CHM 311: PHYSICAL CHEMISTRY I



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CHM 311: Physical Chemistry I

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TABLE OF CONTENTS

Licensing

1: The Path to Quantum Mechanics

- 1.1: Prelude to the Foundations of Quantum Mechanics
- 1.2: Blackbody Radiation Cannot Be Explained Classically
- 1.3: Quantum Hypothesis Used for Blackbody Radiation Law
- 1.4: Photoelectric Effect Explained with Quantum Hypothesis
- 1.5: Matter Has Wavelike Properties
- 1.6: de Broglie Waves can be Experimentally Observed

2: Foundations of Quantum Mechanics

- 2.1: The Schrödinger Equation
- 2.2: The Postulates of Quantum Mechanics
- 2.3: The Wavefunction Specifies the State of a System
- 2.4: Wavefunctions Have a Probabilistic Interpretation
- 2.5: Wavefunctions Must Be Normalized
- 2.6: Linear Operators in Quantum Mechanics
- 2.7: Quantum Operators Represent Classical Variables
- 2.8: The Schrödinger Equation is an Eigenvalue Problem
- 2.9: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators
- 2.10: Eigenfunctions of Operators are Orthogonal
- 2.11: The Heisenberg Uncertainty Principle
- 2.12: Commuting Operators Allow Infinite Precision

3: Model Systems in Quantum Mechanics

- 3.1: The Energy of a Particle in a Box is Quantized
- 3.2: The Free Electron Model
- 3.3: The Average Momentum of a Particle in a Box is Zero
- 3.4: A Particle in a Three-Dimensional Box
- 3.5: Tunneling
- 3.6: A Harmonic Oscillator Obeys Hooke's Law
- 3.7: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule
- 3.8: The Harmonic Oscillator Approximates Molecular Vibrations
- 3.9: The Harmonic Oscillator Energy Levels
- 3.10: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials
- 3.11: Hermite Polynomials are either Even or Odd Functions
- 3.12: Spherical Polar Coordinates
- 3.13: Potential Energy and the Hamiltonian
- 3.14: Solution to the Schrödinger Equation
- 3.15: Spherical Harmonics
- 3.16: Angular Momentum
- 3.17: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision
- 3.18: Application to the Rotation of Real Molecules

4: The Hydrogen Atom

- 4.1: The Hydrogen Atomic Spectrum
- 4.2: The Rydberg Formula and the Hydrogen Atomic Spectrum
- 4.3: Bohr's Hydrogen Atom
- 4.4: The Schrödinger Equation
- 4.5: Other One-Electron Systems
- 4.6: The Wavefunctions
- 4.7: s-orbitals are Spherically Symmetric
- 4.8: Orbital Angular Momentum and the p-Orbitals

5: Many Electron Atoms

- 5.1: The Helium Atom Cannot Be Solved Exactly
- 5.2: Atomic and Molecular Calculations are Expressed in Atomic Units
- 5.3: The Variational Method Approximation
- 5.4: Single-electron Wavefunctions and Basis Functions
- 5.5: An Electron has an Intrinsic Spin Angular Momentum
- 5.6: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
- 5.7: Antisymmetric Wavefunctions can be Represented by Slater Determinants
- 5.8: Electron Configurations, The Pauli Exclusion Principle, The Aufbau Principle, and Slater Determinants
- 5.9: The Self-Consistent Field Approximation (Hartree-Fock Method)
- 5.10: Hartree-Fock Calculations Give Good Agreement with Experimental Data
- 5.11: Term Symbols Gives a Detailed Description of an Electron Configuration
- 5.12: The Allowed Values of J - the Total Angular Momentum Quantum Number
- 5.13: Hund's Rules Determine the Term Symbols of the Ground Electronic States

6: Molecular Structure and Bonding

- 6.1: The Born-Oppenheimer Approximation
- 6.2: The Orbital Approximation and Orbital Configurations
- 6.3: Linear Variational Method and the Secular Determinant
- 6.4: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters
- 6.5: The H_2^+ Prototypical Species
- 6.6: The Overlap Integral
- 6.7: Chemical Bond Stability
- 6.8: Bonding and Antibonding Orbitals
- 6.9: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital
- 6.10: Molecular Orbitals Can Be Ordered According to Their Energies
- 6.11: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule
- 6.12: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle
- 6.13: Diatomic Molecules of the First and Second Periods
- 6.14: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic
- 6.15: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules
- 6.16: Orbital ionization energies
- 6.17: Polar bonds
- 6.18: Molecular Term Symbols Describe Electronic States of Molecules
- 6.19: Molecular Term Symbols Designate Symmetry
- 6.20: The pi-Electron Approximation of Conjugation
- 6.21: Butadiene is Stabilized by a Delocalization Energy
- 6.22: Benzene and Aromaticity

7: Statistical Mechanics

- 7.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System
- 7.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution
- 7.3: Translational Partition Functions of Monotonic Gases
- 7.4: Most Atoms are in the Ground Electronic State
- 7.5: Pressure can be Expressed in Terms of the Canonical Partition Function
- 7.6: Most Molecules are Rotationally Excited at Ordinary Temperatures
- 7.7: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number
- 7.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule
- 7.9: Most Molecules are in the Ground Vibrational State
- 7.10: Vibrational Partition Functions of Polyatomic Molecules Include the Partition Function for Each Normal Coordinate
- 7.11: The Partition Function of Distinguishable, Independent Molecules is the Product of the Molecular Partition Functions
- 7.12: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom
- 7.13: The Average Ensemble Energy is Equal to the Observed Energy of a System
- 7.14: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms
- 7.15: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature
- 7.16: Molar Heat Capacities
- 7.17: The Equipartition Principle
- 7.18: The Famous Equation of Statistical Thermodynamics is S=k ln W
- 7.19: Entropy Can Be Expressed in Terms of a Partition Function
- 7.20: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition
- 7.21: Practical Absolute Entropies of Gases Can Be Calculated from Partition Functions
- 7.22: Standard Entropies Depend Upon Molecular Mass and Structure
- 7.23: Spectroscopic Entropies sometimes disgree with Calorimetric Entropies

8: Molecular Spectroscopy

- 8.1: The Electromagnetic Spectrum
- 8.2: Introduction to Spectroscopy
- 8.3: Rotation of Linear Molecules
- 8.4: Microwave Rotational Spectroscopy
- 8.5: The Selection Rule for the Rigid Rotor
- 8.6: Rotational Spectra of Polyatomic Molecules
- 8.7: The Harmonic Oscillator and Infrared Spectra
- 8.8: The Harmonic Oscillator Selection Rule
- 8.9: Vibrational Overtones
- 8.10: Vibrational Spectroscopy Techniques
- 8.11: Rotations Accompany Vibrational Transitions
- 8.12: Unequal Spacings in Vibration-Rotation Spectra
- 8.13: Unequal Spacings in Pure Rotational Spectra

9: Electronic Spectroscopy

- 9.1: Using Atomic Term Symbols to Interpret Atomic Spectra
- 9.2: The Dynamics of Transitions can be Modeled by Rate Equations
- 9.3: A Two-Level System Cannot Achieve a Population Inversion
- 9.4: Population Inversion can be Achieved in a Three-Level System
- 9.5: What is Inside a Laser?
- 9.6: The Helium-Neon Laser

- 9.7: Modern Applications of Laser Spectroscopy
- 9.8: The Beer-Lambert Law
- 9.9: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
- 9.10: The Franck-Condon Principle
- 9.11: Electronically Excited Molecules can Relax by a Number of Processes

10: Group Theory and Symmetry

- 10.1: Symmetry Elements and Operations Define the Point Groups
- 10.2: Symmetry Operations Define Groups
- 10.3: Symmetry Operations as Matrices
- 10.4: Molecules can be Represented by Reducible Representations
- 10.5: Character Tables Summarize the Properties of a Point Group
- 10.6: Characters of Irreducible Representations
- 10.7: Molecular Orbitals can be Constructed on the Basis of Symmetry
- 10.8: H_2O
- 10.9: The Exploitation of Symmetry Can Help Simplify Numerical Calculations
- 10.10: Normal Modes in Polyatomic Molecules
- 10.11: Irreducible Representation of Point Groups
- 10.12: Group Theory Determines Infrared Activity
- 10.13: Raman- Application
- 10.14: Raman- Theory

Index

Glossary

Detailed Licensing

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CHAPTER OVERVIEW

1: The Path to Quantum Mechanics

1.1: Prelude to the Foundations of Quantum Mechanics
1.2: Blackbody Radiation Cannot Be Explained Classically
1.3: Quantum Hypothesis Used for Blackbody Radiation Law
1.4: Photoelectric Effect Explained with Quantum Hypothesis
1.5: Matter Has Wavelike Properties
1.6: de Broglie Waves can be Experimentally Observed

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1.1: Prelude to the Foundations of Quantum Mechanics

The concepts of quantum mechanics were invented to explain experimental observations that otherwise were totally inexplicable. This period of invention extended from 1900 when Max Planck introduced the revolutionary concept of quantization to 1925 when Erwin Schrödinger and Werner Heisenberg independently introduced two mathematically different but equivalent formulations of a general quantum mechanical theory. The Heisenberg method uses properties of matrices, while the Schrödinger method involves partial differential equations. We will develop and utilize Schrödinger's approach because students usually are more familiar with elementary calculus than with matrix algebra, and because this approach provides direct insight into charge distributions in molecules, which are of prime interest in chemistry.

Heisenberg and Schrödinger were inspired by four key experimental observations: the spectral distribution of black-body radiation, the characteristics of the photoelectric effect, the Compton effect, and the luminescence spectrum of the hydrogen atom. Explanation of these phenomena required the introduction of two revolutionary concepts:

1. physical quantities previously thought to be continuously variable, such as energy and momentum, are quantized, and
2. momentum, p, and wavelength, λ, are related, $p = \frac{h}{\lambda}$, where h is a fundamental constant.

We will use a quasi-historical approach in this chapter to emphasize that individuals created knowledge by inventing new ideas or concepts. What is not apparent here is that these new ideas initially were greeted with considerable skepticism, and acceptance was slow because of counter proposals that were not so revolutionary. Only after some time did inconsistencies in the counter proposals become apparent. By "quantized," we mean that only certain values are possible or allowed. For example, money is quantized. Money does not come in continuous denominations. In the United States the smallest unit of money is a penny, and everything costs some integer multiple of a penny.

From high school and freshman physics, as well as from everyday experience, we learn that particles have momentum, which is mass times velocity. Although more abstract, the wave properties of light are clearly demonstrated by interference, diffraction and refraction effects. That a relationship between momentum (a particle property) and wavelength (a wave property) applies to both particles and light was, and remains, somewhat amazing and revolutionary. This relationship, called the "wave-particle duality," means that particles have wave-like properties and light waves have particle-like properties.

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1.2: Blackbody Radiation Cannot Be Explained Classically

Learning Objectives

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

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

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

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



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

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

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

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

Any body at any temperature above absolute zero **will** radiate to some extent, the intensity and frequency distribution of the radiation depending on the detailed structure of the body. To begin analyzing heat radiation, we need to be specific about the body doing the radiating: *the simplest possible case is an idealized body which is a perfect absorber, and therefore also (from the above argument) a perfect emitter.* So how do we construct a perfect absorber in the laboratory? In 1859 Kirchhoff had a good idea: a small hole in the side of a large box is an excellent absorber, since any radiation that goes through the hole bounces around inside, a

lot getting absorbed on each bounce, and has little chance of ever getting out again. So, we can do this *in reverse*: have an oven with a tiny hole in the side, and presumably the radiation coming out the hole is as good a representation of a perfect emitter as we're going to find (Figure 1.1.2).

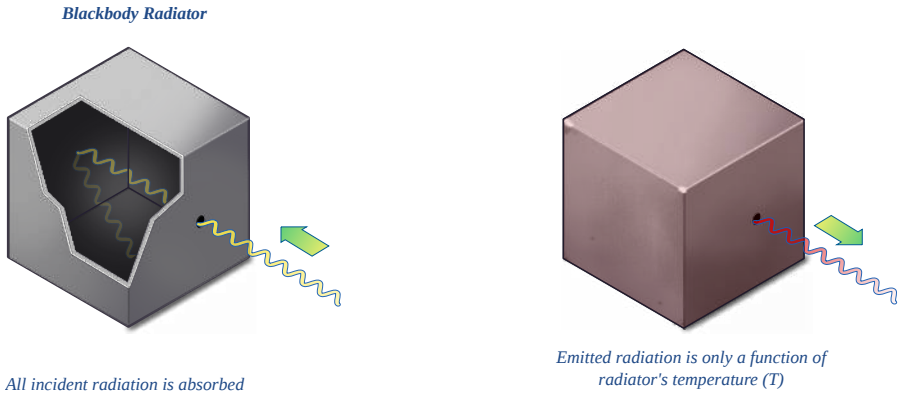


Figure 1.1.2 : Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation. (CC BY-NC; Ümit Kaya via LibreTexts)

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

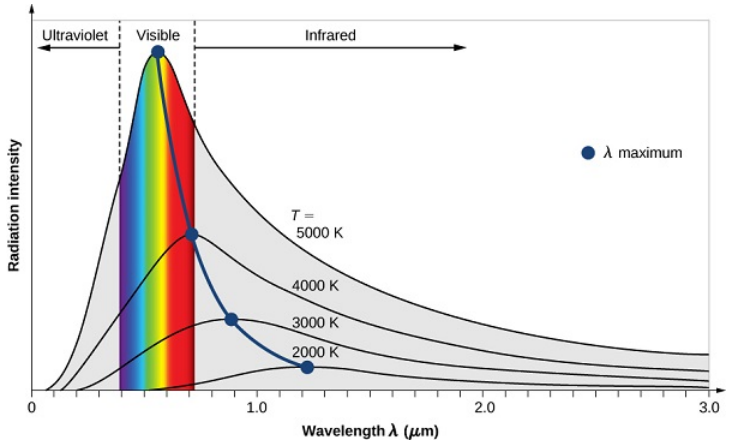
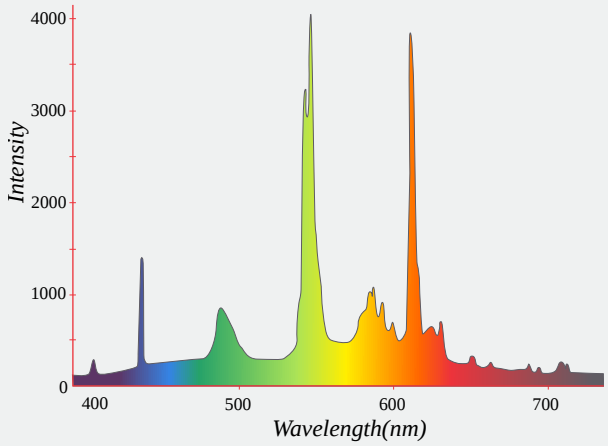


Figure 1.1.3 : Graphic representation of spectral distribution of blackbody radiation at different temperatures. The Stefan-Boltzmann's Law is observed as the increase in the emission amplitude with increasing temperature and the Wien's Displacement Law is observed as the shift to smaller wavelength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

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

Not all radiators are blackbody radiators

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



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

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

1.2.1: 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):

$$P = \sigma T^4 \tag{1.2.1}$$

where

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

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

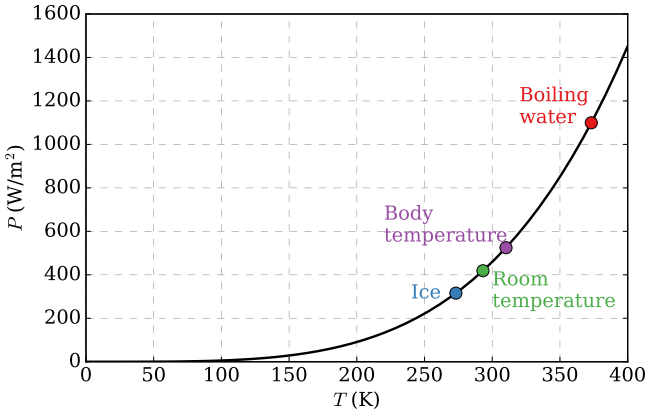


Figure 1.1.4 : Graph of a function of total emitted energy of a blackbody proportional to the fourth power of its thermodynamic temperature T according to the Stefan–Boltzmann law. (CC BY-SA 4.0; Nicoguaro)

Example 1.1.1

The sun's surface temperature is 5700 K.

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

Solution

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

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

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

The power radiated from the sun (via Stefan-Boltzmann Law) is $P = \sigma T^4$ (Equation 1.2.1).

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

This value is per square meter.

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

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

1.2.2: 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:

$$\nu_{max} \propto T \tag{1.2.2}$$

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 1.2.2) in terms of the peak wavelength of light is

$$\lambda_{max} = \frac{b}{T} \tag{1.2.3}$$

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 1.2.1). 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:

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

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 1.2.3, 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 1.2.3 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

1.2.3: The Rayleigh-Jeans Law

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

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

$$=\frac{8\pi k_{B}T}{c^{3}}\nu^{2}d\nu \tag{1.2.5}$$

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 1.2.5). Ehrenfest later dubbed this the "ultraviolet catastrophe". It is important to emphasizing that Equation 1.2.5 is a **classical** result: the only inputs are classical dynamics and Maxwell's electromagnetic theory.

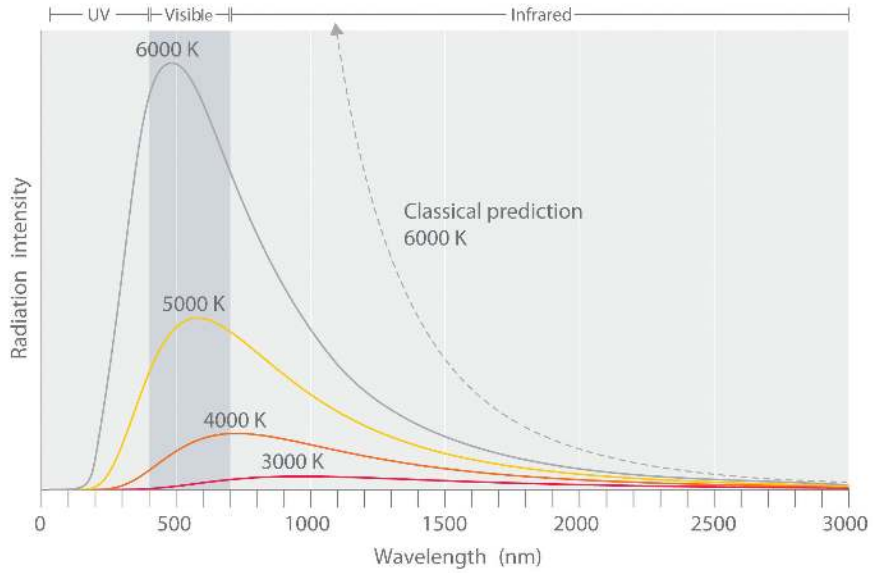


Figure 1.1.5 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the hot metalwork in Figure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

Differential vs. Integral Representation of the Distribution

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

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

However, in practice, we are more interested in frequency intervals. An exact frequency is the limit of a sequence of smaller and smaller intervals. If we make the assumption that, for a sufficiently small interval, $\rho(\nu,T)$ does not vary, we get your definition for the differential $d\rho(\nu,T)$ in Equation 1.2.5:

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

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

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

Example 1.1.4 : The Ultraviolet Catastrophe

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

Solution

The total spectral radiance $\rho_{tot}(T)$ is the combined emission over all possible wavelengths (or equivalently, frequencies), which is an integral over the relevant distribution (Equation 1.2.5 for the Rayleigh-Jeans Law).

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

but the integral

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

does not converge. Worse, it is infinite,

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

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

Contributors and Attributions

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1.3: Quantum Hypothesis Used for Blackbody Radiation Law

Learning Objectives

- To understand how energy is quantized in blackbody radiation

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

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

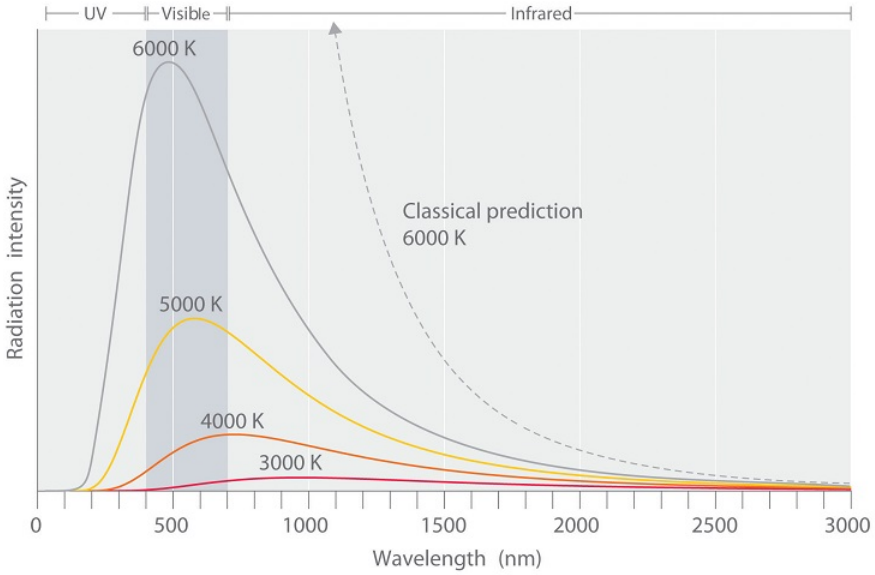


Figure 1.2.1 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases,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

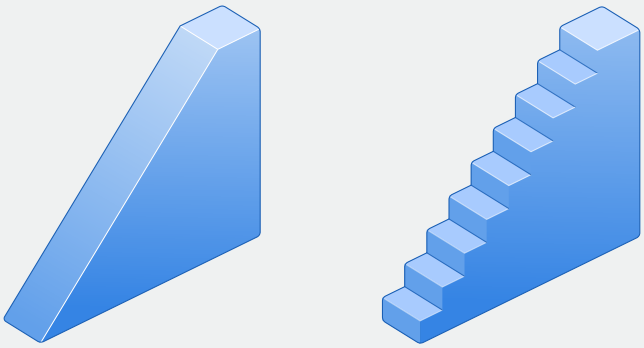
1.3.1: Quantizing Electrons in the Radiator

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

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

Quantization

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



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

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

$$E = h\nu \tag{1.3.1}$$

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

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

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

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

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

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

Max Planck explain the spectral distribution of blackbody radiation as result from oscillations of electrons. Similarly, oscillations of electrons in an antenna produce radio waves. Max Planck concentrated on modeling the oscillating charges that must exist in the oven walls, radiating heat inwards and—in thermodynamic equilibrium—themselves being driven by the radiation field. He found he could account for the observed curve if he required these oscillators not to radiate energy continuously, as the classical theory would demand, but they could **only** lose or gain energy in chunks, called **quanta**, of size $h\nu$, for an oscillator of frequency ν (Equation 1.3.1).

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

$$d\rho(\nu,T) = \rho_\nu(T)d\nu \tag{1.3.2}$$

$$= \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}d\nu \tag{1.3.3}$$

with

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

Planck's radiation energy density (Equation 1.3.3) can also be expressed in terms of wavelength λ.

$$\rho(\lambda,T) = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda k_BT}-1}\right) \tag{1.3.4}$$

With a wavelength of maximum energy density at:

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

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

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

$$= \frac{2h\nu^3}{c^2} \cdot \frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}d\nu \tag{1.3.5}$$

or

$$B_\lambda(\lambda,T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/(\lambda k_BT)}-1} \tag{1.3.6}$$

Planck's equation (Equation 1.3.4) gave an excellent agreement with the experimental observations for all temperatures (Figure 1.2.2).

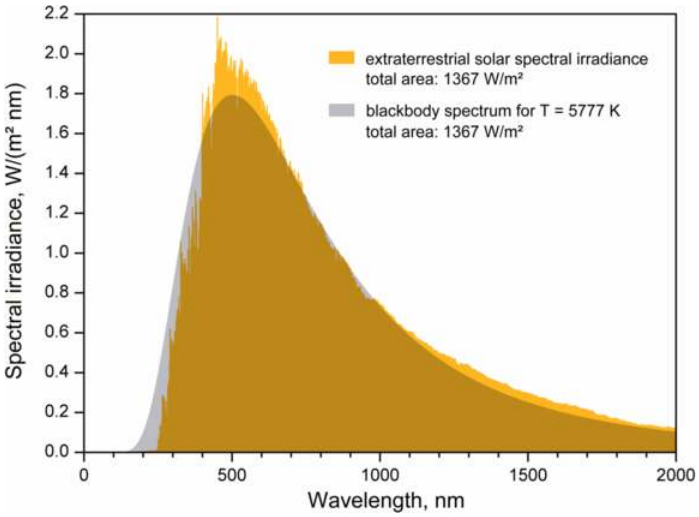
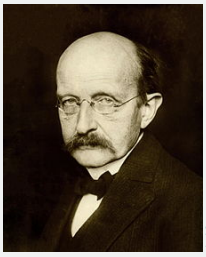


Figure 1.2.2 : The Sun is an excellent approximation of a blackbody. Its effective temperature is ~5777 K. (CC-SA-BY 3.0; Sch).

Max Planck (1858–1947)

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



MAX-PLANCK-GESELLSCHAFT

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

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

Exercise 1.2.1

Use Equation 1.3.4 to show that the units of $\rho(\lambda, T)\, d\lambda$ are J/m^3 as expected for an energy density.

The near perfect agreement of this formula with precise experiments (e.g., Figure 1.2.3), and the consequent necessity of energy quantization, was the most important advance in physics in the century. His blackbody curve was completely accepted as the correct one: more and more accurate experiments confirmed it time and again, yet the radical nature of the quantum assumption did not sink in. Planck was not too upset—he didn't believe it either, he saw it as a technical fix that (he hoped) would eventually prove unnecessary.

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

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

$$E = nh\nu$$

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

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

1.3.2: Summary

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

Contributors and Attributions

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

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1.4: Photoelectric Effect Explained with Quantum Hypothesis

Learning Objectives

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

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

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

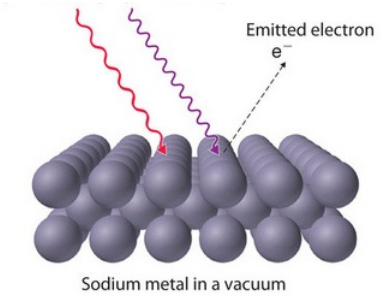


Figure 1.3.1 : The photoelectric effect involves irradiating a metal surface with photons of sufficiently high energy to cause the electrons to be ejected from the metal. (CC BY-SA-NC; anonymous)

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

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

1.4.1: Lenard's Experimental Results (Intensity Dependence)

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

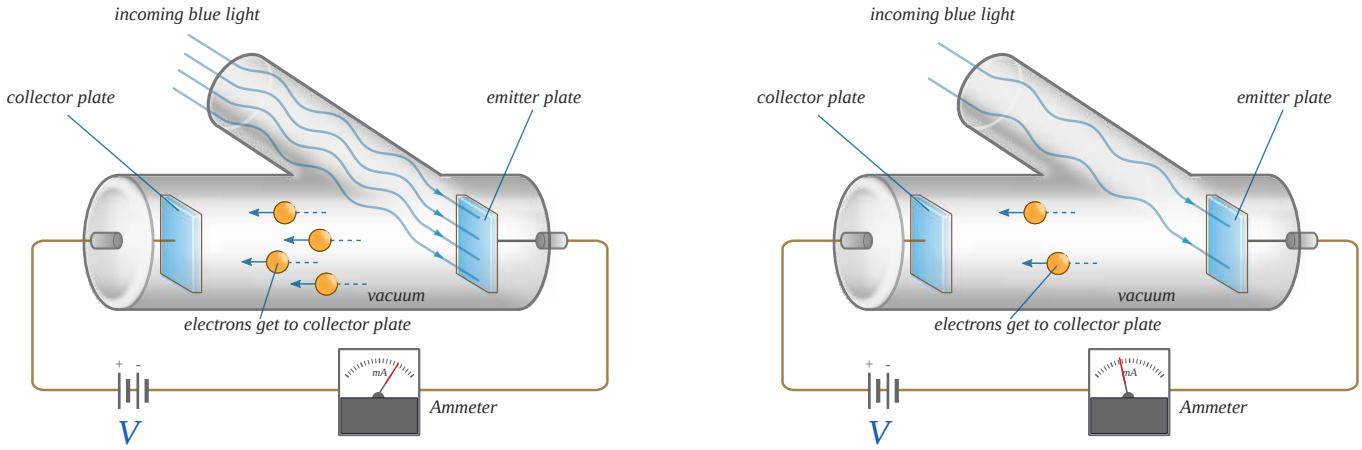


Figure **1.4.2**: Lenard's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

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

1.4.2: Millikan's Experimental Results (Wavelength Dependence)

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

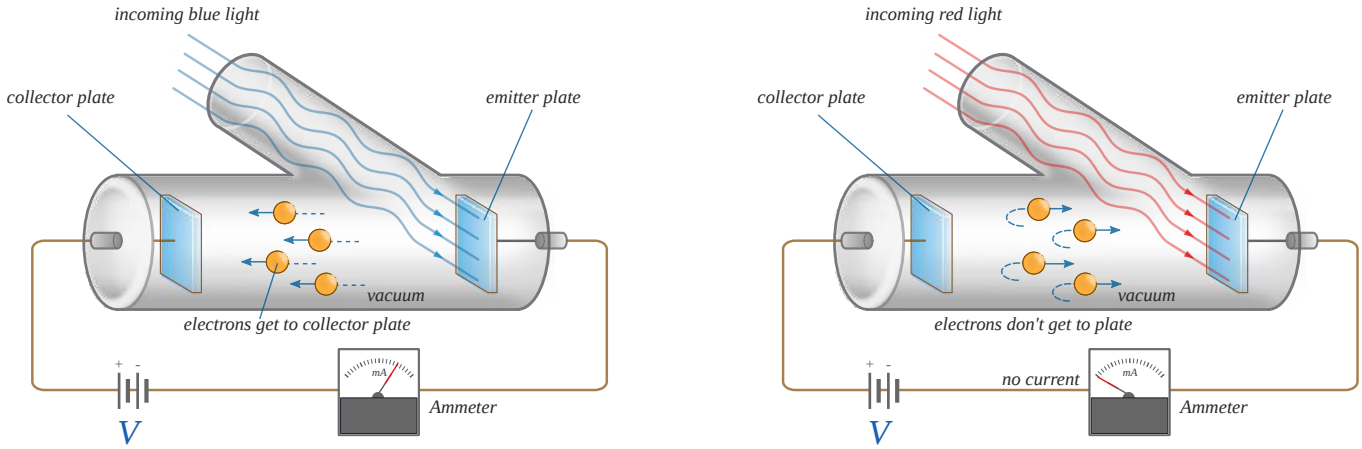


Figure 1.3.3 : Millikan's photoelectric experiment. (left) Incident high-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector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

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

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

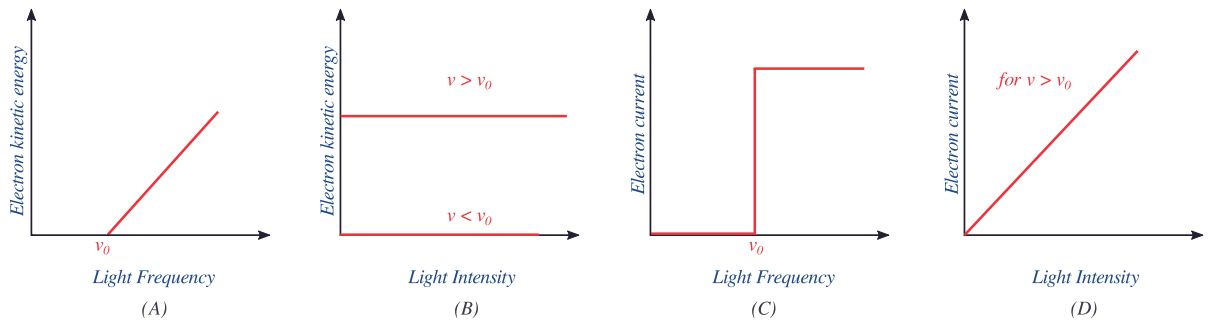


Figure 1.3.4 : Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the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

Classical Theory does not Describe Experiment

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

As with most of the experimental results we discuss in this text, the behavior described above is a simplification of the true experimental results observed in the laboratory. A more complex description involves a greater introduction of more complex physics and instrumentation, which will be ignored for now.

1.4.3: Einstein's Quantum Picture

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

$$KE = h\nu - \Phi \tag{1.4.1}$$

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,

$$eV_{stop} = h\nu - \Phi \tag{1.4.2}$$

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 1.4.4*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 1.4.1). 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 1.4.1 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 1.4.1) 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.

