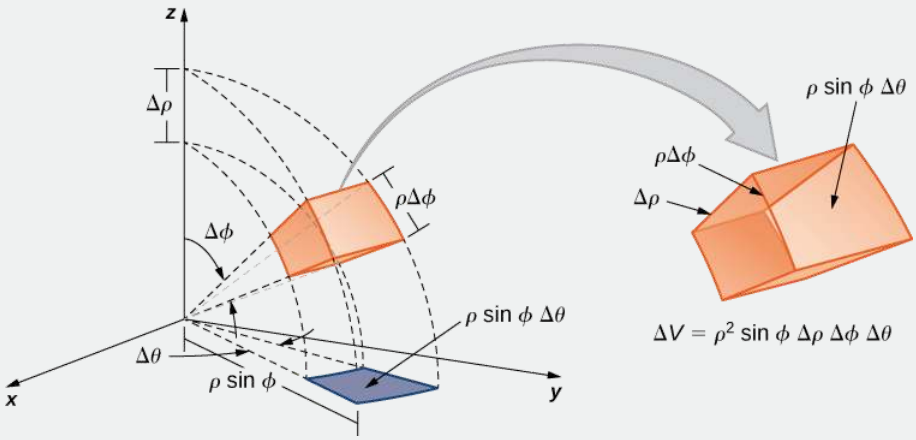
The reader may wonder why the volume of the shell is not taken as:

$$\frac{4}{3}\pi\left[(r+\Delta r)^3 - r^3\right] \tag{6.5.1}$$

the difference in volume between two concentric spheres. When this expression for the volume is expanded, we obtain

$$\frac{4}{3}\pi\left(3r^2\Delta r + 3r\Delta r^2 + \Delta r^3\right) \tag{6.5.2}$$

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.

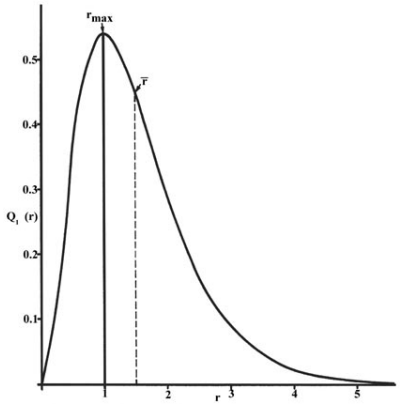


Figure **6.5.5**: The radial distribution function for an H atom. The value of this function at some value of r when multiplied by δr gives the number of electronic charges within the thin shell of space lying between spheres of radius r and $r + \delta r$.

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.

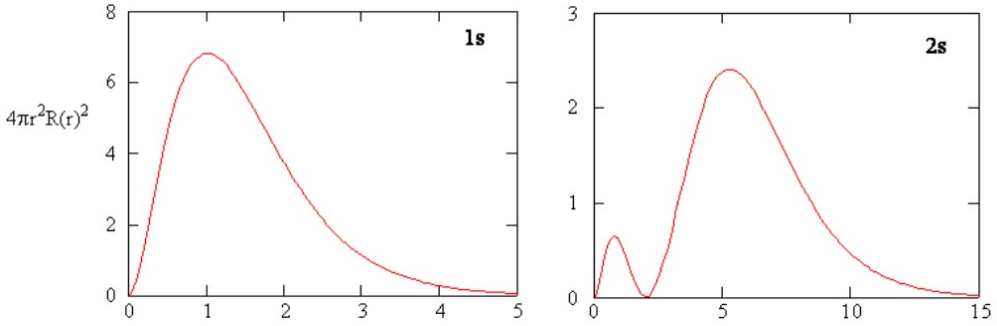


Figure **6.5.6**: The radial distribution function ($4\pi r^2 R(r)^* R(r)$) for the 1s and 2s orbitals. Compare to the radial functions in Figure **6.5.3** or the radial densities in Figure **6.5.4**. For an interactive graph click here.

Example 6.5.1:

Calculate the probability of finding a 1s hydrogen electron being found within distance $2a_o$ from the nucleus.

Solution

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

$$\begin{aligned} prob &= 2 \times 2\pi \times \frac{1}{\pi a_0^3} \int_0^2 a_0(-a_0/2) r^2 de^{-2r/a_0} \\ &= \frac{4}{a_0^3}\left(-\frac{a_0}{2}\right)(r^2 e^{-2r/a_0}|_0^{2a_0} - \int_0^{2a_0} 2re^{-2r/a_0} dr) \\ &= -\frac{2}{a_0^2}[(2a_0)^2 e^{-4} - 0 - 2\int_0^{2a_0} r\left(-\frac{a_0}{2}\right) de^{-2r/a_0}] \\ &= -\frac{2}{a_0^2} 4a_0^2 e^{-4} + \frac{4}{a_0^2}(-\frac{a_0}{2})(re^{-2r/a_0}|_0^{2a_0} - \int_0^{2a_0} e^{-2r/a_0} dr) \\ &= -8e^{-4} - \frac{2}{a_0}\left[2a_0 e^{-4} - 0 - (-\frac{a_0}{2})e^{-2r/a_0}\Big|_0^{2a_0}\right] \\ &= -8e^{-4} - 4e^{-4} - e^{2r/a_0}|_0^{2a_0} \\ &= -12e^{-4} - (e^{-4} - 1) = 1 - 13e^{-4} = 0.762 \end{aligned}$$

There is a 76.2% probability that the electrons will be within $2a_o$ of the nucleus in the 1s eigenstate.

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 wave function 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 wave function, has no physical reality but is a mathematical function which when squared gives the physically measurable electron density distribution.

Contributors

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6.6: Orbital Angular Momentum and the p-Orbitals

Classical 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 ordinary momentum $m\vec{v}$ plays a dominant role in the analysis of linear motion, so angular momentum plays the central role in the analysis of a system with circular motion as found in the model of the hydrogen atom.

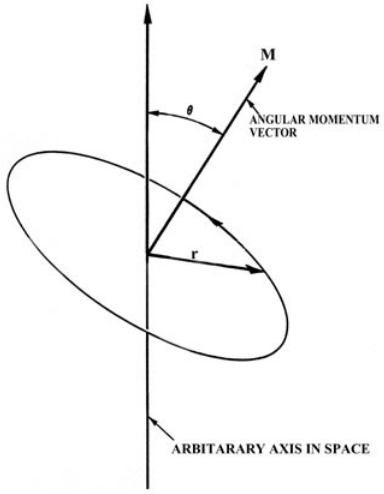


Figure **6.6.1**: The angular momentum vector for a classical model of the atom.

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 as indicated in the figure) 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:

$$|\vec{L}| = mvr \tag{6.6.1}$$

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:

$$|L| = \sqrt{l(l+1)}\hbar \tag{6.6.2}$$

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 6.6.2 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 1*s*, 2*s*, 3*s*, 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 2*s* orbital the hydrogen atom is in a state for which $n = 2$ and $l = 0$.

Comparing these results with those for the 1*s* 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**.

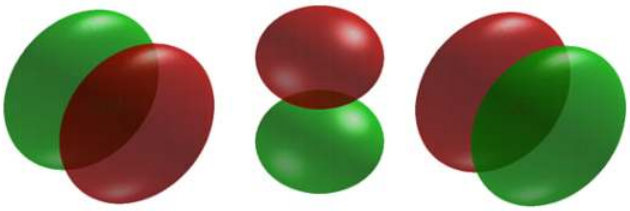


Figure **6.6.2**: The appearance of the three 2p orbitals in three-dimensional space. (CC BY-SA 3.0; I, Sarxos).

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 wave function 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 1*s* 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

$$L_z = m_l \hbar \tag{6.6.3}$$

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.

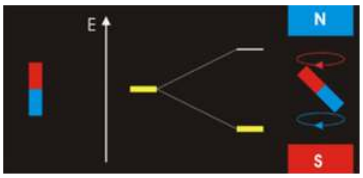


Figure **6.6.3**: The orbiting electron with a non-zero l value acts like a magnetic field with is no energetic difference for any particular orientation (only one energy state, on the left),. However, in external magnetic field there is a high-energy state and a low-energy state depending on the relative orientations of the magnet to the external field. (CC SA-BY 3.0; Darekk2).

Which m_l Mumber 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.

$$|\psi_{2,1,0}\rangle = r\cos\theta R(r) \tag{6.6.4}$$

$$|\psi_{2,1,+1}\rangle = -\frac{r}{2}\sin\theta e^{i\phi} R(r) \tag{6.6.5}$$

$$|\psi_{2,1,-1}\rangle = +\frac{r}{2}\sin\theta e^{-i\phi} R(r) \tag{6.6.6}$$

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.

$$R(r) = \sqrt{\frac{Z^5}{32\pi a_0^5}} e^{-Zr/2a_0} \tag{6.6.7}$$

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:

$$|\psi_{2,1,0}\rangle = zR(r) \tag{6.6.8}$$

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:

$$e^{i\phi} = \cos\phi + i\sin\phi \tag{6.6.9}$$

$$\sin\phi = \frac{e^{i\phi} - e^{-i\phi}}{2i} \tag{6.6.10}$$

$$\cos\phi = \frac{e^{i\phi} + e^{-i\phi}}{2} \tag{6.6.11}$$

We're also going to use $x = \sin\theta\cos\phi$ and $y = \sin\theta\sin\phi$.

$$\begin{aligned}
\psi_{2p_x} &= \frac{1}{\sqrt{2}}\left(\psi_{2,1,+1} - \psi_{2,1,-1}\right) \\
&= \frac{1}{2}\left(e^{i\phi} + e^{-i\phi}\right) r\sin\theta f(r) \\
&= r\sin\theta\cos\phi f(r) = x f(r) \\
\psi_{2p_y} &= \frac{i}{\sqrt{2}}\left(\psi_{2,1,+1} + \psi_{2,1,-1}\right) \\
&= \frac{1}{2i}\left(e^{i\phi} - e^{-i\phi}\right) r\sin\theta f(r) \\
&= r\sin\theta\sin\phi f(r) = y f(r)
\end{aligned}$$

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´ 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 ´ 2+1), seven f orbitals, (2 ´ 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

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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6.7: 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 $\boldsymbol{r_1}$ and $\boldsymbol{r_2}$. The electrons are separated by a distance $\boldsymbol{r_{12} = |r_1 - r_2|}$. 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.

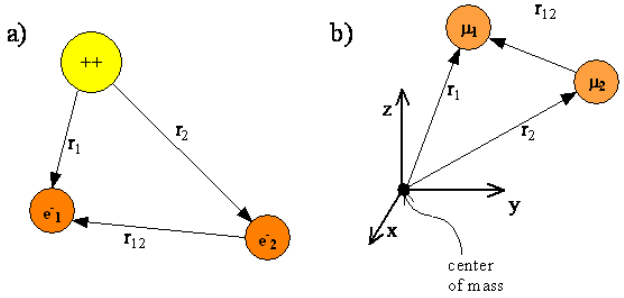


Figure **6.7.1**: (a) The nucleus (++) and electrons (e-) of the helium atom. (b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that μ_1 and $\mu_2 \approx m_e$.

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

$$\hat{H} = \hat{T} + \hat{V} \tag{6.7.1}$$

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

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V_1(r_1) + V_2(r_2) + V_{12}(r_{12}) \tag{6.7.2}$$

where

$$V_1(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{6.7.3}$$

$$V_2(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{6.7.4}$$

$$V_{12}(r_{12}) = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{6.7.5}$$

The two-electron Hamiltonian in Equation 6.7.2 can be extended to any atom or ion by replacing the He nuclear charge of +2 with a general charge Z; e.g.

$$V_1(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{6.7.6}$$

and including terms for the additional electrons. The subsequent multi-electron atom with n electron is

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_i^n \nabla_i^2}_{\text{Kinetic Energy}} + \underbrace{\sum_i^n V_i(r_i)}_{\text{Coulombic Attraction}} + \underbrace{\sum_{i\neq j}^{n,n} V_{ij}(r_{ij})}_{\text{electron-electron Repulsion}} \tag{6.7.7}$$

This multi-electron Hamiltonian is qualitatively similar to the 2-electron Hamiltonian (Equation 6.7.1) with each electron having its own kinetic energy and nuclear potential energy terms (Equations 6.7.3 and 6.7.4). 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 6.7.7):

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 $^{11}\mathbf{B}$ atom.
b. Would it be any different for a $^{11}\mathbf{B}^+$ ion?
c. Would it be any different for a $^{10}\mathbf{B}$ atom?

Answer

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, $^{11}\mathbf{B}^+$ has one less electron than $^{11}\mathbf{B}$. 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

$$\hat{H}_B(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4) = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2m_e}\nabla_3^2 - \frac{\hbar^2}{2m_e}\nabla_4^2 - \frac{-5e^2}{4\pi\epsilon_0 r_1} - \frac{-5e^2}{4\pi\epsilon_0 r_2} - \frac{-5e^2}{4\pi\epsilon_0 r_3} - \frac{-5e^2}{4\pi\epsilon_0 r_4} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{14}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} + \frac{e^2}{4\pi\epsilon_0 r_{24}} + \frac{e^2}{4\pi\epsilon_0 r_{34}}$$

c. No effect. Changing the number of neutrons in the nucleus does not affect kinetic nor potential energies of the electrons. The Hamilitonian for $^{10}\mathbf{B}$ is identical to $^{11}\mathbf{B}$. 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.

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 6.7.7 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**,

$$\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\cdots\vec{r}_n) \tag{6.7.8}$$

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.

$$p(V) = \int_V \left|\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\cdots\vec{r}_n)\right|^2 d\tau \tag{6.7.9}$$

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.

$$\int_{\text{all space}} \left|\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\cdots\vec{r}_i)\right|^2 d\tau = n \tag{6.7.10}$$

Unfortunately, the Coulomb repulsion terms (Equation 6.7.5) 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 6.7.7) involve writing a multi-electron wavefunction ($\psi(r_1,r_2,\cdots,r_n)$) as a simple product of single-electron wavefunctions ($\varphi_i(r_i)$):

$$\psi(r_1,r_2,\cdots,r_n) \approx \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_n(r_n) \tag{6.7.11}$$

or in Dirac notation

$$|\psi(r_1,r_2,\cdots,r_n)\rangle \approx |\varphi_1(r_1)\rangle\,|\varphi_2(r_2)\rangle\cdots|\,\varphi_n(r_n)\rangle \tag{6.7.12}$$

The energy of the atom in the state associated with a specific multi-electron wavefunction (E) is obtained from the multi-electron Schrödinger Equation

$$\hat{H}\psi(r_1,r_2,\cdots,r_n) = E\psi(r_1,r_2,\cdots,r_n) \tag{6.7.13}$$

Within the approximation in Equation 6.7.11, E can be expressed sum of the energies of the one-electron components (ϵ_i).

$$E \approx \sum_i \epsilon_i \tag{6.7.14}$$

> This is called the orbital approximation.

By writing the multi-electron wavefunction as a product of single-electron functions (Equations **6.7.11** or **6.7.12**), 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.

Contributors

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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

$$\sum_{m=-1}^{1}\psi_{31m}^2 = \left(\frac{2}{6561\pi}\right)\left(\frac{z^3}{a_o^3}\right)\sigma^3(6-\sigma)^2\exp^{\frac{-2\sigma}{3}}\left(\cos^2\theta + \sin^2\theta\cos^2\phi + \sin^2\theta\sin^2\phi\right)$$

$$\sum_{m=-1}^{1}\psi_{31m}^2 = \left(\frac{2z^3\sigma^2(6-\sigma)^2\exp^{\frac{-2\sigma}{3}}}{6561\pi a_o^3}\right)\left(\cos^2\theta + \sin^2\theta\left(\cos^2\phi + \sin^2\phi\right)\right)$$

$$\sum_{m=-1}^{1}\psi_{31m}^2 = \left(\frac{2z^3\sigma^2(6-\sigma)^2\exp^{\frac{-2\sigma}{3}}}{6561\pi a_o^3}\right)$$

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

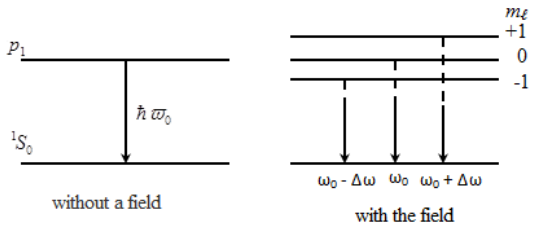
$$I = \frac{q_e m_e v r}{2\pi m_e r^2}$$
$$I = \frac{q_e L}{2\pi m_e r^2}$$

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

$$\hat{L_+}\hat{L_-} - hat{L_-}\hat{L_+} = \hat{L^2} - \hat{L_z^2} + \hbar\hat{L_z} - \hat{L^2} + \hat{L_z^2} - \hbar\hat{L_z}$$

$$\hat{L_+}\hat{L_-} - \hat{L_-}\hat{L_+} = 2\hbar\hat{L_z}$$

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:

$$E_\phi = \frac{\langle \phi \left| \hat{H} \right| \phi \rangle}{\langle \phi | \phi \rangle}$$

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

$$\langle \phi \left| \hat{H} \right| \phi \rangle$$

$$= \frac{n^2 h^2}{8mL^2} \cdot \sqrt{\frac{2}{L}}$$

so

$$E_\phi = \frac{\frac{n^2 h^2}{8mL^2} \cdot \sqrt{\frac{2}{L}}}{\sqrt{\frac{2}{L}}}$$

so

$$E_\phi = \frac{n^2 h^2}{8mL^2}$$

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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CHAPTER OVERVIEW

7: Approximation Methods

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

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

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 (i.e., 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:

$$I_1 = -E_{1s}(\mathrm{He}) = 24.59\ eV \tag{7.1.2}$$

The second ionization energy, I_2 can experimentally determined, but also can be calculated exactly from the hydrogen atom solutions since He^{+} is a hydrogen-like ion with $Z = 2$. Hence, we have

$$I_2 = -E_{1s}(\mathrm{He}^{+}) \tag{7.1.3}$$

$$= \frac{Z^2}{2n^2} \tag{7.1.4}$$

$$= 54.42\ \mathrm{eV} \tag{7.1.5}$$

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

$$E_{true} = -(I_1 + I_2) \tag{7.1.6}$$

$$= -79.02\ \mathrm{eV}. \tag{7.1.7}$$

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

$$E_{true} = -5.8066\, R \tag{7.1.8}$$

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:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \cancel{\frac{e^2}{4\pi\epsilon_0 r_{12}}} \tag{7.1.9}$$

If we simply *ignore* the electron-electron repulsion term, then Equation 7.1.9 can be simplified to

$$\hat{H} \approx -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_2} \tag{7.1.10}$$

$$\approx h_1(r_1) + h_2(r_2) \tag{7.1.11}$$

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 7.1.11 is convenient since electron 1 is *separable* from electron 2, so that the total wavefunction is a product to two one-electron wavefunctions:

$$\Psi_{total} = \psi_{el_1}\psi_{el_2} \tag{7.1.12}$$

or in braket notation

$$|\Psi_{total}\rangle = \hat{H}\Big|\psi_{el_1}\rangle|\psi_{el_2}\rangle \tag{7.1.13}$$

With some operator algebra, something important arises - the one electron energies are **additive**:

$$\hat{H}\Psi_{total} = (\hat{H}_{el_1} + \hat{H}_{el_2})\psi_{n\ el_1}\psi_{n\ el_2} = (E_{n_1} + E_{n_2})\psi_{n\ el_1}\psi_{n\ el_2} \tag{7.1.14}$$

or in bra-ket notation

$$\hat{H}|\Psi_{total}\rangle = \hat{H}\,|\psi_{el_1}\rangle|\,\psi_{el_2}\rangle \tag{7.1.15}$$

$$= (E_{n_1} + E_{n_2})\,|\psi_1\rangle|\,\psi_2\rangle \tag{7.1.16}$$

The energy for a ground state Helium atom (both electrons in lowest state) is then

$$E_{He_{1s}} = \underbrace{E_{n_1}}_{\text{energy of single electron in helium}} + \underbrace{E_{n_2}}_{\text{energy of single electron in helium}} \tag{7.1.17}$$

$$= -R\left(\frac{Z^2}{1}\right) - R\left(\frac{Z^2}{1}\right) \tag{7.1.18}$$

$$= -8R \tag{7.1.19}$$

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**.

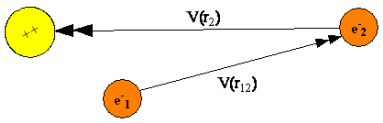


Figure **7.1.1**: Electron-electron shielding leading to a reduced effective nuclear charge. The attractive force of the nucleus on electron 2, $V(r_2)$, is partially countered by the repulsive force between electron 1 and electron 2, $V(r_{12})$.

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

$$E_{trial} \geq E_{true} \tag{7.1.20}$$

where

$$E_{trial} = \frac{\langle \psi_{trial} \left| \hat{H} \right| \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{7.1.21}$$

$$= \frac{\int \psi^*_{trial} \hat{H} \psi_{trial} d\tau}{\int \psi^*_{trial} \psi_{trial} d\tau} \tag{7.1.22}$$

Equation 7.1.20 is call the variational theorem and states that for a time-independent Hamiltonian operator, any trial wave function will have an variational energy (i.e., expectation value) that is **greater than or equal** to the true ground state wave function corresponding to the given Hamiltonian (Equation 7.1.20). 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).

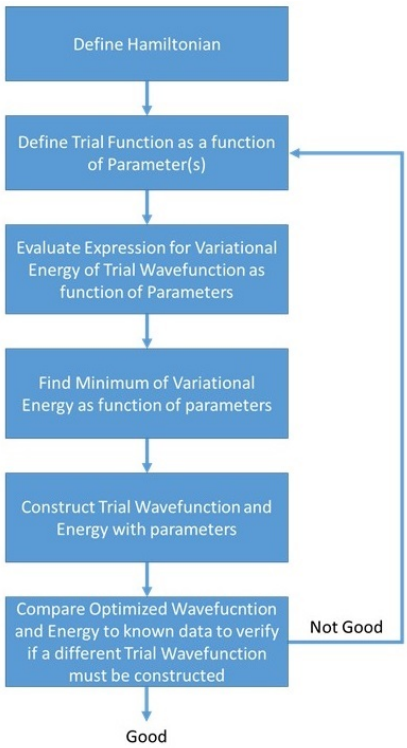


Figure 7.1.2: Simplified algorithmic flowchart of the Variational Method approximation

> *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 7.1.22 can be evaluated analytically. For the case of the He atom, let's consider the trial wavefunction as the product wavefunction given by Equation 7.1.23 (this is called the **orbital approximation**),

$$\psi(r_1, r_2) \approx \varphi(r_1)\varphi(r_2) \tag{7.1.23}$$

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).

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{7.1.24}$$

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 7.1.22) is evaluated for helium, the result is a variational energy that depends on the adjustable parameter, ζ.

$$E_{trial}(\zeta) = \frac{\mu e^4}{4\epsilon_0^2 h}\left(\zeta^2 - \frac{27}{8}\zeta\right) \tag{7.1.25}$$

This function is plotted in Figure 7.1.3 as a function of ζ. According to the variational principle (Equation 7.1.20), 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.

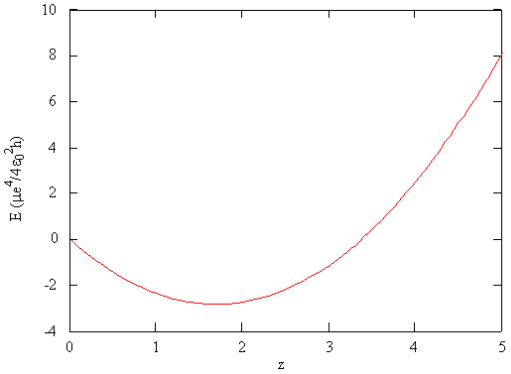


Figure 7.1.3: Graph of trial energies for helium atom as a function of the adjustable parameter ζ in Equation 7.1.25 that represents the effective nuclear charge felt by the electrons.

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 7.1.23 with the Hamiltonian in Equation 7.1.24. 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 7.1.24.
- Step 2: Define the trial wavefunction as a function of at least one parameter - This is given by Equation 7.1.23.
- Step 3: Evaluate variational energy (E_{trial} integral (Equation 7.1.22) - This procedure was already above in Equation 7.1.25.
- 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.

Contributors

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

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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

$$|\psi_{trial}\rangle = \sum_{j=1}^{N} a_j \Big| \phi_j \rangle \tag{7.2.1}$$

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

$$E_{trial} = \frac{\langle \psi_{trial} \Big| \hat{H} \Big| \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{7.2.3}$$

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

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \tag{7.2.6}$$

So the numerator of the right side of Equation 7.2.3 becomes

$$\langle \psi_{trial} | H | \psi_{trial} \rangle = \sum_{i,j}^{N,N} a_i^* a_j H_{ij} \tag{7.2.7}$$

Similarly, the denominator of the right side of Equation 7.2.3 can be expanded

$$\langle \psi_{trial} | \psi_{trial} \rangle = \sum_{i,j}^{N,N} a_i^* a_j \langle \phi_i | \phi_j \rangle \tag{7.2.8}$$

We often simplify the integrals on the right side of Equation 7.2.8 as

$$S_{ij} = \langle \phi_i | \phi_j \rangle \tag{7.2.9}$$

where S_{ij} are **overlap integrals** between the different $\{\phi_j\}$ basis functions. Equation 7.2.8 is thus expressed as

$$\langle \psi_{trial} | \psi_{trial} \rangle = \sum_{i,j}^{N,N} a_i^* a_j S_{ij} \tag{7.2.10}$$

Orthonormality

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 7.2.7 and 7.2.10 into the variational energy formula (Equation 7.2.3) results in

$$E_{trial} = \frac{\sum_{i,j}^{N,N} a_i^* a_j H_{ij}}{\sum_{i,j}^{N,N} a_i^* a_j S_{ij}} \tag{7.2.11}$$

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 7.2.11) can be rearranged

$$E_{trial} \sum_{i,j}^{N,N} a_i^* a_j S_{ij} = \sum_{i,j}^{N,N} a_i^* a_j H_{ij} \tag{7.2.12}$$

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).

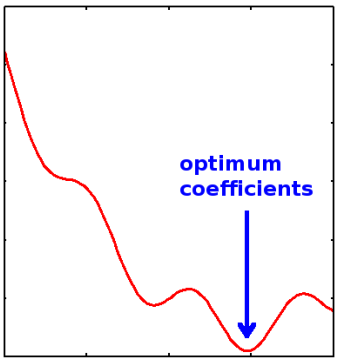


Figure 7.2.1: Linear Variational Principle in action. Two (or more) wavefunctions are mixed by linear combination. The coefficients a_1, a_2 determine the weight each of them is given. The optimum coefficients are found by searching for minima in the potential landscape spanned by a_1 and a_2. (CC BY-SA-NC; Rudolf Winter; Aberystwyth University).

We want to minimize the energy with respect to the linear coefficients $\{a_i\}$, which requires that

$$\frac{\partial E_{trial}}{\partial a_i} = 0 \tag{7.2.13}$$

for all i.

Differentiating both sides of Equation 7.2.12 for the kth coefficient gives,

$$\frac{\partial E_{trial}}{\partial a_k} \sum_{i,j}^{N,N} a_i^* a_j S_{ij} + E_{trial} \sum_i \sum_j \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^* \right] S_{ij} \tag{7.2.14}$$
$$= \sum_{i,j}^{N,N} \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^* \right] H_{ij}$$

Since the coefficients are independent

$$\frac{\partial a_i^*}{\partial a_k} = \delta_{ik} \tag{7.2.15}$$

and

$$S_{ij} = S_{ji} \tag{7.2.16}$$

and also since the Hamiltonian is a Hermitian Operator (see below)

$$H_{ij} = H_{ji} \tag{7.2.17}$$

then Equation 7.2.14 simplifies to

$$\frac{\partial E_{trial}}{\partial a_k} \sum_i \sum_j a_i^* a_j S_{ij} + 2E_{trial} \sum_i a_i S_{ik} = 2 \sum_i a_i H_{ik} \tag{7.2.18}$$

At the minimum variational energy, when

$$\frac{\partial E_{trial}}{\partial a_k} = 0 \tag{7.2.19}$$

then Equation 7.2.18 gives

$$\sum_i^N a_i (H_{ik} - E_{trial} S_{ik}) = 0 \tag{7.2.20}$$

for all k. The equations in 7.2.20 are call the **Secular Equations**.

Hermitian Operators

Hermitian operators are operators that satisfy the general formula

$$\langle \phi_i \left| \hat{A} \right| \phi_j \rangle = \langle \phi_j \left| \hat{A} \right| \phi_i \rangle \tag{7.2.21}$$

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 and a Hermitian operator. Equation 7.2.21 can be rewriten as

$$A_{ij} = A^*_{ji} \tag{7.2.22}$$

where

$$A_{ij} = \langle \phi_i \left| \hat{A} \right| \phi_j \rangle \tag{7.2.23}$$

and

$$A_{ji} = \langle \phi_j \left| \hat{A} \right| \phi_i \rangle \tag{7.2.24}$$

Therefore, when applied to the Hamiltonian operator

$$H^*_{ij} = H_{ji}. \tag{7.2.25}$$

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 7.2.20 reduces to the more familiar Eigenvalue form:

$$\sum_i^N H_{ij} a_j = E_{trial} a_i. \tag{7.2.26}$$

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*'.

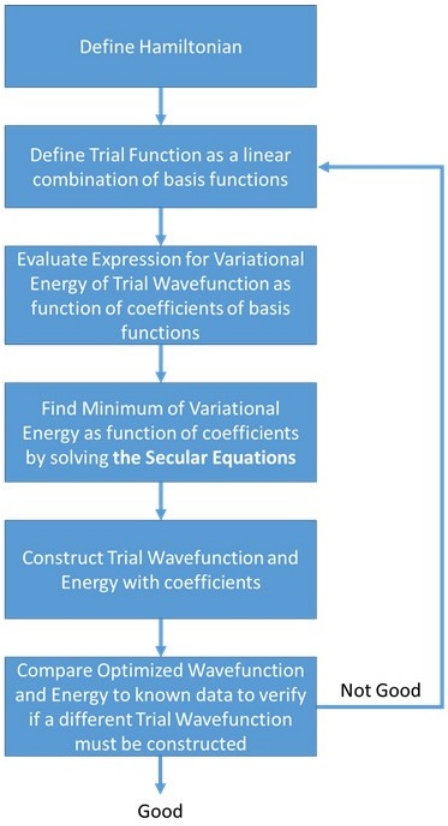


Figure 7.2.2: Simplified algorithmic flowchart of the linear Variational Method approximation. Compared to the similar algorithmic flowchart for the "normal" Variational Method approximation.

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 7.2.26), 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.

$$|H_{ik} - ES_{ik}| = 0 \tag{7.2.27}$$

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

$$|A| = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc. \tag{7.2.28}$$

Similarly, suppose we have a 3×3 matrix A, and we want the specific formula for its determinant $|A|$:

$$\begin{aligned} |A| = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} &= a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \begin{vmatrix} d & e \\ g & h \end{vmatrix} \\ &= aei + bfg + cdh - ceg - bdi - afh. \end{aligned} \tag{7.2.29}$$

To solve Equation 7.2.27, 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,

$$|\psi_{trial}\rangle = \sum_{n=1}^{N=2} a_n \Big| f_n \rangle = a_1 \, |\phi_1\rangle + a_2 | \, \phi_2 \rangle$$

then the secular determinant (Equation 7.2.27), 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

$$a_1^2 H_{11} + 2 a_1 a_2 H_{12} + a_2^2 H_{22} = 0$$

and

$$a_1 (H_{12} - E_{trial} S_{12}) + a_2 (H_{22} - E_{trial} S_{22}) = 0$$

Equation 7.2.27 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

$$|\psi(r)\rangle = \sum_i a_i \Big| \phi_i(r) \rangle$$

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 of the atomic orbitals. Gaussian orbitals form the basis of many quantum chemistry computer codes.

Dec 23, 2018, 11:08 PM

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.

Contributors

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7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters

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 weighting 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

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.

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.

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

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7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

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.

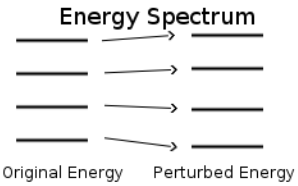


Figure 7.4.1: Perturbed Energy Spectrum. (CC BY-SA 2.0, Frontier).

We begin with a Hamiltonian $\hat{H}^0$ having known eigenkets 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:

$$(\hat{H}^o + \lambda \hat{H}^1)\,(|n^o\rangle + \lambda |n^1\rangle) = (E_n^0 + \lambda E_n^1)\,(|n^o\rangle + \lambda |n^1\rangle) \tag{7.4.11}$$

$$\begin{aligned} \hat{H}^o |n^o\rangle + \lambda \hat{H}^1 |n^o\rangle + \lambda H^o |n^1\rangle + \lambda^2 \hat{H}^1 |n^1\rangle = {} & E_n^0 |n^o\rangle + \lambda E_n^1 |n^o\rangle \\ & + \lambda E_n^0 |n^1\rangle + \lambda^2 E_n^1 |n^1\rangle \end{aligned} \tag{7.4.12}$$

Collecting terms in order of λ and coloring to indicate different orders

$$\begin{aligned} & \underset{\text{zero order}}{\hat{H}^o |n^o\rangle} \\ & + \underset{\text{1st order}}{\lambda(\hat{H}^1 |n^o\rangle + \hat{H}^o |n^1\rangle)} + \underset{\text{2nd order}}{\lambda^2 \hat{H}^1 |n^1\rangle} = \underset{\text{zero order}}{E_n^0 |n^o\rangle} + \underset{\text{1st order}}{\lambda(E_n^1 |n^o\rangle + E_n^0 |n^1\rangle)} + \underset{\text{2nd order}}{\lambda^2 E_n^1 |n^1\rangle} \end{aligned} \tag{7.4.13}$$

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 7.4.10) 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

$$\cancel{E_n^o \langle n^o | n^1 \rangle} + \langle n^o \left| H^1 \right| n^o \rangle = \cancel{E_n^o \langle n^o | n^1 \rangle} + E_n^1 \cancel{\langle n^o | n^{o*1} \rangle} \tag{7.4.19}$$

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

$$E_n^1 = \langle n^o \left| \hat{H}^1 \right| n^o \rangle \tag{7.4.20}$$

> *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

$$E_n \approx E_n^o + E_n^1 \tag{7.4.21}$$

$$\approx \underbrace{E_n^o + \langle n^o | H^1 | n^o \rangle}_{\text{First Order Perturbation}} \tag{7.4.22}$$

Example 7.4.1A: 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

$$E_n^1 = \langle n^o \left| H^1 \right| n^o \rangle$$

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

$$E_n^1 = \langle n^o \left| H^1 \right| n^o \rangle = \langle n^o \left| V_o \right| n^o \rangle = V_o \langle n^o | n^o \rangle = V_o$$

so via Equation 7.4.22, the energy of each perturbed eigenstate is

$$E_n \approx E_n^o + E_n^1$$

$$\approx \frac{h^2}{8mL^2} n^2 + V_o$$

While this is the first order perturbation to the energy, it is also the exact value.

Example 7.4.1B: 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

$$\begin{aligned} E_n^1 &= \frac{2V_o}{L} \left[\frac{-1}{2\frac{\pi n}{a}} \cos\left(\frac{n\pi}{L}x\right) \sin\left(\frac{n\pi}{L}x\right) + \frac{x}{2} \right]_0^{L/2} \\ &= \frac{2V_o}{\cancel{L}} \frac{\cancel{L}}{4} = \frac{V_o}{2} \end{aligned}$$

The energy of each perturbed eigenstate, via Equation 7.4.22, is

$$\begin{aligned} E_n &\approx E_n^o + \frac{V_o}{2} \\ &\approx \frac{h^2}{8mL^2} n^2 + \frac{V_o}{2} \end{aligned}$$

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:

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.31}$$

$$\approx \left| n^o \right\rangle + \sum_{m \neq n} c_{m,n} \left| m^o \right\rangle \tag{7.4.32}$$

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.

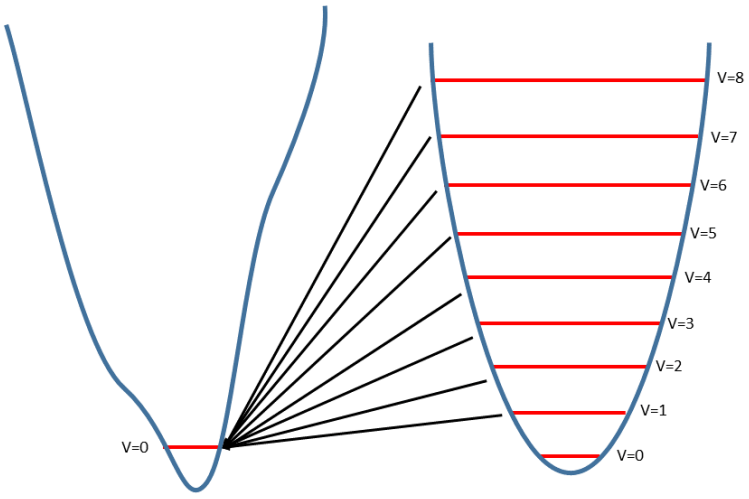


Figure 7.4.2: The first order perturbation of the ground-state wavefunction for a perturbed (left potential) can be expressed as a linear combination of all excited-state wavefunctions of the unperturbed potential (Equation 7.4.32), shown as a harmonic oscillator in this example (right potential). Note that the ground-state harmonic oscillator wavefuncion is not part of this expression and technically all wavefunctions need to be included in the expression, not just the first eight wavefunctions shown here. (CC BY; 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).

Nov 13, 2016, 11:28 PM

http://fizika.unios.hr/~ilukacevic/d...ion_theory.pdf

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 $n = 0$:

$$|0^1\rangle = \frac{\langle 1^o | H^1 | 0^o\rangle}{E_0^o - E_1^o} \Big| 1^o\rangle + \frac{\langle 2^o | H^1 | 0^o\rangle}{E_0^o - E_2^o} \Big| 2^o\rangle + \frac{\langle 3^o | H^1 | 0^o\rangle}{E_0^o - E_3^o} \Big| 3^o\rangle + \frac{\langle 4^o | H^1 | 0^o\rangle}{E_0^o - E_4^o} \Big| 4^o\rangle + \frac{\langle 5^o | H^1 | 0^o\rangle}{E_0^o - E_5^o} \Big| 5^o\rangle$$

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

$$|0^1\rangle = \frac{\langle 1^o | H^1 | 0^o\rangle}{E_0^o - E_1^o} \Big| 1^o\rangle + \frac{\langle 3^o | H^1 | 0^o\rangle}{E_0^o - E_3^o} \Big| 3^o\rangle + \frac{\langle 5^o | H^1 | 0^o\rangle}{E_0^o - E_5^o} \Big| 5^o\rangle$$

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

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

$$\int_0^{\infty} x^{2\pi} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \ldots (2n-1)}{2^{m+1} a^n} \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

Where we plug in $\mathbf{n = 2}$ and $\mathbf{a = \alpha}$ for our integral

$$E^1 = 2\gamma \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} \int_0^{\infty} x^4 e^{-ax^2} dx$$
$$E^1 = 2\gamma \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} \frac{1 \cdot 3}{2^3 a^2} \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

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,

$$E_r^0 = \left(v + \frac{1}{2}\right) hv$$

Where in the ground state $v = 0$ so the energy for the ground state of the quantum harmonic oscillator is

$$E_r^0 = \frac{1}{2} hv$$

Putting both of our energy terms together gives us the ground state energy of the wavefunction of the given Hamiltonian,

$$E = E^0 + E^1$$
$$E = \tfrac{1}{2} hv + \gamma \tfrac{3}{4a^2}$$

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.

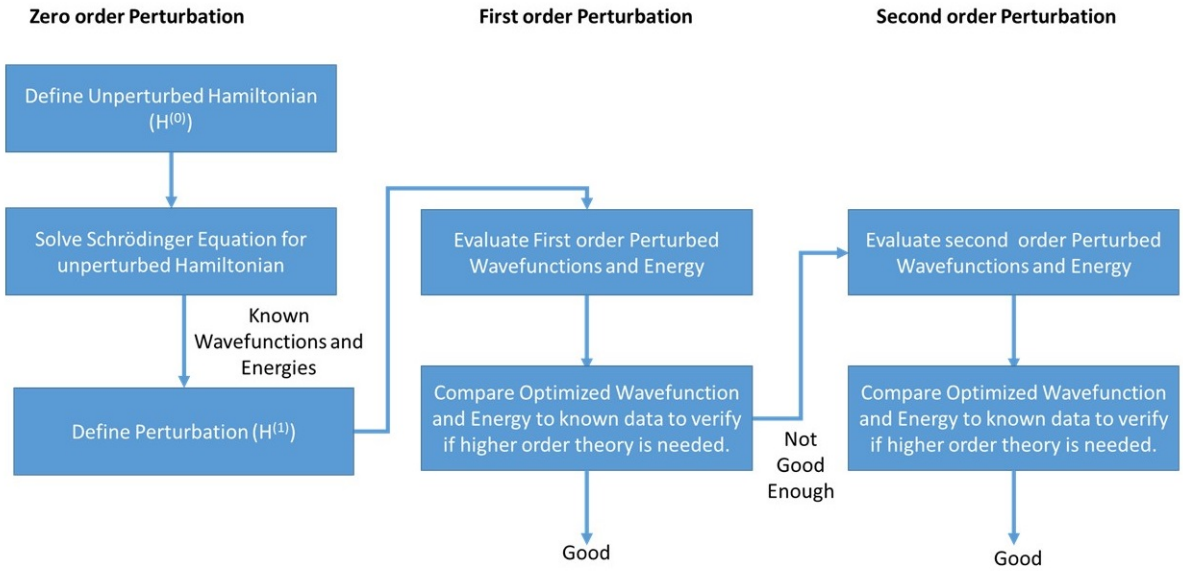


Figure 7.4.1: Simplified algorithmic flowchart of the Perturbation Theory approximation showing the first two perturbation orders. The process can be continued to third and higher orders. (CC BY; Delmar Larsen)

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.

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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_ϕ 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:

$$\int_{-\infty}^{-\infty} \frac{1}{(1+\betax^2)^2[\hbar^2/\mu * 2\beta/(1+\betax^2)^3 - \hbar^2/\mu * 12\beta^2x^2/(1+\betax^2)^4 + \frac{kx^2}{2}(1+\betax^2)^2]}$$

$$= 2\beta\hbar^2/\mu * (7*5*3*1*\pi/8*6*4*2*\beta 1/2) - 12\beta^2\hbar^2/\mu * (7*5*3*1*\pi/10*8*6*4*2*\beta 1/2) + k/2 * (3*1*\pi/6*4*2*\beta^{3/2})$$

$$= \frac{7\pi\beta^{1/2}\hbar}{32\mu + k\pi/32\beta^{3/2}}$$

Now solving the denominator:

$$\int_{\infty}^{\infty} \phi^*\phi\, dx = \int_{\infty}^{\infty} \frac{1}{(1+\beta x^2)^4} = \frac{5*3*1*\pi}{6*4*2*\beta^{1/2}} = /16\beta^{1/2}$$

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:

$$E_{trial}(a) = \frac{\langle \phi(a) \left| \hat{H} \right| \phi(a) \rangle}{\langle \phi(a) | \phi(a) \rangle} \geq E_{true}$$

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

$$\langle \phi \left| \hat{H} \right| \phi \rangle = \int_{-\infty}^{\infty} e^{-ax^2} \left[\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right] e^{-ax^2} dx$$

denominator:

$$\langle \phi | \phi \rangle = \int_{-\infty}^{\infty} e^{-ax^2} e^{-ax^2} dx$$

7.9

Use the trial function

$$|\exp^{\frac{-ax^2}{2}}\rangle$$

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 $s = \frac{l}{a}$ 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 $\langle\phi_n^*\left|\hat{H}\right|\phi_n\rangle$
4. Now that you solved for steps 2 and 3, plug into the equation

$$E_n = \frac{\langle\phi_n^*\left|\hat{H}\right|\phi_n\rangle}{\langle\phi_n^*|\phi_n\rangle}$$

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.

$$E_\phi = \frac{\langle\phi\left|\hat{H}\right|\phi\rangle}{\langle\phi|\phi\rangle} \geq E_o$$

$$\langle\phi|\phi\rangle = 1 = \int_0^L N^2\cos^2\left(\frac{\pi x}{L}\right)$$

Performing this integral and solving for N yields

$$N = \sqrt{\frac{2}{L}}$$

The Hamiltonian for a particle in a one dimensional box is $\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$

$$\begin{aligned}\langle\phi\left|\hat{H}\right|\phi\rangle &= \langle N\cos\left(\frac{\pi x}{L}\right)\left|\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\right|N\cos\left(\frac{\pi x}{L}\right)\rangle \\ &= \int_0^L N\cos\left(\frac{\pi x}{L}\right)\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}N\cos\left(\frac{\pi x}{L}\right)dx \\ &= \frac{N^2\pi^2\hbar^2}{2mL^2}\int_0^L\cos^2\left(\frac{\pi x}{L}\right)dx\end{aligned}$$

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

$$\psi = \phi_A(1) \begin{vmatrix} \phi_B(2) & \phi_B(3) \\ \phi_C(2) & \phi_C(3) \end{vmatrix} - \phi_A(2) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(1) & \phi_B(2) \\ \phi_C(1) & \phi_C(2) \end{vmatrix}$$

$$= \phi_A(1)\left(\phi_B(2)\phi_C(3) - \phi_C(2)\phi_B(3)\right) - \phi_A(2)\left(\phi_B(1)\phi_C(3) - \phi_C(1)\phi_B(3)\right) + \phi_A(3)\left(\phi_B(1)\phi_C(2) - \phi_C(1)\phi_B(2)\right)$$

$$\psi = \phi_A(1)\phi_B(2)\phi_C(3) - \phi_A(1)\phi_C(2)\phi_B(3) - \phi_A(2)\phi_B(1)\phi_C(3) + \phi_A(2)\phi_C(1)\phi_B(3) + \phi_A(3)\phi_B(1)\phi_C(2) - \phi_A(3)\phi_C(1)\phi_B(2)$$

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

$$\phi_{(a)} = \phi_A(2) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} - \phi_A(1) \begin{vmatrix} \phi_B(2) & \phi_B(3) \\ \phi_C(2) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(2) & \phi_B(1) \\ \phi_C(2) & \phi_C(1) \end{vmatrix}$$

$$\phi_{(a)} = \phi_A(2)\phi_B(1)\phi_C(3) - \phi_A(2)\phi_C(1)\phi_B(3) - \phi_A(1)\phi_B(2)\phi_C(3) + \phi_A(1)\phi_C(2)\phi_B(3) + \phi_A(3)\phi_B(2)\phi_C(1) - \phi_A(3)\phi_C(2)\phi_B(1)$$

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

$$\phi_{(b)} = \phi_A(1) \begin{vmatrix} \phi_C(2) & \phi_C(3) \\ \phi_B(2) & \phi_B(3) \end{vmatrix} - \phi_A(2) \begin{vmatrix} \phi_C(1) & \phi_C(3) \\ \phi_B(1) & \phi_B(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_C(1) & \phi_C(2) \\ \phi_B(1) & \phi_B(2) \end{vmatrix}$$

$$\phi_{(b)} = \phi_A(1)\phi_C(2)\phi_B(3) - \phi_A(1)\phi_B(2)\phi_C(3) - \phi_A(2)\phi_C(1)\phi_B(3) + \phi_A(2)\phi_B(1)\phi_C(3) + \phi_A(3)\phi_C(1)\phi_B(2) - \phi_A(3)\phi_B(1)\phi_C(2)$$

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

$$V(x) = -\frac{e^2}{4\pi\epsilon_o r} + (1/2)\epsilon r\cos\theta$$

\[\hat{H} = - ħ ^2/2μ ∂2 /∂x2 ∇^2 -e^2/(4πϵ_o r) + (1/2)ϵrcosθ\nonumber \]

\[\hat{H}^{(0)} = - ħ ^2/2μ ∂2 /∂x2 ∇^2 -e^2/(4πϵ_o r)\nonumber \]

\[\hat{H}^{(1)} =(1/2)ϵrcosθ\nonumber \]

$\Psi^{(0)} = \Psi_{n,l,m}(r,\theta,\phi)$

$E^{(0)} = \mu e^4 / 8\epsilon_o^2 h^2 n^2$

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

$$\psi_1 = \sqrt{\frac{2}{b}}\sin(\frac{\pi x}{b})$$

$$\widehat{H} = \widehat{H}^0 + \widehat{H}^1$$

$$\widehat{H}^1 = ax^3$$

$$E_1 = E_1^0 + E_1^1$$

$$E_1^0 = \frac{h^2}{8mb^2}$$

$$E_1^1 = \langle \psi^1 \left| \widehat{H}^1 \right| \psi^1 \rangle$$

$$= \int_0^b \frac{2a}{b}x^3 \sin^2(\frac{\pi x}{b})dx$$

$$= \frac{2a}{b}\frac{(\pi^2 - 3)b^4}{8\pi^2}$$

$$= \frac{(\pi^2 - 3)ab^3}{4\pi^2}$$

$$E_1 = \frac{h^2}{8mb^2} + \frac{(\pi^2 - 3)ab^3}{4\pi^2}$$

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 $E^0_0 = hv/2$ and $\Psi^0_0 = (\alpha/\pi)^{1/4}e^{-\alpha(x^2)/2}$

$E^0_1 = 3hv/2$ and $\Psi^0_1 = (4\alpha^3/\pi)^{1/4}xe^{-\alpha(x^2)/2}$

$E^0_2 = 5\ hv/2$ 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:

$E_0 = hv/2 + \int (\alpha/\pi)^{1/4}e^{-\alpha(x^2)/2}(bx^3 + cx^4)(\alpha/\pi)^{1/4}e^{-\alpha(x^2)/2}dx$

$= hv/2 + (\alpha/\pi)^{1/2} \int e^{-\alpha(x^2)}(bx^3 + cx^4)dx$

$= hv/2 + (\alpha/\pi)^{1/2} [\int e^{-\alpha(x^2)}bx^3dx + \int e^{-\alpha(x^2)}cx^4dx]$ (The cubic integral is odd so evaluates to 0)

$= hv/2 + (\alpha/\pi)^{1/2} \int e^{-\alpha(x^2)}cx^4dx$

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)

$= hv/2 + 2 * c(\alpha/\pi)^{1/2} * 3/(2^3\alpha^2) * (\pi/\alpha)^{1/2}$

$= hv/2 + 3c/(4\alpha^2)$

$E_1 = 3h\nu/2 + \int (4\alpha^3/\pi)^{1/4} x e^{-\alpha(x^2)/2} (\, bx^3 + cx^4)(4\alpha^3/\pi)^{1/4} x e^{-\alpha(x^2)/2} dx$

$= 3h\nu/2 + (4\alpha^3/\pi)^{1/2} \int x^2 e^{-\alpha(x^2)} (\, bx^3 + cx^4) dx$

$= 3h\nu/2 + (4\alpha^3/\pi)^{1/2} [\int x^2 e^{-\alpha(x^2)}\, bx^3 dx + \int x^2 e^{-\alpha(x^2)}\, cx^4 dx\ ]$ (First integral evaulates to 0)

$= 3h\nu/2 + c(4\alpha^3/\pi)^{1/2} \int x^6 e^{-\alpha(x^2)}\, dx$

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)

$= 3h\nu/2 + 2^* c(4\alpha^3/\pi)^{1/2} {}^* 15/(2^4\alpha^3) * (\pi/\alpha)^{1/2}$

$= 3h\nu/2 + 15c/(4\alpha^2)$

$E_{2o} = 5h\nu/2 + \int (\alpha/4\pi)^{1/4} (2\alpha x^2 - 1) e^{-\alpha(x^2)/2} (\, bx^3 + cx^4)\, (\alpha/4\pi)^{1/4} (2\alpha x^2 - 1) e^{-\alpha(x^2)/2} dx$

$= 5h\nu/2 + (\alpha/4\pi)^{1/2} \int (\, bx^3 + cx^4)(2\alpha x^2 - 1)^2 e^{-\alpha(x^2)} dx$

$= 5h\nu/2 + (\alpha/4\pi)^{1/2} [\int bx^3 (2\alpha x^2 - 1)^2 e^{-\alpha(x^2)} dx + \int cx^4 e^{-\alpha(x^2)} (2\alpha x^2 - 1)^2 dx$

$= 5h\nu/2 + (\alpha/4\pi)^{1/2} \int cx^4 e^{-\alpha(x^2)} (2\alpha x^2 - 1)^2 dx$ (First integral evaluates to 0)

$= 5h\nu/2 + (\alpha/4\pi)^{1/2} \int 4c\alpha^2 x^8 e^{-\alpha(x^2)} - 4\alpha c x^6 e^{-\alpha(x^2)} + cx^4 e^{-\alpha(x^2)} dx$

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)

$= 5h\nu/2 + (\alpha/4\pi)^{1/2} [4c\alpha^2 {}^* 2^* (105/(32\alpha^4))^* (\pi/\alpha)^{1/2} - \alpha c^* 2^* 15/(2^4\alpha^3) * (\pi/\alpha)^{1/2} + c^* 2^* 3/(2^3\alpha^2) * (\pi/\alpha)^{1/2}]$

$= 5h\nu/2 + 39c/4\alpha^2$

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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CHAPTER OVERVIEW

8: Multielectron Atoms

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

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

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 x 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 unites 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			$\hbar/E_h$	2.418×10^{-17} s	
velocity			$a_0 E_h/\hbar = \alpha c$	2.187×10^{6} m·s^{-1}	

Contributors

- Wikipedia

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8.2: Perturbation Theory and the Variational Method for Helium

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

$$\begin{aligned} E^1 &= \langle \psi^0 \left| \hat{H}^1 \right| \psi^0 \rangle \\ &= \int \psi^{0*} \hat{H}^1 \psi^0 \, d\tau \end{aligned}$$

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).

$$|\psi^0\rangle = |\varphi_{1s}(r_1)\varphi_{1s}(r_2)\rangle \tag{8.2.4}$$

So the integral in Equation ??? is

$$E^1 = \iint \varphi_{1s}(r_1)\varphi_{1s}(r_2)\frac{1}{r_{12}}\varphi_{1s}(r_1)\varphi_{1s}(r_2)\, d\tau_1 d\tau_2 \tag{8.2.5}$$

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

$$E_{approx2} = E^0 + E^1 = -74.8eV \tag{8.2.6}$$

The new approximate value for the binding energy represents a substantial (~30%) improvement over the zero-order energy:

$$E^0 = \frac{2}{n^2} + \frac{2}{n^2} = 4 \underbrace{E_h}_{hartrees} = 108.8\, eV \tag{8.2.7}$$

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,

$$E^0 + E^1 + E^2 = -79.2\, eV. \tag{8.2.8}$$

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.

$$E_{trial} = \frac{\langle \psi_{trial} \left| \hat{H} \right| \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{8.2.9}$$

$$= \frac{\int_0^\infty \psi_{trial}^* \hat{H} \psi_{trial} d\tau}{\int_0^\infty \psi_{trial}^2 \, d\tau} \tag{8.2.10}$$

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 8.2.9, 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.

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{8.2.11}$$

$$= \exp\left[-\alpha(r_1 + r_2)\right] \tag{8.2.12}$$

The variational energy obtained after minimizing Equation 8.2.10 after substituting the trial wavefunction (Equation 8.2.12) by varying α is

$$E_{trial} = -2.84766\ E_h \tag{8.2.13}$$

and the experimentally determined ground-state energy for the helium atom is the sum of first and second ionization energies

$$E_{exp} = I_1 + I_2 = -2.90372\ E_h \tag{8.2.14}$$

The deviation of energy for the optimized trial wavefunction from the experimental value is

$$\left|\frac{E_{trial}(\alpha) - E_{exp}}{E_{exp}}\right| = \left|\frac{-2.84766\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.15}$$

$$= 1.93\% \tag{8.2.16}$$

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.

$$\phi(r_1) = \exp(-\alpha r_1) + \exp(-\beta r_1) \tag{8.2.17}$$

Under the orbital approximation this assumption gives a trial wavefunction of the form

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{8.2.18}$$

$$\begin{aligned} &= \exp(-\alpha r_1)\exp(-\alpha r_2) + \exp(-\alpha r_1)\exp(-\beta r_2) \\ &\quad + \exp(-\beta r_1)\exp(-\alpha r_2) + \exp(-\beta r_1)\exp(-\beta r_2) \end{aligned} \tag{8.2.19}$$

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 8.2.10). 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 8.2.10 after substituting the trial wavefunction (Equation 8.2.19) by varying α and β is

$$E_{trial} = -2.86035\ E_h \tag{8.2.20}$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.14) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{exp}}{E_{exp}}\right| = \left|\frac{-2.86035\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.21}$$

$$= 1.49\% \tag{8.2.22}$$

Clearly introducing some electron-electron interactions into the trial wavefunction has improved the agreement between theory and experiment (Equation 8.2.16 vs. 8.2.22).

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 8.2.19). This yields a multi-electron wavefunction of the form,

$$|\psi(1,2)\rangle_{trial} = \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) \tag{8.2.23}$$

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 8.2.10 after substituting the trial wavefunction (Equation 8.2.23) by varying α and β is

$$E_{trial} = -2.87566\ E_h \tag{8.2.24}$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.14) is

$$\left|\frac{E_{trial}(\alpha,\beta)-E_{\exp}}{E_{\exp}}\right| = \left|\frac{-2.87566\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.25}$$

$$= 0.97\% \tag{8.2.26}$$

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.

$$|\psi_{trial}(1,2)\rangle = (\exp[-\alpha(r_1+r_2)])\,(1+\beta r_{12}) \tag{8.2.27}$$

In the trial multi-electron wavefunction of Equation 8.2.27, if the electrons are far apart, then r_{12} is large and the magnitude of the wave function increases to favor that configuration. The variational energy obtained after minimizing Equation 8.2.10 after substituting the trial wavefunction (Equation 8.2.27) by varying α and β is

$$E_{trial} = -2.89112\ E_h \tag{8.2.28}$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.14) is

$$\left|\frac{E_{trial}(\alpha,\beta)-E_{\exp}}{E_{\exp}}\right| = \left|\frac{-2.89112\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.29}$$

$$= 0.43\% \tag{8.2.30}$$

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 wave function (Equation 8.2.23) as shown here.

$$|\psi(1,2)\rangle_{trial} = [\exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2)]\,[1+\gamma r_{12}] \tag{8.2.31}$$

Chandrasakar's three parameter wavefunction gives rise to a fairly complicated variational expression for ground-state energy. The variational energy obtained after minimizing Equation 8.2.10 after substituting the trial wavefunction (Equation 8.2.31) by varying α, β and γ is

$$E_{trial} = -2.90143\ E_h \tag{8.2.32}$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.14) is

$$\left|\frac{E_{trial}(\alpha,\beta,\gamma)-E_{\exp}}{E_{\exp}}\right| = \left|\frac{-2.90143 + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.33}$$

$$= 0.0789\% \tag{8.2.34}$$

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 Module 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 wave function. 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.

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method

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 wavefucntions. 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 a good approximation.

The Unsolvable System

The generic multielectron atom including 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)

$$V_{\text{electron-electron}}(r_{12}) = \frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{8.3.2}$$

with $|\mathbf{r}-\mathbf{r}'|$ is the distance between electron 1 and electron 2. So the proper multi-electron Hamiltonian can be constructed

$$\hat{H}(r_1, r_2, ...r_n) = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V_{\text{nuclear-electron}}(r_i) + \sum_{i\neq j} V_{\text{electron-electron}}(r_{ij}) \tag{8.3.3}$$

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 8.3.3) 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:

$$|\psi(r_1, r_2, \cdots r_i)\rangle \tag{8.3.4}$$

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 8.3.4 can be expanded as a product of single-electron wavefunctions (i.e., orbitals)

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)\rangle \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_N(\mathbf{r}_N) \tag{8.3.5}$$

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \tag{8.3.6}$$

or

$$H_e(r)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \tag{8.3.7}$$

where $V(r)$ is the potential in which the electron moves; this includes both the nuclear-electron interaction

$$V_{nucleus}(\mathbf{r}) = -Ze^2\sum_R \frac{1}{|\mathbf{r}-\mathbf{R}|} \tag{8.3.8}$$

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

$$V_{electron}(\mathbf{r}) = -e\int d\mathbf{r}'\rho(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{8.3.9}$$

where

$$\rho(\mathbf{r}) = \sum_i^{\text{occupied}} |\psi(\mathbf{r})|^2. \tag{8.3.10}$$

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

- **Kinetic Energy:** The Kinetic energy of the electron has an average value is computed by taking the expectation value of the kinetic energy operator

  $$\frac{-\hbar^2}{2m}\nabla^2 \tag{8.3.11}$$

  with respect to any particular solution $\phi_j(r)$ to the Schrödinger equation:

  $$KE = \langle\phi_j\left|\frac{-\hbar^2}{2m}\nabla^2\right|\phi_j\rangle \tag{8.3.12}$$

- **Nuclear-Electron Coulombic Attraction Energy:** Coulombic attraction energy with the nucleus of charge Z:

  $$\langle\phi_j\left|\frac{-Ze^2}{|\mathbf{r}-\mathbf{R}|}\right|\phi_j\rangle \tag{8.3.13}$$

- **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

  $$\sum_{j\neq k}\langle\phi_j(r)\phi_k(r')\left|\frac{e^2}{|r-r'|}\right|\phi_j(r)\phi_k(r')\rangle. \tag{8.3.14}$$

  The Dirac notation $\langle\phi_j(r)\phi_k(r')\left|\frac{e^2}{|r-r'|}\right|\phi_j(r)\phi_k(r')\rangle$ is used to represent the two-electron (six-dimensional) Coulomb integral

  $$J_{j,k} = \int |\phi_j(r)|^2|\phi_k(r')|^2\frac{e^2}{r-r'}drdr' \tag{8.3.15}$$

  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.

The total energy ϵ_j of the orbital ϕ_j, is the sum of the above three contributions:

$$\epsilon_J = \langle \phi_j \left| \frac{-\hbar^2}{2m} \nabla^2 \right| \phi_j \rangle + \langle \phi_j \left| \frac{-Ze^2}{|\mathbf{r} - \mathbf{R}|} \right| \phi_j \rangle + \sum_{j \neq k} \langle \phi_j(r) \phi_k(r') \left| \frac{e^2}{|r - r'|} \right| \phi_j(r) \phi_k(r') \rangle. \tag{8.3.16}$$

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.

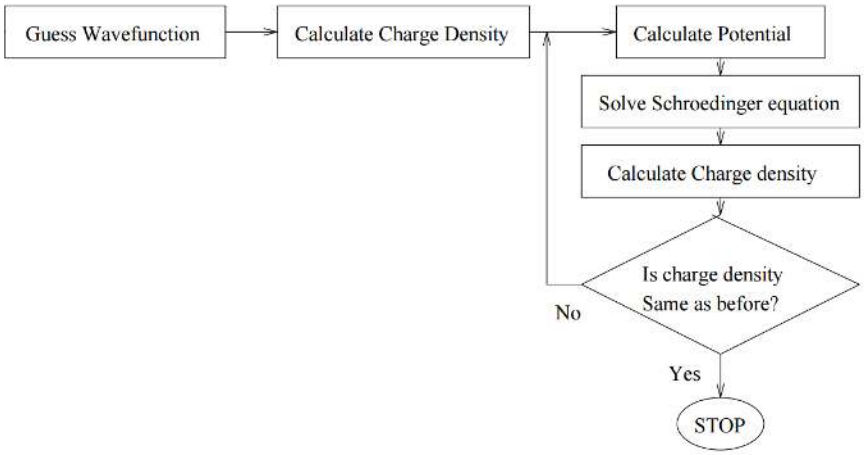


Figure 8.3.1: Algorithm for Self-consistent field theory.

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 from the HF method are Good, but not Good Enough

For an atom, one can approximate the orbitals by using the solutions of the hydrogenic Schrödinger equation. These orbitals are labeled by n, l, and m quantum numbers for the bound states and by l and m quantum numbers and the energy E for the continuum states. These 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

$$|\psi(1, 2, \ldots, 6)\rangle = |\psi_{1s}(1)\psi_{1s}(2)\psi_{2s}(3) \ldots \psi_{1p}(6)\rangle. \tag{8.3.17}$$

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).

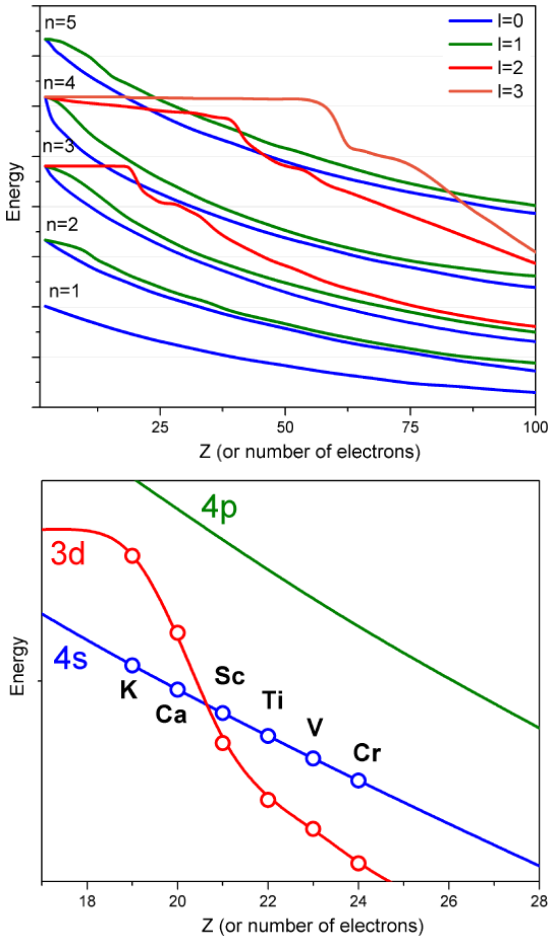


Figure 8.3.2: Energies of Atomic Orbitals as Functions of the number of electrons in Neutral Atoms. (CC BY; Delmar Larsen).

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.

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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8.4: An Electron Has an Intrinsic Spin Angular Momentum

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).

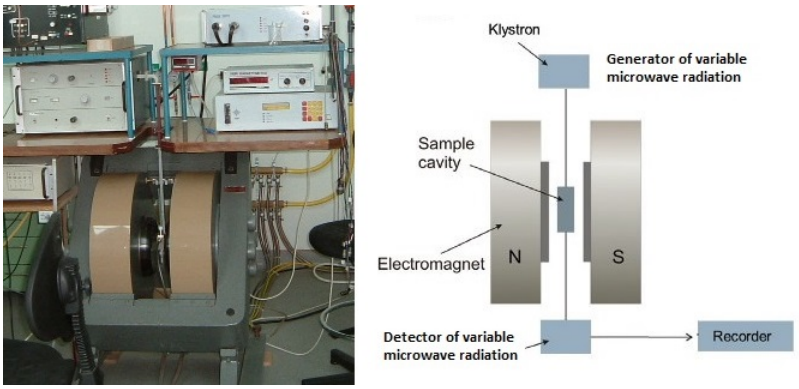


Figure 8.4.1: Schematic diagram of a microwave spectrometer transmission Electron Spin Resonance (ESR) spectrometer with the sample in a magnetic field. (left) ESR spectrometer Faculty of Biochemistry, Biophysics and Biotechnology Jagiellonian University. (right) Schematic of the ESR instrument. The 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 3.0)

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 Degeneracy

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 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).

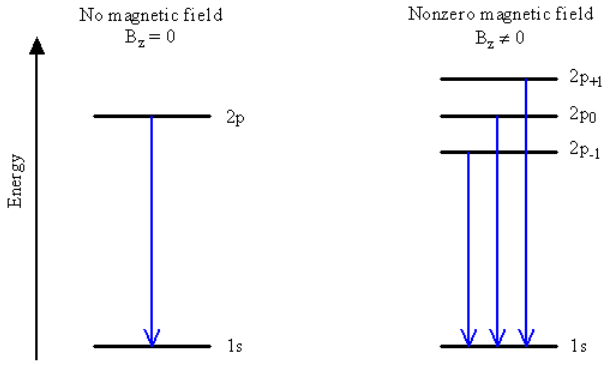


Figure 8.4.2: The Zeeman effect for the $2s \rightarrow 1s$ transition. Emission when an electron switches from a 2p orbital to a 1s orbital occurs at only one energy in the absence of a magnetic field, but can occur at three different energies in the presence of a magnetic field.

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 8.4.3).

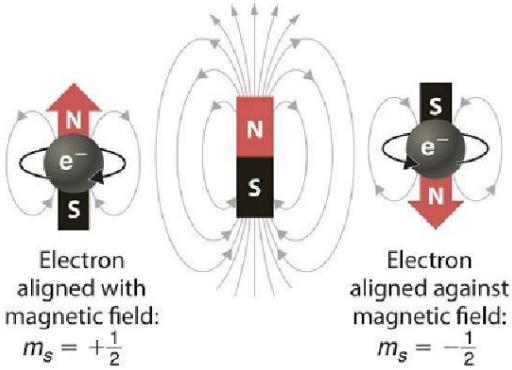


Figure 8.4.3: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden. (CC BY-SA-NC; Anonymous by request).

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 8.4.4).

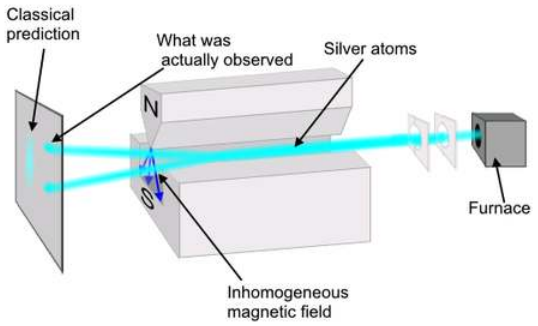


Figure 8.4.4: Stern–Gerlach experiment: silver atoms travel through an inhomogeneous magnetic field and are deflected up or down depending on their spin. (CC BY-SA 3.0 unported; Theresa Knott).

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.

Electron "spin" does not Originate Actual 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.

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

$$\hat{L}^2 \left|Y_l^{m_l}\right\rangle = l(l+1)\hbar^2 \left|Y_l^{m_l}\right\rangle \tag{8.4.2}$$

so by analogy for the spin states, we must have

$$\hat{S}^2 \left|\sigma_s^{m_s}\right\rangle = s(s+1)\hbar^2 \left|\sigma_s^{m_s}\right\rangle \tag{8.4.3}$$

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

$$\hat{L}_z \left|Y_l^{m_l}\right\rangle = m_l\hbar \left|Y_l^{m_l}\right\rangle \tag{8.4.4}$$

so by analogy, we must have a similar projection for the spin angular momentum:

$$\hat{S}_z \left| \sigma_s^{m_s} \right\rangle = m_s \hbar \left| \sigma_s^{m_s} \right\rangle \tag{8.4.5}$$

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. 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 $|\beta\rangle$.

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.

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.

Contributors

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8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

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:

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_1^2)-V(\mathbf{r}_1)-V(\mathbf{r}_2)+V_{12}(\mathbf{r}_1,\mathbf{r}_2)\right]\psi(\mathbf{r}_1,\mathbf{r}_2)=E\psi(\mathbf{r}_1,\mathbf{r}_2) \tag{8.5.1}$$

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

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle=|\varphi_a(\mathbf{r}_1)\rangle|\varphi_b(\mathbf{r}_2)\rangle \tag{8.5.2}$$

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:

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2+V(\mathbf{r}_1)\right]|\varphi_a(\mathbf{r}_1)\rangle=E|\,\varphi_a(\mathbf{r}_1)\rangle \tag{8.5.3}$$

$$\left[-\frac{\hbar^2}{2m}\nabla_2^2+V(\mathbf{r}_2)\right]|\varphi_b(\mathbf{r}_2)\rangle=E|\,\varphi_a(\mathbf{r}_2)\rangle \tag{8.5.4}$$

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

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = \psi(\mathbf{r}_2, \mathbf{r}_1)^* \psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2)^* \psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.5}$$

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 8.5.5 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{i\varphi} \psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.6}$$

so that

$$\left(e^{-i\varphi} \psi(\mathbf{r}_1, \mathbf{r}_2)^*\right) \left(e^{i\varphi} \psi(\mathbf{r}_1, \mathbf{r}_2)^*\right) = \psi(\mathbf{r}_1, \mathbf{r}_2)^* \psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.7}$$

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.,

$$e^{i\varphi} e^{i\varphi} = e^{i2\varphi} = 1 \tag{8.5.8}$$

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:

$$\hat{P}_{12} |\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \pm |\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle \tag{8.5.9}$$

Bosons and femions

Physical solutions must be eigenfunctions of $\hat{P}_{12}$ (i.e., $\hat{H}$ and $\hat{P}_{12}$ commute). Moveover, Equation 8.5.9 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,

$$\hat{P}_{12} |\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = + |\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle \tag{8.5.10}$$

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.

$$\hat{P}_{12}\,|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = -|\,\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle \tag{8.5.11}$$

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

$$|\psi(\mathbf{r}_1,\mathbf{r}_2,\cdots r_i)\rangle \approx \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\cdots\varphi_i(r_i) \tag{8.5.12}$$

? 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).

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 8.5.12 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

$$|\psi^-\rangle = \frac{1}{\sqrt{2}}\Big|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.13}$$

and symmetric combination

$$|\psi^+\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle + C_{aa}\,|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle + C_{bb}|\,\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.14}$$

where the C_{ab} terms are expansion and normalization parameters.

> *Note that the antisymmetric combination (Equation 8.5.13) **cannot** include terms where both particles are in the same state (spin-orbital), but there are three possibilities for the symmetric state (Equation 8.5.14).*

Although any linear combinations of C_{ab}, C_{bb}, and C_{aa} in Equation 8.5.14 is possible, there are three limiting expressions for possible symmetric combinations:

$$|\psi_1^{+i}\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.15}$$

$$|\psi_2^{+i}\rangle = C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle \tag{8.5.16}$$

$$|\psi_3^{+i}\rangle = C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.17}$$

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.

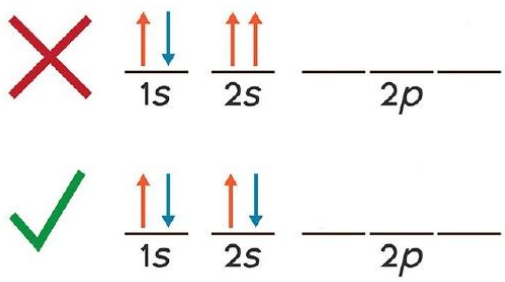


Figure 8.5.1: The 1s and 2s subshells for beryllium atoms can hold only two electrons and when filled, since each electrons is described by a specific spin-orbital and each orbital (spatial) can hold either an α or a β electron (i.e., they must have opposite spins). Otherwise they will have the same 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

$$|\varphi_b(\mathbf{r}_1)\rangle = \varphi_a(\mathbf{r}_2)\rangle \tag{8.5.18}$$

For example, if this were the case for the anti-symmetric combination for helium (Equation 8.5.13), 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.*

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants

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**).

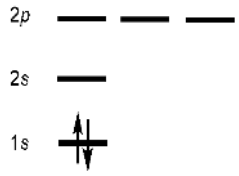


Figure **8.6.1**: Electron configuration for ground state of the helium atom.

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.

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)] \tag{8.6.3}$$

We can introduce a shorthand notation for the arbitrary *spin-orbital*

$$\varphi_{i\alpha}(\mathbf{r}_j) = \varphi_i\alpha(j) \tag{8.6.4}$$

or

$$\varphi_{i\beta}(\mathbf{r}_j) = \varphi_i\beta(j) \tag{8.6.5}$$

as determined by the m_s quantum number. This wavefunction in Equation 8.6.3 can be decomposed into spatial and spin components:

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{1s}(2)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.6}$$

? Exercise 8.6.1

Show that the linear combination 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).

Answer

$|\Psi(r1, r2)>= 1/\sqrt{2}[\varphi 1s\alpha(r))\varphi 1s\beta(r2) - \varphi 1s\beta(r2) - \varphi 1s\alpha(r2)\varphi 1s\beta(r1)](8.6.3) \rightarrow$show this is antisymmetric

Change the minus sign to plus sign show this is symmetric

(1) $|\Psi(r1, r2)>= 1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2) - \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]$
(2) $|\Psi(r1, r2)>= 1/\sqrt{2}[\varphi 1\,sa(r1)\varphi 1s\beta(r2) + \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]$

To see if symmetric $|\Psi_{(r1,r2)}>=|\Psi(r2, r1)> |\Psi(r1, r2)>= 1/\sqrt{2}[\varphi 1sa(r1)\varphi 1s\beta(r2) + \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]=$

$|\Psi(r2, r1)>= 1/\sqrt{2}[\varphi 1s\alpha(r2)\varphi 1s\beta(r1) + \varphi 1s\alpha(r1)\varphi 1s\beta(r2)]$

Can rearrange and $|\Psi(r1, r2)>= 1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2) + \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]=$

$|\Psi(r1, r2)>= 1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2) + \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]$

So $|\Psi(r1, r2)>= 1/\sqrt{2}[\varphi 1\,sa(r1)\varphi 1s\beta(r2) + \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]$ is symmetric

Now for antisymmetric $|\Psi(r1,r2)>=-|\Psi(r2,r1)>$ $|\Psi(r1,r2)>=1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2)-\varphi 1s\alpha(r2)\varphi 1s\beta(r1)]=$ $|\Psi(r2,r1)>=-1/\sqrt{2}[\varphi 1s\alpha(r2)\varphi 1s\beta(r1)-\varphi 1s\alpha(r1)\varphi 1s\beta(r2)]$

Simplify equation above and $1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2)-\varphi 1s\alpha(r2)\varphi 1s\beta(r1)]=1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2)-\varphi 1s\alpha(r2)\varphi 1s\beta(r1)]$

$$|\Psi(r1,r2)> \quad -|\Psi(r2,r1)> \tag{8.6.7}$$

$|\Psi_{(r1,r2)}\rangle=1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2)-\varphi 1s\alpha(r2)\varphi 1s\beta(r1)]\rightarrow$ is antisymmetric

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) that also must satisfy indistinguishability requirement just like the ground state.

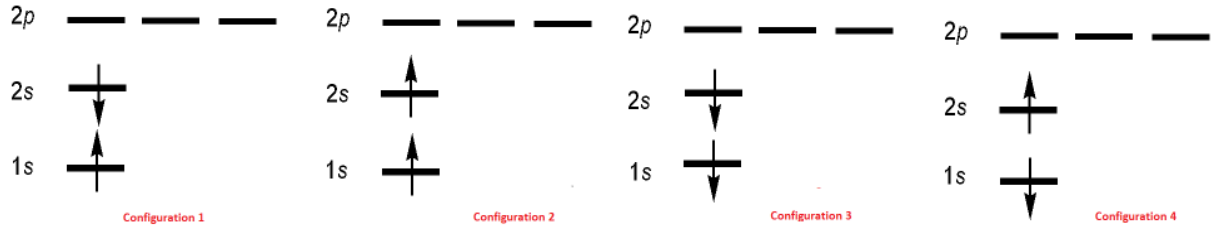


Figure 8.6.2: Electron configurations for first-excited state of the helium atom.

These electron configurations are used to construct four possible excited-state two-electron wavefunctions (but not necessarily in a one-to-on correspondence):

$$|\psi_1(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)+\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)-\alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.8}$$

$$|\psi_2(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\alpha(2)]}_{\text{spin component}} \tag{8.6.9}$$

$$|\psi_3(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)+\alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.10}$$

$$|\psi_4(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\beta(1)\beta(2)]}_{\text{spin component}} \tag{8.6.11}$$

All four wavefunctions are antisymmetric as required for fermionic wavefunctions (which is left to an exercise). Wavefunctions $|\psi_1\rangle$ 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

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2)\end{vmatrix} \tag{8.6.12}$$

A shorthand notation for the determinant in Equation 8.6.12 is then

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = 2^{-\frac{1}{2}}Det\left|\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)\right| \tag{8.6.13}$$

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

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \varphi_2(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_1) \\ \varphi_1(\mathbf{r}_2) & \varphi_2(\mathbf{r}_2) & \cdots & \varphi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(\mathbf{r}_N) & \varphi_2(\mathbf{r}_N) & \cdots & \varphi_N(\mathbf{r}_N) \end{vmatrix} \tag{8.6.14}$$

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

$$|\phi_a(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} \tag{8.6.15}$$

$$|\phi_b(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \tag{8.6.16}$$

$$|\phi_c(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \tag{8.6.17}$$

$$|\phi_d(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} \tag{8.6.18}$$

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 8.6.9 and 8.6.11). 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 8.6.8-8.6.11 can be expressed in term of the four determinants in Equations 8.6.15-8.6.18.

$$\begin{aligned} |\psi_2\rangle &= |\phi_b\rangle \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \\ |\psi_4\rangle &= |\phi_d\rangle \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} \end{aligned}$$

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 8.6.15-8.6.17)

$$\begin{aligned} |\psi_1\rangle &= |\phi_a\rangle - |\phi_c\rangle \\ &= \frac{1}{2}\left(\begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} - \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \right) \\ |\psi_3\rangle &= |\phi_a\rangle + |\phi_c\rangle \\ &= \frac{1}{2}\left(\begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} + \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \right) \end{aligned}$$

Note the expected change in the normalization constants.

Exercise 8.6.3

Show that the determinant wavefunction in Equation 8.6.12 is the same as the form for the helium wavefunction that is given in Equation 8.6.3.

Exercise 8.6.4

Expand the Slater determinant in Equation 8.6.12 for the He atom.

Answer

To expand the Slater determinant of the Helium atom, the wavefunction of Helium in the form of a two-electron system:

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)| = 1/\sqrt{(2)}\,|\Psi_{1s}(1)\mathrm{a}(1) \quad \psi_{1s}(1)\beta(1)| \tag{8.6.19}$$

$$|\psi_{1s}(2)a(2)\Psi_{1s}(2)\beta(2)| \tag{8.6.20}$$

Apply the definition of determinant of a regular 2×2 matrix to this wavefunction. The determinant of a 2×2 matrix is:

$$W = |ab| \rightarrow \det(w) = ad - bc \tag{8.6.21}$$

$$|cd| \tag{8.6.22}$$

Using this definition, expand the Slater determinant of Helium in a similar fashion.

$$\det\left(|\Psi(\mathbf{r}_1,\mathbf{r}_2)|\right) = 1/\sqrt{(2)}\,\left[\Psi_{1s}(1)\mathrm{a}(1)\Psi_{1s}(2)\right]\beta(2) - \Psi_{1s}(1)\beta(1)\Psi_{1s}(2)\mathrm{a}(2)\Big] \tag{8.6.23}$$

Exercise 8.6.5

Write and expand the Slater determinant for the ground-state Li atom.

Answer

Slater determinant for Li atom:

$$\psi(1,2,3) = \frac{1}{\sqrt{6}}\det\begin{pmatrix} 1S\alpha(1) & 1S\beta(1) & 2S\alpha(1) \\ 1S\alpha(2) & 1S\beta(2) & 2S\alpha(2) \\ 1S\alpha(3) & 1S\beta(3) & 2S\alpha(3) \end{pmatrix} \tag{8.6.24}$$

Expansion of Slater determinant (Laplace):

$$\psi(1,2,3) = \frac{1}{\sqrt{6}}[1S\alpha(1)1S\beta(2)2S\alpha(3) - 1S\alpha(1)1S\beta(3)2S\alpha(2) + 1S\alpha(3)1S\beta(1)2S\alpha(2) - 1S\alpha(3)1S\beta(2)2S\alpha(1) + 1S\alpha(2)1S\beta(3)2S\alpha(3) \tag{8.6.25}$$

Exercise 8.6.6

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.

? Exercise 8.6.7

Write the Slater determinant for the $1s^1 2s^1$ excited state orbital configuration of the helium atom.

Answer

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

$$\frac{1}{\sqrt{2}} \begin{bmatrix} \varphi 1_s(1)\alpha(1) & \varphi 2_s(1)\beta(1) \\ \varphi 1_s(2)\alpha(2) & \varphi 2_s(2)\beta(2) \end{bmatrix} \tag{8.6.26}$$

? Exercise 8.6.8

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!)

Contributors

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

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8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

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- eld, but its importance is con ned to the history of physics. In fact the Hartree method is not just approximate: it is wrong, by construction, 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 these *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 (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 single-particle **Hartree-Fock** equations:

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r}) + V_{electron}(\mathbf{r})\psi_i(\mathbf{r}) \\ -\sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = \epsilon_i\psi_i(\mathbf{r}). \end{aligned} \tag{8.7.4}$$

As with the *Hartree* equations, the first term is the kinetic energy of the ith electron

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) \tag{8.7.5}$$

and the second term is the electron-nuclear potential between the ith electron and nucleus

$$V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r}) \tag{8.7.6}$$

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.

$$V_{electron}(\mathbf{r})\psi_i(\mathbf{r}) = J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr' \tag{8.7.7}$$

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:

$$\sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \tag{8.7.8}$$

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. 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:

$$\hat{F}|\varphi_i\rangle = \epsilon_i|\varphi_i\rangle \tag{8.7.9}$$

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 8.7.9. Since the spatial portion of an orbital can be used to describe two electrons, each of the energies and wavefunctions found by solving Equation 8.7.9 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

$$\hat{F} = \hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) \tag{8.7.10}$$

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 8.7.10 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

$$\hat{H}^0(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} \tag{8.7.11}$$

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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.

> *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.*

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.

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:

$$\epsilon_i = \langle \phi_i | h_e | \phi_i \rangle \tag{8.7.12}$$

$$= \langle \phi_i | T + V | \phi_i \rangle + \sum_{j(\text{occupied})} \langle \phi_i | J_j - K_j | \phi_i \rangle \tag{8.7.13}$$

$$= \langle \phi_i | T + V | \phi_i \rangle + \sum_{j(\text{occupied})} [J_{i,j} - K_{i,j}], \tag{8.7.14}$$

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)

$$E_{N-1} - E_N = -\epsilon_k \tag{8.7.15}$$

- and for electron attachment (electron affinities)

$$E_N - E_{N+1} = -\epsilon_k. \tag{8.7.16}$$

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

$$\begin{aligned} E_N - E_{N+1} = & - \langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \frac{1}{2} \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ & - \frac{1}{2} \sum_{j=1}^{N+1} [J_{N+1,j} - K_{N+1,j}] \\ & = - \langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ & = -\epsilon_{N+1}. \end{aligned}$$

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.

> *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.*

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.

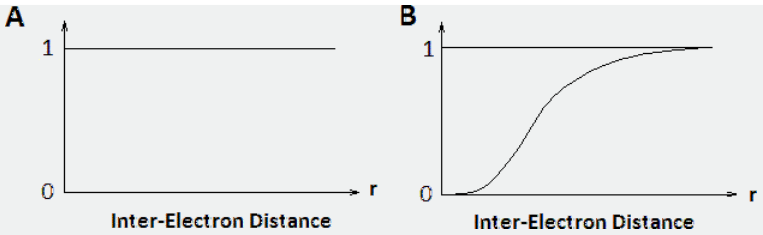


Figure 8.7.2: Normalized Conditional Probability for from electron-electron interactions (excluding coulomb effects) in (A) the Hartree approximation and (B) the Hartree-Fock approximation.

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 8.7.15) and Electron Affinities (Equation 8.7.16) 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.

Contributors

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8.8: Term Symbols Gives a Detailed Description of an Electron Configuration

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 the 2s and 2p electrons. 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 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. If two electrons are revolving in the same direction as each other, you would add their l values.

$$L = \sum_{i}^{n} l_i \tag{8.8.1}$$

If they were revolving opposite to each other, you would subtract them. If they are revolving at some off - angle relative to each other, you would partially subtract them. 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. If you prefer to have a formula, you can use this:

$$L = |l_1 + l_2|, |l_1 + l_2\text{-}1|, \ldots, |l_1\text{-}l_2| \tag{8.8.2}$$

Example 8.8.1: 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

What are the possible L values for the electrons in the $[Xe]6s^2 4f^1 5d^1$?

Solution

We have an $l = 3$ and an $l = 2$ electron.

$$3 + 2 = 5 \tag{8.8.3}$$

and

$$3\text{-}2 = 1 \tag{8.8.4}$$

The possible combinations are 5, 4, 3, 2, 1

The Total Magnetic Quantum Number: M_l

M_l is the total z-component of all of the relevant electrons' orbital momentum. Where L told you how much angular momentum there was, 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.

$$M_l = m_{l1} + m_{l2}, m_{l1} + m_{l2}\text{-}1, \ldots, \text{-}m_{l1}\text{-}m_{l2} \tag{8.8.5}$$

Example 8.8.3: 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.

$$M_s = m_{s1} + m_{s2}, m_{s1} + m_{s2}\text{-}1, ..., m_{s1}\text{-}m_{s2} \tag{8.8.6}$$

Example 8.8.4: 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.

$$S = |s_1 + s_2|, |s_1 + s_2\text{-}1|, ..., |s_1\text{-}s_2| \tag{8.8.7}$$

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 $1s^22s^12p^1$.

Solution

$S = 1, 0$

Example 8.8.7: The Carbon Ground State

Find S for carbon atoms with the $1s^22s^22p^2$ 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 do not necessarily have to be pointing in the same direction (Figure 8.8.1), so J can range from $L + S$ to $|L–S|$.

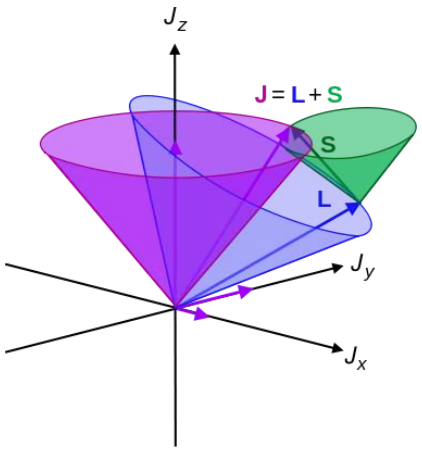


Figure 8.8.1: Illustration of L-S coupling. Total angular momentum J is purple, orbital L is blue, and spin S is green.

Table 8.8.1: Quantum Numbers and associated ranges

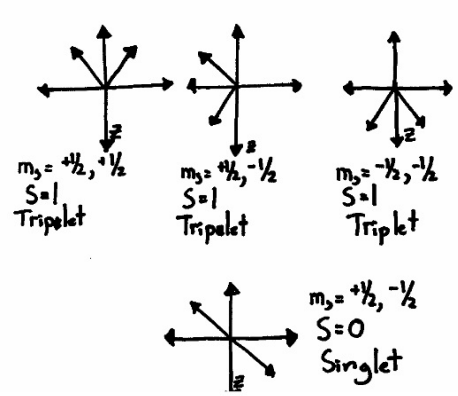
Symbol	Name	Allowed Range
L	Total orbital angular momentum	$\|l_1 + l_2\|, ..., \|l_1\text{-}l_2\|$
M_l	Magnet Quantum number	$[m_{l1} + m_{l2}, ..., \text{-}m_{l1}\text{-}m_{l2}]$
M_s	Spin Magnetic Quantum Number	$\|m_{s1} + m_{s2}\|, ..., \|m_{s1}\text{-}m_{s2}\|$
S	Inherent Spin Number	$\|s_1 + s_2\|, ..., \|s_1\text{-}s_2\|$
M	Multiplicity	2S+1
J	Total Angular Momentum	$L + S, ..., \|L - S\|$

Multiplicity

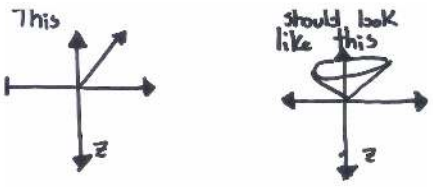
Multiplicity is a simple - sounding concept that defies simple explanations. You know from your first - year education that a singlet is when the net spin (S) is equal to zero (e.g. all the electrons are spin paired), and a triplet happens when the net spin is equal to 1 (e.g. two electrons are pointing 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:

$$L = 4, 3, 2, 1, 0 \tag{8.8.8}$$

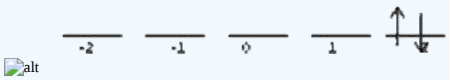
$$M_l = 4, 3, 2, 1, 0, -1, -2, -3, -4 \tag{8.8.9}$$

$$M_s = 1, 0 \tag{8.8.10}$$

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:

$M_s = -1$	$M_s = 0$	$M_s = +1$

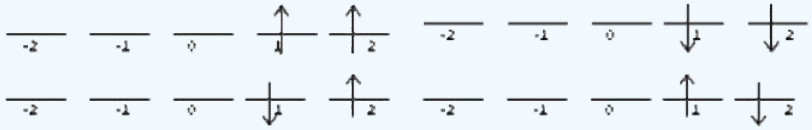
Attacking the chart one row at a time. Ask yourself, how many ways can I arrange the two electrons to give me $M_l = 4$? It turns out there is only one possible combination that does this:



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:

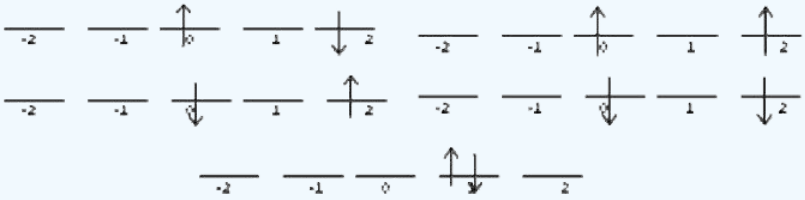
M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0

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

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.

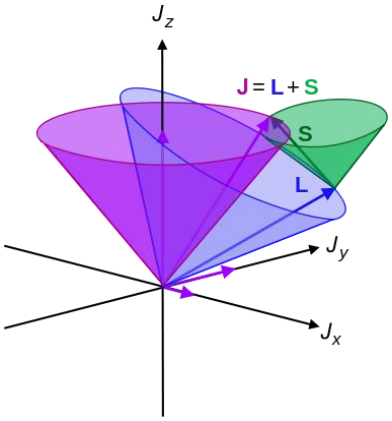


Figure 8.9.1: "Vector cones" of total angular momentum $\boldsymbol{J}$ (purple), orbital $\boldsymbol{L}$ (blue), and spin $\boldsymbol{S}$ (green). The cones arise due to quantum uncertainty between measuring angular momentum components (see vector model of the atom). (Public Domain; Maschen).

However the total angular momentum $\boldsymbol{J}$ 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

$$|\vec{L}| = \hbar\sqrt{\ell(\ell+1)} \tag{8.9.4}$$

with its projection on the z-axis

$$L_z = m_\ell \hbar \tag{8.9.5}$$

Spin Angular Momentum

$$|\vec{S}| = \hbar\sqrt{s(s+1)} \tag{8.9.6}$$

with its projection on the z-axis

$$S_z = m_s \hbar \tag{8.9.7}$$

Total Angular Momentum

$$\left|\vec{J}\right| = \hbar\sqrt{j(j+1)} \tag{8.9.8}$$

with its projection on the z-axis

$$J_z = m_j \hbar \tag{8.9.9}$$

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:

$$m_\ell \in \{-\ell, -(\ell-1) \cdots \ell-1, \ell\}, \quad \ell \in \{0, 1 \cdots n-1\} \tag{8.9.10}$$
$$m_s \in \{-s, -(s-1) \cdots s-1, s\}, \tag{8.9.11}$$
$$m_j \in \{-j, -(j-1) \cdots j-1, j\}, \tag{8.9.12}$$
$$m_j = m_\ell + m_s, \quad j = |\ell + s| \tag{8.9.13}$$

and the magnitudes are:

$$|\mathbf{J}| = \hbar\sqrt{j(j+1)} \tag{8.9.14}$$
$$|\mathbf{J}_1| = \hbar\sqrt{j_1(j_1+1)} \tag{8.9.15}$$
$$|\mathbf{J}_2| = \hbar\sqrt{j_2(j_2+1)} \tag{8.9.16}$$

in which

$$j \in \{|j_1 - j_2|, |j_1 - j_2| - 1 \cdots j_1 + j_2 - 1, j_1 + j_2\} \tag{8.9.17}$$

This process may be repeated for a third electron, then the fourth etc. until the total angular momentum has been found.

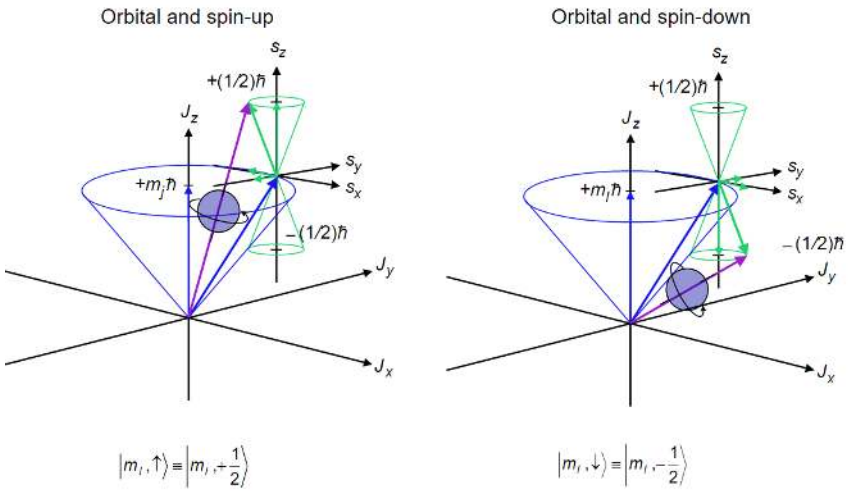


Figure 8.9.2: Vector model of total angular momentum: spin and orbital coupling (spin-1/2 particles). (Public Domain; Maschen).

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

Contributors

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

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8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States

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.

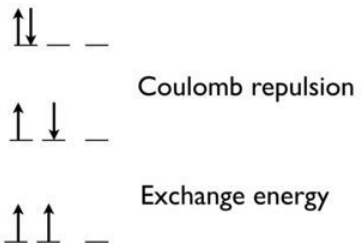


Figure 8.10.1: Origin of Hund's First Rule. Hund's first rule is that for a given electron configuration, a state in which the spins are unpaired has lower total energy than one in which the spins are paired.

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: $[He]2s^2 2p^2$
- N: $[He]2s^2 2p^3$
- O: $[He]2s^2 2p^4$
- Cr^{3+}: $[Ar]3d^3$
- Mn^{3+}: $[Ar]3d^4$
- Fe^{3+}: $[Ar]3d^5$

Answer

$^3P_0$, $^4S_{3/2}$, $^3P_2$, $^4F_{3/2}$, $^5D_0$, and $^6S_{5/2}$, respectively.

8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

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 $\mathbf{He^+}$.

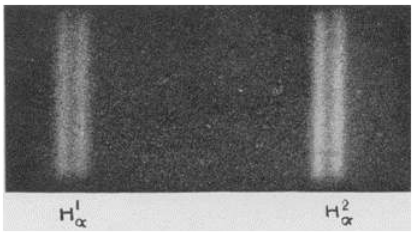


Figure **8.11.1**: Photograph of the first line in the Balmer series for atomic hydrogen and deuterium. These lines are identified as H_α^1 (hydrogen) and H_α^2 (deuterium), respectively. From H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) p. 132 and G.N. Lewis and F.H. Spedding, 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 Couping

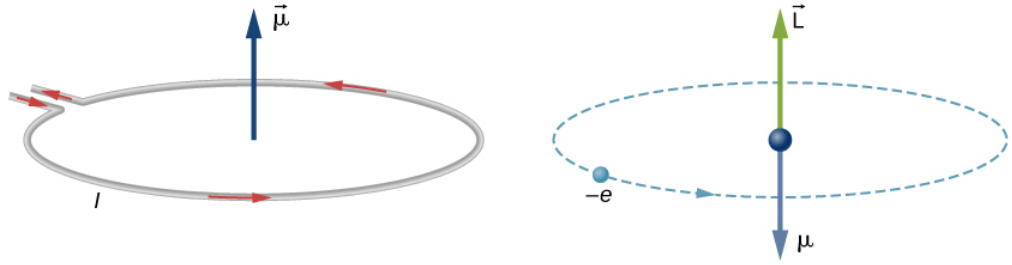
Specifying the orbital configuration of an atom does not uniquely identify the electronic state of the atom because the orbital angular momentum, the spin angular momentum, and the total angular momentum are not precisely specified. For example in the hydrogen $2p^1$ configuration, the electron can be 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.

$$E_{s-o} \propto S \cdot L \tag{8.11.1}$$

with the following terms added to the Hamiltonian

$$\hat{H}_{s-o} \propto \hat{S} \cdot \hat{L} \tag{8.11.2}$$

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**).



(a) Current-carrying loop (b) Hydrogen atom

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

$$\Delta l = \pm 1 \tag{8.11.3}$$

$$\Delta m_l = 0, \pm 1 \tag{8.11.4}$$

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:

$$\Delta S = 0 \tag{8.11.5}$$

$$\Delta L = 0, \pm 1 \tag{8.11.6}$$

$$\Delta J = 0, \pm 1, \tag{8.11.7}$$

but the $J = 0$ to $J = 0$ transition is forbidden

$$\Delta m_J = 0, \pm 1 \tag{8.11.8}$$

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 8.11.6 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 8.11.6.

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 (volition of selection rule in Equation 8.11.5) 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**.

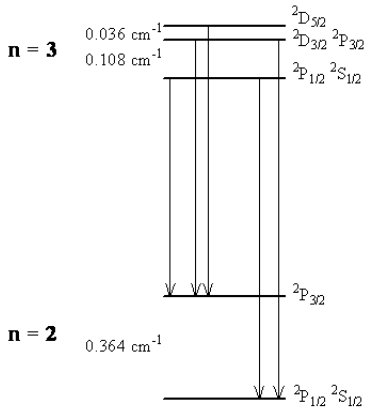


Figure **8.11.2**: Energy level diagram for the electronic states of hydrogen corresponding to an electron with the principal quantum number n = 3 and n = 2. While the relative energies of the terms are drawn to scale, the energy of n = 3 relative to n = 2 is not. Transitions to the $2P_{3/2}$ and ($2P_{1/2}$ 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.

Contributors

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

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1dr_2d\sigma_1d\sigma_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1dr_2d\sigma_1d\sigma_2}$$

can be rewritten as:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1dr_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1dr_2}$$

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:

$$\psi_{ColumnSwap} = \psi_A(2)\psi_B(1) - \psi_A(1)\psi_B(2) = -\psi$$

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 $^3P_0$ 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 $^3P_2$

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 configuration np^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 and M_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

$$J = (L + S), (L + S - 1), (L + S - 2), \ldots\ldots\ldots, (|L + S|),$$

The final results given the term symbols below:

$^3P_2$ $^3P_1$ $^3P_0$ $^1P_1$

$(\boldsymbol{L} + \boldsymbol{S})$ $(\boldsymbol{L} + \boldsymbol{S} - 1)$ $(|\boldsymbol{L} - \boldsymbol{S}|)$ $(|\boldsymbol{L} + \boldsymbol{S}|)$

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.

8.E: Multielectron Atoms (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

9: Chemical Bonding in Diatomic Molecules

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

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.

9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules
9.2: The H_2^+ Prototypical Species
9.3: The Overlap Integral
9.4: Chemical Bond Stability
9.5: Bonding and Antibonding Orbitals
9.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital
9.7: Molecular Orbitals Can Be Ordered According to Their Energies
9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule
9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle
9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic
9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals
9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules
9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently
9.14: Molecular Term Symbols Describe Electronic States of Molecules
9.15: Molecular Term Symbols Designate Symmetry
9.16: Most Molecules Have Excited Electronic States
9.E: Chemical Bond in Diatomic Molecules (Exercises)

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9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules

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.

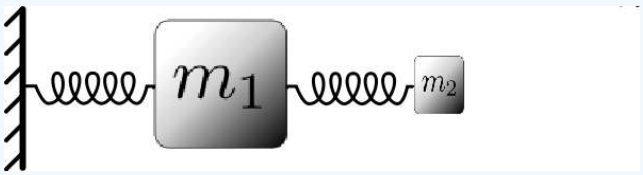
The Born-Oppenheimer Approximation

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

$$\hat{H}(r,R) = \hat{T}_{nuc}(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} + \hat{H}_{elec}(r,R) \tag{9.1.1}$$

where

$$\hat{T}_{nuc}(R) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 \tag{9.1.2}$$

and

$$\hat{H}_{elec}(\vec{r},\vec{R}) = \frac{-\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left(-\sum_i \frac{Z_A}{r_{Ai}} - \sum_i \frac{Z_B}{r_{Bi}} + \frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{r_{ij}}\right) \tag{9.1.3}$$

In Equation 9.1.1, 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 9.1.1 through 9.1.3.

Answer

$$\hat{H}(r,R) = \underbrace{\hat{T}_{nuc}(R)}_{\text{Kinetic Energy Term for nuclei}} + \underbrace{\frac{e^2}{4\pi\epsilon_o}\frac{Z_A Z_B}{R}}_{\text{Repulsion Term for nuclei}} + \underbrace{\hat{H}_{elec}(r,R)}_{\text{Hamiltonian for electrons}}$$

$$\hat{T}_{nuc}(R) = \underbrace{\frac{\hbar^2}{2m_A}\nabla_A^2}_{\text{Kinetic Energy Term for nuclei A}} - \underbrace{\frac{\hbar^2}{2m_b}\nabla_B^2}_{\text{Kinetic Energy Term for nuclei B}}$$

$$\hat{H}_{elec}(\vec{r},\vec{R}) = \underbrace{\frac{-\hbar^2}{2m}\sum_i \nabla_i^2}_{\text{Kinetic Energy Term for electrons}} + \frac{e^2}{4\pi\epsilon_o}\left(\underbrace{-\sum_i \frac{Z_A}{r_{Ai}}}_{\text{Attraction Term between nuclei A and electron i}} \underbrace{-\sum_i \frac{Z_B}{R_{Bi}}}_{\text{Attraction Term between nuclei B and electron i}} + \underbrace{\frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{r_{ij}}}_{\text{Repulsion Term between electrons}}\right)$$

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.

? Exercise 9.1.2

Explain why the factor of 1/2 appears in the last term in Equation 9.1.3.

Answer

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.

The Born-Oppenheimer approximation says that the nuclear kinetic energy terms in the complete Hamiltonian, Equation 9.1.1, 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

$$\hat{H}_{elec}(r,R)\varphi_e(r,R) = E_e(R)\varphi_e(r,R) \tag{9.1.4}$$

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

$$\psi_{ne}(r,R) = X_{ne}(R)\varphi_e(r,R) \tag{9.1.5}$$

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 9.1.5 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 9.1.4 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**.

$$V_e(R) = E_e(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} \tag{9.1.6}$$

Consequently the Schrödinger equation for the vibrational motion is

$$(\hat{T}_{nuc}(R) + V(R))X_{ne}(R) = E_{ne}X_{ne}(R) \tag{9.1.7}$$

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.

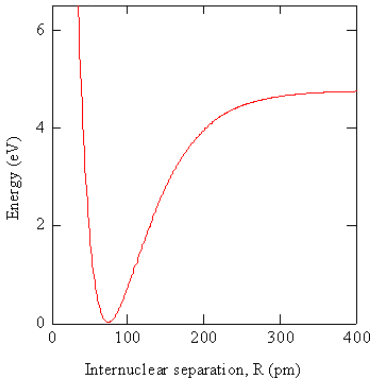


Figure **9.1.1**: The potential energy function for a diatomic molecule.

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 9.1.7 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.

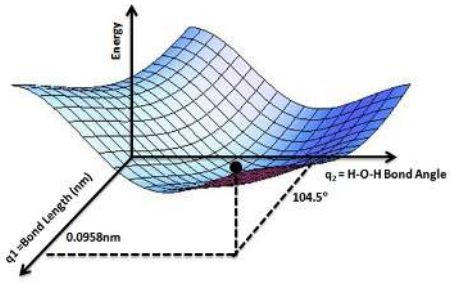


Figure **9.1.2**: The potential energy surface for a water molecule: Shows the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958 nm and H-O-H bond angle of 104.5°. from Wikipeda (AimNature)

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.

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

9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.2: 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 H_2^+.

The Hydrogen Molecular Ion

The simplest conceivable molecule would be made of two protons and one electron, namely 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 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.

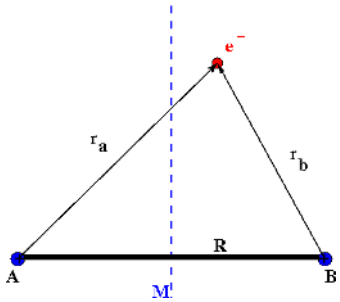


Figure 9.2.1: Hydrogen molecular ion H_2^+ with fixed nuclei A and B, internuclear distance R.

The electronic Hamiltonian for H_2^+ is

$$\hat{H}_{elec}(r,R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \tag{9.2.1}$$

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 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 $\mathbf{r}$ 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

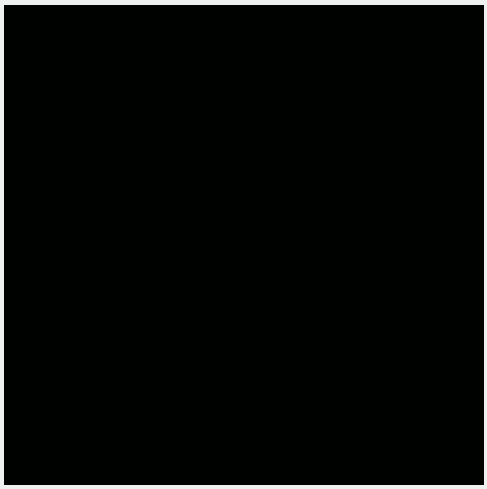
$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \tag{9.2.2}$$

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 9.2.2 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 **2*p*** 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 9.2.2. 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:

$$\psi_+ = C_+(1s_A + 1s_B) \tag{9.2.3}$$

$$\psi_- = C_-(1s_A - 1s_B) \tag{9.2.4}$$

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.

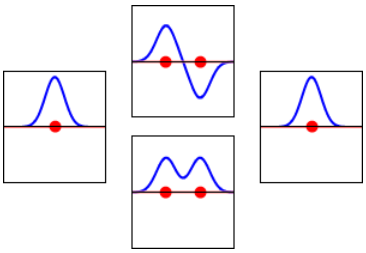


Figure **9.2.2**: Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H_2^+ ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red 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

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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9.3: 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

$$|\psi(r)\rangle = C_A 1s_A(r) + C_B 1s_B(r) \tag{9.3.1}$$

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

$$|C_A|^2 = |C_B|^2 \tag{9.3.2}$$

so $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\underbrace{|\psi_+\rangle = C_+(1s_A + 1s_B)}_{\text{bonding molecular orbital}} \tag{9.3.3}$$

and

$$\underbrace{|\psi_-\rangle = C_-(1s_A - 1s_B)}_{\text{antibonding molecular orbital}} \tag{9.3.4}$$

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 $|\psi_+\rangle$ 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:

$$\int \psi_\pm^* \psi_\pm d\tau = \langle \psi_\pm | \psi_\pm \rangle = 1 \tag{9.3.5}$$

$$\langle C_\pm(1s_A \pm 1s_B) | C_\pm(1s_A \pm 1s_B) \rangle = 1 \tag{9.3.6}$$

$$|C_\pm|^2[\underbrace{\langle 1s_A|1s_A\rangle}_{1} + \underbrace{\langle 1s_B|1s_B\rangle}_{1} \pm \underbrace{\langle 1s_B|1s_A\rangle}_{S} \pm \underbrace{\langle 1s_A|1s_B\rangle}_{S^*}] = 1 \tag{9.3.7}$$

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.

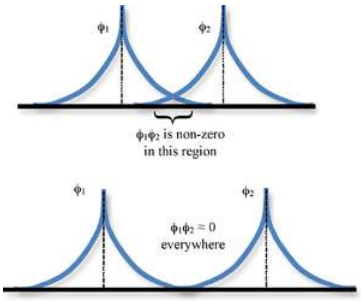


Figure 9.3.1: The wavefunctions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case both S is close to 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

$$\langle 1s_A | 1s_B \rangle = \langle 1s_B | 1s_A \rangle = S \tag{9.3.8}$$

Equation 9.3.7 becomes

$$|C_{\pm}|^2 (2 \pm 2S) = 1 \tag{9.3.9}$$

The solution to Equation 9.3.9 is given by

$$C_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} \tag{9.3.10}$$

Hence, the normalized molecular orbitals in Equations 9.3.3 and 9.3.3 are

$$|\psi_+\rangle = \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B) \tag{9.3.11}$$

and

$$|\psi_-\rangle = \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B) \tag{9.3.12}$$

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:

$$S(R) = \langle 1s_A | 1s_B \rangle \tag{9.3.13}$$

$$= e^{-R/a_o} \left(1 + \frac{R}{a_o} + \frac{R^2}{3a_o^2} \right) \tag{9.3.14}$$

The overlap integral for two 1s atomic orbitals of hydrogen is graphically displayed below

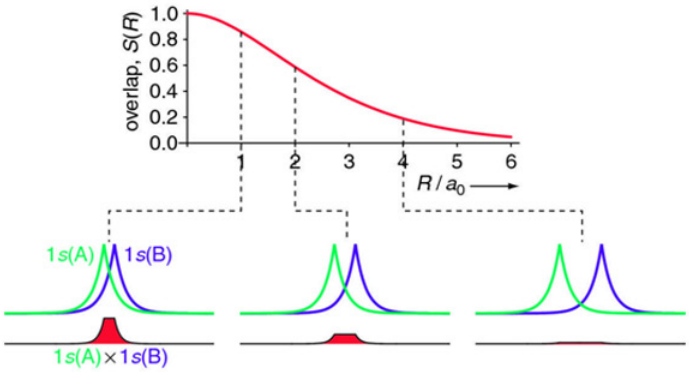


Figure **9.3.2**: The overlap integral at different proton separations.

Example 9.3.1

Calculate the difference in the electronic charge density (C/pm^3) at a point halfway between the two nuclei for $\mathbf{H_2^+}$ 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 9.3.11) 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 9.3.14)

To find the density at halfway between A and B for the bonding orbital evalulate at 1/2 R,

$$r_A = \frac{1}{2}R \text{ and } r_B = \frac{1}{2}R$$

$$\psi_+^2 = 3.7 \times 10^{-7}\ \text{pm}^{-3} \tag{9.3.15}$$

Now multiply this answer by e to generate the electronic charge density,

$$P = \left(3.7 \times 10^{-7}\ \text{pm}^{-3}\right) \times \left(1.602 \times 10^{-19}\right)\ \text{C} = 5.93 \times 10^{-26} C/pm^3 \tag{9.3.16}$$

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 9.3.12 or Figure **9.3.1** shows this will be zero.

$$e\psi_-^2 = 0 \tag{9.3.17}$$

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

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9.4: Chemical Bond Stability

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 ($1s_B$):

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}}(1s_A \pm 1s_B) \tag{9.4.1}$$

The energy of these two molecular orbitals can be calculated from the expectation value integral of the Hamiltonian,

$$E_{\pm} = \left\langle \psi_{\pm} \middle| \hat{H}_{elec} \middle| \psi_{\pm} \right\rangle \tag{9.4.2}$$

which can be expanded using the expanded molecular orbital wavefunctions in Equations 9.4.1 to give

$$E_{\pm} = \frac{1}{2(1 \pm S)} \tag{9.4.3}$$
$$\left[\underbrace{\left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle}_{H_{BA}} \right]$$

where S is the overlap integral between the two atomic orbitals of the basis. The four integrals in Equation 9.4.3 can be represented by H_{AA}, H_{BB}, H_{AB}, and H_{BA}, respectively.

$$E_{\pm} = \frac{1}{2(1 \pm S)} \left[H_{AA} + H_{BB} \pm H_{AB} \pm H_{BA} \right] \tag{9.4.4}$$

Exercise 9.4.1

Show that Equation 9.4.2 expands to give Equation 9.4.3 within the LCAO approximation that uses a basis set of only two 1s atomic orbitals.

Answer

Here we have the wavefunction within the LCAO approximation that uses a basis set of only two 1s atomic orbitals (Equation 9.4.1).

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}} (1_{Sa} \pm 1_{Sb})$$

And our LCAO approximation is equivalent to this if we plug in the wavefunction directly.

$$E_{\pm} = \langle \psi_{\pm} \left| \hat{H} \right| \psi_{\pm} \rangle = N^2 \langle (1_{Sa} \pm 1_{Sb}) \left| \hat{H} \right| (1_{Sa} - 1_{Sb}) \rangle$$

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):

$$\langle 1_{Sa} \left| \hat{H} \right| 1_{Sa} \rangle + \langle 1_{Sb} \left| \hat{H} \right| 1_{Sb} \rangle \pm \langle 1_{Sa} \left| \hat{H} \right| 1_{Sb} \rangle \pm \langle 1_{Sb} \left| \hat{H} \right| 1_{Sa} \rangle$$

Now we can see this is now equivalent to Equation 9.4.3 if the equation above is inserted (and adding a subscript to emphasize this only applies to the electronic wavefunction):

$$E_{\pm} = \frac{1}{2(1 \pm S)} \left[\underbrace{\left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle}_{H_{BA}} \right]$$

Notice that A and B appear equivalently in the Hamiltonian operator. This equivalence means that integrals involving $1s_A$ must be the same as corresponding integrals involving $1s_B$, i.e.

$$H_{AA} = H_{BB} \tag{9.4.5}$$

and since the wavefunctions are real

$$|A\rangle = \langle A| \tag{9.4.6}$$

so

$$H_{AB} = H_{BA} \tag{9.4.7}$$

These two equalities simplify Equation 9.4.4:

$$E_{\pm} = \frac{1}{1 \pm S}(H_{AA} \pm H_{AB}) \tag{9.4.8}$$

Now examine the details of H_{AA} after inserting the Hamiltonian operator for H_2^+ (Equation 9.2.1):

$$H_{AA} = \underbrace{\left\langle 1s_A \middle| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} \middle| 1s_A \right\rangle}_{E_H} + \frac{e^2}{4\pi\epsilon_0 R}\cancelto{1}{\langle 1s_A | 1s_A \rangle} \underbrace{- \left\langle 1s_A \middle| \frac{e^2}{4\pi\epsilon_0 r_B} \middle| 1s_A \right\rangle}_{J_{AB}} \tag{9.4.9}$$

- 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}.

$$= \underbrace{\left\langle 1s_A \middle| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_B} \middle| 1s_B \right\rangle}_{E_H S} + \overbrace{\frac{e^2}{4\pi\epsilon_0 R}\cancelto{S}{\langle 1s_A | 1s_B \rangle}}^{H_{AB}} - \underbrace{\left\langle 1s_A \middle| \frac{e^2}{4\pi\epsilon_0 r_A} \middle| 1s_B \right\rangle}_{K_{AB}} \tag{9.4.10}$$

- 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 9.4.9) and H_{AB} (Equation 9.4.10) and substituting into Equation 9.4.8 produces:

$$E_{\pm} = \frac{1}{1 \pm S}\left[\left(E_H + \frac{e^2}{4\pi\epsilon_0 R}\right)(1 \pm S) + J \pm K\right] \tag{9.4.11}$$

$$= E_H + \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{9.4.12}$$

Equation 9.4.12 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:

$$\Delta E_{\pm} = E_{\pm} - E_H \tag{9.4.13}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{9.4.14}$$

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 9.4.8

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

$$J_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_A}(r)\frac{e^2}{4\pi\epsilon_0 r_B} d\tau \tag{9.4.15}$$

$$K_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_B}(r)\frac{e^2}{4\pi\epsilon_0 r_A} d\tau \tag{9.4.16}$$

Figure 9.4.2 shows graphs of the four terms contributing to the energy of H_2^+ (Equation 9.4.14). In this figure 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.

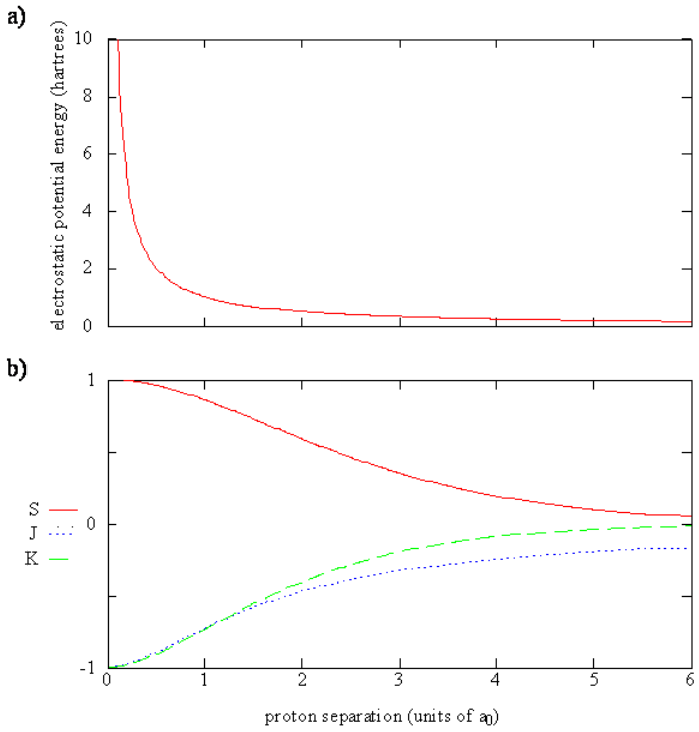


Figure **9.4.2**: (a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance R in units of the Bohr radius (52.92 pm). (b) The overlap (S), Coulomb (J), and exchange (K) integrals at different proton separations. The units for J and K are hartrees; S has no units.

Note that both J and K integrals are **negative** since all quantities in the integrands of Equation 9.4.15 and 9.4.16 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 $\mathbf{H_2^+}$.

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 9.4.12. 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.

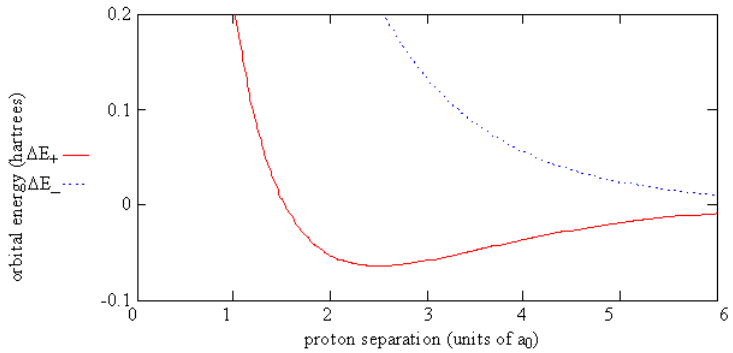


Figure **9.4.3** : Energy of the H2+ bonding molecular orbital ΔE_+ and the molecular orbital ΔE_-, relative to the energy of a separated hydrogen atom and proton.

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 9.4.12 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 9.4.12, 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

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9.5: Bonding and Antibonding Orbitals

The two molecular orbitals 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 jth molecular orbital can be expressed as a linear combination of many atomic orbitals $\{\phi_i\}$:

$$|\psi_J\rangle = \sum_i^N c_{J,i} \Big| \phi_i \rangle \tag{9.5.1}$$

A molecule will have as many molecular orbitals as there are atomic orbitals used in the basis set (N in Equation 9.5.1). 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 1*s* orbitals is called a σ_{1s} combination (parts (a) and (b) of Figure 9.5.1).

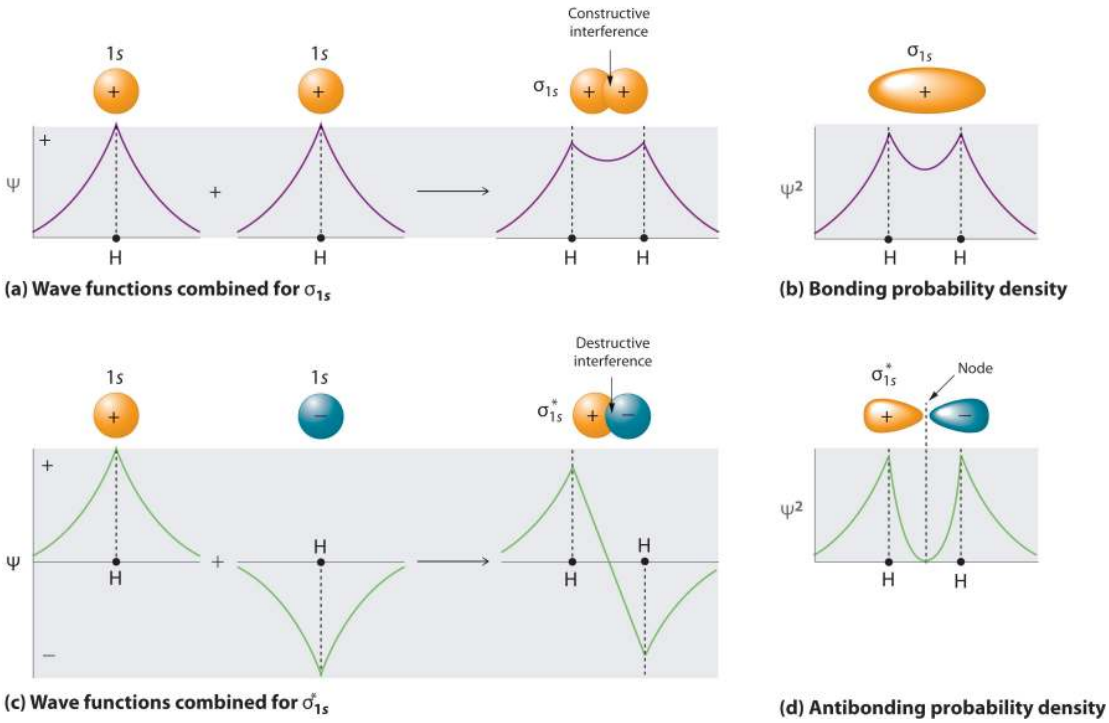


Figure 9.5.1: Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ1s molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wave function.) (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 wave function (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 by request).

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 1*s* denotes the atomic orbitals from which the molecular orbital was derived.

$$|\sigma_{1s}\rangle = \frac{1}{\sqrt{2(1+S)}} \left(|1s_A\rangle + |1s_B\rangle\right) \tag{9.5.2}$$

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:

$$|\sigma_{1s}^{*}\rangle = \frac{1}{\sqrt{2(1-S)}}\left(|1s_A\rangle - |1s_B\rangle\right) \tag{9.5.3}$$

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 wave functions. In contrast, electrons in the σ_{1s}^{*} orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ_{1s}^{*} 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 wave functions).

> *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 1*s* atomic orbitals. Conversely, electrons in the σ_{1s}^{*} 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 1*s* atomic orbitals. Consequently, the σ_{1s}^{*} molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the σ_{1s}^{*} (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**

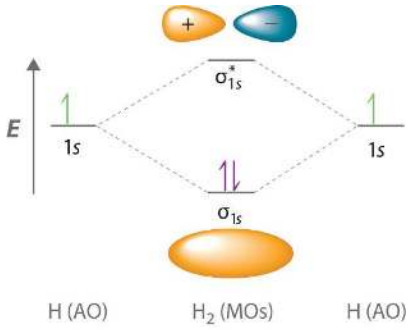


Figure **9.5.2**: Molecular Orbital Energy-Level Diagram for H2. The two available electrons (one from each H atom) in this diagram fill the bonding σ1s molecular orbital. Because the energy of the σ1s molecular orbital is lower than that of the two H 1s atomic orbitals, the H2 molecule is more stable (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,

$$E_J = \frac{\left\langle \psi_J \middle| \hat{H}_{elec} \middle| \psi_J \right\rangle}{\langle \psi_J | \psi_J \rangle} \tag{9.5.4}$$

This is the variational energy using $|\psi_J\rangle$ as the trail wavefunction. After substituting the LCAO expansion for $|\psi_J\rangle$ (Equation 9.5.1) into the energy expression of Equation 9.5.4 results in:

$$E_J = \frac{\left\langle \sum_i c_{J,i}^* \phi_i \left| \hat{H}_{elec} \right| \sum_j c_{J,i} \phi_j \right\rangle}{\left\langle \sum_i c_{J,i}^* \phi_j \right| \sum_j c_{J,j} \phi_j \rangle} \tag{9.5.5}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} \left\langle \phi_i \left| \hat{H}_{elec} \right| \phi_j \right\rangle}{\sum_{i,j} c_{J,i}^* c_{J,j} \langle \phi_i | \phi_j \rangle} \tag{9.5.6}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} H_{ij}}{\sum_{i,j} c_{J,i}^* c_{J,j} S_{ij}} \tag{9.5.7}$$

where H_{ij} is the Hamiltonian matrix element.

$$H_{ij} = \langle \phi_i \left| \hat{H}_{elec} \right| \phi_j \rangle \tag{9.5.8}$$

Following the variational theorem, to determine the coefficients of the LCAO expansion c_i, we need to minimize E_J

$$\frac{\partial E_J}{\partial c_k} = 0 \tag{9.5.9}$$

for all k. This requires solving N linear equations to hold true (where N is the number of atomic orbitals in the basis)

$$\sum_{i=1}^{N} c_i (H_{ki} - E S_{ki}) = 0 \tag{9.5.10}$$

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

$$\begin{aligned} c_1(H_{11} - E S_{11}) + c_2(H_{12} - E S_{12}) &= 0 \\ c_1(H_{12} - E S_{12}) + c_2(H_{22} - E S_{22}) &= 0 \end{aligned} \tag{9.5.11}$$

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

$$\begin{pmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} \\ H_{12} - E S_{12} & H_{22} - E S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{9.5.12}$$

Solving these secular equations with N different atomic orbitals in the expansion (Equation 9.5.1) requires finding the N roots of an N order polynomial.

$$\begin{vmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} & \ldots \\ H_{12} - E S_{12} & H_{22} - E S_{22} & \ldots \\ \ldots & \ldots & \ldots \end{vmatrix} = 0 \tag{9.5.13}$$

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 9.5.1), 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 9.5.1), 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

$$|\psi_J\rangle = c_{J,1}1s_A + c_{J,2}1s_B + c_{J,3}2s_A + c_{J,4}2s_B + c_{J,5}2p_{z,A} + c_{J,6}2p_{z,B} \tag{9.5.14}$$

The reasons that only the p_z atomic orbitals are included in this expansion are discussed later.

Contributors

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

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9.6: 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.

$$|\psi_i\rangle = \sum_j c_{ij}\varphi_j \tag{9.6.1}$$

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,

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_A(r_1)\alpha(1) & \psi_B(r_1)\beta(1)\\ \psi_A(r_2)\alpha(2) & \psi_B(r_2)\beta(2)\end{vmatrix} \tag{9.6.2}$$

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**.

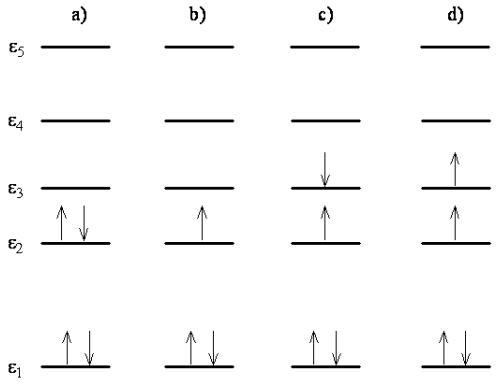


Figure **9.6.1**: a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration.

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

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 \tag{9.6.3}$$

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 wave function 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

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
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9.7: 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.

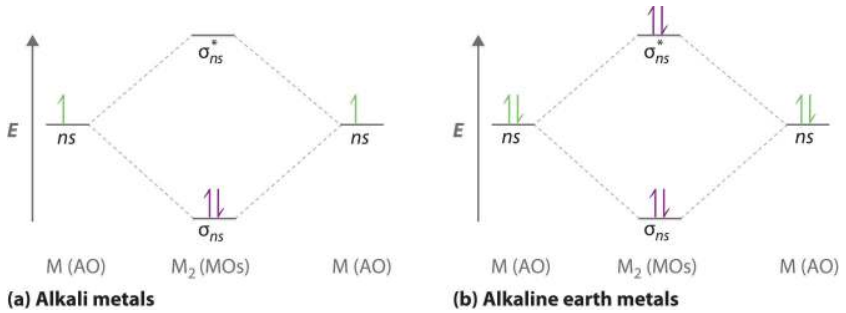


Figure **9.7.1**: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σns (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic 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 by request).

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 **9.7.1***b*, 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.

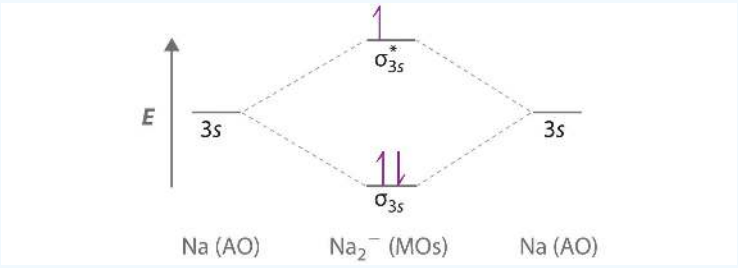
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

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 1*s* 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 $(\sigma_{3s})^2(\sigma^*_{3s})^1$ 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

Ca_2^+ has a $(\sigma_{4s})^2(\sigma^*_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

Molecular Orbitals Formed from n*p* Orbitals

Atomic orbitals other than *ns* 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.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{9.7.1}$$

Just as with *ns* 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 wave functions 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):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{9.7.2}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{9.7.3}$$

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).

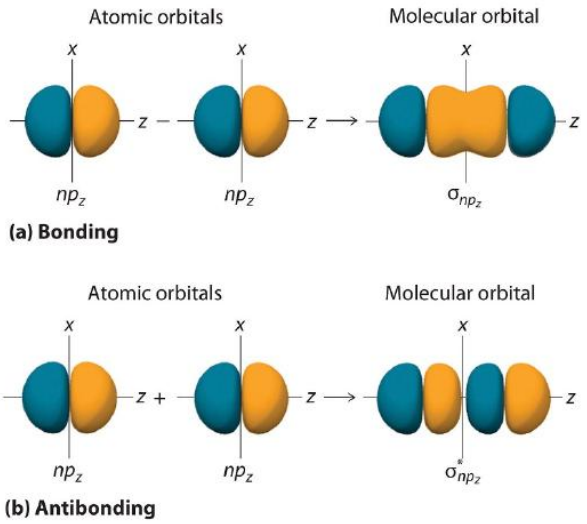


Figure **9.7.2**: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms 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 by request).

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..

$$\pi_{np_z} = np_x\,(A) + np_x\,(B) \tag{9.7.4}$$

$$\pi^*_{np_z} = np_x\,(A) - np_x\,(B) \tag{9.7.5}$$

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 $\pi^*_{np_y}$ 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_z} and π_{np_y}molecular orbitals are a degenerate pair, as are the $\pi^*_{np_z}$ and $\pi^*_{np_y}$ molecular orbitals.

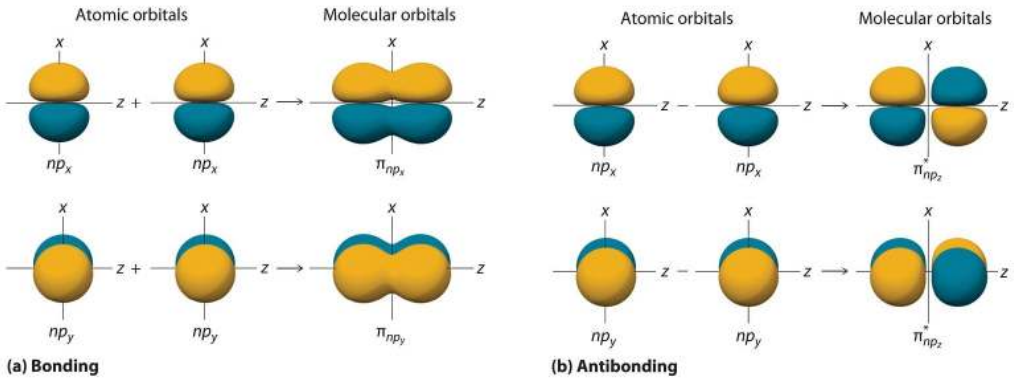


Figure **9.7.3**: Formation of π Molecular Orbitals from npx and npy Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the npx and the npy atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) 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 by request).

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.

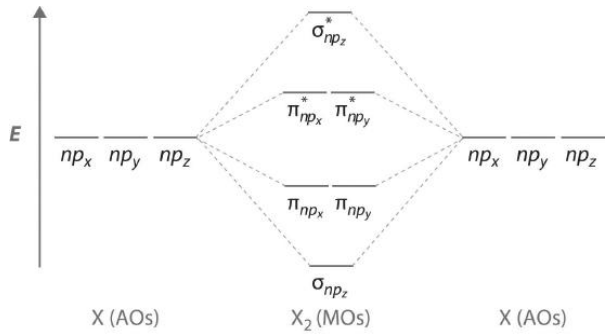


Figure **9.7.4**: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals. (CC BY-SA-NC; anonymous by request).

> *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 **9.7.5***a*; 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 $\sigma^*_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ 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.

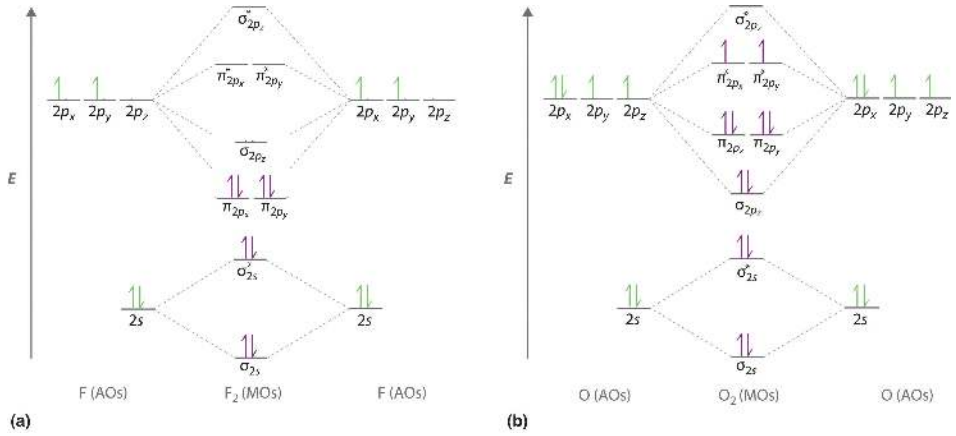


Figure **9.7.5**: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For C_2, with 8 valence electrons (4 from each F atom). This diagram shows 6 electrons in bonding orbitals and 2 in antibonding orbitals, resulting in a bond order of 2. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{np_x}, \pi^*_{np_y}\right)$ 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 by request).