1.4.4: The Workfunction (Φ)

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

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

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

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

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

Table 1.3.1 : Workfunctions and Ionization Energies of Select Elements

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

Example 1.3.1 : Calcium

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

Strategy

To solve part (a), note that the energy of a photon is given by $E = h\nu$. For part (b), once the energy of the photon is calculated, it is a straightforward application of Equation 1.4.1 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 1.4.1. Substituting the photon energy and binding energy yields

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

Discussion

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

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

? Exercise 1.3.1 : Silver

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

Answer

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

? Exercise 1.3.2

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

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 a particle is, the lower its energy.

1.4.5: 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.

1.4.6: Conceptual Questions

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

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1.5: Matter Has Wavelike Properties

Learning Objectives

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

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

$$\lambda = \frac{h}{p} \tag{1.5.1}$$

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

Deriving the de Broglie Wavelength

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

$$E = \sqrt{p^2c^2 + m^2c^4} \tag{1.5.2}$$

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 1.5.2 becomes

$$E = pc.$$

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

$$h\nu = \frac{hc}{\lambda} = pc \tag{1.5.3}$$

Solving for the wavelength λ gives Equation 1.5.1:

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

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

Equation 1.5.1 allows us to associate a wavelength λ to a particle with momentum p. As the momentum increases, the wavelength decreases. In both cases, this means the energy becomes larger. i.e., short wavelengths *and* high momenta correspond to high energies.

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

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

Example 1.6.1 : Electron Waves

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

Solution

To calculate the de Broglie wavelength (Equation 1.5.1), the momentum of the particle must be established and requires knowledge of both the mass and velocity of the particle. The mass of an electron is $9.109383 \times 10^{-28}\ g$ and the velocity is obtained from the given kinetic energy of 1000 eV:

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

Solve for momentum

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

convert to SI units

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

expanding definition of joule into base SI units and cancel

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

Now substitute the momentum into the equation for de Broglie's wavelength (Equation 1.5.1) with Planck's constant ($h = 6.626069 \times 10^{-34}\ J \cdot s$). After expanding units in Plank's constant

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

Exercise 1.6.1 : Baseball Waves

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

Answer

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:

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

Exercise 1.6.2 : Electrons vs. Protons

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

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

Answer

Equation 1.5.1 shows that the de Broglie wavelength of a particle's matter wave is inversely proportional to its momentum (mass times velocity). Therefore the smaller mass particle will have a smaller momentum and longer wavelength. The electron is the lightest and will have the longest wavelength.

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.

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1.6: 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.

1.6.1: Diffraction of Light (Light as a Wave)

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

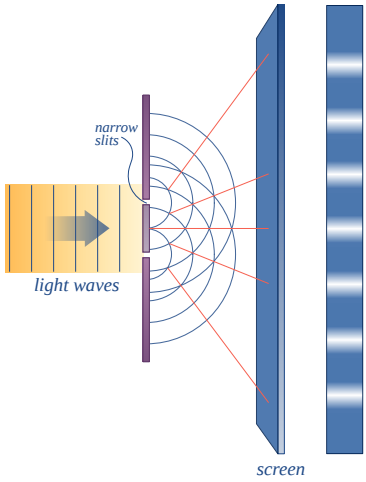


Figure 1.7.1 : Young double slit experiment. Two slits are illuminated by a plane light waves. (CC BY-NC; Ümit Kaya via LibreTexts)

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

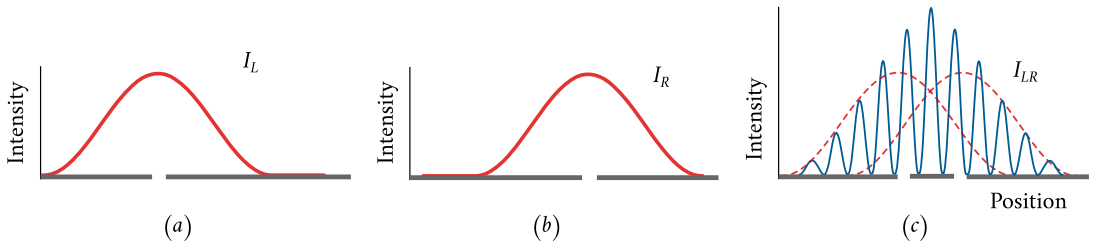


Figure 1.7.2 : Amplitude of particles through (a) left slit, (b) right slit, (c) through both slits. In absence of wavelength interference behavior, the intensity will be the sum of each single slit results (red) and when there is interference, pronounced oscillations in intensity is observed (blue curve).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

The wave nature of light causes the light waves passing through the two slits to interfere, producing bright and dark bands on the screen – a result that would not be expected if light consisted of classical particles (Figure **1.6.0c**). However, the light is always found to be absorbed at the screen at discrete points, as individual particles (not waves); the interference pattern appears via the varying density of these particle hits on the screen. Furthermore, versions of the experiment that include detectors at the slits find that each detected photon passes through one slit (as would a classical particle), and not through both slits (as would a wave).

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

1.6.2: Diffraction of Electrons (Electrons as Waves)

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

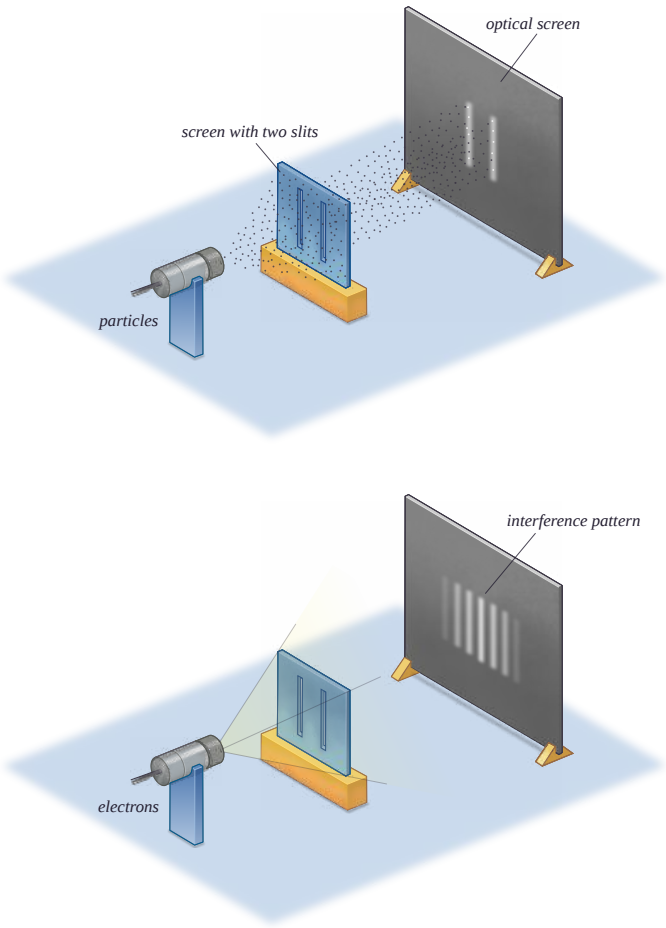


Figure 1.7.3 : (left) classical model of electrons. (right) wave property of electrons. (CC BY-NC; Ümit Kaya via LibreTexts)

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

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



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

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

Is Matter a Particle or a Wave?

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

1.6.3: Neutron Diffraction (Neutrons as Waves)

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

Example 1.7.1 : Neutron Diffraction

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

Solution

This is a simple use of de Broglie's equation

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

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

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

The relationship for kinetic energy is

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

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

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

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 appreciably.

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CHAPTER OVERVIEW

2: Foundations of Quantum Mechanics

2.1: The Schrödinger Equation
2.2: The Postulates of Quantum Mechanics
2.3: The Wavefunction Specifies the State of a System
2.4: Wavefunctions Have a Probabilistic Interpretation
2.5: Wavefunctions Must Be Normalized
2.6: Linear Operators in Quantum Mechanics
2.7: Quantum Operators Represent Classical Variables
2.8: The Schrödinger Equation is an Eigenvalue Problem
2.9: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators
2.10: Eigenfunctions of Operators are Orthogonal
2.11: The Heisenberg Uncertainty Principle
2.12: Commuting Operators Allow Infinite Precision

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2.1: The Schrödinger Equation

Learning Objectives

- To be introduced to the general properties of the Schrödinger equation and its solutions.

De Broglie's doctoral thesis, defended at the end of 1924, created a lot of excitement in European physics circles. Shortly after it was published in the fall of 1925 Pieter Debye, Professor of Theoretical Physics at Zurich and Einstein's successor, suggested to Erwin Schrödinger that he give a seminar on de Broglie's work. Schrödinger gave a polished presentation, but at the end Debye remarked that he considered the whole theory rather childish: why should a wave confine itself to a circle in space? It wasn't as if the circle was a waving circular string, real waves in space diffracted and diffused, in fact they obeyed three-dimensional wave equations, and that was what was needed. This was a direct challenge to Schrödinger, who spent some weeks in the Swiss mountains working on the problem and constructing his equation. There is no rigorous derivation of Schrödinger's equation from previously established theory, but it can be made very plausible by thinking about the connection between light waves and photons, and construction an analogous structure for de Broglie's waves and electrons (and later, other particles).

2.1.1: The Schrödinger Equation: A Better Approach

While the Bohr model is able to predict the allowed energies of any single-electron atom or cation, it by no means, a general approach. Moreover, it relies heavily on classical ideas, clumsily grafting quantization onto an essentially classical picture, and therefore, provides no real insights into the true quantum nature of the atom. Any rule that might be capable of predicting the allowed energies of a quantum system must also account for the *wave-particle duality* and implicitly include a wave-like description for particles. Nonetheless, we will attempt a heuristic argument to make the result at least plausible. In classical electromagnetic theory, it follows from Maxwell's equations that each component of the electric and magnetic fields in vacuum is a solution of the 3-D wave equation for electromagnetic waves:

$$\nabla^2\Psi(x,y,z,t) - \frac{1}{c^2}\frac{\partial^2\Psi(x,y,z,t)}{\partial t^2} = 0 \tag{2.1.1}$$

The wave equation in Equation 2.1.1 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:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{2.1.2}$$

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

$$\Psi(x) = f\left(\frac{2\pi x}{\lambda}\right) \tag{2.1.3}$$

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

$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta \tag{2.1.4}$$

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:

$$T(t) = f(2\pi\nu t) \tag{2.1.5}$$

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

$$\Psi(x,t) = exp\left[2\pi i\left(\frac{x}{\lambda} - \nu t\right)\right] \tag{2.1.6}$$

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

$$\Psi(x,t) = \exp\left[\frac{i(px - Et)}{\hbar}\right] \tag{2.1.7}$$

where

$$\hbar \equiv \frac{h}{2\pi} \tag{2.1.8}$$

Since Planck's constant occurs in most formulas with the denominator 2π, the $\hbar$ symbol was introduced by Paul Dirac. Equation 2.1.5 represents in some way the wavelike nature of a particle with energy E and momentum p. The time derivative of Equation 2.1.7 gives

$$\frac{\partial \Psi}{\partial t} = -\left(\frac{iE}{\hbar}\right)\exp\left[\frac{i(px - Et)}{\hbar}\right] \tag{2.1.9}$$

Thus from a simple comparison of Equations 2.1.7 and 2.1.9

$$i\hbar\frac{\partial \Psi}{\partial t} = E\Psi \tag{2.1.10}$$

or analogously differentiation of Equation 2.1.9 with respect to x

$$-i\hbar\frac{\partial \Psi}{\partial x} = p\Psi \tag{2.1.11}$$

and then the second derivative

$$-\hbar^2\frac{\partial^2 \Psi}{\partial x^2} = p^2\Psi \tag{2.1.12}$$

The energy and momentum for a *nonrelativistic* free particle (i.e., all energy is kinetic with no potential energy involved) are related by

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{2.1.13}$$

Substituting Equations 2.1.12 and 2.1.10 into Equation 2.1.13 shows that $\Psi(x,t)$ satisfies the following partial differential equation

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} \tag{2.1.14}$$

Equation 2.1.14 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

$$E = \frac{p^2}{2m} + V(x) \tag{2.1.15}$$

we postulate that Equation 2.1.3 for matter waves can be generalized to

$$\underbrace{i\hbar\frac{\partial \Psi(x,t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x,t)}_{\text{time-dependent Schrödinger equation in 1D}} \tag{2.1.16}$$

For matter waves in three dimensions, Equation 2.1.6 is then expanded

$$\underbrace{i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\Psi(\vec{r},t)}_{\text{time-dependent Schrödinger equation in 3D}} \tag{2.1.17}$$

Here the potential energy and the wavefunctions Ψ depend on the three space coordinates x, y, z, which we write for brevity as $\vec{r}$. Notice that the potential energy is assumed to depend on position only and not time (i.e., particle motion). This is applicable for conservative forces that a potential energy function $V(\vec{r})$ can be formulated.

The Laplacian Operator

The three second derivatives in parentheses together are called the Laplacian operator, or del-squared,

$$\begin{aligned}\nabla^2 &= \nabla\cdot\nabla \\ &= \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\end{aligned} \tag{2.1.18}$$

with the del operator,

$$\nabla = \left(\vec{x}\frac{\partial}{\partial x}+\vec{y}\frac{\partial}{\partial y}+\vec{z}\frac{\partial}{\partial z}\right) \tag{2.1.19}$$

Remember from basic calculus that when the del operator is direclty operates on a field (e.g, $\nabla f(x,y,x)$, it denotes the gradient (i.e, the locally steepest slope) of the field. The symbols with arrows in Equation 2.1.19 are unit vectors.

Equation 2.1.17 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 2.1.7 can be separated from the space-only factor (via the *Separation of Variables* technique discussed in Section 2.2)

$$\Psi(\vec{r},t) = \psi(\vec{r})e^{-iEt/\hbar} \tag{2.1.20}$$

where $\psi(\vec{r})$ is a wavefunction dependent (or time-independent) wavefuction that only depends on space coordinates. Putting Equation 2.1.20 into Equation 2.1.17 and cancelling the exponential factors, we obtain the time-independent Schrödinger equation:

$$\underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\psi(\vec{r})=E\psi(\vec{r})}_{\text{time-independent Schrödinger equation}} \tag{2.1.21}$$

The overall form of the Equation 2.1.21 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 2.1.17 (i.e., $\Psi(\vec{r},t)$). That does **not imply** that there is no time dependence to the wavefunction. Equation 2.1.20 argues that the time-dependent (i.e., full spatial and temporal) wavefunction ($\Psi(\vec{r},t)$) differs from from the time-independent (i.e., spatial only) wavefunction $\psi(\vec{r})$ by a "phase factor" of constant magnitude. Using the Euler relationship in Equation 2.1.4, the total wavefunction above can be expanded

$$\Psi(\vec{r},t) = \psi(\vec{r})\left(\cos\frac{Et}{\hbar}-i\,\sin\frac{Et}{\hbar}\right) \tag{2.1.22}$$

This means the total wavefunction has a **complex behavior** with a real part and an imaginary part. Moreover, using the trigonometry identity $\sin(\theta)=\cos(\theta-\pi/2)$ Equation 2.1.22 can further simplified to

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

This shows that both the real and the imaginary components of the total wavefunction oscillate, the imaginary part of the total wavefunction oscillates **out of phase** by $\frac{\pi}{2}$ with respect to the real part.

Note that while all wavefunctions have a time-dependence, that dependence may not impact in simple quantum problems as the next sections discuss and can often be ignored.

Before we embark on this, however, let us pause to comment on the validity of quantum mechanics. Despite its weirdness, its abstractness, and its strange view of the universe as a place of randomness and unpredictability, quantum theory has been subject to intense experimental scrutiny. It has been found to agree with experiments to better than $10^{-10}\%$ for all cases studied so far. When the Schrödinger Equation is combined with a quantum description of the electromagnetic field, a theory known as *quantum electrodynamics*, the result is one of the most accurate theories of matter that has ever been put forth. Keeping this in mind, let us forge ahead in our discussion of the quantum universe and how to apply quantum theory to both model and real situations.

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2.2: The Postulates of Quantum Mechanics

There are only a small number of postulates of quantum mechanics. Upon them is built all of the conclusions of this powerful theory.

Postulate 1

The state of a quantum-mechanical system is completely specified by a function $\Psi(\mathbf{r},\mathbf{t})$ that depends on the coordinates of the particle $(\mathbf{r})$ and the time $(\mathbf{t})$. This function, called the wavefunction has the important property that

$$\Psi^*(\mathbf{r},\mathbf{t})\Psi(\mathbf{r},\mathbf{t})\mathbf{dxdydz}$$

is the probability of finding the particle within the infinitesimally small volume element dxdydz located at position $\mathbf{r}$ at time $\mathbf{t}$.

Postulate 2

To every physical observable in classical mechanics, there corresponds an operator in quantum mechanics. This operator will be both linear and Hermitian.

Postulate 3

In any measurement of the observable associated with the operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a which satisfy the eigenvalue equation

$$\hat{A}\phi = a\phi$$

It is important to note that the wavefunction describing the particle need not be an eigenfunction of the operator Â. However, well defined wavefunctions (those meeting the requirements of all of the postulates of quantum mechanics) will have the possibility of being described as a linear combination of eigenfunctions of any of the needed operators. The Superposition Principle is invaluable in working with this concept.

Postulate 4

If a system is in a state described by a normalized wavefunction (Ψ) then the average measured value of the observable corresponding to $\hat{A}$ is given by

$$\langle a\rangle = \int \Psi^*\hat{A}\Psi d\tau \quad \text{or} \quad \langle a\rangle = \frac{\int \Psi^*\hat{A}\Psi d\tau}{\int \Psi^*\Psi d\tau}$$

Postulate 5

The wavefunction of a system evolves in time according to the time dependent Schrödinger equation

$$\hat{H}\Psi(\mathbf{r},t) = i\hbar\frac{\partial}{\partial}\Psi(\mathbf{r},t)$$

Each of these postulates has important consequences and ramifications as to what quantum theory can (and cannot) tell us about a particle or system. In the remainder of this section, we will explore each postulate individually in order to lay a foundation of what quantum mechanics can predict for us about the nature of matter.

Postulate 1: a Squared Wavefunction is a Probability Distribution

This postulate describes the commonly accepted interpretation of a wavefunction. First and foremost, a wavefunction is a mathematical function. It must be single valued in that for each point in space, there is only one value that can be calculated from the function. When considering all space which a particle may occupy, the squared wavefunction must create a smooth [1] and continuous probability distribution describing where the particle might be observed to be located. (for our purposes, "smooth" means that the first derivative of the function must be continuous.) Since the square of the wavefunction is a probability distribution for the location of the particle, any location in space where the squared wavefunction is zero, has a corresponding probability of zero that the particle will be observed at that location.

Example 2.2.1

Consider a particle of mass m in box of length a that is prepared such that it's wave function is given by

$$\psi(x) = \sqrt{\frac{30}{a^5}} \cdot x(a-x)$$

Calculate the probability that the particle will have a position measurement reveal the particle to be in the middle half of the box (with the measured position satisfying $a/4 \leq x \leq 3a/4$.)

Solution

The squared wavefunction gives the probability distribution for where the particle's position will be measured to be.

$$(\psi(x))^2 = \frac{30}{a^5}\left(a^2x^2 - 2ax^3 + x^4\right)$$

The total probability will be given by the following integral.

$$\begin{aligned} P &= \int_{a/4}^{3a/4} [\psi(x)]^2 dx \\ &= \frac{30}{a^5}\int_{a/4}^{3a/4} \left(a^2x^2 - 2ax^3 + x^4\right) dx \\ &= \frac{30}{a^5}\left[\frac{a^2x^3}{3} - \frac{2ax^4}{4} + \frac{x^5}{5}\right]_{a/4}^{3a/4} \\ &= \frac{30}{a^5}\left(\frac{27a^5}{192} - \frac{162a^5}{1024} + \frac{243a^5}{5120} - \frac{a^5}{192} + \frac{2a^5}{1024} - \frac{a^5}{5120}\right) \\ &= \frac{30}{a^5}\left(\frac{26a^5}{192} - \frac{164a^5}{1024} + \frac{242a^5}{5120}\right) \\ &= 0.520 \end{aligned}$$

Note that the final probability is unitless!

[1] The wavefunction will be smooth provided that the potential energy function is not discontinuous. A discontinuous potential energy function (such as a step function) will lead to a wavefunction that which single-valued, will not have a continuous first derivative, and therefore, not be "smooth" in the strictest sense.

The wavefunction contains all of the information about a system that is needed to understand how the system behaves and how it will behave in the future, at least within the limits of the quantum theory! Information on such properties as energy, momentum and position are all contained in the wavefunction.

Postulate 2: Quantum Mechanical Operators

The second postulate describes the nature of quantum mechanical operators and their relationship to those properties of a system which we can observe. The operators are the tools that pull physical information from the wavefunction and reveal the properties of the quantum mechanical system. The following table shows some operators and their corresponding physically observable quantities.

	Physical Observable	One Dimension	Three Dimensions
$\hat{x}$	Position	$\mathbf{x}$	$\mathbf{r}$
$\hat{p}$	Momentum	$-i\hbar\frac{d}{dx}$	$-i\hbar\vec{\nabla}$
$\hat{H}$	Energy	$\hat{T}+\hat{U}$	
$\hat{T}$	Kinetic	$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$	$-\frac{\hbar^2}{2m}\nabla^2$
$\hat{U}$	Potential	$\mathbf{U(x)}$	$\mathbf{U(r)}$

Each of these operators will have two very important properties. 1) Each is **linear** and 2) each is **Hermitian**. In one dimension, an operator ($\hat{A}$) is defined to be linear if the following condition holds:

$$\hat{A}(af(x) + bg(x)) = a\hat{A}f(x) + b\hat{A}g(x)$$

where a and b are scalar values. An example of a linear operator is multiplication by a constant or a function. Taking a derivative (or integrating) is also a linear operation, as is adding a constant or a function. An example of a non-linear operator is taking a logarithm or raising a function to a power other than one.

The Hermitian nature of quantum mechanical operators has many important consequences. An operator ($\hat{A}$) is Hermitian if it satisfies the following relationship:

$$\int g^* \hat{A} f d\tau = \int f \hat{A}^* g^* d\tau$$

for well-behaved [2] functions f and g, where the asterisk ($*$) indicated the complex conjugate of the function or operator. Hermitian operators have the important properties that 1) their

[2] A well-behaved function is one that is normalizable and continuous over the relevant space of the problem.

Example 2.2.1

Is the operator $\frac{d}{dx}$ a Hermitian operator?

Solution

For an operator $\hat{A}$ to be Hermitian, the following relationship must hold (for wellbehaved functions f and g :

$$\int g^* \hat{A} f d\tau = \int f \hat{A}^* g^* d\tau$$

So if we choose arbitrary functions f and g, we can evaluate the left-hand side of the above relationship by noting the pattern $d(uv) = udv + vdu$ and integrating by parts. Using this approach

$$\int udv = uv - \int vdu$$

Making the substitutions that

$$u = g^*$$
$$dv = \frac{d}{dx} f dx$$

it should be clear that

$$du = \frac{d}{dx} g^* dx$$
$$v = f$$

So

$$\int g^* \frac{d}{dx} f dx = g^* f|_{-\infty}^{\infty} - \int f \frac{d}{dx} g^* dx$$

In order for f and g to meet the criteria that they are normalizable, they must vanish as x approaches $\pm\infty$. As such,

$$g^* f|_{-\infty}^{\infty} = 0$$

And we are left with

$$\int g^* \frac{d}{dx} f dx = -\int f \frac{d}{dx} g^* dx$$

Which clearly can not be true. Therefore, the operator $\frac{d}{dx}$ is not Hermitian. You should, however, be able to use the same method to show that the operator $\hat{A} = i\frac{d}{dx}$ is in fact Hermitian!

Postulate 3: Measurable Values

Postulate three states that the only measurable values for a system are those values that are eigenvalues of the corresponding quantum mechanical operator. The first measurable value which we will explore is the energy of the system (see below.) Because the wavefunction provides a probability distribution, it also provides a means of predicting the statistics for a theoretical infinite set of measurements on a system. The ramifications of that point are developed in the discussion of the fourth postulate.

Postulate 4: Expectation Values

An expectation value is an average value that would be expected based on an infinite number of measurements. Since wavefunctions give us probability information, it stands to reason that we can calculate a great deal of statistical information about a system based on the wavefunction and the corresponding operators. This will be discussed in detail in section D with regards to expectation values calculated for position, momentum and energy. It is important to note that the expectation value does not indicate the most probable measurement or observation that will be made, nor must it even give a value that can ever be measured; it just gives the average.

This postulate has very important (and controversial) ramifications. It forms the basis for how the Heisenberg Uncertainty Principle can be discussed. The problem is that quantum mechanics cannot tell you what will be measured, but rather only the probability that a certain value can be measured for a specific property. While a subtle point, it shakes the very nature of our intuition as to what it means for a system to have a certain property. In most cases, the properties we associate with classical particles do not even exist in quantum mechanical particles (at least in any sense to which we are accustomed) until those properties are measured. This has led to numerous debates as to the validity of quantum mechanics as a model, and even led one of the original developers of quantum theory (Erwin Schrödinger) to change his mind completely on the model.

Postulate 5: the evolution of a system in time

The 5^{th} postulate indicates how a system will evolve in time. It also gives the definition of the time dependent Schrödinger equation.

We will explore many of these properties based on the particle in a box problem in order to gain some insight into what quantum mechanics can and can not tell us about a system. The particle in a box problem actually has limited physical application (although it does have some), but does provide a "thought sandbox" in which we can explore the concepts, powers and limitations of the quantum theory. Hopefully then when we apply the theory to problems of greater chemical interest, we can focus more on the conclusions than on the specific mathematics.

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2.3: The Wavefunction Specifies the State of a System

Learning Objectives

- Introduce the first postulate of quantum mechanics
- Recognize invalid wavefunction categories

In classical mechanics, the configuration or state of a system is given by a point (x,p) in the space of coordinates and momenta. This specifies everything else in the system in a fully deterministic way, in that any observable Q that can be expressed as $Q(x,p)$ can be found, and any that cannot is irrelevant. Yet, as we have seen with the diffraction of electrons, it is **impossible** to know both the position and momentum of the electron exactly at every point along the trajectory. This is mathematically expressed as the famous position-momentum uncertainty principle. Hence, specifying a state by (x,p) in classical mechanics clearly will not work in quantum mechanics. So what specifies the state of a quantum system? This is where the **first Postulate of quantum mechanics** comes in.

Postulate I

The state of the system is **completely** specified by ψ. All possible information about the system can be found in the wavefunction ψ.

The properties of a quantum mechanical system are determined by a wavefunction $\psi(r,t)$ that depends upon the spatial coordinates of the system and time, r and t. For a single particle system, r is the set of coordinates of that particle $r=(x_1,y_1,z_1)$. For more than one particle, r is used to represent the complete set of coordinates $r=(x_1,y_1,z_1,x_2,y_2,z_2,\ldots x_n,y_n,z_n)$. 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).

$$P(x)=\psi^*(x)\psi(x) \tag{2.3.1}$$

$$=|\psi(x)|^2 \tag{2.3.2}$$

Hence, for valid (e.g., well-behaved) wavefunctions, the normalized probability in Equation 2.3.2 holds true, such that the integral over all space is equal to 1.

$$\int_{-\infty}^{\infty}\psi^*(x)\psi(x)\,dx=1 \tag{2.3.3}$$

Equation 2.3.3 means that the chance to find a particle is 100% somewhere within all space (e.g. somewhere between $-\infty$ and $+\infty$). A wavefunction is said to be **square-integrable** if Equation 2.3.3 can be satisfied (so that the Born Interpretation to be applicable).

Definition: Square-Integrable Functions

A complex-valued function, $f(x)$, is a *square-integrable* function if the integral of the square of the absolute value is finite.

$$\int_{-\infty}^{\infty}f^*(x)f(x)\,dx<\infty$$

For this to be true, the integrals of the positive and negative portions of the real and imaginary parts of $f(x)$ must both be finite.

Let us examine this set of examples in further detail in Figure 4.1.1 . The first wavefunction ψ_1 is sharply peaked at a particular value of x, and the probability density, being its square, is likewise peaked there as well. This is the wavefunction for a particle well localized at a position given by the center of the peak, as the probability density is high there, and the width of the peak is small, so the uncertainty in the position is very small.

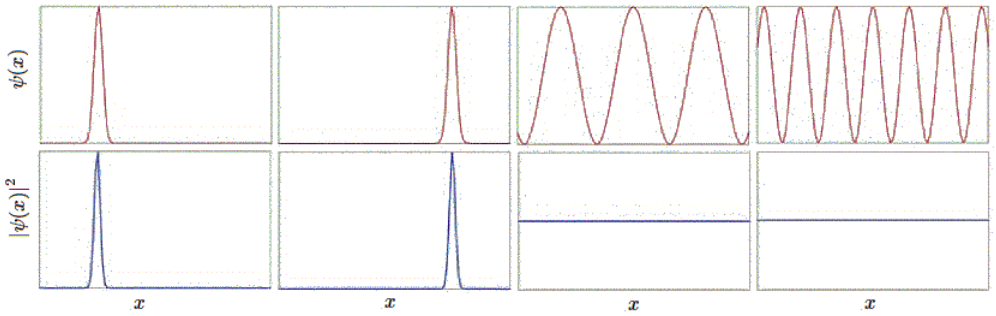


Figure 4.1.1 : Examples of good wavefunctions, $\psi(x)$, (red, top) and corresponding probability densities, $P(x)$, (blue, bottom).

The second wavefunction ψ_2 has the same peak profile, but shifted to a different position center. All of the properties of the first wavefunction hold here too, so this simply describes a particle that is well-localized at that different position. The third and fourth wavefunctions ψ_3 and ψ_4 respectively look like sinusoids of different spatial periods. The wavefunctions are actually complex of the form

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

so only the real part is being plotted in Figure 4.1.1 . Note that even though the periods, k, of the oscillating wavefunctions are different,

$$\begin{aligned} P(x) &= \psi^*(x)\psi(x) \\ &= |e^{ikx}|^2 \\ &= N^2 \left(e^{-ikx}\right)\left(e^{ikx}\right) \\ &= N^2 \end{aligned}$$

for all k, so the corresponding probability densities, $P(x)$, are the same except for the normalization constant (Equation 2.3.2). 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.

2.3.1: Ill-behaved (invalid) Wavefunctions

The Born interpretation in Equation 2.3.2 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 2.3.3 is equal to infinity. This implies that the particle described by such a wavefunction has a zero probability of being anywhere where the wavefunction is not infinite, but is certain to be found at all points where the wavefunction is infinite.

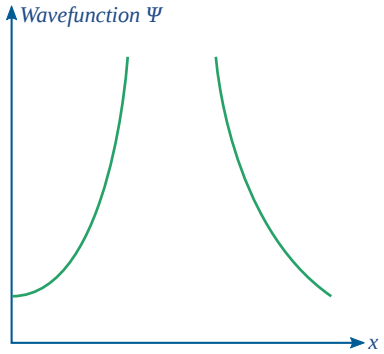


Figure 4.1.2 : This function is an invalid wavefunction since the amplitude is going to infinity over a region (the middle in this case). (CC BY-NC; Ümit Kaya via LibreTexts)

The Born interpretation also renders unacceptable solutions of the Schrödinger equation for which $|\psi(x)|^2$ has more than one value at any point. This would suggest that there were multiple different probabilities of finding the particle at that point, which is clearly absurd. The requirement that the square modulus of the wavefunction must be single-valued usually implies that the wavefunction itself must be single valued. The function in Figure 4.1.3 violates this requirement. The grey lines indicate the region where the wavefunction is multivalued.

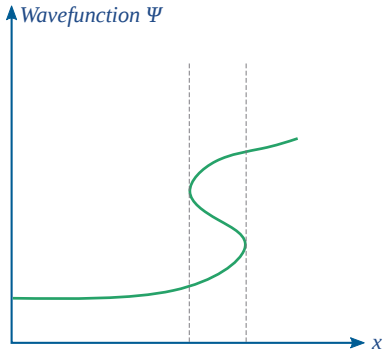


Figure 4.1.3 : This function is an invalid wavefunction since it is not a proper function (i. e., not one-to-one). (CC BY-NC; Ümit Kaya via LibreTexts)

Further restrictions arise because the wavefunction must satisfy the Schrödinger equation, which is a second-order differential equation. This implies that the second derivative of the function must exist, which implies that the first derivative of the wavefunction to exist (otherwise the second derivative is also undefined and the wavefunction cannot be a solution of the Schrödinger equation). The functions in Figure 4.1.4 are also not acceptable for these reasons.

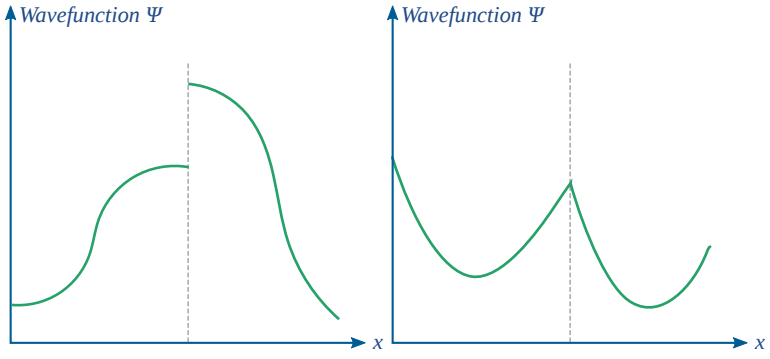


Figure 4.1.4 : These functions are invalid wavefunctions. (left) The first derivative of a function gives its gradient at a given point, and it thus exists as long as the function is continuous - only if there is a break in the function is there a point at which its first derivative does not exist. (right) The second derivative of this wavefunction is discontinuous at the point indicated, where the gradient of the line changes by more than 180°. In practice, this requirement may be somewhat flexible, particularly if the potential energy of the system shows rapid changes with distance. (CC BY-NC; Ümit Kaya via LibreTexts)

Exercise 4.1.1

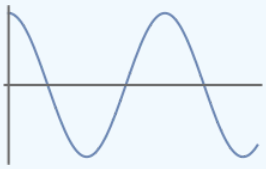
Determine if each of the following functions is acceptable as a wavefunction over the indicated regions:

a. $\cos x$ over $(0, \infty)$
b. e^{x} over $(-\infty, \infty)$
c. e^{-x} over $[0, \infty)$
d. $\tan \theta$ over $[0, 2\theta]$

Solution a

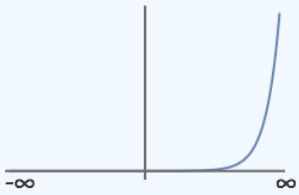
This is not an acceptable wavefunction. It is **single-valued** across the entire range. There is a single value for each value of x. It is **continuous** over the defined limits of integration, as we can see from a plot given below. However, it is not square-integrable.

$$\int_0^{\infty} |\cos(x)|^2 dx \not< \infty$$



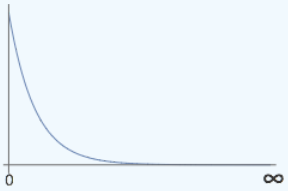
Solution b

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 ∞.



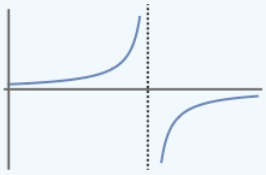
Solution c

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



Solution d

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



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2.4: Wavefunctions Have a Probabilistic Interpretation

Learning Objectives

- To understand that wavefunctions can have probabilistic interpretations.
- To calculate the probabilities directly from a wavefunctions

For a single-particle system, the wavefunction $\Psi(\vec{r},t)$, or $\psi(\vec{r})$ for the time-independent case, represents the amplitude of the still vaguely defined matter waves. Since wavefunctions can in general be complex functions, the physical significance cannot be found from the function itself because the $\sqrt{-1}$ is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e. the absolute square of the wavefunction, which also is called the **square of the modulus** (also called absolute value).

$$P(\vec{r},t) = \Psi^*(\vec{r},t)\Psi(\vec{r},t) \tag{2.4.1}$$

$$= |\Psi(\vec{r},t)|^2 \tag{2.4.2}$$

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 2.4.2) 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

$$P(x \in [a,b]) = \int_a^b |\psi(x)|^2 dx \tag{2.4.3}$$

In three dimensions, Equation 2.4.3 is represented differently

$$P(x \in [a,b]) = \int_V |\psi(\vec{r})|^2 d\tau \tag{2.4.4}$$

This integration extends over a specified volume (V) with the symbol $d\tau$ designating the appropriate volume element (including a Jacobian) of the coordinate system adopted:

- Cartesian:

$$d\tau = dx\,dy\,dz$$

- Spherical:

$$d\tau = r^2 \sin\phi\, dr\, d\theta\, d\phi$$

- Cylindrical:

$$d\tau = r\, dr\, d\phi\, dz.$$

For rectilinear Cartesian space, Equation 2.4.4 can be is expanded with dimension explicitly indicated

$$P(x \in [a,b]) = \int_{a_x}^{b_x} \int_{a_y}^{b_y} \int_{a_z}^{b_z} |\psi(x,y,z)|^2 dx\, dy\, dz \tag{2.4.5}$$

where the limits of integration are selected to encompass the volume V of consideration.

The Born interpretation (Equation 2.4.2) of relating the wavefunction to probability forces certain demands on its mathematical behavior of wavefunctions and not any mathematical function can be a valid wavefunction.

Required Properties of Wavefunction

- The wavefunction must be a *single-valued function* of all its coordinates, since the probability density ought to be *uniquely determined* at each point in space.
- The wavefunction should be both *finite* as an infinite probability has no meaning.
- The wavefunction should be *continuous everywhere*, as expected for a physically-meaningful probability density.

The conditions that the wavefunction be single-valued, finite and continuous--in short, "well behaved"-- lead to restrictions on solutions of the Schrödinger equation such that only certain values of the energy and other dynamical variables are allowed. This is called *quantization* and is in the feature that gives *quantum* mechanics its name.

It is important to note that this interpretation implies the wavefunction does **not** mean the particle is distributed over a large region as a sort of "charge cloud". The wavefunction is used to describe the electron motion that behaves like waves and satisfies a wave equation. This is akin to how a grade distribution in a large class does not represent a smearing of grades for a single student, but only makes sense when taking into account that the distribution is the result of many measurables (e.g., student performances).

Example 3.4.1

Show that the square of the modulus of $\Psi(\vec{r},t) = \psi(\vec{r})e^{-i\omega t}$ is time independent. What insight regarding stationary states do you gain from this proof?

Example 3.4.2

According to the Born interpretation, what is the physical significance of $e\psi^*(r_0)(r_0)d\tau$?

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2.5: Wavefunctions Must Be Normalized

Learning Objectives

- Calculate the probability of an event from the wavefunction
- Understand the utility and importance of normalizing wavefunctions
- Demonstrate how to normalize an arbitrary wavefunction

2.5.1: Extracting Probabilities

Since wavefunctions can in general be complex functions, the physical significance of wavefunctions cannot be found from the functions themselves because the $\sqrt{-1}$ is not a property of the physical world. Rather, the physical significance is found in the product of the wavefunction and its complex conjugate, i.e. the absolute square of the wavefunction, which also is called the **square of the modulus**.

$$\Psi^*(r,t)\Psi(r,t) = |\Psi(r,t)|^2 \tag{2.5.1}$$

where r is a vector specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field. Remember that the Born interpretation is that $\psi^*(r_i)\psi(r_i)\,d\tau$ is the **probability** that the electron is in the volume $d\tau$ located at r_i. The Born interpretation therefore calls the wavefunction the probability amplitude, the absolute square of the wavefunction is called the **probability density**, and the probability density times a volume element in three-dimensional space ($d\tau$) is the probability.

Since the squared magnitude $|\psi|^2$ of the wavefunction of a particle can be interpreted as the probability density, then the probability for a one-dimensional wavefunction between the points $x = a$ and $x = b$ can be calculated by

$$P_{1D} = \int_a^b |\psi(x)|^2 \mathrm{d}x \tag{2.5.2}$$

This is just the area under the under the $|\psi|^2$ curve (Figure 3.6.1).

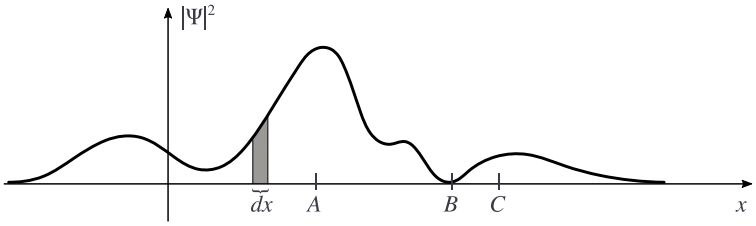


Figure 3.6.1 : The probability can be interpreted as an area under the probability density $|\psi|^2$. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

If the probability of a two-dimensional wavefunction is being evaluated, then Equation 2.5.2 will be amended to included a double integral:

$$P_{2D} = \iint_{a_1,a_2}^{b_1,b_2} |\psi(x,y)|^2 \mathrm{d}x\mathrm{d}y$$

and similarly a triple integral would be used for calculating probabilities of three-dimensional wavefunctions:

$$P_{3D} = \iiint_{a_1,a_2,a_3}^{b_1,b_2,b_3} |\psi(x,y,z)|^2 \mathrm{d}x\mathrm{d}y\mathrm{d}z$$

Example 3.6.1 : Probability of a Particle in a Box

Calculate the probability of finding an electron at $L/2$ in a box of infinite height within an interval ranging from $\frac{L}{2} - \frac{L}{200}$ to $\frac{L}{2} + \frac{L}{200}$ for the $n = 1$ and $n = 2$ states. Since the length of the interval, $L/100$, is small compared to L, you can get an approximate answer without explicitly integrating.

Solution

The wavefunction for the particle in a box is

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

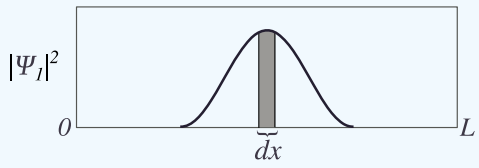
and the wavefunction for the $n = 1$ state is

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

From the interpretation that the wavefunction modulus squared is the probability density, we can establish the following integral to solve the problem (note the limits of integration)

$$|\psi_{n=1}|^2 = \frac{2}{L} \int_{\frac{99L}{200}}^{\frac{101L}{200}} \sin^2\left(\frac{\pi x}{L}\right) dx \tag{2.5.3}$$

We can solve this, but we can also recognize that Equation 2.5.3 is just calculating an area that can be approximated as the area of a rectangle with a height ($\frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)$ at $x = L/2$) and width $\Delta x = L/100$ (Figure 3.6.2).



(a)

Figure 3.6.2 : The probability can be interpreted as an area under the probability density $|\psi_1|^2$. (CC BY-NC; Ümit Kaya via LibreTexts)

This area can be computed:

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

Given that the wavefunction is sinusoidal, the actual probability of finding an electron within the given interval at $\frac{L}{2}$ should be slightly less because of the behavior of the sinusoid at $\frac{L}{2}$ is at its peak of the wavefunction (Figure 3.6.2).

The wavefunction for the $n = 2$ state

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

so the integral that we need to construct and solve is

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

We can use the same graphical interpretation as above, but using the probability density of the ψ_2 wavefunction (Figure 3.6.3).

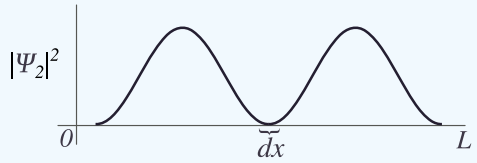


Figure 3.6.3 : The probability can be interpreted as an area under the probability density $|\psi_2|^2$. (CC BY-NC Copyright; Ümit Kaya via LibreTexts)

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

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

Exercise 3.6.1

Show that the square of the modulus of $\Psi(r,t) = \psi(r)e^{-i\omega t}$ is time independent. What insight regarding stationary states do you gain from this proof?

Solution

The square of the modulus of a wavefunction is $\Psi(r,t)^*\Psi(r,t)$ so for wavefunctions of this form, the square of the modulus is

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

Hence, there is no time dependence to the modulus of wavefunctions of this work, which from the probability interpretation of the wavefunction means that the probability density is time-independent.

2.5.2: Normalizing of the Wavefunction

A probability is a real number between 0 and 1, inclusive. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. According to Equation 2.5.1, the probability of a measurement of x yielding a result between $-\infty$ and $+\infty$ is

$$P_{x\in-\infty:\infty}(t) = \int_{-\infty}^{\infty}|\psi(x,t)|^2dx. \tag{2.5.4}$$

However, a measurement of x *must* yield a value between $-\infty$ and $+\infty$, since the particle has to be located somewhere. It follows that $P_{x\in-\infty:\infty}(t) = 1$, or

$$\int_{-\infty}^{\infty}|\psi(x,t)|^2dx = 1, \tag{2.5.5}$$

which is generally known as the **normalization condition** for the wavefunction.

Example 3.6.2 : Normalizing a Gaussian Wavepacket

Normalize the wavefunction of a Gaussian wave packet, centered on $x = x_o$ with characteristic width σ:

$$\psi(x) = \psi_0 e^{-(x-x_0)^2/(4\sigma^2)}. \tag{2.5.6}$$

Solution

To determine the normalization constant ψ_0, we simply substitute Equation 2.5.6 into Equation 2.5.5, 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

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

However, from an integral table we know

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

which implies that

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

Hence, a general normalized Gaussian wavefunction takes the form

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

where ϕ is an arbitrary real phase-angle.

? Exercise 3.6.2

Normalize this wavefunction for a particle in a harmonic well:

$$\psi = xe^{-x^2}$$

Answer

$$\psi = 2\left(\frac{2}{\pi}\right)^{1/4} xe^{-x^2}$$

2.5.3: Time Dependence to the Wavefunction

Now, it is important to demonstrate that if a wavefunction is initially normalized then it stays normalized as it evolves in time according to the time-dependent Schrödinger's equation. If this is not the case then the probability interpretation of the wavefunction is untenable, since it does not make sense for the probability that a measurement of x yields *any* possible outcome (which is, manifestly, unity) to change in time. Hence, we require that

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

for wavefunctions satisfying the time-dependent Schrödinger's equation (this results from the time-dependent Schrödinger's equation and Equation 2.5.5). The above equation gives

$$\frac{d}{dt} \int_{-\infty}^{\infty} \psi^* \psi \, dx = \int_{-\infty}^{\infty} \left(\frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} \right) dx = 0. \tag{2.5.7}$$

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

$$\psi^* \frac{\partial \psi}{\partial t} = \frac{\mathrm{i}}{2m} \psi^* \frac{\partial^2 \psi}{\partial x^2} - \frac{\mathrm{i}}{\hbar} V |\psi|^2 \tag{2.5.8}$$

The complex conjugate of this expression yields

$$\psi \frac{\partial \psi^*}{\partial t} = -\frac{\mathrm{i}}{2m} \psi \frac{\partial^2 \psi^*}{\partial x^2} + \frac{\mathrm{i}}{\hbar} V |\psi|^2 \tag{2.5.9}$$

since

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

- $i^* = -i$.

Summing Equation 2.5.8 and 2.5.9 results in

$$\frac{\partial \psi^*}{\partial t}\psi + \psi^*\frac{\partial \psi}{\partial t} = \frac{\mathrm{i}}{2m}\left(\psi^*\frac{\partial^2 \psi}{\partial x^2} - \psi\frac{\partial^2 \psi^*}{\partial x^2}\right) \tag{2.5.10}$$

$$= \frac{\mathrm{i}}{2m}\frac{\partial}{\partial x}\left(\psi^*\frac{\partial \psi}{\partial x} - \psi\frac{\partial \psi^*}{\partial x}\right). \tag{2.5.11}$$

Equations 2.5.7 and 2.5.11 can be combined to produce

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2 dx = \frac{\mathrm{i}}{2m}\left[\psi^*\frac{\partial \psi}{\partial x} - \psi\frac{\partial \psi^*}{\partial x}\right]_{-\infty}^{\infty} = 0. \tag{2.5.12}$$

The above equation is satisfied provided the wavefunction converges

$$\lim_{|x|\to\infty}|\psi| = 0 \tag{2.5.13}$$

However, this is a necessary condition for the integral on the left-hand side of Equation 2.5.5 to converge. Hence, we conclude that all wavefunctions which are *square-integrable* [i.e., are such that the integral in Equation 2.5.5 converges] have the property that if the normalization condition Equation 2.5.5 is satisfied at one instant in time then it is satisfied at all subsequent times.

Not all Wavefunctions can be Normalized

Not all wavefunctions can be normalized according to the scheme set out in Equation 2.5.5. For instance, a planewave wavefunction for a quantum free particle

$$\Psi(x,t) = \psi_0 \mathrm{e}^{\mathrm{i}(kx-\omega t)}$$

is not square-integrable, and, thus, cannot be normalized. For such wavefunctions, the best we can say is that

$$P_{x\in a:b}(t) \propto \int_a^b |\Psi(x,t)|^2 dx.$$

In the following, all wavefunctions are assumed to be square-integrable and normalized, unless otherwise stated.

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2.6: 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)

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{2.6.1}$$

is called an *operator*. An operator is a generalization of the concept of a function applied to a function. Whereas a function is a rule for turning one number into another, an operator is a rule for turning one function into another. For the time-independent Schrödinger Equation, the operator of relevance is the Hamiltonian operator (often just called the Hamiltonian) and is the most ubiquitous operator in quantum mechanics.

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

We often (but not always) indicate that an object is an operator by placing a 'hat' over it, eg, $\hat{H}$. So time-independent Schrödinger Equation can then be simplified from Equation 2.6.1 to

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \tag{2.6.2}$$

Equation 2.6.2 says that the Hamiltonian operator operates on the wavefunction to produce the energy, which is a scalar (i.e., a number, a quantity and observable) times the wavefunction. Such an equation, where the operator, operating on a function, produces a constant times the function, is called an **eigenvalue equation**. The function is called an eigenfunction, and the resulting numerical value is called the eigenvalue. Eigen here is the German word meaning self or own. We will discuss this in detail in later Sections.

2.6.1: Fundamental Properties of Operators

Most properties of operators are straightforward, but they are summarized below for completeness.

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

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

2. The product of two operators is defined by

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

3. Two operators are equal if

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

   for **all** functions f.
4. The identity operator $\hat{1}$ does nothing (or multiplies by 1)

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

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

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

6. The *associative law* holds for operators

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

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

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}. \tag{2.6.3}$$

To help identify if the inequality in Equation 2.6.3 holds for any two specific operators, we define the commutator.

Definition: The Commutator

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

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

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

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

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

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

2.6.2: Linear Operators

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

$$\hat{A}f(x) = g(x) \tag{2.6.4}$$

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

$$\underset{\text{Condition A}}{\hat{O}(f(x) + g(x)) = \hat{O}f(x) + \hat{O}g(x)} \tag{2.6.5}$$

and

$$\underset{\text{Condition B}}{\hat{O}cf(x) = c\hat{O}f(x)} \tag{2.6.6}$$

where

- $\hat{O}$ is a linear operator,
- c is a constant that can be a complex number ($c = a + ib$), and
- $f(x)$ and $g(x)$ are functions of x

If an operator fails to satisfy either Equations 2.6.5 or 2.6.6 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 2.6.6 must be demonstrated.

Condition A (Equation 2.6.5):

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

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

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

Condition A is confirmed. Does Condition B (Equation 2.6.6) hold?

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

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

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

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 2.6.5 and 2.6.6 must be demonstrated. Let's look first at Condition B.

Does Condition B (Equation 2.6.6) hold?

$$\hat{O}cf(x) = c\hat{O}f(x)$$
$$\sqrt{cf(x)} \neq c\sqrt{f(x)}$$

Condition B does not hold, therefore the square root operator is not linear.

The most operators encountered in quantum mechanics are *linear operators*.

2.6.3: Hermitian Operators

An important property of operators is suggested by considering the Hamiltonian for the particle in a box:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Let $f(x)$ and $g(x)$ be arbitrary functions which obey the same boundary values as the eigenfunctions of $\hat{H}$ (e.g., they vanish at $x = 0$ and $x = a$). Consider the integral

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

Now, using integration by parts,

$$\int_0^a f(x)\,g''(x)\,\mathrm{d}x = -\int_0^a f'(x)\,g'(x)\,\mathrm{d}x + f(x)\,g'(x)\Big|_0^a \tag{2.6.7}$$

The boundary terms vanish by the assumed conditions on f and g. A second integration by parts transforms Equation 2.6.7 to

$$\int_0^a f''(x)\,g(x)\,\mathrm{d}x - f'(x)\,g(x)\Big|_0^a$$

It follows therefore that

$$\int_0^a f(x)\,\hat{H}\,g(x)\,\mathrm{d}x = \int_0^a g(x)\,\hat{H}\,f(x)\,\mathrm{d}x$$

An obvious generalization for complex functions will read

$$\int_0^a f^*(x)\,\hat{H}\,g(x)\,\mathrm{d}x = \left(\int_0^a g^*(x)\,\hat{H}\,f(x)\,\mathrm{d}x\right)^*$$

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

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

for all functions f and g which obey specified boundary conditions is classified as *Hermitian* or *self-adjoint*. Evidently, the Hamiltonian is a **Hermitian operator**. It is postulated that *all* quantum-mechanical operators that represent dynamical variables are Hermitian. The term is also used for specific times of matrices in linear algebra courses.

> *All quantum-mechanical operators that represent dynamical variables are Hermitian.*

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2.7: Quantum Operators Represent Classical Variables

Learning Objectives

- Understand how the correspondence principle argues that a unique quantum operator exist for every classical observable.
- Recognize several of the commonly used quantum operators

An observable is a dynamic variable of a system that can be experimentally measured (e.g., position, momentum and kinetic energy). In systems governed by classical mechanics, it is a real-valued function (never complex), however, in quantum physics, every observable in quantum mechanics is represented by an independent operator that is used to obtain physical information about the observable from the wavefunction. It is a general principle of quantum mechanics that there is an operator for every physical observable. For an observable that is represented in classical physics by a function $Q(x,p)$, the corresponding operator is $Q(\hat{x},\hat{p})$.

Postulate II: The Correspondence Principle

For every observable property of a system there is a corresponding quantum mechanical operator. This is often referred to as the **Correspondence Principle**.

Classical dynamical variables, such as x and p, are represented in quantum mechanics by *linear operators* which act on the wavefunction. The operator for position of a particle in three dimensions is just the set of coordinates x, y, and z, which is written as a vector, r:

$$\vec{r} = (x,y,z) \tag{2.7.1}$$

$$= x\vec{i} + y\vec{j} + z\vec{k} \tag{2.7.2}$$

The operator for a component of linear momentum is

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{2.7.3}$$

and the operator for kinetic energy in one dimension is

$$\hat{T}_x = \left(-\frac{\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} \tag{2.7.4}$$

and in three dimensions

$$\hat{p} = -i\hbar\nabla \tag{2.7.5}$$

and

$$\hat{T} = \left(-\frac{\hbar^2}{2m}\right)\nabla^2 \tag{2.7.6}$$

The total energy operator is called the Hamiltonian operator, $\hat{H}$ and consists of the kinetic energy operator plus the potential energy operator.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{2.7.7}$$

The Hamiltonian Operator

The Hamiltonian operator is named after the Irish mathematician William Hamilton and comes from the his formulation of Classical Mechanics that is based on the total energy:

$$\hat{H} = \hat{T} + \hat{V}$$

rather than Newton's second law,

$$\vec{F} = m\vec{a}$$

In many cases only the kinetic energy of the particles and the electrostatic or Coulomb potential energy due to their charges are considered, but in general all terms that contribute to the energy appear in the Hamiltonian. These additional terms account for such things as external electric and magnetic fields and magnetic interactions due to magnetic moments of the particles and their motion.

Table 4.2.1 : Some common Operators in Quantum Mechanics

Name	Observable Symbol	Operator Symbol	Operation
Position (in 1D)	x	$\hat{X}$	Multiply by x
Position (in 3D)	$\vec{r}$	$\hat{R}$	Multiply by $\vec{r}$
Momentum (in 1D)	p_x	$\hat{P}_x$	$-i\hbar\frac{d}{dx}$
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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2.8: The Schrödinger Equation is an Eigenvalue Problem

Learning Objectives

- To recognize that each quantum mechanical observable is determined by solve by an eigenvalue problem with different operators for different observable
- Confirm if a specific wavefunction is an eigenfunction of a specific operation and extract the corresponding obserable (the eigenvalue)
- To recognize that the Schrödinger equation, just like all measurable, is also an eigenvalue problem with the eigenvalue ascribed to total energy
- Identity and manipulate several common quantum mechanical operators

As per the definition, an operator acting on a function gives another function, however a special case occurs when the generated function is proportional to the original

$$\hat{A}\psi \propto \psi \tag{2.8.1}$$

This case can be expressed in terms of a equality by introducing a proportionality constant k

$$\hat{A}\psi = k\psi \tag{2.8.2}$$

Not all functions will solve an equation like in Equation 2.8.2. 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 ($\hat{A}$):

$$\hat{A}\psi = a\psi \tag{2.8.3}$$

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.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{2.8.4}$$

The object on the left that acts on $\psi(x)$ is an example of an **operator**.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right] \tag{2.8.5}$$

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

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{2.8.6}$$

Therefore, the time-dependent Schrödinger equation can be (and it more commonly) written as

$$\hat{H}\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \tag{2.8.7}$$

and the time-independent Schrödinger equation

$$\hat{H}\psi(x) = E\psi(x) \tag{2.8.8}$$

Note that the functional form of Equation 2.8.8 is the same as the general eigenvalue equation in Equation 2.8.2 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 2.8.8 says that the Hamiltonian operator operates on the wavefunction to produce the energy E, which is a scalar (e.g., expressed in Joules) times the wavefunction.

Correspondence Principle

Note that $\hat{H}$ is derived from the classical energy $p^2/2m + V(x)$ simply by replacing $p \rightarrow -i\hbar(d/dx)$. This is an example of the **Correspondence Principle** initially proposed by Niels Bohr that states that the behavior of systems described by quantum theory reproduces classical physics in the limit of large quantum numbers.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is then the eigenvalue, and the system is said to be in an eigenstate. Equation 2.8.8 states this principle mathematically for the case of energy as the observable. If the wavefunction is not the eigenfunction of the operation, then the measurement will give an eigenvalue (by definition), but not necessarily the same one for each measurement (this will be discussed in more detail in later section).

2.8.1: 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

  $$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{2.8.9}$$

  and can be generalized in three dimensions:

  $$\hat{\vec{p}} = -i\hbar\nabla \tag{2.8.10}$$

- **Position**

  The position operator of a particle moving in one dimension (the x-direction) is

  $$\hat{x} = x \tag{2.8.11}$$

  and can be generalized in three dimensions:

  $$\hat{\vec{r}} = \vec{r} \tag{2.8.12}$$

  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

  $$KE_{classical} = \frac{p_x^2}{2m} \tag{2.8.13}$$

  Quantum mechanically, the corresponding kinetic energy operator is

  $$\hat{KE}_{quantum} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{2.8.14}$$

  and can be generalized in three dimensions:

$$\hat{KE}_{quantum} = -\frac{\hbar^2}{2m}\nabla^2 \tag{2.8.15}$$

- **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 $\hat{p}$

$$\hat{\vec{L}} = -i\hbar(\vec{r} \times \nabla) \tag{2.8.16}$$

- **Hamiltonian:**

  The Hamiltonian operator corresponds to the total energy of the system

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{2.8.17}$$

  and it represents the total energy of the particle of mass m in the potential $V(x)$. The Hamiltonian in three dimensions is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{2.8.18}$$

- **Total Energy:**

  The energy operator from the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t) \tag{2.8.19}$$

  The right hand side of Equation 2.8.6 is the Hamiltonian Operator. In addition determining system energies, the Hamiltonian operator dictates the time evolution of the wavefunction

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{2.8.20}$$

  This aspect will be discussed in more detail elsewhere.

2.8.2: 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 2.8.6).
- If you want to measure the momentum of a particle, you have to operate on wavefunction with the momentum operator (Equation 2.8.9).
- If you want to measure the position of a particle, you have to operate on wavefunction with the position operator (Equation 2.8.11).
- If you want to measure the kinetic energy of a particle, you have to operate on wavefunction with the kinetic energy operator (Equation 2.8.14).

When discussing the eigenstates of the Hamiltonian ($\hat{H}$), the associated eigenvalues represent energies and within the context of the momentum operators, the associated eigenvalues refer to the momentum of the particle. However, not all wavefunctions (ψ) are eigenstates of an operator (ϕ) – and if they are not, they can be usually be written as superpositions of eigenstates.

$$\psi = \sum_i c_i\phi_i$$

This will be discussed in more detail in later sections.

While the wavefunction may not be the eigenstate of an observable, when that operator operates on that wavefunction, the wavefunction **becomes** an eigenstate of that observable and only eigenvalues can be observed. Another way to say this is that the

wavefunction "collapses" into an eigenstate of the observable. Because quantum mechanical operators have different forms, their associated eigenstates are similarly often (i.e., most of the time) different. For example, when a wavefunction is an eigenstate of total energy, it will **not** be an eigenstate of momentum.

> *If a wavefunction is an eigenstate of one operator, (e.g., momentum), that state is not necessarily an eigenstate of a different operator (e.g., energy), although not always.*

The wavefunction immediately after a measurement is an eigenstate of the operator associated with this measurement. What happens to the wavefunction after the measurement is a different topic.

Example 3.3.1

Confirm that the following wavefunctions are eigenstates of linear momentum and kinetic energy (or neither or both):

a. $\psi = A\sin(ax)$
b. $\psi = Ne^{-ix/\hbar}$

Strategy

This question is asking if the eigenvalue equation holds for the operators and these wavefunctions. This is just asking if these wavefunctions are solutions to Equation 2.8.2 using the operators in Equations 2.8.9 and 2.8.14, i.e., are these equations true:

$$\hat{p}_x\psi = p_x\psi \tag{2.8.21}$$

$$\hat{KE}\psi = KE\psi \tag{2.8.22}$$

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

Solution a

Let's evaluate the left side of the linear momentum eigenvalue problem (Equation 2.8.21)

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

and compare to the the right side of Equation 2.8.21

$$p_x A\sin(ax)$$

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

Let's look at the left side of the kinetic energy eigenvalue problem (Equation 2.8.22)

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

and compare to the right side

$$KEA\sin(ax)$$

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

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

Solution b

Let's look at the left side of Equation 2.8.21 for linear momentum

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

and the right side of Equation 2.8.21

$$p_x N e^{-ix/\hbar}$$

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 2.8.22 for kinetic energy

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} N e^{-ix/\hbar} &= +i\frac{\hbar}{2m}\frac{\partial}{\partial x} N e^{-ix/\hbar} \\ &= +\frac{1}{2m} N e^{-ix/\hbar} \end{aligned}$$

and the right side

$$KE N e^{-ix/\hbar}$$

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

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

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

Exercise 3.3.1

Are $\psi = Me^{-bx}$ functions eigenstates of linear momentum and kinetic energy (or neither or both)?

Answer

ψ is an eigenstate of linear momentum with a eigenvalue of $bi\hbar$ and also an eigenstate of kinetic energy with an eigenvalue of b^2.

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2.9: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

Learning Objectives

- To be introduced to the role of eigenvalue equations in obtaining observables from a system
- Understand how expectation values are calculated if the wavefunctions is not an eigenstate of the operator for the observable.

Recall, that we can identify the total energy operator, which is called the Hamiltonian operator, $\hat{H}$, as consisting of the kinetic energy operator plus the potential energy operator.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{2.9.1}$$

Using this notation, we write the Schrödinger Equation as

$$\hat{H}\,|\psi(x,y,z)\rangle = E|\,\psi(x,y,z)\rangle \tag{2.9.2}$$

Equation 2.9.2 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 2.9.2 states this principle mathematically for the case of energy as the observable.

Postulate III: Obtaining Observables Requires Solving Eigenvalue Problems

If a system is described by the eigenfunction Ψ of an operator $\hat{A}$ then the value measured for the observable property corresponding to $\hat{A}$ will always be the eigenvalue a, which can be calculated from the eigenvalue equation.

$$\hat{A}\,|\Psi\rangle = a|\,\Psi\rangle \tag{2.9.3}$$

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

$$A\,|\psi_a(x)\rangle = a|\,\psi_a(x)\rangle \tag{2.9.4}$$

where a is a complex number, then ψ_a is called an **eigenstate** of A corresponding to the eigenvalue a.

Suppose that A is an operator corresponding to some physical dynamical variable. Consider a particle whose wavefunction is ψ_a. The expectation of value A in this state is simply

$$\begin{aligned}\langle A\rangle &= \int_{-\infty}^{\infty}\psi_a^* A\psi_a dx \\ &= a\int_{-\infty}^{\infty}\psi_a^*\psi_a dx \\ &= a.\end{aligned}$$

where use has been made of Equation 2.9.4 and the normalization condition. Moreover,

$$\begin{aligned}\langle A^2\rangle &= \int_{-\infty}^{\infty} \psi_a^* A^2 \psi_a dx \\ &= a\int_{-\infty}^{\infty} \psi_a^* A \psi_a dx \\ &= a^2 \int_{-\infty}^{\infty} \psi_a^* \psi_a dx \\ &= a^2.\end{aligned}$$

So the variance of A is

$$\begin{aligned}\sigma_A^2 &= \langle A^2\rangle - \langle A\rangle^2 = a^2 - a^2 \\ &= 0.\end{aligned}$$

The fact that the variance is *zero* implies that every measurement of A is bound to yield the same result: namely, a. Thus, the eigenstate ψ_a is a state which is associated with a *unique* value of the dynamical variable corresponding to A. This unique value is simply the associated eigenvalue determined by Equation 2.9.4.