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 $\pi^*_{np_x}$ and $\pi^*_{np_y}$ 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.

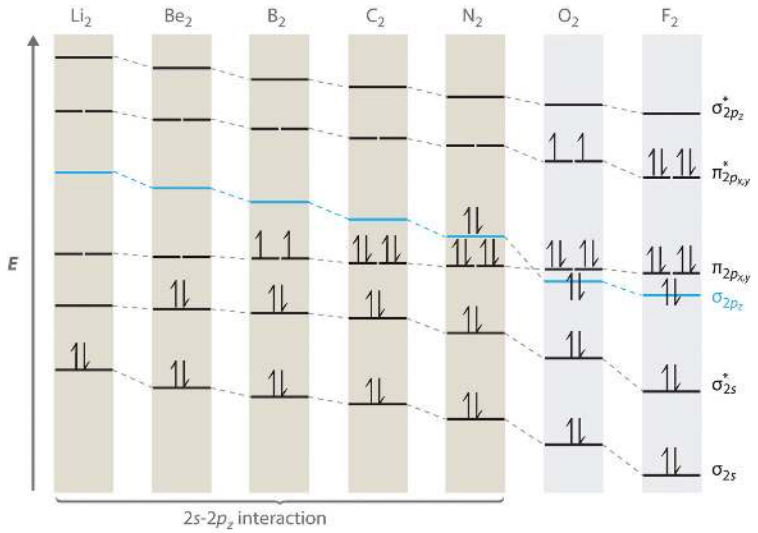


Figure 9.7.6: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. 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 2*s* and 2*p* atomic orbitals as the nuclear charge increases across the row. (CC BY-SA-NC; anonymous by request).

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

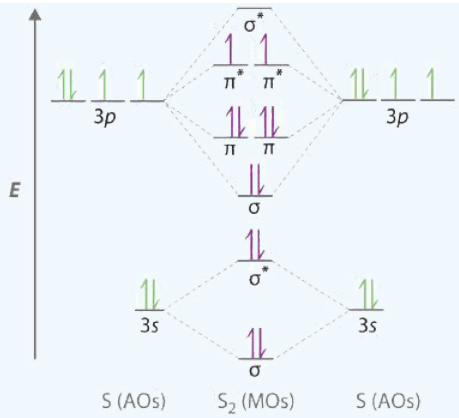
Strategy:

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 $[Ne]3s^23p^4$ 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 by request).

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_z} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^*_{3p_z}$ and $\pi^*_{3p_y}$ 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 $(\sigma_{3s})^2(\sigma^*_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi^*_{3p_{x,y}})^2$ with 2 unpaired electrons. The bond order is $(8-4)\div 2 = 2$, 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

$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_{x,y}})^4(\pi^*_{2p_{x,y}})^4$ bond order of 1; no unpaired electrons

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 wave functions ($ns + np_z$) 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.

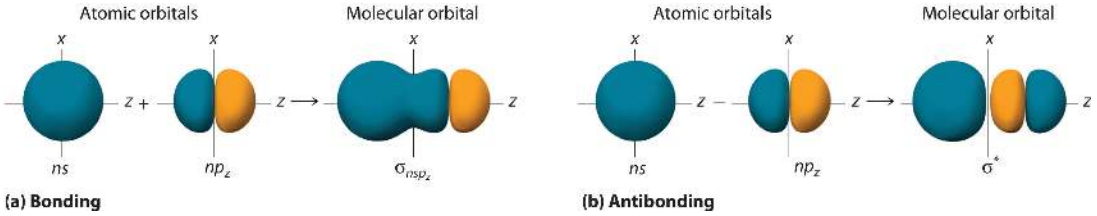


Figure **9.7.7**: Formation of Molecular Orbitals from an *ns* Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous by request).

9.7: Molecular Orbitals Can Be Ordered According to Their Energies is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

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:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \tag{9.8.1}$$

To calculate the bond order of H_2, we know that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ^*_{1s} (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\text{bond order} = \frac{2-0}{2} = 1 \tag{9.8.2}$$

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.

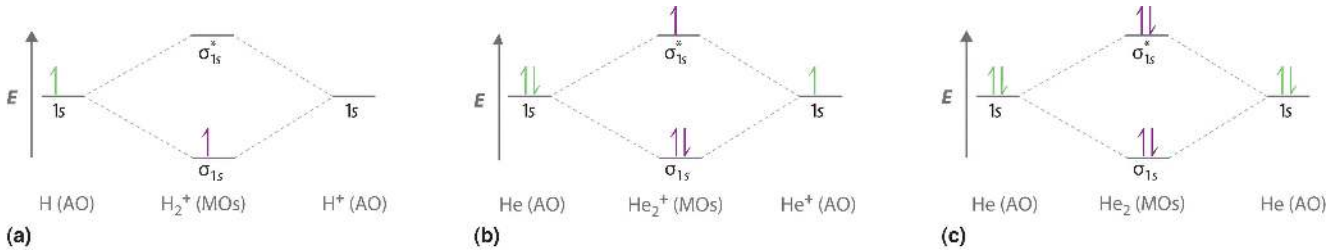


Figure 9.8.1: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here. (CC BY-SA-NC; anonymous by request).

Figure 9.8.1*a* 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 9.8.1)

$$\text{bond order} = \frac{1-0}{2} = 1/2 \tag{9.8.3}$$

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^+	$(\sigma_{1s})^2(\sigma^*_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2$	0	5,500	4.6×10^{-5}

Figure 9.8.1*b* is the molecular orbital energy-level diagram for 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 σ^*_{1s}

antibonding orbital, giving a $(\sigma_{1s})^2 (\sigma^*_{1s})^1$ electron configuration. This electron configuration gives a bond order (via Equation 9.8.1) of

$$\text{bond order} = \frac{2-1}{2} = 1/2 \tag{9.8.4}$$

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 He_2^{2+} ion

Use a molecular orbital energy-level diagrams to predict the bond order and stability of the He_2^{2+} ion.

Given: chemical species

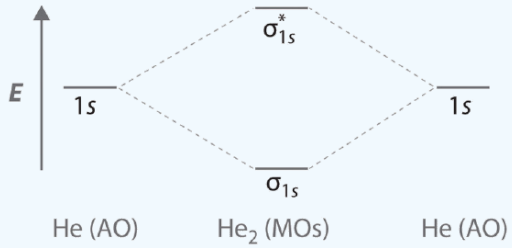
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

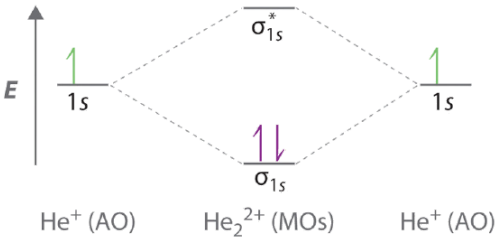
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning 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 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ^*_{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 1*s* 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 9.8.1)

$$\frac{2-0}{2} = 1$$

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 H_2^{2-} Ion

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

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.

The Helium Dimer

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure 9.8.1*c* is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and σ_{1s}^* antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ electron configuration, with a predicted bond order (via Equation 9.8.1) of

$$\text{bond order} = \frac{2-2}{2} = 0 \tag{9.8.5}$$

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 σ_{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 σ_{1s}^* molecular orbital:

$$\Delta E_\pm = E_\pm - E_H \tag{9.8.6}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{9.8.7}$$

Hence, the anti-bonding σ_{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 σ_{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 σ_{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 covalent bonding).*

However, Van der Waals Helium Dimers do exist

Based on molecular orbital theory discussed above, the He_2 molecule should not exist since no covalent bond formed between the helium atoms (Equation 9.8.5). 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, 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 He—He bond is 5,000 times weaker than the covalent bond in the hydrogen molecule (Table 9.8.1).

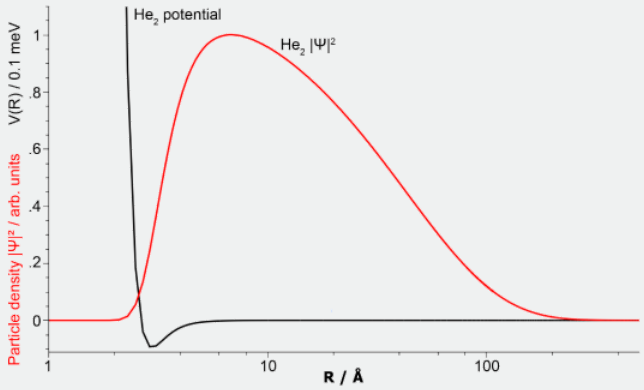


Figure 9.8.2: The weak helium-helium Van der Waals potential decrease leads to the particle probability density distribution leaking more into the classically forbidden region (i..e, tunneling). This effect allows the wavefunction to extend to sizes of fullerenes, the diameter of DNA and even small viruses (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.

9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle

The Pauli exclusion principle plays as important a role in the understanding of the electronic structure of molecules as it does in the case of atoms. The end result of the Pauli principle is to limit the amount of electronic charge density that can be placed at any one point in space. For example, the Pauli principle prevents the 1s orbital in an atom from containing more than two electrons. Since the 1s orbital places most of its charge density in regions close to the nucleus, the Pauli principle, by limiting the occupation of the 1s orbital, limits the amount of density close to the nucleus. Any remaining electrons must be placed in orbitals which concentrate their charge density further from the nucleus.

In an earlier discussion we pointed out that the reason the electron doesn't fall onto the nucleus is because it must possess kinetic energy if Heisenberg's uncertainty principle is not to be violated. This is one reason why matter doesn't collapse. The Pauli principle is equally important in this regard. The electron density of the outer electrons in an atom cannot collapse and move closer to the nucleus since it can do so only if the electrons occupy an orbital with a lower n value. If, however, the inner orbital contains two electrons, then the Pauli principle states that the collapse cannot occur. We must be careful in our interpretation of this aspect of the Pauli principle. The density from a 2s orbital has a small but finite probability of being found well within the density of the 1s orbital. Do not interpret the Pauli principle as implying that the density from an occupied orbital has a clearly defined and distinct region in real space all to its own. This is not the case. The operation of the Pauli principle is more subtle than this. In some simple cases, such as the ones we wish to discuss below, the limiting effect of the Pauli principle on the density distribution can, however, be calculated and pictured in a very direct manner.

The Pauli principle demands that when two electrons are placed in the same orbital their spins must be paired. What restriction is placed on the spins of the electrons during the formation of a molecule, when two orbitals, each on a different atom, overlap one another? For example, consider the approach of two hydrogen atoms to form a hydrogen molecule. Consider atom A to have the configuration $1s^1\alpha$ and atom B the configuration $1s^1\beta$. Even when the atoms approach very close to one another the Pauli principle would be satisfied as the spins of the two electrons are opposed. This is the situation we have tacitly assumed in our previous discussion of the hydrogen molecule. However, what would occur if two hydrogen atoms approached one another and both had the same configuration and spin, say $1s^1\alpha$? When two atoms are relatively close together the electrons become **indistinguishable**. It is no longer possible to say which electron is associated with which atom as both electrons move in the vicinity of both nuclei. Indeed this is the effect which gives rise to the chemical bond. In so far as we can still regard the region around each atom to be governed by its own atomic orbital, distorted as it may be, two electrons with the same spin will not be able to concentrate their density in the binding region. This region is common to the orbitals on both atoms, and since the electrons possess the same spin they cannot both be there simultaneously. In the region of greatest overlap of the orbitals, the binding region, the presence of one electron will tend to exclude the presence of the other if their spins are parallel. Instead of density accumulating in the binding region as two atoms approach, electron density is removed from this region and placed in the antibonding region behind each nucleus where the overlap of the orbitals is much smaller. Thus the approach of two hydrogen atoms with parallel spins does not result in the formation of a stable molecule. This repulsive state of the hydrogen molecule, in which both electrons have the same spin and atomic orbital quantum numbers, can be detected spectroscopically.

> *We can now give the general requirements for the formation of a chemical bond. Electron density must be accumulated in the region between the nuclei to an extent greater than that obtained by allowing the original atomic density distributions to overlap. In general, the increase in charge density necessary to balance the nuclear force of repulsion requires the presence of two electrons.*

We are now in a position to build up and determine the electronic configurations of the homonuclear diatomic molecules by adding electrons two at a time to the molecular orbitals with the spins of the electrons paired, always filling the orbitals of lowest energy first. We shall, at the same time, discuss the effectiveness of each orbital in binding the nuclei and make qualitative predictions regarding the stability of each molecular configuration.

The Pauli Exclusion Principle in Hydrogen Dimer

The two electrons in the hydrogen molecule may both be accommodated in the $1s_g$ orbital if their spins are paired and the molecular orbital configuration for H_2 is $1s_g^2$. Since the $1s_g$ orbital is the only occupied orbital in the ground state of H_2, the density distribution shown previously in Figure **9.9.2** for H_2 is also the density distribution for the $1s_g$ orbital when occupied by two electrons. The remarks made previously regarding the binding of the nuclei in H_2 by the molecular charge distribution apply directly to the properties of the $1s_g$ charge density.

The Pauli Exclusion Principle in Helium Dimer

The electronic configuration of He_2 is $1s_g^2\ 1s_u^2$. A s_u orbital, unlike a s_g orbital, possesses a node in the plane midway between the nuclei and perpendicular to the bond axis. The $1s_u$ orbital and all s_u orbitals in general, because of this nodal property, cannot concentrate charge density in the binding region. It is instead concentrated in the antibinding region behind each nucleus (Figure **9.9.3**).

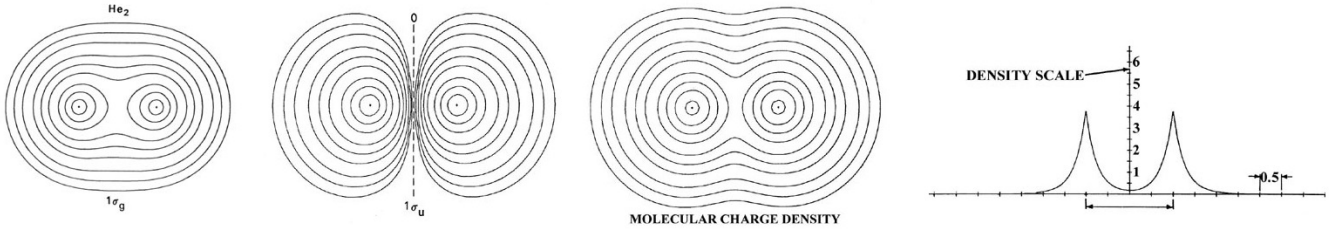


Figure **9.9.3**: Contour maps of the doubly-occupied $1\sigma_g$ and $1\sigma_u$ molecular orbital charge densities and of the total molecular charge distribution of He_2 at R = 2.0 au. A profile of the total charge distribution along the internuclear axis is also shown.

The s_u orbitals are therefore classified as ***antibonding***. It is evident from the form of density distribution for the $1s_u$ orbital that the charge density in this orbital pulls the nuclei apart rather than drawing them together. Generally, the occupation of an equal number of s_g and s_u orbitals results in an unstable molecule. The attractive force exerted on the nuclei by the charge density in the s_g orbitals is not sufficient to balance both the nuclear force of repulsion and the antibinding force exerted by the density in the s_u orbitals. Thus molecular orbital theory ascribes the instability of He_2 to the equal occupation of bonding and antibonding orbitals. Notice that the Pauli exclusion principle is still the basic cause of the instability. If it were not for the Pauli principle, all four electrons could occupy a s_g-type orbital and concentrate their charge density in the region of low potential energy between the nuclei. It is the Pauli principle, and not a question of energetics, which forces the occupation of the $1s_u$ antibonding orbital.

The total molecular charge distribution is obtained by summing the individual molecular orbital densities for single or double occupation numbers as determined by the electronic configuration of the molecule. Thus the total charge distribution for He_2 (Figure **9.9.3**) is given by the sum of the $1s_g$ and $1s_u$ orbital densities for double occupation of both orbitals. The adverse effect which the nodal property of the $1s_u$ orbital has on the stability of He_2 is very evident in the total charge distribution. Very little charge density is accumulated in the central portion of the binding region. The value of the charge density at the mid-point of the bond in He_2 is only 0.164 au compared to a value of 0.268 au for H_2.

We should reconsider in the light of molecular orbital theory the stability of He_2^+ and the instability of the hydrogen molecule with parallel spins. He_2^+ will have the configuration $1s_g^2\ 1s_u^1$. Since the $1s_u$ orbital is only singly occupied in He_2^+, less charge density is accumulated in the antibinding regions than is accumulated in these same regions in the neutral molecule. Thus the binding forces of the doubly-occupied $1s_g$ density predominate and He_2^+ is stable. The electron configuration of (triplet) H_2 is $1s_g^1(\alpha)1s_u^1(\alpha\text{-})$ when the electronic spins are parallel. The electrons **must** occupy separate orbitals because of the Pauli exclusion principle. With equal occupation of bonding and antibonding orbitals, the triplet H_2 species is predicted to be unstable.

Contributors

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9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic

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.

$$\text{bond order} = \frac{\text{number of electrons in bonding MOs} - \text{number of electrons in antbonding MOs}}{2} \tag{9.10.1}$$

For diatomics, the occupations can correlate to bond length, bond energies (Figure **9.10.1**) and behavior in applied magnetic fields.

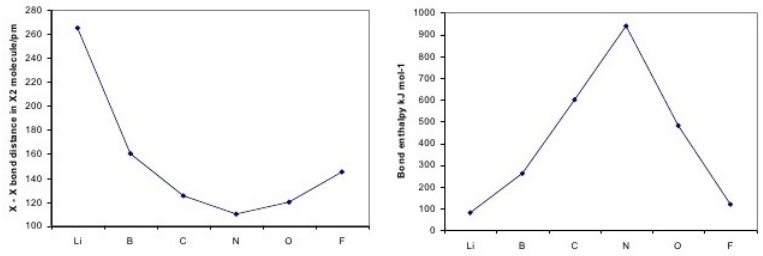


Figure **9.10.1**: Plot of bond length (left) and bond energy (right) for first row diatomics.

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.

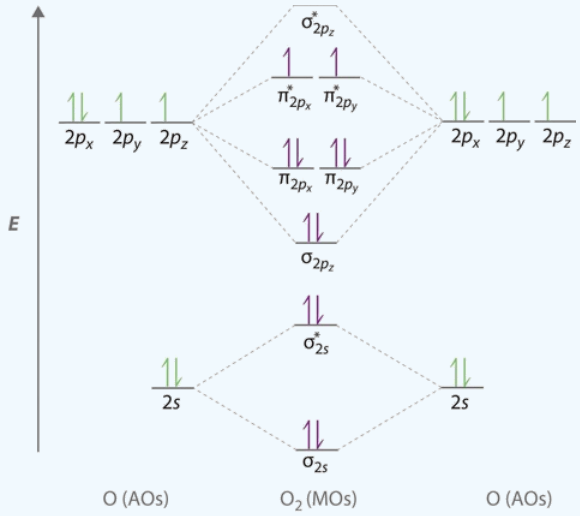


Figure 9.10.1: Molecular Orbital Energy-Level Diagrams for O_2. With 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{np_z}, \pi^*_{np_y}\right)$ pair of orbitals. Hund's first rule dictates that one electron occupies each orbital, and their spins are 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 via Equation 9.10.1. The electron configurations for the four species are contrasted below.

- O_2:

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^1\pi_{2p_y}^{*\,1}$$

  From Equation 9.10.1, the bond order for O_2 is 2 (i.e., a double bond).

- O_2^+:

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^1\pi_{2p_y}^{*\,0}$$

  From Equation 9.10.1, the bond order for O_2^+ is 2.5. An alternative and equally valid configuration is

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^0\pi_{2p_y}^{*\,1}$$

- O_2^-:

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^2\pi_{2p_y}^{*\,1}$$

  From Equation 9.10.1, the bond order for O_2^- is 1.5. An alternative and equally valid configuration is

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^1\pi_{2p_y}^{*\,2}$$

- O_2^{2-}:

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^2\pi_{2p_y}^{*\,2}$$

  From Equation 9.10.1, 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 Figure **9.10.2**, 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.



Figure **9.10.2**: 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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9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{9.11.1}$$

You can see from Equation 9.11.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, 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. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 9.11.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

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9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{9.13.1}$$

You can see from Equation 9.13.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, 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. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 9.13.1

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9.14: 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.

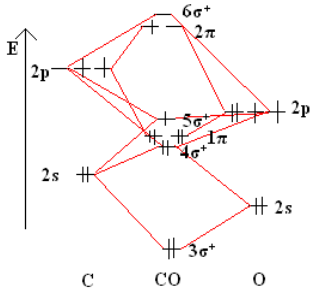
For homonuclear diatomics, the term symbol has the following form:

$$^{2S+1}\Lambda^{(+/-)}_{\Omega,(g/u)} \tag{9.14.1}$$

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.

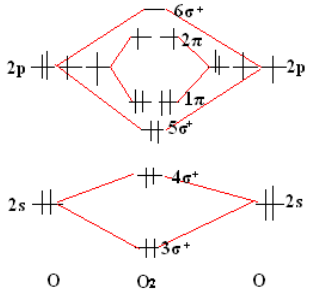
Determining term symbols of diatomics

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 Π x Π = Σ^+ + Σ^- + [Δ], 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. $\Delta\Lambda = 0, \pm1$ except $\Lambda = 0 \ddagger \Lambda' = 0$
2. $\Delta S = 0$
3. $\Delta\Omega = 0; \pm1$ 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

https://www1.udel.edu/pchem/C444/spL...s/05152008.pdf

Excitations between molecular electronic states provide information about properties of molecules. Molecular electronic transitions are induced by UV/VIS radiation, and so these transitions involve much more energy compared to the vibrational-rotational spectroscopies that require microwave and infrared frequencies. However, much as in the case of IR spectroscopy, electronic spectroscopy of molecules includes a ”fine structure” arising from vibrational-rotational transitions associated with changes in electronic states.

Before discussing electronic spectroscopy, we will investigate the description of molecular electronic states in terms of molecular term symbols as in the case of atomic electronic transitions. This should highlight the fact that multiple states are possible given a particular molecular electronic configuration based on the angular momentum and spin.

Molecular Term Symbols: Diatomic Molecules

As with atoms, ML and MS are the ”good” quantum numbers (L and S commute with Hamiltonian for diatomic molecules • Only unfilled subshells contribute to the term orbital and spin angular momentum • For first and second row diatomics, MO’s are either of σ or π type. 1 • ML and MS are generated as follow: – ML = P i mli – MS = P i msi • For MO’s with σ symmetry, ml = 0 • For MO’s with π symmetry, ml = ±1 – Note that there is no ml = 0 for π MO’s since the Pz atomic orbital is associated with the σ MO • As in the atomic case, −L ≤ ML ≤ L and −S ≤ MS ≤ S. • We need to determine the maximum values of ML and MS and generate term symbols • The values of ML corresponding to the various total angular momentum values possible are labelled with Λ. • The possible values of Λ can be 0, 1, 2, 3, ... – As with the atomic case, each numerical value of Λ corresponds to a letter, in the molecular case being Greek letters. • The term symbols are of the form: 2S+1Λ

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9.15: 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:

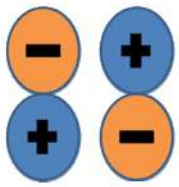
- $\Lambda = 0 \rightarrow \Sigma$
- $\Lambda = 1 \rightarrow \Pi$
- $\Lambda = 2 \rightarrow \Delta$
- $\Lambda = 3 \rightarrow \Phi$

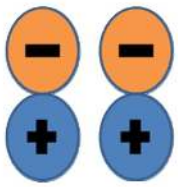
Unlike L, there is not a general formula for finding the possible combinations of Λ. You have to examine the individual microstates. This is easier than it sounds.

- **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 components: 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 +

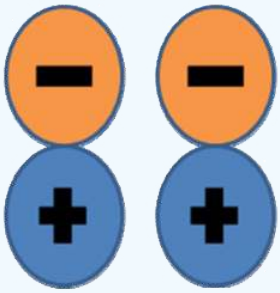
Reflection only applies to Σ states! For Λ > 0, there are no reflection labels! If you experiment with the rules, you will quickly realize why this is the case.

Example 9.15.2

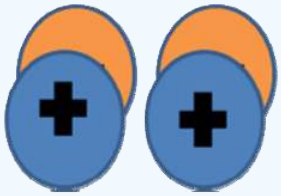
What is the reflection of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

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 -

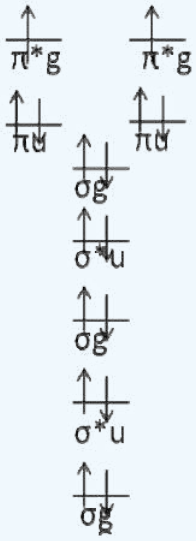
The “vertical” orbital is + The “horizontal” orbital is - Since one is + and one is - , the overall reflection is - . Try using the orthogonal plane and convince yourself that you still get the same answer.

Example 9.15.3: Oxygen

What are the term symbols for O_2 ?

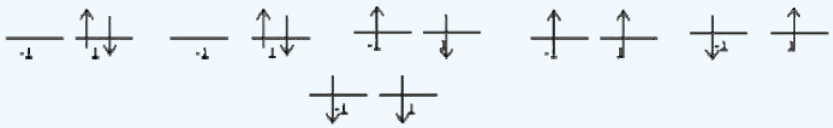
Solution

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

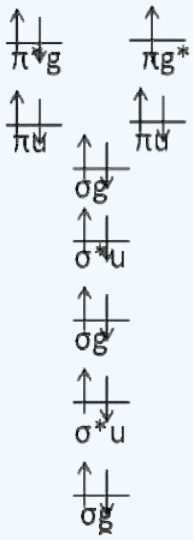
This is a Λ =0 state with three possible spin configurations, so it is $^3\Sigma$. We know that the electrons are in different sub-orbitals (if you cannot see this, try drawing all of the possible combinations that give $\Lambda = 0$). Both of the orbitals are gerade, so the overall parity is gerade. One of the orbitals will be +, the other will be - . The final answer is $^1\Delta_g$\($^3\Sigma_g^+$

? 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 $^2\Pi_g$.

Contributors

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9.16: Most Molecules Have Excited Electronic States

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{9.16.1}$$

You can see from Equation 9.16.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, 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. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 9.16.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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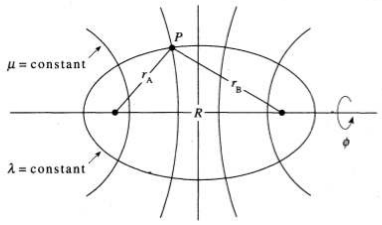
- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

9.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:

$$\begin{aligned}
S &= \frac{Z^3}{\pi} \int dr e^{-Zr_A} e^{-Zr)B} \\
&= \frac{Z^3}{\pi} \int_0^{2\pi} d\phi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu R^3/8(\lambda^2 - \mu^2) e^{-Z(r_A + r_B)} \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (\lambda^2 - \mu^2) e^{-ZR\lambda} \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda e^{-ZR\lambda} \int_{-1}^{1} d\mu (\lambda^2 - \mu^2) \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda e^{-ZR\lambda} (2\lambda^2 - 2/3) \\
&= \frac{R^3 Z^3}{2} \left[(1/ZR + 2/Z^2R^2 + 2/Z^3R^3) e^{-ZR} - 1/3ZRe^{-ZR} \right] \\
&= e^{-ZR}(1 + ZR + Z^2R^2/3)
\end{aligned}$$

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 ν, 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

$$^2\Sigma_g^+ \qquad (9.E.1)$$

$(1\sigma_g)^2$ 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

$$^1\Sigma_g^+ \qquad (9.E.2)$$

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) $(1\pi_g 2p_x)^1(1\pi_g 2py)^1$, 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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CHAPTER OVERVIEW

10: Bonding in Polyatomic Molecules

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

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.

10.1: Hybrid Orbitals Account for Molecular Shape
10.2: Hybrid Orbitals in Water
10.3: Why is BeH_2 Linear and H_2O Bent?
10.4: Photoelectron Spectroscopy
10.5: The \(\pi\)-Electron Approximation of Conjugation
10.6: Butadiene is Stabilized by a Delocalization Energy
10.7: Benzene and Aromaticity
10.E: Bonding in Polyatomic Molecules (Exercises)

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10.1: Hybrid Orbitals Account for Molecular Shape

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

$$V = V_{ee} + V_{en} + V_{nn} \tag{10.1.1}$$

$$= \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{R_{AB}}\right] \tag{10.1.2}$$

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

$$V \to -\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{1A}} + \frac{1}{r_{2B}}\right] \tag{10.1.3}$$

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

$$\psi_u(r_1, r_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)] \tag{10.1.4}$$

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

$$\psi_g(r_1, r_2) = C_g[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)] \tag{10.1.5}$$

(where g designates that this is an even function), 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

$$\psi_u(r_1, r_2, s_1, s_2) = \psi_u(x_1, x_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)] \\ [\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.6}$$

$$\psi_g(r_1, r_2, s_1, s_2) = \psi_g(x_1, x_2) = C_g[\psi^A_{1s}(r_1)\psi_{1s}B(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)] \\ [\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.7}$$

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:

$$\psi^A_{1s}(r_1) = \psi^B_{1s}(r_1) = A \tag{10.1.8}$$

$$\psi^B_{1s}(r_2) = \psi^A_{1s}(r_2) = A' \tag{10.1.9}$$

Substituting these into $\psi_u(x_1, x_2)$, we obtain

$$\psi_u(x_1, x_2) = C_u[AA' - A'A][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] = 0 \tag{10.1.10}$$

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

$$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1 \tag{10.1.11}$$

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 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:

$$\begin{aligned}&\psi_g(r_1, r_2, s_1, s_2) \\ &= C_g[\psi^A_{2p_z}(r_1)\psi^B_{2p_z}(r_2) + \psi^A_{2p_z}(r_2)\psi^B_{2p_z}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]\end{aligned} \tag{10.1.12}$$

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

$$\psi(r_1, r_2, s_1, s_2) = [\psi^H_{1s}(1)\psi^F_{2p_z}(2) + \psi^H_{1s}(2)\psi^F_{2p_z}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]) \tag{10.1.13}$$

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 H_2O illustrates this rather dramatically! Let us consider an even simpler molecule, BeH_2, which has a steric number of 2 and is linear. Let the atoms lie entirely along the z-axis in the arrangement $H - Be - H$.

Although Be 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

$$\psi_1(1,2) = C_1\left[\psi^{H_1}_{1s}(1)\psi^{Be}_{2s}(2) + \psi^{H_1}_{1s}(2)\psi^{Be}_{2s}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.14}$$

$$\psi_2(1,2) = C_2\left[\psi^{H_2}_{1s}(1)\psi^{Be}_{2p_z}(2) + \psi^{H_2}_{1s}(2)\psi^{Be}_{2p_z}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.15}$$

Unfortunately, even this simple scheme does not work entirely because the two $Be - H$ bonds would be different due to their construction from different combinations of orbitals. By symmetry, however, we can see that the two BeH bonds should be equivalent. A solution to this problem was proposed by Linus Pauling in the 30s 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 H, 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

$$\chi(r) = C_1\psi_{2s}(r) + C_2\psi_{2p_z}(r) + C_3\psi_{2p_y}(r) + C_4\psi_{2p_x}(r) \tag{10.1.16}$$

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 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):

$$|\chi_i\rangle = a_1|2s\rangle + b_1|2p_z\rangle \tag{10.1.17}$$

$$|\chi_j\rangle = a_2|2s\rangle + b_2|2p_z\rangle \tag{10.1.18}$$

These two wavefunctions must be orthogonal.

$$\langle\chi_i|\chi_j\rangle = \delta_{ij} \tag{10.1.19}$$

Which can be separated into the following relationships:

$$\langle\chi_i|\chi_i\rangle = 1 \tag{10.1.20}$$

and

$$\langle\chi_j|\chi_j\rangle = 1 \tag{10.1.21}$$

and

$$\langle\chi_i|\chi_j\rangle = \langle\chi_j|\chi_i\rangle = 0 \tag{10.1.22}$$

Equations 10.1.20 and 10.1.21 are the normality requirement and Equation 10.1.22 is the orthogonality requirement for the new hybrid wavefunctions. Substituting 10.1.17 into 10.1.20 results in

$$\langle\chi_i|\chi_i\rangle = a_1^2 \cancelto{1}{\langle 2s|2s\rangle} + a_1b_1 \cancelto{0}{\langle 2s|2p_z\rangle} + a_1b_1 \cancelto{0}{\langle 2p_z|2s\rangle} + b_1^2 \cancelto{1}{\langle 2p_z|2p_z\rangle} = 1 \tag{10.1.23}$$

and similarly for $\langle\chi_j|\chi_j\rangle$

$$\langle\chi_j|\chi_j\rangle = a_2^2 \cancelto{1}{\langle 2s|2s\rangle} + a_2b_2 \cancelto{0}{\langle 2s|2p_z\rangle} + a_2b_2 \cancelto{0}{\langle 2p_z|2s\rangle} + b_2^2 \cancelto{1}{\langle 2p_z|2p_z\rangle} = 1 \tag{10.1.24}$$

results in the following relationships

$$\langle\chi_i|\chi_i\rangle = a_1^2 + b_1^2 = 1 \tag{10.1.25}$$

$$\langle\chi_j|\chi_j\rangle = a_2^2 + b_2^2 = 1 \tag{10.1.26}$$

and

$$\langle\chi_i|\chi_j\rangle = a_1a_2 + b_1b_2 = 0 \tag{10.1.27}$$

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.

$$a_1 = a_2 \tag{10.1.28}$$

Equations 10.1.25 to 10.1.27 revert to

$$a_1^2 + b_1^2 = 1 \tag{10.1.29}$$

$$a_1^2 + b_2^2 = 1 \tag{10.1.30}$$

$$b_1^2 = b_2^2 \tag{10.1.31}$$

Therefore

$$b_1 = -b_2 \tag{10.1.32}$$

and

$$a_1 = b_1 \tag{10.1.33}$$

Insert Equation \refPeq231} into 10.1.31 to get

$$a_1 = \frac{1}{\sqrt{2}} \tag{10.1.34}$$

and the two hybrid orbitals are

$$\chi_1(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) + \psi_{2p_z}(r)] \tag{10.1.35}$$

$$\chi_2(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) - \psi_{2p_z}(r)] \tag{10.1.36}$$

Note that these orbitals are both normalized and orthogonal:

$$\int |\chi_1(r)|^2 dV = 1\ ;\ \int |\chi_2(r)|^2 dV = 1\ ;\ \int \chi_1^*(r)\chi_2(r) dV = 0 \tag{10.1.37}$$

These orbitals appear as shown in Figure 10.1.3

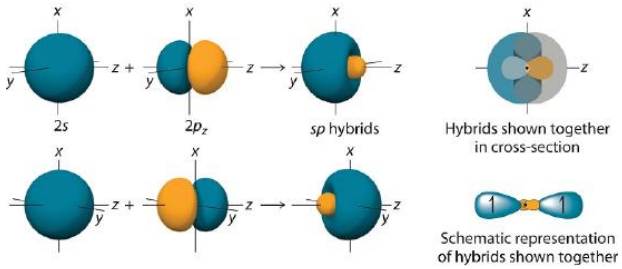


Figure 10.1.3: *The Formation of sp Hybrid Orbitals. Taking the sum and difference of an ns and an np atomic orbital where n = 2 gives two equivalent sp hybrid orbitals oriented at 180° to each other.*

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:

$$\psi_1(1,2) = C_1[\psi_{1s}^{H_1}(1)\chi_1^{Be}(2) + \psi_{1s}^{H_1}(2)\chi_1^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.38}$$

$$\psi_2(1,2) = C_2[\psi_{1s}^{H_2}(1)\chi_2^{Be}(2) + \psi_{1s}^{H_2}(2)\chi_2^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.39}$$

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 hydrogens lies along the positive x axis. The remaining hydrogens would be in the 3rd and 4th quadrants, respectively, as shown in Figure 10.1.4.

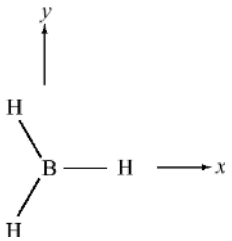


Figure 10.1.4: Geometry of BH_3.

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

$$\psi_{2p_x} \sim \cos\phi \; ; \; \psi_{2p_y} \sim \sin\phi \tag{10.1.40}$$

If we rotate $2p_y$ by -30 degrees (Figure 10.1.5; blue is positive and red is negative), the ϕ dependence becomes

$$\psi_{2p_y}^{(rot)} \sim \sin(\phi + 30) \tag{10.1.41}$$

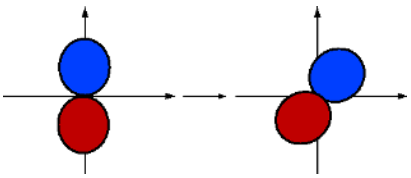


Figure 10.1.5: Rotation of a $2p_y$ orbital by -30 degrees.

Using the fact that

$$\sin(\alpha \pm \beta) = \sin\alpha\cos\beta \pm cos\alpha sin\beta \tag{10.1.42}$$

this rotation gives

$$\psi_{2p_y}^{(rot,1)} \sim sin\phi\cos 30 + \cos\phi\sin 30 \tag{10.1.43}$$

$$\sim \left[\frac{\sqrt{3}}{2}\sin\phi + \frac{1}{2}\cos\phi\right] \tag{10.1.44}$$

$$\sim \left[\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_z}\right] \tag{10.1.45}$$

Similarly, consider rotating $-\psi_{2p_y}$ by $+30$ degrees (Figure 10.1.6). This gives

$$-\psi_{2p_y}^{(rot,2)} \sim -\sin(\phi - 30) \tag{10.1.46}$$

$$\sim -\left[\frac{\sqrt{3}}{2}\sin\phi - \frac{1}{2}\cos\phi\right] \tag{10.1.47}$$

$$\sim -\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_z} \tag{10.1.48}$$

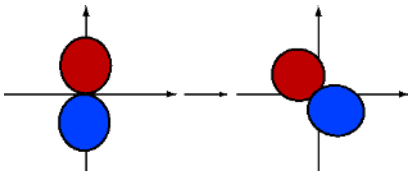


Figure 10.1.6: *Rotation of a $-2p_y$ orbital by 30 degrees.*

So, we now take the hybrid orbitals to be of the form

$$\chi_1(r) = a\psi_{2s}(r) - b\psi_{2p_z} \tag{10.1.49}$$

$$\chi_2(r) = c\psi_{2s}(r) + d\psi_{2p_y}^{(rot,1)}(r) \tag{10.1.50}$$

$$\chi_3(r) = c\psi_{2s}(r) - d\psi_{2p_y}^{(rot,2)}(r) \tag{10.1.51}$$

The coefficients a, b, and c are determined by requiring that the orbitals are normalized and mutually orthogonal:

$$\int |\chi_1(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_2(r)dV = 0 \tag{10.1.52}$$

$$\int |\chi_2(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_3(r)dV = 0 \tag{10.1.53}$$

$$\int |\chi_3(r)|^2 dV = 1 \; ; \; \int \chi_2^*(r)\chi_3(r)dV = 0 \tag{10.1.54}$$

Carrying out the algebra, we obtain the following sp^2 hybrid orbitals:

$$\chi_1(r) = \frac{1}{\sqrt{3}}[\psi_{2s}(r) - \sqrt{2}\psi_{2p_x}(r)] \tag{10.1.55}$$

$$\chi_2(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) + \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.56}$$

$$\chi_3(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) - \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.57}$$

The sp^2 hybrids allow bonding at $120°$ degrees, and these orbitals appear as shown in Figure 10.1.7:

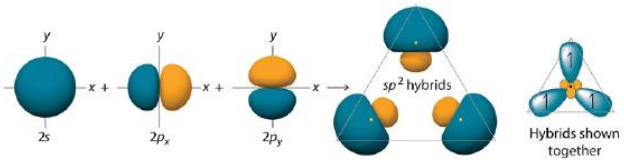


Figure 10.1.7: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

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:

$$\chi_1(r) = \frac{1}{2}[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)] \tag{10.1.58}$$

$$\chi_2(r) = \frac{1}{2}[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)] \tag{10.1.59}$$

$$\chi_3(r) = \frac{1}{2}[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)] \tag{10.1.60}$$

$$\chi_4(r) = \frac{1}{2}[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)] \tag{10.1.61}$$

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.

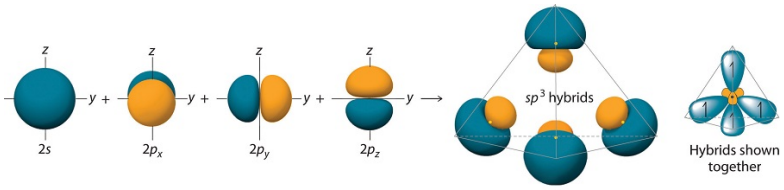


Figure 10.1.8: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

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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10.2: Hybrid Orbitals in Water

The goal of applying Valence Bond Theory to water is to describe the bonding in 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):

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + b_1|2p_y\rangle_O \tag{10.2.1}$$

$$|\chi_2\rangle = a_2|1s\rangle_{H_2} + b_2|2p_z\rangle_O \tag{10.2.2}$$

However, with a 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.

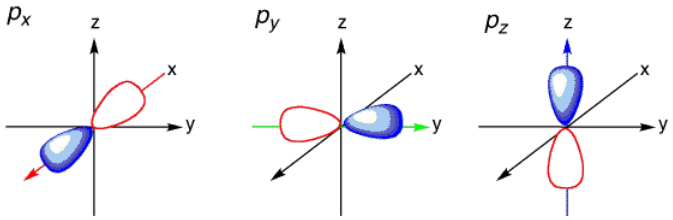


Figure **10.2.1**: The three p-orbitals are aligned along perpendicular axis (CC-SA-BY-NC; Nick Greeves ChemTube3D);

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.

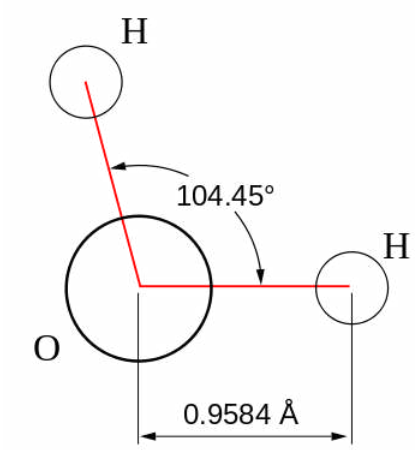


Figure **10.2.2:** Experimentally determined geometry of the water molecule (CC BY-SA 3.0 Booyabazooka).

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°.

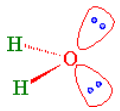


Figure 10.2.4: Among the four hybrid orbitals, two are half filled and the remaining two are completely filled.

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.

Note: A few cautionary words about hybridization.

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.

Estimating Character of Hybrid Orbitals

The terminology we use for hybridization actually is just an abbreviation:

$$\mathrm{sp}^x = \mathrm{s}^{\frac{1}{x+1}}\mathrm{p}^{\frac{x}{x+1}} \tag{10.2.3}$$

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:

$$|\chi_i\rangle = N(p + \gamma s) \tag{10.2.4}$$

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:

$$\langle \chi_i | \chi_i \rangle = 1 \tag{10.2.5}$$

and substituting Equation 10.2.4 into to get

$$\langle N(p + \gamma s) | N(p + \gamma s) \rangle = 1 \tag{10.2.6}$$

which in integral notation is

$$\int N^2 (p + \gamma s)^2 d\tau = 1 \tag{10.2.7}$$

where $d\tau$ represents all space. This is then expanded to

$$N^2 \int p^2 d\tau + N^2 2\gamma \int sp\, d\tau + N^2 \gamma^2 \int s^2 d\tau = 1 \tag{10.2.8}$$

These terms simplify either due to orthogonality or normality of the constitute atomic orbitals. Equation 10.2.8 simplifies to

$$N^2 + N^2 \gamma^2 = 1 \tag{10.2.9}$$

and thus the normalization factor can be expressed in terms of γ

$$N = \frac{1}{\sqrt{1 + \gamma^2}} \tag{10.2.10}$$

and the generic normalized sp^x hybrid orbital (Equation 10.2.4) is

$$|\chi_i\rangle = \frac{1}{\sqrt{1 + \gamma^2}} (p + \gamma s) \tag{10.2.11}$$

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

$$\left(\frac{1}{\sqrt{1+\gamma^2}} \right)^2 = \frac{1}{1 + \gamma^2} \tag{10.2.12}$$

  as $\gamma \rightarrow 0$, then the p character of the hybrid goes to 100%
- The magnitude of s-character is

$$\left(\frac{1}{\sqrt{1+\gamma^2}} \gamma^2 \right)^2 = \frac{\gamma^2}{1 + \gamma^2} \tag{10.2.13}$$

  as $\gamma \rightarrow 1$, 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:

$$\cos\theta = -\gamma^2 \tag{10.2.14}$$

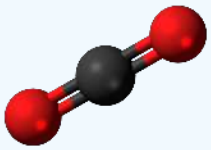
Equation 10.2.14 is an important equation as it related experimentally determined structure to the nature of the bonding and specifically, the composition of the atomic orbitals that create the hybrid orbitals used in the bonding.

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 $\theta = 180°$ and via Equation 10.2.14, $\gamma = 1$ since $\cos 180° = -1$. Hence, Equation 10.2.13 argues that the hybrid orbitals used in the bonding of CO_2 have 50% character; i.e., they are sp hybrid orbitals

$$|\chi_1\rangle = \frac{1}{\sqrt{2}}(s + p) \tag{10.2.15}$$

and

$$|\chi_2\rangle = \frac{1}{\sqrt{2}}(s - p) \tag{10.2.16}$$

Now, let's apply Equation 10.2.13 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

$$\cos 104.5° = -0.25 \tag{10.2.17}$$

and

$$\gamma = \sqrt{0.25} = 0.5 \tag{10.2.18}$$

From Equation 10.2.12, then the amount of p character in the hybrid orbitals are

$$\frac{1}{1+\gamma^2} = \frac{1}{1+0.5^2} = 0.80\% \tag{10.2.19}$$

which leave 20% for s character (Equation 10.2.13).

$$\frac{\gamma^2}{1+\gamma^2} = \frac{0.5^2}{1+0.5^2} = 0.20 \tag{10.2.20}$$

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:

$$0.8 + 0.8 + x + x = 3 \tag{10.2.21}$$

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 10.2.12 and 10.2.14

- p-character:

$$\frac{1}{1+\gamma^2} = 0.7 \tag{10.2.22}$$

so

$$-\gamma^2 = \frac{1}{0.7 - 1} = -0.42 \tag{10.2.23}$$

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.

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10.3: Why is BeH_2 Linear and H_2O 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:

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_2\,|1s\rangle_{H_2} + a_3|\,2s\rangle_A + a_4\,|2p_x\rangle_A + a_5|\,2p_y\rangle_A + a_6|2p_z\rangle_A \tag{10.3.1}$$

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 10.3.1 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 10.3.1 can be simplified to consider the combination

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_1\,|1s\rangle_{H_2} + a_3|\,2s\rangle_A + a_6|2p_z\rangle_A \tag{10.3.2}$$

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.

> 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 10.3.1 are shown in Figure 10.3.1.

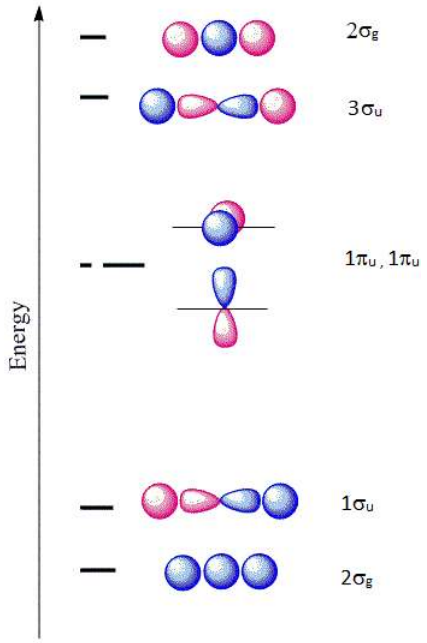


Figure 10.3.1: The six molecular orbitals for the AH_2 molecule constrained to a linear geometry. The symmetry labels for each molecular orbital are indicated.

The first molecular orbital $|\chi_1\rangle$ constructed from Equation 10.3.1 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:

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A \tag{10.3.3}$$

$$|\chi_6\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} - a_3|2s\rangle_A \tag{10.3.4}$$

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

$$|\chi_2\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A \tag{10.3.5}$$

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

$$|\chi_5\rangle = a_1|1s\rangle_{H_1} - a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A \tag{10.3.6}$$

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:

$$|\chi_3\rangle = |2p_x\rangle_A \tag{10.3.7}$$

$$|\chi_4\rangle = |2p_y\rangle_A \tag{10.3.8}$$

Beryllium Hydride (BeH_2) is Linear

Consider the 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 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 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 2 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**.

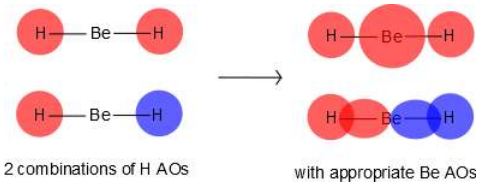


Figure **10.3.2**: Forming molecular orbitals for BeH_2.

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.

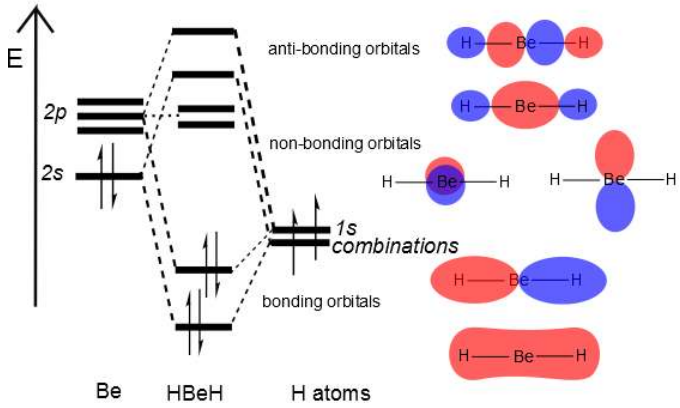


Figure **10.3.3**: *Molecular orbitals diagram for BeH_2.*

Walsh Correlation Diagrams

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).

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 H_2O and 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.

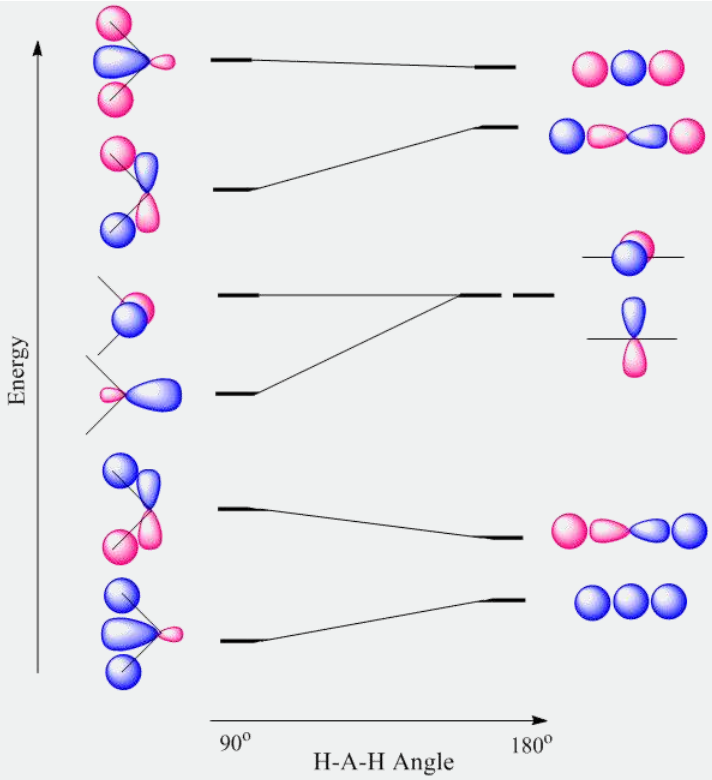


Figure **10.3.4**: A Walsh diagram for an AH_2 molecule. (public domain).

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.

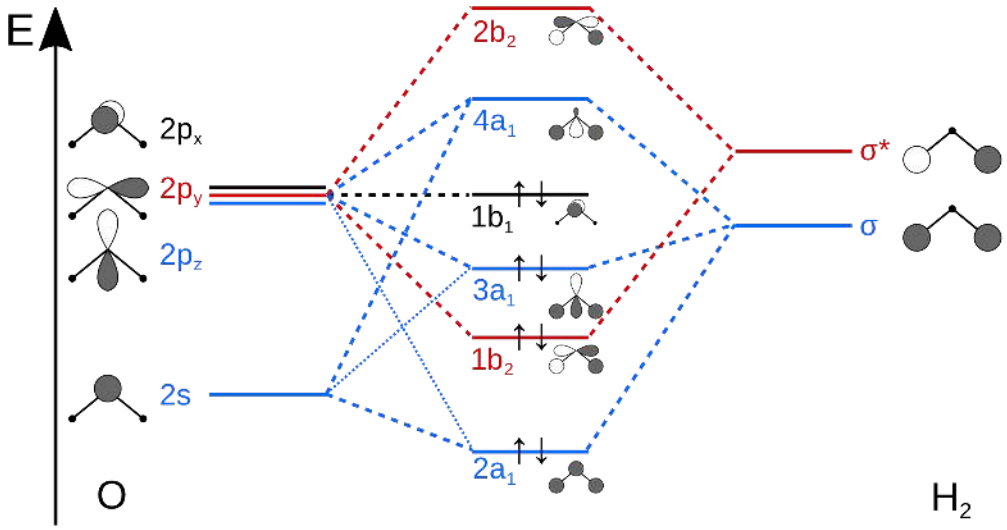


Figure **10.3.5**: MO diagram for water. (CC-SA-BY-3.0; Officer781).

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

$$(a_1)^2(b_2)^2(a_1)^2(b_1)^2 \tag{10.3.9}$$

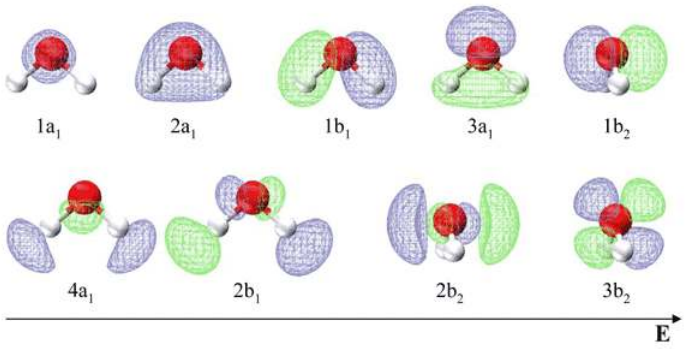


Figure **10.3.5**. Image from Anna Krylov (USC)

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 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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10.4: Photoelectron Spectroscopy

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 spectroscopy is 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:

$$E = h\nu \tag{10.4.1}$$

where h is Planck constant (6.62 x 10^{-34} J s) 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 Module.

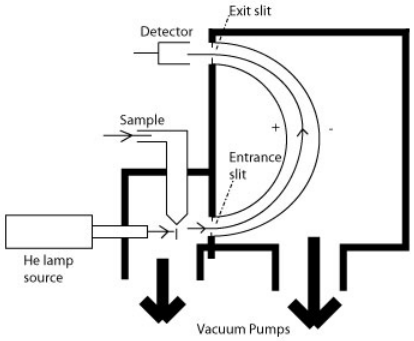


Figure 10.4.1: Diagram of a basic, typical PES instrument used in UPS, where the radiation source is an UV light source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit.

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. The process of photoionization can be considered in several ways. One way is to look at the overall process as follows:

$$A + \text{photon} \rightarrow A^+ + e^- \tag{10.4.2}$$

Conservation of energy then requires that (after using Equation 10.4.1):

$$E(A) + h\nu = E(A^+) + E(e^-) \tag{10.4.3}$$

Since the free electron's energy is present solely as kinetic energy (KE)

$$E(e^-) = KE \tag{10.4.4}$$

Equation 10.4.3 can then be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - [E(A^+) - E(A)] \tag{10.4.5}$$

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:

$$KE = h\nu - IE \tag{10.4.6}$$

or

$$IE = h\nu - KE \tag{10.4.7}$$

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 (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.

At the molecular orbitalst 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.

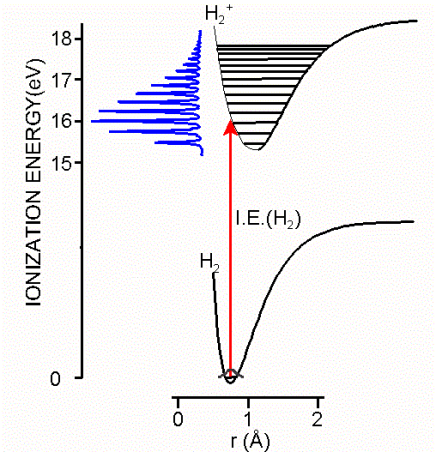


Figure **10.4.2**: Vertical ionization process for molecular hydrogen.

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states as shown in Equation 10.4.7 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.

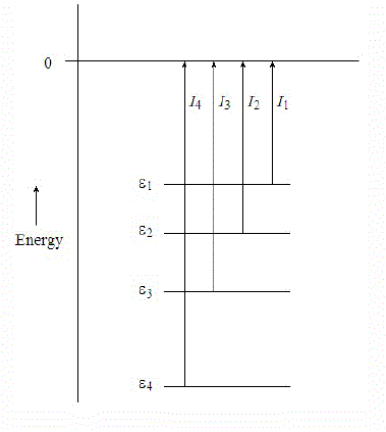


Figure **10.4.3**: Within Koopmans' Theorem, the energies of the orbitals have an attractively simple physical interpretation: they give the amount of energy necessary to remove (ionize) the electron out of the molecular orbital, which corresponds to the negative of the experimentally observable ionization potential:

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, provided the distributions of the remaining electrons do not change (i.e., frozen).

$$I_j = -\epsilon_j \tag{10.4.8}$$

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.

Koopmans' Theorem

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

$$M(X, v''=0) + h\nu \rightarrow M^+(x, v'=0) + e^- \tag{10.4.9}$$

  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

$$M(X, v''=0) + h\nu \rightarrow M^+(x, v'=n) + e^- \tag{10.4.10}$$

  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.

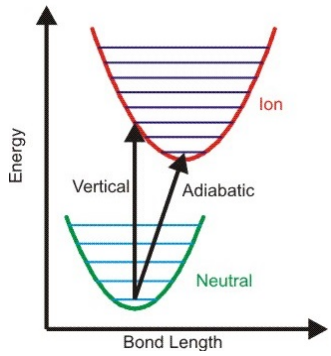


Figure **10.4.4**: Difference between vertical and adiabatic ionization energies for a simple harmonic oscillator system.

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

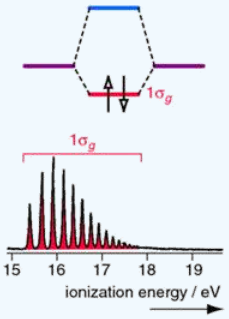
You have been exposed to three metrics of ionization energies already, which are similar, but with distinct differences:

- 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

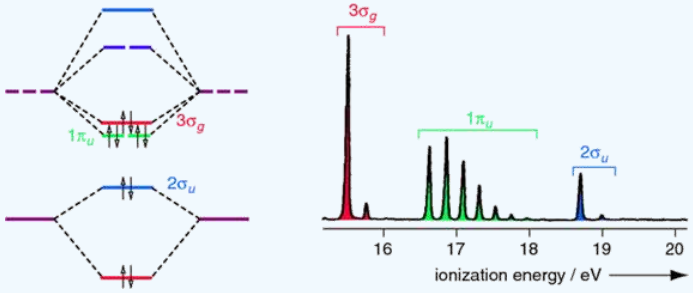
As you remember, the molecular orbital description of hydrogen involves two $|1s\rangle$ atomic orbitals generating a bonding $1\sigma_g$ and antibonding $2\sigma_u^*$ molecular orbitals. The two electrons that are responsible for the H_2 bond are occupied in the $1\sigma_g$.



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.



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

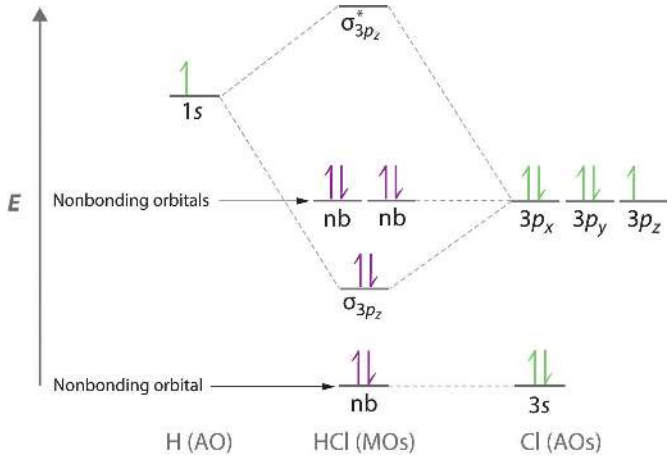


Figure 10.4.5: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts molecular orbitals strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

Important aspects of molecular orbital diagram in Figure 10.4.5:

- The H 1*s* 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 1*s* 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 primairly of H 1*s* 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 3*s* bonding molecular orbital (vibrational structure).

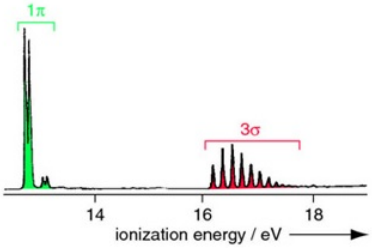


Figure 10.4.6: Photoelectron spectrum and MO diagram of HCl.

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 $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^2$.

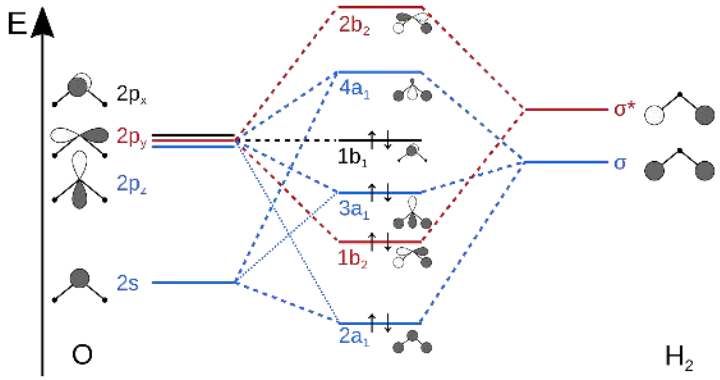


Figure **10.4.7**: MO diagram for water. (CC-SA-BY-3.0; Officer781).

The Hartree–Fock orbital energies (with sign changed) of these orbitals are tablulated 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.

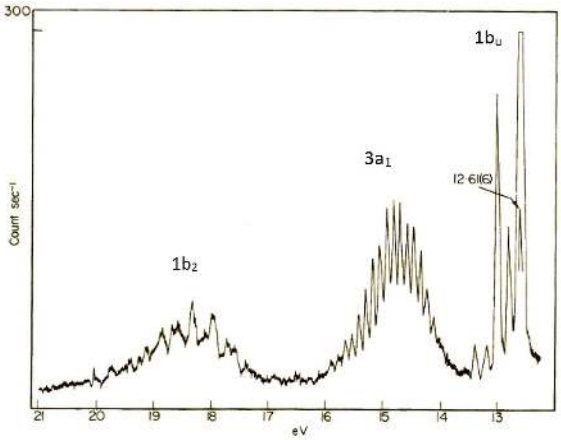


Figure **10.4.8**: Photoelectron spectrum of water. Note the energy axes is flipped compared to other spectra on this page.his spectrum does not go to high enough energy to show the deep $2a_1$ molecular orbital.

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. Despire 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 ner structure showing ionization to di erent vibrational levels.

Contributors

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- http://www.forgottenplanet.com (permission pending)

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10.5: The π -Electron Approximation of Conjugation

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 H–C–H and 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**).

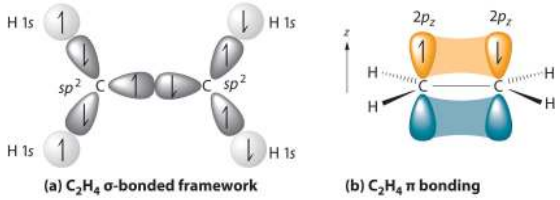


Figure **10.5.1**: (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1*s* orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one 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.)

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, 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**).

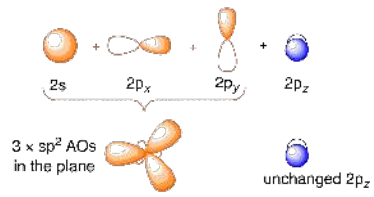


Figure **10.5.2**: Hybridizing of the carbon atomic orbitals to give sp^2 hybrid orbitals for bonding to hydrogen atoms in ethylene. from ChemTube (CC-SA-BY-NC; Nick Greeves).

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.

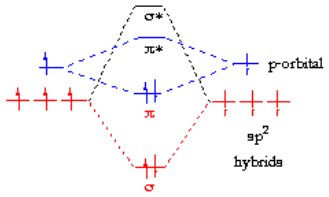


Figure 10.5.3: Molecular orbitals demonstrating the *sigma-pi separability* of the π-*bonding framework (blue) and the* σ-*bonding frameworks (red) of ethylene.*

> *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:

$$|\psi_i\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \tag{10.5.1}$$

This equation is substituted in the Schrödinger equation:

$$\hat{H}\,|\psi_i\rangle = E_i|\,\psi_i\rangle \tag{10.5.2}$$

with $\hat{H}$ the Hamiltonian and E_i the energy corresponding to the molecular orbital to give:

$$\hat{H}c_1\left|\phi_1\right\rangle + \hat{H}c_2\left|\,\phi_2\right\rangle = Ec_1\,|\phi_1\rangle + Ec_2|\,\phi_2\rangle \tag{10.5.3}$$

If Equation 10.5.3 is multiplied by $\langle\phi_1|$ (and integrated), then

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{10.5.4}$$

where H_{ij} are the Hamiltonian matrix elements (see note below)

$$H_{ij} = \langle\phi_i\left|\hat{H}\right|\phi_j\rangle = \int \phi_i H \phi_j \mathrm{d}v \tag{10.5.5}$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle\phi_i|\phi_j\rangle = \int \phi_i\phi_j \mathrm{d}v \tag{10.5.6}$$

If Equation 10.5.3 is multiplied by $\langle\phi_2|$ (and integrated), then

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \tag{10.5.7}$$

Both Equations 10.5.4 and 10.5.7 can better represented in matrix notation,

$$\begin{bmatrix} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) \\ c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) \end{bmatrix} = 0 \tag{10.5.8}$$

or more simply as a product of matrices.

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.9}$$

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 10.5.9 are called the *secular equations* and will also have the trivial solution of

$$c_1 = c_2 = 0 \tag{10.5.10}$$

Within linear algebra, the secular equations in Equation 10.5.9 will also have a non-trivial solution, if and only if, the secular determinant is zero

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{10.5.11}$$

or in shorthand notation

$$\det(H - ES) = 0 \tag{10.5.12}$$

Everything in Equation 10.5.11 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)

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{21} - ES_{21})(H_{12} - ES_{12}) = 0 \tag{10.5.13}$$

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 10.5.1). 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

$$H_{11} = H_{22} = \alpha \tag{10.5.14}$$

$$H_{12} = H_{21} = \beta \tag{10.5.15}$$

Assumptions 1 means that the overlap integral between the two atomic orbitals is 0

$$S_{11} = S_{22} = 1 \tag{10.5.16}$$

$$S_{12} = S_{21} = 0 \tag{10.5.17}$$

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 10.5.9 in two homogeneous equations:

$$\begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.18}$$

if Equation 10.5.18 is divided by β:

$$\begin{bmatrix} \frac{\alpha - E}{\beta} & 1 \\ 1 & \frac{\alpha - E}{\beta} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.19}$$

and then a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{10.5.20}$$

then Equation 10.5.18 simplifies to

$$\begin{bmatrix} x & 1 \\ 1 & x \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.21}$$

The trivial solution gives both wavefunction coefficients equal to zero and the other (non-trivial) solution is determined by solving the secular determinant

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \tag{10.5.22}$$

which when expanded is

$$x^2 - 1 = 0 \tag{10.5.23}$$

so

$$x = \pm 1 \tag{10.5.24}$$

Knowing that $E = \alpha - x\beta$ from Equation 10.5.20, the energy levels can be found to be

$$E = \alpha - \pm 1 \times \beta \tag{10.5.25}$$

or

$$E = \alpha \mp \beta \tag{10.5.26}$$

Since β is negative, the two energies are ordered (Figure 10.5.4)

- For π_1: $E_1 = \alpha + \beta$

- For π_2: $E_2 = \alpha - \beta$

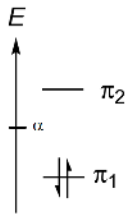


Figure 10.5.4: π energies of ethylene with occupation.

To extract the coefficients attributed to these energies, the corresponding x values can be substituted back into the Secular Equations (Equation 10.5.21). For the lower energy state ($x = -1$)

$$\begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.27}$$

This gives $c_1 = c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 10.5.1):

$$\psi_1\rangle = N_1(\phi_1\rangle + |\phi_2\rangle) \tag{10.5.28}$$

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

$$\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.29}$$

This gives $c_1 = -c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 10.5.1):

$$\psi_2\rangle = N_2(\phi_1\rangle - |\phi_2\rangle) \tag{10.5.30}$$

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

$$N_1 = N_2 = \frac{1}{\sqrt{2}} \tag{10.5.31}$$

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.

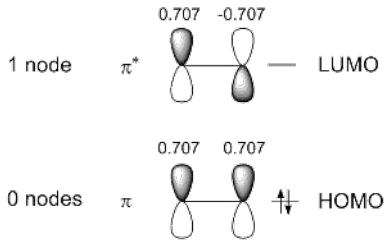


Figure 10.5.5: Schemetic representation of the π molecular orbitals framework for ethylene . Notice that the antibonding molecular orbital has one more node than the bonding molecular orbital as expected since it is higher in energy.

> *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.

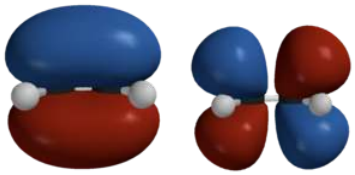


Figure* 10.5.6*: *Calculated π molecular orbitals for ethylene . (left) the bonding orbital (\|\psi_1 \rangle\) and (right) the antibonding ($|\psi_2\rangle$) orbital.*

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.

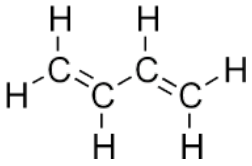
Contributors

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- Wikipedia
- StackExchange (Philipp)

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10.6: Butadiene is Stabilized by a Delocalization Energy

1,3-Butadiene is a simple conjugated diene with the formula C_4H_6 and can be viewed structurally as two vinyl groups ($CH_2=CH_2$) 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 4 $|p\rangle$ atomic orbitals at on the carbon atoms:

$$|\Psi_i\rangle = \sum_i^4 c_{ij}\Big|p_i\rangle \tag{10.6.1}$$

or explicitly

$$|\Psi_i\rangle = c_{i1}|p_1\rangle + c_{i2}\,|p_2\rangle + c_{i3}|\,p_3\rangle + c_{i4}|p_4\rangle \tag{10.6.2}$$

for the ith molecular orbital $|\Psi_i\rangle$. The secular equations that need to be solved are

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{10.6.3}$$

If the standard Hückel theory approximations were used

$$H_{ii} - ES_{ii} = \alpha \tag{10.6.4}$$

and

$$H_{ij} - ES_{ij} = \beta \tag{10.6.5}$$

when $i = j \pm 1$, otherwise

$$H_{ij} - ES_{ij} = 0 \tag{10.6.6}$$

then the secular equations for butadience in Equation 10.6.3 become

$$\begin{bmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{10.6.7}$$

Solving Equation 10.6.7 for $\{c_i\}$ coefficients and energy secular equation requires extracting the roots of the secular determinant:

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0 \tag{10.6.8}$$

If both sides of Equation 10.6.8 were divided by β^4 and a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{10.6.9}$$

then Equation 10.6.8 simplifies further to

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{10.6.10}$$

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 10.6.10 gives the 4th order polynomial equation

$$x^4 - 3x^2 + 1 = 0 \tag{10.6.11}$$

While solving 4th order equations typically require numerical estimation, Equation 10.6.11 can be further simplified by recognizing that it is a quadratic equation in terms of x^2. Therefore, the roots are

$$x^2 = \frac{3 \pm \sqrt{5}}{2} \tag{10.6.12}$$

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):

$$E_1 = \alpha + 1.618\beta \tag{10.6.13}$$

$$E_2 = \alpha + 0.618\beta \tag{10.6.14}$$

$$E_3 = \alpha - 0.618\beta \tag{10.6.15}$$

$$E_4 = \alpha - 1.618\beta \tag{10.6.16}$$

This sequence of energies is displayed in the energy diagram of Figure 10.6.1.

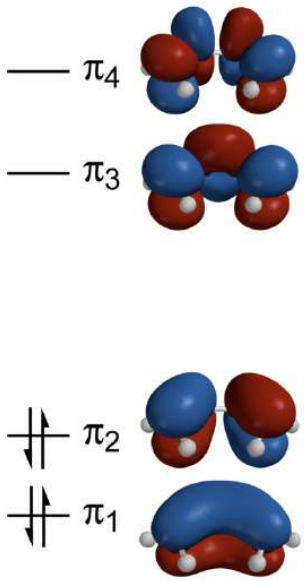


Figure 10.6.1: The π molecular orbital energies from Hückel theory for butadiene with ground-state configuration. Structures calculated and images produced using HF/6-31G* (Public Domain; Ben Mills).

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 10.6.13-10.6.16 and scaling by their occupations to get

$$E_\pi(butadiene) = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) = 4\alpha + 4.472\beta \tag{10.6.17}$$

If butadiene were described as two localized double bond (as in its dominant valence-bond structure), then its π-electron energy would be given by twice the E_π predicted for the ethlyene molecule:

$$2 \times E_{\pi}(ethylene) = 2 \times 2(\alpha + \beta) = 4\alpha + 4\beta \tag{10.6.18}$$

Comparing Equation 10.6.17 with Equation 10.6.17, 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

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.

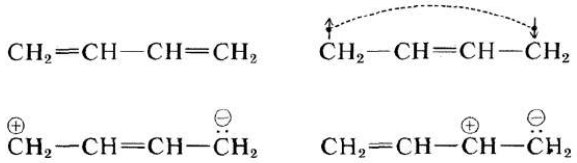


Figure **10.6.2**: Several resonance structures that can be written for 1,3-butadiene. The resonance structure in the upper left dominates, but does not exclusively describe the system since a delocalization energy is experimentally observed compared to two ethylene molecules. (John D. Robert and Marjorie C. Caserio).

In general, the true description of the bonidng 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 also gives the $\{c_{ij}\}$ coefficients for the molecular orbitals in Equation 10.6.2 (not demonstrated):

$$|\Psi_1\rangle = 0.37|p_1\rangle + 0.60\,|p_2\rangle + 0.60|\,p_3\rangle + 0.37|p_4\rangle \tag{10.6.19}$$

$$|\Psi_3\rangle = 0.60|p_1\rangle + 0.37\,|p_2\rangle - 0.37|\,p_3\rangle - 0.60|p_4\rangle \tag{10.6.20}$$

$$|\Psi_3\rangle = 0.60|p_1\rangle - 0.37\,|p_2\rangle - 0.37|\,p_3\rangle + 0.60|p_4\rangle \tag{10.6.21}$$

$$|\Psi_4\rangle = 0.37|p_1\rangle - 0.60\,|p_2\rangle + 0.60|\,p_3\rangle - 0.37|p_4\rangle \tag{10.6.22}$$

These are depicted in Figure **10.6.3**.

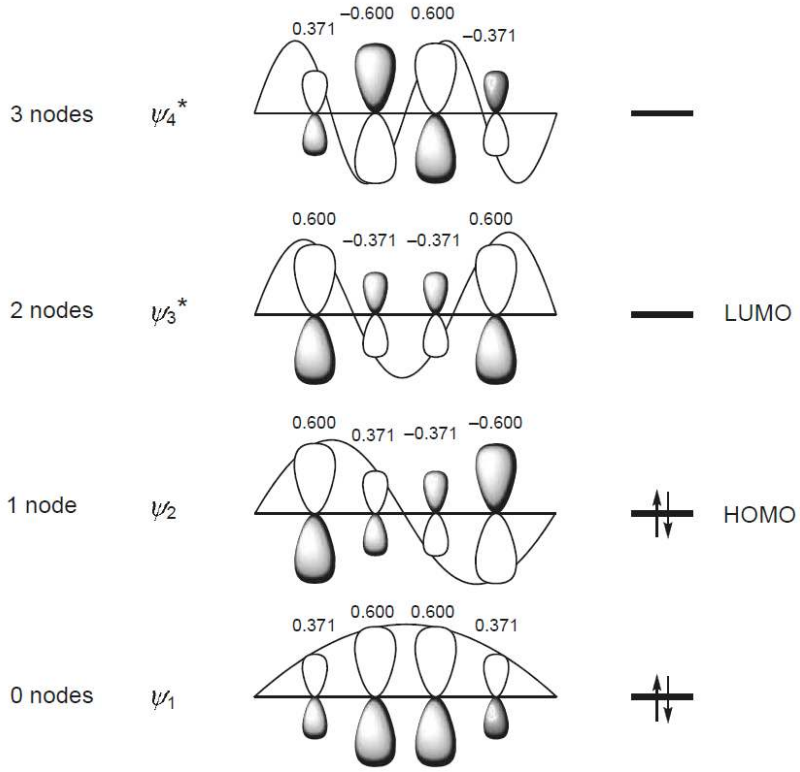


Figure **10.6.3**: Energy level diagram and decomposition of the π molecular orbitals of butadiene.

Not the correlation of the energy of the wavefunctions to the number of nodes in the wavefunction; this is the general trend observed in previous systems like the particles in the box and atomic orbitals. The four 3-D calculated molecular orbitals are contrasted in Figure **10.6.1**:

Aromaticity in Benzene

Aromatic systems provide the most significant applications of Hückel theory. For benzene, we find the secular equation

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{10.6.23}$$

with the **six roots** $x = \pm 2, \pm 1, \pm 1$. The energy levels are $E = \alpha \pm 2\beta$ and two-fold degenerate $E = \alpha \pm \beta$. With the three lowest MO's occupied, we have

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta \tag{10.6.24}$$

Since the energy of three localized double bonds is $6\alpha + 6\beta$, the delocalization energy equals 2β. The thermochemical value is -152 kJmol^{-1}.

Contributors

- Wikipedia
- Anonymous

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10.7: Benzene and Aromaticity

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 C_nH_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 (C_6H_6) with $n = 6$, although many other molecules exist like cyclobutadiene (C_4H_4) with $n = 4$ (Figure 10.7.1).

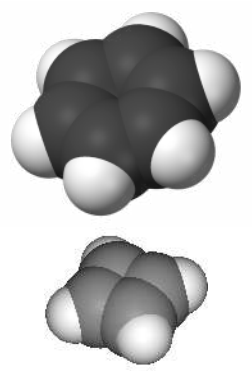


Figure 10.7.1: Space-filling model of benzene (left) and cyclobutadiene (right). Carbon atoms are indicated in black, while hydrogen atoms are indicated in white. (Public domain; Benjah-bmm27 and Edgar181, *respectively).*

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.

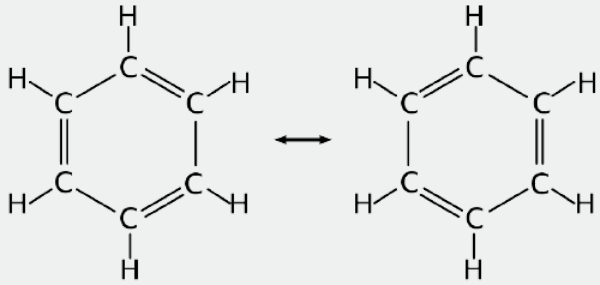


Figure 10.7.2: Resonance structures of benzene.

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 structures 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

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{10.7.1}$$

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**).

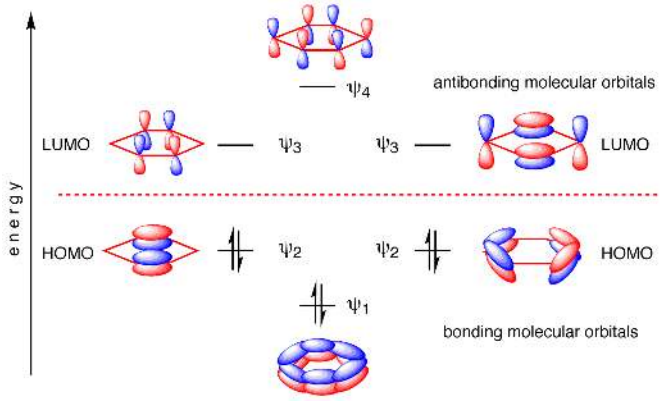


Figure **10.7.3**: The π molecular orbitals for benzene. The dashed lines represenet teh energy of an isolated p orbitals and all orbitals below this line are bonding. All orbitals above it are antibonding. Image used withpermission (CC-SA_BY-NC; ChemTube3D by Nick Greeves).

The resulting wavefunctions are below (expanded in terms of carbon $|2p\rangle$ atomic orbitals).

$$|\psi_1\rangle = \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle\right] \tag{10.7.2}$$

$$|\psi_2\rangle = \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle\right] \tag{10.7.3}$$

$$|\psi_3\rangle = \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle + \frac{1}{2}\left|2p_{z2}\right\rangle - \frac{1}{2}\left|2p_{z3}\right\rangle - \left|2p_{z4}\right\rangle - \frac{1}{2}\left|2p_{z5}\right\rangle + \frac{1}{2}|2p_{z6}\rangle\right] \tag{10.7.4}$$

$$|\psi_4\rangle = \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle\right] \tag{10.7.5}$$

$$|\psi_5\rangle = \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle - \frac{1}{2}\left|2p_{z2}\right\rangle - \frac{1}{2}\left|2p_{z3}\right\rangle + \left|2p_{z4}\right\rangle - \frac{1}{2}\left|2p_{z5}\right\rangle - \frac{1}{2}|2p_{z6}\rangle\right] \tag{10.7.6}$$

$$|\psi_6\rangle = \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle\right] \tag{10.7.7}$$

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

$$E_{tot}(benzene) = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta \tag{10.7.8}$$

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

$$\Delta E = E_{tot}(benzene) - 3E_{tot}(ethylene) = (6\alpha + 8\beta) - 3 \times 2(\alpha + \beta) = 2\beta \tag{10.7.9}$$

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) π 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 10.7.8), 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) 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. 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**). 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 additonal stability is a characteristic of all aromatic compounds.

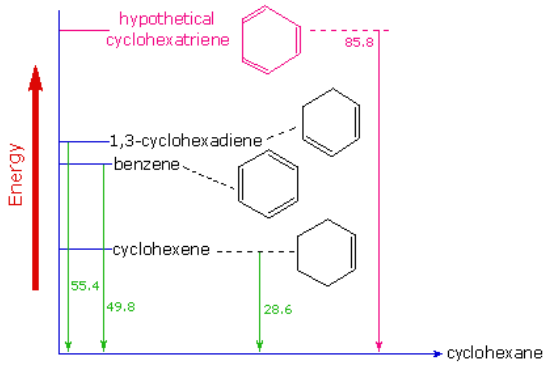


Figure **10.7.4**: Experimental evidence for aromatic stabilization energy in benenze from the heat of hydrogenation. Energies are in kcal/mol. (CC-SA-BY-NC; William Resuch);

Contributors

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Wikipedia

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10.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:

$$|1\rangle = \frac{1}{2}(|s\rangle + \left|p_x\right\rangle + |p_y\rangle + |p_z\rangle)$$

$$|2\rangle = \frac{1}{2}(|s\rangle - \left|p_x\right\rangle - |p_y\rangle + |p_z\rangle)$$

$$|3\rangle = \frac{1}{2}(|s\rangle + \left|p_x\right\rangle - |p_y\rangle - |p_z\rangle)$$

$$|4\rangle = \frac{1}{2}(|s\rangle - \left|p_x\right\rangle + |p_y\rangle - |p_z\rangle)$$

Normality:

$$\langle 1|1\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| + \langle p_y| + \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{10.E.1}$$

$$= \frac{1}{4}(\langle s|s\rangle + \langle s|p_x\rangle + \langle s|p_y\rangle + \langle s|p_z\rangle + \langle p_x|s\rangle + \langle p_x|p_x\rangle + \langle p_x|p_y\rangle + \langle p_x|p_z\rangle + \langle p_y|s\rangle + \langle p_y|p_x\rangle + \langle p_y|p_y\rangle + \langle p_y|p_z\rangle + \langle p_z|s\rangle + \langle p_z|p_x\rangle + \langle p_z|p_y\rangle + \langle p_z|p_z\rangle) \tag{10.E.2}$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{10.E.3}$$

$$\langle 2|2\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| - \langle p_y| + \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle)\right) \tag{10.E.4}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle s|p_x\rangle - \langle s|p_y\rangle + \langle s|p_z\rangle - \langle p_x|s\rangle + \langle p_x|p_x\rangle + \langle p_x|p_y\rangle - \langle p_x|p_z\rangle - \langle p_y|s\rangle + \langle p_y|p_x\rangle + \langle p_y|p_y\rangle - \langle p_y|p_z\rangle + \langle p_z|s\rangle - \langle p_z|p_x\rangle - \langle p_z|p_y\rangle + \langle p_z|p_z\rangle) \tag{10.E.5}$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{10.E.6}$$

$$\langle 3|3\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| - \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle)\right) \tag{10.E.7}$$

$$= \frac{1}{4}(\langle s|s\rangle + \langle s|p_x\rangle - \langle s|p_y\rangle - \langle s|p_z\rangle + \langle p_x|s\rangle + \langle p_x|p_x\rangle - \langle p_x|p_y\rangle - \langle p_x|p_z\rangle - \langle p_y|s\rangle - \langle p_y|p_x\rangle + \langle p_y|p_y\rangle + \langle p_y|p_z\rangle - \langle p_z|s\rangle - \langle p_z|p_x\rangle + \langle p_z|p_y\rangle + \langle p_z|p_z\rangle) \tag{10.E.8}$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{10.E.9}$$

$$\langle 4|4\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| + \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle)\right) \tag{10.E.10}$$

$$= \frac{1}{4} \tag{10.E.11}$$
$$(\langle s|s\rangle - \langle s|p_x\rangle + \langle s|p_y\rangle - \langle s|p_z\rangle - \langle p_x|s\rangle + \langle p_x|p_x\rangle - \langle p_x|p_y\rangle + \langle p_x|p_z\rangle + \langle p_y|s\rangle$$
$$- \langle p_y|p_x\rangle + \langle p_y|p_y\rangle - \langle p_y|p_z\rangle - \langle p_z|s\rangle + \langle p_z|p_x\rangle - \langle p_z|p_y\rangle + \langle p_z|p_z\rangle)$$

$$= \frac{1}{4}(1+0+0+0+0+1+0+0+0+0+1+0+0+0+0+1) = 1 \tag{10.E.12}$$

Orthogonality:

For the longer wavefunctions, only surviving terms in the dot product are included:

$$\langle 1|2\rangle = \langle 2|1\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| - \langle p_y| + \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{10.E.13}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle - \langle p_y|p_y\rangle + \langle p_z|p_z\rangle) = \frac{1}{4}(1-1-1+1) = 0 \tag{10.E.14}$$

$$\langle 1|3\rangle = \langle 3|1\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| - \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{10.E.15}$$

$$= \frac{1}{4}(\langle s|s\rangle + \langle p_x|p_x\rangle - \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1+1-1-1) = 0 \tag{10.E.16}$$

$$\langle 1|4\rangle = \langle 4|1\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| + \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle)\right) \tag{10.E.17}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle + \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1-1+1-1) = 0 \tag{10.E.18}$$

$$\langle 2|3\rangle = \langle 3|2\rangle = \left(\frac{1}{2}(\langle s| + \langle p_x| - \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle)\right) \tag{10.E.19}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle + \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1-1+1-1) = 0 \tag{10.E.20}$$

$$\langle 2|4\rangle = \langle 4|2\rangle = \left(\frac{1}{2}(\langle s| - \langle p_x| + \langle p_y| - \langle p_z|)\right)\left(\frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle)\right) \tag{10.E.21}$$

$$= \frac{1}{4}(\langle s|s\rangle + \langle p_x|p_x\rangle - \langle p_y|p_y\rangle - \langle p_z|p_z\rangle) = \frac{1}{4}(1+1-1-1) = 0 \tag{10.E.22}$$

$$\langle 3|4\rangle = \langle 4|3\rangle = (\frac{1}{2}(\langle s\Big| - \langle p_x\Big| + \langle p_y| - \langle p_z|))(\frac{1}{2}(|s\rangle + |p_x\rangle - \Big|p_y\rangle - \Big|p_z\rangle)) \tag{10.E.23}$$

$$= \frac{1}{4}(\langle s|s\rangle - \langle p_x|p_x\rangle - \langle p_y|p_y\rangle + \langle p_z|p_z\rangle) = \frac{1}{4}(1-1-1+1) = 0 \tag{10.E.24}$$

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:

$$\psi_1 = \left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{4}}\right)\mathbf{i} + \frac{1}{\sqrt{4}}\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k} \tag{10.E.25}$$

$$\psi_2 = \left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{4}}\right)\mathbf{i} + \frac{1}{\sqrt{4}}\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k}$$

$$\psi_3 = -\frac{1}{\sqrt{4}}\mathbf{i} + \left(-\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{4}}\right)\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k} \tag{10.E.26}$$

$$\psi_4 = -\frac{1}{\sqrt{4}}\mathbf{i} + \left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{4}}\right)\mathbf{j} - \frac{1}{\sqrt{12}}\mathbf{k}$$

$$\psi_5 = \left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\mathbf{k} \qquad \psi_6 = \left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\mathbf{k} \tag{10.E.27}$$

For any two ψ the angel can be calculated using:

$$\left(\sqrt{A_x^2 + A_y^2 + A_z^2}\right)\left(\sqrt{B_x^2 + B_y^2 + B_z^2}\right) cos\theta = A_xB_x + A_yB_y + A_zB_z \tag{10.E.28}$$

So, choosing ψ_5 and ψ_6 we get:

$$\left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right) cos\theta = \left(-\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right)\left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{12}}\right) \tag{10.E.29}$$

$$-\frac{5}{12} cos\theta = -\frac{5}{12} \tag{10.E.30}$$

$$cos\theta = 0 \tag{10.E.31}$$

$$\theta = 90^\circ \tag{10.E.32}$$

Q10.10

Given

$$\xi_1 = \frac{1}{\sqrt{4}}2s + \sqrt{\frac{3}{4}}2p_z \tag{10.E.33}$$

$$\xi_2 = \frac{1}{\sqrt{4}}2s + \sqrt{\frac{2}{3}}2p_x - \frac{1}{\sqrt{12}}2p_z \tag{10.E.34}$$

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

$$(\sqrt{A_x^2 + A_y^2 + A_z^2})(\sqrt{B_x^2 + B_y^2 + B_z^2}) \cos\theta = A_xB_x + A_yB_y + A_zB_z \tag{10.E.35}$$

When we plug in our constants in the x, y, and z directions for the two equations we get

$$(\sqrt{\frac{2}{3} + \frac{1}{12}})(\sqrt{\frac{3}{4}}) \cos\theta = -\sqrt{\frac{1}{12}}\sqrt{\frac{3}{4}} \tag{10.E.36}$$

isolating the theta term we get

$$\theta = \arccos(-\sqrt{\frac{1}{12}}/\sqrt{\frac{12}{9}} \tag{10.E.37}$$

yielding

$$\theta = 109.47^{\circ} \tag{10.E.38}$$

The square root constants are the necessary normalization constants.

Q10.11

Given that

$$\psi_1 = 0.71j + 0.55k \tag{10.E.39}$$

and

$$\psi_2 = -0.71j + 0.55k \tag{10.E.40}$$

Find the bond angle between ψ_1 and ψ_2 using the vector approach.

S10.11

Using this equation below:

$$\left(\sqrt{A_x^2 + A_y^2 + A_z^2}\right)\left(\sqrt{B_x^2 + B_y^2 + B_z^2}\right) cos\theta = A_xB_x + A_yB_y + A_zB_z \tag{10.E.41}$$

use to find the angle between the orbitals,

$$(0.71^2 + 0.55^2)^{0.5}(0.71^2 + 0.55^2)^{0.5} cos\theta = -0.71^2 + 0.55^2 \tag{10.E.42}$$

$$cos\theta = -0.25 \tag{10.E.43}$$

$$\theta = 104.5^{\circ} \tag{10.E.44}$$

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

$$\psi_1 = N[\gamma 2s + (sin[\theta]2p_y + cos[\theta]2p_z] \tag{10.E.45}$$

and

$$\psi_2 = N[\gamma 2s - (sin[\theta]2p_y + cos[\theta]2p_z]. \tag{10.E.46}$$

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.

$$\psi_{bonding} = N[\gamma 2_s + c_1 2p_y + c_2 2p_z] \tag{10.E.47}$$

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

$$\psi_1 = N[\gamma 2s + (sin[\theta]2p_y + cos[\theta]2p_z) \tag{10.E.48}$$

and

$$\psi_2 = N[\gamma 2s - (sin[\theta]2p_y + cos[\theta]2p_z) \tag{10.E.49}$$

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.

$$\langle \psi_1 | \psi_2 \rangle = 0 \tag{10.E.50}$$

$$N^2(\gamma^2 + cos^2[\theta] - sin^2[\theta]) \tag{10.E.51}$$

$$\gamma^2 = sin^2[\theta] - cos^2[\theta] \tag{10.E.52}$$

The bond angles in water are 104.5° which can be substituted into θ.

$$\gamma = 0.5 \tag{10.E.53}$$

Q10.13

The lone pair wave functions of H2O can be described as:

$$\psi_{l1} = 0.54(2s) - 0.44(2pz) + 0.72(2px) \tag{10.E.54}$$

$$\psi_{l2} = 0.54(2s) - 0.44(2pz) - 0.72(2px) \tag{10.E.55}$$

Confirm the orthonormality of these wave functions.

S10.13

The two wave functions must be normalized and orthogonal to each other.

$$\int d\tau \psi_{l1}^* \psi_{l1} = 1 \tag{10.E.56}$$

$$= (0.54)^2(2s) + (-0.44)^2(2pz) + (0.72)^2(2px) = 1 \tag{10.E.57}$$

$$\int d\tau \psi_{l2}^* \psi_{l2} = 1 \tag{10.E.58}$$

$$= (0.54)^2(2s) + (-0.44)^2(2pz) + (-0.72)^2(2px) = 1 \tag{10.E.59}$$

$$\int d\tau \psi_{l1}^* \psi_{l2} = 0 \tag{10.E.60}$$

$$= (0.54)^2(2s) + (-0.44)^2(2pz) - (0.72)^2(2px) = 0 \tag{10.E.61}$$

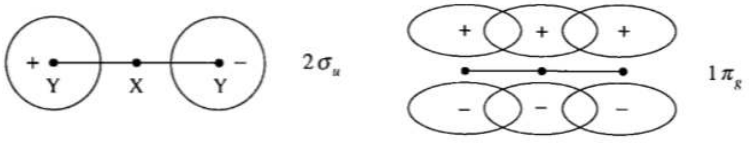
The atomic orbitals within the linear combination of the lone pair wave functions are normalized and orthogonal, zeroing out cross products and leaving only the squares of the coefficients.

10.14

Molecular orbitals for a linear

$$XY_2 \tag{10.E.62}$$

molecule can be represented as



Draw a schematic representation for the

$$3\sigma_g, 4\sigma_g, 1\pi_g, 2\sigma_g \tag{10.E.63}$$

orbitals

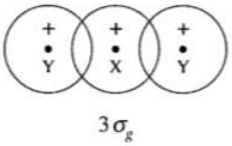
Which has the highest energy?

S10.14

$$3\sigma_g \tag{10.E.64}$$

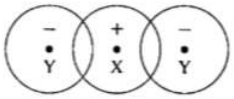
NOTE:

$3\sigma_g$ (10.E.65)



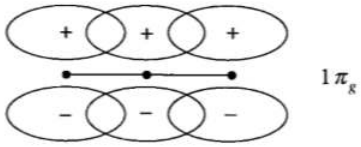
$3\sigma_g$

$4\sigma_g$ (10.E.66)



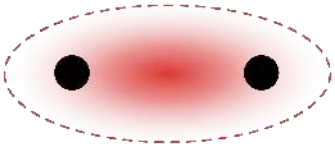
$4\sigma_g$

$1\pi_g$ (10.E.67)



$1\pi_g$

$2\sigma_g$ (10.E.68)



$4\sigma_g$ (10.E.69)

has the highest energy

The

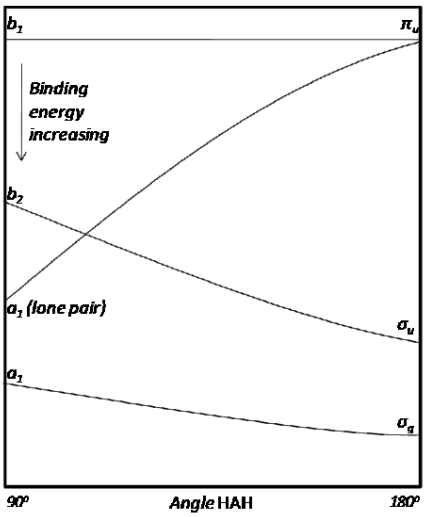
$4\sigma_g$ (10.E.70)

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

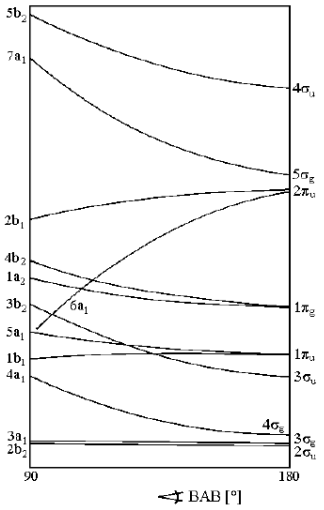
S10.18

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** (90º) 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** (180º) 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

$$\psi_\pi = c_1 2p_{z1} + c_2 2p_{z2} \tag{10.E.71}$$

the relationship of the coefficients can be defined as the following from the secular determinate:

$$c_1(\alpha - E) + c_2\beta = 0 \tag{10.E.72}$$

$$c_1\beta + c_2(\alpha - E) = 0 \tag{10.E.73}$$

Substituting $E = \alpha + \beta$ into these expressions and solving gives

$$-c_1\beta + c_2\beta = 0 \tag{10.E.74}$$

$$c_1 = c_2 \tag{10.E.75}$$

Then plugging back into the original equation gives

$$\psi_\pi = c_1(2p_{zA} + 2p_{zB}) \tag{10.E.76}$$

Now we can solve for c_1 by normalizing the wavefunction

$$c_1^2(1 + 2S + 1) = 1 \tag{10.E.77}$$

where S = 0 so solving yields

$$c_1 = \frac{1}{\sqrt{2}} \tag{10.E.78}$$

.

The final wave function can be written as

$$\psi_\pi = \frac{1}{\sqrt{2}}(2p_{z1} + 2p_{z2}) \tag{10.E.79}$$

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

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{10.E.80}$$

making a substitution for $x = \frac{\alpha - E}{\beta}$ the secular determinant becomes

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \tag{10.E.81}$$

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

$$E = \alpha \pm \sqrt{2}\beta \tag{10.E.82}$$

and

$$E = 0 \tag{10.E.83}$$

To find the wave function of propene you must find the constants

$$\begin{vmatrix} c_1(x) & c_2 & 0 \\ c_1 & c_2(x) & c_3 \\ 0 & c_2 & c_3(x) \end{vmatrix} = 0 \tag{10.E.84}$$

solving the determinant yields

$$c_1 = c_3 = \frac{1}{2} \tag{10.E.85}$$

$$c_2 = \frac{1}{\sqrt{2}} \tag{10.E.86}$$

therefore the wave function is

$$\psi = \frac{1}{2}1s + \frac{1}{\sqrt{2}}2s + \frac{1}{2}2p_z \tag{10.E.87}$$

Q10.26

Show that the six molecular orbitals for Benzene consturcted from the $2Pp_x$ atomic orbital on each of the six carbon atoms:

$$\psi_i = \sum_{j=1}^{6} c_{ij} 2p_{xj} \tag{10.E.88}$$

leads to a secular determinant.

S10.26

The above equation for benzene is :

$$\psi_i = c_{i1}2p_{z1} + c_{i2}2p_{z2} + c_{i3}2p_{z3} + c_{i4}2p_{z4} + c_{i5}2p_{z5} + c_{i6}2p_{z6} \tag{10.E.89}$$

The secular determinant for the benzene is :

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES_{14} & H_{15} - ES_{15} & H_{16} - ES_{16} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & H_{23} - ES_{23} & H_{24} - ES_{24} & H_{25} - ES_{25} & H_{26} - ES_{26} \\ H_{13} - ES_{13} & H_{23} - ES_{23} & H_{33} - ES_{33} & H_{34} - ES_{34} & H_{35} - ES_{35} & H_{36} - ES_{36} \\ H_{14} - ES_{14} & H_{24} - ES_{24} & H_{34} - ES_{34} & H_{44} - ES_{44} & H_{45} - ES_{45} & H_{46} - ES_{46} \\ H_{15} - ES_{15} & H_{25} - ES_{25} & H_{35} - ES_{35} & H_{45} - ES_{45} & H_{55} - ES_{55} & H_{56} - ES_{56} \\ H_{16} - ES_{16} & H_{26} - ES_{26} & H_{36} - ES_{36} & H_{46} - ES_{46} & H_{56} - ES_{56} & H_{66} - ES_{66} \end{vmatrix} = 0 \tag{10.E.90}$$

$H_{11} = H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = \alpha$

$H_{12} = H_{23} = H_{34} = H_{45} = H_{56} = \beta$ 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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CHAPTER OVERVIEW

11: Computational Quantum Chemistry

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

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.

11.1: Overview of Quantum Calculations
11.2: Gaussian Basis Sets
11.3: Extended Basis Sets
11.4: Orbital Polarization Terms in Basis Sets
11.5: The Ground-State Energy of H_2
11.6: Quantum Calculations
11.E: Computational Quantum Chemistry (Exercises)

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11.1: 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_1) 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

$$|\psi(r_1, r_2)|^2 = \psi(r_2, r_1)^* \psi(r_2, r_1) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{11.1.1}$$

Equation 11.1.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(r_1, r_2) = e^{i\varphi} \psi(r_1, r_2) \tag{11.1.2}$$

so that

$$\left(e^{-i\varphi} \psi(r_1, r_2)^*\right) \left(e^{i\varphi} \psi(r_1, r_2)^*\right) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{11.1.3}$$

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.,

$$e^{i\varphi} e^{i\varphi} = e^{i2\varphi} = 1 \tag{11.1.4}$$

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, 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.

$$\psi(r_2, r_1) = e^{i\varphi} \psi(r_1, r_2) = -\psi(r_1, r_2) \tag{11.1.5}$$

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, $1s^2$.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) \tag{11.1.6}$$

After permutation of the electrons, this becomes

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1) \tag{11.1.7}$$

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 11.1.7 from the right-hand side of Equation 11.1.6 has the desired antisymmetric behavior. The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1)] \tag{11.1.8}$$

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)

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}\begin{vmatrix}\sigma_{1s}(1)\alpha(1) & \sigma_{1s}(1)\beta(1)\\ \sigma_{1s}(2)\alpha(2) & \sigma_{1s}(2)\beta(2)\end{vmatrix} \tag{11.1.9}$$

We can introduce a shorthand notation for the arbitrary **spin-orbital**

$$\chi_{i\alpha}(\mathbf{r})=\varphi_i\alpha \tag{11.1.10}$$

or

$$\chi_{i\beta}(\mathbf{r})=\varphi_i\beta \tag{11.1.11}$$

as determined by the m_s quantum number. A shorthand notation for the determinant in Equation 8.6.4 is then

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=2^{-\frac{1}{2}}Det|\chi_{1s\alpha}(\mathbf{r}_1)\alpha\chi_{1s\beta}(\mathbf{r}_2)\beta| \tag{11.1.12}$$

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

$$\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\chi_1(\mathbf{r}_1)\alpha & \chi_1(\mathbf{r}_1)\beta & \cdots & \chi_{N/2}(\mathbf{r}_1)\beta\\ \chi_1(\mathbf{r}_2)\alpha & \chi_2(\mathbf{r}_2)\beta & \cdots & \chi_{N/2}(\mathbf{r}_2)\beta\\ \vdots & \vdots & \ddots & \vdots\\ \chi_1(\mathbf{r}_N)\alpha & \chi_2(\mathbf{r}_N)\beta & \cdots & \chi_{N/2}(\mathbf{r}_N)\beta\end{vmatrix} \tag{11.1.13}$$

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

$$\varphi_j=\sum_k c_{jk}\psi_k \tag{11.1.14}$$

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

$$E=\frac{\int\Psi^*\hat{H}\Psi d\tau}{\int\Psi^*\Psi d\tau} \tag{11.1.15}$$

or in bra-ket notation

$$E=\frac{\left\langle\Psi\left|\hat{H}\right|\Psi\right\rangle}{\langle\psi|\psi\rangle} \tag{11.1.16}$$

The the optimum coefficients c_{jk} for each molecular orbital in Equation 11.1.14 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 11.1.13). 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 11.1.14. The ground state wavefunction Ψ is written as the Slater Determinant of the five lowest energy molecular orbitals ψ_k. Equation 11.1.15 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.

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

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11.2: Gaussian Basis Sets

A basis set in theoretical and computational chemistry is a set of functions (called basis functions) which are combined in linear combinations (generally as part of a quantum chemical calculation) to create molecular orbitals. For convenience these functions are typically atomic orbitals centered on atoms, but can theoretically be any function; plane waves are frequently used in materials calculations.

The Variational Method and Basis Sets

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.

$$\psi_i = \sum_j c_{ij}\varphi_j \tag{11.2.1}$$

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. For example, an active area of research in industry involves calculating changes in chemical properties of pharmaceutical drugs as a result of changes in chemical structure.

> *Selecting the ab initio model for a chemical system is almost always involves a trade-off between accuracy and computational cost. More accurate methods and larger basis sets make jobs run longer.*

In modern computational chemistry, quantum chemical calculations are typically performed using a finite set of basis functions. In these cases, the wavefunctions of the system in question are represented as vectors, the components of which correspond to coefficients in a linear combination of the basis functions in the basis set used.

The molecular spin-orbitals that are used in the Slater determinant usually are expressed as a linear combination of some chosen functions, which are called *basis functions*. This set of functions is called the *basis set*. The fact that one function can be represented by a linear combination of other functions is a general property. All that is necessary is that the basis functions *span-the-space*, which means that the functions must form a complete set and must be describing the same thing. For example, spherical harmonics cannot be used to describe a hydrogen atom radial function because they do not involve the distance r, but they can be used to describe the angular properties of anything in three-dimensional space.

This span-the-space property of functions is just like the corresponding property of vectors. The unit vectors $(\vec{x}, \vec{y}, \vec{z})$ describe points in space and form a complete set since any position in space can be specified by a linear combination of these three unit vectors. These unit vectors also could be called basis vectors.

? Exercise 11.2.1: "Spanning the Space"

Explain why the unit vectors $(\vec{x}, \vec{y})$ do not form a complete set to describe your (three-dimensional) classroom.

Just as we discussed for atoms, parameters in the basis functions and the coefficients in the linear combination can be optimized in accord with the Variational Principle to produce a self-consistent field (SCF) for the electrons. This optimization means that the ground state energy calculated with the wavefunction is minimized with respect to variation of the parameters and coefficients

defining the function. As a result, that ground state energy is larger than the exact energy, but is the best value that can be obtained with that wavefunction.

Slater Type Orbitals (STOs)

Intuitively one might select hydrogenic atomic orbitals as the basis set for molecular orbitals. After all, molecules are composed of atoms, and hydrogenic orbitals describe atoms exactly if the electron-electron interactions are neglected. At a better level of approximation, the nuclear charge that appears in these functions can be used as a variational parameter to account for the shielding effects due to the electron-electron interactions. Also, the use of atomic orbitals allows us to interpret molecular properties and charge distributions in terms of atomic properties and charges, which is very appealing since we picture molecules as composed of atoms. As described in the previous chapter, calculations with hydrogenic functions were not very efficient so other basis functions, *Slater-type atomic orbitals* (STOs), were invented.

A minimal basis set of STOs for a molecule includes only those STOs that would be occupied by electrons in the atoms forming the molecule. A larger basis set, however, improves the accuracy of the calculations by providing more variable parameters to produce a better approximate wavefunction, but at the expense of increased computational time. STOs have the following radial part (the spherical harmonic functions are used to describe the angular part)

$$R(r) = Nr^{n-1}e^{-\zeta r} \tag{11.2.2}$$

where

- n is a natural number that plays the role of principal quantum number, n = 1,2,...,
- N is a normalizing constant,
- r is the distance of the electron from the atomic nucleus, and ζ is a constant related to the effective charge of the nucleus, the nuclear charge being partly shielded by electrons. Historically, the effective nuclear charge was estimated by Slater's rules.

Double-zeta basis Sets

One can use more than one STO to represent one atomic orbital, as shown in Equation 11.2.3, and rather than doing a nonlinear variational calculation to optimize each ζ value, use two STOs with different ζ variables. The linear variation calculation then will produce the coefficients (C_1 and C_2) for these two functions in the linear combination that **best** describes the charge distribution in the molecule (for the ground state). The function with the large zeta accounts for charge near the nucleus, while the function with the smaller zeta accounts for the charge distribution at larger values of the distance from the nucleus. This expanded basis set is called a *double-zeta basis set*.

$$R_{2s}(r) = C_1 re^{-\zeta_1 r} + C_2 re^{-\zeta_2 r} \tag{11.2.3}$$

The use of double zeta functions in basis sets is especially important because without them orbitals of the same type are constrained to be identical even though in the molecule they may be chemically inequivalent. For example, in acetylene the p_z orbital along the internuclear axis is in a quite different chemical environment and is being used to account for quite different bonding than the p_x and p_y orbitals. With a double zeta basis set the p_z orbital is not constrained to be the same size as the p_x and p_y orbitals.

Example 11.2.1

Explain why the p_x, p_y, and p_z orbitals in a molecule might be constrained to be the same in a single-zeta basis set calculation, and how the use of a double-zeta basis set would allow the p_x, p_y, and p_z orbitals to differ.

Gaussian Orbitals

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. A Gaussian basis function has the form shown in Equation 11.2.4. Note that in all the basis sets, only the radial part of the orbital changes, and the spherical harmonic functions are used in all of them to describe the angular part of the orbital.

$$G_{nlm}(r,\theta,\psi) = N_n \underbrace{r^{n-1}e^{-\alpha r^2}}_{\text{radial part}} \underbrace{Y_l^m(\theta,\psi)}_{\text{angular part}} \tag{11.2.4}$$

Unfortunately Gaussian functions do not match the shape of an atomic orbital very well. In particular, they are flat rather than steep near the atomic nucleus at $r = 0$, and they fall off more rapidly at large values of r (Figure 11.2.1).

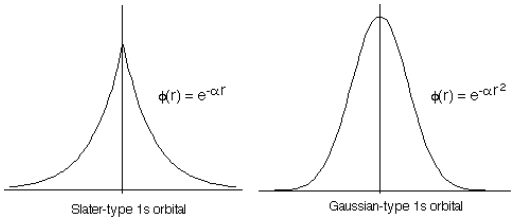


Figure 11.2.1: Radial Dependence of Slater and Gaussian Basis Functions. .

To compensate for this problem, each STO is replaced with a number of Gaussian functions with different values for the exponential parameter. These Gaussian functions form a *primitive Gaussian basis set*. Linear combinations of the primitive Gaussians are formed to approximate the radial part of an STO. This linear combination is not optimized further 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*. Although more functions and more integrals now are part of the calculation, the integrals involving Gaussian functions are quicker to compute than those involving exponentials, so there is a net gain in the efficiency of the calculation.

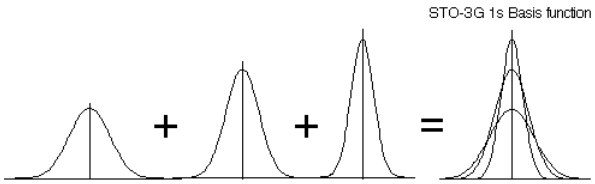


Figure 11.2.2: To better represent the cusp in the electron density at the nuclei, GTO basis sets are constructed from fixed linear-combinations of Gaussian functions, contracted GTOs (CGTO). The earliest CGTO basis sets, where constructed from N GTOs that best fit the desired STO. These are called STO-NG basis sets.

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 elswhere) 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 11.2.1 for other examples).

Table 11.2.1: 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

When molecular calculations are performed, it is common to use a basis composed of a finite number of atomic orbitals (Equation 11.2.1), centered at each atomic nucleus within the molecule (linear combination of atomic orbitals ansatz). These atomic orbitals are well described with Slater-type orbitals (STOs), as STOs decay exponentially with distance from the nuclei, accurately describing the long-range overlap between atoms, and reach a maximum at zero, well describing the charge and spin at the nucleus. 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

Contributors

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

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11.3: Extended Basis Sets

Today, there are hundreds of basis sets composed of Gaussian Type Orbitals (GTOs). 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 literally dozens to hundreds of basis functions on each atom.

Minimum Basis sets

A minimum basis set is one in which a **single** basis function is used for each orbital in a Hartree-Fock calculation on the atom. However, for atoms such as lithium, basis functions of p type are added to the basis functions corresponding to the 1s and 2s orbitals of each atom. For example, each atom in the first row of the periodic system (Li - Ne) would have a basis set of five functions (two s functions and three p functions).

> *In a minimum basis set, a single basis function is used for each atomic orbital on each constituent atom in the system.*

The most common minimal basis set is STO-nG, where n is an integer. This n value represents the number GTOs used to approximate the Slater Type orbital (STO) for both core and valence orbitals. Minimal basis sets typically give rough results that are insufficient for research-quality publication, but are much cheaper (less calculations requires) than the larger basis sets discussed below. Commonly used minimal basis sets of this type are: STO-3G, STO-4G, and STO-6G.

Two is Often Better than One

Minimal basis sets are not flexible enough for accurate representation of, which requires the use multiple functions to represent each atomic orbital. The distribution of the electron density of valence electrons is better represented by the sum of two orbitals with different "effective charges". This is a double-ζ basis sets and includes split-valence set (inner and valence) and linear combination of two orbitals of same type, but with different effective charges (i.e., ζ). This flexibility can be used to generate atomic orbital of adjustable sizes.

For example, the double-zeta basis set allows us to treat each orbital separately when we conduct the Hartree-Fock calculation.

$$\phi_i = a_1\phi_{2s}^{STO}(r,\zeta_1) + a_2\phi_{2s}^{STO}(r,\zeta_2) \tag{11.3.1}$$

The 2s atomic orbital approximated as a sum of two STOs. The two equations are the same except for the value of ζ which accounts for how large the orbital is. The constants a_1 and a_2 determines how much each STO contributes to the final atomic orbital, which will vary depending on the type of atom that the atomic orbit (i.e., hydrogen and lithium orbitals will have different a_1, a_2, ζ_1, and ζ_2 values).

Extended Basis Sets

The triple and quadruple-zeta basis sets work the same way, except use three and four STOs instead of two like in **11.3.1**. The typical trade-off applies here as well, better accuracy, however with more expensive calculations. There are several different types of extended basis sets including: n split-valence, n polarized sets, n diffuse sets, and n correlation consistent sets. The notation of this sort of basis set (with a Gaussian basis) is

$$N-MPG \tag{11.3.2}$$

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).

A minimal basis set is when one basis function for each atomic orbital in the atom, while a double-ζ, has two two basis functions for each atomic orbital. Correspondingly, a triple and dquarupe-ζ set had three and four basis functions for each atomic orbital, respectively. Higher order basis set have been constructed too, e.g., 5Z, 6Z,)..

There are hundreds of basis sets composed of Gaussian-type orbitals (Figure Figure **11.3.1**). 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.

Figure **11.3.1**: 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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11.4: Orbital Polarization Terms in Basis Sets

Polarization functions denoted in Pople's sets by an asterisk. Two asterisks, indicate that polarization functions are also added to light atoms (hydrogen and helium). n Polarization functions have one additional node. For example, the only basis function located on a hydrogen atom in a minimal basis set would be a function approximating the 1 s atomic orbital. When polarization is added to this basis set, a p -function is also added to the basis set. The 6-31G** is synonymous to 6-31 G(d,p).

The use of a minimal basis set with fixed zeta parameters severely limits how much the electronic charge can be changed from the atomic charge distribution to describe molecules and chemical bonds. This limitation is removed if STOs with larger n values and different spherical harmonic functions, the $Y_l^m(\theta, \varphi)$ in the definition of STO's are included. Adding such functions is another way to expand the basis set and obtain more accurate results. Such functions are called polarization functions because they allow for charge polarization away form the atomic distribution to occur.

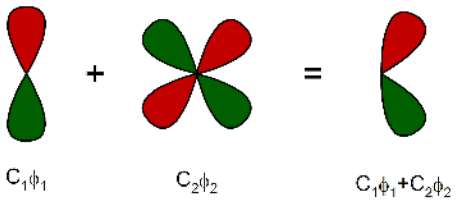


Figure **11.4.1**: A d-polarization function added to a p orbital. (CC-BY-SA-3.0; Rifleman 82)

The most common addition to minimal basis sets is probably the addition of polarization functions, denoted (in the names of basis sets developed by Pople) by an asterisk, *. Two asterisks, **, indicate that polarization functions are also added to light atoms (hydrogen and helium). These are auxiliary functions with one additional node. For example, the only basis function located on a hydrogen atom in a minimal basis set would be a function approximating the 1s atomic orbital. When polarization is added to this basis set, a p-function is also added to the basis set. This adds some additional needed flexibility within the basis set, effectively allowing molecular orbitals involving the hydrogen atoms to be more asymmetric about the hydrogen nucleus.

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. 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. Another, more precise notation indicates exactly which and how many functions are added to the basis set, such as (d, p).

Diffuse Functions

Another common addition to basis sets is the addition of **diffuse functions**, denoted in Pople-type sets by a plus sign, +, and in Dunning-type sets by "aug" (from "augmented"). Two plus signs indicate that diffuse functions are also added to light atoms (hydrogen and helium). 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.

Contributors

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11.5: The Ground-State Energy of H_2

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11.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

$$\int_0^\infty e^{-(x-x_0)^2}dx = \int_0^\infty e^{-x^2}dx = \frac{1}{2}\int_{-\infty}^\infty e^{-x^2}dx = \sqrt{\pi} \tag{11.E.1}$$

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

$$I_0 = \int_{-\infty}^\infty e^{-4x^2}dx \tag{11.E.2}$$

Convert the integration variables from Cartesian coordinates to polar coordinates and show that

$$I_0 = \frac{\sqrt{\pi}}{2} \tag{11.E.3}$$

S11.3

We first write

$$I_0^2 = \left(\int_{-\infty}^{\infty} e^{-4x^2} dx\right)^2 = \int_{-\infty}^{\infty} e^{-4x^2} dx \int_{-\infty}^{\infty} e^{-4y^2} dy \tag{11.E.4}$$

the product of two integrals can be expressed as a double integral

$$I_0^2 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-4(x^2+y^2)} dxdy \tag{11.E.5}$$

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

$$I_0^2 = \int_0^{\infty}\int_0^{2\pi} e^{-4r^2} rdrd\theta = 2\pi \int_0^{\infty} e^{-4r^2} rdr. \tag{11.E.6}$$

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

$$\int_0^{\infty} e^{-4r^2} rdr = \frac{1}{8}\int_0^{\infty} e^{-u^2} du = \frac{1}{8} \tag{11.E.7}$$

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:

$$I_o = \int_{-\infty}^{\infty} e^{-ax^2} dx$$

$$\tfrac{dI_o}{da} = \int_{-\infty}^{\infty} -x^2 e^{-ax^2} dx = -\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx$$

$$\tfrac{d^2I_o}{da^2} = \int_{-\infty}^{\infty} -x^{2\cdot 2} e^{-ax^2} dx = \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx$$

solve the integrals for the first I_{2n} starting with I_o,

$$I_o = \int_{-\infty}^{\infty} e^{-ax^2} dx = \tfrac{1}{2}\left(\tfrac{\pi}{a}\right)^{\frac{1}{2}}$$

$$I_2 = \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \tfrac{dI_o}{da} = \tfrac{1}{4a}\left(\tfrac{\pi}{a}\right)^{\frac{1}{2}}$$

$$I_4 = \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx = \tfrac{d^2I_o}{da^2} = -\tfrac{dI_2}{da} = \tfrac{3}{8a}\left(\tfrac{\pi}{a}\right)^{\frac{1}{2}}$$

$$I_6 = \int_{-\infty}^{\infty} x^6 e^{-ax^2} dx = -\frac{d^3 I_o}{da^3} = -\frac{dI_4}{da} = \frac{3 \cdot 5}{16a} \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

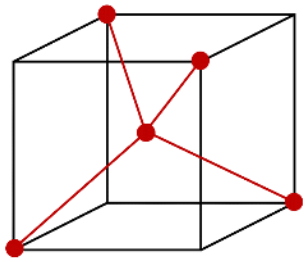
in general

$$I_{2n} = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \left(\frac{a}{2}\right)^{\frac{1}{2}}$$

(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

$$\frac{109.1\ pm}{\sqrt{3}} = 63\ pm = a \tag{11.E.8}$$

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:

$$a = \frac{146\,pm}{\sqrt{3}} = 84.29\,pm \tag{11.E.9}$$

For florine:

$$a = \frac{159.5\,pm}{\sqrt{3}} = 92.09\,pm \tag{11.E.10}$$

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

$$\tilde{\nu} = (2c\pi)^{-1}\sqrt{\frac{k}{\mu}} \tag{11.E.11}$$

which can be rewritten as

$$k = 4\mu(\tilde{\nu}c\pi)^2. \tag{11.E.12}$$

The reduced masses can be found to be

$$\mu_{H_2} = 8.38 \times 10^{-28}\text{kg},\ \mu_{CO} = 1.14 \times 10^{-26}\text{kg, and } \mu_{HCl} = 1.626 \times 10^{-27}\text{kg.}$$

Now we can find our force constants by plugging in the given values.

- $k_{H_2} = 642 N/m$
- $k_{CO} = 2404 N/m$
- $k_{HCl} = 481 N/m$

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:

$$\phi(r) = xe^{-\alpha r^2} \tag{11.E.13}$$

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

$$\int A^2 x^2 e^{-2\alpha r^2} d\tau = 1 \tag{11.E.14}$$

or in bra-ket notation

$$\langle \phi(r) | \phi(r) \rangle = 1.$$

where A is the normalization constant. In spherical coordinates,

$$1 = \int A^2 r^2 \sin^2\theta \cos^2\phi e^{-2\alpha r^2} d\tau \tag{11.E.15}$$

$$= A^2 \int_0^\infty r^4 e^{-2\alpha r^2} dr \int_0^\pi \sin^3\theta d\theta \int_0^{2\pi} \cos^2\phi d\phi \tag{11.E.16}$$

$$\frac{1}{A^2} = \frac{3}{8(2\alpha)^2}\left(\frac{\pi}{2\alpha}\right)^{1/2}\left(\frac{4}{3}\right)(\pi) \tag{11.E.17}$$

$$= \frac{\pi^{3/2}}{2^{7/2}\alpha^{5/2}} \tag{11.E.18}$$

Therefore, the nomalization constant will the inverse of this result:

$$A = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} \tag{11.E.19}$$

Q11.21

Which hydrogen atomic orbital corresponds to the following normalized Gaussian orbital?

$$G(x,y,z;\alpha) = \left(\frac{128\alpha^5}{\pi^3}\right)^{0.25} y e^{-\alpha r^2} \tag{11.E.20}$$

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:

$$G_{nlm}(r,\theta,\phi) = N_n r^{n-1} e^{-\alpha r^2} Y_l^m(\theta,\phi) \tag{11.E.21}$$

.

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,

$$\chi_{nlm} = R_n(r) Y_{lm}(\theta,\phi) \tag{11.E.22}$$

where the second term is the spherical harmonic given by

$$R_n(r) = \frac{(2\alpha)^{(n+1/2)}}{\sqrt{(2n)!}} r^{(n-1)} e^{(-\alpha r)} \tag{11.E.23}$$

Define the 1s-slater type orbital.

S11-22

For n=1, the slater-type orbital is

$$\phi_{nlm} = \frac{(2\zeta)^{(n+1/2)}}{\sqrt{(2n)!}} r^{(n-1)} e^{(-\zeta r)} Y_{lm}(\theta,\phi) \tag{11.E.24}$$

$$\phi_{1s}(r,\zeta) = S_{100}(r,\zeta) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r} \tag{11.E.25}$$

11.23

Consider the normalized functions

$$G_1(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})(\frac{1}{4})x^2 e^(-\alpha r^2) \tag{11.E.26}$$

$$G_2(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})(\frac{1}{4})y^2 e^(-\alpha r^2) \tag{11.E.27}$$

$$G_3(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})(\frac{1}{4})z^2 e^(-\alpha r^2) \tag{11.E.28}$$

$$G_4(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})(\frac{1}{4})(x^2-y^2) e^(-\alpha r^2) \tag{11.E.29}$$

Which hydrogen atomic orbital corresponds to the linear combination

$$G_3(x,y,z;\alpha) + G_1(x,y,z;\alpha)? \tag{11.E.30}$$

S11.23

$$G_3(x,y,z;\alpha) + G_1(x,y,z;\alpha) = (\frac{2048\alpha^7}{9\pi^3})(\frac{1}{4})(z^2+x^2) e^(-\alpha r^2) \tag{11.E.31}$$

Corresponds to the

$$3d_{z^2+x^2} \tag{11.E.32}$$

hydrogen atomic orbital.

This is a good tricky question because usually people would think that

$$H_2 \tag{11.E.33}$$

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

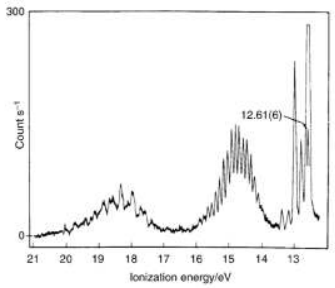
To calculate the dipole moment of a molecule, one needs an accurate description of the electron densities and molecular orbitals. This description becomes **more accurate when a larger basis set is used**, which is why the 6-31G* basis set gave more accurate calculations than did the STO-3G basis set.

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

$$1D = 1 * 10^{-18} esu \bullet cm \left(\frac{1.6022 * 10^{-19}\, C}{4.803 * 10^{-10}\, esu} * \frac{1m}{100cm} \right) = 3.3407 * 10^{-30}\, C \bullet m \tag{11.E.34}$$

Q11.30

Determine the dipole moment $SnCl_2$ by using the geometry and charges:

$$z = e \sum X_i r_i \tag{11.E.35}$$

S11.30

$$e((0.41sin(52.57)i + .041cos(52.75)j)94.7 * 10^{-12}m \\ + (0.41sin(52.57)i + 0.41cos(52.75)j)94.7x10^{-12}m) \tag{11.E.36}$$

$$= 2.3D \tag{11.E.37}$$

Notes:

The equation I found for dipole moment is:

$$\vec{\mu} = \sum_i q_i \vec{r}_i \tag{11.E.38}$$

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CHAPTER OVERVIEW

12: Group Theory - The Exploitation of Symmetry

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

Group Theory is a branch of the mathematical field of algebra. One important application, the theory of symmetry groups, is a powerful tool for the prediction of physical properties of molecules and crystals. It is for example possible to determine whether a molecule can have a dipole moment. Many important predictions of spectroscopic experiments (optical, IR or Raman) can be made purely by group theoretical considerations. The qualitative properties of molecular orbitals can be obtained from group theory (whereas their precise energetics and ordering have to be determined by a quantum chemical method). In quantum chemistry, group theory can applied to *ab initio* or semi-empirical calculations to significantly reduce the computational cost.

12.1: The Exploitation of Symmetry
12.2: Symmetry Elements
12.3: Symmetry Operations Define Groups
12.4: Symmetry Operations as Matrices
12.5: The \(C_{3V}\) Point Group
12.6: Character Tables
12.7: Characters of Irreducible Representations
12.8: Using Symmetry to Solve Secular Determinants
12.9: Generating Operators
12.E: Group Theory - The Exploitation of Symmetry (Exercises)

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12.1: The Exploitation of Symmetry

Previously, we used Hückel theory to explore the π bonding network of benzene by constructing linear combinations of $2p_x$ atomic orbitals on the carbon atoms. In doing so, the roots of the secular equations were found via solving the 6×6 secular determinant.

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{12.1.1}$$

Since the secular determinant is a 6×6 matrix, there are six solutions or values of x that can be determined after expanding the determinant into the resulting (6th-order) polynomial.

$$x^6 - 6x^4 + 9x^2 - 4 = 0 \tag{12.1.2}$$

Secular determinants are formulated in terms of a specific basis set; i.e., a set of functions that describe the wavefunctions. For the determinnat in Equation 12.1.1, that basis set is the the $\{|2p_z\rangle\}$ orbitals on the carbons. However, any basis set can be used to represent the determinant (long as it span the same space). For example, the following linear combination of $\{|2p_z\rangle\}$ orbitals could also be used:

$$|\phi_1\rangle = \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle\right] \tag{12.1.3}$$

$$|\phi_2\rangle = \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle\right] \tag{12.1.4}$$

$$|\phi_3\rangle = \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle + \frac{1}{2}\left|2p_{z2}\right\rangle - \frac{1}{2}\left|2p_{z3}\right\rangle - \left|2p_{z4}\right\rangle - \frac{1}{2}\left|2p_{z5}\right\rangle + \frac{1}{2}|2p_{z6}\rangle\right] \tag{12.1.5}$$

$$|\phi_4\rangle = \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle\right] \tag{12.1.6}$$

$$|\phi_5\rangle = \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle - \frac{1}{2}\left|2p_{z2}\right\rangle - \frac{1}{2}\left|2p_{z3}\right\rangle + \left|2p_{z4}\right\rangle - \frac{1}{2}\left|2p_{z5}\right\rangle - \frac{1}{2}|2p_{z6}\rangle\right] \tag{12.1.7}$$

$$|\phi_6\rangle = \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle\right] \tag{12.1.8}$$

In this new basis set $\{\phi\rangle\}$, the secular determinant Equation 12.1.1 is represented as

$$\begin{vmatrix} x+2 & 0 & 0 & 0 & 0 & 0 \\ 0 & x-2 & 0 & 0 & 0 & 0 \\ 0 & 0 & x+1 & \frac{x+1}{2} & 0 & 0 \\ 0 & 0 & \frac{x+1}{2} & x+1 & 0 & 0 \\ 0 & 0 & 0 & 0 & x-1 & \frac{x-1}{2} \\ 0 & 0 & 0 & 0 & \frac{x-1}{2} & x-1 \end{vmatrix} = 0 \tag{12.1.9}$$

This is the determinant into a bock diagonal form; which can be expanded into a product of smaller determinants to give the polynomial

$$\frac{9}{16}(x+2)(x-2)(x+1)^2(x-1)^2 = 0 \tag{12.1.10}$$

The roots to this equation are ± 2, ± 1 and ± 1. This is not surprising since these are the same roots obtained from expanding the determinant in the original basis set (Equation 12.1.2). You may remember that the selection of a specific basis set to represent a

function does not change the fundamental nature of the function (e.g., a parabola in 2D space is the same curve if represented in terms of Cartesian coordinates (x and y) or polar coordinates (θ and r), which both span 2-D space.

As you recall, Hückel theory (irrespective of the basis set) was used to simplify the general secular determinant (e.g., for benzene)

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} & H_{15}-ES_{15} & H_{16}-ES_{16} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} & H_{25}-ES_{25} & H_{26}-ES_{26} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} & H_{35}-ES_{35} & H_{36}-ES_{36} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} & H_{45}-ES_{45} & H_{46}-ES_{46} \\ H_{51}-ES_{51} & H_{52}-ES_{52} & H_{53}-ES_{53} & H_{54}-ES_{54} & H_{55}-ES_{55} & H_{56}-ES_{56} \\ H_{61}-ES_{61} & H_{62}-ES_{62} & H_{63}-ES_{63} & H_{64}-ES_{64} & H_{65}-ES_{65} & H_{66}-ES_{6} \end{vmatrix} = 0 \tag{12.1.11}$$

where H_{ij} are the Hamiltonian matrix elements

$$H_{ij} = \langle \phi_i \left| \hat{H} \right| \phi_j \rangle = \int \phi_i H \phi_j \mathrm{d}v \tag{12.1.12}$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \int \phi_i \phi_j \mathrm{d}v \tag{12.1.13}$$

In general, this involves solving 36 Hamiltonian matrix elements (H_{ij}) and 36 overlap integrals (S_{ij}), which can be a daunting task to do by hand without the assumptions of Hückel theory to help out. As with the application of Hückel theory, which was used to set most of these integrals to zero, solving for the energies from Equation 12.1.11 can be simplified by using the intrinsic symmetry of the benzene system to demonstrate (rigorously) that many of these integrals are zero. This is the subject of group theory.

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12.2: Symmetry Elements

A *symmetry operation* is an action that leaves an object looking the same after it has been carried out. For example, if we take a molecule of water and rotate it by 180° about an axis passing through the central O atom (between the two H atoms) it will look the same as before. Each symmetry operation has a corresponding *symmetry element*, which is the axis, plane, line or point with respect to which the symmetry operation is carried out. The symmetry element consists of all the points that stay in the same place when the symmetry operation is performed. In a rotation, the line of points that stay in the same place constitute a *symmetry axis*; in a reflection the points that remain unchanged make up a *plane of symmetry*. The symmetry elements that a molecule (and any other 3-D object) may possess are discussed below.

Symmetry Operations

A symmetry operation is a permutation of atoms such that the molecule is transformed into a state **indistinguishable** from the starting state.

E: The Identity Symmetry

The identity operation consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule has at least this element. For example, the $CHFClBr$ molecule in Figure 12.2.1. The identify symmetry is not indicated since all molecule exhibit this symmetry.

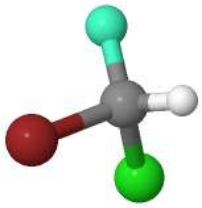


Figure 12.2.1: Example of Identify Symmetry: The $CHFClBr$ molecule contain no other symmetry other than identity. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

C_n: an n-fold Axis of Rotation

Rotation by $360°/n$ leaves the molecule unchanged. The H_2O molecule has a C_2 axis (Figure 12.2.2). Some molecules have more than one C_n axis, in which case the one with the highest value of n is called the *principal axis*. Note that by convention rotations are *counterclockwise* about the axis. C_n rotations are indicated via vectors with labels as indicated below.

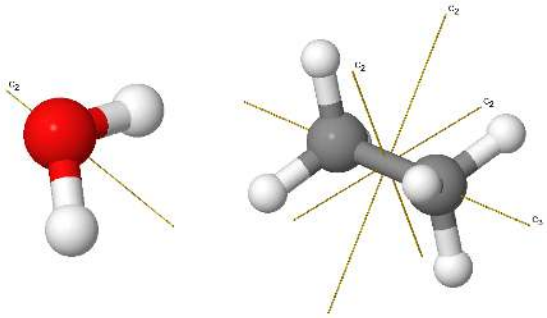


Figure 12.2.2: Examples of n-fold Axis of Rotation: (left) The water molecule contains a C_2 axis. (right) Ethane contains both C_2 and C_3 axes. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

σ: a Plane of Symmetry

Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a vertical mirror plane and is labeled σ_v, while one perpendicular to the axis is called a horizontal mirror plane and is labeled σ_h. A vertical mirror plane that bisects the angle between two C_2 axes is called a dihedral mirror plane, σ_d. σ symmetry is indicated as a plane on molecules; since they often bisect atoms, which should be clearly indicated.

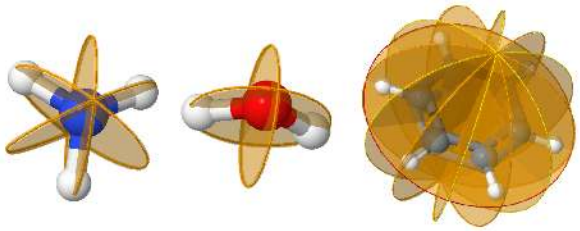


Figure 12.2.3: Examples of reflection symmetry. (left) The ammonia molecule contains three identical reflection planes. All are designated as vertical symmetry planes (σ_v) because they contain the principle rotation axis.(middle) The water molecule contains two different reflection planes. (right) benzene contains a total of seven reflection planes, one horizontal plane (σ_h) and six vertical planes (σ_v and σ_d). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

i: a Center of Inversion Symmetry

Inversion through the center of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the center of inversion and out to the same distance on the other side of the molecule. Examples of molecules with centers of inversion is shown in Figure 12.2.4. Centers of inversion are indicated via a point, which may or may not overlap with an atoms. The centers of inversion in the examples below do not overlap with atoms.

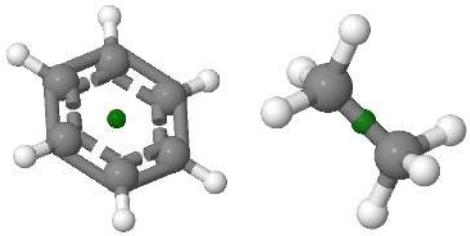


Figure 12.2.4: Examples of Center of Inversion Symmetry. (left) Benzene and (right) staggard ethane have centers of inversion (green balls). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

S_n: an n-fold axis of improper rotation Symmetry

Improper rotations are also called a rotary-reflection axis. The rotary reflection operation consists of rotating through an angle $360\,°/n$ about the axis, followed by reflecting in a plane perpendicular to the axis. Improper rotation symmetry is indicated with both an axis and a plan as demonstrated in the examples in Figure 12.2.5.

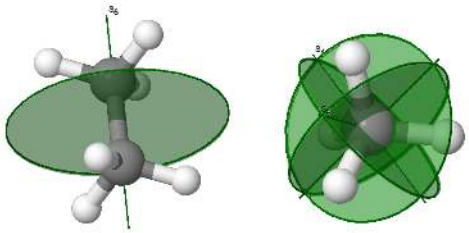


Figure 12.2.5: Examples of Improper axis of rotation. (left) Staggered ethane contains an S_6 axis of improper rotation. (right) Methane contains three S_4 axes of improper rotation. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

> **Note**
>
> S_1 is the same as reflection and S_2 is the same as inversion.