2.9.1: 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

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi|^2 dx \tag{2.9.5}$$

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

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)|\psi|^2 dx. \tag{2.9.6}$$

Postulate IV

The average value of an observable measurement of a state in (*normalized*) wavefunction ψ with operator $\hat{A}$ is given by the expectation value $\langle a\rangle$:

$$\langle a\rangle = \langle \psi\,|a|\,\psi\rangle \tag{2.9.7}$$

$$= \int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx \tag{2.9.8}$$

If an unnormalized wavefunction where used, then Equation 2.9.8 changes to

$$\langle a\rangle = \frac{\langle \psi\,|a|\,\psi\rangle}{\langle\psi|\psi\rangle} \tag{2.9.9}$$

$$= \frac{\int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx}{\int_{-\infty}^{\infty} \psi^*\psi dx} \tag{2.9.10}$$

The denominator is just the normalization requirement discussed earlier. In general, the results of the various different measurements of x will be scattered around the expectation value $\langle x\rangle$. The degree of scatter is parameterized by the quantity

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x - \langle x\rangle)^2 |\psi|^2 dx \tag{2.9.11}$$

$$\equiv \langle x^2\rangle - \langle x\rangle^2, \tag{2.9.12}$$

which is known as the *variance* of x. The square-root of this quantity, σ_x, is called the *standard deviation* of x. We generally expect the results of measurements of x to lie within a few standard deviations of the expectation value (Figure 4.3.1).

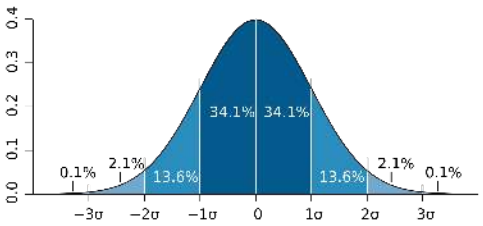


Figure 4.3.1 : A plot of a normal distribution (or bell-shaped curve) where each band has a width of 1 standard deviation. image usd with permission from Wikipedia.

Example 4.3.1

For a particle in a box in its ground state, calculate the expectation value of the

a. *position*,
b. the *linear momentum*,
c. the *kinetic energy*, and
d. the total energy

Solution

First the wavefunction needs to be defined. From the particle in the box solutions, the ground state wavefunction ($n = 1$) is

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

We can confirm that the wavefunction is normalized.

$$\int \psi^* \psi \, d\tau = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx = 1$$

Hence, the Equation 2.9.8 is the relevant equation to use.

Solution a

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

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

Solution b

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

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

Solution c

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

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

A position "on average" is in the middle of the box ($L/2$). It has equal probability of traveling towards the left or right, so the average momentum and velocity must be zero.

Solution d

The average kinetic energy must be equal to the total energy of the ground state of the particle in the box, as there is no other energy component (i.e, $V = 0$).

2.9.2: Expanding the Wavefunction

It is also possible to demonstrate that the eigenstates of an operator attributed to a observable form a **complete set** (*i.e.*, that any general wavefunction can be written as a linear combination of these eigenstates). However, the proof is quite difficult, and we shall not attempt it here.

In summary, given an operator $\hat{A}$, any general wavefunction, $\psi(x)$, can be written

$$\psi = \sum_i c_i \phi_i$$

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

$$A\phi_i = a_i \phi_i$$

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

$$\int_{-\infty}^{\infty} \phi_i^* \phi_j dx = \delta_{ij}. \tag{2.9.13}$$

Here, δ_{ij} is called the **Kronecker delta-function**, and takes the value unity when its two indices are equal, and zero otherwise. It follows from Equations 2.9.10 and 2.9.13 that

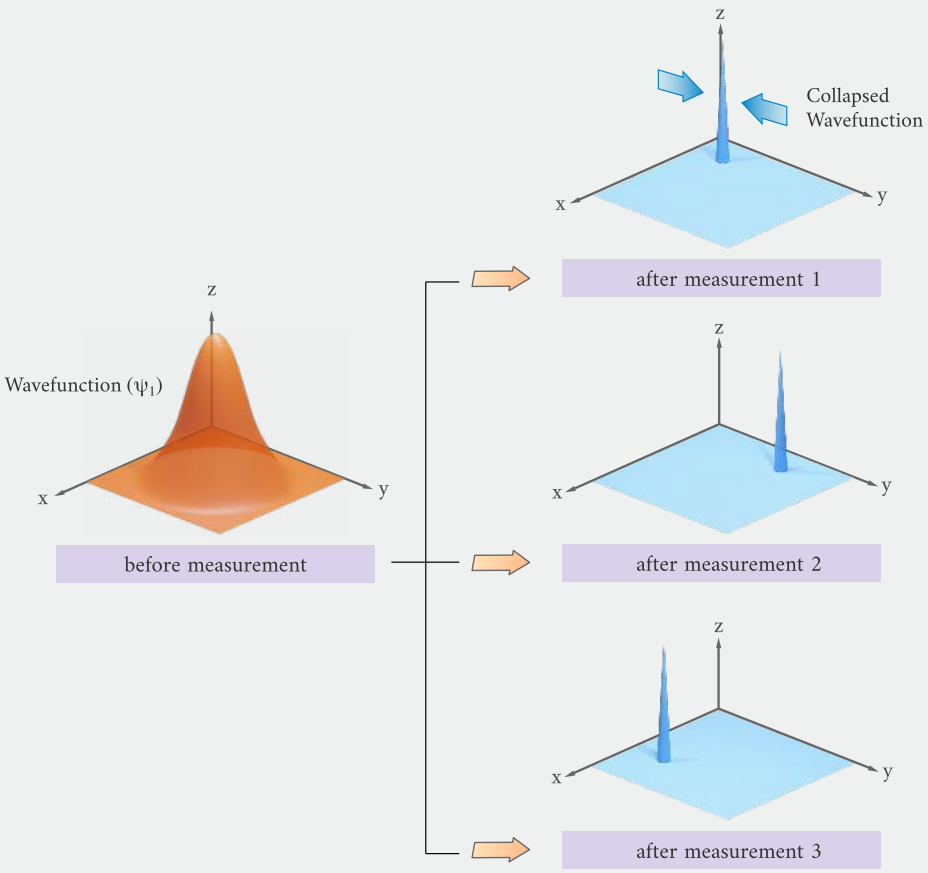
$$c_i = \int_{-\infty}^{\infty} \phi_i^* \psi dx. \tag{2.9.14}$$

Thus, the expansion coefficients in Equation 2.9.14 are easily determined, given the wavefunction ψ and the eigenstates ϕ_i. Moreover, if ψ is a properly normalized wavefunction then Equations 2.9.10 and 2.9.13 yield

$$\sum_i |c_i|^2 = 1.$$

Collapsing the Wavefunction

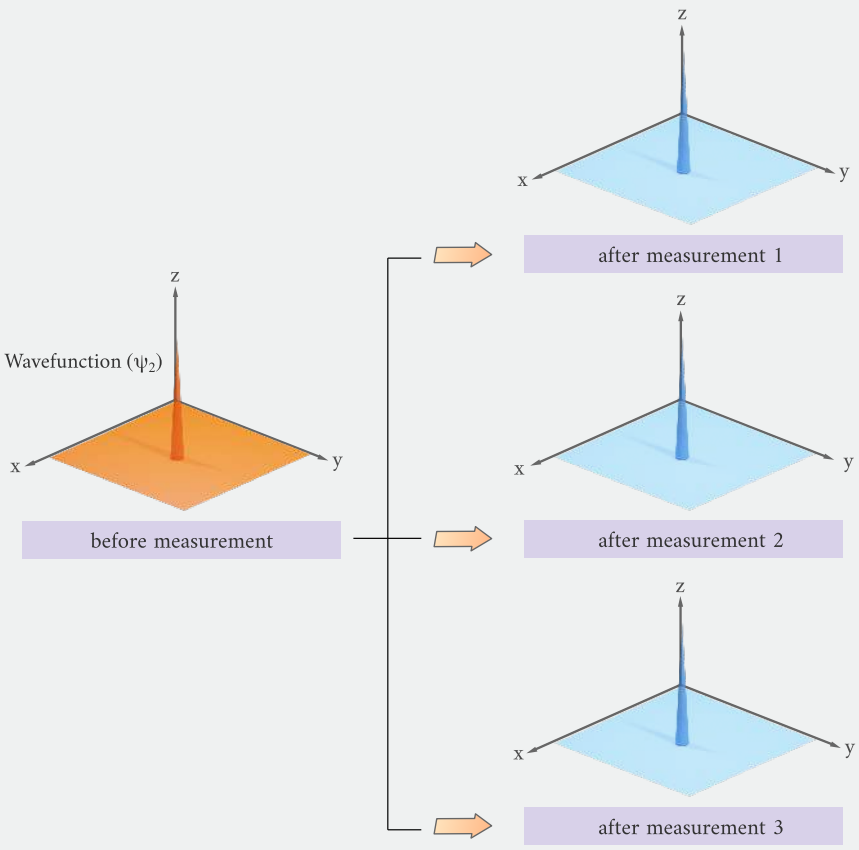
Wavefunction collapse is said to occur when a wavefunction—initially in a superposition of several eigenstates—appears to reduce to a single eigenstate (by "observation"). A particle (or a system in general) can be found in a given state $\psi(x,t)$. Suppose now a measurement is performed on the wavefuction to characterize a specific property of the system.



The measurement of position (with the position operator) effectively collapses this wavefunction that is a superposition of position eigenstates, which are delta-functions and are continuous - i.e. not quantized. Using a different measurement operation may in quantized values (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Mathematically, an operator $\hat{A}$ is associated with this measurement process, which you suppose has a *complete orthonormal set* of eigenvalues: $\{\phi_i\}$ that is typically an infinite set of functionals that depend on quantum number n. The wavefunction Ψ can be expand and a set of basis functions can be selected to specifies the wavefunction is the coefficients $\{c_n\}$ of the expansion. Therefore, if the system is perturbed, then your wavefunction will have another set of coefficients $\{c'_n\}$.

https://chem.libretexts.org/@go/page/478071



The measurement of position (with the position operator) does not collapse this wavefunction since it is in a position eigenstate in contrast to the wavefunction above. Using a different measurement operation (e.g., kinetic energy) may "collapse" the wavefunction into a different eigenstate (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

If you wavefunction is in the eigenstate of the operator, then each measurement via that operator will give the same result.

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2.10: Eigenfunctions of Operators are Orthogonal

Learning Objectives

- Understand the properties of a Hermitian operator and their associated eigenstates
- Recognize that all experimental obervables are obtained by Hermitian operators

Consideration of the quantum mechanical description of the particle-in-a-box exposed two important properties of quantum mechanical systems. We saw that the eigenfunctions of the Hamiltonian operator are orthogonal, and we also saw that the position and momentum of the particle could not be determined exactly. We now examine the generality of these insights by stating and proving some fundamental theorems. These theorems use the Hermitian property of quantum mechanical operators that correspond to observables, which is discuss first.

2.10.1: 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

$$\int \psi^* \hat{A} \psi \, d\tau = \int (\hat{A}^* \psi^*) \psi \, d\tau \tag{2.10.1}$$

This equation means that the complex conjugate of $\hat{A}$ can operate on ψ^* to produce the same result after integration as $\hat{A}$ operating on φ, followed by integration. To prove that a quantum mechanical operator $\hat{A}$ is Hermitian, consider the eigenvalue equation and its complex conjugate.

$$\hat{A}\psi = a\psi \tag{2.10.2}$$

$$\hat{A}^* \psi^* = a^* \psi^* = a\psi^* \tag{2.10.3}$$

Note that $a^* = a$ because the eigenvalue is real. Multiply Equation 2.10.2 and 2.10.3 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

$$\int \psi^* \hat{A} \psi \, d\tau = a \int \psi^* \psi \, d\tau = a \tag{2.10.4}$$

$$\int \psi \hat{A}^* \psi^* \, d\tau = a \int \psi \psi^* \, d\tau = a \tag{2.10.5}$$

Since both integrals equal a, they must be equivalent.

$$\int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau \tag{2.10.6}$$

The operator acting on the function,

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

produces a new function. Since functions commute, Equation 2.10.6 can be rewritten as

$$\int \psi^* \hat{A} \psi d\tau = \int (\hat{A}^* \psi^*) \psi d\tau \tag{2.10.7}$$

This equality means that $\hat{A}$ is Hermitian.

Orthogonality Theorem

Eigenfunctions of a Hermitian operator are orthogonal if they have different eigenvalues.

Because of this theorem, we can identify orthogonal functions easily without having to integrate or conduct an analysis based on symmetry or other considerations.

Proof

ψ and φ are two eigenfunctions of the operator $\hat{A}$ with real eigenvalues a_1 and a_2, respectively. Since the eigenvalues are real, $a_1^* = a_1$ and $a_2^* = a_2$.

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

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

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

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

$$\int \psi \hat{A}^*\psi^* \, d\tau = a_2 \int \psi\psi^* \, d\tau \tag{2.10.8}$$

Subtract the two equations in Equation 2.10.8 to obtain

$$\int \psi^* \hat{A}\psi \, d\tau - \int \psi \hat{A}^*\psi^* \, d\tau = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{2.10.9}$$

The left-hand side of Equation 2.10.9 is zero because $\hat{A}$ is Hermitian yielding

$$0 = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{2.10.10}$$

If a_1 and a_2 in Equation 2.10.10 are not equal, then the integral **must** be zero. This result proves that **nondegenerate eigenfunctions** of the same operator are orthogonal.

□

Two wavefunctions, $\psi_1(x)$ and $\psi_2(x)$, are said to be *orthogonal* if

$$\int_{-\infty}^{\infty} \psi_1^* \psi_2 \, dx = 0. \tag{2.10.11}$$

Consider two eigenstates of $\hat{A}$, $\psi_a(x)$ and $\psi_{a'}(x)$, which correspond to the two *different* eigenvalues a and a', respectively. Thus,

$$A\psi_a = a\psi_a \tag{2.10.12}$$

$$A\psi_a' = a'\psi_a' \tag{2.10.13}$$

Multiplying the complex conjugate of the first equation by $\psi_{a'}(x)$, and the second equation by $\psi_{a'}^*(x)$, and then integrating over all x, we obtain

$$\int_{-\infty}^{\infty} (A\psi_a)^* \psi_{a'} dx = a \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx, \tag{2.10.14}$$

$$\int_{-\infty}^{\infty} \psi_a^* (A\psi_{a'}) dx = a' \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx. \tag{2.10.15}$$

However, from Equation 2.10.9, the left-hand sides of the above two equations are equal. Hence, we can write

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

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

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

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

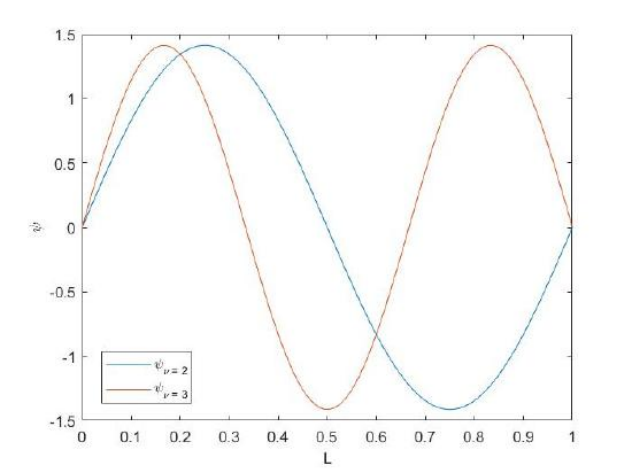
> The eigenvalues of operators associated with experimental measurements are all *real*.

Example4.5.1

Draw graphs and use them to show that the particle-in-a-box wavefunctions for $\psi(n=2)$ and $\psi(n=3)$ are orthogonal to each other.

Solution

The two PIB wavefunctions are qualitatively similar when plotted



These wavefunctions are orthogonal when

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

and when the PIB wavefunctions are substituted this integral becomes

$$\int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{2n}{L}x\right) \sqrt{\frac{2}{L}} \sin\left(\frac{2n}{L}x\right) dx = ?$$

$$\frac{2}{L}\int_0^L \sin\left(\frac{2}{L}x\right) \sin\left(\frac{3}{L}x\right) = ?$$

We can expand the integrand using trigonometric identities to help solve the integral, but it is easier to take advantage of the symmetry of the integrand, specifically, the $\psi(n=2)$ wavefunction is even (blue curves in above figure) and the $\psi(n=3)$ is odd (purple curve). Their product (even times odd) is an odd function and the integral over an odd function is zero. Therefore $\psi(n=2)$ and $\psi(n=3)$ wavefunctions are orthogonal.

This can be repeated an infinite number of times to confirm the entire set of PIB wavefunctions are mutually orthogonal as the Orthogonality Theorem guarantees.

2.10.2: Orthogonality of Degenerate Eigenstates

Consider two eigenstates of $\hat{A}$, ψ_a and ψ'_a, which correspond to the *same* eigenvalue, a. Such eigenstates are termed **degenerate**. The above proof of the orthogonality of different eigenstates fails for degenerate eigenstates. Note, however, that *any* linear combination of ψ_a and ψ'_a is also an eigenstate of $\hat{A}$ corresponding to the eigenvalue a. Thus, even if ψ_a and ψ'_a are not orthogonal, we can always choose two linear combinations of these eigenstates which are orthogonal. For instance, if ψ_a and ψ'_a are properly normalized, we can define the **overlap integral**

$$S = \int_{-\infty}^{\infty} \psi_a^* \psi_a' dx, \tag{2.10.16}$$

It is easily demonstrated (but not here) that

$$\psi_a'' = \frac{|S|}{\sqrt{1-|S|^2}} \left(\psi_a - S^{-1}\psi_a'\right) \tag{2.10.17}$$

is a properly normalized eigenstate of $\hat{A}$, corresponding to the eigenvalue a, which is orthogonal to ψ_a. It is straightforward to generalize the above argument to three or more degenerate eigenstates. Hence, we conclude that the eigenstates of a Hermitian operator are, or can be chosen to be, **mutually orthogonal.**

Theorem: Gram-Schmidt Orthogonalization

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

The above theorem argues that if the eigenvalues of two eigenfunctions are the same then the functions are said to be degenerate and linear combinations of the degenerate functions can be formed that will be orthogonal to each other. Since the two eigenfunctions have the same eigenvalues, the linear combination also will be an eigenfunction with the same eigenvalue. The proof of this theorem shows us one way to produce orthogonal degenerate functions.

Proof

If ψ_a and ψ_a' are degenerate, but not orthogonal, we can define a new composite wavefunction $\psi_a'' = \psi_a' - S\psi_a$ where S is the overlap integral:

$$S = \langle \psi_a | \psi_a' \rangle$$

then ψ_a and ψ_a'' will be orthogonal.

$$\begin{aligned} \langle \psi_a | \psi_a'' \rangle &= \langle \psi_a | \psi_a' - S\psi_a \rangle \\ &= \cancel{\langle \psi_a | \psi_a' \rangle}^{S} - S \cancel{\langle \psi_a | \psi_a \rangle}^{1} \\ &= S - S = 0 \end{aligned}$$

$$\int \psi_a^* \psi_a d\tau$$

then ψ_a and Φ will be orthogonal.

$$\begin{aligned} \int \psi_A^* \Phi d\tau &= \int \psi_a^* (\psi_a' - S\psi_a) d\tau \\ &= \int \psi_a^* \psi_a' d\tau - S \int \psi_a^* \psi_a d\tau \\ &= S - S = 0 \end{aligned}$$

□

Exercise 4.5.2

Find N that normalizes ψ if $\psi = N(\varphi_1 - S\varphi_2)$ where φ_1 and φ_2 are normalized wavefunctions and S is their overlap integral.

$$S = \langle \varphi_1 | \varphi_2 \rangle$$

Answer

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:

$$\langle\psi|\psi\rangle = \langle N(\varphi_1 - S\varphi_2)|N(\varphi_1 - S\varphi_2)\rangle = 1$$

$$N^2\langle(\varphi_1 - S\varphi_2)|(\varphi_1 - S\varphi_2)\rangle = 1$$

$$N^2\left[\cancelto{1}{\langle\varphi_1|\varphi_1\rangle} - S\cancelto{S}{\langle\varphi_2|\varphi_1\rangle} - S\cancelto{S}{\langle\varphi_1|\varphi_2\rangle} + S^2\cancelto{1}{\langle\varphi_2|\varphi_2\rangle}\right] = 1$$

$$N^2(1 - S^2 \cancel{- S^2} + \cancel{S^2}) = 1$$

$$N^2(1 - S^2) = 1$$

therefore

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

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

Contributors and Attributions

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2.11: 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.

2.11.1: Probability

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

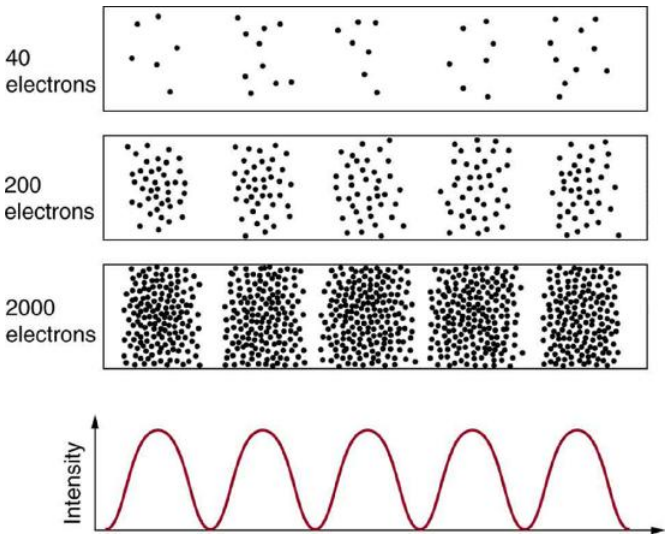


Figure 1.9.1 : The building up of the diffraction pattern of electrons scattered from a crystal surface. Each electron arrives at a definite location, which cannot be precisely predicted. The overall distribution shown at the bottom can be predicted as the diffraction of waves having the de Broglie wavelength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

After de Broglie proposed the wave nature of matter, many physicists, including Schrödinger and Heisenberg, explored the consequences. The idea quickly emerged that, *because of its wave character, a particle's trajectory and destination cannot be precisely predicted for each particle individually*. However, each particle goes to a definite place (Figure 1.9.1). After compiling enough data, you get a distribution related to the particle's wavelength and diffraction pattern. There is a certain *probability* of finding the particle at a given location, and the overall pattern is called a **probability distribution**. Those who developed quantum mechanics devised equations that predicted the probability distribution in various circumstances.

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

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

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

2.11.2: 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,

$$\Delta p = \frac{h}{\lambda} \tag{2.11.1}$$

$$\Delta x = \lambda \tag{2.11.2}$$

By substituting Δx for λ into Equation 2.11.1, we derive

$$\Delta p = \frac{h}{\Delta x} \tag{2.11.3}$$

or,

$$\Delta p \Delta x = h \tag{2.11.4}$$

early form of uncertainty principle

A Common Trend in Quantum Systems

Equation 2.11.4 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 2.11.4.

Equation 2.11.4 was further refined by Heisenberg and his colleague Niels Bohr, and was eventually rewritten as

$$\Delta p_x \Delta x \geq \frac{h}{4\pi} = \frac{\hbar}{2} \tag{2.11.5}$$

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

Equation 2.11.5 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).

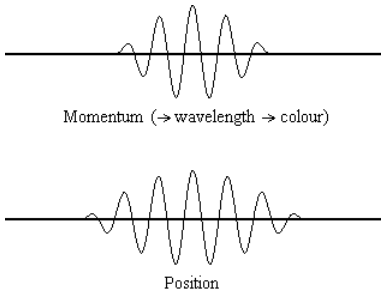


Figure 1.9.2 : The animation shows the relevant spreads in the uncertainty for position and momentum of light/photons (light wave's corresponding photon particle). From the result of de Broglie, we know that for a particle with known momentum, p will have a precise value for its de Broglie wavelength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

What is the Proper Definition of Uncertainty?

Equation 2.11.5 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 2.11.5 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 2.11.5 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 2.11.5):

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

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: $\Delta x = 150 \times 10^{-12} m$

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

$$= 3.9 \times 10^5\ m/s$$

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.

2.11.3: 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 $10^{-6}\ m/s$.

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

Solution a

From Equation 2.11.5, the $\Delta p_x = m\Delta v_x$ with $m = 1.0\ g$. Solving for Δx to get

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

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

Solution b

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

Exercise 1.9.2

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

Answer

We need to quantify the uncertainty of the electron in position. We can estimate that as $\pm 5 \times 10^{-10} m$. Hence, substituting the relavant numbers into Equation 2.11.5 and solving for Δv we get

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

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

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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2.12: Commuting Operators Allow Infinite Precision

Learning Objectives

- To connect the Heisenberg Uncertainty principle to the commutation relations.
- Develop proficiency in calculating the commutator of two operators.

If two operators commute then both quantities can be measured at the same time with infinite precision, if not then there is a tradeoff in the accuracy in the measurement for one quantity vs. the other. This is the mathematical representation of the Heisenberg Uncertainty principle.

2.12.1: Commuting Operators

One important property of operators is that the order of operation matters. Thus in general

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

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

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

To determine whether two operators commute first operate $\hat{A}\hat{E}$ on a function $f(x)$. Then operate$\hat{E}\hat{A}$ the same function $f(x)$. If the same answer is obtained subtracting the two functions will equal zero and the two operators will commute.on

If two operators commute, then they can have the same set of eigenfunctions. By definition, two operators $\hat{A}$ and $\hat{B}$ commute if the effect of applying $\hat{A}$ then $\hat{B}$ is the same as applying $\hat{B}$ then $\hat{A}$, i.e.

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

For example, the operations brushing-your-teeth and combing-your-hair commute, while the operations getting-dressed and taking-a-shower do not. This theorem is very important. If two operators commute and consequently have the same set of eigenfunctions, then the corresponding physical quantities can be evaluated or measured exactly simultaneously with no limit on the uncertainty. As mentioned previously, the eigenvalues of the operators correspond to the measured values.

If $\hat{A}$ and $\hat{B}$ commute and ψ is an eigenfunction of $\hat{A}$ with eigenvalue b, then

$$\hat{B}\hat{A}\psi = \hat{A}\hat{B}\psi = \hat{A}b\psi = b\hat{A}\psi \tag{2.12.1}$$

Equation 2.12.1 says that $\hat{A}\psi$ is an eigenfunction of $\hat{B}$ with eigenvalue b, which means that when $\hat{A}$ operates on ψ, it cannot change ψ. At most, $\hat{A}$ operating on ψ can produce a constant times ψ.

$$\hat{A}\psi = a\psi \tag{2.12.2}$$

$$\hat{B}(\hat{A}\psi) = \hat{B}(a\psi) = a\hat{B}\psi = ab\psi = b(a\psi) \tag{2.12.3}$$

Equation 2.12.3 shows that Equation 2.12.2 is consistent with Equation 2.12.1. Consequently ψ also is an eigenfunction of $\hat{A}$ with eigenvalue a.

Example 4.6.1

Do the following pairs of operators commute?

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

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.

2.12.2: 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

$$\sigma_A \sigma_B \geq \left| \int \psi^* [\hat{A}\hat{B} - \hat{B}\hat{A}] \psi \, d\tau \right| \tag{2.12.4}$$

where the integral inside the square brackets is called the **commutator**, and $\left|\ \right|$ signifies the modulus or absolute value. If $\hat{A}$ and $\hat{B}$ commute, then the right-hand-side of Equation 2.12.4 is zero, so either or both σ_A and σ_B could be zero, and there is no restriction on the uncertainties in the measurements of the eigenvalues a and b. If $\hat{A}$ and $\hat{B}$ do not commute, then the right-hand-side of Equation 2.12.4 will not be zero, and neither σ_A nor σ_B can be zero unless the other is infinite. Consequently, both a and b cannot be eigenvalues of the same wavefunctions and cannot be measured simultaneously to arbitrary precision.

? Exercise4.6.1

Show that the commutator for position and momentum in one dimension equals $-i\hbar$ and that the right-hand-side of Equation 2.12.4 therefore equals $\hbar/2$ giving $\sigma_x\sigma_{px} \geq \frac{\hbar}{2}$.

2.12.3: Applications

Operators are very common with a variety of purposes. They are used to figure out the energy of a wavefunction using the Schrödinger Equation.

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

They also help to explain observations made in the experimentally. An example of this is the relationship between the magnitude of the angular momentum and the components.

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

However the components do not commute themselves. An additional property of commuters that commute is that both quantities can be measured simultaneously. Thus, the magnitude of the angular momentum and ONE of the components (usually z) can be known at the same time however, NOTHING is known about the other components.

> *The physical quantities corresponding to operators that commute can be measured simultaneously to any precision.*

2.12.2A Example

Determine whether the following two operators commute:

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

and

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

Solution

Evaluate

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

2.12.2B Example

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 and commutes with everything. Thus, these two operators commute. We can also directly evaluate the commutator:

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

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

2.12.2C Exercise

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

This requires evaluating the following commucators:

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

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

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

2.12.4: References

1. Gohberg, I. Basic Operator Theory; Birkhäuser: Boston, 2001
2. McQuarrie, D.A. Quantum Chemistry, 2nd Edition; University Science Books:Sausalito, 2008
3. Schechter, M. Operator Methods in Quantum Mechanics; Dover Publications, 2003

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CHAPTER OVERVIEW

3: Model Systems in Quantum Mechanics

3.1: The Energy of a Particle in a Box is Quantized
3.2: The Free Electron Model
3.3: The Average Momentum of a Particle in a Box is Zero
3.4: A Particle in a Three-Dimensional Box
3.5: Tunneling
3.6: A Harmonic Oscillator Obeys Hooke's Law
3.7: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule
3.8: The Harmonic Oscillator Approximates Molecular Vibrations
3.9: The Harmonic Oscillator Energy Levels
3.10: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials
3.11: Hermite Polynomials are either Even or Odd Functions
3.12: Spherical Polar Coordinates
3.13: Potential Energy and the Hamiltonian
3.14: Solution to the Schrödinger Equation
3.15: Spherical Harmonics
3.16: Angular Momentum
3.17: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision
3.18: Application to the Rotation of Real Molecules

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

Learning Objectives

- Solve the particle-in-a-box model used to describing a trapped particle in 1 D well
- Characterize the particle-in-a-box eigenstates (i.e., wavefunctions) and the eigenenergies as a function of the quantum number
- Demonstrate that the eigenstates are orthogonal

The *particle in the box* model system is the simplest non-trivial application of the Schrödinger equation, but one which illustrates many of the fundamental concepts of quantum mechanics. For a particle moving in one dimension (again along the x- axis), the Schrödinger equation can be written

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

Assume that the particle can move freely between two endpoints $x = 0$ and $x = L$, but cannot penetrate past either end. This is equivalent to a potential energy dependent on x with

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

This potential is represented in Figure 3.5.1 . The infinite potential energy constitutes an impenetrable barrier since the particle would have an infinite potential energy if found there, which is clearly impossible.

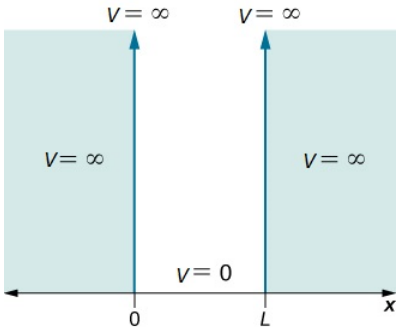


Figure 3.5.1 : The barriers outside a one-dimensional box have infinitely large potential, while the interior of the box has a constant, zero potential. (CC-BY 4.0; OpenStax).

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

$$\psi(x) = 0 \quad for \;\; x < 0 \;\; and \;\; x > L \tag{3.1.1}$$

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

$$\psi(0) = 0 \quad and \quad \psi(L) = 0 \tag{3.1.2}$$

which constitutes a pair of boundary conditions on the wavefunction within the box. Inside the box, $V(x) = 0$, so the Schrödinger equation reduces to the free-particle form:

$$-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x) \tag{3.1.3}$$

with $0 \le x \le L$.

We again have the differential equation

$$\psi''(x) + k^2\psi(x) = 0 \tag{3.1.4}$$

with

$$k^2 = \frac{2mE}{\hbar^2} \tag{3.1.5}$$

The general solution can be written

$$\psi(x) = A \sin\ kx + B \cos\ kx \tag{3.1.6}$$

where A and B are constants to be determined by the boundary conditions in Equation 3.1.2. By the first condition, we find

$$\psi(0) = A \sin 0 + B \cos 0 = B = 0 \tag{3.1.7}$$

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

$$\psi(a) = A \sin kL = 0 \tag{3.1.8}$$

It is assumed that $A \neq 0$, for otherwise $\psi(x)$ would be zero everywhere and the particle would disappear (i.e., the trivial solution). The condition that $\sin kx = 0$ implies that

$$kL = n\pi \tag{3.1.9}$$

where n is a integer, positive, negative or zero. The case $n = 0$ must be excluded, for then $k = 0$ and again $\psi(x)$ would vanish everywhere. Eliminating k between Equation 3.1.4 and 3.1.9, we obtain

$$E_n = \frac{\hbar^2\pi^2}{2mL^2} n^2 = \frac{h^2}{8mL^2} n^2 \tag{3.1.10}$$

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

These are the only values of the energy which allows solutions of the Schrödinger Equation 3.1.3 consistent with the boundary conditions in Equation 3.1.2. The integer n, called a **quantum number**, is appended as a subscript on E to label the allowed energy levels. Negative values of n add nothing new because the energies in Equation 3.1.10 depends on n^2.

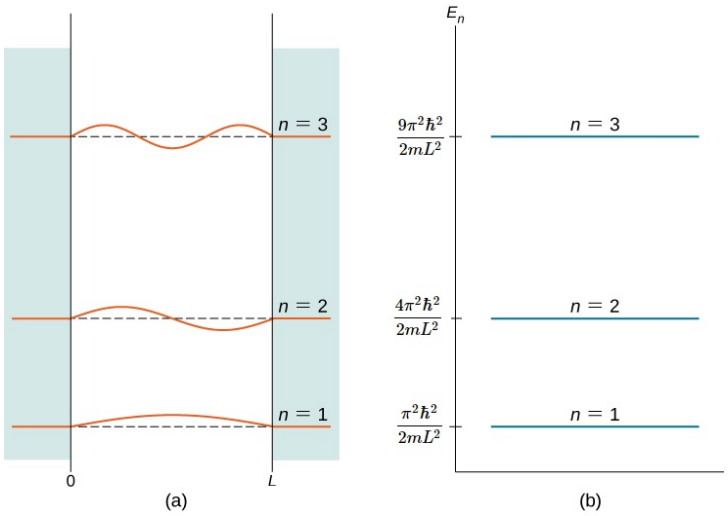


Figure 3.5.2 : A plot of $\psi_n(x)$ for the first four wavefunctions. (CC-BY 4.0; OpenStax).

Figure 3.5.2 shows part of the energy-level diagram for the particle in a box. The occurrence of discrete or quantized energy levels is characteristic of a bound system, that is, one confined to a finite region in space. For the free particle, the absence of confinement allowed an energy continuum. Note that, in both cases, the number of energy levels is infinite-denumerably infinite for the particle in a box, but nondenumerably infinite for the free particle.

The particle in a box assumes its lowest possible energy when $n = 1$, namely

$$E_1 = \frac{h^2}{8mL^2} \tag{3.1.11}$$

The state of lowest energy for a quantum system is termed its *ground state*.

Zero Point Energy

An interesting point is that $E_1 > 0$, whereas the corresponding classical system would have a minimum energy of zero. This is a recurrent phenomenon in quantum mechanics. The residual energy of the ground state, that is, the energy in excess of the classical minimum, is known as **zero point energy**. In effect, the kinetic energy, hence the momentum, of a bound particle cannot be reduced to zero. The minimum value of momentum is found by equating E_1 to $p^2/2m$, giving $p_{min} = \pm h/2L$. This can be expressed as an *uncertainty* in momentum given by $\Delta p \approx h/L$. Coupling this with the uncertainty in position, $\Delta x \approx L$, from the size of the box, we can write

$$\Delta x \Delta p \approx h \tag{3.1.12}$$

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

The particle-in-a-box eigenfunctions are given by Equation 3.1.13, with $B = 0$ and $k = n\pi/L = a$, in accordance with Equation 3.1.9

$$\psi_n(x) = A \sin \frac{n\pi x}{L} \tag{3.1.13}$$

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

These, like the energies, can be labeled by the quantum number n. The constant A, thus far arbitrary, can be adjusted so that $\psi_n(x)$ is normalized. The normalization condition is, in this case,

$$\int_0^a [\psi_n(x)]^2 \, dx = 1 \tag{3.1.14}$$

the integration running over the domain of the particle $0 \le x \le L$. Substituting Equation 3.1.13 into Equation 3.1.14,

$$A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = A^2 \frac{L}{n\pi} \int_0^{n\pi} \sin^2 \theta \, d\theta \tag{3.1.15}$$

$$= A^2 \frac{L}{2} = 1 \tag{3.1.16}$$

We have made the substitution $\theta = n\pi x/L$ and used the fact that the average value of $\sin^2 \theta$ over an integral number of half wavelengths equals 1/2 (alternatively, one could refer to standard integral tables). From Equation 3.1.16, we can identify the general normalization constant

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

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

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \tag{3.1.17}$$

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

The first few eigenfunctions and the corresponding probability distributions are plotted in Figure 3.5.3 . There is a close analogy between the states of this quantum system and the modes of vibration of a violin string. The patterns of standing waves on the string are, in fact, identical in form with the wavefunctions in Equation 3.1.17.

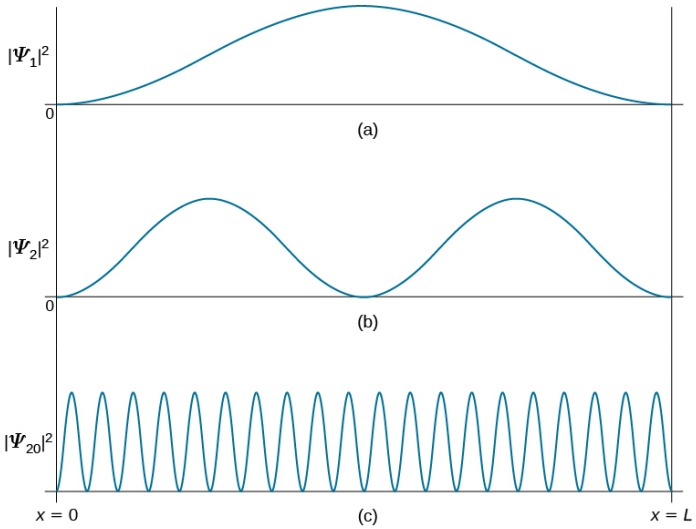


Figure 3.5.3 : The probability density distribution $|\psi_n(x)|^2$ for a quantum particle in a box for: (a) the ground state, $n = 1$; (b) the first excited state, $n = 2$; and, (c) the nineteenth excited state, $n = 20$. (CC-BY 4.0; OpenStax).

Nodes and Curvature

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

Strategy

Probability that the particle will be found between a and b is

$$P(a,b) = \int_a^b \psi^2 \, dx$$

For this problem,

$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

therefore,

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

Solution a

The probability that the particle is in the left half of the box is

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

Solution 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 wavefunction is

$$\psi_1 = \sqrt{\frac{2}{L}}\sin\frac{x\pi}{L}$$

What is the probability that the particle is in the left half of the box in the ground state?

Answer

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

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 Nature of Wavefunctions

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

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

so for the particle in a box, these are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} e^{-iE_n t/\hbar} \tag{3.1.18}$$

with E_n given by Equation 3.1.10.

The phase part of Equation 3.1.18 can be expanded into a real part and a complex components. So the total wavefunction for a particle in a box is

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

which can be simplified (slightly) to

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

As discussed previously, the imaginary part of the total wavefunction oscillates out of phase by $\pi/2$ with respect to the real part (we call this "out of phase"). This is demonstrated in the time-dependent behavior of the first three eigenfunctions in Figure 3.5.4 .

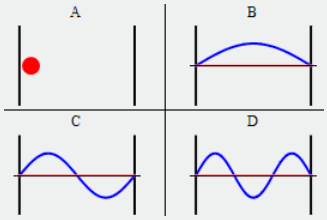


Figure 3.5.4 : Some trajectories of a particle in a box according to Newton's laws of classical mechanics (A), and according to the Schrödinger equation of quantum mechanics (B-D). In (B-D), the horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the wavefunction. The states (B, C, D) are energy eigenstates. (Public Domain; Sbyrnes321 via Wikipedia).

Note that as n increased, the energy of the wavefunction increases (Equation 3.1.10) and both the number of nodes and antinodes increase and the frequency of oscillation of the wavefunction increases.

> *It is generally true in quantum systems (not just for particles in boxes) that the number of nodes in a wavefunction increases with the energy of the quantum state.*

3.1.1: Orthonormality of the Eigenstates

Another important property of the eigenfunctions in Equation 3.1.17 applies to the integral over a product of two *different* eigenfunctions (Equation 3.1.17). It is easy to see from Figure 3.5.5 that the integral

$$\int_0^L \psi_2(x)\psi_1(x)dx = 0 \tag{3.1.19}$$

The integral in Equation 3.1.19 is zero when the two eignestates differ and when integrated over the entire range of the system (from $-\infty$ to ∞ for a 1-D particle in the box, but this can be a narrow region of 0 to L since the eigenstates are zero outside of the box).

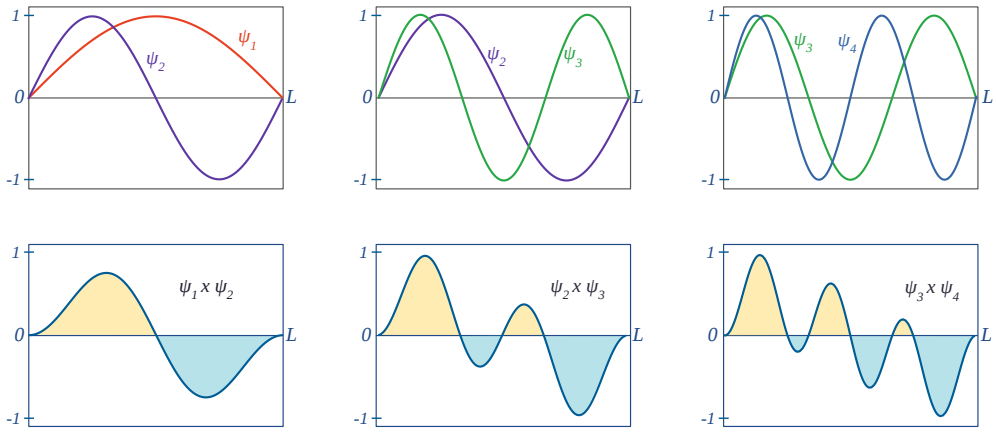


Figure 3.5.5 : (Top Row): Select plots of the $n = 1$ (red curves), $n = 2$ (purple curves), $n = 3$ (green curves), and $n = 4$ (blue curves) eigenfunctions. (Bottom Row): Product of different eigenstates with positive (tan) and negative (cyan) areas emphasized. Note that the negative and positive areas perfectly cancel when added together. Created via fooplot (CC BY-NC; Ümit Kaya via LibreTexts)

To prove Equation 3.1.19 for a particle in a box model, we can use the trigonometric identity

$$\sin\alpha \sin\beta = \frac{1}{2}[\cos(\alpha-\beta) - \cos(\alpha+\beta)] \tag{3.1.20}$$

to show that

$$\int_0^L \psi_m(x)\psi_n(x)dx = 0 \quad if \quad m \neq n \tag{3.1.21}$$

This property is called **orthogonality**. We will show in the next chapter, that this is a general result from quantum-mechanical eigenfunctions. The normalization (Equation 3.1.19) together with the orthogonality (Equation 3.1.21) can be combined into a single relationship

$$\int_0^L \psi_m(x)\psi_n(x)dx = \delta_{mn} \tag{3.1.22}$$

In terms of the *Kronecker delta*

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \tag{3.1.23}$$

A set of functions $\{\psi_n\}$ which obeys Equation 3.1.22 is called *orthonormal*.

Example 3.5.2

Evaluate

a. $\langle\psi_3|\psi_3\rangle$
b. $\langle\psi_4|\psi_4\rangle$
c. $\langle\psi_3|\psi_4\rangle$
d. $\langle\psi_4|\psi_3\rangle$

for the normalized wavefunctions:

$$|\psi_3\rangle = \sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L}$$

and

$$|\psi_4\rangle = \sqrt{\frac{2}{L}}\sin\frac{4\pi x}{L}$$

Strategy

These are four different integrals and we can solve them directly or use orthonormality (Equation 3.1.23) to evaluate.

Solution a

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

This is an integration over an even function, so it cannot be tossed out via symmetry. We can use the Trigonometry relationship in Equation 3.1.20 to get

$$\frac{2}{L}\int_{-\infty}^{+\infty}\sin^2\frac{3\pi x}{L}\,dx = \frac{2}{L}\int_{-\infty}^{+\infty}\frac{1}{2}\left(1-\cos\frac{6\pi x}{L}\right)dx$$

and we can continue the fun. However, there is no need. Since the we can recognize that $\langle\psi_3|\psi_3\rangle$ is 1 by the normalization criteria which is folded into the orthonormal criteria (Equation 3.1.23).

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

Solution b

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

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

Solution c

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

We can expand this integral and evaluate, but since the integrand is odd (and even function times an odd), this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.1.23).

Solution d

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

We can expand this integral and evaluate, but since the integrand is odd (and even function times an odd function), this integral is zero. Alternatively, we can use the orthogonality criteria into the greater orthonormal criteria (Equation 3.1.23).

However, since the wavefunctions are real, then

$$\langle\psi_4|\psi_3\rangle = \langle\psi_3|\psi_4\rangle$$

which also means

$$\langle\psi_4|\psi_3\rangle = 0$$

from the results of section c.

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3.2: The Free Electron Model

Consider a long molecule that is a conjugated polyene. Kuhn (Kuhn, 1949) has suggested a model for the electrons involved in this π-bond system in which an electron is said to have a finite potential energy when it is "on" the molecule and an infinite potential energy when it is "off" the molecule. The model (known as the free electron model) is very much analogous to the particle in a box problem as we have presented it in class.

Let's consider a conjugated polyene molecule in which there are twelve atoms in the conjugated polyene chain. Each atom contributes one π electron and each bond contributes $\mathbf{0.139\ nm}$ (the $\mathbf{C=C}$ bond length in benzene.) We can consider each energy level in the system as one orbital. As in all other cases involving electrons, each orbital can contain two electrons. Using the model, we can predict the wavelength of light the molecule will absorb to excite one electron from the HOMO to the LUMO (highest occupied molecular orbital to the lowest unoccupied molecular orbital.)

First, there are 11 bonds in the chain. Since each bond contributes $\mathbf{0.139\ nm}$, the "box" is $\mathbf{1.529\ nm}$ long. The energy levels of the molecular orbitals are then given by:

$$E_n = \frac{n^2h^2}{8ma^2}$$

where $n = 1, 2, 3 \ldots, h$ is Plank's constant $\left(h = 6.63 \times 10^{-34}\text{Js}\right), m$ is the mass of an electron $\left(m_e = 9.11 \times 10^{-31}\ \text{kg}\right)$ and a is the length of the box $\left(a = 1.529 \times 10^{-9}\ \text{m}\right)$.

The energy levels will be filled with the 12π electrons packing two electrons per orbital. Thus, the HOMO will be the state with $n = 6$. The LUMO will be the state with $n = 7$ - the next state up in energy. The difference in energy is what we want in order to predict the wavelength of light the molecule will absorb.

$$E_6 = \frac{6^2\left(6.63\times10^{-34}\text{Js}\right)^2}{8\left(9.11 \times 10^{-31}\ \text{kg}\right)\left(1.529\times10^{-9}\ \text{m}\right)^2} = 9.288 \times 10^{-19}\ \text{J}$$

$$E_7 = \frac{7^2\left(6.63\times10^{-34}\text{Js}\right)^2}{8\left(9.11 \times 10^{-31}\ \text{kg}\right)\left(1.529\times10^{-9}\ \text{m}\right)^2} = 1.2642 \times 10^{-18}\ \text{J}$$

So the energy of excitation will be $\mathbf{3.354 \times 10^{-19}\ J}$. This corresponds to an absorption wavelength of $\mathbf{593\ nm}$ (which is in the visible region of the spectrum.) How would the absorption wavelength change for more or fewer atoms in the conjugated polyene chain? The solution is left as an exercise.

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

Learning Objectives

- Calculate the expectation value for a measurement
- Apply the expectation value concept to calculate average properties of a participle in a box model
- Understand the origin of a zero-point energy/zero-point motion.
- Extend the concept of orthogonality from vectors to mathematical functions (and wavefunctions).

Now that we have mathematical expressions for the wavefunctions and energies for the particle-in-a-box, we can answer a number of interesting questions. The answers to these questions use quantum mechanics to predict some important and general properties for electrons, atoms, molecules, gases, liquids, and solids. Key to addressing these questions is the formulation and use of expectation values. This is demonstrated below and used in the context of evaluating average properties (momentum of the particle in a box for the case below).

3.3.1: Classical Expectation Values

The expectation value is the probabilistic expected value of the result (measurement) of an experiment. It is not the most probable value of a measurement; indeed the expectation value may even have zero probability of occurring. The expected value (or expectation, mathematical expectation, mean, or first moment) refers to the value of a variable one would "expect" to find if one could repeat the random variable process an infinite number of times and take the average of the values obtained. More formally, the expected value is a weighted average of all possible values.

Example 3.7.1 : Classical Expectation Value of Exam Scores (a discretized example)

A classical example is calculating the expectation value (i.e. average) of the exam grades in the class. For example if the class scores for an exam were

65	67	94	43	67	76	94	67

The discrete way is to sum up all scores and divide by the number of students:

$$\langle s \rangle = \frac{\sum_i^N s(i)}{N} \tag{3.3.1}$$

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 3.3.1 can be rewritten with "probability" or "probability weights"

$$\langle s \rangle = \sum_i^N s(i) P_s(i) \tag{3.3.2}$$

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 3.3.2 to the set of scores, we need to calculate these weights:

Score	65	67	94	43	76
P_s	1/8	3/8	2/8	1/8	1/8

As with all probabilities, the sum of all probabilities possible must be one. These confirm that for the weights here:

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

This is the discretized "normalization" criterion (the same as why we normalize wavefunctions).

So, now we can use Equation 3.3.2 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 3.3.2 gives the same result, as expected, from Equation 3.3.1.

3.3.2: Quantum Expectation Values

The extension of the classical expectation (average) approach in Example 3.7.1 using Equation 3.3.2 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

$$\langle o\rangle = \int_{-\infty}^{+\infty}\psi^*\hat{O}\psi\,dx \tag{3.3.3}$$

where x is the range of space that is integrated over (i.e., an integration over all possible probabilities). The expectation value changes as the wavefunction changes and the operator used (i.e, which observable you are averaging over).

> *In general, changing the wavefunction changes the expectation value for that operator for a state defined by that wavefunction.*

3.3.3: 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 3.3.3. In the equation below, the symbol $\langle H\rangle$ is used to denote the average value for the total energy.

$$\langle H\rangle = \int_{-\infty}^{\infty}\psi^*(x)\hat{H}\psi(x)dx \tag{3.3.4}$$

$$= \int_{-\infty}^{\infty}\psi^*(x)\hat{KE}\psi(x)dx+\int_{-\infty}^{\infty}\psi^*(x)\hat{V}\psi(x)dx \tag{3.3.5}$$

$$= \underbrace{\int_{-\infty}^{\infty}\psi^*(x)\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x)dx}_{\text{average kinetic energy}}+\underbrace{\int_{-\infty}^{\infty}\psi^*(x)\hat{V}(x)\psi(x)dx}_{\text{average potential energy}} \tag{3.3.6}$$

The Hamiltonian operator consists of a kinetic energy term and a potential energy term. The kinetic energy operator involves differentiation of the wavefunction to the right of it. This step must be completed before multiplying by the complex conjugate of the wavefunction. The potential energy, however, usually depends only on position and not momentum (i.e., it involves conservative forces). The potential energy operator therefore only involves the coordinates of a particle and does not involve differentiation. For this reason we do not need to use a caret over V in Equation 3.3.6.

Equation 3.3.6 can be simplified

$$\langle H\rangle = \langle KE\rangle+\langle V\rangle \tag{3.3.7}$$

The potential energy integral then involves only products of functions, and the order of multiplication does not affect the result, e.g. 6×4 = 4×6 = 24. This property is called the **commutative property**. The average potential energy therefore can be written as

$$\langle V \rangle = \int_{-\infty}^{\infty} V(x)\psi^*(x)\psi(x)dx \tag{3.3.8}$$

This integral is telling us to take the probability that the particle is in the interval dx at x, which is $\psi^*(x)\psi(x)dx$, multiply this probability by the potential energy at x, and sum (i.e., integrate) over all possible values of x. This procedure is just the way to calculate the average potential energy $\langle V \rangle$ of the particle.

Exercise 3.7.2 : Particle in Box

Evaluate the two integrals in Equation 3.3.6 for the PIB wavefunction $\psi(x) = \sqrt{\frac{2}{L}}\sin(kx)$ with the potential function $V(x) = 0$ from 0 to the length of a box L with $k = \frac{\pi}{L}$.

Solution

The *average kinetic energy* is

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

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

$$\begin{aligned}
\langle KE \rangle &= \left(\frac{2}{L}\right)\left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \sin^2(kx)dx \\
&= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \left(\frac{2}{L}\right)\sin^2(kx)dx \\
&= \left(\frac{k^2\hbar^2}{2m}\right)\int_0^L \psi^*(x)\psi(x)dx \quad (\to 1) \\
&= \frac{k^2\hbar^2}{2m}
\end{aligned}$$

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 3.3.7 for this system and set of wavefunctions

$$\langle H \rangle = \frac{\pi^2 \hbar^2}{2mL^2}$$

This is the same result obtained from solving the eigenvalue equation for the PIB. However, if the wavefunctions used were NOT eigenstates of energy, then we cannot use the eigenvalue approach and need to rely on the expectation values to describe the energy of the system.

What is the lowest energy for a particle in a box? The lowest energy level is E_1, and it is important to recognize that this lowest energy of a particle in a box is not zero. This finite energy is called the **zero-point energy**, and the motion associated with this energy is called the zero-point motion. Any system that is restricted to some region of space is said to be bound. The zero-point energy and motion are manifestations of the wave properties and the Heisenberg Uncertainty Principle, and are general properties of bound quantum mechanical systems.

? Exercise 3.7.2 : Progressing to the Classical Limit

What happens to the energy level spacing for a particle-in-a-box when mL^2 becomes much larger than h^2? What does this result imply about the relevance of quantization of energy to baseballs in a box between the pitching mound and home plate? What implications does quantum mechanics have for the game of baseball in a world where h is so large that baseballs exhibit quantum effects?

Answer

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?

3.3.4: 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 3.3.1*a*)

$$\psi_{n=1} = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \tag{3.3.9}$$

This state has the following probability distribution (Figure **3.3.1***b*):

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

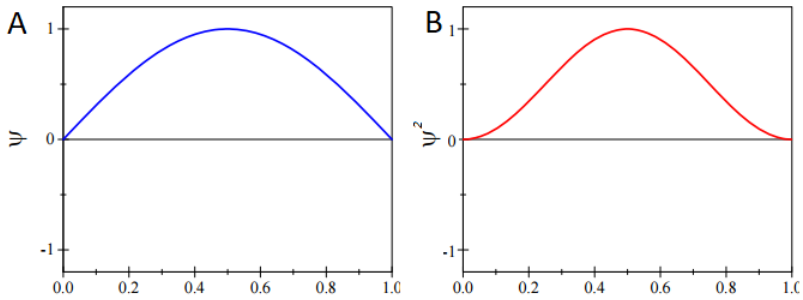


Figure 3.7.1 : (left) The ground-state ($n = 1$) wavefunction for a particle in a box. (right) The ground-state ($n = 1$) probability for a particle in a box.

The expectation value for position with the $\hat{x} = x$ operation for any wavefunction (Equation 3.3.3) is

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

which for the ground-state wavefunction (Equation 3.3.9) shown in Figure 3.7.1 is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) x \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx \tag{3.3.10}$$

$$= \frac{2}{L} \int_{-\infty}^{+\infty} x \sin^2\left(\frac{\pi x}{L}\right) \tag{3.3.11}$$

Solution by Inspection

Without even having to evaluate Equation 3.3.11, we can get the expectation value from simply inspecting $\psi^*_{n=1}\psi_{n=1}$ in (Figure **3.3.1**;). 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. Moreover, specifically at any point a fixed distance away from the mean, i.e.

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

Therefore, the particle is most likely to be found at the center of the box. So

$$\langle x \rangle = \frac{L}{2}$$

Exercise 3.7.4

Use the general form of the particle-in-a-box wavefunction for any n to find the mathematical expression for the position expectation value $\langle x \rangle$ for a box of length L. How does $\langle x \rangle$ depend on n?

3.3.5: Average Momentum of a Particle in a Box

What is the average momentum of a particle in the box? We start with Equation 3.3.3 and use the momentum operator

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{3.3.12}$$

We note that the particle-in-a-box wavefunctions are **not** eigenfunctions of the momentum operator (Exercise 3.7.4). However, this does not mean that Equation 3.3.3 is inapplicable as Example 3.7.2 demonstrates.

Example 3.7.3 : The Average Momentum of a Particle in a Box is Zero

Even though the wavefunctions are not momentum eigenfunctions, we can calculate the expectation value for the momentum. Show that the expectation or average value for the momentum of an electron in the box is zero in every state (i.e., arbitrary values of n).

Strategy

First write the expectation value integral (Equation 3.3.3) with the momentum operator. Then insert the expression for the wavefunction and evaluate the integral as shown here.

Solution

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

Note that this makes sense since the particles spends an equal amount of time traveling in the $+x$ and $-x$ direction.

Interpretation

It may seem that this means the particle in a box does not have any momentum, which is incorrect because we know the energy is never zero. In fact, the energy that we obtained for the particle-in-a-box is entirely kinetic energy because we set the potential energy at 0. Since the kinetic energy is the momentum squared divided by twice the mass, it is easy to understand how the average momentum can be zero and the kinetic energy finite

Exercise 3.7.5

Show that the particle-in-a-box wavefunctions are not eigenfunctions of the momentum operator (Equation 3.3.12).

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 the following PIB wavefunctions

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

and

$$\hat{p} = -i\hbar\frac{d}{dx}$$

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

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

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

Alternative Solution

An alternative, albeit more complicated, approach is to recognize that the uncertainty of p must be zero if the wavefunction is an eigenstate of the momentum operator. Hence

$$\sqrt{\langle p^2\rangle - \langle p\rangle^2} = 0$$

This requires calculating the $\langle p^2\rangle$ and $\langle p\rangle$ expectation values:

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

This integral is zero via orthonormality of the sine and cosine functions (although you can expand the integrand and confirm this).

$$\begin{aligned}\langle p^2\rangle &= \int_0^L \psi^*\left[-i\hbar\frac{d}{dx}\right]^2\psi dx\\ &= \frac{\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\frac{d^2}{dx^2}\sin\left(\frac{n\pi x}{L}\right)dx\\ &= \frac{-\mathrm{h}^2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx\\ &= -\frac{\mathrm{h}^2}{L}\end{aligned}$$

Now the integral above is 1 using orthonormality (although you can expand the integrand and confirm this). Now we calculate the uncertainty in momentum in the PIB wavefunctions:

$$\begin{aligned}\sqrt{\langle p^2\rangle - \langle p\rangle^2} &= \sqrt{\frac{-\mathrm{h}^2}{L} - 0^2}\\ &= \sqrt{\frac{-\mathrm{h}^2}{L}}\\ &\neq 0 \rightarrow\end{aligned}$$

Since the uncertainty is not 0, different measurements (experiments) will results in different values of momentum being quantified. Hence, the PIB wavefunctions are **not** eigenfunctions of the momentum operator.

It must be equally likely for the particle-in-a-box to have a momentum $-p$ as $+p$. The average of $+p$ and $-p$ is zero, yet p^2 and the average of p^2 are not zero. The information that the particle is equally likely to have a momentum of $+p$ or $-p$ is contained in the wavefunction. In fact, the sine function is a representation of the two momentum eigenfunctions e^{+ikx} and e^{-ikx} (Figure 3.7.2).

? 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).

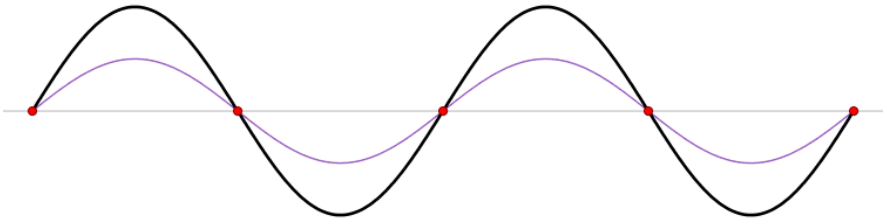


Figure 3.7.2 : Two waves traveling in opposite directions across the same medium combine linearly. In this animation, both waves have the same wavelength and the sum of amplitudes results in a standing wave. (Public Domain; LucasVB).

> *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.

3.3.6: Orthogonality

In vector calculus, *orthogonality* is the relation of two lines at right angles to one another (i.e., perpendicularity), but is generalized into n dimensions via zero amplitude "dot products" or "inner products." Hence, orthogonality is thought of as describing **non-overlapping**, **uncorrelated**, or **independent** objects of some kind. The concept of orthogonality extends to functions (wavefunctions or otherwise) too. Two functions ψ_A and ψ_B are said to be orthogonal if

$$\int_{allspace} \psi_A^* \psi_B d\tau = 0 \tag{3.3.13}$$

In general, eigenfunctions of a quantum mechanical operator with different eigenvalues are orthogonal. Are the eigenfunctions of the particle-in-a-box Hamiltonian orthogonal?

? Exercise 3.7.7

Evaluate the integral $\int \psi_1^* \psi_3 dx$ for all possible pairs of particle-in-a-box eigenfunctions from $n = 1$ to $n = 3$ (use symmetry arguments whenever possible) and explain what the results say about orthogonality of the functions.

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3.4: A Particle in a Three-Dimensional Box

Learning Objectives

- To demonstrate how the particle in 1-D box problem can extend to a particle in a 3D box
- Introduction to nodal surfaces (e.g., nodal planes)

The quantum particle in the 1D box problem can be expanded to consider a particle within a higher dimensions as demonstrated elsewhere for a quantum particle in a 2D box. Here we continue the expansion into a particle trapped in a 3D box with three lengths L_x, L_y, and L_z. As with the other systems, there is NO FORCE (i.e., no potential) acting on the particles *inside* the box (Figure 3.9.1).

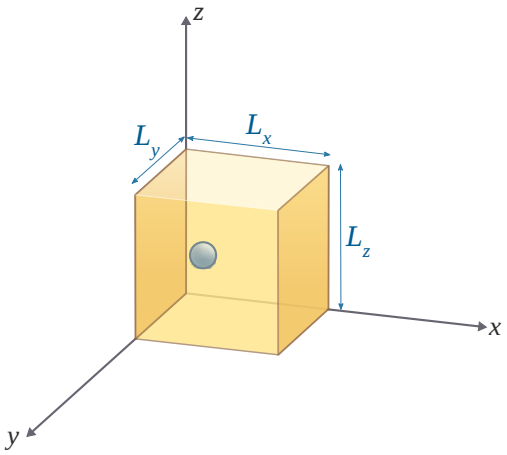


Figure 3.9.1 : A particle in 3D box with three lengths L_x, L_y, and L_z. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The potential for the particle inside the box

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

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

$\vec{r}$ is the vector with all three components along the three axes of the 3-D box: $\vec{r} = L_x\hat{x} + L_y\hat{y} + L_z\hat{z}$. When the potential energy is infinite, then the wavefunction equals zero. When the potential energy is zero, then the wavefunction obeys the Time-Independent Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r) \tag{3.4.1}$$

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

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2}\right) = E\psi(r) \tag{3.4.2}$$

The easiest way in solving this partial differential equation is by having the wavefunction equal to a **product** of individual function for each independent variable (e.g., the Separation of Variables technique):

$$\psi(x,y,z) = X(x)Y(y)Z(z) \tag{3.4.3}$$

Now each function has its own variable:

- $X(x)$ is a function of variable x only

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

Now substitute Equation 3.4.3 into Equation 3.4.2 and divide it by the xyz product:

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

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

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

$$\left(-\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2}\right) + \left(-\frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2}\right) + \left(-\frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2}\right) = E \tag{3.4.4}$$

E is an energy constant, and is the sum of x, y, and z. For this to work, each term must equal its own constant. For example,

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

Now separate each term in Equation 3.4.4 to equal zero:

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0$$
$$\frac{d^2Y}{dy^2} + \frac{2m}{\hbar^2}\varepsilon_y Y = 0$$
$$\frac{d^2Z}{dz^2} + \frac{2m}{\hbar^2}\varepsilon_z Z = 0$$

Now we can add all the energies together to get the total energy:

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E \tag{3.4.5}$$

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

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}E_x X = 0 \approx \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \tag{3.4.6}$$

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

$$n = 1, 2, ..\infty$$

Use the normalization wavefunction equation for each variable:

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

Normalization wavefunction equation for each variable (that substitute into Equation 3.4.3):

$$X(x) = \sqrt{\frac{2}{L_x}}\sin\left(\frac{n_x\pi x}{L_x}\right) \tag{3.4.7}$$

$$Y(y) = \sqrt{\frac{2}{L_y}}\sin\left(\frac{n_y\pi y}{L_y}\right) \tag{3.4.8}$$

$$Z(z) = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n_z\pi z}{L_z}\right) \tag{3.4.9}$$

The limits of the three quantum numbers

- $n_x = 1, 2, 3, ...\infty$
- $n_y = 1, 2, 3, ...\infty$

- $n_z = 1, 2, 3, ...\infty$

For each constant use the de Broglie Energy equation:

$$\varepsilon_x = \frac{n_x^2 h^2}{8mL_x^2} \tag{3.4.10}$$

with $n_x = 1...\infty$

Do the same for variables n_y and n_z. Combine Equation 3.4.3 with Equations 3.4.7-3.4.9 to find the wavefunctions inside a 3D box.

$$\psi(r) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \tag{3.4.11}$$

with

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

To find the Total Energy, add Equation 3.4.10 and Equation 3.4.5.