The identity E and rotations C_n are symmetry operations that could actually be carried out on a molecule. For this reason they are called *proper symmetry operations*. Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic rearrangement of chemical bonds) and as such, are termed *improper symmetry operations*. These five symmetry elements are tabulated in Table 12.2.1 with their corresponding operators.

Table 12.2.1: The five principal symmetry elements and their operators for 3D space

Symbol Elements	Description	Symbol Operator	Symbol
E	identity	$\hat{E}$	no change
C_n	n-fold axis of rotation	$\hat{C}_n$	Rotation by $360°/n$ leaves the molecule unchanged
σ	plane of symmetry	$\hat{\sigma}$	Reflection in the plane leaves the molecule unchanged
i	center of symmetry.	$\hat{i}$	Inversion through the center of symmetry leaves the molecule unchanged.
S_n	n-fold improper rotation	$\hat{S}_n$	The rotary reflection operation consists of rotating through an angle $360°/n$ about the axis, followed by reflecting in a plane perpendicular to the axis.

Axis Definitions

Conventionally, when imposing a set of Cartesian axes on a molecule (as we will need to do later on in the course), the z axis lies along the principal axis of the molecule, the x axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the y axis makes up a right handed axis system.

Molecular Point Groups

It is only possible for certain combinations of symmetry elements to be present in a molecule (or any other object). As a result, we may group together molecules that possess the same symmetry elements and classify molecules according to their symmetry. These groups of symmetry elements are called *point groups* (due to the fact that there is at least one point in space that remains unchanged no matter which symmetry operation from the group is applied). There are two systems of notation for labeling symmetry groups, called the Schoenflies and Hermann-Mauguin (or International) systems. The symmetry of individual molecules is usually described using the **Schoenflies** notation, which is used below.

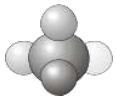
Table **12.2.2**: Common Point Groups for Molecules

Nonaxial groups	C_1	C_s	C_i	-	-	-	-	-	-
C_n groups	C_2	C_3	C_4	C_5	C_6	C_7	C_8	-	-
D_n groups	D_2	D_3	D_4	D_5	D_6	D_7	D_8	-	-
C_{nv} groups	C_{2v}	C_{3v}	C_{4v}	C_{5v}	C_{6v}	C_{7v}	C_{8v}	-	-
C_{nh} groups	C_{2h}	C_{3h}	C_{4h}	C_{5h}	C_{6h}	-	-	-	-
D_{nh} groups	D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}	D_{7h}	D_{8h}	-	-
D_{nd} groups	D_{2d}	D_{3d}	D_{4d}	D_{5d}	D_{6d}	D_{7d}	D_{8d}	-	-
S_n groups	S_2	-	S_4	-	S_6		S_8	S_{10}	S_{12}
Cubic groups	T	T_h	T_d	O	O_h	I	I_h	-	-
Linear groups	$C_{\infty v}$	$D_{\infty h}$	-	-	-	-	-	-	-

Shared Names

Some of the point groups share their names with symmetry operations, so be careful you do not mix up the two. It is usually clear from the context which one is being referred to.

1. C_1 - contains only the identity (a C_1 rotation is a rotation by 360° and is the same as the identity operation) e.g. CHDFCl.



2. C_i - contains the identity E and a center of inversion i.



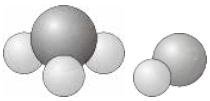
3. C_S - contains the identity E and a plane of reflection σ.



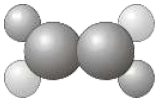
4. C_n - contains the identity and an n-fold axis of rotation.



5. C_{nv} - contains the identity, an n-fold axis of rotation, and n vertical mirror planes σ_v.



6. C_{nh} - contains the identity, an n-fold axis of rotation, and a horizontal reflection plane σ_h (note that in C_{2h} this combination of symmetry elements automatically implies a center of inversion).



7. D_n - contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.



8. D_{nh} - contains the same symmetry elements as D_n with the addition of a horizontal mirror plane.



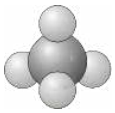
9. D_{nd} - contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.



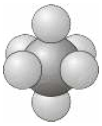
10. S_n - contains the identity and *one* S_n axis. Note that molecules only belong to S_n if they have not already been classified in terms of one of the preceding point groups (e.g. S_2 is the same as C_i, and a molecule with this symmetry would already have been classified).

The following groups are the cubic groups, which contain more than one principal axis. They separate into the tetrahedral groups (T_d, T_h and T) and the octahedral groups (O and O_h). The icosahedral group also exists, but is not included below.

11. T_d - contains all the symmetry elements of a regular tetrahedron, including the identity, 4 C_3 axes, 3 C_2 axes, 6 dihedral mirror planes, and 3 S_4 axes e.g. CH_4.



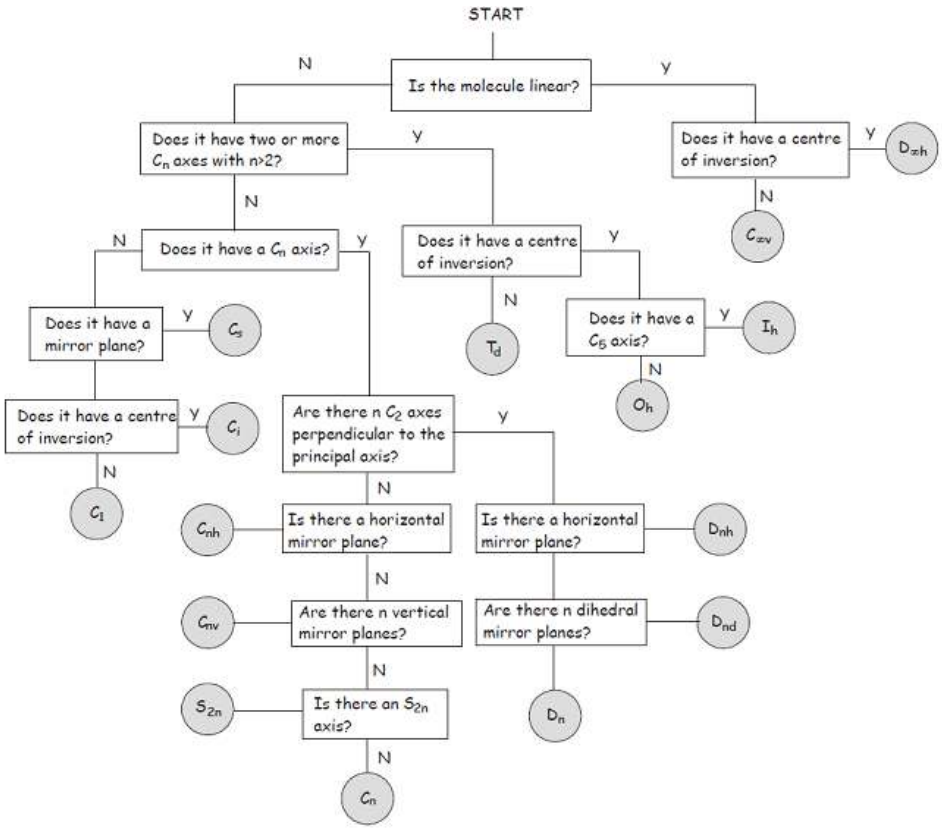
12. T - as for T_d but no planes of reflection.
13. T_h - as for T but contains a center of inversion.
14. O_h - the group of the regular octahedron e.g. SF_6.



15. O - as for O_h, but with no planes of reflection.

The final group is the full rotation group R_3, which consists of an infinite number of C_n axes with all possible values of n and describes the symmetry of a sphere. Atoms (but no molecules) belong to R_3, and the group has important applications in atomic quantum mechanics. However, we won't be treating it any further here.

Once you become more familiar with the symmetry elements and point groups described above, you will find it quite straightforward to classify a molecule in terms of its point group. In the meantime, the flowchart shown below provides a step-by-step approach to the problem.



[1]Though the Hermann-Mauguin system can be used to label point groups, it is usually used in the discussion of crystal symmetry. In crystals, in addition to the symmetry elements described above, translational symmetry elements are very important. Translational symmetry operations leave no point unchanged, with the consequence that crystal symmetry is described in terms of *space groups* rather than *point groups*.

Symmetry and physical properties

Carrying out a symmetry operation on a molecule must not change any of its physical properties. It turns out that this has some interesting consequences, allowing us to predict whether or not a molecule may be chiral or polar on the basis of its point group.

For a molecule to have a permanent dipole moment, it must have an asymmetric charge distribution. The point group of the molecule not only determines whether the molecule may have a dipole moment, but also in which direction(s) it may point. If a molecule has a C_n axis with $n > 1$, it **cannot** have a dipole moment perpendicular to the axis of rotation (for example, a C_2 rotation would interchange the ends of such a dipole moment and reverse the polarity, which is not allowed – rotations with higher values of n would also change the direction in which the dipole points). Any dipole must lie parallel to a C_n axis.

Also, if the point group of the molecule contains any symmetry operation that would interchange the two ends of the molecule, such as a σ_h mirror plane or a C_2 rotation perpendicular to the principal axis, then there cannot be a dipole moment along the axis. The only groups compatible with a dipole moment are C_n, C_{nv} and C_s. In molecules belonging to C_n or C_{nv} the dipole must lie along the axis of rotation.

One example of symmetry in chemistry that you will already have come across is found in the isomeric pairs of molecules called enantiomers. Enantiomers are non-superimposable mirror images of each other, and one consequence of this symmetrical relationship is that they rotate the plane of polarized light passing through them in opposite directions. Such molecules are said to be chiral,[2] meaning that they cannot be superimposed on their mirror image. Formally, the symmetry element that precludes a molecule from being chiral is a rotation-reflection axis S_n. Such an axis is often implied by other symmetry elements present in a group.

For example, a point group that has C_n and σ_h as elements will also have S_n. Similarly, a center of inversion is equivalent to S_2. As a rule of thumb, a molecule definitely cannot have be chiral if it has a center of inversion or a mirror plane of any type (σ_h, σ_v or σ_d), but if these symmetry elements are absent the molecule should be checked carefully for an S_n axis before it is assumed to be chiral.

Chirality

The word chiral has its origins in the Greek word for hand (χειρ, pronounced ‘cheri’ with a soft ch as in ‘loch’). A pair of hands is also a pair of non-superimposable mirror images, and you will often hear chirality referred to as ‘handedness’ for this reason.

Summary

All molecules can be described in terms of their symmetry or lack thereof, which may contain symmetry elements (point, line, plane). Reflection, rotation, and inversion are symmetry operations (movement of the molecules such that after the movement, all the atoms of the molecules is coincidental with equivalent atom of the molecule in original).

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12.3: Symmetry Operations Define Groups

Now that we have explored some of the properties of symmetry operations and elements and their behavior within point groups, we are ready to introduce the formal mathematical definition of a group. A mathematical group is defined as a set of elements (g_1, g_2, g_3...) together with a rule for forming combinations g_j. The number of elements h is called the **order** of the group. For our purposes, the elements are the symmetry operations of a molecule and the rule for combining them is the sequential application of symmetry operations investigated in the previous section. The elements of the group and the rule for combining them must satisfy the following criteria.

1. The group must include the identity E, for which

$$Eg_i = g_i \tag{12.3.1}$$

   for all the elements of the group.
2. The elements must satisfy the **group property** that the combination of any pair of elements is also an element of the group.
3. Each element g_i must have an inverse g_i^{-1}, which is also an element of the group, such that

$$g_i g_i^{-1} = g_i^{-1} g_i = E \tag{12.3.2}$$

   (e.g. in C_{3v} the inverse of C_3^+ is C_3^-, the inverse of (σ_v is σ_v', the inverse g_i^{-1} effectively 'undoes' the effect of the symmetry operation g_i).
4. The rule of combination must be associative i.e.

$$(g_i g_j)(g_k) = g_i(g_j g_k) \tag{12.3.3}$$

The above definition **does not** require the elements to commute, which would require

$$g_i g_k = g_k g_i \tag{12.3.4}$$

As we discovered in the C_{3v} example above, in many groups the outcome of consecutive application of two symmetry operations depends on the order in which the operations are applied.

Commuting is not a Requirement of Group Elements

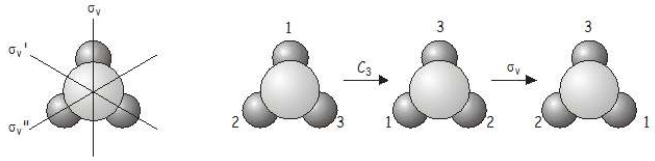
Groups for which the elements do not commute are called **non-Abelian** groups; those for which they elements do commute are *Abelian*.

Group theory is an important area in mathematics, and luckily for chemists the mathematicians have already done most of the work for us. Along with the formal definition of a group comes a comprehensive mathematical framework that allows us to carry out a rigorous treatment of symmetry in molecular systems and learn about its consequences.

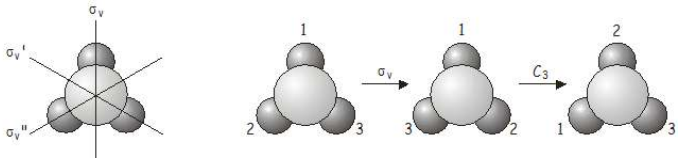
Many problems involving operators or operations (such as those found in quantum mechanics or group theory) may be reformulated in terms of matrices. Any of you who have come across transformation matrices before will know that symmetry operations such as rotations and reflections may be represented by matrices. It turns out that the set of matrices representing the symmetry operations in a group obey all the conditions laid out above in the mathematical definition of a group, and using matrix representations of symmetry operations simplifies carrying out calculations in group theory. Before we learn how to use matrices in group theory, it will probably be helpful to review some basic definitions and properties of matrices.

Group Multiplication

Now we will investigate what happens when we apply two symmetry operations in sequence. As an example, consider the NH_3 molecule, which belongs to the C_{3v} point group. Consider what happens if we apply a C_3rotation followed by a σ_v reflection. We write this combined operation $\sigma_v C_3$ (when written, symmetry operations operate on the thing directly to their right, just as operators do in quantum mechanics – we therefore have to work backwards from right to left from the notation to get the correct order in which the operators are applied). As we shall soon see, the order in which the operations are applied is important.



The combined operation $\sigma_v C_3$ is equivalent to σ_v'', which is also a symmetry operation of the C_{3v} point group. Now let's see what happens if we apply the operators in the reverse order i.e. $C_3\sigma_v$ (σ_v followed by C_3).



Again, the combined operation $C_3\sigma_v$ is equivalent to another operation of the point group, this time σ_v'.

There are two important points that are illustrated by this example:

1. The order in which two operations are applied is important. For two symmetry operations A and B, AB is not necessarily the same as BA, i.e. symmetry operations do not in general commute. In some groups the symmetry elements do commute; such groups are said to be *Abelian*.
2. If two operations from the same point group are applied in sequence, the result will be equivalent to another operation from the point group. Symmetry operations that are related to each other by other symmetry operations of the group are said to belong to the same *class*. In NH_3, the three mirror planes σ_v, σ_v' and σ_v'' belong to the same class (related to each other through a C_3 rotation), as do the rotations C_3^+ and C_3^- (anticlockwise and clockwise rotations about the principal axis, related to each other by a vertical mirror plane

The effects of applying two symmetry operations in sequence within a given point group are summarized in *group multiplication tables*. As an example, the complete group multiplication table for C_{3v} using the symmetry operations as defined in the figures above is shown below. The operations written along the first row of the table are carried out first, followed by those written in the first column (note that the table would change if we chose to name σ_v, σ_v' and σ_v'' in some different order).

C_{3v}	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
E	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
C_3^+	C_3^+	C_3^-	E	σ_v'	σ_v''	σ_v
C_3^-	C_3^-	E	C_3^+	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^-	C_3^+
σ_v'	σ_v'	σ_v	σ_v''	C_3^+	E	C_3^-
σ_v''	σ_v''	σ_v'	σ_v	C_3^-	C_3^+	E

(12.3.5)

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12.4: Symmetry Operations as Matrices

Matrices can be used to map one set of coordinates or functions onto another set. Matrices used for this purpose are called *transformation matrices*. In group theory, we can use transformation matrices to carry out the various symmetry operations discussed previously. As a simple example, we will investigate the matrices we would use to carry out some of these symmetry operations on a vector in 2D space (x, y).

The Identity Operation

The identity operation leaves the vector unchanged, and as you may already suspect, the appropriate matrix is the identity matrix.

$$(x, y)\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} = (x, y) \tag{12.4.1}$$

Reflection in a plane

The simplest example of a reflection matrix corresponds to reflecting the vector (x, y) in either the x or y axes. Reflection in the x axis maps y to $-y$, while reflection in the y axis maps x to $-x$. The appropriate matrix is very like the identity matrix but with a change in sign for the appropriate element. Reflection in the x axis transforms the vector (x, y) to $(x, -y)$, and the appropriate matrix is

$$(x, y)\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = (x, -y) \tag{12.4.2}$$

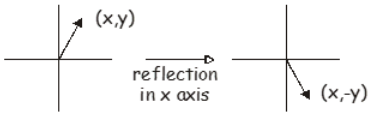


Figure 12.4.1: Reflection across the x-axis in 2D space.

Reflection in the y axis transforms the vector (x, y) to $(-x, y)$, and the appropriate matrix is

$$(x, y)\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix} = (-x, y) \tag{12.4.3}$$

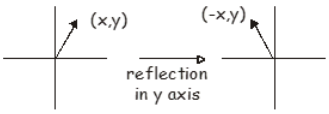


Figure 12.4.2: Reflection across the y-axis *in 2D space.*

More generally, matrices can be used to represent reflections in any plane (or line in 2D). For example, reflection in the 45° axis shown below maps (x, y) onto $(-y, -x)$.

$$(x, y)\begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix} = (-y, -x) \tag{12.4.4}$$

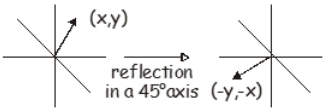


Figure 12.4.3: Reflection across the axis that is rotated 45° with with respect to x-axis *in 2D space.*

Rotation about an Axis

In two dimensions, the appropriate matrix to represent rotation by an angle θ about the origin is

$$R(\theta) = \begin{pmatrix}\cos\theta & -\sin\theta\\ \sin\theta & \cos\theta\end{pmatrix} \tag{12.4.5}$$

In three dimensions, rotations about the x, y and z axes acting on a vector (x, y, z) are represented by the following matrices.

$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \tag{12.4.6}$$

$$R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \tag{12.4.7}$$

$$R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{12.4.8}$$

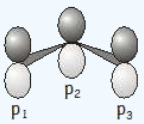
Matrix Representation

The symmetry operations in a group may be represented by a set of transformation matrices $\Gamma(g)$, one for each symmetry element g. Each individual matrix is called a *representative* of the corresponding symmetry operation, and the complete set of matrices is called a *matrix representation* of the group. The matrix representatives act on some chosen *basis set* of functions, and the actual matrices making up a given representation will depend on the basis that has been chosen. The representation is then said to *span* the chosen basis. In the examples above we were looking at the effect of some simple transformation matrices on an arbitrary vector (x, y). The basis was therefore a pair of unit vectors pointing in the x and y directions. In most of the examples we will be considering in this course, we will use sets of atomic orbitals as basis functions for matrix representations. Before proceeding any further, we must check that a matrix representation of a group obeys all of the rules set out in the formal mathematical definition of a group.

1. The first rule is that the group must include the identity operation E (the 'do nothing' operation). We showed above that the matrix representative of the identity operation is simply the identity matrix. As a consequence, every matrix representation includes the appropriate identity matrix.
2. The second rule is that the combination of any pair of elements must also be an element of the group (the *group property*). If we multiply together any two matrix representatives, we should get a new matrix which is a representative of another symmetry operation of the group. In fact, matrix representatives multiply together to give new representatives in exactly the same way as symmetry operations combine according to the group multiplication table. For example, in the C_{3v} point group, we showed that the combined symmetry operation $C_3\sigma_v$ is equivalent to σ_v''. In a matrix representation of the group, if the matrix representatives of C_3 and σ_v are multiplied together, the result will be the representative of σ_v''.
3. The third rule states that every operation must have an inverse, which is also a member of the group. The combined effect of carrying out an operation and its inverse is the same as the identity operation. It is fairly easy to show that matrix representatives satisfy this criterion. For example, the inverse of a reflection is another reflection, identical to the first. In matrix terms we would therefore expect that a reflection matrix was its own inverse, and that two identical reflection matrices multiplied together would give the identity matrix. This turns out to be true, and can be verified using any of the reflection matrices in the examples above. The inverse of a rotation matrix is another rotation matrix corresponding to a rotation of the opposite sense to the first.
4. The final rule states that the rule of combination of symmetry elements in a group must be associative. This is automatically satisfied by the rules of matrix multiplication.

✔ Example 12.4.1: matrix representation of the C_{2v} point group (the allyl radical)

In this example, we'll take as our basis a p orbital on each carbon atom (p_1, p_2, p_3).



Note that the p orbitals are *perpendicular* to the plane of the carbon atoms (this may seem obvious, but if you're visualizing the basis incorrectly it will shortly cause you a not inconsiderable amount of confusion). The symmetry operations in the C_{2v} point group, and their effect on the three p orbitals, are as follows:

$$\begin{array}{ll} E & (p_1, p_2, p_3) \rightarrow (p_1, p_2, p_3) \\ C_2 & (p_1, p_2, p_3) \rightarrow (-p_3, -p_2, -p_1) \\ \sigma_v & (p_1, p_2, p_3) \rightarrow (-p_1, -p_2, -p_3) \\ \sigma_v' & (p_1, p_2, p_3) \rightarrow (p_3, p_2, p_1) \end{array} \tag{12.4.9}$$

The matrices that carry out the transformation are

$$\begin{array}{ll} \Gamma(E) & (p_1, p_2, p_3) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = (p_1, p_2, p_3) \\ \Gamma(C_2) & (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} = (-p_3, -p_2, -p_1) \\ \Gamma(\sigma_v) & (p_1, p_2, p_3) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = (-p_1, -p_2, -p_3) \\ \Gamma(\sigma_v') & (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} = (p_3, p_2, p_1) \end{array} \tag{12.4.10}$$

We have written the vectors representing our basis as *row vectors*. This is important. If we had written them as column vectors, the corresponding transformation matrices would be the transposes of the matrices above, and would not reproduce the group multiplication table (try it as an exercise if you need to convince yourself).

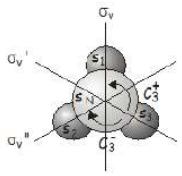
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12.5: The C_{3v} Point Group

The first thing we need to do before we can construct a matrix representation is to choose a basis. For NH_3, we will select a basis (s_N, s_1, s_2, s_3) that consists of the valence s orbitals on the nitrogen and the three hydrogen atoms. We need to consider what happens to this basis when it is acted on by each of the symmetry operations in the C_{3v} point group, and determine the matrices that would be required to produce the same effect. The basis set and the symmetry operations in the C_{3v} point group are summarized in the figure below.



The effects of the symmetry operations on our chosen basis are as follows:

$$\begin{array}{ll} E & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3) \\ C_3^+ & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1) \\ C_3^- & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2) \\ \sigma_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2) \\ \sigma_v' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3) \\ \sigma_v'' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1) \end{array} \tag{12.5.1}$$

By inspection, the matrices that carry out the same transformations are:

$$\begin{array}{ll} \Gamma(E) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_1, s_2, s_3) \\ \Gamma(C_3^+) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_2, s_3, s_1) \\ \Gamma(C_3^-) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_1, s_2) \\ \Gamma(\sigma_v) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_1, s_3, s_2) \\ \Gamma(\sigma_v') & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_2, s_1, s_3) \\ \Gamma(\sigma_v'') & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_2, s_1) \end{array} \tag{12.5.2}$$

These six matrices therefore form a representation for the C_{3v} point group in the (s_N, s_1, s_2, s_3) basis. They multiply together according to the group multiplication table and satisfy all the requirements for a mathematical group.

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12.6: Character Tables

Now that we've learnt how to create a matrix representation of a point group within a given basis, we will move on to look at some of the properties that make these representations so powerful in the treatment of molecular symmetry.

Similarity Transforms

Suppose we have a basis set $(x_1, x_2, x_3, ...x_n)$, and we have determined the matrix representatives for the basis in a given point group. There is nothing particularly special about the basis set we have chosen, and we could equally well have used any set of linear combinations of the original functions (provided the combinations were linearly independent). The matrix representatives for the two basis sets will certainly be different, but we would expect them to be related to each other in some way. As we shall show shortly, they are in fact related by a *similarity transform*. It will be far from obvious at this point why we would want to carry out such a transformation, but similarity transforms will become important later on when we use group theory to choose an optimal basis set with which to generate molecular orbitals.

Consider a basis set $(x'_1, x'_2, x'_3, ...x'_n)$, in which each basis function x'_i is a linear combination of our original basis $(x_1, x_2, x_3, ...x_n)$.

$$x'_j = \Sigma_i x_i c_{ji} = x_1 c_{j1} + x_2 c_{j2} + ... \tag{11.1}$$

The c_{ji} appearing in the sum are coefficients; c_{ji} is the coefficient multiplying the original basis function x_i in the new linear combination basis function x'_j. We could also represent this transformation in terms of a matrix equation $\mathbf{x'} = \mathbf{x}C$:

$$(x'_1, x'_2, ...x'_n) = (x_1, x_2, ...x_n) \begin{pmatrix} c_{11} & c_{12} & ... & c_{1n} \\ c_{21} & c_{22} & ... & c_{2n} \\ ... & ... & ... & ... \\ c_{n1} & c_{n2} & ... & c_{nn} \end{pmatrix} \tag{11.2}$$

Now we look at what happens when we apply a symmetry operation g to our two basis sets. If $\Gamma(g)$ and $\Gamma'(g)$ are matrix representatives of the symmetry operation in the $\mathbf{x}$ and $\mathbf{x'}$ bases, then we have:

$$\begin{aligned} g\mathbf{x'} &= \mathbf{x'}\Gamma'(g) & & \\ g\mathbf{x}C &= \mathbf{x}C\Gamma'(g) & & \text{since } \mathbf{x'} = \mathbf{x}C \\ g\mathbf{x} &= \mathbf{x}C\Gamma'(g)C^{-1} & & \text{multiplying on the right by } C^{-1} \text{and using } CC^{-1} = I \\ &= \mathbf{x}\Gamma(g) & & \end{aligned} \tag{11.3}$$

We can therefore identify the similarity transform relating $\Gamma(g)$, the matrix representative in our original basis, to $\Gamma'(g)$, the representative in the transformed basis. The transform depends only on the matrix of coefficients used to transform the basis functions.

$$\Gamma(g) = C\Gamma'(g)C^{-1} \tag{11.4}$$

Also,

$$\Gamma'(g) = C^{-1}\Gamma(g)C \tag{11.5}$$

Characters of Representations

The trace of a matrix representative $\Gamma(g)$ is usually referred to as the *character* of the representation under the symmetry operation g. We will soon come to see that the characters of a matrix representation are often more useful than the matrix representatives themselves. Characters have several important properties.

1. The character of a symmetry operation is invariant under a similarity transform
2. Symmetry operations belonging to the same class have the same character in a given representation. Note that the character for a given class may be different in different representations, and that more than one class may have the same character.

Proofs of the above two statements are given in the Appendix.

Character Tables

A character table summarizes the behavior of all of the possible irreducible representations of a group under each of the symmetry operations of the group. The character table for C_{3v} is shown below.

$C_{3v}, 3m$	E	$2C_3$	$3\sigma_v$	$h = 6$
A_1	1	1	1	$z, z^2, x^2 + y^2$
A_2	1	1	−1	R_z
E	2	−1	0	$(x, y), (xy, x^2 + y^2), (xz, yz), (R_x, R_y)$

(12.6.1)

The various sections of the table are as follows:

i. The first element in the table gives the name of the point group, usually in both Schoenflies (C_{3v}) and Hermann-Mauguin ($3m$) notation.
ii. Along the first row are the symmetry operations of the group, E, $2C_3$ and $3\sigma_v$, followed by the order of the group. Because operations in the same class have the same character, symmetry operations are grouped into classes in the character table and not listed separately.
iii. In the first column are the irreducible representations of the group. In C_{3v} the irreducible representations are A_1, A_2 and E (the representation we considered above spans $2A_1$ + E).
iv. The characters of the irreducible representations under each symmetry operation are given in the bulk of the table.
v. The final column of the table lists a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products $(z^2, x^2 + y^2, xy, yz)$, and the rotations (R_x, R_y, R_z).

The functions listed in the final column of the table are important in many chemical applications of group theory, particularly in spectroscopy. For example, by looking at the transformation properties of x, y and z (sometimes given in character tables as T_x, T_y, T_z) we can discover the symmetry of translations along the x, y, and z axes. Similarly, R_x, R_y and R_z represent rotations about the three Cartesian axes. As we shall see later, the transformation properties of x, y, and z can also be used to determine whether or not a molecule can absorb a photon of x-, y-, or z-polarized light and undergo a spectroscopic transition. The Cartesian products play a similar role in determining selection rules for Raman transitions, which involve two photons.

Character tables for common point groups are given in Appendix B.

A simple way to determine the characters of a representation

In many applications of group theory, we only need to know the characters of the representative matrices, rather than the matrices themselves. Luckily, when each basis function transforms as a 1D irreducible representation (which is true in many cases of interest) there is a simple shortcut to determining the characters without having to construct the entire matrix representation. All we have to do is to look at the way the individual basis functions transform under each symmetry operation. For a given operation, step through the basis functions as follows:

i. Add 1 to the character if the basis function is unchanged by the symmetry operation (i.e. the basis function is mapped onto itself);
ii. Add −1 to the character if the basis function changes sign under the symmetry operation (i.e the basis function is mapped onto minus itself);
iii. Add 0 to the character if the basis function moves when the symmetry operation is applied (i.e the basis function is mapped onto something different from itself).

Try this for the s orbital basis we have been using for the C_{3v} group. You should find you get the same characters as we obtained from the traces of the matrix representatives.

We can also work out the characters fairly easily when two basis functions transform together as a 2D irreducible representation. For example, in the C_{3v} point group x and y axes transform together as E. If we carry out a rotation about z by an angle θ, our x and y axes are transformed onto new axes x' and y'. However, the new axes can each be written as a linear combination of our original x and y axes. Using the rotation matrices introduced in Section 9, we see that:

$$\begin{aligned} x' &= \cos\theta\, x + \sin\theta\, y \\ y' &= -\sin\theta\, x + \cos\theta\, y \end{aligned} \tag{12.6.2}$$

For one-dimensional irreducible representations we asked if a basis function/axis was mapped onto itself, minus itself, or something different. For two-dimensional irreducible representations we need to ask how much of the 'old' axis is contained in the new one. From the above we see that the x' axis contains a contribution $\cos\theta$ from the x axis, and the y' axis contains a contribution $\cos\theta$ from the y axis. The characters of the x and y axes under a rotation through θ are therefore $\cos\theta$, and the overall character of the E irreducible representation is therefore $\cos\theta + \cos\theta = 2\cos\theta$. For a C_3 rotation through 120 degrees, the character of the E irreducible representation is therefore $2\cos 120° = -1$.

In general, *when an axis is rotated by an angle θ by a symmetry operation, its contribution to the character for that operation is* $\cos\theta$.

Irreducible representations with complex characters

In many cases (see Appendix B), the characters for rotations C_n and improper rotations S_n are complex numbers, usually expressed in terms of the quantity $\epsilon = \exp(2\pi i/n)$. It is fairly straightforward to reconcile this with the fact that in chemistry we are generally using group theory to investigate physical problems in which all quantities are real. It turns out that whenever our basis spans an irreducible representation whose characters are complex, it will also span a second irreducible representation whose characters are the complex conjugates of the first irreducible representation i.e. complex irreducible representations occur in pairs. According to the strict mathematics of group theory, each irreducible representation in the pair should be considered as a separate representation. However, when applying such irreducible representations in physical problems, we add the characters for the two irreducible representations together to get a single irreducible representation whose characters are real.

As an example, the 'correct' character table for the group C_3 takes the form:

C_3	E	C_3	C_3^2
A	1	1	1
E	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\\epsilon*\end{matrix}$	$\begin{matrix}\epsilon*\\\epsilon\end{matrix}$

(12.6.3)

Where $\epsilon = \exp(2\pi i/3)$. However, as chemists we would usually combine the two parts of the E irreducible representation to give:

C_3	E	C_3	C_3^2
A	1	1	1
E	2	−1	1

(12.6.4)

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12.7: Characters of Irreducible Representations

The two one-dimensional irreducible representations spanned by s_N and s_1' are seen to be identical. This means that s_N and s_1' have the 'same symmetry', transforming in the same way under all of the symmetry operations of the point group and forming bases for the same matrix representation. As such, they are said to belong to the same *symmetry species*. There are a limited number of ways in which an arbitrary function can transform under the symmetry operations of a group, giving rise to a limited number of symmetry species. Any function that forms a basis for a matrix representation of a group must transform as one of the symmetry species of the group. The irreducible representations of a point group are labeled according to their symmetry species as follows:

i. 1D representations are labeled A or B, depending on whether they are symmetric (character $+1$) or antisymmetric (character -1) under rotation about the principal axis.
ii. 2D representations are labeled E, 3D representations are labeled T.
iii. In groups containing a center of inversion, g and u labels (from the German *gerade* and *ungerade*, meaning symmetric and antisymmetric) denote the character of the irreducible representation under inversion ($+1$ for g, -1 for u)
iv. In groups with a horizontal mirror plane but no center of inversion, the irreducible representations are given prime and double prime labels to denote whether they are symmetric (character $+1$ or antisymmetric (character -1) under reflection in the plane.
v. If further distinction between irreducible representations is required, subscripts 1 and 2 are used to denote the character with respect to a C_2 rotation perpendicular to the principal axis, or with respect to a vertical reflection if there are no C_2 rotations.

The 1D irreducible representation in the C_{3v} point group is symmetric (has character $+1$) under all the symmetry operations of the group. It therefore belongs to the irreducible representation A_1. The 2D irreducible representation has character 2 under the identity operation, -1 under rotation, and 0 under reflection, and belongs to the irreducible representation E.

Sometimes there is confusion over the relationship between a function f and its irreducible representation, but it is quite important that you understand the connection. There are several different ways of stating the relationship. For example, the following statements all mean the same thing:

- "f has A_2 symmetry"
- "f transforms as A_2"
- "f has the same symmetry

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12.8: Using Symmetry to Solve Secular Determinants

As we continue with this course, we will discover that there are many times when we would like to know whether a particular integral is necessarily zero, or whether there is a chance that it may be non-zero. We can often use group theory to differentiate these two cases.

You will have already used symmetry properties of functions to determine whether or not a one-dimensional integral is zero. For example, cos(x) is an 'even' function (symmetric with respect to reflection through the origin), and it follows from this that

$$\int_{-\infty}^{\infty} \cos(x)dx = 0 \tag{12.8.1}$$

In general integral between these limits for any other even function will be also be zero.

In the general case we may have an integral of more than one dimension. The key to determining whether a general integral is necessarily zero lies in the fact that because an integral is just a number, it must be invariant to any symmetry operation. For example, bonding in a diatomic (see next section) depends on the presence of a non-zero overlap between atomic orbitals on adjacent atoms, which may be quantified by an *overlap integral*. You would not expect the bonding in a molecule to change if you rotated the molecule through some angle θ, so the integral must be invariant to rotation, and indeed to any other symmetry operation.

In group theoretical terms, for an integral to be non-zero, *the integrand must transform as the totally symmetric irreducible representation in the appropriate point group*. In practice, the integrand may not transform as a single irreducible representation, but it **must include** the totally symmetric irreducible representation. These ideas should become more clear in the next section.

> It should be noted that even when the irreducible representations spanned by the integrand do include the totally symmetric irreducible representation, it is still possible for the integral to be zero. All group theory allows us to do is identify integrals that are *necessarily* zero based on the symmetry (or lack thereof) of the integrand.

Secular Equations

As we have seen already, any set of linear equations may be rewritten as a matrix equation $\mathbf{Ax} = \mathbf{b}$. Linear equations are classified as *simultaneous linear equations* or *homogeneous linear equations*, depending on whether the vector $\mathbf{b}$ is non-zero or zero. For a set of simultaneous linear equations (non-zero $\mathbf{b}$) it is fairly apparent that if a unique solution exists, it can be found by multiplying both sides by the inverse matrix $\mathbf{A}^{-1}$ (since $\mathbf{A}^{-1}\mathbf{A}$ on the left hand side is equal to the identity matrix, which has no effect on the vector $\mathbf{x}$)

$$\begin{aligned} \mathbf{Ax} &= \mathbf{b} \\ \mathbf{A}^{-1}\mathbf{Ax} &= \mathbf{A}^{-1}\mathbf{b} \\ \mathbf{x} &= \mathbf{A}^{-1}\mathbf{b} \end{aligned} \tag{12.8.2}$$

In practice, there are easier matrix methods for solving simultaneous equations than finding the inverse matrix, but these need not concern us here. We previously argued that in order for a matrix to have an inverse, **it must have a non-zero determinant**. Since $\mathbf{A}^{-1}$ must exist in order for a set of simultaneous linear equations to have a solution, this means that the determinant of the matrix $\mathbf{A}$ must be non-zero for the equations to be solvable.

> *For a matrix to have an inverse, it must have a non-zero determinant.*

The reverse is true for homogeneous linear equations. In this case the set of equations only has a solution if the determinant of $\mathbf{A}$ *is* equal to zero. The secular equations we want to solve are homogeneous equations, and we will use this property of the determinant to determine the molecular orbital energies. An important property of homogeneous equations is that if a vector $\mathbf{x}$ is a solution, so is any multiple of $\mathbf{x}$, meaning that the solutions (the molecular orbitals) can be normalized without causing any problems.

Solving for the orbital energies and expansion coefficients

Recall the secular equations for the A_1 orbitals of NH_3 derived in the previous section

$$\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) &= 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) &= 0 \end{aligned} \tag{12.8.3}$$

where c_1 and c_2 are the coefficients in the linear combination of the SALCs $\phi_1 = s_N$ and $\phi_2 = \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3)$ used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{12.8.4}$$

In order for the equations to have a solution, the determinant of the matrix must be equal to zero. Writing out the determinant will give us a polynomial equation in E that we can solve to obtain the orbital energies in terms of the Hamiltonian matrix elements H_{ij} and overlap integrals S_{ij}. The number of energies obtained by 'solving the secular determinant' in this way is equal to the order of the matrix, in this case two.

The secular determinant for Equation (21.3) is (noting that S_{11} = $S_{22} = 1$ since the SALCs are normalized)

$$(H_{11} - E)(H_{22} - E) - (H_{12} - ES_{12})^2 = 0 \tag{12.8.5}$$

Expanding and collecting terms in E gives

$$E^2(1 - S_{12}^2) + E(2H_{12}S_{12} - H_{11} - H_{22}) + (H_{11}H_{22} - H_{12}^2) = 0 \tag{12.8.6}$$

which can be solved using the quadratic formula to give the energies of the two molecular orbitals.

$$\begin{aligned} E_{\pm} &= \\ &= \frac{-(2H_{12}S_{12} - H_{11} - H_{22}) \pm \sqrt{(2H_{12}S_{12} - H_{11} - H_{22})^2 - 4(1 - S_{12}^2)(H_{11}H_{22} - H_{12}^2)}}{2(1 - S_{12}^2)} \end{aligned} \tag{12.8.7}$$

To obtain numerical values for the energies, we need to evaluate the integrals H_{11}, H_{22}, H_{12}, and S_{12}. This would be quite a challenge to do analytically, but luckily there are a number of computer programs that can be used to calculate the integrals. One such program gives the following values.

$$\begin{aligned} H_{11} &= -26.0000\ eV \\ H_{22} &= -22.2216\ eV \\ H_{12} &= -29.7670\ eV \\ S_{12} &= 0.8167\ eV \end{aligned} \tag{12.8.8}$$

When we substitute these into our equation for the energy levels, we get:

$$\begin{aligned} E_+ &= 29.8336\ eV \\ E_- &= -31.0063\ eV \end{aligned} \tag{12.8.9}$$

We now have the orbital energies and the next step is to find the orbital coefficients. The coefficients for an orbital of energy E are found by substituting the energy into the secular equations and solving for the coefficients c_i. Since the two secular equations are not linearly independent (i.e. they are effectively only one equation), when we solve them to find the coefficients what we will end up with is the *relative* values of the coefficients. This is true in general: in a system with N coefficients, solving the secular equations will allow all N of the coefficients c_i to be obtained in terms of, say, c_1. The absolute values of the coefficients are found by normalizing the wavefunction.

Since the secular equations for the orbitals of energy E_+ and E_- are not linearly independent, we can choose to solve either one of them to find the orbital coefficients. We will choose the first.

$$(H_{11} - E_{\pm})c_1 + (H_{12} - E_{\pm}S_{12})c_2 = 0 \tag{12.8.10}$$

For the orbital with energy E_- = -31.0063 eV, substituting numerical values into this equation gives

$$\begin{aligned} 5.0063c_1 - 4.4442c_2 &= 0 \\ c_2 &= 1.1265c_1 \end{aligned} \tag{12.8.11}$$

The molecular orbital is therefore

$$\Psi = c_1(\phi_1 + 1.1265\phi_2) \tag{12.8.12}$$

Normalizing to find the constant c_1 (by requiring $< \Psi | \Psi >$ = 1) gives

$$\begin{aligned} \Psi_1 &= 0.4933\phi_1 + 0.5557\phi_2 \\ &= 0.4933s_N + 0.3208(s_1 + s_2 + s_3) \quad \text{(substituting the SALCs for } \phi_1 \text{ and } \phi_2) \end{aligned} \tag{12.8.13}$$

For the second orbital, with energy E_+ = 29.8336 eV, the secular equation is

$$\begin{aligned} -55.8336c_1 - 54.1321c_2 &= 0 \\ c_2 &= -1.0314c_1 \end{aligned} \tag{12.8.14}$$

giving

$$\begin{aligned} \Psi_2 &= c_1(\phi_1 - 1.0314\phi_2) \\ &= 1.6242\phi_1 - 1.6752\phi_2 \qquad \text{(after normalization)} \\ &= 1.6242s_N - 0.9672(s_1 + s_2 + s_3) \end{aligned} \tag{12.8.15}$$

These two A_1 molecular orbitals Ψ_1 and Ψ_2, one bonding and one antibonding, are shown below.



The remaining two SALCs arising from the s orbitals of NH_3 ($\phi_3 = \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3)$ and $\phi_4 = \frac{1}{\sqrt{2}}(s_2 - s_3)$), form an orthogonal pair of molecular orbitals of E symmetry. We can show this by solving the secular determinant to find the orbital energies. The secular equations in this case are:

$$\begin{aligned} c_1(H_{33} - ES_{33}) + c_2(H_{34} - ES_{34}) &= 0 \\ c_1(H_{34} - ES_{34}) + c_2(H_{44} - ES_{44}) &= 0 \end{aligned} \tag{12.8.16}$$

Solving the secular determinant gives

$$E_\pm = \frac{-(2H_{34}S_{34} - H_{33} - H_{44}) \pm \sqrt{(2H_{34}S_{34} - H_{33} - H_{44})^2 - 4(1 - S_{34}^2)(H_{33}H_{44} - H_{34}^2)}}{2(1 - S_{34}^2)} \tag{12.8.17}$$

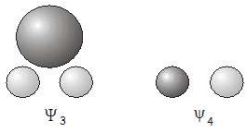
The integrals required are

$$\begin{aligned} H_{33} &= -9.2892\ eV \\ H_{44} &= -9.2892\ eV \\ H_{34} &= 0 \\ S_{34} &= 0 \end{aligned} \tag{12.8.18}$$

Using the fact that H_{34} = $S_{34} = 0$, the expression for the energies reduces to

$$E_\pm = \frac{(H_{33} + H_{44}) \pm (H_{33} - H_{44})}{2} \tag{12.8.19}$$

giving E_+ = H_{33} = -9.2892 eV and E_- = H_{44} = -9.2892 eV. Each SALC therefore forms a molecular orbital by itself, and the two orbitals have the same energy; the two SALCs form an orthogonal pair of degenerate orbitals. These two molecular orbitals of E symmetry are shown below.



Summary of the steps involved in constructing molecular orbitals

1. Choose a basis set of functions f_i consisting of the valence atomic orbitals on each atom in the system, or some chosen subset of these orbitals.
2. With the help of the appropriate character table, determine which irreducible representations are spanned by the basis set using Equation (15.20) to determine the number of times a_k that the kth irreducible representation appears in the representation.

$$a_k = \frac{1}{h}\sum_C n_C \chi(g)\chi_k(g) \tag{12.8.20}$$

3. Construct the SALCs ϕ_i that transform as each irreducible representation using Equation 16.1

$$\phi_i = \sum_g \chi_k(g) g f_i \tag{12.8.21}$$

4. Write down expressions for the molecular orbitals by taking linear combinations of all the irreducible representations of the same symmetry species.
5. Write down the secular equations for the system.
6. Solve the secular determinant to obtain the energies of the molecular orbitals.
7. Substitute each energy in turn back into the secular equations and solve to obtain the coefficients appearing in your molecular orbital expressions in step 4.
8. Normalize the orbitals.

Contributors

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12.9: Generating Operators

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12.E: Group Theory - The Exploitation of Symmetry (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 12 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q12.1

Normalize the following equation:

$$\psi(x) = Zxe^{-kx^2} \tag{12.E.1}$$

S12.1

$$\int_{-\infty}^{\infty} \psi(x)^* \psi(x) dx \tag{12.E.2}$$

$$1 = Z^2 \frac{1}{4} \sqrt{\frac{\pi}{2}} \alpha^{\frac{-3}{2}} \tag{12.E.3}$$

$$Z^2 = 4 \sqrt{\frac{2}{\pi}} \left(\frac{m\omega}{2\hbar}\right)^{3/2} \tag{12.E.4}$$

notes:

When I integrated $(xe^{-kx^2})^2$ the answer had an erf term in it. I think that the normalization of this specific function is more complex than was intended

Q12.3

List the symmetry elements for the bent molecule H_2O.

S12.3

Identity element E, two reflection planes σ_{xz} and σ_{yz}, one 2-fold rotation axis C_2, and it belongs to the point group C_2v.

Q12.4

Verify that an ethene molecule has the symmetry elements given in Table 12.2.

S12.4

The point group of ethene is D_{2h}. The identity of element is given. There are three C_2 axes and three vertical axes.

Q12.5

Verify that a water molecule has the symmetry elements given in Table 12.2.

S12.5

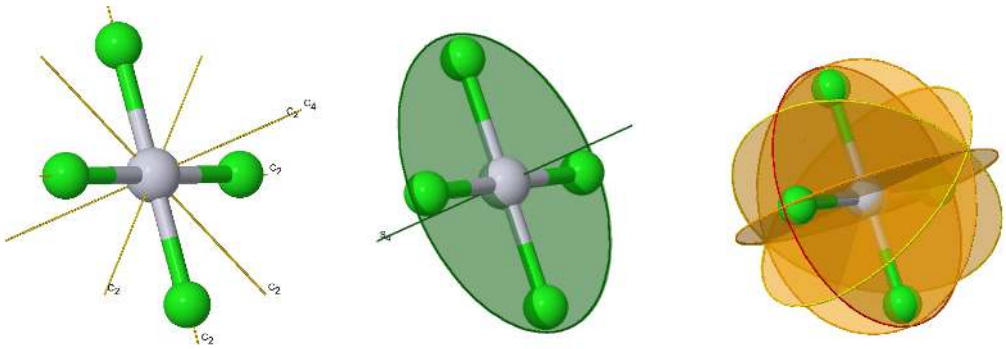
The point group of water is C_{2v}. A water molecule contains the symmetry elements E, C_2, and $2\sigma_v$. Water contains a two- fold C_2 axis through the oxygen molecule located directly on the Z axis. Water also contains two vertical planes of symmetry. The first mirror plane cuts vertically through all three molecules, H-O-H. The second mirror plane cuts through the water molecule perpendicular to the other vertical plane. The C_2 axis lies along the intersection of the two σ planes.

Q12.6

What is the point group of tetrachlropalladate $[PdCl_4]^{2-}$ and show the symmetry elements.

S12.6

The symmetry elements for tetrachlropalladate are $E, i, C_4, 4C_2, S_4, \sigma_h, 2\sigma_v, 2\sigma_d$.



(left): proper rotations (C_2 and C_4), (center) improper S_4 rotation, (right) relection planes (σ_h σ_d and σ_h)

Q12.31

Considering the allyl anion, $CH_2CHCH_2^-$, which belongs to the C_{2v} point group, calculate the Huckel secular determinant using $|\psi_1\rangle$, $|\psi_2\rangle$, and $|\psi_3\rangle$ (2_{pz} on each carbon atom). Then find the reducible representation for the allyl anion using $|\psi_j\rangle$ as the basis.

Show that the reducible representation Γ = $A_2 + 2B_1$. What does this say about the expected secular determinant? Now, use the generating operator (Equation 13.2) to derive three symmetry orbitals for the allyl anion. Normalize them and calculate the Huckel secular determinant equation and solve for the π electron energies.

S12.31

Applying the Huckel theory to the allyl anion yields the secular determinant given as

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{12.E.5}$$

Dividing the matrix by β and using the variable $x = \frac{\alpha - E}{\beta}$, we can solve a determinant of the form:

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \tag{12.E.6}$$

Expanding this determinant gives the equation

$$x^3 - 2x = 0 \tag{12.E.7}$$

Solving this equation gives $x = 0, \pm\sqrt{2}$.

The reducible representation can be found by looking at the four operators in the C_{2v} point group, which are $E, C_2, \sigma_v, \sigma_v'$. The operator E leaves all three orbitals unchanged (reducible representation of 3). The C_{2v} operator inverts just one of the orbitals (a reducible representation of -1). The σ_v operator leaves just one of the orbitals unchanged but does not invert any (reducible representation of 1). Lastly, the σ_v' operator inverts all three orbitals (reducible representation of -3). Thus, the reducible representation of the C_{2v} point group is

$$\Gamma = 3 \quad -1 \quad 1 \quad -3$$

Using equation 12.23, we find the irreducible representations to be

$$a_{A_1} = \frac{1}{4}(3 - 1 + 1 - 3) = 0 \tag{12.E.8}$$

$$a_{A_2} = \frac{1}{4}(3-1-1+3) = 1 \tag{12.E.9}$$

$$a_{B_1} = \frac{1}{4}(3+1+1+3) = 2 \tag{12.E.10}$$

$$a_{B_2} = \frac{1}{4}(3+1-1-3) = 0 \tag{12.E.11}$$

We therefore yield the reducible representation $\Gamma = A_2 + 2B_1$. This result shows us that the secular determinant can be written in either a 1 x 1 or 2 x 2 block diagonal form corresponding to the A_2 or B_1 representation, respectively. The three symmetry orbitals are found by

$$P_{A_2}\psi_1 = \frac{1}{4}(\psi_1 - \psi_3 - \psi_3 + \psi_1) \propto \psi_1 - \psi_3 \tag{12.E.12}$$

$$P_{B_1}\psi_1 = \frac{1}{4}(\psi_1 + \psi_3 + \psi_3 + \psi_1) \propto \psi_1 + \psi_3 \tag{12.E.13}$$

$$P_{B_1}\psi_2 = \frac{1}{4}(\psi_2 + \psi_2 + \psi_2 + \psi_2) = \psi_2 \tag{12.E.14}$$

using generating operators for A_2 and B_1.

The three normalized symmetry orbitals are

$$\Phi_1 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_3) \tag{12.E.15}$$

$$\Phi_2 = \psi_2 \tag{12.E.16}$$

$$\Phi_3 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_3) \tag{12.E.17}$$

Thus, these three orbitals give the symmetry elements below.

$$H_{11} = \frac{1}{2}(2\alpha) = \alpha \tag{12.E.18}$$

$$H_{22} = \alpha \tag{12.E.19}$$

$$H_{33} = \frac{1}{2}(2\alpha) = \alpha \tag{12.E.20}$$

$$H_{12} = \frac{1}{2}(\beta - \beta) = 0 \tag{12.E.21}$$

$$H_{13} = \frac{1}{2}(\alpha - \alpha) = 0 \tag{12.E.22}$$

$$H_{23} = \frac{1}{\sqrt{2}}(2\beta) = \sqrt{2}\beta \tag{12.E.23}$$

$$S_{11} = S_{22} = S_{33} = 1 \tag{12.E.24}$$

$$S_{12} = S_{13} = S_{23} = 0 \tag{12.E.25}$$

This gives the secular determinant

$$\begin{vmatrix} \alpha - E & 0 & 0 \\ 0 & \alpha - E & \sqrt{2}\beta \\ 0 & \sqrt{2}\beta & \alpha - E \end{vmatrix} = 0 \tag{12.E.26}$$

Dividing the matrix by β and using the variable $x = \frac{\alpha - E}{\beta}$, we can solve a determinant of the form:

$$\begin{vmatrix} x & 0 & 0 \\ 0 & x & \sqrt{2} \\ 0 & \sqrt{2} & x \end{vmatrix} = 0 \tag{12.E.27}$$

which gives roots $x = 0, \pm\sqrt{2}$. Using the substitution that $x = \dfrac{\alpha - E}{\beta}$, we get the energies to be

$$E_1 = \alpha - \sqrt{2}\beta \tag{12.E.28}$$

$$E_2 = \alpha \tag{12.E.29}$$

$$E_3 = \alpha + \sqrt{2}\beta \tag{12.E.30}$$

Q12.32

How will the secular determinant for SF_6 look if we use group theory to generate symmetry orbitals?

S12.32

The reducible representation for an octahedral is

$$\begin{array}{cccccccccccc} O_h & E & 8C_3 & 6C_2 & 6C_4 & 3C_2 & i & 6S_4 & 8S_6 & 3\sigma_h & 6\sigma_d \\ \Gamma & 6 & 0 & 0 & 2 & 2 & 0 & 0 & 0 & 4 & 2 \end{array} \tag{12.E.31}$$

Use this equation:

$$a_i = \frac{1}{h}\sum \chi(\hat{R})\chi_i(\hat{R}) \tag{12.E.32}$$

to get:

$$a_E = \frac{1}{10}\left(6 + 2 + 2 + 4 + 2\right) \tag{12.E.33}$$

However, the reducible representation is better represented in a table format:

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ	6	0	0	2	2	0	0	0	4	2

Q12.33

Apply the *Great Orthogonality Theorem*,

$$\sum_{\hat{R}} \Gamma_i(\hat{R})_{nm}\Gamma_{ij}(\hat{R})_{n'm'} = \frac{h}{d_i}\delta_{ij}\delta_{mm'}\delta_{nn'} \tag{12.E.34}$$

,

to C_{3v} point group given in which

$$\Gamma_E = [E_1 E_2 E_3 E_4 E_5 E_6] \tag{12.E.35}$$

where

$$E_1 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{12.E.36}$$

$$E_2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} \tag{12.E.37}$$

$$E_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} \tag{12.E.38}$$

$$E_4 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{12.E.39}$$

$$E_5 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix} \tag{12.E.40}$$

$$E_6 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix} \tag{12.E.41}$$

(h is the number of elements of Γ_i and d_i is the length of the diagonal of the matrix element of Γ_i)

S12.33

If we assume that $i = j = E_i$ and that $m = m', n = n'$, the general equation looks like

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{nm}]^2 \tag{12.E.42}$$

we must to pick the same element of each matrix, square it, and add them all together. All of them should equal $/frachl = 3$.

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{11}]^2 = 1 + 1/4 + 1/4 + 1 + 1/4 + 1/4 = 3 \tag{12.E.43}$$

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{12}]^2 = 0 + 3/4 + 3/4 + 0 + 3/4 + 3/4 = 3 \tag{12.E.44}$$

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{21}]^2 = 0 + 3/4 + 3/4 + 0 + 3/4 + 3/4 = 3 \tag{12.E.45}$$

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{22}]^2 = 1 + 1/4 + 1/4 + 1 + 1/4 + 1/4 = 3 \tag{12.E.46}$$

for unequal cases,($m \neq m'$ and $n \neq n'$) we can use the products of the elements and they should sum to zero.

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{11} \Gamma_E(\hat{R})_{12} = 0 + \sqrt{3}/4 - \sqrt{3}/4 + 0 - \sqrt{3}/4 + \sqrt{3}/4 = 0 \tag{12.E.47}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{11} \Gamma_E(\hat{R})_{21} = 0 - \sqrt{3}/4 + \sqrt{3}/4 + 0 - \sqrt{3}/4 + \sqrt{3}/4 = 0 \tag{12.E.48}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{12} \Gamma_E(\hat{R})_{21} = 0 - 3/4 - 3/4 + 0 + 3/4 + 3/4 = 0 \tag{12.E.49}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{12} \Gamma_E(\hat{R})_{22} = 1 + 1/4 + 1/4 - 1 - 1/4 - 1/4 = 0 \tag{12.E.50}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{21} \Gamma_E(\hat{R})_{22} = 0 - \sqrt{3}/4 + \sqrt{3}/4 + 0 + \sqrt{3}/4 - \sqrt{3}/4 = 0 \tag{12.E.51}$$

Q12.34

Using the Great Orthogonality Theorem, let $i = j$, $m = n$, and $m' = n'$ and sum over n and n' to show that

$$\sum_{\hat{R}} [\chi_j(\hat{R}]^2 = h \tag{12.E.52}$$

.

S12.34

Recall that $\chi_j(\hat{R})$ is defined as the character of the jth irreducible representation of $\hat{R}$, which in terms of matrix elements, is given by

$$\chi_i(\hat{R}) = \sum_m \Gamma_i(\hat{R})_{mm} \tag{12.E.53}$$

We now use the **great orthogonality theorem** to find the summed equation:

$$\sum_{\hat{R}} \Gamma_i(\hat{R})_{mn} \Gamma_j(\hat{R})_{m'n'} = \frac{h}{l_i} \delta_{ij} \delta_{mm'} \delta_{nn'} \tag{12.E.54}$$

Let $i = j$, $m = n$, and $m' = n'$. Then

$$\sum_{\hat{R}} \Gamma_i(\hat{R})_{nn} \Gamma_i(\hat{R})_{n'n'} = \frac{h}{l_i} \delta_{nn'} \tag{12.E.55}$$

$$\sum_{\hat{R}} \sum_n \Gamma_i(\hat{R})_{nn} \sum_{n'} \Gamma_i(\hat{R})_{n'n'} = \frac{h}{l_i} \delta_{nn'} \tag{12.E.56}$$

$$\sum_{\hat{R}} [\chi_i(\hat{R})]^2 = \frac{h}{l_i} = h \tag{12.E.57}$$

Q12.35

Determine the character table for C_i which has the symmetry elements E and *i*.

S12.35

Because there are two symmetry elements, there are two rows to the character table also to have a 2x2. The first row is completely symmetric to both operations while the second is antisymmetric with respect to the inversion center. Therefore, the character table is as shown below.



Q12-36

The C_i point group character table is given by

Ci	E	i
Ag	+1	+1
Au	+1	-1

Show that the basis for this point group are the even and odd functions over an interval (-a,a). Evaluate the integrals of this basis set using group theory in order to establish symmetry principles.

S12-36

Applying the inversion operator to a function,

$$i f_{even} = f_{even} \tag{12.E.58}$$

$$i f_{odd} = -f_{odd} \tag{12.E.59}$$

This demonstrates that f(even) belongs to Ag and f(odd) belongs to Au. As a result these functions are a basis of the C_i point group.

$$S_{ij} = \int \phi_i^* \phi_j d\tau \tag{12.E.60}$$

$$RS_{ij} = \int R\phi_i^* R\phi_j d\tau = S_{ij} = \int \phi_i^* \phi_j d\tau \tag{12.E.61}$$

with the value of Sij unchanged by the symmetry operation of the point group.

$$S_{ij} = \int_{-a}^{a} f_{even}(x) f_{even}(x) dx \tag{12.E.62}$$

$$iS_{ij} = \int_{-a}^{a} if_{even}(x) if_{even}(x) dx = \int_{-a}^{a} f_{even}(x) f_{even}(x) dx = 1 \tag{12.E.63}$$

$$S_{ij} = \int_{-a}^{a} f_{odd}(x) f_{odd}(x) dx \tag{12.E.64}$$

$$iS_{ij} = \int_{-a}^{a} if_{odd}(x) if_{odd}(x) dx = \int_{-a}^{a} -f_{odd}(x) - f_{odd}(x) dx = 1 \tag{12.E.65}$$

$$S_{ij} = \int_{-a}^{a} f_{even}(x) f_{odd}(x) dx \tag{12.E.66}$$

$$iS_{ij} = \int_{-a}^{a} if_{even}(x) if_{odd}(x) dx = -\int_{-a}^{a} f_{even}(x) f_{odd}(x) dx = 0 \tag{12.E.67}$$

12.37

Derive the symmetry orbitals for the pi- orbitals of butadiene by applying the generating operator

$$P_j = \frac{d_j}{h} \sum_R \chi_j(R) R \tag{12.E.68}$$

to the atomic 2pz orbital on each carbon atom. Identify the irreducible representation to which each resulting symmetry orbital belong. Derive the Huckel secular determinant.

S12.37

Butadiene belongs to the C2h point-group. Denote the 2pz orbital on

$$C_i \tag{12.E.69}$$

by

$$\psi_i \tag{12.E.70}$$

$$P\psi_1 = \frac{1}{4} \sum_R \chi(R) R \tag{12.E.71}$$

$$= \frac{1}{4} [(1) E\psi_1 + (1) C_2\psi_1 + (1) i\psi_1 + (1) \sigma\psi_1] \tag{12.E.72}$$

$$= \frac{1}{4} (\psi_1 + \psi_4 - \psi_4 + \psi_2) = 0 \tag{12.E.73}$$

Similarly,

$$P\psi_2 = \frac{1}{4} (\psi_2 + \psi_3 - \psi_3 - \psi_2) = 0 \tag{12.E.74}$$

$$P\psi_2 = \frac{1}{4} (\psi_2 + \psi_3 - \psi_3 - \psi_2) = 0 \tag{12.E.75}$$

Using Psi 1 and 2 (things get very confusing after this line, especially the part of the equation "=0 $\alpha\psi_1 - \psi_4$? -RM)

$$P\psi_1 = \frac{1}{4} (\psi_1 - \psi_4 - \psi_4 + \psi_1) = 0 \alpha\psi_1 - \psi_4 \tag{12.E.76}$$

$$P\psi_2 = \frac{1}{4} (\psi_2 - \psi_3 - \psi_3 + \psi_2) = 0 \alpha\psi_2 - \psi_3 \tag{12.E.77}$$

$$P\psi_3 = \frac{1}{4} (\psi_1 + \psi_4 + \psi_4 + \psi_1) = 0 \alpha\psi_1 + \psi_4 \tag{12.E.78}$$

$$P\psi_4 = \frac{1}{4} (\psi_2 + \psi_3 + \psi_3 + \psi_2) = 0 \alpha\psi_2 + \psi_3 \tag{12.E.79}$$

$$P\psi_1 = \backslash\hat{}P\psi_2 = 0 \tag{12.E.80}$$

The process isnt very clear as to how you got to the solution...perhaps explain a little better how the math works.

Q12.41

An arbitrary tetrahedral molecule (AB_4) belonging to the T_d point group has the reducible representation: Γ = 4 1 0 0 2. Show that:

a. the symmetry elements of the point group give this representation, and
b. it can be reduced as $\Gamma = A_1 + T_2$.

Finally, prove that an sp^3 orbital with T_d symmetry can be formed.

S12.41

a.) Applying the symmetry elements, we see that:

- $\hat{E}$ leaves all 4 bonds unmoved
- $\hat{C}_3$ leaves 1 bond unmoved
- $\hat{C}_2$ leaves 0 bonds unmoved
- $\hat{S}_4$ leaves 0 bonds unmoved
- $\hat{\sigma}_d$ leaves 2 bonds unmoved

The result is the reducible representation Γ = 4 1 0 0 2.

b.) Rewriting the symmetry elements in terms of the irreducible representations, we see that:

- $\alpha_{A_1} = \frac{1}{24}(4+8+0+0+12) = 1$
- $\alpha_{A_2} = \frac{1}{24}(4+8+0+0-12) = 0$
- $\alpha_{E} = \frac{1}{24}(8-8+0+0+0) = 0$
- $\alpha_{T_1} = \frac{1}{24}(12+0+0+0-12) = 0$
- $\alpha_{T_2} = \frac{1}{24}(12+0+0+0+12) = 1$

Using α as a coefficient and taking the sum of these 5 equations, we can rewrite the reducible representation as $\Gamma = A_1 + T_2$.

c.) The 2 p orbitals all have T_2 symmetry for a T_d molecule, so they can combine to form a hybrid T_2 orbital. All s orbitals are totally symmetric due to their spherical shape, making them A_1. Summing the 3 p orbitals and an s orbital will give a hybrid orbital of the desired $A_1 + T_2$ symmetry.

-Interesting question. I like the explanation on how an Sp3 orbital with T_2 symmetry can be formed

Q12.42

Consider an octahedral molecule XY6 whose point group is O_h. Prove the irreducible representation of O_h is $\Gamma = A_{1g} + E_g + T_{1u}$.

S12.43

(12.E.81)

$$a_{A_{1g}} = \frac{1}{48}(6+0+0+12+6+0+0+0+12+12) = 1$$
$$a_{A_{2g}} = \frac{1}{48}(6+0+0-12+6+0+0+0+12-12) = 0$$
$$a_{E_g} = \frac{1}{48}(12+0+0+0+12+0+0+0+24+0) = 1$$
$$a_{T_{1g}} = \frac{1}{48}(18+0+0+12-6+0+0+0-12-12) = 0$$
$$a_{T_{2g}} = \frac{1}{48}(18+0+0-12-6+0+0+0-12+12) = 0$$
$$a_{A_{1u}} = \frac{1}{48}(6+0+0+12+6+0+0+0-12-12) = 0$$
$$a_{A_{2u}} = \frac{1}{48}(6+0+0-12+6+0+0+0-12+12) = 0$$
$$a_{E_u} = \frac{1}{48}(12+0+0+0+12+0+0+0-24+0) = 0$$
$$a_{T_{1u}} = \frac{1}{48}(18+0+0+12-6+0+0+0+12+12) = 1$$
$$a_{T_{2u}} = \frac{1}{48}(18+0+0-12-6+0+0+0+12-12) = 0$$

= $\mathbf{\Gamma} = A_{1g} + E_g + T_{1u}$.

Q12.43

Consider an octahedral molecule XY6 whose point group is O_h. Prove the irreducible representation of O_h is $\mathbf{\Gamma} = A_{1g} + E_g + T_{1u}$.

S12.43

(12.E.82)

$$a_{A_{1g}} = \frac{1}{48}(6+0+0+12+6+0+0+0+12+12) = 1$$
$$a_{A_{2g}} = \frac{1}{48}(6+0+0-12+6+0+0+0+12-12) = 0$$
$$a_{E_g} = \frac{1}{48}(12+0+0+0+12+0+0+0+24+0) = 1$$
$$a_{T_{1g}} = \frac{1}{48}(18+0+0+12-6+0+0+0-12-12) = 0$$
$$a_{T_{2g}} = \frac{1}{48}(18+0+0-12-6+0+0+0-12+12) = 0$$
$$a_{A_{1u}} = \frac{1}{48}(6+0+0+12+6+0+0+0-12-12) = 0$$
$$a_{A_{2u}} = \frac{1}{48}(6+0+0-12+6+0+0+0-12+12) = 1$$
$$a_{E_u} = \frac{1}{48}(12+0+0+0+12+0+0+0-24+0) = 0$$
$$a_{T_{1u}} = \frac{1}{48}(18+0+0+12-6+0+0+0+12+12) = 1$$
$$a_{T_{2u}} = \frac{1}{48}(18+0+0-12-6+0+0+0+12-12) = 0$$

Therefore, the irreducible representation becomes $\mathbf{\Gamma} = A_1 + A_2 + E$

12.E: Group Theory - The Exploitation of Symmetry (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

13: 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.

13.1: The Electromagnetic Spectrum
13.2: Rotations Accompany Vibrational Transitions
13.3: Unequal Spacings in Vibration-Rotation Spectra
13.4: Unequal Spacings in Pure Rotational Spectra
13.5: Vibrational Overtones
13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
13.7: The Franck-Condon Principle
13.8: Rotational Spectra of Polyatomic Molecules
13.9: Normal Modes in Polyatomic Molecules
13.10: Irreducible Representation of Point Groups
13.11: Time-Dependent Perturbation Theory
13.12: The Selection Rule for the Rigid Rotor
13.13: The Harmonic Oscillator Selection Rule
13.14: Group Theory Determines Infrared Activity
13.E: Molecular Spectroscopy (Exercises)

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13.1: 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.[1] 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 2.997 92 × 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 × 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.

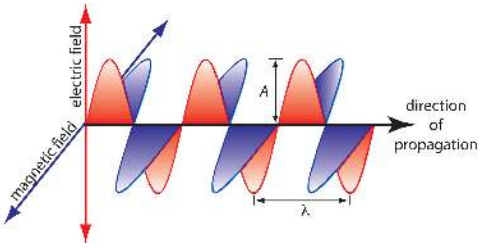


Figure **13.1.1**: Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, A, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic 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

$$A_t = A_e \sin(2\pi\nu t + \phi) \tag{13.1.1}$$

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

$$A_t = A_m \sin(2\pi\nu t + \phi) \tag{13.1.2}$$

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.