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{3.4.12}$$

Notice the similarity between the energies a particle in a 3D box (Equation 3.4.12) and a 1D box.

3.4.1: Degeneracy in a 3D Cube

The energy of the particle in a 3-D cube (i.e., $L_x = L_y = L$) in the *ground state* is given by Equation 3.4.12 with $n_x = 1$, $n_y = 1$, and $n_z = 1$. This energy ($E_{1,1,1}$) is hence

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

The ground state has only one wavefunction and no other state has this specific energy; the ground state and the energy level are said to be **non-degenerate**. However, in the 3-D cubical box potential the energy of a state depends upon the sum of the squares of the quantum numbers (Equation 3.4.11). The particle having a particular value of energy in the excited state *MAY* has several different stationary states or wavefunctions. If so, these states and energy eigenvalues are said to be **degenerate**.

For the first excited state, three combinations of the quantum numbers (n_x, n_y, n_z) are (2, 1, 1), (1, 2, 1), (1, 1, 2). The sum of squares of the quantum numbers in each combination is same (equal to 6). Each wavefunction has same energy:

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

Corresponding to these combinations three different wavefunctions and **three** different states are possible. Hence, the first excited state is said to be three-fold or triply degenerate. The number of independent wavefunctions for the stationary states of an energy level is called as the **degree of degeneracy** of the energy level. The value of energy levels with the corresponding combinations and sum of squares of the quantum numbers

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

as well as the degree of degeneracy are depicted in Table 3.9.1 .

Table 3.9.1 : Degeneracy properties of the particle in a 3-D cube with $L_x = L_y = L$.

$n_x^2+n_y^2+n_z^2$	Combinations of Degeneracy (n_x, n_y, n_z)						Total Energy (E_{n_x,n_y,n_z})	Degree of Degeneracy
3	(1,1,1)						$\frac{3h^2}{8mL^2}$	1
6	(2,1,1)	(1,2,1)	(1,1,2)				$\frac{6h^2}{8mL^2}$	3
9	(2,2,1)	(1,2,2)	(2,1,2)				$\frac{9h^2}{8mL^2}$	3
11	(3,1,1)	(1,3,1)	(1,1,3)				$\frac{11h^2}{8mL^2}$	3
12	(2,2,2)						$\frac{12h^2}{8mL^2}$	1
14	(3,2,1)	(3,1,2)	(2,3,1)	(2,1,3)	(1,3,2)	(1,2,3)	$\frac{14h^2}{8mL^2}$	6
17	(2,2,3)	(3,2,2)	(2,3,2)				$\frac{17h^2}{8mL^2}$	3
18	(1,1,4)	(1,4,1)	(4,1,1)				$\frac{18h^2}{8mL^2}$	3
19	(1,3,3)	(3,1,3)	(3,3,1)				$\frac{19h^2}{8mL^2}$	3
21	(1,2,4)	(1,4,2)	(2,1,4)	(2,4,1)	(4,1,2)	(4,2,1)	$\frac{21h^2}{8mL^2}$	6

Example 3.9.1 : Accidental Degeneracies

When is there degeneracy in a 3-D box when none of the sides are of equal length (i.e., $L_x \neq L_y \neq L_z$)?

Solution

From simple inspection of Equation 3.4.12 or Table 3.9.1 , it is clear that degeneracy originates from different combinations of n_x^2/L_x^2, n_y^2/L_y^2 and n_z^2/L_z^2 that give the same value. These will occur at common multiples of at least two of these quantities (the Least Common Multiple is one example). For example

if

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2}$$

there will be a degeneracy. Also degeneracies will exist if

$$\frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}$$

or if

$$\frac{n_x^2}{L_x^2} = \frac{n_z^2}{L_z^2}$$

and especially if

$$\frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2}.$$

There are two general kinds of degeneracies in quantum mechanics: degeneracies due to a symmetry (i.e., $L_x = L_y$) and accidental degeneracies like those above.

Exercise 3.9.1

The 6^{th} 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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3.5: Tunneling

Tunneling is a quantum mechanical phenomenon when a particle is able to penetrate through a potential energy barrier that is higher in energy than the particle's kinetic energy. This amazing property of microscopic particles play important roles in explaining several physical phenomena including radioactive decay. Additionally, the principle of tunneling leads to the development of Scanning Tunneling Microscope (STM) which had a profound impact on chemical, biological and material science research.

Violating Classical Mechanics

Consider a ball rolling from one valley to another over a hill (Figure **3.5.1**). If the ball has enough energy (E) to overcome the potential energy (V) at the top of the barrier between each valley, then it can roll from one valley to the other. This is the classical picture and is controlled by the simple Law of Conservation of Energy approach taught in beginning physics courses. However, If the ball does not have enough kinetic energy ($E < V$), to overcome the barrier it will never roll from one valley to the other. In contrast, when quantum effects are taken into effect, the ball can "tunnel" through the barrier to the other valley, even if its kinetic energy is less than the potential energy of the barrier to the top of one of the hills.

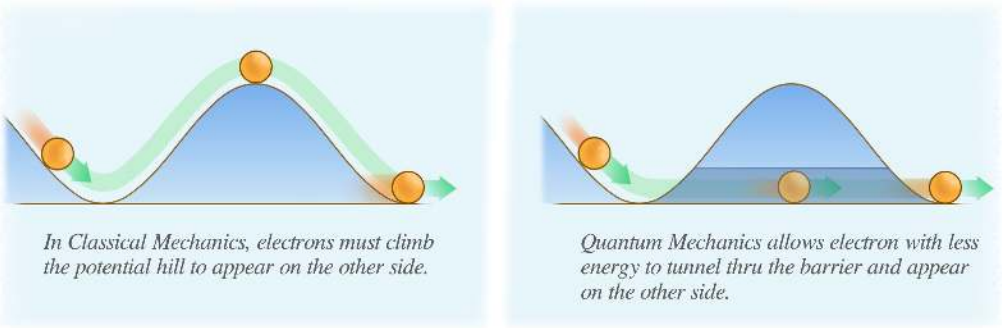


Figure **3.5.1**: Contrasting classical (over the barrier) motion vs. quantum (through the barrier) motion. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The Heisenberg Uncertainty Principle in Action

The reason for the difference between classical and quantum motion comes from wave-particle nature of matter. One interpretation of this duality involves the Heisenberg uncertainty principle, which defines a limit on how precisely the position and the momentum of a particle can be known at the same time. This implies that there are no solutions with a probability of exactly zero (or one), though a solution may approach infinity if, for example, the calculation for its position was taken as a probability of 1, the other, i.e. its speed, would have to be infinity. Hence, the probability of a given particle's existence on the opposite side of an intervening barrier is non-zero, and such particles will appear on the 'other' (a semantically difficult word in this instance) side with a relative frequency proportional to this probability.

Microscopic particles such as protons, or electrons would behave differently as a consequence of wave-particle duality. Consider a particle with energy E that is confined in a box which has a barrier of height V. Classically, the box will prevent these particles from escaping due to the insufficiency in kinetic energy of these particles to get over the barrier. However, if the thickness of the barrier is thin, the particles have some probability of penetrating through the barrier **without** sufficient energy and appear on the other side of the box (Figure **3.5.2**).

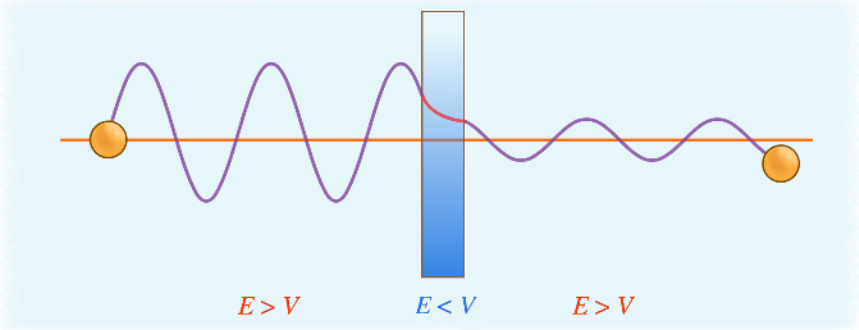


Figure 3.5.2: Quantum tunneling through a barrier. The energy of the tunneled particle is the same but the amplitude is decreased. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

When it reaches a barrier it cannot overcome, a particle's wave function changes from sinusoidal to exponentially diminishing in form. The solution for the Schrödinger equation in such a medium (Figure 3.5.2; blue region) is:

$$\psi = Ne^{-\beta x} \tag{3.5.1}$$

where

- N is a normalization constant and
- $\beta = \sqrt{\frac{2m(V-E)}{\hbar^2}}$

For a quantum particle to *appreciably* tunnel through a barrier three conditions must be met (Figure 3.5.2):

1. The height of the barrier must be **finite** and the thickness of the barrier should be **thin**.
2. The potential energy of the barrier exceeds the kinetic energy of the particle ($E < V$).
3. The particle has wave properties because the wavefunction is able to penetrate through the barrier. This suggests that quantum tunneling only apply to microscopic objects such protons or electrons and does not apply to macroscopic objects.

If these conditions are met, there would be some probability of finding the particles on the other side of the barrier. Beginning as a sinusoidal wave, a particle begins tunneling through the barrier and goes into exponential decay until it exits the barrier and gets transmitted out the other side as a final sinusoidal wave with a smaller amplitude. The act of tunneling decreases the wave amplitude due the reflection of the incident wave when it comes into the contact with the barrier but does not affect the wave equation.

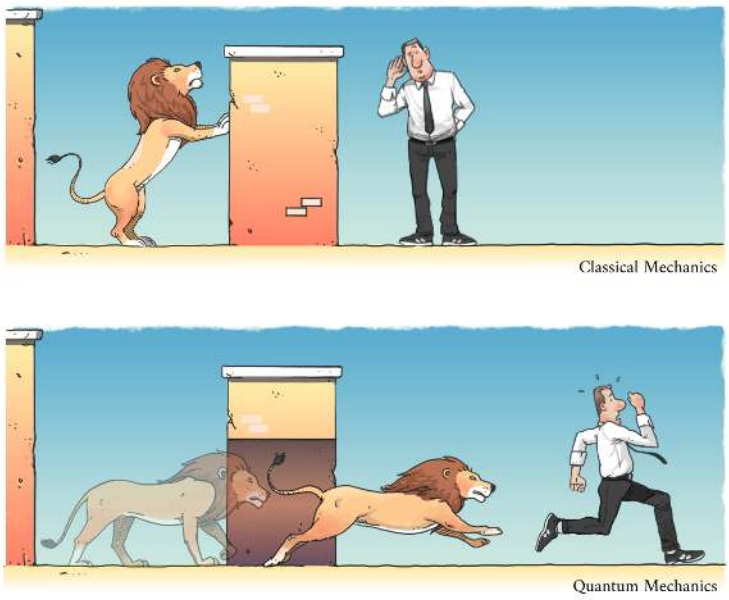


Figure 3.5.3: Quantum tunnelling of alion through a barrier is a quantum effect with no classical analog. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The probability, P, of a particle tunneling through the potential energy barrier is derived from the Schrödinger Equation and is described as,

$$P = \exp\left(\frac{-4a\pi}{h}\sqrt{2m(V-E)}\right) \tag{3.5.2}$$

with $E < V$

where

- V is the potential barrier,
- E is the kinetic energy possessed by the particle, and
- a is the thickness of the barrier.
- m is mass of the particle
- h is Planks Constant ($6.6260 \times 10^{-34} m^2 kg/s$)

Therefore, the probability of an object tunneling through a barrier decreases with the object's increasing mass and with the increasing gap between the energy of the object and the energy of the barrier. And although the wave function never quite reaches 0 (as can be determined from the functionality), this explains how tunneling is frequent on nanoscale, but negligible at the macroscopic level. Equation 3.5.2 argues that the probability of tunneling decreases exponentially with the square root of the particles mass (particles with a small mass can effectively tunnel through barriers more easily than those with larger mass) and the thickness of the barrier (a)

Example 3.5.1

An electron having total kinetic energy E of 4.50 eV approaches a rectangular energy barrier with $V = 5.00\,eV$ and $L = 950\,pm$. Classically, the electron cannot pass through the barrier because $E < V$. Calculate probability of tunneling of this electron through the barrier.

Solution

This is a straightforward application of Equation 3.5.2.

$$P = \exp\left(\frac{-4a\pi}{h}\sqrt{2m(V-E)}\right)$$

The electronvolt (eV) is a unit of energy that is equal to approximately $1.6 \times 10^{-19}\ J$, which is the conversion used below.

The mass of an electron is $9.10 \times 10^{-31}\ kg$

$$P = \exp\left[\left(-\frac{(4)(950 \times 10^{-12}\ m)(\pi)}{6.6260 \times 10^{-34} m^2 kg/s}\right)\right.$$
$$\left.\sqrt{(2)(9.10 \times 10^{-31}\ kg)(5.00 - 4.50\ \cancel{eV})(1.60 \times 10^{-19} J/\cancel{eV})}\right]$$
$$= \exp^{-6.88} = 1.03 \times 10^{-3}$$

There is a ~0.1% probability of the electrons tunneling though the barrier.

Alpha Decay Radioactivity

Protons and neutrons in a nucleus have kinetic energy, but it is about 8 MeV less than that needed to get out from attractive nuclear potential (Figure 3.5.4). Hence, they are bound by an average of 8 MeV per nucleon. The slope of the hill outside the bowl is analogous to the repulsive Coulomb potential for a nucleus, such as for an α particle outside a positive nucleus. In α decay, two protons and two neutrons spontaneously break away as a ^{4}He unit. Yet the protons and neutrons do not have enough kinetic energy to classically get over the rim.

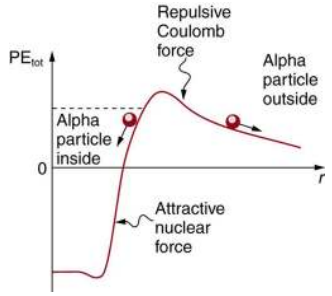


Figure 3.5.4: Nucleons within an atomic nucleus are bound or trapped by the attractive nuclear force, as shown in this simplified potential energy curve. An particle outside the range of the nuclear force feels the repulsive Coulomb force. The α particle inside the nucleus does not have enough kinetic energy to get over the rim, yet it does manage to get out by quantum mechanical tunneling. (CC BY; OpenStax)

The α article tunnels through a region of space it is forbidden to be in, and it comes out of the side of the nucleus. Like an electron making a transition between orbits around an atom, it travels from one point to another without ever having been in between (Figure 3.5.5). The wave function of a quantum mechanical particle varies smoothly, going from within an atomic nucleus (on one side of a potential energy barrier) to outside the nucleus (on the other side of the potential energy barrier). Inside the barrier, the wave function does not become zero but decreases exponentially, and we do not observe the particle inside the barrier. The probability of finding a particle is related to the square of its wave function, and so there is a small probability of finding the particle outside the barrier, which implies that the particle can tunnel through the barrier.

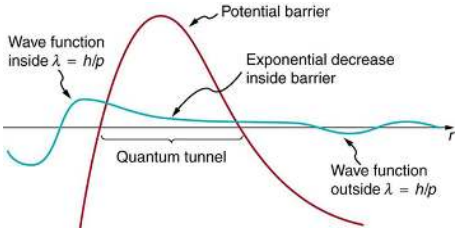


Figure 3.5.5: The wave function representing a quantum mechanical particle must vary smoothly, going from within the nucleus (to the left of the barrier) to outside the nucleus (to the right of the barrier). Inside the barrier, the wave function does not abruptly become zero; rather, it decreases exponentially. Outside the barrier, the wave function is small but finite, and there it smoothly becomes sinusoidal. Owing to the fact that there is a small probability of finding the particle outside the barrier, the particle can tunnel through the barrier. (CC BY; OpenStax)

Scanning Tunneling Microscopy (STM)

A metal tip usually made out of tungsten is placed between a very small distance above a conducting or semiconducting surface. This distance acts as a potential barrier for tunneling. The space between the tip and the surface normally is vacuum. When electrons tunnel from the metal tip to the surface, a current is created and monitored by a computer (Figure **3.5.6**). The current depends on the distance between the tip and the surface, which is controlled by a piezoelectric cylinder. If there is a strong current, the tip will move away from the surface. The increase of the potential barrier will decrease the probability of tunneling and decrease the current. If the current becomes too weak, the tip moves closer to the surface. The potential barrier will be reduced and the current will increase. The variations in the current as the tip moves over the sample are reconstructed by the computer to produce topological image of the scanned surface.

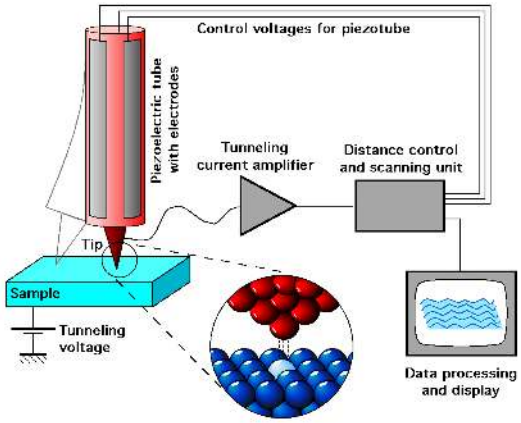


Figure **3.5.6**: Schematic diagram of a scanning tunneling microscope. (CC BY-SA 2.0 Austria; Michael Schmid via Wikipedia).

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3.6: 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.

3.6.1: The Classical Harmonic Oscillator

Simple harmonic oscillators about a potential energy minimum can be thought of as a ball rolling frictionlessly in a curved dish or a pendulum swinging frictionlessly back and forth (Figure 5.1.2). The restoring forces are precisely the same in either horizontal direction.

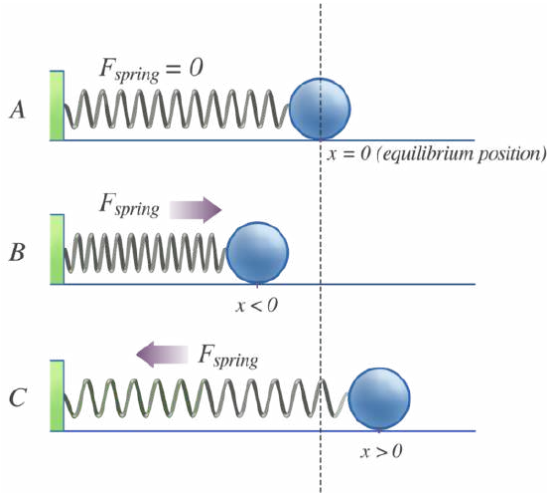


Figure 5.1.2 : A mass connected to a spring that follows Hooke's law is a system that, when displaced from its equilibrium position ($x_o = 0$), experiences a restoring force, F that is proportional to the displacement, x from the equilibrium length (x_o). (CC BY-NC; Ümit Kaya via LibreTexts)

If we consider the bond to behave like a mass on a spring (Figure 5.1.2), then this restoring force (F) is proportional to the displacement (x) from the equilibrium length (x_o) - this is *Hooke's Law*:

$$F = -kx \tag{3.6.1}$$

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.

$$V(x) = \frac{1}{2}kx^2 \tag{3.6.2}$$

Hooke's Law or the harmonic (i.e. quadratic) potential given by Equation 3.6.2 is an excellent *approximation* for the vibrational oscillations of molecules. The magnitude of the force constant k depends upon the nature of the chemical bond in molecular systems just as it depends on the nature of the spring in mechanical systems. The larger the force constant, the stiffer the spring or the stiffer the bond. Since it is the electron distribution between the two positively charged nuclei that holds them together, a double bond with more electrons has a larger force constant than a single bond, and the nuclei are held together more tightly.

Caution

A stiff bond with a large force constant is not necessarily a strong bond with a large dissociation energy. A harmonic oscillator has no dissociation energy since it CANNOT be broken - there is always a restoring force to keep the molecule together. This is one of many deficiencies in using the harmonic oscillator model to describe molecular vibrations.

Two atoms or one?

You may have questioned the applicability of the harmonic oscillator model involving one moving mass bound to a fix wall via a spring like in Figure 5.1.2 for the vibration of a diatomic molecule with two moving masses like in Figure 5.1.1 . It turned out the two are mathematically the same with internal vibration motion described by a single reduced particle with a reduced mass μ.

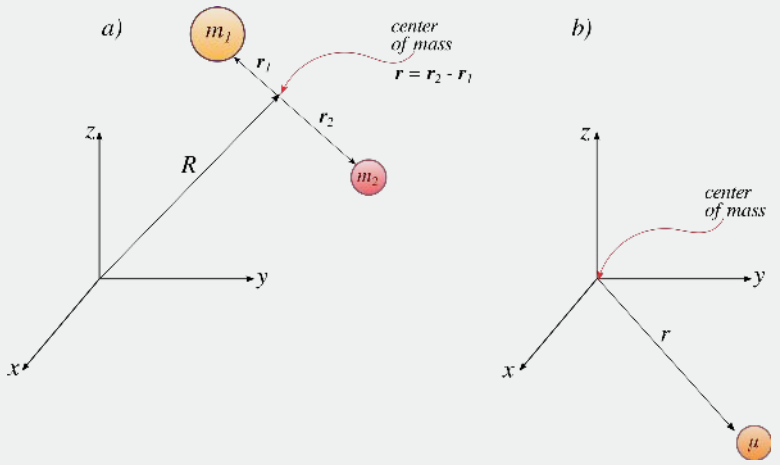


Figure 5.1.3 : Diagrams of the coordinate systems and relevant vectors for the motion of (a) a two-particle diatomic molecule with atoms of mass m_1 and m_2 and (b) the equivalent one-particle pseudo-particle of reduced mass μ. (CC BY-NC; Ümit Kaya via LibreTexts)

For a diatomic molecule, Figure 5.1.3 , the vector $\vec{r}$ corresponds to the internuclear axis. The magnitude or length of r is the bond length, and the orientation of r in space gives the orientation of the internuclear axis in space. Changes in the orientation correspond to rotation of the molecule, and changes in the length correspond to vibration. The change in the bond length from the equilibrium bond length is the **vibrational coordinate** for a diatomic molecule.

Example 5.1.1

a. Show that minus the first derivative of the harmonic potential energy function in Equation 3.6.2 with respect to x is the Hooke's Law force in Equation 3.6.1.
b. Show that the second derivative is the force constant, k.
c. At what value of x is the potential energy a minimum; at what value of x is the force zero?
d. Sketch graphs to compare the potential energy and the force for a system with a large force constant to one with a small force constant.

Solution a

Hooke's Law for a spring entails that the force applied on a spring F is equal to the force constant, $-k$ times the distance compressed or stretched, x (Equation 3.6.1). The derivative of $V(x) = 0.5kx^2$ is

$$V'(x) = (2)\left(\frac{1}{2}\right)kx = kx.$$

The negative of this is $-V'(x) = -kx$ which is exactly equal to Hooke's Law.

Solution b

The second derivative

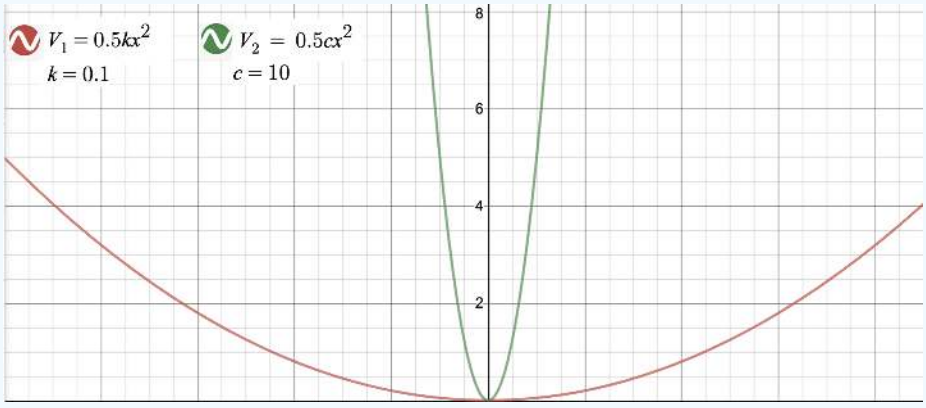
$$V''(x) = \frac{d}{dx}kx = k$$

Thus, the second derivative of this equation for potential energy is equal to the force constant, k.

Solution c

To find the minimum potential energy, it is easiest to set the first derivative equal to zero and solve for x. When $V'(x) = kx = 0$ then x must be equal to zero. Thus, the minimum potential energy is when x=0. Plugging this into Hooke's Law, $F(0) = -k(0) = 0$ so this is also the value for x when the force is zero.

Solution d



The force constant has a drastic effect on both the potential energy and the force. A system with a large force constant requires minimal change in x to have a drastic change in potential energy or force, whereas a system with a small force constant is the exact opposite phenomenon.

3.6.2: 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

$$m\frac{d^2x(t)}{dt^2} = -kx(t) \tag{3.6.3}$$

which can be rewritten in the standardform:

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0 \tag{3.6.4}$$

Equation 3.6.3 is a linear second-order differential equation that can be solved by the standard method of factoring and integrating. The resulting solution to Equation 3.6.3 is

$$x(t) = x_o \sin(\omega t + \phi) \tag{3.6.5}$$

with

$$\omega = \sqrt{\frac{k}{m}} \tag{3.6.6}$$

and the momentum has time dependence

$$\begin{aligned} p &= mv \\ &= mx_o\omega\cos(\omega t + \phi) \end{aligned}$$

Figure 5.1.4 show the displacement of the bond from its equilibrium length as a function of time. Such motion is called **harmonic**.

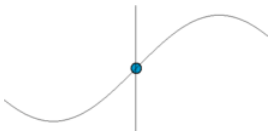


Figure 5.1.4 : Solution to the Harmonic Oscillator. Displacement (y-axis) is plotted as a function of time.

Example 5.1.2

Substitute the following functions into Equation 3.6.4 to demonstrate that they are both possible solutions to the classical equation of motion.

a. $x(t) = x_0e^{i\omega t}$
b. $x(t) = x_0e^{-i\omega t}$

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 $x(t) = x_0e^{i\omega t}$ into Equation 3.6.4.

$$\begin{aligned} \frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) &= 0 \\ \frac{d^2}{dt^2}\left(x_oe^{i\omega t}\right) + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_o\frac{d^2}{dt^2}\left(e^{i\omega t}\right) + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_oi^2\omega^2\left(e^{i\omega t}\right) + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_oi^2\omega^2e^{i\omega t} + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_oi^2\omega^2 + \frac{k}{m}x_o &= 0 \\ -x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \quad &\text{with} \quad \omega = \sqrt{\frac{k}{m}} \end{aligned}$$

Solution b

This requires simply placing the given function $x(t) = x_0e^{-i\omega t}$ into Equation 3.6.4.

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

$$\frac{d^2}{dt^2}\left(x_o e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o\frac{d^2}{dt^2}\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 e^{-i\omega t} + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 + \frac{k}{m}x_o = 0$$

$$-x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \quad \text{with} \quad \omega = \sqrt{\frac{k}{m}}$$

? Exercise 5.1.1

Show that sine and cosine functions also are solutions to Equation 3.6.4.

Answer

Using Equation 3.6.4

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

with $\omega = \sqrt{\frac{k}{m}}$.

For

$$x(t) = x_o\sin(\omega t + \phi)$$

Take the second derivative of $x(t)$

$$\begin{aligned}\frac{d^2x(t)}{dt} &= -\omega^2 x_o\sin(\omega t + \phi)\\ &= \omega^2 x_o\sin(\omega t + \phi)\\ &= -\frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right)\end{aligned}$$

Plug in $x(t)$ and the second derivative of $x(t)$ into Equation 3.6.4

$$-\frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right) + \frac{k}{m}x_o\sin\left(\sqrt{\frac{k}{m}}t + \phi\right) = 0$$

Hence, the sine equation is a solution to Equation 3.6.4

We do the same for the cosine function

$$x(t) = x_o\cos(\omega t + \phi)$$

Take the second derivative of $x(t)$

$$\begin{aligned}\frac{d^2x(t)}{dt} &= -\omega^2 x_o\cos(\omega t + \phi)\\ &= -\omega^2 x_o\cos(\omega t + \phi)\\ &= -\frac{k}{m}x_o\cos\left(\sqrt{\frac{k}{m}}t + \phi\right)\end{aligned}$$

Plug in $x(t)$ and the second derivative of $x(t)$ into Equation 3.6.4

$$-\frac{k}{m}x_o\cos\left(\sqrt{\frac{k}{m}}t+\phi\right)+\frac{k}{m}x_o\cos\left(\sqrt{\frac{k}{m}}t+\phi\right)=0$$

The cosine equation is also a solution to Equation 3.6.4.

Exercise 5.1.2

Identify what happens to the frequency of the motion as the force constant increases in one case and as the mass increases in another case. If the force constant is increased 9-fold and the mass is increased by 4-fold, by what factor does the frequency change?

Answer

This is a simple application of Equation 3.6.6. 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.

3.6.3: 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

$$p=m\frac{dx}{dt} \tag{3.6.7}$$

so combining Equations 3.6.7 and 3.6.2, the total energy can be written as

$$E=T+V \tag{3.6.8}$$

$$=\frac{p^2}{2m}+\frac{k}{2}x^2 \tag{3.6.9}$$

The total energy of the harmonic oscillator is equal to the maximum potential energy stored in the spring when $x=\pm A$, called the *turning points (*Figure 5.1.5). The total energy (Equation 3.6.9) is continuously being shifted between potential energy stored in the spring and kinetic energy of the mass.

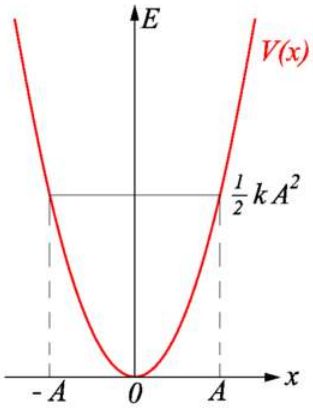


Figure 5.1.5 : The potential $V(x)$ for a harmonic oscillator. Vertical axis energy; horizontal axis displacement x. The potential energy $V(x)=½kx^2$ is shown in red. (Paul Wormer Wikipedia).

The motion of a classical oscillator is confined to the region where its kinetic energy is nonnegative, which is what the energy relation Equation 3.6.9 says. Physically, it means that a classical oscillator can never be found beyond its turning points, and its energy depends only on how far the turning points are from its equilibrium position. The energy of a classical oscillator changes in a continuous way. The lowest energy that a classical oscillator may have is zero, which corresponds to a situation where an object is at rest at its equilibrium position. The zero-energy state of a classical oscillator simply means no oscillations and no motion at all (a classical particle sitting at the bottom of the potential well in Figure 5.1.5). When an object oscillates, no matter how big or small its energy may be, it spends the longest time near the turning points, because this is where it slows down and reverses its direction of motion. Therefore, the probability of finding a classical oscillator between the turning points is highest near the turning points and lowest at the equilibrium position. (Note that this is not a statement of preference of the object to go to lower energy. It is a statement about how quickly the object moves through various regions.)

Example5.1.3

a. What happens to the frequency of the oscillation as the vibration is excited with more and more energy?
b. What happens to the maximum amplitude of the vibration as it is excited with more and more energy?

Solution

a. Frequency

The energy of the harmonic oscillator can be written as

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$

and the frequency of oscillation is $\omega = \sqrt{\frac{k}{m}}$. Notice that the frequency depends only on the stiffness (k) and reduced mass (μ) of the oscillator and not on the energy. Hence, increasing the energy of the vibrations does not affects its frequency.

b. Amplitude

The kinetic and potential terms for energy of the harmonic oscillator can be written as

$$\begin{aligned} E &= K + V \\ &= \frac{1}{2}m\omega^2 A^2 \sin^2 \omega t + \frac{1}{2}kA^2 \cos^2 \omega t \end{aligned}$$

with $\omega = \sqrt{\frac{k}{m}}$ so

$$\begin{aligned} E &= \frac{1}{2}kA^2\left(\sin^2 \omega t + \cos^2 \omega t\right) \\ &= \frac{1}{2}kA^2 \end{aligned}$$

The maximum amplitude of the vibration will **increase** as the energy **increases.**

Exercise 5.1.3

If a molecular vibration is excited by collision with another molecule and is given a total energy E_{hit} as a result, what is the maximum amplitude of the oscillation? Is there any constraint on the magnitude of energy that can be introduced?

Answer

The equation that defines the energy of a molecular vibration can be approximated is:

$$E_{hit} = T + V = \frac{p^2}{2m} + \frac{k}{2}x$$

The maximum amplitude of a harmonic oscillator is equal to x when the kinetic energy term of total energy equals zero

$$E_{hit} = \frac{k}{2}x$$

Solving for x gives the maximum amplitude:

$$x = \sqrt{\frac{2}{k} E_{hit}}$$

The constraint for the energy that can be introduced cannot be greater than the energy required to break the bond between atoms.

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3.7: 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:

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} \tag{3.7.1}$$

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.

3.7.1: Reduced Mass

Viewing the multi-body system as a single particle allows the separation of the motion: vibration and rotation, of the particle from the displacement of the center of mass. This approach greatly simplifies many calculations and problems.

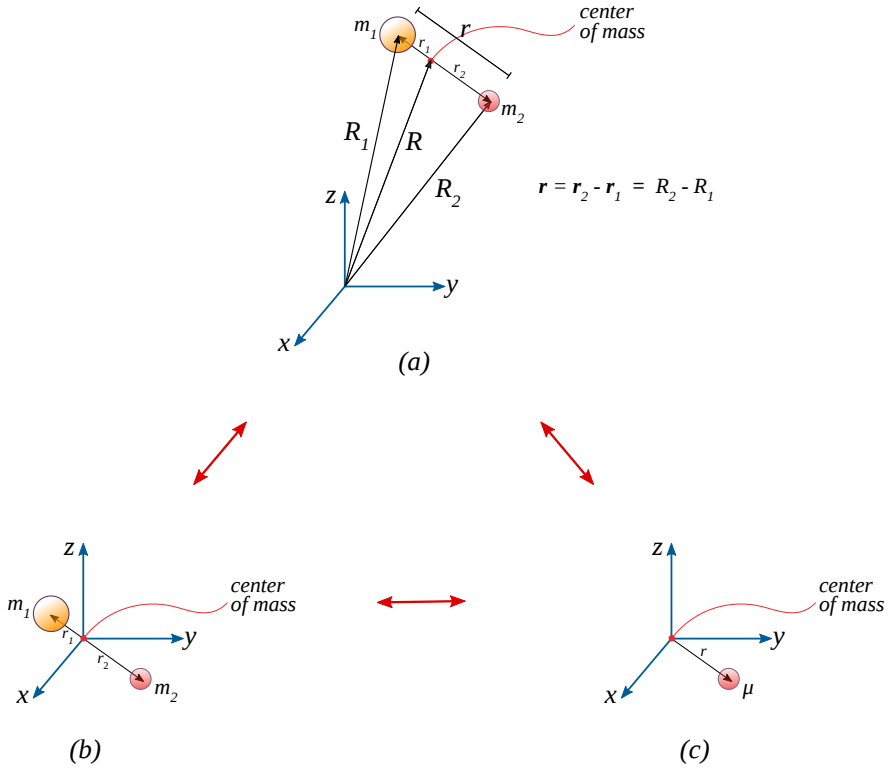


Figure 5.2.1 : a) the individual vectors to the particles m_1 and m_2 in the coordinate space and the resultant vector. b) center of mass. c) reduced mass. (CC BY-NC; Ümit Kaya via LibreTexts)

This concept is readily used in the general motion of diatomics, i.e. simple harmonic oscillator (vibrational displacement between two bodies, following Hooke's Law), the rigid rotor approximation (the moment of inertia about the center of mass of a two-body system), spectroscopy, and many other applications.

Example 5.2.1 : Reduced Mass

Determine the reduced mass of the two body system of a proton and electron with $m_{proton} = 1.6727 \times 10^{-27}\ kg$ and $m_{electron} = 9.110 \times 10^{-31}\ kg$).

Answer

$$\mu_{pe} = \frac{(1.6727 \times 10^{-27})(9.110 \times 10^{-31})}{1.6727 \times 10^{-27} + 9.110 \times 10^{-31}}$$
$$= 9.105 \times 10^{-31} kg$$

3.7.2: 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

$$V(x) \approx \frac{1}{2}kx^2 \tag{3.7.2}$$

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 3.7.2.

$$\hat{H}\left|\psi\right\rangle = \left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]\left|\psi\right\rangle = E|\psi\rangle$$

Solving this quantum harmonic oscillator is appreciably harder than solving the Schrödinger Equation for the simpler particle-in-the-box model and is outside the scope of this text. However, as with most quantum modules (and in contrast to the classical harmonic oscillator), the energies are quantized in terms of a quantum number (v in this case):

$$E_v = \hbar\left(\sqrt{\frac{k}{\mu}}\right)\left(v + \frac{1}{2}\right) \tag{3.7.3}$$
$$= h\nu\left(v + \frac{1}{2}\right) \tag{3.7.4}$$

with the natural vibrational frequency of the system given as

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{3.7.5}$$

and the mass, μ, is the reduced mass of the system (Equation 3.7.1).

Warning

Be careful to distinguish ν, the symbol for the natural frequency (as a Greek nu) from v the quantum harmonic oscillator quantum number (Latin v).

Caution: Do Not Use Atomic Weights to Calculate Reduced Masses

The vibrational frequencies given by Equation 3.7.5 depend on the force constants (k) and the atomic masses of the vibrating nuclei via the reduced mass (μ). It should be clear that the substitution of one isotope of an atom in a molecule for another isotope will affect the atomic masses and therefore the reduced mass (via Equation 3.7.1) and therefore the vibrational frequencies (via Equation 3.7.5).

It is important to remember that the Periodic Table gives only atomic weights of elements, which are scaled averages of atoms normally encountered in the laboratory (Table 5.2.1). To properly discuss vibrational frequencies of molecules, we need to know (or denote) the specific isotopes in the molecule. Check Table A4 for that information.

Table 5.2.1: Atomic Mass and Isotope Composition. Consult Table A4 for more extensive table.

isotope	atomic mass (in amu)	isotopic abundance (%)
^{1}H	1.007825	99.985
^{2}H	2.0140	0.015
^{35}Cl	35.968852	75.77
^{37}Cl	36.965903	24.23
^{79}Br	78.918336	50.69
^{81}Br	80.916289	49.31

Example 5.2.1 : Isotope Effect

What are the reduced mass for $^{1}H^{35}Cl$ and $^{1}H^{37}Cl$? If the spring constants for vibrations of both molecules are equal and estimated at $478\,N/m$, what are the natural vibrational frequencies of these two molecules?

Solution

The periodic table gives an atomic weight of 35.45 amu for chlorine, but remember this is the the average of the natural abundances of different chlorine isotopes which is dictated primary by two isotopes: ^{35}Cl and ^{37}Cl. For this problem, we need the exact mass of the ^{1}H, ^{35}Cl, and ^{37}Cl isotopes. Check Table A4 for that information.

For $^{1}H^{35}Cl$:

$$\begin{aligned}\text{Reduced mass} &= \frac{m_1 m_2}{m_1 + m_2} \\ &= \frac{m_H m_{^{35}Cl}}{m_H + m_{^{35}Cl}} \\ &= \frac{(1.0078)(34.9688)}{1.0078 + 34.9688)}\,amu \\ &= 0.9796\,amu\end{aligned}$$

or when converted into kg is $1.629 \times 10^{-27}\,kg$.

For $^{1}H^{37}Cl$:

$$\begin{aligned}\text{Reduced mass} &= \frac{m_1 m_2}{m_1 + m_2} \\ &= \frac{m_H m_{^{37}Cl}}{m_H + m_{^{37}Cl}} \\ &= \frac{(1.0078)(36.965)}{1.0078 + 36.965)}\,amu \\ &= 0.9810\,amu\end{aligned}$$

or when converted into kg is $1.6291 \times 10^{-27}\,kg$. This is only 0.29% bigger.

Equation 3.7.5 is used to predict the respective vibrational frequencies of these two molecules.

For $^{1}H^{35}Cl$:

$$\begin{aligned}\nu &= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \\ &= \frac{1}{2\pi}\sqrt{\frac{478\,N/m}{1.629 \times 10^{-27}\,kg}} \\ &= 8.6394 \times 10^{13} s^{-1}\end{aligned}$$

For $^{1}H^{37}Cl$:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{478\,N/m}{1.629 \times 10^{-27}\,kg}}$$

$$= 8.621 \times 10^{13} s^{-1}$$

As with the differences in the reduced masses, the differences in the vibrational frequencies of these two molecules is quite small. However, high resolution IR spectroscopy can easily distinguish the vibrations between these two molecules. Exercise 5.2.1 will demonstrate that this "**isotope effect**" is not always a small effect.

? Exercise 5.2.1 : Hydrogen Chloride

The force constant is weakly sensitive to the specific isotopes in a molecule (and we typically assume it is isotope independent). If the $k = 478\ N/m$ for both $H^{35}Cl$ and $H^{37}Cl$. What are the vibration frequencies in these two diatomic molecules.

Answer

$H^{35}Cl$: 2886 cm^{-1}

$D^{35}Cl$: 2081 cm^{-1}

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3.8: The Harmonic Oscillator Approximates Molecular Vibrations

Learning Objectives

- Understand the utility and limits of using the quantum harmonic oscillator as a model for molecular vibrations

The quantum harmonic oscillator is one of the most important model systems in quantum mechanics. This is due in partially to the fact that an arbitrary potential curve $V(x)$ can usually be *approximated* as a harmonic potential at the vicinity of a stable equilibrium point. Furthermore, it is one of the few quantum-mechanical systems for which an exact, analytical solution exists. Solving other potentials typically require either approximations or numerical approaches to identify the corresponding eigenstates and eigenvalues (i.e., wavefunctions and energies).

A general potential energy ($V(x)$) curve for a molecular vibration can be expanded as a Taylor series

$$V(x) = V(x_0) + \left.\frac{dV(x)}{dx}\right|_{x_0}^{x}(x - x_0) + \frac{1}{2!}\left.\frac{d^2V(x)}{dx^2}\right|_{x_0}^{x}(x - x_0)^2 + \ldots + \frac{1}{n!}\left.\frac{d^nV(x)}{dx^n}\right|_{x_0}^{x}(x - x_0)^n \tag{3.8.1}$$

It is important to note that this approximation is only good for x near x_0, and that x_0 stands for the equilibrium bond distance. $V(x)$ is often (but not always) shortened to the cubic term and can be rewritten as

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 \tag{3.8.2}$$

where $V(x_0) = 0$, k is the harmonic force constant (harmonic term), and γ is the first anharmonic term (i.e., cubic). As Figure 5.3.2 demonstrates, the harmonic oscillator (red curve) is a good approximation for the exact potential energy of a vibration (blue curve).

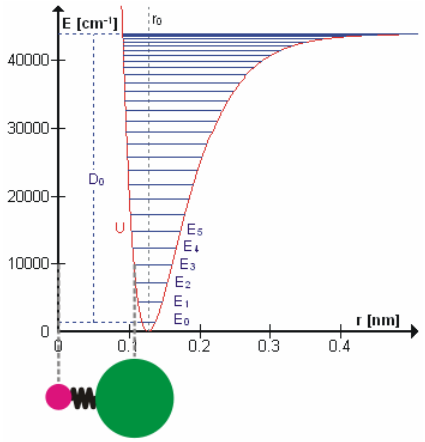


Figure 5.3.1 : The vibration of the **HCl** molecule is really an anharmonic oscillator, but can be approximated as a harmonic oscillator at low energies. In this animation, **HCl** is vibrating at the E_3 energy level. D_0 is dissociation energy here, r_0 bond length, V potential energy. Energy is expressed in wavenumbers. The hydrogen chloride molecule is attached to the coordinate system to show bond length changes on the curve. (CC BY-SA 3.0; Darekk2 via Wikipedia).

Adding anharmonic perturbations to the harmonic oscillator (Equation 3.8.2) better describes molecular vibrations. Anharmonic oscillation is defined as the deviation of a system from harmonic oscillation, or an oscillator not oscillating in simple harmonic motion. Anharmonic oscillation is described as the restoring force is no longer proportional to the displacement. Adding the cubic term (Figure 5.3.2 ; green curve) improves the harmonic oscillation approximation especially under greater displacement from equilibrium.

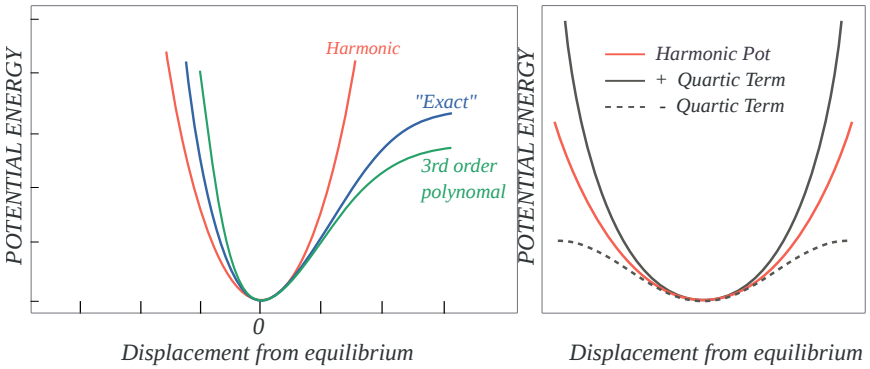


Figure 5.3.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

Naturally, adding higher order anharmonic terms, like quartic terms (Figure **3.8.2;**) improve the approximation. Almost all diatomics have experimentally determined potentials for their lowest energy states. $\mathbf{H_2}$, $\mathbf{Li_2}$, $\mathbf{O_2}$, $\mathbf{N_2}$, and $\mathbf{F_2}$ with terms up to $n < 10$ determined of Equation 3.8.1.

Figure 5.3.1 shows the the general potential with (numerically) calculated energy levels (E_0, E_1 etc.). D_o is the dissociation energy, which is different from the well depth D_e. These vibrational energy levels of this plot can be calculated using the harmonic oscillator model (i.e., Equation 5.3.1 with the Schrödinger equation) and have the general form

$$E_v = \left(v + \frac{1}{2}\right) v_e - \left(v + \frac{1}{2}\right)^2 v_e x_e + \left(v + \frac{1}{2}\right)^3 v_e y_e + \textbf{higher terms}$$

where v is the vibrational quantum number and x_e and y_e are the first and second anharmonicity constants, respectively.

The $v = 0$ level is the vibrational ground state. Because this potential is less confining than a parabola used in the harmonic oscillator, the energy levels become **less widely** spaced at high excitation (Figure 5.3.1 ; top of potential).

Limitations of the Harmonic Oscillator Model for Molecular Vibrations

The harmonic oscillation is a great approximation of a molecular vibration, but has key limitations:

- Due to equal spacing of energy, all transitions occur at the **same** frequency (i.e. single line spectrum). However experimentally many lines are often observed (called overtones).
- The harmonic oscillator does not predict bond dissociation; you cannot break it no matter how much energy is introduced.

Morse Potentials are better Approximations of Vibrational Motion

A more powerful approach than just "patching up" the harmonic oscillator solution with anharmonic corrections is to adopt a different potential ($V(x)$). One such approach is the Morse potential, named after physicist Philip M. Morse, and a better approximation for the vibrational structure of the molecule than the harmonic oscillator because it explicitly includes the effects of *bond breaking* and accounts for the anharmonicity of real bonds (Figure 5.3.4).

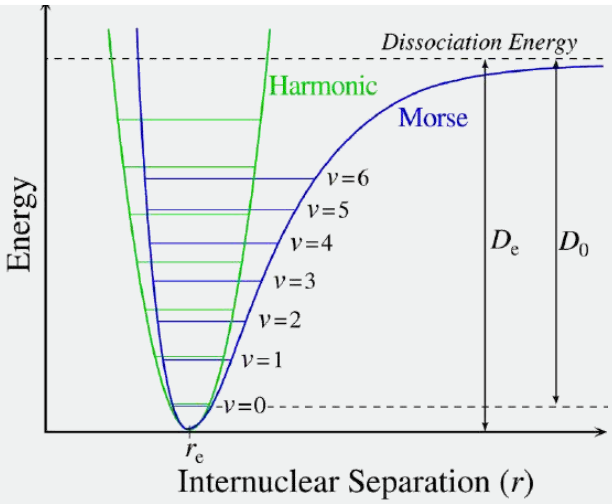


Figure 5.3.4 : The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by ħω, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e is larger than the true energy required for dissociation D_0 due to the zero point energy of the lowest ($v = 0$) vibrational level. from Wikipedia.

The Morse Potential is a good approximation to $V(x)$ and is best when looking for a general formula for all x from 0 to ∞, not just applicable for the local region around the x_o:

$$V(x) = D(1 - e^{-\beta(x-x_0)})^2 \tag{3.8.3}$$

with $V(x = x_0) = 0$ and $V(x = \infty) = D$.

The Morse Potential (Figure 5.3.4) approaches zero at infinite r_e and equals $-D_e$ at its minimum (i.e. $r = r_e$). It clearly shows that the Morse potential is the combination of a short-range repulsion term (small r values) and a long-range attractive term (large r values).

Solving the Schrödinger Equation with the Morse Potential (Equation **3.8.3**) is not trivial, but can be done analytically.

$$\hat{H}\,|\psi\rangle = E_n|\,\psi\rangle$$

with

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} \\ &= \frac{-\hbar^2 d^2}{2m\,dx^2} + D(1 - e^{-\beta(x-x_0)})^2\end{aligned}$$

The solutions and energies for the Morse potential will not be used in this course and will not be discussed in more detail.

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3.9: The Harmonic Oscillator Energy Levels

For a classical oscillator, we know exactly the position, velocity, and momentum as a function of time. The frequency of the oscillator (or normal mode) is determined by the reduced mass μ and the effective force constant k of the oscillating system and does not change unless one of these quantities is changed. There are no restrictions on the energy of the oscillator, and changes in the energy of the oscillator produce changes in the amplitude of the vibrations experienced by the oscillator.

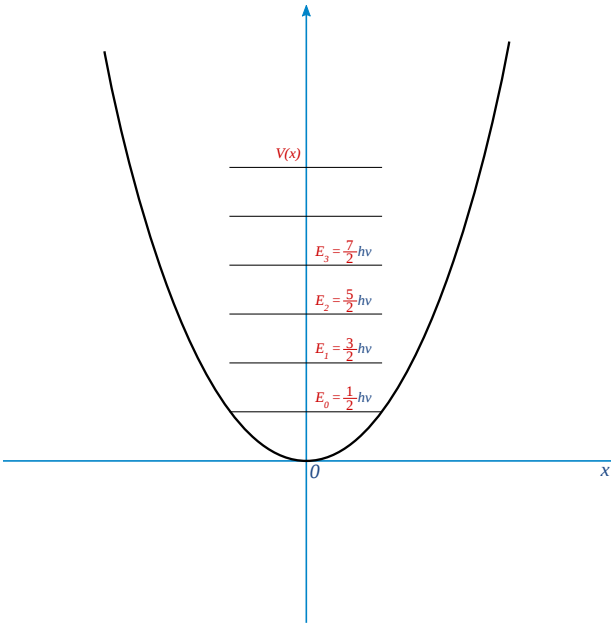


Figure 5.4.1 : Potential energy function and first few energy levels for harmonic oscillator. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

For the quantum mechanical oscillator, the oscillation frequency of a given normal mode is still controlled by the mass and the force constant (or, equivalently, by the associated potential energy function). However, the energy of the oscillator is limited to certain values. The allowed quantized energy levels are equally spaced and are related to the oscillator frequencies as given by Equation **3.9.1** and Figure 5.4.1 .

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega = \left(v + \frac{1}{2}\right)h\nu \tag{3.9.1}$$

with

$$v = 0, 1, 2, 3, \cdots \infty$$

In a quantum mechanical oscillator, we cannot specify the position of the oscillator (the exact displacement from the equilibrium position) or its velocity as a function of time; we can only talk about the probability of the oscillator being displaced from equilibrium by a certain amount. This probability is given by

$$P_{Q \to Q+dQ} = \int_{Q}^{Q+dQ} \psi_v^*(Q)\psi_v(Q)dQ \tag{3.9.2}$$

We can, however, calculate the average displacement and the mean square displacement of the atoms relative to their equilibrium positions. This average is just $\langle Q \rangle$, the expectation value for Q, and the mean square displacement is $\langle Q^2 \rangle$, the expectation value for Q^2. Similarly we can calculate the average momentum $\langle P_Q \rangle$, and the mean square momentum $\left\langle P_Q^2 \right\rangle$, but we cannot specify the momentum as a function of time.

Physically what do we expect to find for the average displacement and the average momentum? Since the potential energy function is *symmetric* around $Q = 0$, we expect values of $Q > 0$ to be equally as likely as $Q < 0$. The average value of Q therefore should be zero.

These results for the average displacement and average momentum do not mean that the harmonic oscillator is sitting still. As for the particle-in-a-box case, we can imagine the quantum mechanical harmonic oscillator as moving back and forth and therefore having an average momentum of zero. Since the lowest allowed harmonic oscillator energy, E_0, is $\frac{\hbar\omega}{2}$ and not 0, the atoms in a molecule must be moving even in the lowest vibrational energy state. This phenomenon is called the zero-point energy or the zero-point motion, and it stands in direct contrast to the classical picture of a vibrating molecule. Classically, the lowest energy available to an oscillator is zero, which means the momentum also is zero, and the oscillator is not moving.

? Exercise 5.4.1

Compare the quantum mechanical harmonic oscillator to the classical harmonic oscillator at $v = 1$ and $v = 50$.

Answer

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

$$\int_{-\infty}^{\infty} \psi_v^*(x)\psi_v(x)dx = 1 \tag{3.9.3}$$

and are orthogonal to each other.

$$\int_{-\infty}^{\infty} \psi_{v'}^*(x)\psi_v(x)dx = 0 \text{ for } v' \neq v \tag{3.9.4}$$

The fact that a family of wavefunctions forms an orthonormal set is often helpful in simplifying complicated integrals. We will use these properties when we determine the harmonic oscillator selection rules for vibrational transitions in a molecule and calculate the absorption coefficients for the absorption of infrared radiation.

Finally, we can calculate the probability that a harmonic oscillator is in the classically forbidden region. What does this tantalizing statement mean? Classically, the maximum extension of an oscillator is obtained by equating the total energy of the oscillator to the potential energy, because at the maximum extension all the energy is in the form of potential energy. If all the energy weren't in the form of potential energy at this point, the oscillator would have kinetic energy and momentum and could continue to extend further away from its rest position. Interestingly, as we show below, the wavefunctions of the quantum mechanical oscillator extend beyond the classical limit, i.e. beyond where the particle can be according to classical mechanics.

The lowest allowed energy for the quantum mechanical oscillator is called the **zero-point energy,** $E_0 = \frac{\hbar\omega}{2}$. Using the classical picture described in the preceding paragraph, this total energy must equal the potential energy of the oscillator at its maximum

extension. We define this classical limit of the amplitude of the oscillator displacement as Q_0. When we equate the zero-point energy for a particular normal mode to the potential energy of the oscillator in that normal mode, we obtain

$$\frac{\hbar\omega}{2} = \frac{kQ_0^2}{2} \tag{3.9.5}$$

> *The zero-point energy is the **lowest** possible energy that a quantum mechanical physical system may have. Hence, it is the energy of its ground state.*

Recall that k is the effective force constant of the oscillator in a particular normal mode and that the frequency of the normal mode is given by Equation 3.9.1 which is

$$\omega = \sqrt{\frac{k}{\mu}} \tag{3.9.6}$$

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3.10: 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, $\hat{V}$.

$$\hat{H} = \hat{T} + \hat{V} \tag{3.10.1}$$

For the free particle and the particle in a box, the potential energy term used in the Hamiltonian was zero. As shown in Equation 3.10.1, 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,

$$\hat{H}(q) = \frac{1}{2\mu}\hat{P}_q^2 + \frac{k}{2}\hat{q}^2 \tag{3.10.2}$$

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

$$\hat{H}(q) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2} + \frac{k}{2}q^2 \tag{3.10.3}$$

since the operator for position or displacement is just the position or displacement. The time-independent Schrödinger Equation then becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_v(q)}{dq^2} + \frac{k}{2}q^2\psi_v(q) = E_v\psi_v(q) \tag{3.10.4}$$

or upon rearranging

$$\frac{d^2\psi_v(q)}{dq^2} + \frac{2\mu}{\hbar^2}\left(E_v - \frac{k}{2}q^2\right)\psi_v(q) = 0 \tag{3.10.5}$$

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 3.10.5 are to simplify the equation by collecting constants in the parameter β

$$\beta^2 = \frac{\hbar}{\sqrt{\mu k}} \tag{3.10.6}$$

and then changing the variable from q to x where

$$x = \frac{q}{\beta} \tag{3.10.7}$$

so that

$$\frac{d^2}{dq^2} = \frac{1}{\beta^2}\frac{d^2}{dx^2} \tag{3.10.8}$$

After substituting Equations 3.10.6 and 3.10.8 into Equation 3.10.5, the differential equation for the harmonic oscillator becomes

$$\frac{d^2\psi_v(x)}{dx^2} + \left(\frac{2\mu\beta^2 E_v}{\hbar^2} - x^2\right)\psi_v(x) = 0 \tag{3.10.9}$$

? Exercise 5.6.1

Make the substitutions given in Equations 3.10.6 and 3.10.8 into Equation 3.10.5 to get Equation 3.10.9.

3.10.1: Solving for the Quantum Wavefunctions

A common strategy for solving differential equations, which is employed here, is to find a solution that is valid for large values of the variable and then develop the complete solution as a product of this asymptotic solution and a power series. Since the potential energy approaches infinity as x and the coordinate q approach infinity, the wavefunctions must approach zero (this is, the wavefunctions must **converge to zero**):

$$\lim_{x\to\infty} \psi_v(x) = 0 \tag{3.10.10}$$

The function that has this property and satisfies the differential equation for large values of x is the exponential function, i.e.,

$$\lim_{x\to\infty} \phi_v(x)\exp\left(\frac{-x^2}{2}\right) = 0 \tag{3.10.11}$$

where the wavefunctions are

$$\psi_v(x) \propto \phi_v(x)\exp\left(\frac{-x^2}{2}\right)$$

The general expression for a power series of $\phi_v(x)$ is

$$\begin{aligned}\phi_v(x) &= \sum_{n=0}^{\infty} c_n(v)x^n \\ &= c_n(v)x + c_n(v)x^2 + c_n(v)x^3 + \cdots\end{aligned}$$

which can be truncated after the first term, after the second term, after the third term, etc. to produce a set of polynomials. There is one polynomial for each value of v where v can be equal to any integer value including zero.

$$\sum_{n=0}^{v} c_n x^n \tag{3.10.12}$$

Each of the truncations of the power series in Equation 3.10.12 can be multiplied by the exponential function in Equation 3.10.11 to create a family of valid solutions to the differential equation in Equation 3.10.9.

$$\psi_v(x) = \sum_{n=0}^{v} c_n x^n \exp\left(\frac{-x^2}{2}\right) \tag{3.10.13}$$

? Exercise 5.6.2

Write the first four polynomials, $v = 0$ to $v = 1$, $v = 12$, $v = 13$, $v = 14$ for Equation 3.10.12 and use suitable software to prepare plots of these polynomials. Identify the curves in the plots.

? Exercise 5.6.3

Confirm that the wavefunction given by Equation 3.10.13 is a solution to the harmonic oscillator Schrödinger Equation in Equation 3.10.9 for $v = 0$ and $v = 1$.

3.10.1.1: Hermite Polynomials

While polynomials in general approach ∞ (or $-\infty$) as x approaches ∞, the decreasing exponential term overpowers the polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of x or $-x$. The exact forms of

polynomials that solve Equation 3.10.9 are the **Hermite polynomials**, which are standard mathematical functions known from the work of Charles Hermite. The first eight Hermite polynomials, $H_v(x)$, are given below.

- $H_0 = 1$
- $H_1 = 2x$
- $H_2 = -2 + 4x^2$
- $H_3 = -12x + 8x^3$
- $H_4 = 12 - 48x^2 + 16x^4$
- $H_5 = 120x - 160x^3 + 32x^5$
- $H_6 = -120 + 720x^2 - 480x^4 + 64x^6$
- $H_7 = -1680x + 3360x^3 - 1344x^5 + 128x^7$

The first six Hermite polynomials are plotted in Figure 5.6.1 . Hermite polynomials will be discussed in more detail in the following Section.

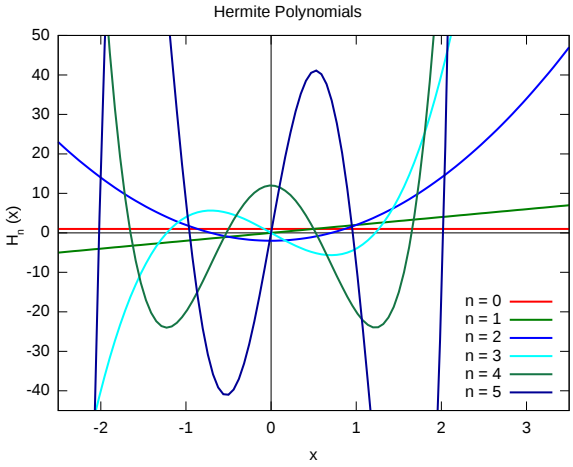


Figure 5.6.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

? Exercise 5.6.4

Determine the units of β and the units of x in the Hermite polynomials.

Because of the association of the wavefunction with a probability density, it is necessary for the wavefunction to include a normalization constant, N_v.

$$N_v = \frac{1}{(2^v v! \sqrt{\pi})^{1/2}} \tag{3.10.14}$$

The final form of the harmonic oscillator wavefunctions is thus

$$\psi_v(x) = N_v H_v(x) e^{-x^2/2} \tag{3.10.15}$$

Alternative and More Common Formulation of Harmonic Oscillator Wavefunctions

The harmonic oscillator wavefunctions are often written in terms of Q, the unscaled displacement coordinate (Equation 3.10.7) and a different constant α:

$$\alpha = 1/\sqrt{\beta} = \sqrt{\frac{k\mu}{\hbar^2}}$$

so Equation 3.10.15 becomes

$$\psi_v(x) = N_v'' H_v(\sqrt{\alpha} Q) e^{-\alpha Q^2/2}$$

with a slightly different normalization constant

$$N_v'' = \sqrt{\frac{1}{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

Exercise 5.6.5

Compute the normalization factor for $\psi_v(x)$ where $v = 0$ and $v = 4$. What is the purpose of N_v?

The energy eigenvalues for a quantum mechanical oscillator also are obtained by solving the Schrödinger equation. The energies are restricted to discrete values

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \tag{3.10.16}$$

with $v = 0, 1, 2, 3, \cdots$.

The energies depend both on the quantum number, v, and the oscillator frequency

$$\omega = \sqrt{\frac{k}{\mu}}$$

which in turn depends on the spring constant k and the reduced mass of the vibration μ.

Exercise 5.6.6

Determine the energy for the first ten harmonic oscillator energy levels in terms of $\hbar\omega$. Sketch an energy level diagram of these energies.

1. What insights do you gain from Equation 3.10.16, your calculations, and your diagram?
2. Is it possible to have a molecule that is not vibrating?
3. In terms of $\hbar\omega$, what is the energy of the photon required to cause a transition from one vibrational state to the next higher one?
4. If a transition from energy level $v = 9$ to $v = 10$ were observed in a spectrum, where would that spectral line appear relative to the one for the transition from level $v = 0$ to $v = 1$?
5. If a vibrational transition is observed at 3000 cm-1 in an infrared spectrum, what is the value of $\hbar\omega$ for the normal mode?
6. Identify all the possible meanings of $\Delta E = h\nu$ and the definition of the frequency, ν, in each case.

The normalized wavefunctions for the first four states of the harmonic oscillator are shown in Figure 5.6.2 , and the corresponding probability densities are shown in Figure 5.6.3 . You should remember the mathematical and graphical forms of the first few harmonic oscillator wavefunctions, and the correlation of v with E_v. The number of nodes in the wavefunction will help you to remember these characteristics. Also note that the functions fall off exponentially and that the symmetry alternates. For v equal to an even number, ψ_v is gerade; for v equal to an odd number, ψ_v is ungerade.