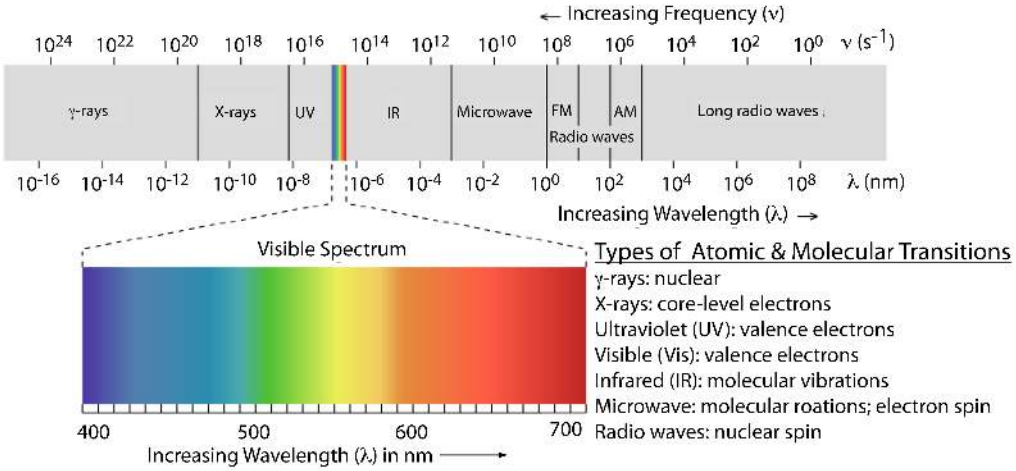


Figure **13.1.2**: The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.Wikipedia.org).

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

$$\lambda = \frac{c}{\nu} \tag{13.1.3}$$

Another unit useful unit is the **wavenumber**, $\tilde{\nu}$, which is the reciprocal of wavelength

$$\tilde{\nu} = \frac{1}{\lambda} \tag{13.1.4}$$

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

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{589 \times 10^{-9} \text{ m}} = 5.09 \times 10^{14} \text{ s}^{-1} \tag{13.1.5}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{589 \times 10^{-9} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 1.70 \times 10^4 \text{ cm}^{-1} \tag{13.1.6}$$

? 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?

Click here to review your answer to this exercise.

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 Techniquea
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:

$$\Delta E = E_u - E_l = h\nu \tag{13.1.7}$$

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.

References

1. McQuarrie, Donald A. Physical Chemistry. 2nd ed. United States Of America: University Science Books, 2008. 321-24.

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- U. L.

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13.2: 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

$$E_v = h\nu\left(v + \frac{1}{2}\right) \tag{13.2.1}$$

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:

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}} \tag{13.2.2}$$

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

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{13.2.3}$$

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

$$E_r = \frac{h^2}{8\pi^2 I}J(J+1) \tag{13.2.4}$$

In which I is the moment of inertia, given by

$$I = \mu r^2 \tag{13.2.5}$$

where μ is the reduced mass (Equation 13.2.3) 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

$$F(J) = \frac{E_r}{h} = \frac{h}{8\pi^2 I}J(J+1) = BJ(J+1) \tag{13.2.6}$$

or wavenumbers

$$\tilde{F}(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 cI}J(J+1) = \tilde{B}J(J+1) \tag{13.2.7}$$

> 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 $\Delta v = +1$. The full selection rule is technically that $\Delta v = \pm 1$, 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**).

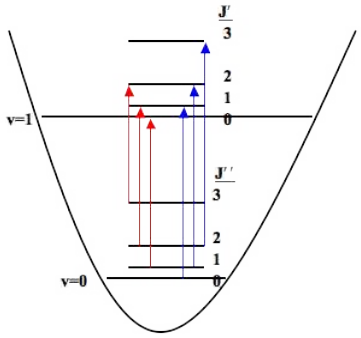


Figure **13.2.1**: *Rotation-Vibration Transitions. Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels.*

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:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{13.2.8}$$
$$= h\nu_0 + hB\left[(J+1)(J+2) - J(J+1)\right] \tag{13.2.9}$$
$$= h\nu_0 + 2hB(J+1) \tag{13.2.10}$$

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:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{13.2.11}$$
$$= h\nu_0 + hB\left[J(J-1) - J(J+1)\right] \tag{13.2.12}$$
$$= h\nu_0 - 2hBJ \tag{13.2.13}$$

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:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \tag{13.2.14}$$
$$= h\nu_0 \tag{13.2.15}$$

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.

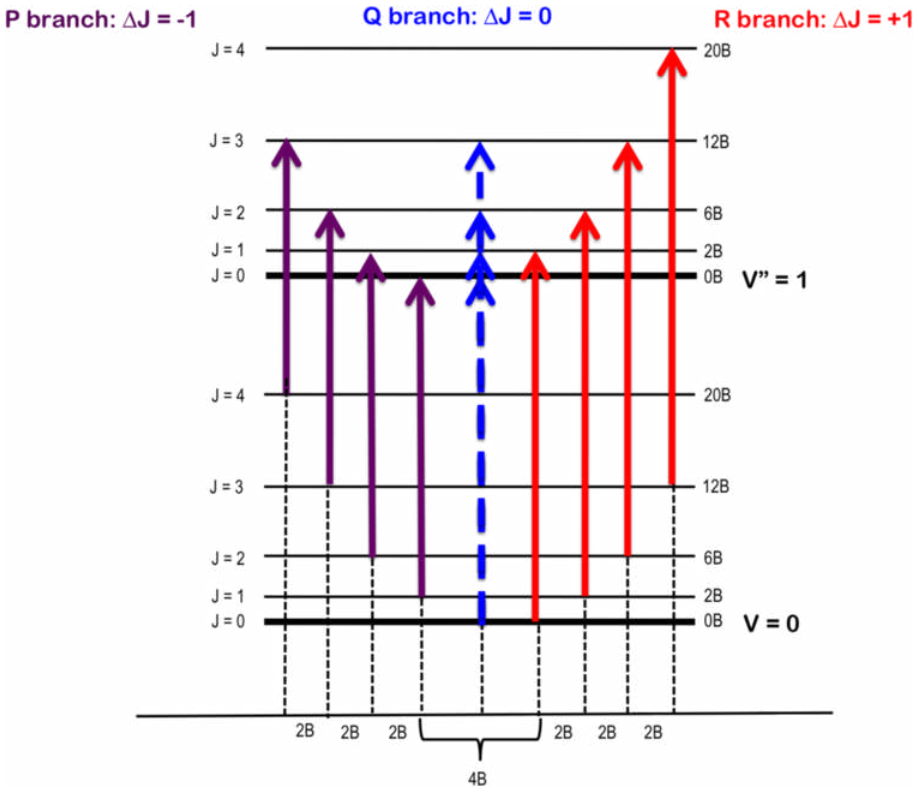


Figure **13.2.3**: *Cartoon depiction of rotational energy levels, J, imposed on vibrational energy levels, v. The transitions between levels that would result in the P- and R-branches are depicted in purple and red, respectively, in addition to the theoretical Q-branch line in blue.*

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

$$S(v, J) = G(v) + F(J) \tag{13.2.16}$$

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

$$S(v, J) = \nu_0 \left(v + \frac{1}{2}\right) + BJ(J+1) \tag{13.2.17}$$

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.

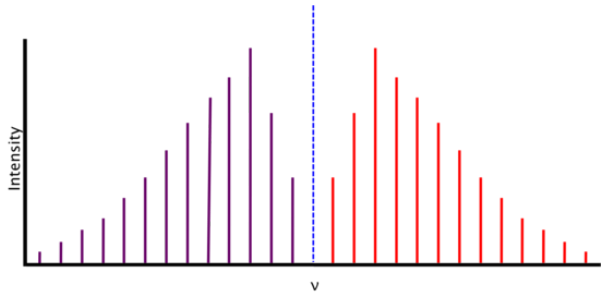


Figure **13.2.3**: A cartoon depiction of an ideal rovibrational spectrum.

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:

$$\frac{N_J}{N_0} = (2J+1)e^{\left(-\frac{E_r}{kT}\right)} \tag{13.2.18}$$

(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

$$\frac{d}{dJ}\left(\frac{N_J}{N_0}\right) = 0 \tag{13.2.19}$$

by differentiation, we obtain

$$J_{max} = \left(\frac{kT}{2hB}\right)^{\frac{1}{2}} - \frac{1}{2} \tag{13.2.20}$$

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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13.3: 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*.

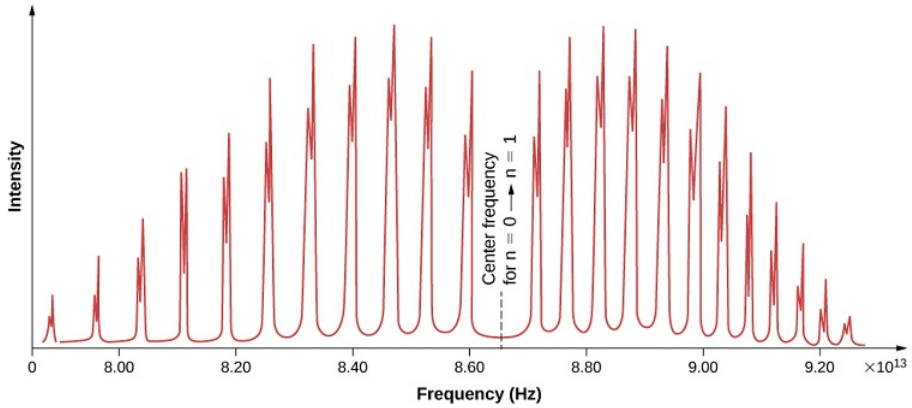


Figure **13.3.1**: Absorption spectrum of hydrogen chloride (**HCl**) from the $n = 0$ to $n = 1$ vibrational levels. The discrete peaks indicate a quantization of the angular momentum of the molecule. The bands to the left indicate a decrease in angular momentum, whereas those to the right indicate 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.

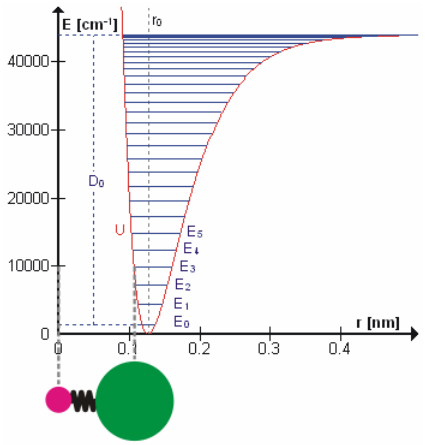


Figure **13.3.2** : Anharmonic Oscillator and Bond Length. Figure used with permission from Wikipedia.

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

$$\tilde{E}_{v,J} = G(v) + F(J) = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}J(J+1) \tag{13.3.1}$$

or in term of $\tilde{B}_v$

$$\tilde{E}_{v,J} = \tilde{\nu}\left(v + \frac{1}{2}\right) + \tilde{B}_v J(J+1) \tag{13.3.2}$$

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 $J = 0, 1, 2, ...$

$$\tilde{\nu}_R(\Delta J = +1) = \tilde{E}_{1,J+1} - \tilde{E}_{0,J} \tag{13.3.3}$$

$$= \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1) \tag{13.3.4}$$

$$= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.5}$$

For P branch, allowed $J = 1, 2, 3, ...$

$$\tilde{\nu}_P(\Delta J = -1) = \tilde{E}_{1,J-1} - \tilde{E}_{0,J} \tag{13.3.6}$$

$$= \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.7}$$

Decrease in Spacing of Lines in the R Branch with Increasing J

A closer look at

$$\tilde{\nu}_R = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.8}$$

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,

$$\tilde{\nu}_P = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.9}$$

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.

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13.4: 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.

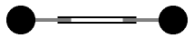


Figure **13.4.1**: This animation can serve as an illustration of one of the aspects of the conservation of angular momentum. The animation is a schematic representation of two weights that are connected to each other. The two weights are circling around their common center of mass, the center of mass 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,

$$F_c = \mu r_c \omega^2 = L^2/\mu {r_c}^3 \tag{13.4.1}$$

Equating the restoring force to the centrifugal force, one gets

$$k(r_c - r_e) = \frac{L^2}{\mu {r_c}^3} \tag{13.4.2}$$

$$r_c - r_e = \frac{L^2}{k\mu {r_c}^3} \cong \frac{L^2}{k\mu {r_e}^3} \tag{13.4.3}$$

Total energy, on adding kinetic energy, as expressed in Equation 13.4.3 to the potential energy,

$$\frac{1}{2}k(r_c - r_e)^2 \tag{13.4.4}$$

is given by

$$E_r = \frac{L^2}{2\mu {r_c}^2} + \frac{1}{2}k\,(r_c - r_e)^2 \tag{13.4.5}$$

Using $(r_c - r_e) = \Delta r$ and eliminating r_c from equation 13.4.5, one gets

$$E_r = \frac{L^2}{2\mu\ {r_e}^2(1 + \Delta r/r_e)^2} + \frac{1}{2}k\Delta r^2 \tag{13.4.6}$$

$$= \frac{L^2(1 - 2\Delta r/r_e)}{2\mu\ {r_e}^2} + \frac{1}{2}k\Delta r^2 \tag{13.4.7}$$

using

$$(1 + \Delta r/r_e)^{-2} \approx (1 - 2\Delta r/r_e) \tag{13.4.8}$$

$$E_r = \frac{L^2}{2\mu {r_e}^2} - \frac{L^4}{k\mu^2 {r_e}^6} + \frac{1}{2}k\frac{L^4}{k^{2\mu 2}{r_e}^6} \tag{13.4.9}$$

$$= \frac{L^2}{2\mu {r_e}^2} - \frac{1}{2}\frac{L^4}{k\mu^2 {r_e}^6} \tag{13.4.10}$$

$$= \frac{\hbar^2\, J(J+1)}{2\mu {r_e}^2} - \frac{\hbar^4\, J^2(J+1)^2}{2k\mu^2 {r_e}^6} \tag{13.4.11}$$

Use of Equation 13.4.3 and of the relation regarding angular momentum of a rotor

$$L = \hbar\sqrt{J(J+1)} \tag{13.4.12}$$

has been made to obtain relation in Equation 13.4.11, which may be expressed in cm^{-1} as

$$F(J) = \underbrace{\tilde{B}J(J+1)}_{\text{rigid rotator term}} - \underbrace{\tilde{D}J^2(J+1)^2 cm^{-1}}_{\text{centrifugal stretching}} \tag{13.4.13}$$

where

$$\tilde{B} = \frac{\hbar}{4\pi\,\mu\, {r_e}^2 c}\ (\text{in cm}^{-1}) \tag{13.4.14}$$

and

$$\tilde{D} = \frac{\hbar^3}{4\pi k\,\mu^2\, {r_e}^6\, c}\ (\text{in cm}^{-1}) \tag{13.4.15}$$

First term in the Equation 13.4.13 is same as for the rigid rotator; second term is the consequence of the centrifugal stretching. Recall Equation 13.4.3 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 13.4.13 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 13.4.2.

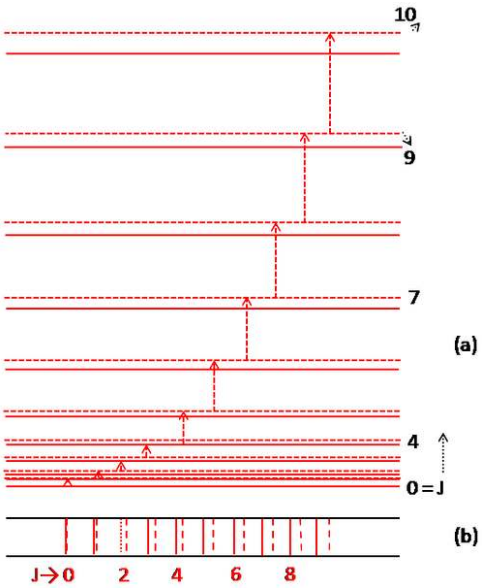


Figure 13.4.2: Energy levels and the transitions of rigid rotator (broken red lines) & of non-rigid rotator (solid red lines). (b) resulting spectra from both the models

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 **13.4.2**. 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 $B \sim 10.4 \ \ cm^{-1}$ and $D \sim 0.0004\, cm^{-1}$. Usually, D is ignored in the calculations. Figure **13.4.2** 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.

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13.5: Vibrational Overtones

Although the harmonic oscillator proves useful at lower energy levels, like n=1, it fails at higher numbers of n, failing not only to properly model atomic bonds and dissociations, but also unable to match spectra showing additional lines than is 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 transition from $\Delta v = \pm 1$. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator approximation (Figure 13.5.1). For exaple, unlike the parabola given in the Harmonic Oscillator approximation, atoms that are too far apart will dissociate.

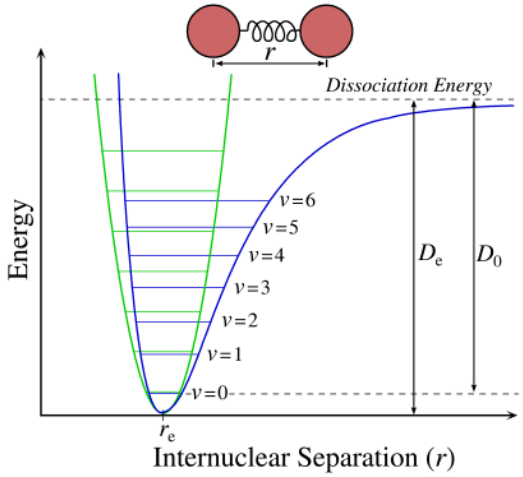


Figure 13.5.1: Pictured above is the Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left 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 13.5.1, the harmonic oscillator potential (in green) well only roughly fits over the more accurate anharmonic oscillator well (in blue). The solid line accounts for dissociation at large R values, which the dotted lines 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.

$$V(R) = V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}(R-R_e)^4 + \ldots \tag{13.5.1}$$

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

$$V_{HO}(R) \approx V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 \tag{13.5.2}$$

or in terms of a spring constant (and ignore the absolute energy term) and defining r to equal the displacement from equilibrium ($r = R - R_e$), then we get the "standard" harmonic oscillator potential:

$$V_{HO}(R) = \frac{1}{2}kr^2 \tag{13.5.3}$$

Alternatively, the expansion in Equation 13.5.1 can be shortened to the cubic term

$$V(x) = \frac{1}{2}kr^2 + \frac{1}{6}\gamma r^3 \tag{13.5.4}$$

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.

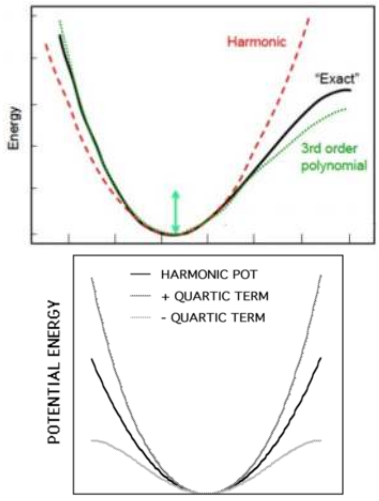


Figure 13.5.2: *(left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (black curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. Images used with permission from Heather Kulik (MIT) via OpenCourseWare.*

The harmonic oscillator approximation and gives by the following energies:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right) \tag{13.5.5}$$

When cubic terms in the expansion (Equation 13.5.4) is included, then Schrödinger equation solved, using perturbation theory, gives:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right) - \tilde{\chi_e}\tilde{\nu}\left(v + \frac{1}{2}\right)^2 \tag{13.5.6}$$

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 $G(n)$ 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 13.5.1.

Overtones

The Harmonic Oscillator approximation predicts that there will be only one line the spectrum of a diatomic molecule, and while experimental data shows there is in fact one dominant line--the fundamental--there are also other, weaker lines. How can we account for these extra lines?

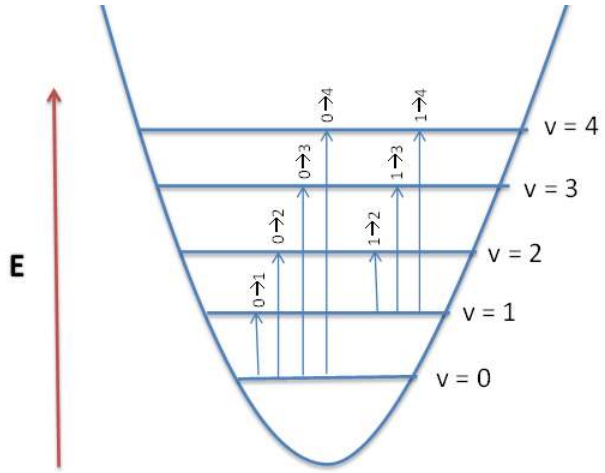


Figure 1 shows a diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potenital energy for the harmonic (quadratic) oscillator. The transition $0 \rightarrow 1$ is fundamental, transitions $0 \rightarrow n$ (n>1) are called overtones, and transitions $1 \rightarrow n$ (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 $v = 1 \rightarrow 2$ is (approximately) twice the energy of the fundamental, $v = 0 \rightarrow 1$.

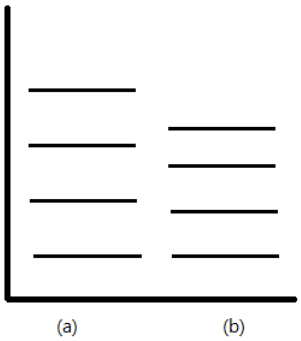


Figure **13.5.4**: An exaggerated view of the energy levels. (a) would be the harmonic oscillator, with the evenly spaced out energy levels. (b) would be the anharmonic, with the energy levels compressing until they converge.

The levels are not equally spaced, like in the harmonic oscillator, but decrease as n increases, until it ultimately converges, is implied by Figure **13.5.4**. 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 $v = 2$, which is called the first overtone, or $v = 0$ to $v = 3$, the second overtone. The fundamental transitions, v=±1, are the most commonly occurring, and the probability of overtones rapid decreases as $\Delta v > \pm 1$ gets bigger. Based on the harmonic oscillator approximation, the energy of the overtone transition will be about n 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 **13.5.1**: 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
$0 \rightarrow 4$ (thirdovertone)	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 **13.5.1** 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 being occupied).

? 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?

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13.6: 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.

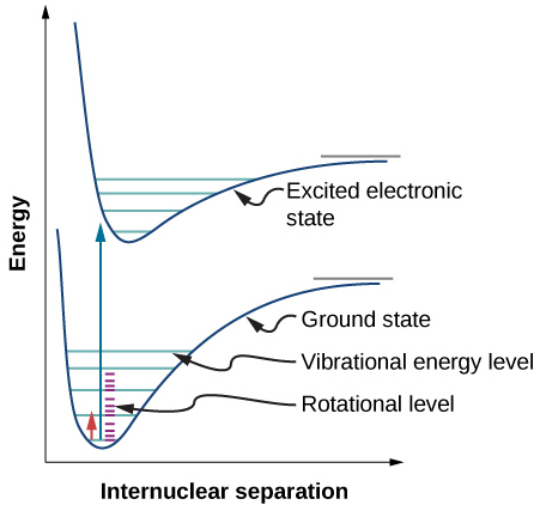


Figure **13.6.1**: Three types of energy levels in a diatomic molecule: electronic, vibrational, and rotational. If the vibrational quantum number (n) changes by one unit, then the rotational quantum number (l) changes by one unit. (CC BY 3.0; OpenStax).

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:

$$\tilde{E}_{total} = \tilde{\nu}_{el} + G(v) + F(J) \tag{13.6.1}$$

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 13.6.1 can be expanded accordingly:

$$= \underbrace{\tilde{\nu}_{el}}_{\text{electronic}} + \underbrace{\tilde{\nu}_e\left(v+\frac{1}{2}\right) - \tilde{\chi}_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^2}_{\text{vibrational}} + \underbrace{\tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2}_{\text{rotational}} \tag{13.6.2}$$

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.

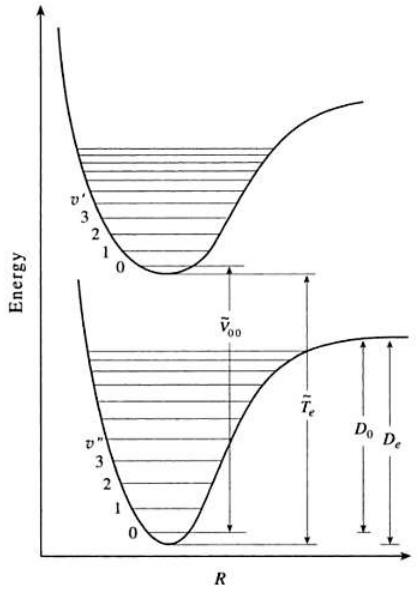


Figure **13.6.2**: As you can see, electronic transitions involve two energy potential wells! The vibrational levels are included, but rotational levels are excluded.

The eigenstate-to-eigenstate transitions (e.g., $\mathbf{1} \rightarrow \mathbf{2}$) possible are numerous and have absorption lines at

$$\tilde{\nu}_{obs} = \tilde{E}_2 - \tilde{E}_1 \tag{13.6.3}$$

and for simplification, we refer to constants associated with these states as $|'\rangle$ and $|''\rangle$, respectively. So Equation 13.6.3 is

$$\tilde{\nu}_{obs} = E''\tilde{(v'')} - E'\tilde{(v')} \tag{13.6.4}$$

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 13.6.2 can be used with Equation 13.6.3 to get

$$\tilde{\nu}_{obs} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right) + \tilde{\nu}'_e v'' - \tilde{\chi}'_e\tilde{\nu}'_e v''(v''+1) \tag{13.6.5}$$

A common transition of importance is the $\tilde{\nu}_{00}$, which is the $\mathbf{0} \rightarrow \mathbf{0}$ transition and include no vibrational change. For this case, equation 13.6.5 is then

$$\tilde{\nu}_{00} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right) \tag{13.6.6}$$

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.

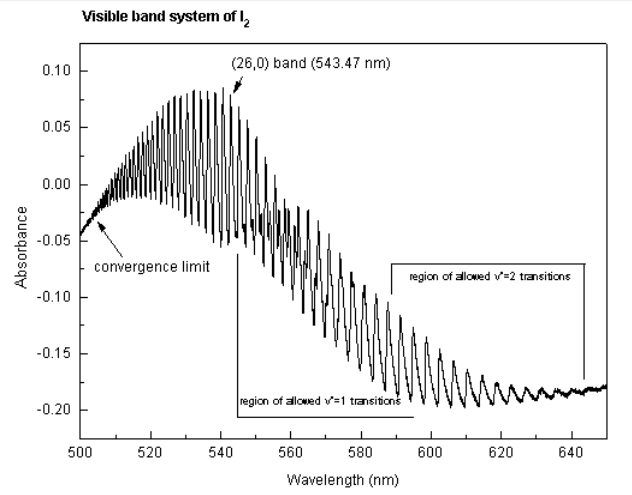
Iodine

The absorption spectrum of iodine yields information about the excited state well rather than the ground state well (notice that equation 13.6.5 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.

13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

13.7: The Franck-Condon Principle

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 wave function 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 wave function 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.

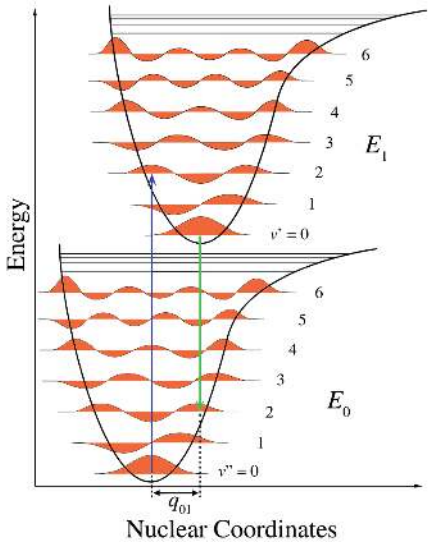


Figure **13.7.1**: Franck–Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v' = 2$. (CC-SA-BY-3.0; Samoza).

In Figure **13.7.1**, 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 probablity of a vibrational transition to the overlap of the vibrational wave functions. It states that the probability of a vibrational transition occurring is

weighted by the Franck-Condon overlap integral:

$$P_{i\rightarrow f} = \left|\langle \psi^*_{final} \left|\mu\right| \psi_{initial}\rangle\right|^2 = \left| \int \psi^*_{final} \mu \psi_{initial} d\tau \right|^2 \tag{13.7.1}$$

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 **13.7.1**).

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 wave functions given the total wavefunction.

$$|\psi_{total}(Q,q) = |\psi_{nuc}(Q))\psi_{el}(Q;q)\rangle \tag{13.7.2}$$

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 occuring:

$$\langle \psi^*_{total,f} \left|\hat{\mu}\right| \psi_{total,i}\rangle = \langle \psi^*_{nuc,f} \left|\langle \psi^*_{el,f} \left|\mu\right| \psi_{el,i}\rangle\right| \psi_{nuc,i}\rangle \tag{13.7.3}$$

$$= \underbrace{\langle \psi^*_{nuc,f} | \psi_{nuc,i}\rangle}_{\text{nuclear overlap}} \langle \psi^*_{el,f} \left|\mu\right| \psi_{el,i}\rangle \tag{13.7.4}$$

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

$$|\psi(R)\rangle = |\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2}\rangle \tag{13.7.5}$$

The zero-point wavefunction in the excited electronic state is

$$|\psi(R)\rangle = |\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-Q_e)^2/2}\rangle \tag{13.7.6}$$

where

- $\alpha = \frac{\sqrt{mk}}{\hbar}$
- 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

$$S_{00} = \langle \psi^*_{nuc,f} | \psi_{nuc,i}\rangle = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} e^{-\alpha(R-Q_e)^2/2} dR \tag{13.7.7}$$

The exponent in Equation **13.7.7** can be expanded as

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(2R^2 - RR_e - 2RQ_e + R_e^2 + Q_e^2)/2} dR \tag{13.7.8}$$

and we use

$$(R_e + Q_e)^2 = R_e^2 + Q_e^2 + 2R_eQ_e \tag{13.7.9}$$

and

$$(R_e - Q_e)^2 = R_e^2 + Q_e^2 - 2R_eQ_e \tag{13.7.10}$$

to substitute and complete the square inside the integral. We can express

$$R_e^2 + Q_e^2 = \frac{1}{2}[(R_e + Q_e)^2 + (R_e - Q_e)^2]. \tag{13.7.11}$$

Thus, the integral in Equation 13.7.8 is

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \int_{-\infty}^{\infty} e^{-\alpha\{R - 1/2(R_e + Q_e)\}^2} dR \tag{13.7.12}$$

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

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \frac{1}{\sqrt{\alpha}} \int_{-\infty}^{\infty} e^{z^2} dz \tag{13.7.13}$$

this integral has been solved already, from a table of integrals, Equation 13.7.13 becomes

$$S_{00} = e^{-\alpha(R_e - Q_e)^2/4} \tag{13.7.14}$$

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 $x = \sqrt{\alpha}(R - Q_e)$.

$$S_{01} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle \tag{13.7.15}$$

with the zero-point wavefunction in the ground electronic state is

$$|\psi(R)\rangle = \left| \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R - R_e)^2/2} \right\rangle \tag{13.7.16}$$

The first excited-state wavefunction in the excited electronic state is

$$|\psi(R)\rangle = \left| \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{\alpha} 2(R - Q_e) e^{-\alpha(R - Q_e)^2/2} \right\rangle \tag{13.7.17}$$

The overlap of zeroth ground state level with the first excited state level (Equation 13.7.15) is then

$$S_{01} = \frac{1}{\sqrt{2}} \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha(R - R_e)^2/2} \sqrt{\alpha} 2(R - Q_e) e^{-\alpha(R - Q_e)^2/2} \tag{13.7.18}$$

and

$$S_{01} = \sqrt{\frac{2\alpha^2}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \int_{-\infty}^{\infty} (R - Q_e) e^{-\alpha\{R - 1/2(R_e + Q_e)^2\}} \tag{13.7.19}$$

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

$$S_{01} = \sqrt{\frac{\alpha^2}{2}} (R_e - Q_e) e^{-\alpha(R_e - Q_e)^2/4} \tag{13.7.20}$$

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.

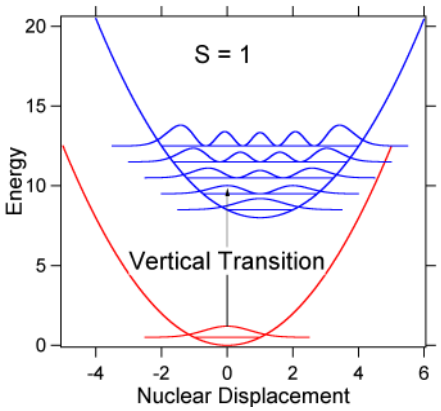


Figure **13.7.2**: Wavefunctions transitions for a harmonic oscillator model system with moderate displacement (S=1).

According to the above model for the Franck-Condon factor we would generate a "stick" spectrum (Figure **13.7.3**) 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.

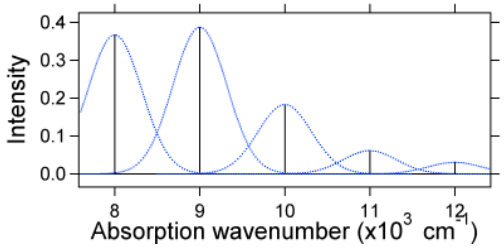


Figure **13.7.3**: Stick spectrum, dressed with Gaussians, for the moderate displacement (S=1) harmonic oscillator system from Figure **13.7.2**.

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:

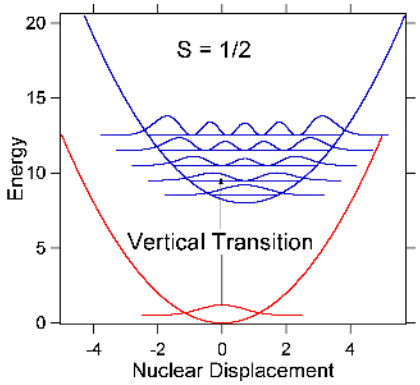


Figure **13.7.4**: Wavefunctions transitions for a harmonic oscillator model system with small displacement (S=1/2).

For this case the "stick" spectrum has the appearance in Figure **13.7.5**

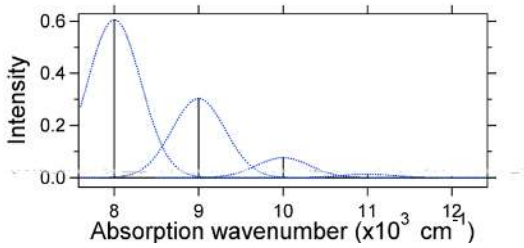


Figure **13.7.5**: Stick spectrum, dressed with Gaussians, for the small displacement (S=1/2) harmonic oscillator system from Figure **13.7.4**.

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.

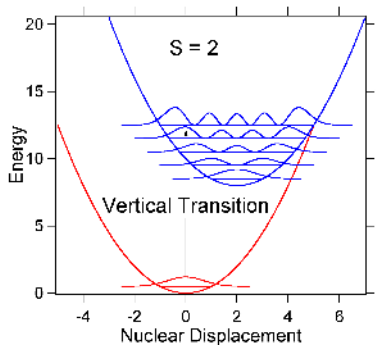


Figure **13.7.6**: Wavefunctions transitions for a harmonic oscillator model system with strong displacement (S=2).

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.

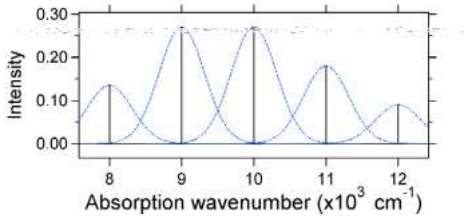


Figure **13.7.7**: Stick spectrum, dressed with Gaussians, for the large displacement (S=2) harmonic oscillator system from Figure **13.7.6**.

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.

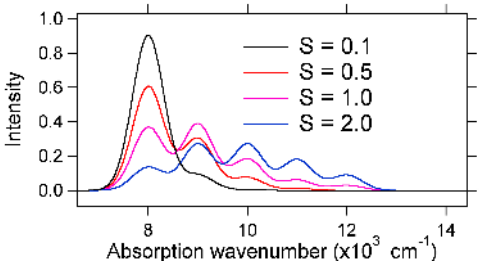


Figure **13.7.8**: Stick spectra, dressed with Gaussians, for the small to large displacements in harmonic oscillator system described above.

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.

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13.8: 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

$$\frac{\hbar^2}{2\mu}\left[\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{R^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\psi\rangle = E|\psi\rangle \tag{13.8.1}$$

or

$$\frac{L^2}{2\mu R^2}|\psi\rangle = E|\psi\rangle \tag{13.8.2}$$

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

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{13.8.3}$$

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:

$$E_J = \frac{\hbar^2 J(J+1)}{2\mu R^2} = BJ(J+1) \tag{13.8.4}$$

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 13.8.4 can be expressed in terms of the moment of inertia I

$$I = \sum_i m_i R_i^2 \tag{13.8.5}$$

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 13.8.4:

$$E_J = \frac{\hbar^2 J(J+1)}{2I} = BJ(J+1) \tag{13.8.6}$$

Rotation of Polyatomic Molecules

In contrast to diatomic molecules (Equation 13.8.5), 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.

$$I = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix} \tag{13.8.7}$$

The components of this tensor can be assembled into a matrix given by

$$I_{xx} = \sum_{k=1}^{N} m_k(y_k^2 + z_k^2) \tag{13.8.8}$$

$$I_{yy} = \sum_{k=1}^{N} m_k(x_k^2 + z_k^2) \tag{13.8.9}$$

$$I_{zz} = \sum_{k=1}^{N} m_k (x_k^2 + y_k^2) \tag{13.8.10}$$

$$I_{yx} = I_{xy} = -\sum_{k=1}^{N} m_k x_k y_k \tag{13.8.11}$$

$$I_{zx} = I_{xz} = -\sum_{k=1}^{N} m_k x_k z_k \tag{13.8.12}$$

$$I_{zy} = I_{yz} = -\sum_{k=1}^{N} m_k y_k z_k. \tag{13.8.13}$$

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 13.8.7) is a constant real symmetric matrix, which can be decomposed into a diagonal matrix, given by

$$I = \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix} \tag{13.8.14}$$

These labels are assigned so that I_c is the **largest** principal moment of inertia with an order of the three moments set as

$$I_a < I_b < I_c \tag{13.8.15}$$

The rotational kinetic energy operator for a rigid non-linear polyatomic molecule is then expressed as

$$H_{rot} = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} \tag{13.8.16}$$

The components of the quantum mechanical angular momentum operators along the three principal axes are:

$$J_a = -i\hbar \cos\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi}\right] - -i\hbar \sin\chi \frac{\partial}{\partial\theta} \tag{13.8.17}$$

$$J_b = i\hbar \sin\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi}\right] - -i\hbar \cos\chi \frac{\partial}{\partial\theta} \tag{13.8.18}$$

$$J_c = -\frac{ih\partial}{\partial\chi} \tag{13.8.19}$$

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

$$J^2 = J_a^2 + J_b^2 + J_c^2 \tag{13.8.20}$$

$$= -\frac{\partial^2}{\partial\theta^2} - \cot\theta \frac{\partial}{\partial\theta} - \left(\frac{1}{\sin\theta}\right)\left(\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial\chi^2} - 2\cos\theta \frac{\partial^2}{\partial\varphi\partial\chi}\right) \tag{13.8.21}$$

and the component along the lab-fixed Z axis is

$$J_Z = -ih \frac{\partial}{\partial\varphi}. \tag{13.8.22}$$

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 13.8.16 can be expressed in terms of the total angular momentum operator J^2

$$H_{rot} = \frac{J^2}{2I} \tag{13.8.23}$$

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

$$J_Z = -ih\frac{\partial}{\partial\varphi} \tag{13.8.24}$$

and

$$J_a = -ih\frac{\partial}{\partial\chi} \tag{13.8.25}$$

act on different angles. The energies associated with such eigenfunctions are

$$E(J,K,M) = \frac{\hbar^2 J(J+1)}{2I^2} \tag{13.8.26}$$

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 $D_{J,M,K}$:

$$|J,M,K\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D^*_{J,M,K}(\theta,\varphi,\chi) \tag{13.8.27}$$

which obey

$$J^2\,|J,M,K\rangle = \hbar^2 J(J+1)|\,J,M,K\rangle \tag{13.8.28}$$

$$J_a\,|J,M,K\rangle = \hbar K|\,J,M,K\rangle \tag{13.8.29}$$

$$J_Z\,|J,M,K\rangle = \hbar M|\,J,M,K\rangle \tag{13.8.30}$$

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.

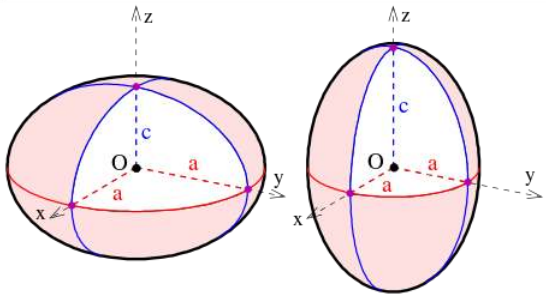


Figure 13.8.1: The assignment of semi-axes on a spheroid. It is oblate if c < a (left) and prolate if c > a (right). (CC BY-SA 4.0; Ag2gaeh)

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 13.8.16 becomes

$$H_{rot} = \frac{J^2}{2I} + J_a^2\left(\frac{1}{2I_a} - \frac{1}{2I}\right) \tag{13.8.31}$$

For oblate tops, Equation 13.8.16 becomes

$$H_{rot} = \frac{J^2}{2I} + J_c^2\left(\frac{1}{2I_c} - \frac{1}{2I}\right) \tag{13.8.32}$$

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

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I^2} + h^2 K^2 \left(\frac{1}{2I_a} - \frac{1}{2I}\right) \tag{13.8.33}$$

and the energies for oblate tops are

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I2} + h^2 K^2 \left(\frac{1}{2I_c} - \frac{1}{2I}\right) \tag{13.8.34}$$

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 13.8.16 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

$$\psi_n(\theta,\varphi,\chi) = \sum_{J,M,K} C_{n,J,M,K} |J,M,K\rangle \tag{13.8.35}$$

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:

$$\psi_{n,J}(\theta,\varphi,\chi) = \sum_{M,K} C_{n,J,M,K} |J,M,K\rangle \tag{13.8.36}$$

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:

$$\langle j,\rangle = \langle j,\rangle = 1/2 < j,\rangle = h2[J(J+1) - K2], \tag{13.8.37}$$

$$\langle j,\rangle = h^2 K^2 \tag{13.8.38}$$

$$\langle j\rangle = -\langle j\rangle = h^2[J(J+1) - K(K\pm1)]1/2[J(J+1) - (K\pm1)(K\pm2)]1/2\langle j\rangle = 0 \tag{13.8.39}$$

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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13.9: 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:

$$3N - 6 = 3(8) - 6 = 18 \tag{13.9.1}$$

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:

$$3N - 5 = 3(3) - 5 = 4 \tag{13.9.2}$$

The normal modes of vibration are: asymmetric, symmetric, wagging, twisting, scissoring, and rocking for polyatomic molecules.

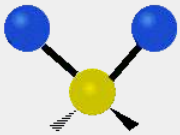
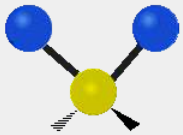
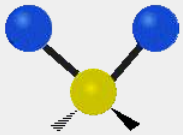
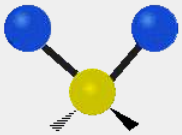
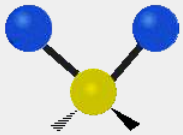
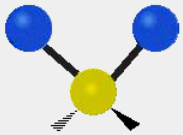
Symmetricical Stretching	Asymmetrical Stretching	Wagging
		
Twisting	**Scissoring**	**Rocking**
		

Figure* 13.9.1*: *Six types of Vibrational Modes. Taken from publisher http://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:

$$\Delta V = V(q_1, q_2, q_3, ..., q_n) - V(0, 0, 0, ..., 0) \tag{13.9.3}$$

$$= \frac{1}{2}\sum_{i=1}^{N_{vib}}\sum_{j=1}^{N_{vib}}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right) q_i q_j \tag{13.9.4}$$

$$= \frac{1}{2}\sum_{i=1}^{N_{vib}}\sum_{j=1}^{N_{vib}} f_{ij} q_i q_j \tag{13.9.5}$$

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 {Q_j} can be found such that

$$\Delta V = \frac{1}{2}\sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{13.9.6}$$

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:

$$\hat{H}_{vib} = -\sum_{j=1}^{N_{vib}} \frac{\hbar^2}{2\mu_i}\frac{d^2}{dQ_j^2} + \frac{1}{2}\sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{13.9.7}$$

The total wavefunction is a product of the individual wavefunctions and the energy is the sum of independent energies. This leads to:

$$\hat{H}_{vib} = \sum_{j=1}^{N_{vib}} \hat{H}_{vib,j} = \sum_{j=1}^{N_{vib}} \left(\frac{-\hbar^2}{2\mu_j} \frac{d^2}{dQ_i^2} + \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \right) \tag{13.9.8}$$

and the wavefunction is then

$$\psi_{vib} = Q_1, Q_2, Q_3 ..., Q_{vib} = \psi_{vib,1}(Q_1)\psi_{vib,2}(Q_2)\psi_{vib,3}(Q_3), ..., \psi_{vib,N_{vib}}(Q_{N_{vib}}) \tag{13.9.9}$$

and the total vibrational energy of the molecule is

$$E_{vib} = \sum_{j=1}^{N_{vin}} h\nu_j \left(v_j + \frac{1}{2} \right) \tag{13.9.10}$$

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 $\mathbf{\Delta r_0(C)}$, and the displacement of the O atom, denoted by $\mathbf{\Delta r_0(O)}$, occur at the same frequency. The displacement of atoms is measured from the equilibrium distance in ground vibrational state, r_o.

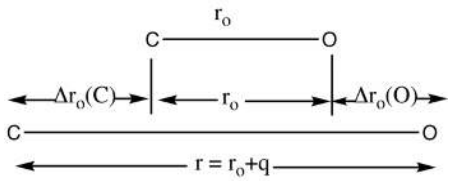


Figure **13.9.2**: The Normal coordinate for CO is equation to $\Delta r(C) + \Delta r(O)$

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13.10: Irreducible Representation of Point Groups

There exists an important fact about normal coordinates. Each of these coordinates belongs to an irreducible representation of the point the molecule under investigation. Vibrational wavefunctions associated with vibrational energy levels share this property as well. The normal coordinates and the vibration wavefunction can be categorized further according to the point group they belong to. From the character table predictions can be made for which symmetries can exist. The irreducible representation offers insight into the IR and/or Raman activity of the molecule in question.

Symmetry of normal modes

It is important to realize that every normal mode has a certain type of symmetry associated with it. Identifying the point group of the molecule is therefore an important step. With this in mind it is not surprising that every normal mode forms a basis set for an irreducible representation of the point group the molecule belongs to. For a molecule such as water, having a structure of XY_2, three normal coordinates can be determined. The two stretching modes are equivalent in symmetry and energy. The figure below shows the three normal modes for the water molecule:

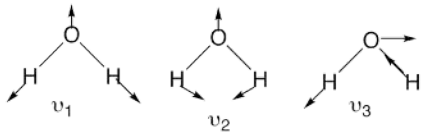


Figure* 13.10.1: Three normal modes of water*

By convention, with nonlinear molecules, the symmetric stretch is denoted v_1 whereas the asymmetric stretch is denoted v_2. Bending motions are v_3. With linear molecules, the bending motion is v_2 whereas asymmetric stretch is v_3.

The water molecule has C_{2v} symmetry and its symmetry elements are E, C_2, σ(xz) and σ(yz). To determine the symmetries of the three vibrations and how they each transform, symmetry operations will be performed. As an example, performing C_2 operations using the two normal mode v_2 and v_3 gives the following transformation:

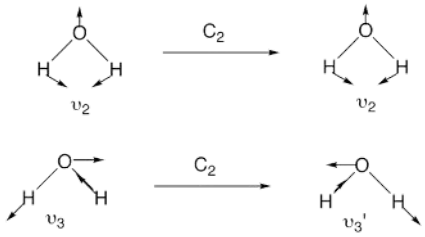


Figure 13.10.2: Symmetry operations on the symmetric and asymmetric stretches of water

Once all the symmetry operations have been performed in a systematic manner for each modes the symmetry can be assigned to the normal mode using the character table for C_{2v}:

Table 13.10.2*: Character table for the C_{2v} point group*

C_{2v}	E	C2	σ (xz)	σ (yz)	
v_1	1	1	1	1	= a_1
v_2	1	1	1	1	= a_1
v_3	1	-1	-1	1	= b_2

Water has three normal modes that can be grouped together as the reducible representation

$$\Gamma_{vib} = 2a_1 + b_2. \tag{13.10.1}$$

Determination of normal modes becomes quite complex as the number of atoms in the molecule increases. Nowadays, computer programs that simulate molecular vibrations can be used to perform these calculations. The example of $[PtCl_4]^{2-}$ shows the

increasing complexity (Figure **13.10.2**). The molecule has five atoms and therefore 15 degrees of freedom, 9 of these are vibrational degrees of freedom. The nine normal modes are exemplified below along with the irreducible representation the normal mode belongs to (D_{4h} point group).

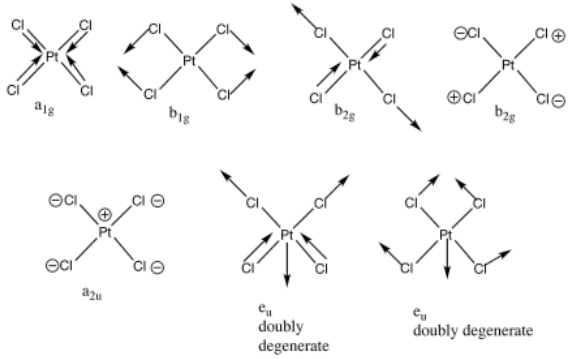


Figure **13.10.3**: A_{1g}, b_{1g} and e_u are stretching vibrations whereas b_{2g}, a_{2u}, b_{2u} and e_u are bending vibrations.

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13.11: Time-Dependent Perturbation Theory

Time-independent perturbation theory is one of two categories of perturbation theory, the other being time-dependent perturbation. In time-independent perturbation theory the perturbation Hamiltonian is static (i.e., possesses no time dependence). Time-independent perturbation theory was presented by Erwin Schrödinger in a 1926 paper,shortly after he produced his theories in wave mechanics. 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)

$$|j(t)\rangle = e^{-iE_j t/\hbar}\Big|j\rangle \tag{13.11.1}$$

Now, introduce a time-dependent perturbing Hamiltonian $H_1(t)$. The Hamiltonian of the perturbed system is

$$H = H_0 + H_1(t) \tag{13.11.2}$$

Let $|\psi(t)\rangle$ denote the quantum state of the perturbed system at time t and obeys the time-dependent Schrödinger equation,

$$H\Big|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}\Big|\psi(t)\rangle \tag{13.11.3}$$

The quantum state at each instant can be expressed as a linear combination of the complete eigenbasis of $|n\rangle$:

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}\Big|n\rangle \tag{13.11.4}$$

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

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}\Big|n\rangle \tag{13.11.5}$$

Plugging into the Schrödinger equation and using the fact that $\partial/\partial t$ acts by a chain rule, one obtains

$$\sum_n \left(i\hbar\frac{\partial c_n}{\partial t} - c_n(t)V(t)\right)e^{-iE_n t/\hbar}|n\rangle = 0\ . \tag{13.11.6}$$

By resolving the identity in front of V, this can be reduced to a set of partial differential equations for the amplitudes,

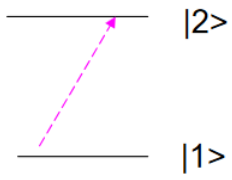
$$\frac{\partial c_n}{\partial t} = \frac{-i}{\hbar}\sum_k \langle n\,|H_1(t)|\,k\rangle\, c_k(t)\, e^{-i(E_k - E_n)t/\hbar}\ . \tag{13.11.7}$$

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. $n = 1, 2$)

$$|\psi\rangle = \sum_{n=1,2} c_n(t) \Big| n \rangle_o \tag{13.11.8}$$



Solution of time-dependent perturbation for two level system:

$$i\hbar \frac{\partial c_1(t)}{\partial t} = c_1(t) H_{11}(t) + c_2 e^{-i\omega_o t} H_{12}(t) \tag{13.11.9}$$

$$i\hbar \frac{\partial c_2(t)}{\partial t} = c_2(t) H_{22}(t) + c_1 e^{+i\omega_o t} H_{21}(t) \tag{13.11.10}$$

where the matrix elements of the permutation (in terms of the eigenstates of $H(0)$) are

$$\langle m | H_1(t) | n \rangle = H_{mn}(t) \tag{13.11.11}$$

Assume initial state is $n = 1$, and $H_{11} = H_{22} = 0$

$$|\psi(t = 0)\rangle = |1\rangle \tag{13.11.12}$$

Probability of particle at $n = 2$ at time t after the perturbation is turned on (i.e., incident light):

$$c_2(t) = \frac{-i}{\hbar} \int_o^t e^{i\omega_o t} dt' H_{21}(t') \tag{13.11.13}$$

where

$$H_1(t) = \cos(\omega t) V(r) \tag{13.11.14}$$

$V(r)$ 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

$$\omega \approx \omega_o \tag{13.11.15}$$

then Equation 13.11.13 can be simplified to

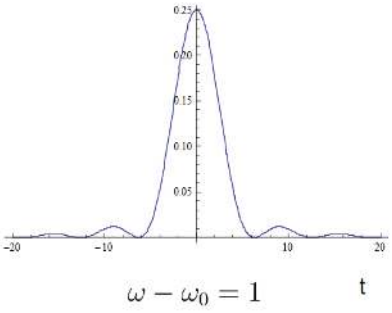
$$c_2(t) = -\frac{2i}{\hbar} \frac{\sin(\omega - \omega_o)t/2}{(\omega - \omega_o)t} e^{i(\omega_0 - \omega)t/2} H_{21} \tag{13.11.16}$$

Transition Probability

Assume initial state is $n = 1$, and probability of transition from $n = 1$ state to $n = 2$ state is:

$$P_{12}(t) = |c_2(t)|^2 = \frac{4}{\hbar^2} \left| \frac{\sin(\omega - \omega_o)t/2}{(\omega - \omega_o)t} \right|^2 |H_{21}|^2 \tag{13.11.17}$$

What does this mean? Strangely, it means that the probability of makinga 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.

Contributors

- Wikipedia

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13.12: 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

$$\mu_z = \int \Psi_1{}^* \mu_z \Psi_1 \, d\tau \tag{13.12.1}$$

A transition dipole moment is a transient dipolar polarization created by an interaction of electromagnetic radiation with a molecule

$$(\mu_z)_{12} = \int \Psi_1{}^* \mu_z \Psi_2 \, d\tau \tag{13.12.2}$$

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.

$$(\mu_z)_{J,M,J',M'} = \int_0^{2\pi} \int_0^{\pi} Y_{J'}^{M'}(\theta,\phi) \mu_z Y_J^M(\theta,\phi) \sin\theta \, d\phi, d\theta \tag{13.12.3}$$

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

$$Y_J^M(\theta,\phi) = N_{JM} P_J^{|M|}(\cos\theta) e^{iM\phi} \tag{13.12.4}$$

where N_{JM} is a normalization constant. Using the standard substitution of $x = \cos q$ we can express the rotational transition moment as

$$(\mu_z)_{J,M,J',M'} = \mu N_{JM} N_{J'M'} \int_0^{2\pi} e^{I(M-M')\phi} \, d\phi \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx \tag{13.12.5}$$

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

$$(\mu_z)_{J,M,J',M'} = 2\pi\mu N_{JM} N_{J'M'} \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx \tag{13.12.6}$$

We can evaluate this integral using the identity

$$(2J+1) x \, P_J^{|M|}(x) = (J - |M| + 1) P_{J+1}^{|M|}(x) + (J - |M|) P_{J-1}^{|M|}(x) \tag{13.12.7}$$

Substituting into the integral one obtains an integral which will vanish unless $J' = J+1$ or $J' = J-1$.

$$\int_{-1}^{1} P_{J'}^{|M'|}(x) \left(\frac{(J - |M| + 1)}{(2J+1)} P_{J+1}^{|M|}(x) + \frac{(J - |M|)}{(2J+1)} P_{J-1}^{|M|}(x) \right) dx \tag{13.12.8}$$

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 ($\Delta l = \pm 1$, $\Delta m = 0$).

13.12: The Selection Rule for the Rigid Rotor is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

13.13: 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

$$\Psi_v(x) = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2} \tag{13.13.1}$$

A transition dipole moment can be written to describe a transition along the z-axis.

$$\mu_z = \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}\mu_z(\alpha^{1/2}x)e^{-\alpha x^2/2}dx \tag{13.13.2}$$

μ is the dipole moment, so we pull it out of the integral.

$$\mu_z = \mu_z \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx \tag{13.13.3}$$

Using the idea that the transition moment μ_z changes on x, we express it as a derivative.

$$\mu_z = \frac{d\mu}{dx} \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx \tag{13.13.4}$$

To evaluate the integral, we take advantage of a special Hermite relationship: $\sqrt{\alpha}xH_v(\sqrt{\alpha}x) = vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)$

$$\mu_z = \frac{N_v N_{v+1}}{\sqrt{\alpha}}\left(\frac{d\mu}{dx}\right) \int_{-\infty}^{\infty} H_{v+1}(\sqrt{\alpha}x)e^{(}-\alpha x^2/2) \tag{13.13.5}$$
$$[vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)]dx$$

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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13.14: Group Theory Determines Infrared Activity

Determining if a Normal Modes is IR or Raman Active

A transition from v --> 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:

$$M(v \rightarrow v') = \langle \text{final wavefunction} \left|\vec{\mu}\right| \text{initial wavefunction} \rangle \tag{13.14.1}$$

or in terms of vibrational wavefunctions for a specific normal mode $|\phi(v)\rangle$

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) \left|\vec{\mu}\right| \phi(v = 0) \rangle \tag{13.14.2}$$

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 13.14.2 becomes

$$M(v \rightarrow v') = \vec{\mu} \langle \phi(v' \neq 0) | \phi(v = 0) \rangle \tag{13.14.3}$$

Since $|\phi(v = 0)\rangle$ and $|\phi(v =\neq 0)\rangle$ are mutually orthogonal to each other, the integral in Equation 13.14.2 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):

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) \left|\alpha\right| \phi(v = 0) \rangle \tag{13.14.4}$$

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 $\mathbf{\Gamma}_{tot}$ - $\mathbf{\Gamma}_{trans}$ - $\mathbf{\Gamma}_{rot}$.

$$\mathbf{\Gamma}_{vib}(H_2O) = (3a_1 + a_2 + 2b_1 + 3b_2) - (a_1 + b_1 + b_2) - (a_2 + b_1 + b_2) = 2a_1 + b_2 \tag{13.14.5}$$

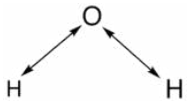
In order to determine which modes are IR active, a simple check of the irreducible representation that corresponds to x,y and z and a cross check with the reducible representation Γ_{vib} is necessary. If they contain the same irreducible representation, the mode is IR active.

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	$= a_1 + b_2$

$$\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch} = 2a_1 + b_2 - a_1 - b_2 = a_1 \quad (13.14.6)$$

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.

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13.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

$$G(v) = (v + \frac{1}{2})\nu_e - (v + \frac{1}{2})^2 \chi_e \nu_e \tag{13.E.1}$$

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

$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{13.E.2}$$

Use this result to show that the dissociation energy of the diatomic molecule can be written as

$$D_e = \frac{\nu_e - \nu_e \chi_e^2}{4\chi_e} \approx \frac{\nu_e}{4\chi_e} \tag{13.E.3}$$

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
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 $38269.48 cm^{-1}$.

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

$$0 = \nu_e - 2\chi_e\nu_e(v_{max}+1) \tag{13.E.4}$$

$$2\chi_e(v_{max}+1) = 1 \tag{13.E.5}$$

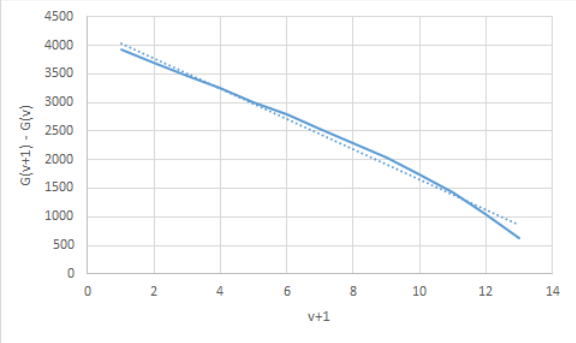
$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{13.E.6}$$

The molecule dissociates in the limit $\Delta G \to 0$, so the dissociation energy is given by

$$D_e = G(v_{max}) = (\frac{1}{2\chi_e} - \frac{1}{2})\nu_e - (\frac{1}{2\chi_e} - \frac{1}{2})^2\chi_e\nu_e = \frac{\nu_e}{2\chi_e}(1-\chi_e) - \frac{\nu_e}{4\chi_e}(1-\chi_e)^2 \tag{13.E.7}$$
$$= \frac{\nu_e}{4\chi_e}(2-2\chi_e-1+2\chi_e-\chi_e^2) = \frac{\nu_e}{4\chi_e}(1-\chi_e^2) \approx \frac{\nu_e}{4\chi_e}$$

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

$$D_e = \frac{\nu_e}{4\chi_e} = 37400cm^{-1} \tag{13.E.8}$$

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 $\nu_{max} = \frac{1}{2\tilde{x}_e} - 1$ to determine the number of bound vibrational levels for ground state of Na_2.

S13.21

First solve for $\tilde{x}$:

$$\tilde{x} = \frac{0.7255\ cm^{-1}}{159.125\ cm^{-1}} = 4.5593 \times 10^{-3}\ cm^{-1} \tag{13.E.9}$$

Then plug it in to the equation:

$$\nu_{max} = \frac{1}{2 \times 4.5593 \times 10^{-3}\ cm^{-1}} - 1 = 109.67\ cm^{-1} \tag{13.E.10}$$

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

$$U(q) = D_e(1 - e^{-/betaq})^2 \tag{13.E.11}$$

where $q = R - R_e$. Prove the force constant for the Morse Potential is evaluated

$$k = 2D_e\beta^2 \tag{13.E.12}$$

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

$$U(q) = D_e(1 - e^{-\beta q})^2 = D_e(1 - (1 - \beta q + \frac{\beta^2 q^2}{2}O(q)^3))^2 = D_e(\beta^2 q^2 + O(q)^3) \tag{13.E.13}$$

We know that

$$U(q) = \frac{kq^2}{2} \tag{13.E.14}$$

assuming that $O(q)^3$ approaches zero, we get

$$\frac{kq^2}{2} = D_e(\beta^2 q^2 + O(q)^3) \implies k = 2D_e\beta^2 \tag{13.E.15}$$

Plugging in our given values, we get

$$l = 2(6.23 \times 10^{-19} J \cdot Molecule^{-1})(1.37 \times 10^{10})^2 = 234 N \cdot m^{-1} \tag{13.E.16}$$

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:

$$\tilde{v}_e = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{13.E.17}$$

We can find k from the parameters given in the problem. Solving for k gives

$$k = (2\pi c \tilde{v}_e)^2 \mu \tag{13.E.18}$$

$$= [2\pi(3 \times 10^{10} cm \cdot s^{-1})(1580.0 cm^{-1})]^2 \\ (7.9975 amu)(1.661 x 10^{-27} kg \cdot amu^{-1}) \tag{13.E.19}$$

$$= 1176.3 N \cdot m^{-1} \tag{13.E.20}$$

Using the equation:

$$\beta = \left(\frac{k}{2D_e}\right)^{1/2} \tag{13.E.21}$$

We can solve for β using the information above

$$\beta = \left[\frac{1176.3 N \cdot m^{-1}}{2(7.33 \times 10^{-19} J)}\right]^{1/2} \tag{13.E.22}$$

$$= 2.84 \times 10^{10} m^{-1} \tag{13.E.23}$$

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

$$\tilde{v} = \tilde{v}_e - 2\tilde{x}_e\tilde{v}_e \tag{13.E.24}$$

and

$$\tilde{v} = 2\tilde{v}_e - 6\tilde{x}_e\tilde{v}_e, \tag{13.E.25}$$

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.

$$\tilde{v}_e = [3(2143.0) - 4260.0] cm^{-1} = 2169.0 cm^{-1} \tag{13.E.26}$$

Then multiply the fundamental frequency by 2 and subtract from the overtone.

$$\tilde{x}_e\tilde{v}_e = 13.0cm^{-1} \tag{13.E.27}$$

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

$$H^{35}Cl \tag{13.E.28}$$

given

$$\tilde{v_e} = 2990.946cm^{-1} \tag{13.E.29}$$

$$\tilde{x_e}\tilde{v_e} = 52.819cm^{-1} \tag{13.E.30}$$

S13-25

Use equation,

$$\tilde{v_{obs}} = \tilde{v_e}\nu - \tilde{x_e}\tilde{v_e}\nu(\nu+1) \tag{13.E.31}$$

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:

$$\tilde{v_{obs}} = \tilde{v_e} - 2\tilde{x_e}\tilde{v_e} = 2990.946cm^{-1} - 2(52.819cm^{-1}) = 2885.308cm^{-1} \tag{13.E.32}$$

First overtone:

$$\tilde{v_{obs}} = 2\tilde{v_e} - 6\tilde{x_e}\tilde{v_e} = 2990.946cm^{-1} - 6(52.819cm^{-1}) = 5664.978cm^{-1} \tag{13.E.33}$$

Second overtone:

$$\tilde{v_{obs}} = 3\tilde{v_e} - 12\tilde{x_e}\tilde{v_e} = 3(2990.946cm^{-1}) - 12(52.819cm^{-1}) = 8339.01cm^{-1} \tag{13.E.34}$$

Q13.26

Plot the

$$\frac{\nu_{obs}}{\nu} \tag{13.E.35}$$

versus

$$(\nu+1) \tag{13.E.36}$$

for the anharmonic oscillator approximation and use it to determine the values of

$$\nu_e \tag{13.E.37}$$

and

$$x_e\nu_e \tag{13.E.38}$$

for

$$H^{3}5Cl \tag{13.E.39}$$

. Use the information in Table13.4.

S13.26

$$\nu_{obs} = \nu_{obs}\nu - x_e\nu_e\nu(\nu+1) \tag{13.E.40}$$

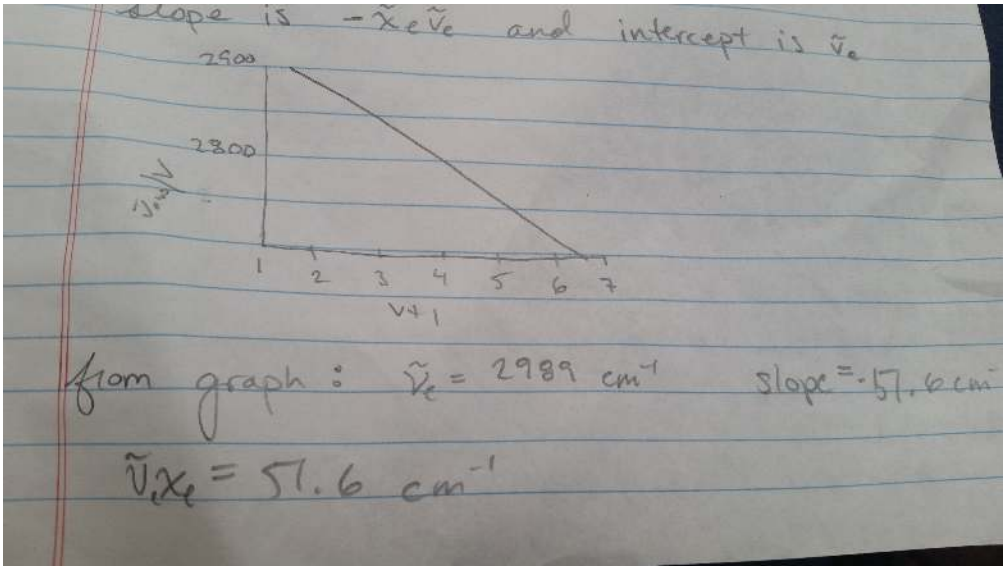
$$\frac{\nu_{obs}}{\nu} = \nu_e - x_e\nu_e(\nu+1) \tag{13.E.41}$$

The slope is

$$-x_e\nu_e \tag{13.E.42}$$

and the intercept is

$$\nu_e \tag{13.E.43}$$



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	$\tilde{\nu}_{abs}$ [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:

$$\tilde{\nu_{abs}} = \tilde{\nu_{0,0}}' + \tilde{\nu}_e'\tilde{\nu}' - \tilde{\chi}_e'\tilde{\nu}_e'\tilde{\nu}'(\nu'+1) \tag{13.E.44}$$

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.

- $\nu' = 0$:

$$\tilde{\nu_{0,0}}' = 29,699.10\ cm^{-1} \quad (1)$$

- $\nu' = 1$:

$$\tilde{\nu_{0,0}}' + \tilde{\nu_e}' - 2\tilde{\chi_e}'\tilde{\nu_e}' = 40,786.80\ cm^{-1} \quad (2)$$

- $\nu' = 2$:

$$\tilde{\nu_{0,0}}' + 2\tilde{\nu_e}' - 6\tilde{\chi_e}'\tilde{\nu_e}' = 41,858.90\ cm^{-1} \quad (3)$$

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:

$$\tilde{\chi_e}'\tilde{\nu_e}' = 1103.3\ cm^{-1} \quad (13.E.45)$$

and

$$\tilde{\nu_e}' = 7.80\ cm^{-1} \quad (13.E.46)$$

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	$0 \rightarrow 0$	$0 \rightarrow 1$	$0 \rightarrow 2$
$\tilde{\nu}_{obs}/cm^{-}1$	12376	89706	15219

*not accurate values for NaCl

Use these data to calculate the values of $\tilde{\nu}_e$ and $\tilde{\nu}_e\tilde{x}_e$ for the excited state of NaCl

S13.32

$A = \tilde{\nu}'_e, B = \tilde{\nu}'_e\tilde{x}'_e$

$12376 = \tilde{\nu}_0, 0$

$89706 = \tilde{\nu}_0, 0 + \tilde{\nu}'_e - 2\tilde{\nu}'_e\tilde{x}'_e - 12376 = \tilde{\nu}_0, 0 = 77330 = +\tilde{\nu}'_e - 2\tilde{\nu}'_e\tilde{x}'_e$ (1)

$15219 = \tilde{\nu}_0, 0 + 2\tilde{\nu}'_e - 6\tilde{\nu}'_e\tilde{x}'_e - 12376 = \tilde{\nu}_0, 0 = 2843 = 2\tilde{\nu}'_e - 6\tilde{\nu}'_e\tilde{x}'_e$ (2)

77330 + 2B = A (1a)

2843 = 2A - 6B (2a)

77330+2B = A

2843 - 154660 = -2B

B = 75908.5 cm^{-1} = $\tilde{\nu}'_e$

A = 229147 cm^{-1} = $\tilde{\nu}'_e\tilde{x}'_e$

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

$$I_{xx} = \sum m_j y_j^2 = m(1)^2 + 2m(sin^2 30°) = \frac{3}{2}m \tag{13.E.47}$$

$$I_{yy} = \sum m_j x_j^2 = m(0)^2 + 2m(cos^2 30°) = \frac{3}{2}m \tag{13.E.48}$$

$$I_{zz} = \sum m_j x_j^2 + \sum m_j y_j^2 = 3m \tag{13.E.49}$$

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

$$I_{xx} = 2\cos^2\theta + 8\sin^2\theta \tag{13.E.50}$$

$$I_{yy} = 8\cos^2\theta + 2\sin^2\theta \tag{13.E.51}$$

$$I_{xy} = -6\cos\theta\sin\theta \tag{13.E.52}$$

Solve the secular determinant equation for λ

$$\begin{vmatrix} I_{xx} - \lambda & I_{xy} \\ I_{xy} & I_{yy} - \lambda \end{vmatrix} = 0 \tag{13.E.53}$$

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 $\theta = 180°$. 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

$$I_{xx} = \sum m_i y_i^2 = 2(1)(2\sin\theta)^2 + 2(1)\left[\sin\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\sin^2\theta + 2\cos^2\theta \tag{13.E.54}$$

$$I_{yy} = \sum m_i x_i^2 = 2(1)(2\cos\theta)^2 + 2(1)\left[\cos\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\cos^2\theta + 2\sin^2\theta \tag{13.E.55}$$

$$\begin{aligned} I_{xy} = -\sum m_i x_i y_i &= -(2\cos\theta)(2\sin\theta) - 2\left[\cos(\pi) + \theta\right]\left[\sin(\pi) + \theta\right] \\ &\quad - \left[\sin\left(\frac{\pi}{2}\right) - \theta\right]\left[\cos\left(\frac{\pi}{2}\right) - \theta\right] - \left[\cos\left(\frac{\pi}{2}\right) + \theta\right]\left[\sin\left(\frac{\pi}{2}\right) + \theta\right] \\ &= -6\cos\theta\sin\theta \end{aligned} \tag{13.E.56}$$

The secular determinantal equation becomes

$$\begin{vmatrix} 8\sin^2\theta + 2\cos^2\theta - \lambda & -6\cos\theta\sin\theta \\ -6\cos\theta\sin\theta & 8\cos^2\theta + 2\sin^2\theta - \lambda \end{vmatrix} = 0 \tag{13.E.57}$$

Expanding the determinant gives

$$0 = \lambda^2 - \lambda(10)(\sin\theta^2 + \cos\theta^2) + 16(\sin\theta^2 + \cos\theta^2)^2 \tag{13.E.58}$$

$$0 = \lambda^2 - 10\lambda + 16 \tag{13.E.59}$$

$$\lambda = 5 \pm 3 \tag{13.E.60}$$

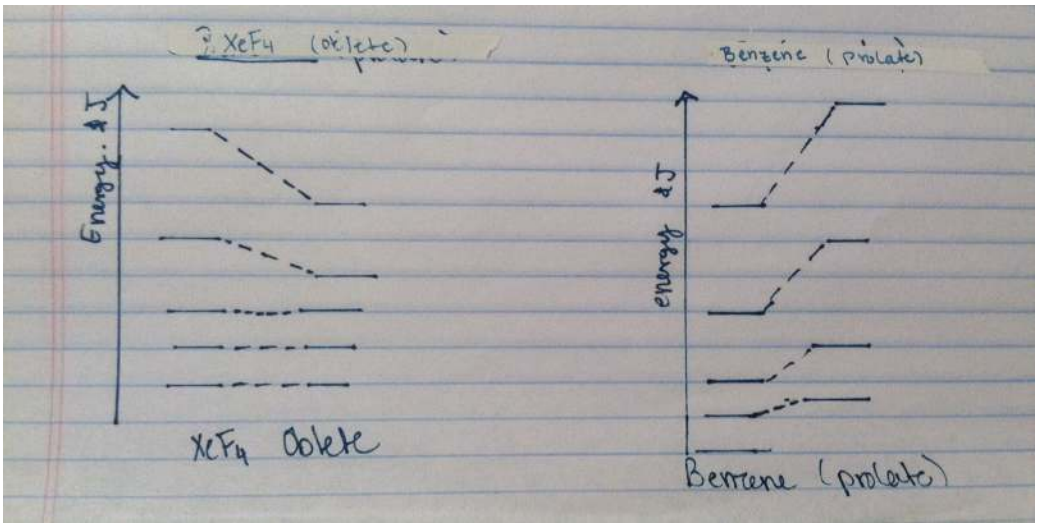
If $\theta = 180°$ then $I_{xx} = 2, I_{yy} = 8, and I_{xy} = 0$. If $\theta = 90°$ then $I_{xx} = 8, I_{yy} = 2, and I_{xy} = 0$. This tells us that the coordinate system does not affect the values of the principal momentum of inertia.

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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CHAPTER OVERVIEW

14: Nuclear Magnetic Resonance Spectroscopy

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

Nuclear magnetic resonance (NMR) is a physical phenomenon in which nuclei in a magnetic field absorb and re-emit electromagnetic radiation. This energy is at a specific resonance frequency which depends on the strength of the magnetic field and the magnetic properties of the isotope of the atoms. Many scientific techniques exploit NMR phenomena to study molecular physics, crystals, and non-crystalline materials through nuclear magnetic resonance spectroscopy. NMR is also routinely used in advanced medical imaging techniques, such as in magnetic resonance imaging (MRI).

14.1: Nuclei Have Intrinsic Spin Angular Momenta
14.2: Magnetic Moments Interact with Magnetic Fields
14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz
14.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded
14.5: Chemical Shifts Depend upon the Chemical Environment of the Nucleus
14.6: Spin-Spin Coupling Can Lead to Multiplets in NMR Spectra
14.7: Spin-Spin Coupling Between Chemically Equivalent Protons is Not Observed
14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method
14.E: Nuclear Magnetic Resonance Spectroscopy (Exercises)

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14.1: Nuclei Have Intrinsic Spin Angular Momenta

The electron, as well as certain other fundamental particles, possesses an intrinsic angular momentum or *spin*, in addition to its orbital angular momentum. These two types of angular momentum are analogous to the daily and annual motions, respectively, of the Earth around the Sun. To distinguish the spin angular momentum from the orbital, we designate the quantum numbers as s and m_s, in place of ℓ and m. For the electron, the quantum number s always has the value $\frac{1}{2}$, while m_s can have one of two values, $\pm\frac{1}{2}$. The electron is said to be an elementary particle of spin $\frac{1}{2}$. The proton and neutron also have spin $\frac{1}{2}$ and belong to the classification of particles called *fermions*, which are governed by the Pauli exclusion principle. Other particles, including the photon, have integer values of spin and are classified as *bosons*. These do *not* obey the Pauli principle, so that an arbitrary number can occupy the same quantum state. A complete theory of spin requires relativistic quantum mechanics. For our purposes, it is sufficient to recognize the two possible internal states of the electron, which can be called `spin up' and `spin down.' These are designated, respectively, by α and β as factors in the electron wavefunction. Spins play an essential role in determining the possible electronic states of atoms and molecules.

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14.2: Magnetic Moments Interact with Magnetic Fields

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.2.1}$$

You can see from Equation 14.2.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, 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. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 14.2.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz

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14.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded

An isolated nucleus in an external magnetic field experiences the external magnetic field. However, a nucleus in a molecule, when the molecule is placed in an external magnetic field, does not experience the external magnetic field, due to interference by the magnetic field generated by the surrounding electrons. The magnetic field experienced by the nucleus is either slightly lower than the external magnetic field or slightly higher. If the magnetic field experienced by the nucleus is lower than the external magnetic field, the nucleus is said to be shielded; if it is higher, the nucleus is said to be deshielded.

- B_x = the external magnetic field
- B_y = the magnetic field experienced by the nucleus

If $B_y < B_x$, the nucleus is shielded. If $B_y > B_x$, the nucleus is deshielded.

- http://www.chem.ucla.edu/~harding/ec...tutorial51.pdf
- http://personal.tcu.edu/bjanesko/NMR.htm

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14.5: Chemical Shifts Depend upon the Chemical Environment of the Nucleus

The chemical shift in NMR is extremely important, as it gives vital information about the local structure surrounding the nucleus of interest. For a majority of scientists, the chemical shift is used exlusivley to determine structure, especially in organic systems. Additional information may be gained by examining the anisotropy of the chemical shift. This section will be devoted to looking at chemical shift from a mathematical standpoint including a full treatment of the chemical shift tensor and the relation to the NMR lineshape.

The Chemical Shift

The local magnetic field is the field felt by a particular nucleus, where the applied field $\boldsymbol{B}$ induces currents in the electrons surrounding the nucleus give rise to a shielding. The shielding constant is σ. The local magnetic field is reduced by shielding by a factor $1-\sigma$.

$$B_{loc} = B + \delta B = (1-\sigma)B \tag{14.5.1}$$

The chemical shift is the difference between the resonance frequency of a nucleus and that of a standard.

The Larmor frequency of a shielded nucleus is:

$$\nu_L = \frac{\gamma B_{loc}}{2\pi} \tag{14.5.2}$$

Chemical shifts are reported on the δ-scale.

$$\delta = \frac{\nu - \nu_0}{\nu_0} \times 10^6 \tag{14.5.3}$$

The resonance frequency of the standard is ν_0.

The shielding constant is the sum of three contributions.

$$\sigma = \sigma(local) + \sigma(molecule) + \sigma(solvent) \tag{14.5.4}$$

The local contribution is due to electrons on the atom that contains the nucleus. The molecular contribution is from the rest of the molecule. The solvent contribution is from surrounding solvent molecules.

The Local Contribution

The local contribution is a sum of both diamagnetic σ_d and paramagnetic σ_p parts. The diamagnetic part arises from circulation of the electrons in response to $\boldsymbol{B}$. The Lamb formula gives the magnitude of σ_d,

$$\sigma_d = \frac{e^2 \mu_0}{3m_e} \int_o^\infty \rho(r) r \, dr \tag{14.5.5}$$

where ρ is the electron probability density $|\Psi^2|$. σ_d is inversely proportional to the **Bohr radius**. The magnetic moment of a current loop is proportional to a_o^2 and the magnetic field generated at the nucleus is proportional $\frac{1}{a_o^3}$.

The Molecular Contribution

The applied magnetic field generates currents in neighboring groups proportional to the magnetic susceptibility χ of a group. The induced magnetic moment gives rise to a magnetic field that is inversely proportional to the cube of the distance from the nucleus.

Contributors

- Stefan Franzen (North Carolina State University)

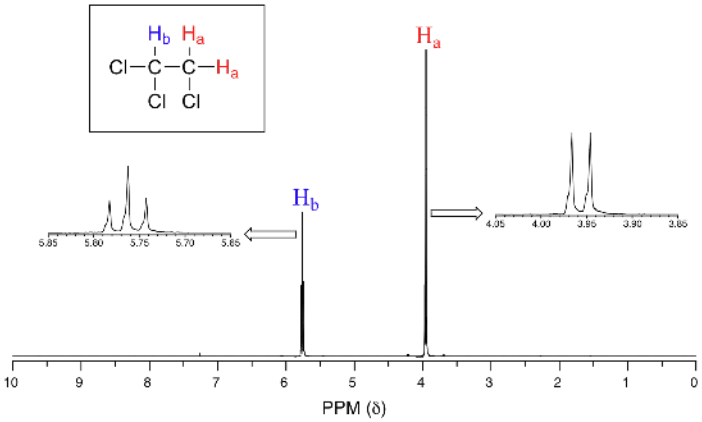
14.5: Chemical Shifts Depend upon the Chemical Environment of the Nucleus is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

14.6: Spin-Spin Coupling Can Lead to Multiplets in NMR Spectra

5.5A: The source of spin-spin coupling

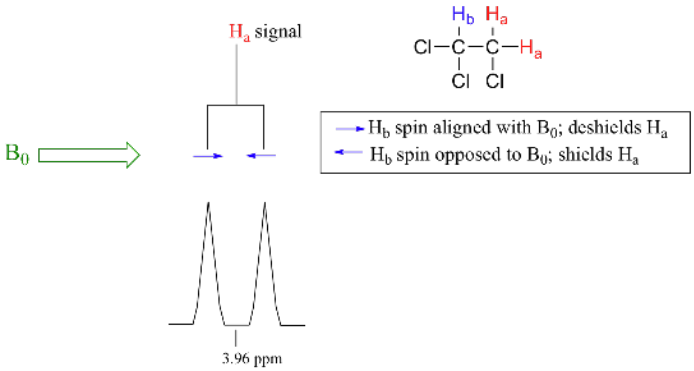
The ^{1}H-NMR spectra that we have seen so far (of methyl acetate and *para*-xylene) are somewhat unusual in the sense that in both of these molecules, each set of protons generates a single NMR signal. In fact, the ^{1}H-NMR spectra of most organic molecules contain proton signals that are 'split' into two or more sub-peaks. Rather than being a complication, however, this splitting behavior actually provides us with more information about our sample molecule.

Consider the spectrum for 1,1,2-trichloroethane. In this and in many spectra to follow, we show enlargements of individual signals so that the signal splitting patterns are recognizable.

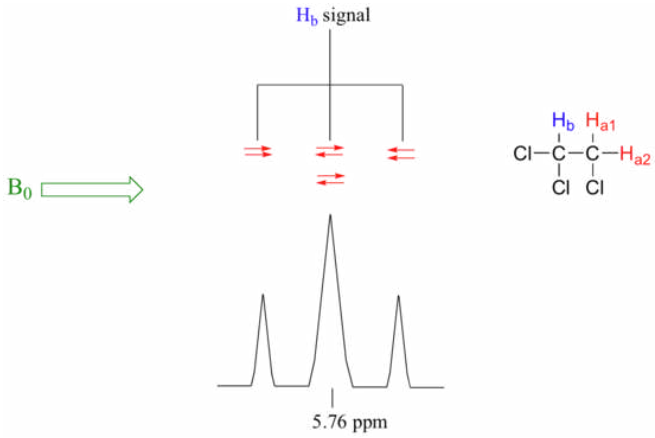


The signal at 3.96 ppm, corresponding to the two H_a protons, is split into two subpeaks of equal height (and area) – this is referred to as a **doublet**. The H_b signal at 5.76 ppm, on the other hand, is split into three sub-peaks, with the middle peak higher than the two outside peaks - if we were to integrate each subpeak, we would see that the area under the middle peak is twice that of each of the outside peaks. This is called a **triplet**.

The source of signal splitting is a phenomenon called **spin-spin coupling**, a term that describes the magnetic interactions between neighboring, non-equivalent NMR-active nuclei. In our 1,1,2 trichloromethane example, the H_a and H_b protons are spin-coupled to each other. Here's how it works, looking first at the H_a signal: in addition to being shielded by nearby valence electrons, each of the H_a protons is also influenced by the small magnetic field generated by H_b next door (remember, each spinning proton is like a tiny magnet). The magnetic moment of H_b will be aligned *with* B_0 in (slightly more than) half of the molecules in the sample, while in the remaining half of the molecules it will be opposed to B_0. The B_{eff} 'felt' by H_a is a slightly weaker if H_b is aligned against B_0, or slightly stronger if H_b is aligned with B_0. In other words, in half of the molecules H_a is *shielded* by H_b (thus the NMR signal is shifted slightly upfield) and in the other half H_a is *deshielded* by H_b(and the NMR signal shifted slightly downfield). What would otherwise be a single H_a peak has been split into two sub-peaks (a doublet), one upfield and one downfield of the original signal. These ideas an be illustrated by a **splitting diagram**, as shown below.

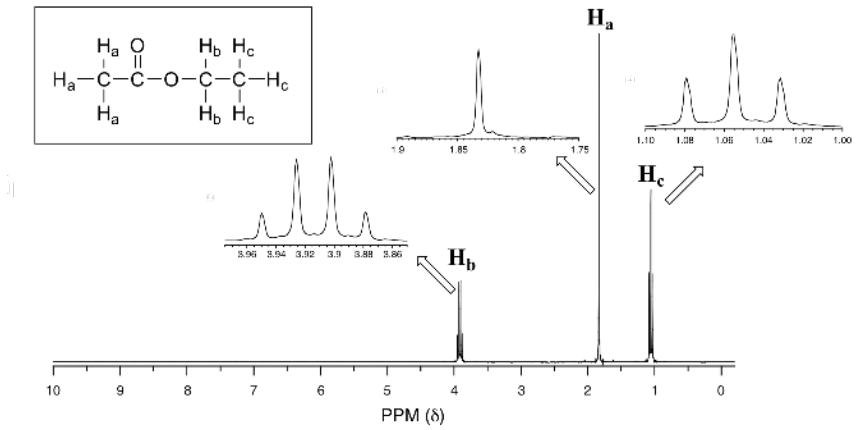


Now, let's think about the $H_b$signal. The magnetic environment experienced by H_b is influenced by the fields of both neighboring H_a protons, which we will call H_{a1} and H_{a2}. There are four possibilities here, each of which is equally probable. First, the magnetic fields of both H_{a1} and H_{a2} could be aligned with B_0, which would deshield H_b, shifting its NMR signal slightly downfield. Second, both the H_{a1} and H_{a2} magnetic fields could be aligned opposed to B_0, which would shield H_b, shifting its resonance signal slightly upfield. Third and fourth, H_{a1} could be with B_0 and H_{a2} opposed, or H_{a1}opposed to B_0 and H_{a2} with B_0. In each of the last two cases, the shielding effect of one H_a proton would cancel the deshielding effect of the other, and the chemical shift of H_b would be unchanged.



So in the end, the signal for H_b is a **triplet**, with the middle peak twice as large as the two outer peaks because there are *two* ways that H_{a1} and H_{a2} can cancel each other out.

Now, consider the spectrum for ethyl acetate:



We see an unsplit '**singlet**' peak at 1.833 ppm that corresponds to the acetyl (H_a) hydrogens – this is similar to the signal for the acetate hydrogens in methyl acetate that we considered earlier. This signal is unsplit because there are no adjacent hydrogens on the molecule. The signal at 1.055 ppm for the H_c hydrogens is split into a triplet by the two H_b hydrogens next door. The explanation here is the same as the explanation for the triplet peak we saw previously for 1,1,2-trichloroethane.

The $H_b$hydrogens give rise to a **quartet** signal at 3.915 ppm – notice that the two middle peaks are taller then the two outside peaks. This splitting pattern results from the spin-coupling effect of the *three* H_c hydrogens next door, and can be explained by an analysis similar to that which we used to explain the doublet and triplet patterns.

Example 5.6

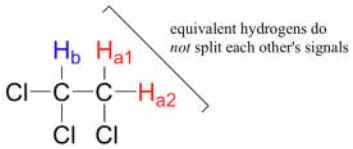
a. Explain, using left and right arrows to illustrate the possible combinations of nuclear spin states for the H_c hydrogens, why the H_b signal in ethyl acetate is split into a quartet.

b. The integration ratio of doublets is 1:1, and of triplets is 1:2:1. What is the integration ratio of the H_b quartet in ethyl acetate? (Hint – use the illustration that you drew in part a to answer this question.)

Solution

By now, you probably have recognized the pattern which is usually referred to as the ***n* + 1 rule**: if a set of hydrogens has *n* neighboring, non-equivalent hydrogens, it will be split into *n* + 1 subpeaks. Thus the two H_b hydrogens in ethyl acetate split the H_c signal into a triplet, and the three H_c hydrogens split the H_b signal into a quartet. This is very useful information if we are trying to determine the structure of an unknown molecule: if we see a triplet signal, we know that the corresponding hydrogen or set of hydrogens has two `neighbors`. When we begin to determine structures of unknown compounds using ^{1}H-NMR spectral data, it will become more apparent how this kind of information can be used.

Three important points need to be emphasized here. First, signal splitting only occurs between non-equivalent hydrogens – in other words, H_{a1} in 1,1,2-trichloroethane is *not* split by H_{a2}, and vice-versa.

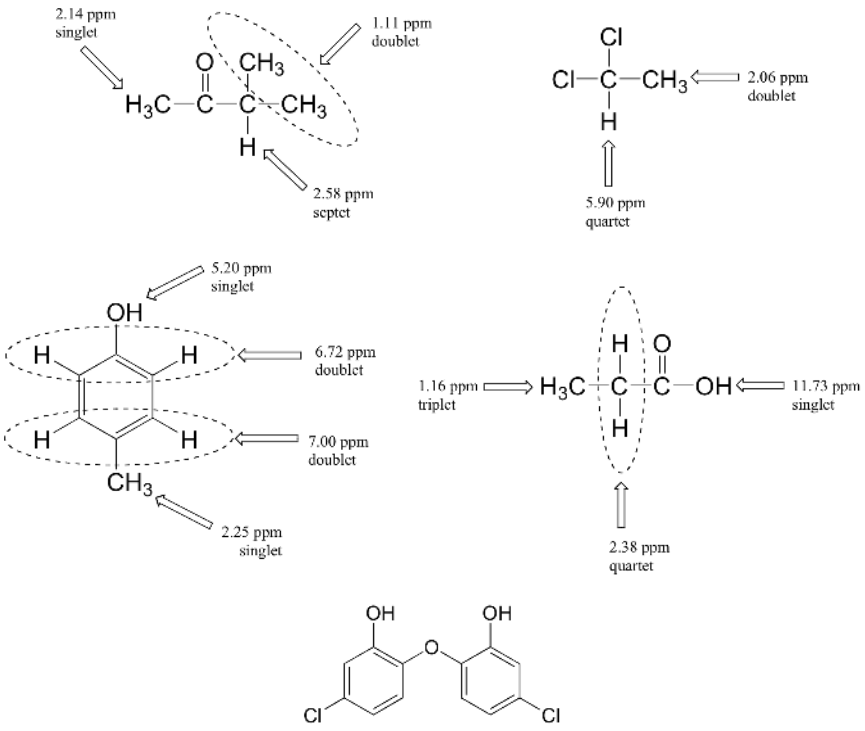


Second, splitting occurs primarily between hydrogens that are separated by three bonds. This is why the H_a hydrogens in ethyl acetate form a singlet– the nearest hydrogen neighbors are five bonds away, too far for coupling to occur.



Occasionally we will see four-bond and even 5-bond splitting, but in these cases the magnetic influence of one set of hydrogens on the other set is much more subtle than what we typically see in three-bond splitting (more details about how we quantify coupling interactions is provided in section 5.5B). Finally, splitting is most noticeable with hydrogens bonded to carbon. Hydrogens that are bonded to heteroatoms (alcohol or amino hydrogens, for example) are coupled weakly - or not at all - to their neighbors. This has to do with the fact that these protons exchange rapidly with solvent or other sample molecules.

Below are a few more examples of chemical shift and splitting pattern information for some relatively simple organic molecules.



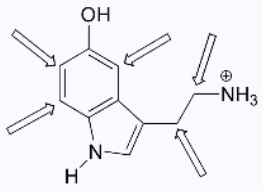
Example 5.7

a. How many proton signals would you expect to see in the ^{1}H-NMR spectrum of triclosan (a common antimicrobial agent found in detergents)? For each of the proton signals, predict the splitting pattern. Assume that you see only 3-bond coupling.

Solution

Example 5.8

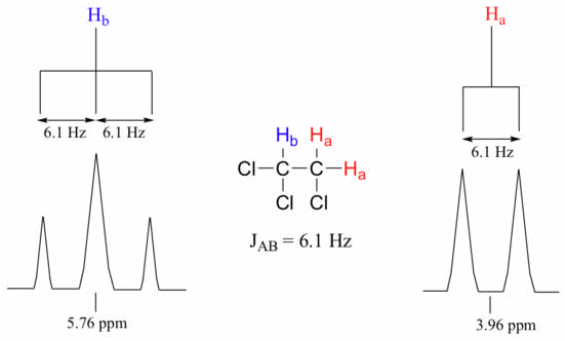
Predict the splitting pattern for the ^{1}H-NMR signals corresponding to the protons at the locations indicated by arrows (the structure is that of the neurotransmitter serotonin).



Solution

5.5B: Coupling constants

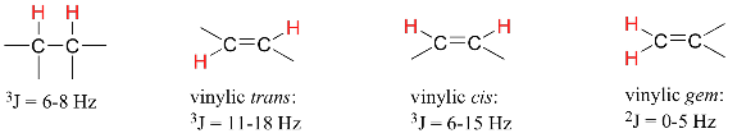
Chemists quantify the spin-spin coupling effect using something called the **coupling constant**, which is abbreviated with the capital letter *J*. The coupling constant is simply the difference, expressed in Hz, between two adjacent sub-peaks in a split signal. For our doublet in the 1,1,2-trichloroethane spectrum, for example, the two subpeaks are separated by 6.1 Hz, and thus we write $^3J_{a\text{-}b}$ = 6.1 Hz.



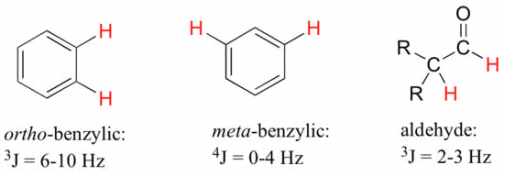
The superscript 3 tells us that this is a three-bond coupling interaction, and the a-b subscript tells us that we are talking about coupling between H_a and H_b. Unlike the chemical shift value, *the coupling constant, expressed in Hz, is the same regardless of the applied field strength of the NMR magnet*. This is because the strength of the magnetic moment of a neighboring proton, which is the source of the spin-spin coupling phenomenon, does *not* depend on the applied field strength.

When we look closely at the triplet signal in 1,1,2-trichloroethane, we see that the coupling constant - the `gap` between subpeaks - is 6.1 Hz, the same as for the doublet. This is an important concept! The coupling constant $^3J_{a\text{-}b}$ quantifies the magnetic interaction between the H_a and H_b hydrogen sets, and *this interaction is of the same magnitude in either direction*. In other words, H_a influences H_b to the same extent that H_b influences H_a. When looking at more complex NMR spectra, this idea of **reciprocal coupling constants** can be very helpful in identifying the coupling relationships between proton sets.

Coupling constants between proton sets on neighboring sp^3-hybridized carbons is typically in the region of 6-8 Hz. With protons bound to sp^2-hybridized carbons, coupling constants can range from 0 Hz (no coupling at all) to 18 Hz, depending on the bonding arrangement.



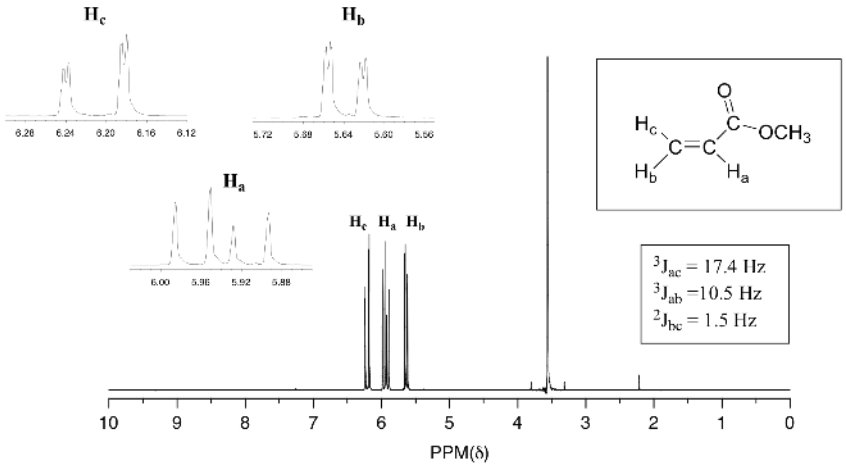
For vinylic hydrogens in a *trans* configuration, we see coupling constants in the range of ^3J = 11-18 Hz, while *cis* hydrogens couple in the ^3J = 6-15 Hz range. The 2-bond coupling between hydrogens bound to the same alkene carbon (referred to as geminal hydrogens) is very fine, generally 5 Hz or lower. *Ortho* hydrogens on a benzene ring couple at 6-10 Hz, while 4-bond coupling of up to 4 Hz is sometimes seen between *meta* hydrogens.



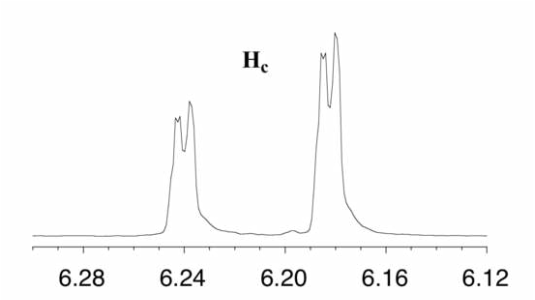
Fine (2-3 Hz) coupling is often seen between an aldehyde proton and a three-bond neighbor. Table 4 lists typical constant values.

5.5C: Complex coupling

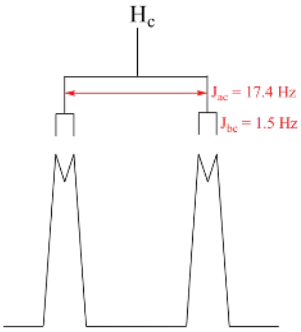
In all of the examples of spin-spin coupling that we have seen so far, the observed splitting has resulted from the coupling of one set of hydrogens to *just one* neighboring set of hydrogens. When a set of hydrogens is coupled to *two or more* sets of nonequivalent neighbors, the result is a phenomenon called **complex coupling**. A good illustration is provided by the ^{1}H-NMR spectrum of methyl acrylate:



First, let's first consider the H_c signal, which is centered at 6.21 ppm. Here is a closer look:

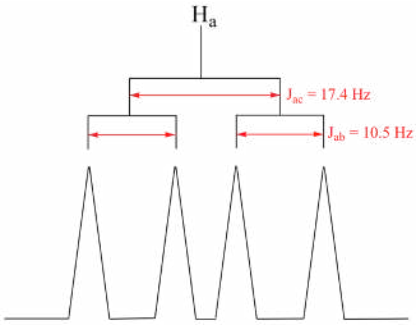


With this enlargement, it becomes evident that the Hc signal is actually composed of four sub-peaks. Why is this? H_c is coupled to both H_a and H_b , but with *two different coupling constants*. Once again, a splitting diagram can help us to understand what we are seeing. H_a is *trans* to H_c across the double bond, and splits the H_c signal into a doublet with a coupling constant of $^3J_{ac}$ = 17.4 Hz. In addition, each of these H_c doublet sub-peaks is split again by H_b (*geminal* coupling) into two more doublets, each with a much smaller coupling constant of $^2J_{bc}$ = 1.5 Hz.

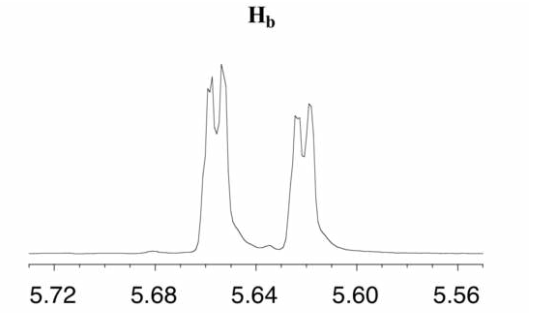


The result of this `double splitting` is a pattern referred to as a **doublet of doublets**, abbreviated `**dd**`.

The signal for H_a at 5.95 ppm is also a doublet of doublets, with coupling constants $^3J_{ac}$= 17.4 Hz and $^3J_{ab}$ = 10.5 Hz.



The signal for H_b at 5.64 ppm is split into a doublet by H_a, a *cis* coupling with $^3J_{ab}$ = 10.4 Hz. Each of the resulting sub-peaks is split again by H_c, with the same *geminal* coupling constant $^2J_{bc}$ = 1.5 Hz that we saw previously when we looked at the H_c signal. The overall result is again a doublet of doublets, this time with the two `sub-doublets` spaced slightly closer due to the smaller coupling constant for the *cis* interaction. Here is a blow-up of the actual $H_b$signal:



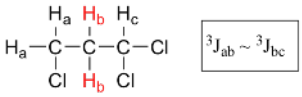
Example 5.9

Construct a splitting diagram for the H_b signal in the ^{1}H-NMR spectrum of methyl acrylate. Show the chemical shift value for each sub-peak, expressed in Hz (assume that the resonance frequency of TMS is exactly 300 MHz).

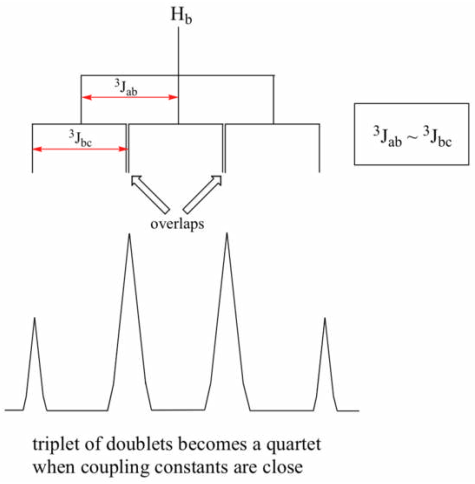
Solution

When constructing a splitting diagram to analyze complex coupling patterns, it is usually easier to show the larger splitting first, followed by the finer splitting (although the reverse would give the same end result).

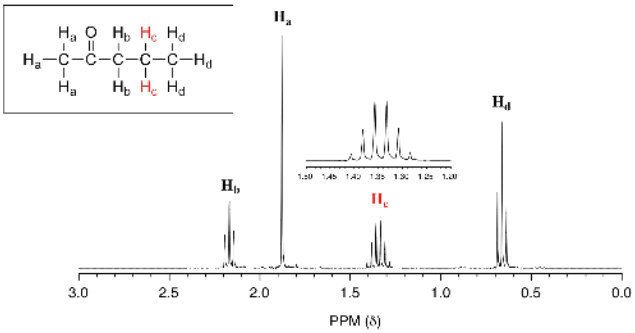
When a proton is coupled to two different neighboring proton sets with identical or very close coupling constants, the splitting pattern that emerges often appears to follow the simple `*n* + 1 rule` of non-complex splitting. In the spectrum of 1,1,3-trichloropropane, for example, we would expect the signal for H_b to be split into a triplet by H_a, and again into doublets by H_c, resulting in a 'triplet of doublets'.



H_a and H_c are not equivalent (their chemical shifts are different), but it turns out that $^3J_{ab}$ is very close to $^3J_{bc}$. If we perform a splitting diagram analysis for H_b, we see that, due to the overlap of sub-peaks, the signal appears to be a quartet, and for all intents and purposes follows the $n + 1$ rule.

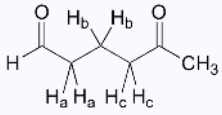


For similar reasons, the H_c peak in the spectrum of 2-pentanone appears as a sextet, split by the five combined H_b and H_d protons. Technically, this 'sextet' could be considered to be a 'triplet of quartets' with overlapping sub-peaks.



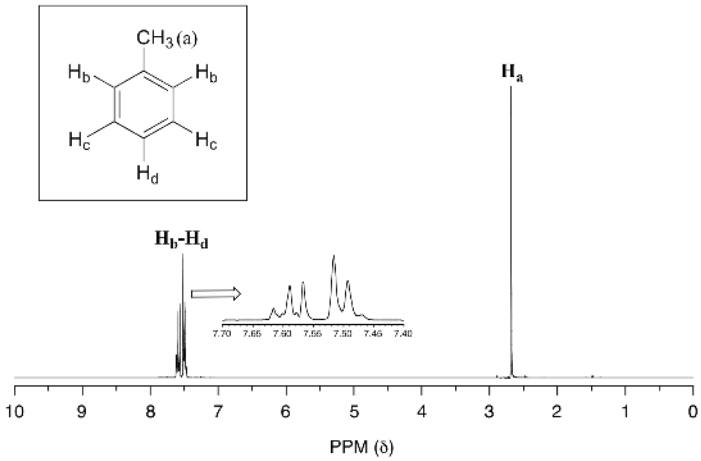
Example 5.10

What splitting pattern would you expect for the signal coresponding to H_b in the molecule below? Assume that $J_{ab} \sim J_{bc}$. Draw a splitting diagram for this signal, and determine the relative integration values of each subpeak.



Solution

In many cases, it is difficult to fully analyze a complex splitting pattern. In the spectrum of toluene, for example, if we consider only 3-bond coupling we would expect the signal for H_b to be a doublet, H_d a triplet, and H_c a triplet.



In practice, however, all three aromatic proton groups have very similar chemical shifts and their signals overlap substantially, making such detailed analysis difficult. In this case, we would refer to the aromatic part of the spectrum as a **multiplet**.

When we start trying to analyze complex splitting patterns in larger molecules, we gain an appreciation for why scientists are willing to pay large sums of money (hundreds of thousands of dollars) for higher-field NMR instruments. Quite simply, the stronger our magnet is, the more resolution we get in our spectrum. In a 100 MHz instrument (with a magnet of approximately 2.4 Tesla field strength), the 12 ppm frequency 'window' in which we can observe proton signals is 1200 Hz wide. In a 500 MHz (~12 Tesla) instrument, however, the window is 6000 Hz - five times wider. In this sense, NMR instruments are like digital cameras and HDTVs: better resolution means more information and clearer pictures (and higher price tags!)

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

14.6: Spin-Spin Coupling Can Lead to Multiplets in NMR Spectra is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

14.7: Spin-Spin Coupling Between Chemically Equivalent Protons is Not Observed

When doing NMR spectroscopy, it is an observed fact that equivalent hydrogens do not split one another. Why don't equivalent hydrogens split each other's signals? For example, why is the NMR spectrum for ethane a singlet instead of a quartet or even a dodecuplet (due to the hydrogens on the same carbon)? What is so special about hydrogens being equivalent to one another that causes no splitting to be observed?

Finding the states between which transitions occur

The Hamiltonian for two coupled spins is

$$\hat{H} = \omega_1 \hat{I}_{1z} + \omega_2 \hat{I}_{2z} + \frac{2\pi J_{12}}{\hbar}(\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2) \tag{14.7.1}$$

where ω_1 and ω_2 are the Larmor frequencies[2] of the two nuclei and J_{12} is the coupling constant (in Hz) between the two nuclei. (The factor of $2\pi/\hbar$ is simply there to bring it into energy units.) $\hat{I}_i$ is the operator for the spin angular momentum of nucleus i and $\hat{I}_{iz}$ is the operator for its projection along the z-axis.

However, in NMR, it is customary to work in frequency units instead of energy units. Since $E = h\nu$, we simply need to divide through by h. Bearing in mind that $\omega = 2\pi\nu$ and $h = 2\pi\hbar$, we get:

$$\hat{H}_{\text{freq}} = \frac{\nu_1}{\hbar}\hat{I}_{1z} + \frac{\nu_2}{\hbar}\hat{I}_{2z} + \frac{J_{12}}{\hbar^2}(\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2) \tag{14.7.2}$$

On top of that, to make the math easier, it is also quite common to set $\hbar = 1$. Therefore, we have

$$\hat{H}_{\text{freq}} = \nu_1 \hat{I}_{1z} + \nu_2 \hat{I}_{2z} + J_{12}(\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2) \tag{14.7.3}$$

We will deal with two spin-$1/2$ nuclei here, where $|\alpha\rangle$ and $|\beta\rangle$ represent the "up" and "down" spins (recall we set $\hbar = 1$ so it doesn't appear in the eigenvalues):

$$\hat{I}_{iz}|\alpha_i\rangle = \frac{1}{2}|\alpha_i\rangle \qquad \hat{I}_{iz}|\beta_i\rangle = -\frac{1}{2}|\beta_i\rangle \qquad (i = 1, 2) \tag{14.7.4}$$

Furthermore since we are dealing with equivalent nuclei we can simply set $\nu_1 = \nu_2 = \nu$ and drop the subscript in J_{12} just to make it a bit cleaner:

$$\hat{H} = \nu(\hat{I}_{1z} + \hat{I}_{2z}) + J(\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2) \tag{14.7.5}$$

Now, we need to find the eigenstates and eigenvalues of $\hat{H}$. To do so, we will adopt the basis set of product functions $(|\alpha_1\alpha_2\rangle, |\alpha_1\beta_2\rangle, |\beta_1\alpha_2\rangle, |\beta_1\beta_2\rangle)$. From equation (4) we have

$$\hat{I}_{1z}|\alpha_1\alpha_2\rangle = \frac{1}{2}|\alpha_1\alpha_2\rangle \qquad \hat{I}_{2z}|\alpha_1\alpha_2\rangle = \frac{1}{2}|\alpha_1\alpha_2\rangle \tag{14.7.6}$$

$$\hat{I}_{1z}|\alpha_1\beta_2\rangle = \frac{1}{2}|\alpha_1\beta_2\rangle \qquad \hat{I}_{2z}|\alpha_1\beta_2\rangle = -\frac{1}{2}|\alpha_1\beta_2\rangle \tag{14.7.7}$$

$$\hat{I}_{1z}|\beta_1\alpha_2\rangle = -\frac{1}{2}|\beta_1\alpha_2\rangle \qquad \hat{I}_{2z}|\beta_1\alpha_2\rangle = \frac{1}{2}|\beta_1\alpha_2\rangle \tag{14.7.8}$$

$$\hat{I}_{1z}|\beta_1\beta_2\rangle = -\frac{1}{2}|\beta_1\beta_2\rangle \qquad \hat{I}_{2z}|\beta_1\beta_2\rangle = -\frac{1}{2}|\beta_1\beta_2\rangle \tag{14.7.9}$$

The action of the scalar product $\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2$ is more complicated. We need to introduce the *shift operators* (or *ladder operators*).

$$\hat{I}_{i+} = \hat{I}_{ix} + \mathrm{i}\hat{I}_{iy} \qquad \hat{I}_{i-} = \hat{I}_{ix} - \mathrm{i}\hat{I}_{iy} \tag{14.7.10}$$

from which we can obtain

$$\hat{I}_{ix} = \frac{\hat{I}_{i+} + \hat{I}_{i-}}{2} \qquad \hat{I}_{iy} = \frac{\hat{I}_{i+} - \hat{I}_{i-}}{2\mathrm{i}} \tag{14.7.11}$$

So, finally, we can write

$$\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2 = \hat{I}_{1x}\hat{I}_{2x} + \hat{I}_{1y}\hat{I}_{2y} + \hat{I}_{1z}\hat{I}_{2z} \tag{14.7.12}$$

$$= \frac{\hat{I}_{1+}\hat{I}_{2-} + \hat{I}_{1-}\hat{I}_{2+}}{2} + \hat{I}_{1z}\hat{I}_{2z} \tag{14.7.13}$$

where in going from (12) to (13) one simply substitutes in (11) and does a fair bit of algebraic manipulation. The action of the shift operators are

Label '14' multiply defined

This allows you to work out the effect of $\hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2$ on our basis states. The actual math is left to the reader and I will simply quote the results:

$$\hat{H}|\alpha_1\alpha_2\rangle = \left(\nu + \frac{J}{4}\right)|\alpha_1\alpha_2\rangle \tag{14.7.15}$$

$$\hat{H}|\alpha_1\beta_2\rangle = -\frac{J}{4}\left|\alpha_1\beta_2\right\rangle + \frac{J}{2}\left|\beta_1\alpha_2\right\rangle \tag{14.7.16}$$

$$\hat{H}|\beta_1\alpha_2\rangle = \frac{J}{2}\left|\alpha_1\beta_2\right\rangle - \frac{J}{4}\left|\beta_1\alpha_2\right\rangle \tag{14.7.17}$$

$$\hat{H}|\beta_1\beta_2\rangle = \left(-\nu + \frac{J}{4}\right)|\beta_1\beta_2\rangle \tag{14.7.18}$$

Therefore in this basis the Hamiltonian matrix is

$$\mathbf{H} = \begin{pmatrix} \nu + J/4 & 0 & 0 & 0 \\ 0 & -J/4 & J/2 & 0 \\ 0 & J/2 & -J/4 & 0 \\ 0 & 0 & 0 & -\nu + J/4 \end{pmatrix} \tag{14.7.19}$$

Finding the eigenvectors and eigenvalues of this matrix is again left to the reader (it is not a difficult task) and they are (eigenvalues denoted \(E_i$)

$$|1\rangle = |\alpha_1\alpha_2\rangle \qquad E_1 = \nu + \frac{J}{4} \tag{14.7.20}$$

$$|2\rangle = \frac{1}{\sqrt{2}}(|\alpha_1\beta_2\rangle + |\beta_1\alpha_2\rangle) \qquad E_2 = \frac{J}{4} \tag{14.7.21}$$

$$|3\rangle = \frac{1}{\sqrt{2}}(|\alpha_1\beta_2\rangle - |\beta_1\alpha_2\rangle) \qquad E_3 = -\frac{3J}{4} \tag{14.7.22}$$

$$|4\rangle = |\beta_1\beta_2\rangle \qquad E_4 = -\nu + \frac{J}{4} \tag{14.7.23}$$

The form of the eigenstates should be familiar: they are simply the triplet and singlet states of two spin-$1/2\) particles. These states arise from the coupling of two sources of angular momenta, I_1 and I_2, to form one overall angular momentum denoted I.

$$\vec{I} = \vec{I}_1 + \vec{I}_2 \tag{14.7.24}$$

The allowed values of I are determined by the **Clebsch-Gordan series**:

$$I = I_1 + I_2, I_1 + I_2 - 1, \cdots, |I_1 - I_2| \tag{14.7.25}$$

Since $I_1 = I_2 = 1/2$, I can take the values 1 and 0. The values of M_I, the projection of the total angular momentum along the \(z$-axis, are as usual

$$M_I = I, I-1, \cdots, -I \tag{14.7.26}$$

so the states with $I = 1$ ("triplet") have $M_I = 1, 0, -1$ and the state with $I = 0$ ("singlet") has $M_I = 0$. One can use more quantum mechanics to work out which state is associated with which quantum numbers, but I will not do it here. They are:

State	I	M_I
$\|1\rangle$	1	1
$\|2\rangle$	1	0
$\|3\rangle$	0	0
$\|4\rangle$	1	-1

(14.7.27)

Selection rules

We have four different states, which leads to $\binom{4}{2} = 6$ different possible transitions. However, not all of these transitions are allowed.

The intensity of the transition is proportional to the square of the matrix element $\langle \psi_f \left| \hat{H}' \right| \psi_i \rangle$ (the so-called "transition dipole moment"), where $\hat{H}'$ is the Hamiltonian for the process that induces the transition. In the case of NMR transitions, the transition arises due to a magnetic field aligned along the \(x$-axis.[3] The corresponding Hamiltonian is therefore

$$\hat{H}' = \omega'(\hat{I}_{1x} + \hat{I}_{2x}) = \omega' \hat{I}_x \tag{14.7.28}$$

Exactly what ω' represents is not important here because we are only really concerned about whether the transition dipole moment is zero or not.[4] Making use of the relations established in equations 14.7.10 and 14.7.11,[5] one can find that the selection rules are

$$\Delta I = 0; \Delta M_I = \pm 1 \tag{14.7.29}$$

which means that the allowed transitions are $|4\rangle \leftrightarrow |2\rangle$ and $|2\rangle \leftrightarrow |1\rangle$. Transitions to and from the singlet state $|3\rangle$ are forbidden. The energies of the transitions are

$$E_{4 \leftrightarrow 2} = \frac{J}{4} - \left(-\nu + \frac{J}{4}\right) = \nu \tag{14.7.30}$$

$$E_{2 \leftrightarrow 1} = \left(\nu + \frac{J}{4}\right) - \frac{J}{4} = \nu \tag{14.7.31}$$

i.e. the two transitions are degenerate and only one line in the spectrum at frequency ν is observed. This is exactly what is depicted in the diagrams posted in the other answers.

> *the two transitions are degenerate and only one line in the spectrum at frequency ν is observed.*

Notes and references

[1] I am assuming the reader has some knowledge of the quantum mechanical treatment of angular momentum, which is a topic that is treated thoroughly in most quantum mechanics textbooks. See, for example, chapter 4 of Atkins's *Molecular Quantum Mechanics* (5th ed.).

[2] The Larmor frequency is given by $\omega = -\gamma B_0$, where γ is the magnetogyric ratio of the nucleus in question and B_0 is the strength of the external magnetic field. It represents the frequency with which a magnetic moment precesses about a magnetic field. See any textbook on magnetism for further details.

[3] I am glossing over some details here. The so-called magnetic field in the \(x$-axis is a component of the radiofrequency pulse applied in the \(xy$-plane. If you are interested please consult a textbook on the vector model of NMR. In particular I recommend Keeler's *Understanding NMR Spectroscopy* (2nd ed.).

[4] It is related to the strength of the magnetic field in the $x\$ - axis, \(B_1$, by $w' = |\gamma| B_1$. The usual symbol is ω_1, but I chose not to use this here to avoid potential confusion. Again, please consult a textbook on the vector model of NMR if you wish to find out more.

[5] A full proof can be found in *J. Chem. Educ.* **1982,** *59* (10), 819. There is also some discussion of the selection rules in Gunther's *NMR Spectroscopy* (3rd ed.), p 156 onwards.

Note

The first important point to note is that *magnetically* equivalent nuclei do in fact couple to each other, however no splitting is *observed* in the spectrum. The second point is that *chemically equivalent, but magnetically non-equivalent*, nuclei couple to each other, and this coupling *is* observable in the NMR spectrum.

Spin coupling comes from a magnetic interaction between nuclear spins transmitted through the bonding electrons. Signals observed in the NMR spectrum are a transition between energy levels of allowed spin states. When two nuclei 'couple', the energy levels are stabilised or destabilsed slightly based on the relative orientations of the nuclear moments, so that (for a

doublet) one transition is now δ+J/2, and the other transition is δ-J/2. These two transitions constitute the two lines of the doublet signal. When two equivalent nuclei couple, transitions between energy levels do not change because the interactions between the nuclear moments are the same, as are all other contributing factors such as the Fermi contact. As long as the transitions remain the same, all possible transitions will be equivalent.

The diagram below hopefully explains it a little clearer. The middle energy levels are for two non-coupled spins. Spin A (shown in red) has two possible transitions, both of which are equivalent. When the two spins are coupled, the energy levels are stabilised/destabilised as shown on the right. The transitions for spin A are now no longer equivalent, and they will appear as two lines (doublet). On the left, the equivalent nuclei have an overall change in energy level, but the transition between the levels remains the same, hence the observed line is still a singlet.



When there are two distinct nuclei (The AX case) and there is spin-spin interaction (J coupling) between them (in addition to chemical shift) then fine structure can be observed in the nmr spectrum. The first diagram shows the energy levels and how they interact. Note how the J coupling moves the levels up and down in addition to chemical shift.



Now there are selection rules that allow the radio frequency radiation to couple different levels together and so produce a spectrum. The rule is that the m_z quantum number (variously called magnetic, or azimuthal or projection quantum number) has to change by $+1$ or -1. This means that in the first diagram only levels in which one alpha changes to beta or vice versa, as shown by the vertical arrows, are allowed transitions. (The selection rule occurs because the photon (even if at radio frequency) has one unit of angular momentum and total angular momentum is conserved.)

In the equivalent nuclei case (called A2) the interaction between spins is still present but because of the magnetically identical nuclei the spin states are not either symmetrical or anti symmetrical to exchange of nuclei and a linear combination has to be made. This is shown on the left of the figure below. The reason that the splitting in energy levels is not observed is that selection rules make the transitions unobservable



Advanced: Liouville–von Neumann Equation

An alternative answer using the product operator formalism:

The fundamental equation describing NMR quantum mechanically (neglecting relaxation) is the **Liouville–von Neumann Equation** (in frequency units, i.e. setting $\hbar = 1$):

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho} = -\mathrm{i}[\hat{H}, \hat{\rho}] \tag{14.7.32}$$

For a 2-spin system with identical chemical shifts and a coupling

$$\hat{H} = \Omega\hat{I}_{1z} + \Omega\hat{I}_{2z} + J(\vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2) \tag{14.7.33}$$

After a 90 degree pulse on both nuclei the density matrix $\hat{\rho}$ is of the form $\hat{I}_{1\chi} + \hat{I}_{2\chi}$, where $\chi = x$ or y. Now it is a bit lengthy but easy to show that

$$[\hat{I}_{1\chi} + \hat{I}_{2\chi}, J(\vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2)] = 0, \quad \text{with } \chi = x, y, z \tag{14.7.34}$$

meaning that the coupling Hamiltonian does not influence the signal after a 90 degree pulse, as $[\hat{H}_{\text{coupling}}, \hat{\rho}] = 0$.

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14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.9.1}$$

You can see from Equation 14.9.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, 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. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 14.9.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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14.E: Nuclear Magnetic Resonance Spectroscopy (Exercises)

These are homework exercises to accompany Chapter 14 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q14.1

Write the equation for a magnetic dipole in the angular momentum form starting from $\mu = \frac{q(\mathbf{r} \times \mathbf{v})}{2}$.

S14.1

μ can be expressed in terms of angular momentum by using the fact $\mathbf{L} = \mathbf{r}$ x $\mathbf{p}$ and that $\mathbf{p} = m\mathbf{v}$.

By substituting $\mathbf{p} = m\mathbf{v}$ in to $\mathbf{L}$ gives :

$$\mathbf{L} = \mathbf{r} \text{ x } m\mathbf{v}$$

by dividing out the $\mathbf{m}$ becuse it is a scalar μ becomes:

$$\mu = \frac{q}{2m}\mathbf{L}.$$

Q14.3

Show that the frequency from $\nu_{1\to3}$ given in Table 14.6 reduces to Equation 14.66 when $J \ll \nu_0(\sigma_1 - \sigma_2)$

S14.35

$$\nu_{1\to3} = \frac{\nu_0}{2}(2-\sigma_1-\sigma_2) - \frac{J}{2} + \frac{1}{2}\left[\nu_0^2(\sigma_1-\sigma_2)^2+J^2\right]^{\frac{1}{2}}$$

$$= \frac{\nu_0}{2}(2-\sigma_1-\sigma_2) - \frac{J}{2} + \frac{\nu_0(\sigma_1-\sigma_2)}{2}\left[1+\frac{J^2}{\nu_0^2(\sigma_1-\sigma_2)^2}\right]^{\frac{1}{2}}$$

Since $J \ll \nu_0(\sigma_1 - \sigma_2)$, we can use a Taylor expansion and keeping only the terms that are linear in J gives

$$\frac{\nu_0}{2}(2-\sigma_1-\sigma_2) - \frac{J}{2} + \frac{\nu_0(\sigma_1-\sigma_2)}{2} - O(J^2)$$

$$= \nu_0(1-\sigma_2) - \frac{J}{2}$$

Q14.18

Nuclear spin operators I_x, I_y, I_z all obey the commutation relations, that

$$[I_x, I_y] = ihI_z$$

$$[I_y, I_z] = ihI_x$$

$$[I_z, I_x] = ihI_y$$

Show that

$$I_zI_+ = I_+I_z + hI_+ \qquad \textit{and} \qquad I_zI_- = I_-I_z - hI_-$$

S14.18

We know that the commutation relations are as follows:

$$I_xI_y - I_yI_x = ihI_z$$

$$I_yI_z - I_zI_y = ihI_x$$

$$I_zI_x - I_xI_z = ihI_y$$

Therefore,

$$I_zI_+ = I_z(I_x + iI_y) = ihI_y + I_xI_z + iI_zI_y = ihI_y + I_xI_z + i(I_yI_z - ihI_x) = I_xI_z + iI_yI_z + hI_x + ihI_y = I_+I_z + hI_+$$

and

$$I_zI_- = I_z(I_x - iI_y) = ihI_y + I_xI_z - iI_zI_y = ihI_y + I_xI_z - i(I_yI_z - ihI_x) = I_xI_z - iI_yI_z - hI_x + ihI_y = I_-I_z - hI_-$$

Q14.19

Given:

$$\hat{I}_+\hat{I}_- = \hat{I}_x^2 + i\hat{I}_x\hat{I}_y - i\hat{I}_x\hat{I}_y + \hat{I}_y^2$$

and

$$\hat{I}^2 = \hat{I}_x^2 + \hat{I}_y^2 + \hat{I}_z^2$$

Show:

$$\hat{I}_+\hat{I}_- = \hat{I}^2 - \hat{I}_z^2 + \hbar\hat{I}_z$$

and

$$\hat{I}_-\hat{I}_+ = \hat{I}^2 - \hat{I}_z^2 - \hbar\hat{I}_z$$

S14.19

$\hat{I}^2 - \hat{I}_z^2 = \hat{I}_x^2 + \hat{I}_y^2$, so

$$\hat{I}_+\hat{I}_- = \hat{I}^2 - \hat{I}_z^2 + i\hat{I}_y\hat{I}_x - i\hat{I}_x\hat{I}_y$$

$$= \hat{I}^2 - \hat{I}_z^2 - i(i\hbar\hat{I}_z)$$

$$= \hat{I}^2 - \hat{I}_z^2 + \hbar\hat{I}_z$$

and

$$\hat{I}_-\hat{I}_+ = \hat{I}_x^2 + \hat{I}_y^2 + i\hat{I}_x\hat{I}_y - i\hat{I}_y\hat{I}_x$$

$$= \hat{I}^2 - \hat{I}_z^2 + i(i\hbar\hat{I}_z)$$

$$= \hat{I}^2 - \hat{I}_z^2 - \hbar\hat{I}_z$$

Q14.20

Using

$$\hat{I}_z\hat{I}_+ = \hat{I}_+\hat{I}_z + \hbar\hat{I}_+$$

$$\hat{I}_z\beta = -\frac{\hbar}{2}\beta$$

$$\hat{I}_+\beta = \hbar\alpha$$

and $c = \hbar$,
derive $\hat{I}_x\alpha$, $\hat{I}_y\alpha$, $\hat{I}_x\beta$, and $\hat{I}_y\beta$ in terms of $\alpha, \beta, \hbar$.

S14.20

We know

$$\hat{I}_+ = \hat{I}_x + i\hat{I}_y \text{ and } \hat{I}_- = \hat{I}_x - i\hat{I}_y$$

So we can show that

$$\hat{I}_+\alpha = \hat{I}_x\alpha + i\hat{I}_y\alpha = 0 \text{ and } \hat{I}_-\alpha = \hat{I}_x\alpha - i\hat{I}_y\alpha = \hbar\beta$$

by adding the equations we can show that

$$\hat{I}_x\alpha = \frac{\hbar}{2}\beta \text{ and } \hat{I}_y\alpha = \frac{i\hbar}{2}\beta$$

if we apply the same methodology as above but with \(\beta)\ we can see that

$$\hat{I}_x\beta = \frac{\hbar}{2}\alpha \text{ and } \hat{I}_y\beta = \frac{i\hbar}{2}\alpha$$

Q14.21

This problem shows that the proportionality constant c in

$$\hat{I}_+\beta = c\alpha \; or \; \hat{I}_-\alpha = c\beta$$

is equal to $\hbar$. Start with

$$\int \alpha^*\alpha d\tau = 1 = \frac{1}{c^2}\int (\hat{I}_+\beta)^*(\hat{I}_+\beta)d\tau$$

Let $\hat{I}_+ = \hat{I}_x + i\hat{I}_y$ in the second factor in the above integral and use the fact that $\hat{I}_x$ and $\hat{I}_y$ are Hermitian to get

$$\int (\hat{I}_x\hat{I}_+\beta)^*\beta d\tau + i\int (\hat{I}_y\hat{I}_+\beta)^*\beta d\tau = c^2$$

Now take the complex conjugate of both sides to get

$$\int \beta^*\hat{I}_x\hat{I}_+\beta d\tau - i\int \beta^*\hat{I}_y\hat{I}_+\beta d\tau = c^2 = \int \beta^*\hat{I}_-\hat{I}_+\beta d\tau$$

Using the given equation:

$$\hat{I}_-\hat{I}_+ = \hat{I}^2 - \hat{I}_z^2 - \hbar\hat{I}_z$$

Show that:

$$c^2 = \int \beta^*\hat{I}_-\hat{I}_+\beta d\tau = \int \beta^*(\hat{I}^2 - \hat{I}_z^2 - \hbar\hat{I}_z)\beta d\tau = \int \beta^*\left(\frac{3}{4}\hbar^2 - \frac{1}{4}\hbar^2 + \frac{\hbar^2}{2}\right)\beta d\tau = \hbar^2$$

or that $c = \hbar$

S14.21

Recall that for a Hermitian operator $\hat{A}$,

$$\int f^*(x)\hat{A}g(x)dx = \int g(x)\hat{A}^*f^*(x)dx$$

Begin with the expression

$$\int \alpha^*\alpha d\tau = 1 = \frac{1}{c^2}\int (\hat{I}_+\beta)^*(\hat{I}_+\beta)d\tau$$

Solving for c^2 gives

$$c^2 = \int (\hat{I}_+\beta)^*(\hat{I}_+\beta)d\tau = \int (\hat{I}_+\beta)^*(\hat{I}_x\beta + i\hat{I}_y\beta)d\tau = \int (\hat{I}_+\beta)^*(\hat{I}_+\beta d\tau + i\int (\hat{I}_+\beta)^*\hat{I}_y\beta d\tau$$

We can use the fact that $\hat{I}_x$ and $\hat{I}_y$ are Hermitian to write this as

$$c^2 = \int \beta\hat{I}_+^*(\hat{I}_+\beta)^* d\tau + i\int \beta\hat{I}_y^*(\hat{I}_+\beta)^* d\tau$$

Take the complex conjugate of both sides of the last equation to find

$$c^2 = \int \beta^*\hat{I}_x\hat{I}_+\beta d\tau - i\int \beta^*\hat{I}_y\hat{I}_+\beta d\tau = \int \beta^*(\hat{I}_x - i\hat{I}_y)\hat{I}_+\beta d\tau = \int \beta^*\hat{I}_-\hat{I}_+\beta d\tau$$

Substituting $\hat{I}_-\hat{I}_+ = \hat{I}^2 - \hat{I}_z^2 - \hbar\hat{I}_z$, we obtain

$$c^2 = \int \beta^* \hat{I}_- \hat{I}_+ \beta d\tau = \int \beta^* (\hat{I}^2 - \hat{I}_z^2 - \hbar \hat{I}_z) \beta d\tau = \int \beta^* \left(\frac{3\hbar^2}{4} - \frac{1\hbar^2}{4} + \frac{\hbar^2}{2} \right) \beta d\tau = \hbar^2$$

where we have used the given equation to evaluate the various terms involving $\hat{I}^2$ and $\hat{I}_z$.

Taking the squareroot of both sides of the final equation proves that $c = \hbar$.

Q14.22

Show that $H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) \hat{I}_{y1} \hat{I}_{y2} \alpha(1) \alpha(2) = 0$.

S14.22

$$H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) \hat{I}_{y1} \hat{I}_{y2} \alpha(1) \alpha(2)$$

$$H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) [\hat{I}_{y1} \alpha(1)][\hat{I}_{y2} \alpha(2)]$$

$$H_{y,11} = \frac{hJ_{12}}{\bar{h}^2} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) \left[\frac{i\bar{h}}{2} \beta(1) \right] \left[\frac{i\bar{h}}{2} \beta(2) \right]$$

$$= -\frac{hJ_{12}}{4} \int \int d\tau_1 \tau_2 \alpha^*(1) \alpha^*(2) \beta(1) \beta(2) = 0$$

Orthogonality of spin functions is used so that the equation equates to zero.

Q14-23 Nice work! Correct

The energy levels of a two-spin system can be calculated using first-order perturbation theory. Show this for the first energy level.

S14-23

$$E_j = E_j^{(0)} + \int d\tau_1 d\tau_2 \psi_j^* H^{(1)} \psi_j \tag{14.E.1}$$

$$H^{(0)} \psi_j = E_j^{(0)} \psi_j \tag{14.E.2}$$

$$E_j = E_j^{(0)} + H_{xjj}^{(1)} + H_{yjj}^{(1)} + H_{zjj}^{(1)} \tag{14.E.3}$$

The unperturbed first-order energy is calculated using

$$I_{zj} \alpha(j) = \frac{\hbar}{2} \alpha(j) \tag{14.E.4}$$

$$H^{(0)} \psi_1 = H^{(0)} \alpha(1) \alpha(2) \tag{14.E.5}$$

$$= -\gamma B_0 (1 - \sigma_1) I_{z1} \alpha(1) \alpha(2) - \gamma B_0 (1 - \sigma_2) I_{z2} \alpha(1) \alpha(2) \tag{14.E.6}$$

$$E_1^{(0)} \alpha(1) \alpha(2) = E_1^{(0)} \psi_1 \tag{14.E.7}$$

$$E_1^{(0)} = -\hbar \gamma B_0 (1 - \frac{\sigma_1 + \sigma_2}{2}) \tag{14.E.8}$$

The first-order correction is defined as

$$H_{ii} = \frac{hJ_{12}}{\hbar^2} \int d\tau_1 d\tau_2 \psi_i^* I_1 I_2 \psi_i \tag{14.E.9}$$

with the x and y terms in I1 and I2 not contributing to the first-order energy.

Considering the unperturbed wave function for a two-spin system

$$\psi_1 = \alpha(1) \alpha(2) \tag{14.E.10}$$

$$I_{z1}I_{z2}\alpha(1)\alpha(2) = \frac{\hbar^2}{4}\alpha(1)\alpha(2) \tag{14.E.11}$$

Furthermore, the perturbation to the first-order energy becomes

$$H_{z,11} = \frac{hJ_{12}}{\hbar^2}\int d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2) I_{z1}I_{z2}\alpha(1)\alpha(2) = \frac{hJ_{12}}{4} \tag{14.E.12}$$

As a result the first order energy energy can be represented by

$$E_1 = -h\nu_0(1 - \frac{\sigma_1 + \sigma_2}{2}) + \frac{hJ_{12}}{4} \tag{14.E.13}$$

.

Q14.24

Derive the frequencies associated with the allowed transitions between nuclear spin up to n = 4.

S14.24

(its good that you started from the beginning to derive the frequencies good job--RM)

$$E = h\nu \tag{14.E.14}$$

$$E_{1=>2} = E_2 - E_1 \tag{14.E.15}$$

$$= \frac{h\nu}{2}(\sigma_2 - \sigma_1) - \frac{hJ_{12}}{4} + h\nu_0(1 - \frac{\sigma_1 + \sigma_2}{2}) - \frac{hJ_{12}}{4} \tag{14.E.16}$$

$$= h\nu_0(1 - \sigma_1) - \frac{hJ_{12}}{2} \tag{14.E.17}$$

$$\nu_{1=>2} = \nu_0(1 - \sigma_1) - \frac{hJ_{12}}{2} \tag{14.E.18}$$

$$E_{1=>3} = E_3 - E_1 \tag{14.E.19}$$

$$= \frac{h\nu}{2}(\sigma_1 - \sigma_2) - \frac{hJ_{12}}{4} + h\nu_0(1 - \frac{\sigma_1 + \sigma_2}{2}) - \frac{hJ_{12}}{4} \tag{14.E.20}$$

$$= h\nu_0(1 - \sigma_3) - \frac{hJ_{12}}{2} \tag{14.E.21}$$

$$\nu_{1=>3} = \nu_0(1 - \sigma_2) - \frac{hJ_{12}}{2} \tag{14.E.22}$$

$$E_{2=>4} = E_4 - E_2 \tag{14.E.23}$$

$$= h\nu(\sigma_1 + \sigma_2) - \frac{hJ_{12}}{4} - \frac{h\nu_0}{2}(\sigma_2 - \sigma_1) + \frac{hJ_{12}}{4} \tag{14.E.24}$$

$$= h\nu_0(1 - \sigma_2) + \frac{hJ_{12}}{2} \tag{14.E.25}$$

$$\nu_{2=>4} = \nu_0(1 - \sigma_2) + \frac{hJ_{12}}{2} \tag{14.E.26}$$

$$E_{3=>4} = E_4 - E_3 \tag{14.E.27}$$

$$= h\nu(1 - \frac{\sigma_1 + \sigma_2}{2}) + \frac{hJ_{12}}{4} - \frac{h\nu_0}{2}(\sigma_1 - \sigma_2) + \frac{hJ_{12}}{4} \tag{14.E.28}$$

$$= h\nu_0(1 - \sigma_1) + \frac{hJ_{12}}{2} \tag{14.E.29}$$

$$\nu_{2=>4} = \nu_0(1 - \sigma_1) + \frac{hJ_{12}}{2} \tag{14.E.30}$$

Q14.28

Using the Hamiltonian for an H_2 molecule with 2 nonequivalent hydrogen atoms, prove that $H_{13} = \iint d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2)\hat{H}\beta(1)\alpha(2) = 0$.

S14.28

The necessary Hamiltonian is:

$$\hat{H} = -\gamma B_0(1-\sigma_1)\hat{I}_1 - \gamma B_0(1-\sigma_2)\hat{I}_2 + \frac{hJ_{12}}{\hbar^2}\hat{I}_1 \cdot \hat{I}_2.$$

We can then plug in the Hamiltonian and write the second half of the equation as:

$$\begin{aligned}\hat{H}\beta(1)\beta(2) &= -\gamma B_0(1-\sigma_1)(-\frac{\hbar}{2})\beta(1)\alpha(2) - \gamma\beta_0(1-\sigma_2)(\frac{\hbar}{2})\beta(1)\beta(2) \\ &+ \frac{hJ_{23}}{\hbar^2}[\frac{\hbar^2}{4}\alpha(1)\beta(2) + \frac{\hbar^2}{4}\alpha(1)\beta(2) - \frac{\hbar^2}{4}\beta(1)\alpha(2)] \\ &= \frac{\hbar}{2}\gamma B_0\beta(1)\alpha(2)[(1-\sigma_1)-(1-\sigma_2)] + \frac{hJ_{12}}{4}[2\alpha(1)\beta(2) - \beta(1)\alpha(2)]\end{aligned}$$

Doing some algebra, we get that:

$$H_{13} = \iint d\tau_1 d\tau_2 \alpha^*(1)\alpha^*(2)\left[\frac{\hbar}{2}\gamma B_0\beta(1)\alpha(2)[(1-\sigma_1)-(1-\sigma_2)] + \frac{hJ_{12}}{4}[2\alpha(1)\beta(2) - \beta(1)\alpha(2)]\right]$$

Because α and β are orthonormal, **the integral goes to zero**. Therefore, we have proved that $H_{13} = 0$.

Q14.29

Prove that

$$\begin{aligned}H_{44} &= \iint d\tau_(1) d\tau_(2)\beta^*(1)\beta^*(2)\hat{H}\beta(1)\beta(2) \\ &= -\frac{1}{2}h\nu_0(1-\sigma_1) - \frac{1}{2}h\nu_0(1-\sigma_2) + \frac{hJ_12}{4}\end{aligned}$$

with

$$\hat{H} = -\gamma B_0(1-\sigma_1)\hat{I}_1 - \gamma B_0(1-\sigma_2)\hat{I}_2 + \frac{hJ_{12}}{\hbar^2}\hat{I}_1 \cdot \hat{I}_2.$$

S14.29

$$\begin{aligned}\hat{H}\beta(1)\beta(2) &= -\gamma B_0(1-\sigma_1)(\frac{\hbar}{2})\beta(1)\beta(2) - \gamma\beta_0(1-\sigma_2)(\frac{\hbar}{2})\beta(1)\beta(2) \\ &+ \frac{hJ_{12}}{\hbar^2}[\frac{\hbar^2}{4}\beta(1)\beta(2) - \frac{\hbar^2}{4}\beta(1)\beta(2) + \frac{\hbar^2}{4}\alpha(1)\alpha(2)] \\ &= \left[\frac{-\hbar\gamma B_0}{2}(1-\sigma_1) - \frac{-\hbar\gamma B_0}{2}(1-\sigma_2) + \frac{hJ_{12}}{4}][2\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]\beta(1)\beta(2)\end{aligned}$$

Calculated with matlab,

$$\begin{aligned}H_{44} &= \iint d\tau_1 d\tau_2\left[\frac{-\hbar\gamma B_0}{2}(1-\sigma_1) - \frac{-\hbar\gamma B_0}{2}(1-\sigma_2) + \frac{hJ_{12}}{4}][2\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]\beta(1)\beta(2) \\ &= \frac{1}{2}h\nu_0(1-sigma_1) - \frac{1}{2}h\nu_0(1-\sigma_2) + h\frac{J_{12}}{4}\end{aligned}$$

Q14.30

Using Equation 14.58, prove that

$$H_{44} = -\frac{1}{2}hv_0(1-\sigma_1) + \frac{1}{2}h_v0(1-\sigma_2) + \frac{hJ_{12}}{4}$$

S14.30

To find this matrix element, you must complete the integral given by $\langle \psi_4 | H | \psi_4 \rangle$. By using the relationships in Table 14.4 to evaluate parts of the integral, Equation 14.45 and Equation 14.58, algebra, and calculus, this integral can be solved to give the final answer above.

Q14.31

Given the following matrix, expand the determinants to solve for the energies:

$$\begin{pmatrix} \alpha - E & \beta & 0 & 0 & 0 & 0 \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ 0 & 0 & 0 & 0 & \beta & \alpha - E \end{pmatrix}$$

S14.31

\[x_{i} = \frac{\alpha E}{\beta}\nonumber \]

$$E_j = \alpha - \beta x_j$$

$$x_j = -2cos(\frac{j\pi}{n_c + 1})$$

$$E_j = \alpha + 2\beta * cos(\frac{j\pi}{n_c} + 1)$$

$$E_1 = \alpha + 2\beta * cos(\frac{\pi}{6+1}) = \alpha + 1.8\beta$$

$$E_2 = \alpha + 2\beta * cos(\frac{2\pi}{6+1}) = \alpha + 1.24\beta$$

$$E_3 = \alpha + 2\beta * cos(\frac{3\pi}{6+1}) = \alpha + 0.44\beta$$

$$E_4 = \alpha + 2\beta * cos(\frac{4\pi}{6+1}) = \alpha - 0.44\beta$$

$$E_5 = \alpha + 2\beta * cos(\frac{5\pi}{6+1}) = a - 1.25\beta$$

$$E_6 = \alpha + 2\beta * cos(\frac{6\pi}{6+1}) = \alpha - 1.8\beta$$

Q14.33

Show that a two-spin system with $J = 0$ consists of only two peaks with frequencies $v_0(1 - \sigma_1)$ and $v_0(1 - \sigma_2)$.

S14.33

The resonance frequencies is given by

$$v_{1 \rightarrow 2} = \frac{v_0}{2} (2 - \sigma_1 - \sigma_2) - \frac{J}{2} - \frac{1}{2} [v_0^2(\sigma_1 - \sigma_2)^2 + J^2]^{\frac{1}{2}}$$

with J = 0, this leads to

$$v_{1 \rightarrow 2} = \frac{v_0}{2} (2 - \sigma_1 - \sigma_2) - \frac{0}{2} - \frac{1}{2} [v_0^2(\sigma_1 - \sigma_2)^2 + 0^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2} (2 - \sigma_1 - \sigma_2) - \frac{1}{2} [v_0^2(\sigma_1 - \sigma_2)^2]^{\frac{1}{2}}$$

$$= v_0(1 - \sigma_1)$$

Similarly, for the other transitions:

$$v_{1 \rightarrow 3} = \frac{v_0}{2} (2 - \sigma_1 - \sigma_2) - \frac{J}{2} + \frac{1}{2} [v_0^2(\sigma_1 - \sigma_2)^2 + J^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2}\,(2-\sigma_1-\sigma_2) - \frac{0}{2}+\frac{1}{2}\,[v_0^2(\sigma_1-\sigma_2)^2+0^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2}\,(2-\sigma_1-\sigma_2) +\frac{1}{2}\,[v_0^2(\sigma_1-\sigma_2)^2]^{\frac{1}{2}}$$

$$= v_0(1-\sigma_2)$$

$$v_2 \rightarrow_4 = \frac{v_0}{2}\,(2-\sigma_1-\sigma_2) + \frac{J}{2}+\frac{1}{2}\,[v_0^2(\sigma_1-\sigma_2)^2+J^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2}\,(2-\sigma_1-\sigma_2) + \frac{0}{2}+\frac{1}{2}\,[v_0^2(\sigma_1-\sigma_2)^2+0^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2}\,(2-\sigma_1-\sigma_2) +\frac{1}{2}\,[v_0^2(\sigma_1-\sigma_2)^2]^{\frac{1}{2}}$$

$$= v_0(1-\sigma_2)$$

$$v_3 \rightarrow_4 = \frac{v_0}{2}\,(2-\sigma_1-\sigma_2) + \frac{J}{2}-\frac{1}{2}\,[v_0^2(\sigma_1-\sigma_2)^2+J^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2}\,(2-\sigma_1-\sigma_2) + \frac{0}{2}-\frac{1}{2}\,[v_0^2(\sigma_1-\sigma_2)^2+0^2]^{\frac{1}{2}}$$

$$= \frac{v_0}{2}\,(2-\sigma_1-\sigma_2) -\frac{1}{2}\,[v_0^2(\sigma_1-\sigma_2)^2]^{\frac{1}{2}}$$

$$= v_0(1-\sigma_1)$$

Q14.34

Show that

$$\nu_{2\rightarrow 4} = \frac{\nu_0}{2}(2-\sigma_1-\sigma_2) + \frac{J}{2}) + \frac{1}{2}[\nu_0^2()\sigma_1-\sigma_2)^2+J^2]^{1/2}$$

for a general two-spin system.

S14.34

$$E_4 - E_2 = [h\nu_0(1-\frac{\sigma_1+\sigma_2}{2}) + \frac{hJ}{4}] - [-\frac{hJ}{4} - \frac{h}{2}[\nu_0^2(\sigma_1-\sigma_2)^2+J^2]^{1/2}]$$

$$= h\nu_0(1-\frac{\sigma_1+\sigma_2}{2}) + \frac{hJ}{2} - \frac{h}{2}[\nu_0^2(\sigma_1-\sigma_2)^2+J^2]^{1/2}$$

$$\frac{E_4-E_2}{2} = \frac{\nu_0}{2}(2-\sigma_1-\sigma_2) + \frac{J}{2}) + \frac{1}{2}[\nu_0^2()\sigma_1-\sigma_2)^2+J^2]^{1/2}$$

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CHAPTER OVERVIEW

15: Lasers, Laser Spectroscopy, and Photochemistry

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

15.1: Electronically Excited Molecules can Relax by a Number of Processes
15.2: The Dynamics of Transitions can be Modeled by Rate Equations
15.3: A Two-Level System Cannot Achieve a Population Inversion
15.4: Population Inversion can be Achieved in a Three-Level System
15.5: What is Inside a Laser?
15.6: The Helium-Neon Laser
15.7: High-Resolution Laser Spectroscopy
15.8: Pulsed Lasers Can by Used to Measure the Dynamics of Photochemical Processes
15.E: Lasers, Laser Spectroscopy, and Photochemistry (Exercises)

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15.1: Electronically Excited Molecules can Relax by a Number of Processes

Fluorescence and phosphorescence are types of molecular luminescence methods. A molecule of analyte absorbs a photon and excites a species. The emission spectrum can provide qualitative and quantitative analysis. The term fluorescence and phosphorescence are usually referred as photoluminescence because both are alike in excitation brought by absorption of a photon. Fluorescence differs from phosphorescence in that the electronic energy transition that is responsible for fluorescence does not change in electron spin, which results in short-live electrons ($<10^{-5}$ s) in the excited state of fluorescence. In phosphorescence, there is a change in electron spin, which results in a longer lifetime of the excited state (second to minutes). Fluorescence and phosphorescence occurs at longer wavelength than the excitation radiation.

Introduction

Fluorescence can occur in gaseous, liquid, and solid chemical systems. The simple kind of fluorescence is by dilute atomic vapors. A fluorescence example would be if a 3s electron of a vaporized sodium atom is excited to the 3p state by absorption of a radiation at wavelength 589.6 and 589.0 nm. After 10^{-8} s, the electron returns to ground state and on its return it emits radiation of the two wavelengths in all directions. This type of fluorescence in which the absorbed radiation is remitted without a change in frequency is known as resonance fluorescence. Resonance fluorescence can also occur in molecular species. Molecular fluorescence band centers at wavelengths longer than resonance lines. The shift toward longer wavelength is referred to as the **Stokes Shift**.

Singlet and Triplet Excited States

Understanding the difference between fluorescence and phosphorescence requires the knowledge of electron spin and the differences between singlet and triplet 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) and only two electrons can occupy each orbital where they must have opposite spin states. These opposite spin states are called spin pairing. Because of this spin pairing, most molecules do not exhibit a magnetic field and are diamagnetic. In diamagnetic molecules, electrons are not attracted or repelled by the static electric field. Free radicals are paramagnetic because they contain unpaired electrons have magnetic moments that are attracted to the magnetic field.

Singlet state is defined 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 into a magnetic field. A doublet state occurs when there is an unpaired electron that gives two possible orientations when exposed in a magnetic field and imparts different energy to the system. A singlet or a triplet can form when one electron is excited to a higher energy level. In an excited singlet state, the electron is promoted in the same spin orientation as it was in the ground state (i.e., paired). In a triplet excited stated, the electron that is promoted has the same spin orientation (parallel) to the other unpaired electron. The difference between the spins of ground singlet, excited singlet, and excited triplet is shown in Figure **15.1.1**. Singlet, doublet and triplet is 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 calculated the S for the excited singlet state, the equation would be

$$2(+1/2 + -1/2) + 1 = 2(0) + 1 = 1 \tag{15.1.1}$$

therefore making the center orbital in the figure a singlet state. If the spin multiplicity for the excited triplet state was calculated, we obtain

$$2(+1/2 + +1/2) + 1 = 2(1) + 1 = 3 \tag{15.1.2}$$

which gives a triplet state as expected.

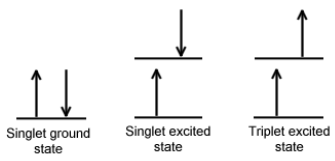


Figure **15.1.1**: Spin in the ground and excited states

The difference between a molecule in the ground and excited state is that the electrons is diamagnetic in the ground state and paramagnetic in the triplet state.This difference in spin state makes the transition from singlet to triplet (or triplet to singlet) more

improbable than the singlet-to-singlet transitions. This singlet to triplet (or reverse) transition involves a change in *electronic* state. For this reason, the lifetime of the triplet state is longer the singlet state by approximately 10^4 seconds fold difference.The radiation that induced the transition from ground to excited triplet state has a low probability of occurring, thus their absorption bands are less intense than singlet-singlet state absorption. The excited triplet state can be populated from the excited singlet state of certain molecules which results in phosphorescence. These spin multiplicities in ground and excited states can be used to explain transition in photoluminescence molecules by the Jablonski diagram.

Jablonski Diagrams

The Jablonski diagram that drawn below is a partial energy diagram that represents the energy of 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, majority of the molecules in a solution are in this state.

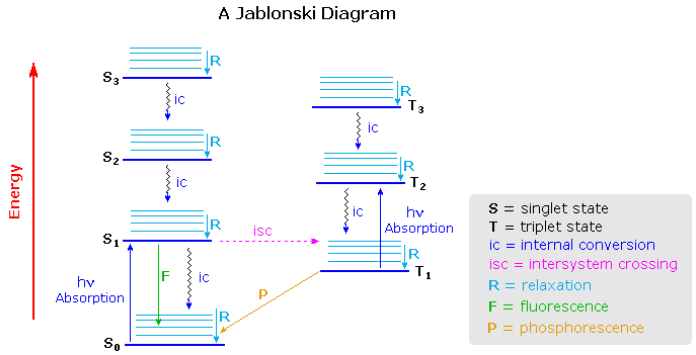


Figure **15.1.2**: *Partial Jablonski Diagram for Absorption, Fluorescence, and Phosphorescence. from Bill Reusch.*

The upper lines represent the energy state of the three excited electronic states: S_1 and S_2 represent the electronic singlet state (left) and T_1 represents the first electronic triplet state (right). The upper darkest line represents the ground vibrational state of the three excited electronic state.The energy of the triplet state is lower than the energy of the corresponding singlet state.

There are numerous vibrational levels that can be associated with each electronic state as denoted by the thinner lines. Absorption transitions (blues lines in Figure **15.1.2**) can occur from the ground singlet electronic state (S_o) to various vibrational levels in the singlet excited vibrational states. It is unlikely that a transition from the ground singlet electronic state to the triplet electronic state because the electron spin is parallel to the spin in its ground state (Figure **15.1.1**). This transition leads to a change in multiplicity and thus has a low probability of occurring which is a **forbidden transition.** Molecules also go through vibration relaxation to lose any excess vibrational energy that remains when excited to the electronic states (S_1 and S_2) as demonstrated in wavy lines in Figure **15.1.2**. The knowledge of forbidden transition is used to explain and compare the peaks of absorption and emission.

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	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

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 **15.1.2**.The deactivation process of fluorescence and phosphorescence involve an emission of a photon radiation as shown by the straight arrow in Figure **15.1.2**. The wiggly arrows in Figure **15.1.2** are deactivation processes without the use of radiation. The favored deactivation process is the route that is most rapid and spends less time in the excited state.If the rate constant for fluorescence is more favorable in the radiationless path, the fluorescence will be less intense or absent.

- **Vibrational Relaxation:** A molecule maybe to promoted to several vibrational levels during the electronic excitation process.Collision of molecules with the excited species and solvent leads to rapid energy transfer and a slight increase in temperature of the solvent. Vibrational relaxation is so rapid that the lifetime of a vibrational excited molecule ($<10^{-12}$) is less than the lifetime of the electronically excited state. For this reason, fluorescence from a solution always involves the transition of the lowest vibrational level of the excited state. Since the space of the emission lines are so close together, the transition of the vibrational relaxation can terminate in any vibrational level of the ground state.
- **Internal Conversion:** Internal conversion is an intermolecular process of molecule that passes to a lower electronic state without the emission of radiation.It is a crossover of two states with the same multiplicity meaning singlet-to-singlet or triplet-to-triplet states.The internal conversion is more efficient when two electronic energy levels are close enough that two vibrational energy levels can overlap as shown in between S_1 and S_2. Internal conversion can also occur between S_0 and S_1 from a loss of energy by fluorescence from a higher excited state, but it is less probable. The mechanism of internal conversion from S_1 to S_0 is poorly understood. For some molecules, the vibrational levels of the ground state overlaps with the first excited electronic state, which leads to fast deactivation.These usually occur with aliphatic compounds (compound that do not contain ring structure), which would account for the compound is seldom fluorescing. Deactivation by energy transfer of these molecules occurs so rapidly that the molecule does not have time to fluoresce.
- **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 leads to enhanced fluorescence because they reduce the number of collision between molecules, thus slowing down the deactivation process.
- **Intersystem Crossing:** Intersystem crossing is a process where there is a crossover between electronic states of different multiplicity as demonstrated in the singlet state to a triplet state (S_1 to T_1) on Figure **15.1.1**. The probability of intersystem crossing is enhanced if the vibration levels of the two states overlap. Intersystem crossing is most commonly observed with molecules that contain heavy atom such as iodine or bromine. The spin and orbital interaction increase and the spin become more favorable.Paramagnetic species also enhances intersystem crossing, which consequently decreases fluorescence.
- **Phosphorescence**: Deactivation of the electronic excited state is also involved in phosphorescence. After the molecule transitions through intersystem crossing to the triplet state, further deactivation occurs through internal or external fluorescence or phosphorescence. A triplet-to-singlet transition is more probable than a singlet-to-singlet internal crossing. In phosphorescence, the excited state lifetime is inversely proportional to the probability that the molecule will transition back to the ground state. Since the lifetime of the molecule in the triplet state is large (10^{-4} to 10 second or more), transition is less

probable which suggest that it will persist for some time even after irradiation has stopped. Since the external and internal conversion compete so effectively with phosphorescence, the molecule has to be observed at lower temperature in highly viscous media to protect the triplet state.

Variables that affect Fluorescence

After discussing all the possible deactivation processes, variable that affect the emissions to occur. Molecular structure and its chemical environment influence whether a substance will fluoresce and the intensities of these emissions. The **quantum yield** or **quantum efficiency** is used to measure the probability that a molecule will fluoresce or phosphoresce. For fluorescence and phosphorescence is the ratio of the number of molecules that luminescent to the total number of excited molecules. For highly fluoresce molecules, the quantum efficiency approaches to one.Molecules that do not fluoresce have quantum efficiencies that approach to zero.

Fluorescence quantum yield (ϕ) for a compound is determined by the relative rate constants (k) of various deactivation processes by which the lowest excited singlet state is deactivated to the ground state. The deactivation processes including fluorescence (kf), intersystem crossing (k_i), internal conversion (kic), predissociation (kpd), dissociation (kd), and external conversion (kec) allows one to qualitatively interpret the structural and environmental factors that influence the intensity of the fluorescence. They are related by the quantum yield equation given below:

$$\frac{k_f}{k_f + k_i + k_{ec} + k_{ic} + k_{pd} + k_d} \tag{15.1.3}$$

Using this equation as an example to explain fluorescence, a high fluorescence rate (k_f) value and low values of the all the other relative rate constant terms ($k_f + k_i + k_{ec} + k_{ic} + k_{pd} + k_d$) will give a large ϕ, which suggest that fluorescence is enhanced. The magnitudes of kf , kd, and kpd depend on the chemical structure, while the rest of the constants ki, kec, and kic are strongly influenced by the environment.

Fluorescence rarely results from absorption of ultraviolet radiation of wavelength shorter than 250 nm because radiation at this wavelength has sufficient energy to deactivate the electron in the excited state by predissociation or dissociation. The bond of some organic molecules would rupture at 140 kcal/mol, which corresponds to 200-nm of radiation. For this reason, $\sigma \rightarrow \sigma^*$ transition in fluorescence are rarely observed. Instead, emissions from the less energetic transition will occur which are either $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transition.

Molecules that are excited electronically will return to the lowest excited state by rapid vibrational relaxation and internal conversion, which produces no radiation emission. Fluorescence arises from a transition from the lowest vibrational level of the first excited electronic state to one of the vibrational levels in the electronic ground state. In most fluorescent compounds, radiation is produced by a $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transition depending on which requires the least energy for the transition to occur.

Fluorescence is most commonly found in compounds in which the lowest energy transition is $\pi \rightarrow \pi^*$ (excited singlet state) than $n \rightarrow \pi^*$ which suggest that the quantum efficiency is greater for $\pi \rightarrow \pi^*$ transitions. The reason for this is that the molar absorptivity, which measures the probability that a transition will occur, of the $\pi \rightarrow \pi^*$ transition is 100 to 1000 fold greater than $n \rightarrow \pi^*$ process. The lifetime of $\pi \rightarrow \pi^*$ (10^{-7} to 10^{-9} s) is shorter than the lifetime of $n \rightarrow \pi^*$ (10^{-5} to 10^{-7}).

Phosphorescent quantum efficiency is the opposite of fluorescence in that it occurs in the $n \rightarrow \pi^*$ excited state which tends to be short lived and less suceptable to deactivation than the $\pi \rightarrow \pi^*$ triplet state. Intersystem crossing is also more probable for $\pi \rightarrow \pi^*$ excited state than for the $n \rightarrow \pi^*$state because the energy difference between the singlet and triplet state is large and spin-orbit coupling is less likely to occur.

References

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15.2: The Dynamics of Transitions can be Modeled by Rate Equations

The Phenomenological Rate Laws

Before closing this chapter, it is important to emphasize the context in which the transition rate expressions obtained here are most commonly used. The perturbative approach used in the above development gives rise to various contributions to the overall rate coefficient for transitions from an initial state Φ_i to a final state Φ_f ; these contributions include the electric dipole, magnetic dipole, and electric quadrupole first order terms as well contributions arising from second (and higher) order terms in the perturbation solution.

In principle, once the rate expression

$$R_{i,f} = 2\pi g(\omega_{f,i})|\alpha_{f,i}|^2$$

has been evaluated through some order in perturbation theory and including the dominant electromagnetic interactions, one can make use of these **state-to-state rates** , which are computed on a per-molecule basis, to describe the time evolution of the populations of the various energy levels of the molecule under the influence of the light source's electromagnetic fields.

For example, given two states, denoted i and f, between which transitions can be induced by photons of frequency wf,i, the following kinetic model is often used to describe the time evolution of the numbers of molecules ni and nf in the respective states:

$$\frac{dn_i}{dt} = -R_{i,f}n_i + R_{f,i}n_f$$

$$\frac{dn_f}{dt} = -R_{f,i}n_f + R_{i,f}n_i.$$

Here, $R_{i,f}$ and $R_{f,i}$ are the rates (per molecule) of transitions for the $\mathrm{i} \rightarrow \mathrm{f}$ and $\mathrm{f} \rightarrow \mathrm{i}$ transitions respectively. As noted above, these rates are proportional to the intensity of the light source (i.e., the photon intensity) at the resonant frequency and to the square of a matrix element connecting the respective states. This matrix element square is $|\alpha_{i,f}|^2$ in the former case and $|\alpha_{f,i}|^2$ in the latter. Because the perturbation operator whose matrix elements are $\alpha_{i,f}$ and $\alpha_{f,i}$ is Hermitian (this is true through all orders of perturbation theory and for all terms in the long-wavelength expansion), these two quantities are complex conjugates of one another, and, hence $|\alpha_{i,f}|^2 = |\alpha_{f,i}|^2$, from which it follows that $R_{i,f} = R_{f,i}$. This means that the state-to-state absorption and stimulated emission rate coefficients (i.e., the rate per molecule undergoing the transition) are identical. This result is referred to as the principle of **microscopic reversibility.**

Quite often, the states between which transitions occur are members of levels that contain more than a single state. For example, in rotational spectroscopy a transition between a state in the J = 3 level of a diatomic molecule and a state in the J = 4 level involve such states; the respective levels are 2J+1 = 7 and 2J+1 = 9 fold degenerate, respectively.

To extend the above kinetic model to this more general case in which degenerate levels occur, one uses the number of molecules in each **level** (N_i and N_f for the two levels in the above example) as the time dependent variables. The kinetic equations then governing their time evolution can be obtained by summing the state-to-state equations over all states in each level

$$\sum_{\text{i in level 1}} \left(\frac{dn_i}{dt}\right) = \frac{dN_I}{dt}$$

$$\sum_{\text{f in level F}} \left(\frac{dn_f}{dt}\right) = \frac{dN_F}{dt}$$

and realizing that each state within a given level can undergo transitions to all states within the other level (hence the total rates of production and consumption must be summed over all states to or from which transitions can occur). This generalization results in a set of rate laws for the populations of the respective levels:

$$\frac{dN_i}{dt} = -g_f R_{i,f} N_i + g_i R_{f,i} N_f$$

$$\frac{dN_f}{dt} = -g_i R_{f,i} N_f + g_f R_{i,f} N_i.$$

Here, g_i and g_f are the degeneracies of the two levels (i.e., the number of states in each level) and the $R_{i,f}$ and $R_{f,i}$, which are equal as described above, are the state-to-state rate coefficients introduced earlier.

Spontaneous and Stimulated Emission

It turns out (the development of this concept is beyond the scope of this text) that the rate at which an excited level can emit photons and decay to a lower energy level is dependent on two factors:

i. the rate of **stimulated** photon emission as covered above and
ii. the rate of **spontaneous** photon emission.

The former rate $g_f R_{i,f}$ (per molecule) is proportional to the light intensity $g(\omega_{f,i})$ at the resonance frequency. It is conventional to separate out this intensity factor by defining an intensity independent rate coefficient $B_{i,f}$ for this process as:

$$g_f R_{i,f} = g(\omega_{f,i}) B_{i,f}.$$

Clearly, $B_{i,f}$ embodies the final-level degeneracy factor g_f, the perturbation matrix elements, and the 2π factor in the earlier expression for $R_{i,f}$. The spontaneous rate of transition from the excited to the lower level is found to be **independent** of photon intensity, because it deals with a process that does not require collision with a photon to occur, and is usually denoted $A_{i,f}$. The rate of photon-stimulated upward transitions from state f to state i ($g_i R_{f,i} = g_i R_{i,f}$ in the present case) is also proportional to $g(\omega_{f,i})$, so it is written by convention as:

$$g_i R_{f,i} = g(\omega_{f,i}) B_{f,i}.$$

An important relation between the $B_{i,f}$ and $B_{f,i}$ parameters exists and is based on the identity $R_{i,f} = R_{f,i}$ that connects the state-to-state rate coefficients:

$$\frac{(B_{i,f})}{(B_{f,i})} = \frac{(g_f R_{i,f})}{(g_i R_{f,i})} = \frac{g_f}{f_i}.$$

This relationship will prove useful in the following sections.

Saturated Transitions and Transparency

Returning to the kinetic equations that govern the time evolution of the populations of two levels connected by photon absorption and emission, and adding in the term needed for spontaneous emission, one finds (with the initial level being of the lower energy):

$$\frac{dN_i}{dt} = -gB_{i,f}N_i + (A_{f,i} + gB_{f,i})N_f$$

$$\frac{dN_f}{dt} = -(A_{f,i} + gB_{f,i})N_f + gB_{i,f}N_i$$

where g = g(ω) denotes the light intensity at the resonance frequency. At steady state, the populations of these two levels are given by setting

$$\frac{dN_i}{dt} = \frac{dN_f}{dt} = 0:$$

$$\frac{N_f}{N_i} = \frac{(gB_{i,f})}{(A_{f,i} + gB_{f,i})}.$$

When the light source's intensity is so large as to render $gB_{f,i} >> A_{f,i}$ (i.e., when the rate of spontaneous emission is small compared to the stimulated rate), this population ratio reaches $(B_{i,f}/B_{f,i})$, which was shown earlier to equal (g_f/g_i). In this case, one says that the populations have been **saturated** by the intense light source. Any further increase in light intensity will result in **zero** increase in the rate at which photons are being absorbed. Transitions that have had their populations saturated by the application of intense light sources are said to display optical **transparency** because they are unable to absorb (nor emit) any further photons because of their state of saturation.

Equilibrium and Relations Between A and B Coefficients

When the molecules in the two levels being discussed reach **equilibrium** (at which time the $\frac{dN_i}{dt} = \frac{dN_f}{dt} = 0$ also holds) with a photon source that itself is in **equilibrium** characterized by a temperature T, we must have:

$$\frac{N_f}{N_i} = \frac{g_f}{g_i} e^{\frac{-(E_f - E_i)}{kT}} = \frac{g_f}{g_i} e^{\frac{\hbar\omega}{kT}}$$

where g_f and g_i are the degeneracies of the states labeled f and i. The photon source that is characterized by an equilibrium temperature T is known as a **black body** radiator, whose intensity profile $g(\omega)$ (in erg cm^{-3} sec) is know to be of the form:

$$g(\omega) = \frac{2(\hbar\omega)^3}{\pi c^3 \hbar^2} \left(e^{\frac{\hbar\omega}{kT}} - 1 \right)^{-1}.$$

Equating the kinetic result that must hold at equilibrium:

$$\frac{N_f}{N_i} = \frac{(gB_{i,f})}{(A_{f,i} + gB_{f,i})}$$

to the thermodynamic result:

$$\frac{N_f}{N_i} = \frac{g_f}{g_i} e^{\frac{-\hbar\omega}{kT}},$$

and using the above black body g(ω) expression and the identity

$$\frac{B_{i,f}}{B_{f,i}} = \frac{g_f}{g_i},$$

one can solve for the $A_{f,i}$ rate coefficient in terms of the $B_{f,i}$ coefficient. Doing so yields:

$$A_{f,i} = B_{f,i} \frac{2(\hbar\omega)^3}{\pi^3 \hbar^2}$$

Summary

In summary, the so-called **Einstein A and B rate coefficients** connecting a lower-energy initial state i and a final state f are related by the following conditions:

$$B_{i,f} = \frac{g_f}{g_i} B_{f,i}$$

and

$$A_{f,i} = \frac{2(\hbar\omega)^3}{\pi c^3 \hbar^2 B_{f,i}}.$$

These phenomenological level-to-level rate coefficients are related to the state-to-state $R_{i,f}$ coefficients derived by applying perturbation theory to the electromagnetic perturbation through

$$g_f R_{i,f} = g(\omega_{f,i}) B_{i,f}.$$

The A and B coefficients can be used in a kinetic equation model to follow the time evolution of the populations of the corresponding levels:

$$\frac{dN_i}{dt} = -gB_{i,f} N_i + (A_{f,i} + gB_{f,i}) N_f$$

$$\frac{dN_f}{dt} = -(A_{f,i} + gB_{f,i}) N_f + gB_{i,f} N_i.$$

These equations possess steady state solutions

$$\frac{N_f}{N_i} = \frac{(gB_{i,f})}{(A_{f,i} + gB_{f,i})}$$

which, for large $g(\omega)$, produce saturation conditions:

$$\frac{N_f}{N_i} = \frac{(B_{i,f})}{(B_{f,i})} = \frac{g_f}{g_i}.$$

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15.3: A Two-Level System Cannot Achieve a Population Inversion

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 monochromaticlight, 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-stablestate, 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.

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 water fall. 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.

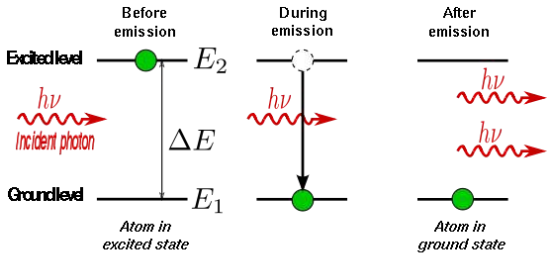


Figure 1: Stimulated emission in a two-level transition. (CC BY-SA 4.0; V1adis1av)

It is clear, from the above diagram, 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 a continuous laser action we need to consider other possibilities, such as a three-level atom.

Contributors

Jay Newman and Seyffie Maleki (Union College)

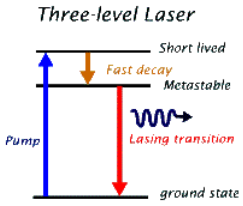
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15.4: Population Inversion can be Achieved in a Three-Level System

Optical pumping will at most only achieve equal population of 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 (simulated 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 use a third metastable level. The pumping will be between the other two, but electrons in the upper energy level will quickly decay into the metastable level, leaving the upper level practically unpopulated at all times. The transition from the metastable level to the ground level has a different frequency: the laser frequency. The pumping frequency is between upper level and the ground level, so the pumping is off-resonant to the laser transition and will, thus, not trigger stimulated emission.

In fact, the first laser that was demonstrated to operate was a three-level laser, Maiman's ruby laser.



In the above diagram of a three level laser the 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. [Decays back to the ground state also occur, 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 any short-lived upper level.t 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.

Contributors

- Jonas from chemistry StackEchange
- Jay Newman and Seyffie Maleki (Union College)

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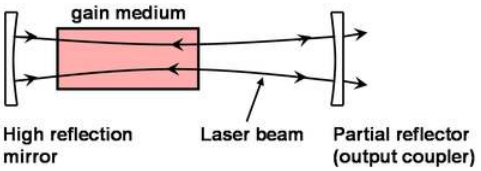
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15.5: What is Inside a Laser?

Laser Operation and Components

- The process of light *stimulated emission* is fundamental to laser operation.
- Laser light is produced by an *active medium*, or *gain medium* inside the *laser optical cavity*. The 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.
- For lasing to take place, the active 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.
- To induce stimulated emission, the laser cavity must provide a means to reflect, or *feedback* emitted light into the gain medium.
- A laser must have an *output coupler* to allow a portion of the laser light to leave the optical cavity.

Laser Optical Cavity



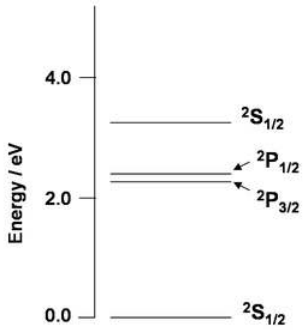
Sketch showing the main components of a laser optical (or resonator) cavity. The optical cavity is formed by a pair of mirrors that surround the gain medium and enable feedback of light into the medium. The output coupler is a partially reflective mirror that allows a portion of the laser radiation to leave the cavity. The gain medium is excited by an external source (not shown), such as a flash lamp, electric current or another laser. 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 References 7-10 and the "Laser Radiation Properties" section.

Stimulated Emission [7-10, 12, 13]

- *Stimulated emission* occurs when a photon of light induces an atom or molecule to lose energy by producing a second photon. The second photon has the same phase, frequency, direction of travel and polarization state as the stimulating photon.
- Since from one photon a second identical photon is produced, stimulated emission leads to *light amplification*.
- Stimulated emission can be understood from an *energy level diagram* within the context of the competing optical processes of *stimulated absorption* and *spontaneous emission*.
- For stimulated emission to take place, a *population inversion* must be created in the laser gain medium.
- For more on stimulated emission, see energy level diagrams and subsequent sections.

Energy Level Diagrams

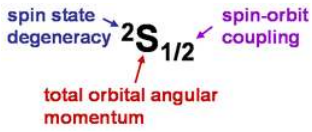
- An energy level diagram displays states of an atom, molecule or material as levels ordered vertically according to energy.
- The states contain contributions from several sources, as appropriate for the matter considered. Sources include the orbital and spin angular momentum of electrons, vibrations of nuclei, molecular rotations, and spin contributions from nuclei.
- The lowest energy level is called the *ground state*.
- Absorption and emission of energy occurs when matter undergoes *transitions between states*.



Energy level diagram showing states of a sodium atom. Each state is labeled by a *term symbol* and includes effects of electron orbital and spin angular momentum.

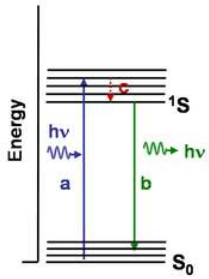
Term Symbols

- Term symbols are a shorthand for describing the angular momentum and coupling interactions among electrons in atoms and molecules.
- As a starting point for understanding a term symbol, write the electron configuration for the state considered. For Na, the electron configuration of the ground state is: $1s^2 2s^2 2p^6 3s^1$
- The central letter describes the total orbital angular momentum. Only the valence electrons need to be considered. For Na, there is one valence electron, and it occupies an s-orbital. The angular momentum quantum number for an s-orbital is l = 0. The total orbital angular momentum for ground state Na is L = l = 0. Symbols are assigned to the values of L as follows: L = 0 (S), L = 1 (P), L = 2 (D), etc.
- The left superscript reflects the coupling of valence electron spin angular momentum and gives the degeneracy of spin states. For Na, s = 1/2 for the valence electron; therefore, the total spin, S = 1/2 and the degeneracy = (2 S + 1) = 2.
- The right subscript reflects the coupling between spin and orbital angular momentum. For ground state Na, J = L + S = 1/2.
- For a detailed discussion of term symbols, see Ref 11.



Absorption and Emission Processes and Transitions Between Energy States

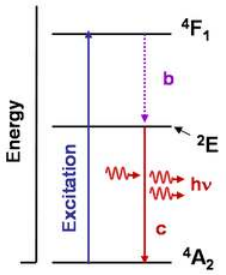
- *Stimulated absorption* (a) occurs when light, or a photon of light (hν), excites matter to a higher energy (or *excited*) state.
- *Spontaneous emission* (b) is a process whereby energy is spontaneously released from matter as light.
- Molecules typically transition to vibrationally excited levels within the excited electronic state.
- Following excitation, the vibrational energy is quickly released by *non-radiative* pathways (c).
- In molecules, spontaneous emission known as *fluorescence* (b) occurs by transition from the lowest level in the excited electronic state, to upper vibrational levels of the lower electronic state.



Energy level diagram for a typical dye molecule. The vibrational levels of each electronic state, labeled by S_0 and S_1, are included.

Stimulated Emission - Details [7-10, 12, 13]

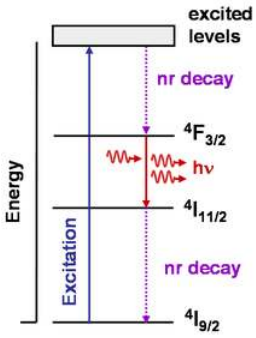
- Laser radiation is produced when energy in atoms or molecules is released as *stimulated emission* (c).
- Stimulated emission requires a *population inversion* in the laser gain medium.
- A *population inversion* occurs when the number of atoms or molecules in an excited state exceeds the number in lower levels (usually the ground state).
- To create the population inversion, the gain medium must transition to a *metastable state*, which is long lived relative to spontaneous emission.
- The three-level diagram (below) shows excitation followed by *non-radiative (nr) decay* (b) to ^2E states. The ^2E states are long lived, because the transition to $^4A_2$ requires a change in the electron spin state.
- A photon of the same energy as the $^2E \rightarrow {}^4A_2$ transition can stimulate the emission of a second photon (c), leading to *light amplification*, or lasing.



Three-level energy diagram. Simplified diagram showing transitions for Cr^{3+} in a ruby laser.

Three and Four Level Lasers [7-10, 12, 13]

- Three-level lasers require intense pumping to maintain the population inversion, because the lasing transition re-populates the ground state.
- Lasers based on transitions between four energy levels (see below), can be more efficiently pumped, because the lower level of the lasing transition is not the ground state.
- Only four-level lasers provide continuous output. HeNe and Nd:YAG are common four-level lasers.
- A population inversion is necessary for lasing, because without one, the photon inducing stimulated emission would instead have a greater probability of undergoing absorption in the gain medium.
- For more in depth information about laser transitions and population inversion, Refs 7-10, 12 (pg 96) and 13 can be consulted.



Four-level energy diagram. Simplified diagram showing transitions for Nd^{3+} in a Nd:YAG laser.

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15.6: The Helium-Neon Laser

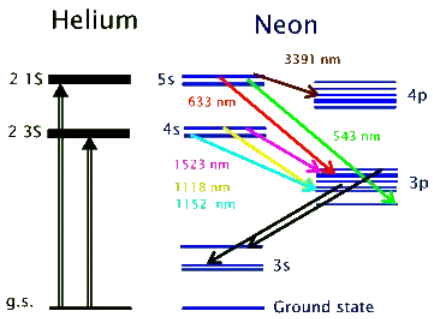
http://laser.physics.sunysb.edu/~dli/hnwork.html

http://web.physics.ucsb.edu/~phys128...aserFall06.pdf

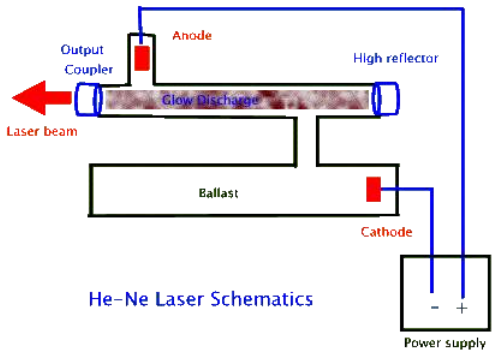
https://www.physics.ohio-state.edu/~...tishshort.html

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 use helium atoms to excite neon atoms. It is the atomic transitions in the neon that produces the laser light. The most commonly used neon transition in these lasers produces red light at 632.8 nm. But these lasers can also produce green and yellow light in the visible as well as UV and IR (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.

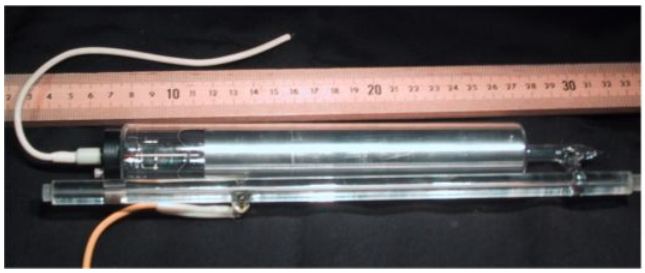
He-Ne lasers typically produce a few to tens of mW (milli-Watt, or 10^{-3} W) of power. They are not sources of high power laser light. Probably one of the most important features of these lasers is that they are highly stable, both in terms of their wavelength (mode stability) and intensity of their 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.



The above energy level diagram shows the two excited states of helium atom, the 2 3S and 2 1S, that get populated as a result of the electromagnetic pumping in the discharge. 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. These are the two upper lasing levels, each for a separate set of lasing transitions. Radiative decay from the 5s to the 4s levels are forbidden. So, 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. The 632.8 nm laser transition, for example, involves the 5s and 3p levels, as shown above.



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 that is connected to a larger size tube called a ballast, as shown above. 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. The function of the ballast is to maintain the desired gas mixture. Since some of the atoms may get imbedded in the glass and/or the electrodes as they accelerate within the discharge, in the absence of a ballast the tube would not last very long. To further prolong tube lifetime some of these lasers also use "getters", often metals such as titanium, that absorb impurities in the gas.



Above photograph shows 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.

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.

Jay Newman and Seyffie Maleki (Union College)

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15.7: High-Resolution Laser Spectroscopy

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{15.7.1}$$

You can see from Equation 15.7.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, 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. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 15.7.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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15.8: Pulsed Lasers Can by Used to Measure the Dynamics of Photochemical Processes

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

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You can see from Equation 15.8.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

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15.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

$$|\mu| = \sqrt{\frac{3A\epsilon_0 h c^3 g_2}{16\pi^3 v^3 g_1}} \tag{15.E.1}$$

Since we know the wavelength and the radiative lifetime, we can find frequency (v) and amplitude (A) with the following equations, respectively.

$$v = \frac{c}{\lambda} = 2.46 \times 10^{15} s^{-1} \tag{15.E.2}$$

$$A = \frac{1}{\tau} = 6.25 \times 10^{8} s^{-1} \tag{15.E.3}$$

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

$$|\mu| = \sqrt{\frac{3A\epsilon_0 h c^3 g_2}{16\pi^3 v^3 g_1}} \tag{15.E.4}$$

$$|\mu| = 1.1 \times 10^{-29} C * m \tag{15.E.5}$$

Q15.10

$$A = \frac{16\pi^3 \nu^3 g_1}{3\varepsilon_0 h c^3 g_2}|\mu|^2 \tag{15.E.6}$$

$$A_{21} = \frac{8h\pi\nu_{12}^3}{c^3}B_{21} \tag{15.E.7}$$

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

$$\mu = \frac{h\nu}{4\pi}n_2 A_{21} \tag{15.E.8}$$

$$A = \frac{32h\pi^3\nu^7}{c^3\varepsilon_0}n_2 B_{21} \tag{15.E.9}$$

$$B_{21} = \frac{c^3 \varepsilon_0}{n_2 A32 h \pi^3 \nu^7} \tag{15.E.10}$$

$$730nm = 7.3 * 10^{-7} m \tag{15.E.11}$$

$\lambda = 7.3 * 10^{-7} m$ and thus $\nu = c\lambda = 2.189 * 10^{16} s^{-1}$

$$B_{21} = \frac{c^3 \varepsilon_0}{n_2 A32 h \pi^3 \nu^7} \tag{15.E.12}$$

$$B_{21} = \frac{c^3 A}{8 h \pi \nu^3} \tag{15.E.13}$$

$$B_{21} = \frac{(2.998 * 10^8 m * s^{-1})^3 * (0.48 * 10^6 s^{-1})}{8 h \pi (2.189 * 10^{16})^3} \tag{15.E.14}$$

$$B_{21} = 7.420 * 10^{13} kg^{-1} m \tag{15.E.15}$$

Q15.11

Given

$$N_{total} = N_1(t) + N_2(t) + N_3(t) \tag{15.E.16}$$

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.

$$\frac{dN_1}{dt} = -B_{31}\rho_v\nu_{31}N_1 + B_{31}\rho_v\nu_{31}N_3 + A_{31}N_3 + A_21N_2 \tag{15.E.17}$$

the others follow as

$$\frac{dN_2}{dt} = -B_{32}\rho_v\nu_{32}N_2 + B_{32}\rho_v\nu_{32}N_3 + A_{32}N_3 - A_21N_2 \tag{15.E.18}$$

and

$$\begin{aligned} &\frac{dN_3}{dt} \\ &= -B_{31}\rho_v\nu_{31}N_1 + -B_{31}\rho_v\nu_{31}N_3 - A_{32}N_3 - A_31N_3 - B_{32}\rho_v\nu_{32}N_3 + B_{32}\rho_v\nu_{32}N_2 \end{aligned} \tag{15.E.19}$$

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

$$N_3(t) = N_3^0 e^{-(A_{32}+A_{31})t} \tag{15.E.20}$$

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:

$$N_3 = Ce^{-(A_{32}+A_{31})t} \tag{15.E.21}$$

At t = 0 (when the light is turned off), $N_3(t) = N_3^0 = C$, so

$$N_3(t) = N_3^0 e^{-(A_{32}+A_{31})t} \tag{15.E.22}$$

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,

$$1s^2 2p^1 \tag{15.E.23}$$

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:

$$^2P_{1/2} \tag{15.E.24}$$

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)

$$E = \frac{-Z^2}{2n^2} \tag{15.E.25}$$

$$He^+ = -2E_h \tag{15.E.26}$$

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:

$$\frac{2.6W}{85\frac{pulses}{MHz}} = \frac{2.6\frac{J}{s}}{85\cdot10^{6}\frac{pulses}{s}} = 3.059\cdot10^{-8}\frac{J}{pulse} \tag{15.E.27}$$

Using this, we can then calculate the radiant energy of each laser pulse:

$$\frac{3.059\cdot10^{-8}\frac{J}{pulse}}{15\cdot10^{-15}s} = 2039.216\frac{kW}{pulse} \tag{15.E.28}$$

Finally, we can calculate the radiant energy of a single photon:

$$E_{photon} = \frac{hc}{\lambda} = \frac{(6.626\cdot10^{-34}J\cdot s)(2.988\cdot10^{8}\frac{m}{s})}{640\cdot10^{-9}m} = 3.094\cdot10^{-19}J \tag{15.E.29}$$

Using this energy, we can calculate the the number of photons produced per second by the laser:

$$\frac{E_{laser}}{E_{photon}} = \frac{2.6\frac{J}{s}}{3.094\cdot10^{-19}\frac{J}{photon}} = 8.40\cdot10^{18}\frac{photons}{second} \tag{15.E.30}$$

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 = $\mathbf{6.626*10^{-34}J\cdot s}$
- $\mathbf{c}$ = speed of light = $\mathbf{3.00*10^{8}\frac{m}{s}}$
- $\boldsymbol{\lambda}$ = wavelength = 945 nm or 230 nm = $\mathbf{540*10^{-9}m\,or\,230*10^{-9}m}$

$$E_{photon} = \frac{(6.626*10^{-34}J\cdot s)*(3.00*10^{8}\frac{m}{s})}{945*10^{-9}\,m} = 2.104x10^{-19}\,J/photon$$

$$E_{pulse} = 9.45\,mJ = 9.45*10^{-3}J$$

$$\#_{photon} = \frac{E_{pulse}}{E_{photon}} = \frac{9.45*10^{-3}J}{2.104*10^{-19}\,J/photon} = \mathbf{4.493*10^{16}\,photons}$$

$$E_{photon} = \frac{(6.626*10^{-34}J\cdot s)*(3.00*10^{8}\frac{m}{s})}{230*10^{-9}\,m} = 8.64*10^{-19}J$$

$$E_{pulse} = 2.30\,mJ = 2.30*10^{-3}J$$

$$\#_{photon} = \frac{E_{pulse}}{E_{photon}} = \frac{2.30*10^{-3}J}{8.64*10^{-19}\,J/photon} = \mathbf{2.66*10^{15}\,photons}$$

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:

$$Q_p = \frac{hc}{\lambda} \tag{15.E.31}$$

$$= \frac{(6.626 \times 10^{-34})(3 \times 10^{8})}{760 \times 10^{-9}} \tag{15.E.32}$$

$$= 2.62 \times 10^{-19} \tag{15.E.33}$$

Number of photon in 1.6 mJ pulse is:

$$N_1 = \frac{Q}{Q_p} = 6.12 \times 10^{15} \tag{15.E.34}$$

For 500-ms, 1.60-mJ pulse at 5320 nm:

$$Q_p = 3.75 \times 10^{-18} \tag{15.E.35}$$

Number of photon in 1.6 mJ pulse is:

$$N_2 = \frac{Q}{Q_p} = 0.4 \times 10^{15} \tag{15.E.36}$$

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:

$$\frac{5200 J * s^{-1}}{20 s^{-1}} = 260 J * pulse^{-1}$$

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

$$n = \frac{(260J)(0.29)(9.0 * 10^{-6} m)}{(6.626 * 10^{-34} J * s)(2.998 * 10^{8} m * s^{-1})}$$

$$= 3.42 * 10^{37} \text{ photons}$$

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.

$$Fundamental frequency (J' = 0 \rightarrow 0) 100 \rightarrow 001 = 960.80 cm^{-1} \tag{15.E.37}$$

$$\tilde{B}(001) = 0.3871 cm^{-1} \tilde{B}(100) = 0.3902 cm^{-1} \tag{15.E.38}$$

The fundamental frequency is \(960.80cm^{-1}

S15.25

Using the following equation F(J) for J = 2 and J = 3 can calculated:

$$F(J) = \tilde{B} J(J+1) \tag{15.E.39}$$

$$F_{001}(3) = (0.3871 cm^{-1})(3)(3+1) = 4.645 cm^{-1} \tag{15.E.40}$$

$$F_{100}(2) = (0.3902 cm^{-1})(2)(2+1) = 2.341 cm^{-1} \tag{15.E.41}$$

Therefore the spacing is

$$960.80 cm^{-1} + 4.645 cm^{-1} - 2.341 cm^{-1} = 963.10 cm^{-1} \tag{15.E.42}$$

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:

$$G(v) = \tilde{\nu}_e \left(v + \frac{1}{2} \right) - \tilde{x}_e \tilde{\nu}_e \left(v + \frac{1}{2} \right)^2 \tag{15.E.43}$$

$$G''(13) = (4401.2 cm^{-1})(13.5) - (121.34 cm^{-1})(13.5)^2 = 37,301.98 cm^{-1} \tag{15.E.44}$$

$$G''(6) = (1356.9 cm^{-1})(6.5) - (19.93 cm^{-1})(6.5)^2 = 7,977.81 cm^{-1} \tag{15.E.45}$$

the transition is as follows

$$\tilde{\nu} = \tilde{T}_e + G''(6) - G''(13) \tag{15.E.46}$$

$$= 91,689.9 cm^{-1} + 7,977.81 cm^{-1} - 37,301.98 cm^{-1} = 62,365.73 cm^{-1} \tag{15.E.47}$$

therefore

$$\lambda = 160.34 nm \tag{15.E.48}$$

The radiant energy of the laser pulse is found using dimensional analysis

$$\left(200\frac{kJ}{s}\right)\left(2\times10^{-9}s\right)=1x10^{-4}J \tag{15.E.49}$$

the number of photons per pulse is determined using $E=nhv=8.06\times10^{13}$ 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 :

$$G''(0)=(\frac{1}{2})(2291cm^{-1})-(\frac{1}{2})^262.4cm^{-1}$$

$$G''(0)=1129.9cm^{-1}$$

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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Index

A

Anharmonicity
- 5.3: The Harmonic Oscillator Approximates Vibrations
- 13.5: Vibrational Overtones

antibonding molecular orbital
- 9.5: Bonding and Antibonding Orbitals

aromaticity
- 10.6: Butadiene is Stabilized by a Delocalization Energy

Asymmetric Tops
- 13.8: Rotational Spectra of Polyatomic Molecules

atomic term symbols
- 8.8: Term Symbols Gives a Detailed Description of an Electron Configuration
- 8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

Atomic units
- 8.1: Atomic and Molecular Calculations are Expressed in Atomic Units

B

Balmer series
- 1.4: The Hydrogen Atomic Spectrum

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

bond order
- 9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

bonding molecular orbital
- 9.5: Bonding and Antibonding Orbitals

bosons
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

bracketing theorem
- 7.2: Linear Variational Method and the Secular Determinant

C

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

Commuting Operators
- 4.6: Commuting Operators Allow Infinite Precision

conservative forces
- 1.8: The Bohr Theory of the Hydrogen Atom

correspondence principle
- 3.3: The Schrödinger Equation is an Eigenvalue Problem

Coulomb integral
- 10.5: 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

de Broglie wavelength
- 1.6: Matter Has Wavelike Properties

degeneracy
- 3.9: A Particle in a Three-Dimensional Box

delocalization energy
- 10.6: Butadiene is Stabilized by a Delocalization Energy

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

eigenfunction
- 3.3: The Schrödinger Equation is an Eigenvalue Problem

eigenvalue problem
- 3.3: The Schrödinger Equation is an Eigenvalue Problem
- 4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

Exchange Operator
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

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

G

Gaussian Type Orbitals
- 11.3: Extended Basis Sets

Generating Operators (Group Theory)
- 12.9: Generating Operators

H

Hückel theory
- 10.5: The \(\pi\)-Electron Approximation of Conjugation

Hamiltonian
- 4.2: Quantum Operators Represent Classical Variables

Harmonic oscillator
- 5.3: The Harmonic Oscillator Approximates 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

Hund's Rules
- 8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States

hybridization
- 10.1: Hybrid Orbitals Account for Molecular Shape

Hylleraas Wavefunction
- 8.2: Perturbation Theory and the Variational Method for Helium

I

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
- 10.4: Photoelectron Spectroscopy

L

Lamb formula
- 14.5: Chemical Shifts Depend upon the Chemical Environment of the Nucleus

laplacian
- 4.2: Quantum Operators Represent Classical Variables

LCAO
- 9.4: Chemical Bond Stability
- 9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently

lenard
1.3: Photoelectric Effect Explained with Quantum Hypothesis
lone pairs
10.2: Hybrid Orbitals in Water

M
microscopic reversibility
15.2: 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
13: Molecular Spectroscopy
molecular term symbols
9.14: Molecular Term Symbols Describe Electronic States of Molecules
9.15: Molecular Term Symbols Designate Symmetry
moment of inertia tensor
13.8: Rotational Spectra of Polyatomic Molecules
Morse potential
5.3: The Harmonic Oscillator Approximates Vibrations
5.5: The Harmonic Oscillator and Infrared Spectra

N
node
2.5: A Vibrating Membrane
nodes
3.7: The Average Momentum of a Particle in a Box is Zero
Nonstationary States
4.4: The Time-Dependent Schrödinger Equation
normal modes
13.9: Normal Modes in Polyatomic Molecules

O
oblate top
13.8: Rotational Spectra of Polyatomic Molecules
Operators
3.2: Linear Operators in Quantum Mechanics
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
6.7: The Helium Atom Cannot Be Solved Exactly
orthogonality
3.5: The Energy of a Particle in a Box is Quantized
Orthonormality
3.5: The Energy of a Particle in a Box is Quantized
overlap
9.3: The Overlap Integral
overlap integral
9.3: The Overlap Integral
overtones
13.5: Vibrational Overtones

P
Particle in a 3D Box
3.9: A Particle in a Three-Dimensional Box
Particle in a box
3.5: The Energy of a Particle in a Box is Quantized
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
photoelectric effect
1.3: Photoelectric Effect Explained with Quantum Hypothesis
photoelectron spectroscopy
10.4: Photoelectron Spectroscopy
photons
1.3: Photoelectric Effect Explained with Quantum Hypothesis
physical
13.1: The Electromagnetic Spectrum
13.3: Unequal Spacings in Vibration-Rotation Spectra
13.5: Vibrational Overtones
13.E: Molecular Spectroscopy (Exercises)
Planck's constant
1.2: Quantum Hypothesis Used for Blackbody Radiation Law
plane of symmetry
12.2: Symmetry Elements
population inversion
15.4: Population Inversion can be Achieved in a Three-Level System
Probabilistic Interpretation
3.4: Wavefunctions Have a Probabilistic Interpretation
probability density
3.4: Wavefunctions Have a Probabilistic Interpretation
prolate top
13.8: 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

R
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
10.5: The \(\pi\)-Electron Approximation of Conjugation
Rigid rotor
5.8: The Energy Levels of a Rigid Rotor
5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
13.12: The Selection Rule for the Rigid Rotor
rotational constant
5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
Rotational of Polyatomic Molecules
13.8: Rotational Spectra of Polyatomic Molecules
rovibrational spectroscopy
13.2: Rotations Accompany Vibrational Transitions

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
7.2: Linear Variational Method and the Secular Determinant
9.5: Bonding and Antibonding Orbitals
Selection rules
5.5: The Harmonic Oscillator and Infrared Spectra
13.12: The Selection Rule for the Rigid Rotor
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 harmonics
5.8: The Energy Levels of a Rigid Rotor
6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics
Spherical Tops
13.8: Rotational Spectra of Polyatomic Molecules
standing wave
2.1: The One-Dimensional Wave Equation
STO
7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters
Stokes shift
15.1: 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
13.8: 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

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

U

Ultraviolet Catastrophe

1.1: Blackbody Radiation Cannot Be Explained Classically

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

10.4: Photoelectron Spectroscopy

vertical transition

13.7: The Franck-Condon Principle

W

Walsh diagrams

10.3: Why is BeH_2 Linear and H_2O Bent?

Wave equations

2.1: The One-Dimensional Wave Equation

Wavefunction Normalization

3.6: Wavefunctions Must Be Normalized

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

Glossary

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    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
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  - 1: The Dawn of the Quantum Theory - *Undeclared*
    - 1.1: Blackbody Radiation Cannot Be Explained Classically - *CC BY 4.0*
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    - 1.3: Photoelectric Effect Explained with Quantum Hypothesis - *Undeclared*
    - 1.4: The Hydrogen Atomic Spectrum - *Undeclared*
    - 1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum - *Undeclared*
    - 1.6: Matter Has Wavelike Properties - *Undeclared*
    - 1.7: de Broglie Waves can be Experimentally Observed - *Undeclared*
    - 1.8: The Bohr Theory of the Hydrogen Atom - *Undeclared*
    - 1.9: The Heisenberg Uncertainty Principle - *Undeclared*
    - 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 - *Undeclared*
    - 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 - *Undeclared*
    - 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 - *Undeclared*
    - 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 - *Undeclared*
- 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 - *Undeclared*
  - 5.3: The Harmonic Oscillator Approximates Vibrations - *Undeclared*
  - 5.4: The Harmonic Oscillator Energy Levels - *Undeclared*
  - 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 - *Undeclared*
  - 5.8: The Energy Levels of a Rigid Rotor - *Undeclared*
  - 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 - *Undeclared*
  - 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 Helium Atom Cannot Be Solved Exactly - *Undeclared*
  - 6.E: The Hydrogen Atom (Exercises) - *Undeclared*
- 7: Approximation Methods - *Undeclared*
  - 7.1: The Variational Method Approximation - *Undeclared*
  - 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 - *Undeclared*
  - 7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems - *Undeclared*
  - 7.E: Approximation Methods (Exercises) - *Undeclared*
- 8: Multielectron Atoms - *Undeclared*
  - 8.1: Atomic and Molecular Calculations are Expressed in Atomic Units - *Undeclared*
  - 8.2: Perturbation Theory and the Variational Method for Helium - *Undeclared*
  - 8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method - *Undeclared*
  - 8.4: An Electron Has an Intrinsic Spin Angular Momentum - *Undeclared*
  - 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons - *Undeclared*
  - 8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants - *Undeclared*
  - 8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data - *Undeclared*
  - 8.8: Term Symbols Gives a Detailed Description of an Electron Configuration - *Undeclared*
  - 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: Chemical Bonding in Diatomic Molecules - *Undeclared*
  - 9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules - *Undeclared*
  - 9.2: The H_2^+ Prototypical Species - *Undeclared*
  - 9.3: The Overlap Integral - *Undeclared*
  - 9.4: Chemical Bond Stability - *Undeclared*
  - 9.5: Bonding and Antibonding Orbitals - *Undeclared*
  - 9.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital - *Undeclared*
  - 9.7: Molecular Orbitals Can Be Ordered According to Their Energies - *Undeclared*
  - 9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule - *Undeclared*

- 9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle - *Undeclared*
- 9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic - *Undeclared*
- 9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals - *Undeclared*
- 9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules - *Undeclared*
- 9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently - *Undeclared*
- 9.14: Molecular Term Symbols Describe Electronic States of Molecules - *Undeclared*
- 9.15: Molecular Term Symbols Designate Symmetry - *Undeclared*
- 9.16: Most Molecules Have Excited Electronic States - *Undeclared*
- 9.E: Chemical Bond in Diatomic Molecules (Exercises) - *Undeclared*

10: Bonding in Polyatomic Molecules - *Undeclared*

- 10.1: Hybrid Orbitals Account for Molecular Shape - *CC BY-NC-SA 4.0*
- 10.2: Hybrid Orbitals in Water - *Undeclared*
- 10.3: Why is BeH_2 Linear and H_2O Bent? - *Undeclared*
- 10.4: Photoelectron Spectroscopy - *Undeclared*
- 10.5: The \(\pi\)-Electron Approximation of Conjugation - *Undeclared*
- 10.6: Butadiene is Stabilized by a Delocalization Energy - *Undeclared*
- 10.7: Benzene and Aromaticity - *Undeclared*
- 10.E: Bonding in Polyatomic Molecules (Exercises) - *Undeclared*

11: Computational Quantum Chemistry - *Undeclared*

- 11.1: Overview of Quantum Calculations - *Undeclared*
- 11.2: Gaussian Basis Sets - *Undeclared*
- 11.3: Extended Basis Sets - *Undeclared*
- 11.4: Orbital Polarization Terms in Basis Sets - *Undeclared*
- 11.5: The Ground-State Energy of H_2 - *Undeclared*
- 11.6: Quantum Calculations - *Undeclared*
- 11.E: Computational Quantum Chemistry (Exercises) - *Undeclared*

12: Group Theory - The Exploitation of Symmetry - *Undeclared*

- 12.1: The Exploitation of Symmetry - *Undeclared*
- 12.2: Symmetry Elements - *Undeclared*
- 12.3: Symmetry Operations Define Groups - *Undeclared*
- 12.4: Symmetry Operations as Matrices - *Undeclared*
- 12.5: The \(C_{3V}\) Point Group - *Undeclared*
- 12.6: Character Tables - *Undeclared*
- 12.7: Characters of Irreducible Representations - *Undeclared*
- 12.8: Using Symmetry to Solve Secular Determinants - *Undeclared*
- 12.9: Generating Operators - *Undeclared*
- 12.E: Group Theory - The Exploitation of Symmetry (Exercises) - *Undeclared*

13: Molecular Spectroscopy - *Undeclared*

- 13.1: The Electromagnetic Spectrum - *Undeclared*
- 13.2: Rotations Accompany Vibrational Transitions - *Undeclared*
- 13.3: Unequal Spacings in Vibration-Rotation Spectra - *Undeclared*
- 13.4: Unequal Spacings in Pure Rotational Spectra - *Undeclared*
- 13.5: Vibrational Overtones - *Undeclared*
- 13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information - *Undeclared*
- 13.7: The Franck-Condon Principle - *Undeclared*
- 13.8: Rotational Spectra of Polyatomic Molecules - *Undeclared*
- 13.9: Normal Modes in Polyatomic Molecules - *Undeclared*
- 13.10: Irreducible Representation of Point Groups - *Undeclared*
- 13.11: Time-Dependent Perturbation Theory - *Undeclared*
- 13.12: The Selection Rule for the Rigid Rotor - *Undeclared*
- 13.13: The Harmonic Oscillator Selection Rule - *Undeclared*
- 13.14: Group Theory Determines Infrared Activity - *Undeclared*
- 13.E: Molecular Spectroscopy (Exercises) - *Undeclared*

14: Nuclear Magnetic Resonance Spectroscopy - *Undeclared*

- 14.8: The n+1 Rule Applies Only to First-Order Spectra - *Undeclared*
- 14.1: Nuclei Have Intrinsic Spin Angular Momenta - *Undeclared*
- 14.2: Magnetic Moments Interact with Magnetic Fields - *Undeclared*

- 14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz - *Undeclared*
- 14.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded - *Undeclared*
- 14.5: Chemical Shifts Depend upon the Chemical Environment of the Nucleus - *Undeclared*
- 14.6: Spin-Spin Coupling Can Lead to Multiplets in NMR Spectra - *Undeclared*
- 14.7: Spin-Spin Coupling Between Chemically Equivalent Protons is Not Observed - *Undeclared*
- 14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method - *Undeclared*
- 14.E: Nuclear Magnetic Resonance Spectroscopy (Exercises) - *Undeclared*

- 15: Lasers, Laser Spectroscopy, and Photochemistry - *Undeclared*
  - 15.1: Electronically Excited Molecules can Relax by a Number of Processes - *Undeclared*
  - 15.2: The Dynamics of Transitions can be Modeled by Rate Equations - *Undeclared*
  - 15.3: A Two-Level System Cannot Achieve a Population Inversion - *Undeclared*
  - 15.4: Population Inversion can be Achieved in a Three-Level System - *Undeclared*
  - 15.5: What is Inside a Laser? - *Undeclared*
  - 15.6: The Helium-Neon Laser - *Undeclared*
  - 15.7: High-Resolution Laser Spectroscopy - *Undeclared*
  - 15.8: Pulsed Lasers Can by Used to Measure the Dynamics of Photochemical Processes - *Undeclared*
  - 15.E: Lasers, Laser Spectroscopy, and Photochemistry (Exercises) - *Undeclared*
- Back Matter - *Undeclared*
  - Index - *Undeclared*
  - Glossary - *Undeclared*
  - Detailed Licensing - *Undeclared*