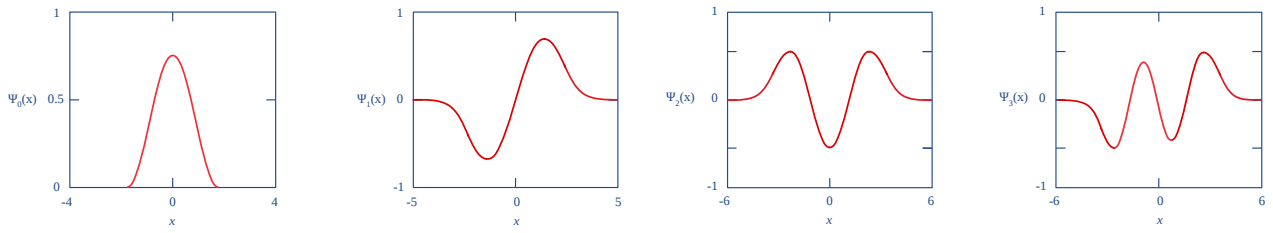


Figure 5.6.2 : The harmonic oscillator wavefunctions describing the four lowest energy states.

Exercise 5.6.7

Write a few sentences describing and comparing the plots in Figure 5.6.2 . How many nodes are there as a function of v? Do the wavefunctions converge at extreme displacement? Where is the most likely displacements for the oscillator to be found?

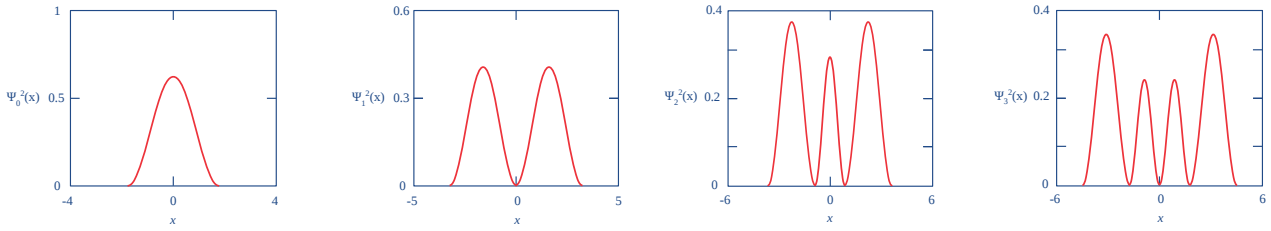


Figure 5.6.3 : The probability densities for the four lowest energy states of the harmonic oscillator.

Exercise 5.6.8

Explain how Figure 5.6.3 is related to Figure 5.6.2 . Explain the physical significance of the plots in Figure 5.6.3 in terms of the magnitude of the normal coordinate Q. Couch your discussion in terms of the HCl molecule. How would you describe the location of the atoms in each of the states? How does the oscillator position correspond to the energy of a particular level?

Answer

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?

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.

3.10.2: Tunneling in the Quantum Harmonic Oscillator

The observation that the wavefunctions are not zero at the classical limit means that the quantum mechanical oscillator has a finite probability of having a displacement that is larger than what is classically possible. The oscillator can be in a region of space where the potential energy is greater than the total energy. Classically, when the potential energy equals the total energy, the kinetic energy and the velocity are zero, and the oscillator cannot pass this point. A quantum mechanical oscillator, however, has a finite

probability of passing this point. For a molecular vibration, this property means that the amplitude of the vibration is larger than what it would be in a classical picture. In some situations, a larger amplitude vibration could enhance the chemical reactivity of a molecule.

? Exercise 5.6.10

Plot the probability density for $v = 0$ and $v = 1$ states. Mark the classical limits on each of the plots, since the limits are different because the total energy is different for $v = 0$ and $v = 1$. Shade in the regions of the probability densities that extend beyond the classical limit.

We should be able to calculate the probability that the quantum mechanical harmonic oscillator is in the classically forbidden region for the lowest energy state of the harmonic oscillator, the state with $v = 0$. The classically forbidden region is shown by the shading of the regions beyond Q_0 in the graph you constructed for Exercise 5.6.3 . The area of this shaded region gives the probability that the bond oscillation will extend into the forbidden region (Figure 5.6.3). To calculate this probability, we use

$$P[\text{forbidden}] = 1 - P[\text{allowed}] \tag{3.10.17}$$

because the integral from 0 to Q_0 for the allowed region can be found in integral tables and the integral from Q_0 to ∞ cannot. The form of the integral, $P[\text{allowed}]$, to evaluate is

$$P[\text{allowed}] = 2\int_0^{Q_0} \psi_0^*(Q)\psi_0(Q)dQ \tag{3.10.18}$$

The factor 2 appears in Equation 3.10.18 from the chancing the limits of integration from $-Q_0$ to $+Q_0$ into 0 to $+Q_0$; we can do this since the integrand is an even function, i. e., $f(-x) = f(x)$. To evaluate the integral in Equation 3.10.18, use the wavefunction and do the integration in terms of x. Recall that for $v = 0$, $Q = Q_0$ corresponds to $x = 1$. Including the normalization constant, Equation 3.10.18 produces

$$P[\text{allowed}] = \frac{2}{\sqrt{\pi}}\int_0^1 \exp(-x^2)dx \tag{3.10.19}$$

The integral in Equation 3.10.19 is called an error function (ERF) and can only be evaluated numerically. Values can be found in books of mathematical tables. When the limit of integration is 1, ERF(l) = 0.843 and P[forbidden] = 0.157. This result means that the quantum mechanical oscillator can be found in the forbidden region 16% of the time. This effect is substantial and leads to the phenomenon called *quantum mechanical tunneling*.

? Exercise 5.6.11

Numerically verify that $P[\text{allowed}]$ in Equation 3.10.19 equals 0.843. To obtain a value for the integral do not use symbolic integration or symbolic equals.

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3.11: Hermite Polynomials are either Even or Odd Functions

Learning Objectives

- Understand key properties of the Hermite polynomials including orthogonality and symmetry.
- Be proficient at using symmetries of integrands to quickly solve integrals.

Hermite polynomials were defined by Laplace (1810) though in scarcely recognizable form, and studied in detail by Chebyshev (1859). Chebyshev's work was overlooked and they were named later after Charles Hermite who wrote on the polynomials in 1864 describing them as new. They were consequently not new although in later 1865 papers Hermite was the first to define the multidimensional polynomials. The first six Hermite polynomial are plotted in Figure 5.7.1 .

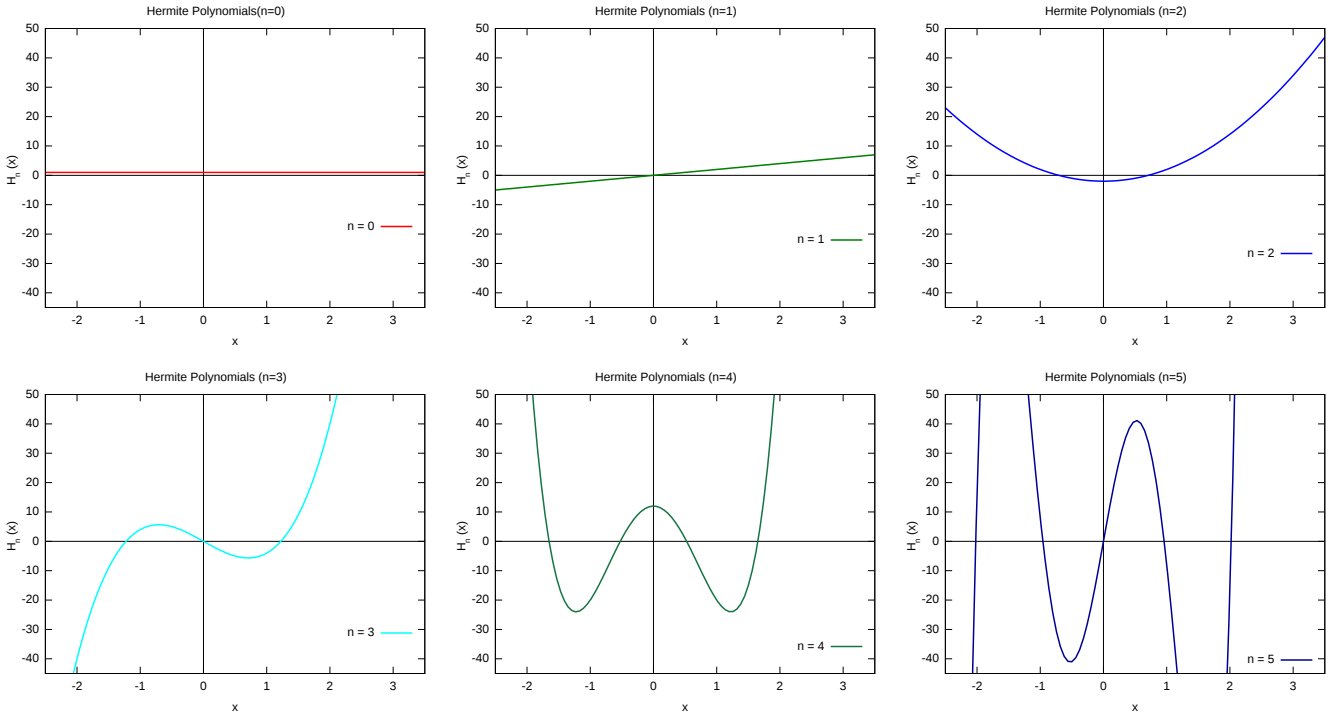


Figure 5.7.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

Generating Formula

Any Hermite polynomial $H_n(x)$ can be generated from a previous one $H_{n-1}(x)$ via the following using the recurrence relation

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x). \tag{3.11.1}$$

3.11.1: Hermite Polynomials are Symmetric

Let $f(x)$ be a real-valued function of a real variable.

- Then f is **even** if the following equation holds for all x and -x in the domain of f

$$f(x) = f(-x)$$

- Then f is **odd** if the following equation holds for all x and -x in the domain of f

$$-f(x) = f(-x)$$

Even and odd are terms used to describe particularly well-behaved functions. An *even* function is symmetric about the y-axis (Figure 5.7.2 ; left). That is, if we reflect the graph of the function in the y-axis, then it does not change. Formally, we say that f is

even if, for all x and $-x$ in the domain of f, we have

$$f(-x) = f(x)$$

Two examples of even functions are $f(x) = x^2$ and $f(x) = \cos x$.

An *odd* function has rotational symmetry of order two about the origin (Figure 5.7.2 ; middle). That is, if we rotate the graph of the function 180° about the origin, then it does not change. Formally, we say that ff is odd if, for all x and $-x$ in the domain of f, we have

$$f(-x) = -f(x)$$

Examples of odd functions are $f(x) = x^3$ and $f(x) = \sin x$.

Naturally, not all functions can be classified as even or odd. For example $f = x^3 + 1$ shown in the right side of Figure 5.7.2 , is neither.

> You can also think of these properties as symmetry conditions at the origin. More symmetries in 3D space are discussed in Group Theory.

Without proof, we can identify several key features involving multiplication properties of even and odd functions:

- The product of two **even** functions is an **even** function.
- The product of two **odd** functions is an **even** function.
- The product of an **even** function and an **odd** function is an odd function.

This can be shown graphically as a product table like that in Table 5.7.1 .

Table 5.7.1 : Product table of 1D Functions

Product table	Odd Function (anti-symmetric)	Even Function (symmetric)	No symmetry (neither)
Odd Function (anti-symmetric)	Even Function (symmetric)	Odd Function (anti-symmetric)	who knows
Even Function (symmetric)	Odd Function (anti-symmetric)	Even Function (symmetric)	who knows
No symmetry (neither)	who knows	who knows	who knows

Notice that the Hermite polynomials in Figure 5.7.1 oscillate from even to odd. We can take advantage of that aspect in our calculation of Harmonic Oscillator wavefunctions. Hermite Polynomial is an even or odd function depends on its degree n. Based on

$$H_n(-x) = (-1)^n H_n(x) \tag{3.11.2}$$

- $H_n(x)$ is an even function, when n is even.
- $H_n(x)$ is an odd function, when n is odd.

3.11.2: Integration over Symmetric Functions

You often consider integrals of the form

$$I = \int_{-a}^{a} f(x)\,\mathrm{d}x$$

If f is odd or even, then sometimes you can make solving this integral easier. For example, we can rewrite that integral in the following way:

$$I = \int_{-a}^{a} f(x)\,\mathrm{d}x = \int_{-a}^{0} f(x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{3.11.3}$$

$$= \int_{0}^{a} f(-x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{3.11.4}$$

For an even function, we have $f(-x) = f(x)$ and Equation 3.11.4 can be simplified

$$\begin{aligned} I &= \int_0^a f(-x)\,dx + \int_0^a f(x)\,dx \\ &= 2\int_0^a f(x)\,dx \end{aligned}$$

For an odd function, we have $f(-x) = -f(x)$ and Equation 3.11.4 can be simplified

$$\begin{aligned} I &= -\int_0^a f(x)\,dx + \int_0^a f(x)\,dx \\ &= 0 \end{aligned}$$

That's what it means to simplify the integration: the integral of an odd or even function over the interval $[-L, L]$ can be put into a nicer form (and sometimes we can see that it vanishes without ever computing an integral).

Example 5.7.1

Technically, evaluating the orthogonality of Hermite polynomials requires integrating over the $\exp(-x^2)$ weight function (Equations 3.11.5 and 3.11.6).

Solution

For the Hermite polynomials $H_n(x)$, the relevant inner product (using Dirac Notation)

$$\langle f, g\rangle = \int_{-\infty}^{\infty} f(x)g(x)\exp(-x^2)\,dx$$

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:

$$\int_{-\infty}^{\infty} f(x)\,dx = 0$$

This simplifies calculations greatly as demonstrated in the following chapters.

3.11.3: Hermite Polynomials are Orthogonal

Hermite polynomials $H_n(x)$ are *n*th-degree polynomials for *n* = 0, 1, 2, 3 and form an orthogonal set of functions for the weight function $e^{-x^2/2}$. The exact relation is:

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 0 \tag{3.11.5}$$

if $m \neq n$ and

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 2^n n!\sqrt{\pi} \tag{3.11.6}$$

if $m = n$.

This will not be proved, but can the demonstrated using any of the Hermite polynomials listed in the previous section. The orthogonality property becomes important when solving the Harmonic oscillator problems. Note that the integral of Equation 3.11.6 is important for normalizing the quantum harmonic oscillator wavefunctions discussed in last Section.

Example 5.7.2 : Hermite Polynomials are Orthogonal

Demonstrate that $H_2(x)$ and $H_3(x)$ are orthogonal.

Solution

We need to confirm

$$\int_{-\infty}^{\infty} H_2(x)H_3(x)dx = 0$$

or when substituted

$$\int_{-\infty}^{\infty} (4x^2-2)(8x^3-12x)dx = 0$$

because it says I need to show it's orthogonal on $[-\infty, \infty]$ or we can just evaluate it on a finite interval $[-L, L]$, where L is a constant.

$$\begin{aligned}\int_{-L}^{L} (4x^2-2)(8x^3-12x)dx &= 8\left(\frac{2x^6}{3} - 2x^4 + \frac{3x^2}{2}\right)\Bigg|_{-L}^{L} \\ &= 8\left(\frac{2L^6}{3} - 2L^4 + \frac{3L^2}{2}\right) - 8\left(\frac{2(-L)^6}{3} - 2(-L)^4 + \frac{3(-L)^2}{2}\right) \\ &= 0.\end{aligned}$$

3.11.4: 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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3.12: Spherical Polar Coordinates

The description of a rotating molecule in Cartesian coordinates would be very cumbersome. The problem is actually much easier to solve in **spherical polar coordinates**. Consider a particle that is located in space at some arbitrary point (x,y,z). In spherical polar coordinates, the position of a particle is also described by three variables, namely $\mathbf{r}, \theta$, and ϕ. These variables are defined according to the diagram. The distance from the origin to the point is specified by r. θ gives the angle formed by the position vector of the point and the positive z-axis. ϕ give the angle of rotation from the positive x-axis of the projection of the position vector into the xy plane. The ranges of possible values for $\mathbf{r}, \theta$ and ϕ are given by

$$\begin{aligned} 0 \leq r &\leq \infty \\ 0 \leq \theta &\leq \pi \\ 0 \leq \phi &\leq 2\pi \end{aligned} \tag{3.12.1}$$

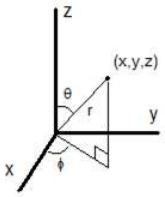


Figure 3.12.1

The coordinates of any point can be transformed from spherical polar coordinates to Cartesian coordinates using the following equations.

$$\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned}$$

The coordinates can be transformed from Cartesian coordinates to spherical polar coordinates by these equations.

$$\begin{aligned} r &= \sqrt{x^2 + y^2 + z^2} \\ \theta &= \tan^{-1}\left(\frac{y}{x}\right) \\ \phi &= \cos^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right) \end{aligned}$$

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3.13: Potential Energy and the Hamiltonian

Since there is no energy barrier to rotation, there is no potential energy involved in the rotation of a molecule. All of the energy is kinetic energy. This simplifies the writing of the Hamiltonian.

In Cartesian coordinates, the Hamiltonian can be written

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\mu}\nabla^2 \\ &= -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\end{aligned}$$

In spherical polar coordinates, the Hamiltonian can be written

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\mu}\nabla^2 \\ &= -\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\end{aligned}$$

For the rigid rotor problem, $\mathbf{r}$ is taken to be a constant, simplifying the operator.

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

The expression $\mu\mathbf{r}^2$ is the **moment of inertia** for the molecule. This value shows up often in problems involving the rotation of a molecule.

$$I = \mu r^2$$

While the expression for the Hamiltonian in spherical polar coordinates looks considerably more cumbersome than the Hamiltonian expressed in Cartesian coordinates, it will still be simpler to solve the problem describing the rotation of a molecule.

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3.14: Solution to the Schrödinger Equation

The time-independent Schrödinger equation can be written as follows.

$$\hat{H}\psi(\theta,\phi) = E\psi(\theta,\phi)$$
$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi(\theta,\phi) = E\psi(\theta,\phi)$$

Since the Hamiltonian can be expressed as a sum of operators, one in θ and the other in ϕ, it follows that the wavefunction should be able to be expressed as a product of two functions.

$$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

Making this substitution, the equation becomes

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Theta(\theta)\Phi(\phi) = E\Theta(\theta)\Phi(\phi)$$

With minimal rearrangement, the following result can be derived

$$\frac{\Phi(\phi)}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\Theta(\theta) + \frac{\Theta(\theta)}{\sin^2\theta}\frac{d^2}{d\phi^2}\Phi(\phi) = -\frac{2\mu r E}{\hbar^2}\Theta(\theta)\Phi(\phi)$$

And dividing both sides by $\Theta(\theta)\Phi(\phi)$ produces

$$\left(\frac{1}{\Theta(\theta)\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\Theta(\theta)\right) + \left(\frac{1}{\Phi(\phi)\sin^2\theta}\frac{d^2}{d\phi^2}\Phi(\phi)\right) = -\frac{2\mu r^2 E}{\hbar^2}$$

This expression suggests that the sum of two functions, one only in θ and the other only in ϕ, when added together, yields a constant. As the two variables θ and ϕ are independent of one another, the only way this can be true is if each equation is itself equal to a constant.

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\Theta(\theta) = -\lambda_1^2\Theta(\theta)$$
$$\frac{1}{\sin^2\theta}\frac{d^2}{d\phi^2}\Phi(\phi) = -\lambda_2^2\Phi(\phi)$$

where λ_1 and λ_2 are constants of separation (the form of which is chosen for convenience) which satisfy the following relationship.

$$-\lambda_1^2 - \lambda_2^2 = -\lambda^2$$
$$= -\frac{2\mu r^2 E}{\hbar^2}$$

Rotation in the xy plane ($\theta = \pi/2$)

We'll tackle the equation in ϕ first. One way to picture this part of the equation is that it describes the rotation of a molecule in the xy plane only (defined by $\theta = \pi/2$.) Given this constraint, it is clear that the $\sin^2(\theta)$ term becomes unity, $\text{since}\sin(\pi/2) = 1$. The problem then becomes

$$\frac{d^2}{d\phi^2}\Phi(\phi) = -\frac{2\mu r^2 E}{\hbar^2}\Phi(\phi)$$

If a substitution is made for the constants on the right-hand side of the equation,

$$-m_l^2 = -\frac{2\mu r^2 E}{\hbar^2}$$

we get

$$\frac{d^2}{d\phi^2}\Phi(\phi) = -m_l^2\Phi(\phi)$$

which should look like a familiar problem. Instead of using sine and cosine functions this time though, we will use an imaginary exponential function instead.

$$\Phi(\phi) = A_{m_l} e^{im_l\phi}$$

The boundary condition for this problem is that the function $\Phi(\phi)$ must be single valued. Therefore

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

So

$$A_{m_l} e^{im_1\phi} = A_{m_1} e^{im_l(\phi+2\pi)}$$

Dividing both sides by A_{m_l} and expressing the second exponential as a product yields

$$e^{im_l\phi} = e^{im_l\phi} e^{im_l 2\pi}$$
$$1 = e^{im_l 2\pi}$$

Using the Euler relationship

$$e^{i\alpha} = \cos\alpha + i\sin\alpha$$

we see that

$$1 = \cos(2m_l\pi) + i\sin(2m_l\pi)$$

In order for this to be true, the sine term must vanish and the cosine term must become unity. This is true if m_l is an integer, either positive or negative and including zero.

$$m_l = \ldots, -2, -1, 0, 1, 2, \ldots$$

Energy Levels

As such, the energy of a rigid rotator limited to rotation in the xy plane is given by

$$E_{m_l} = \frac{m_l^2\hbar^2}{2\mu r^2} \quad m_l = 0, \pm1, \pm2, \ldots$$

It is important to note that these functions are doubly degenerate for any non-zero value of m_l as there are always two values of m_l that yield the same energy.

Normalization

The wavefunctions can be normalized in the usual way.

$$\begin{aligned}\int_0^{2\pi} \left(A_{m_l} e^{im_l\phi}\right)^* \left(A_{m_l} e^{im_l\phi}\right) d\phi &= 1 \\ &= A_{m_l}^2 \int_0^{2\pi} e^{-im_l\phi} e^{im_l\phi} d\phi \\ &= A_{m_l}^2 \int_0^{2\pi} d\phi \\ &= A_{m_l}^2 [\phi]_0^{2\pi} \\ &= 2\pi A_{m_l}^2 \\ \sqrt{\frac{1}{2\pi}} &= A_{m_l}\end{aligned}$$

As was the case with the particle in a box problem, the normalization factor does not depend on the quantum number. The wavefunctions can be expressed

$$\Phi(\phi) = \sqrt{\frac{1}{2\pi}} e^{im_l\phi} \quad m_l = 0, \pm1, \pm2, \ldots$$

Rotation in three dimensions

We are now ready to tackle the more complicated problem of rotation in three dimensions. Recall the Schrödinger equation as was previously written.

$$\frac{\Phi(\phi)}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\Theta(\theta)+\frac{\Theta(\theta)}{\sin^2\theta}\frac{d^2}{d\phi^2}\Phi(\phi)=-\frac{2\mu r E}{\hbar^2}\Theta(\theta)\Phi(\phi)$$

We already know the form of the solutions for the $\Phi(\phi)$ part of the equation. However, due to the $1/\sin^2\theta$ term in the Φ equation, it is possible that the solution to the Θ part of the equation will introduce a new constraint on the quantum number m_l.

Energy Levels

The only well-behaved functions (functions that satisfy all of the boundary conditions) have energies given by

$$E_l=\frac{l(l+1)\hbar^2}{2\mu r^2}\quad l=0,1,2,...$$

The quantum number l indicated the angular momentum. m_l is the z-axis component of angular momentum. The z-axis is treated differently than the x - or y-axes due to the unique manner in which the z-axis is treated in the choice of the spherical polar coordinate system (since θ is taken as the angle of the position vector with the positive z-axis.) Also, as will be shown later, the operator $\hat{L}_z$, the z-axis angular momentum component operator, has a special relationship with the Hamiltonian (as does the squared angular momentum operator, $\hat{L}^2$.)

Degeneracy

The interpretation of the quantum number m_l is that it gives the magnitude of the z-axis component of the angular momentum vector. And since no vector can have a component with a magnitude greater than that of the vector itself, the constraint on m_l that is introduced by this solution is

$$|m_l|\le l$$

so for a given value of l, there are $(2l+1)$ values of m_l that fit the constraint. And since the energy expression does not depend on m_l, it is clear that each energy level has a degeneracy that is given by $(2l+1)$. That can be demonstrated as in the diagram below for an angular momentum vector of magnitude $2(l=2)$.

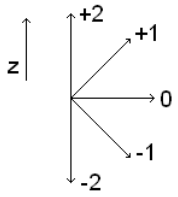


Figure 3.14.1

As can be seen in the diagram, there are five possible values of $m_l, +2, +1, 0, -1$ and -2. These five values correspond to the $(2l+1)$ degeneracy predicted for a state with total angular momentum given by $l=2$ (and therefore $2l+1=5$). When we see the wavefunctions in more detail, there will be a new reason for this constraint on the quantum number m_l.

Wavefunctions

For convenience, we'll first look at the solutions where $m_l=0$. The wavefunctions under this constraint have two parts, a normalization constant and a Legendre polynomial in $\cos(\theta)$. The Legendre polynomials are another set of orthogonal polynomials, similar to the Hermite polynomials that occur in the solution to the harmonic oscillator problem. The Legendre polynomials can be generated by the following relationship

$$P_l(x)=\frac{1}{2^l l!}\frac{d^l}{dx^l}\left(x^2-1\right)^l$$

The first few Legendre polynomials are given below.

l	$P_l(x)$	$P_l(\cos\theta)$
0	1	1
1	x	$\cos(\theta)$
2	$\frac{1}{2}(3x^2-1)$	$\frac{1}{2}[3\cos^2(\theta)-1]$
3	$\frac{1}{2}(5x^3-3x)$	$\frac{1}{2}[5\cos^3(\theta)-3\cos(\theta)]$

A recursion relation for the Legendre Polynomials is given by

$$(l+1)P_{l+1}(x) = (2l+1)xP_l(x) - lP_{l-1}(x)$$

When $m_l = 0$, the spherical harmonic function $Y_l^m(\theta,\phi) = \Theta(\theta)\Phi(\phi)$ becomes just $\Theta(\theta)$, since the ϕ dependence disappears. The $\Theta(\theta)$ part of the wavefunctions are given by

$$\Theta(\theta) = \left[\frac{(2l+1)}{2}\right]^{\frac{1}{2}} P_l(\cos\theta)$$

The functions are slightly different for $m_l \neq 0$. In this case, the functions involve a set of functions that are related to the Legendre Polynomials called the associated Legendre polynomials. These functions are generated from the Legendre polynomials via the following relationship.

$$P_l^{|m_l|}(x) = (-1)^{|m_l|}\left(1-x^2\right)^{\backslash m_l//2}\frac{d^{|m_l|}}{dx^{|m_l|}}P_l(x)$$

Note that for any value of $|m_l| > l$, the derivative of $P_l(x)$ vanishes.

$$\frac{d^{|m_l|}}{dx^{|m_l|}}P_l(x) = 0 \quad \text{for } |m_l| > l$$

And this is the origin of the constraint on m_l.

The associated Legendre polynomials depend on both l and m_l. Also, given the $|m_l|$ dependence, the sign of m_l does not matter. (The only place that the sign of m_l matter is in the $\Phi(\phi)$ function.) The first few associated Legendre Polynomials are given in the table below.

I	$\lvert m_l\rvert$	$P^{\lvert m\rvert}(x)$	$P^{\lvert m\rvert}(\cos\theta)$
0	0	1	1
1	0	x	$\cos(\theta)$
	1	$(1-x^2)^{\frac{1}{2}}$	$\sin(\theta)$
2	0	$\frac{1}{2}(3x^2-1)$	$\frac{1}{2}(3\cos^2(\theta)-1)$
	1	$3x(1-x^2)^{\frac{1}{2}}$	$3\cos(\theta)\sin(\theta)$
	2	$3(1-x^2)$	$3\sin^2(\theta)$

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3.15: Spherical Harmonics

The rigid rotor problem was solved using the Schrödinger equation

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi(\theta,\phi)=E\psi(\theta,\phi)$$

As it turns out, the solutions to this equation are very important in a number of areas in chemistry and physics. The eigenfunctions are known as the **spherical harmonics** $(Y_l^{m_l}(\theta,\phi))$ and they appear in every problem that has spherical symmetry. The Spherical Harmonics satisfy the relationship

$$\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y_l^{m_l}(\theta,\phi)=\hbar^2 l(l+1)Y_l^{m_l}(\theta,\phi)$$

Each function $Y_l^{m_l}(\theta,\phi)$ has three parts: 1) a normalization constant, 2) an associated Legendre polynomial in $\cos(\theta)$, and 3) an imaginary (for $m_l \neq 0$) exponential in ϕ.

$$Y_l^{m_l}(\theta,\phi)=\left[\frac{(2l+1)(l-|m_l|)}{4\pi(l+|m_l|)}\right]^{\frac{1}{2}}P_l^{|m_l|}(\cos\theta)e^{im_l\phi}$$

The first few Spherical harmonics are shown in the table below.

l	m_l	$Y_l^{m_l}(\theta,\phi)$
0	0	$\sqrt{\frac{1}{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}}\cos(\theta)$
	±1	±1
2	±1	$\sqrt{\frac{5}{16\pi}}(3\cos^2(\theta)-1)$
	0	$\sin(\theta)\cos(\theta)e^{\pm i\phi}$
	±2	$\sqrt{\frac{15}{32\pi}}\sin^2(\theta)e^{\pm 2i\phi}$

Notice the $(2l+1)$ degeneracy in these functions, due to the $(2l+1)$ values of m_l for each value of l. Also, it is useful to not that these functions all have l angular nodes (values of θ that cause the wavefunction to vanish.) For the $l=1$ wavefunctions, these nodes occur at $\theta=\pi/2$ for $m_l=0$ and at $\theta=0$ for $m_l=\pm1$. The number of nodes in each wavefunction is a useful property to know when discussing how these functions related to the radial wavefunction in the Hydrogen atom.

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3.16: Angular Momentum

The Spherical Harmonics are involved in a number of problems where **angular momentum** is important (including the Rigid Rotor problem, the H-atom problem and anything else where spherical symmetry is involved.) Angular momentum is a vector quantity that is given by the cross product of position and momentum.

$$\vec{\mathbf{L}} = \vec{\mathbf{r}} \times \vec{\mathbf{p}}$$

This quantity can be calculated from the following determinant.

$$\begin{aligned}\vec{\mathbf{L}} = \vec{\mathbf{r}} \times \vec{\mathbf{p}} &= \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \\ &= (yp_z - zp_y)\,\mathbf{i} + (zp_x - xp_z)\,\mathbf{j} + (xp_y - yp_x)\,\mathbf{k}\end{aligned}$$

Substituting the operators for the components of linear momentum, the operators that correspond to the three components of angular momentum are

$$\begin{aligned}\widehat{L_x} &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \widehat{L_y} &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \widehat{L_z} &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\end{aligned}$$

These can be used to determine the square of the angular momentum, which is given by the dot product of $\vec{\mathbf{L}}$ with itself.

$$\vec{\mathbf{L}} \cdot \vec{\mathbf{L}} = L^2 = L_x^2 + L_y^2 + L_z^2$$

Similarly, the operator for the square of the angular momentum is given by

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

In spherical polar coordinates, the angular momentum operators are given by the expressions

$$\begin{aligned}\hat{L}_x &= -i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\ \hat{L}_y &= -i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\ \hat{L}_z &= -i\hbar\frac{\partial^2}{\partial\phi^2}\end{aligned}$$

And the angular momentum squared operator is given by

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

For the Rigid-Rotator problem, it is interesting to note that the Hamiltonian is very closely related to the angular momentum squared operator.

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\mu r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \\ &= \frac{1}{2I}\hat{L}^2\end{aligned}$$

The eigenfunctions of the $\hat{L}^2$ operator are the Spherical Harmonics, $Y_l^{m_l}(\theta,\phi)$. These functions have the important properties that

$$\begin{aligned}\hat{H}Y_l^{m_l}(\theta,\phi) &= \frac{\hbar^2 l(l+1)}{2\mu r^2}Y_l^{m_l}(\theta,\phi) \\ \hat{L}^2Y_l^{m_l}(\theta,\phi) &= \hbar^2 l(l+1)Y_l^{m_l}(\theta,\phi) \\ \hat{L}_zY_l^{m_l}(\theta,\phi) &= \hbar m_l Y_l^{m_l}(\theta,\phi)\end{aligned}$$

Seeing as the spherical harmonics are eigenfunctions of all three of these operators, what is implied about the commutator of these two operators?

There are important relationships between the angular momentum operators. Each of the operators corresponding to the components of angular momentum commutes with the $\hat{L}^2$ operator, but they do not commute with one another. This implies that one can measure the squared angular momentum and only one component of angular momentum. This is generally taken as the z-axis component of angular momentum as the z-axis has special properties due to the manner in which the spherical polar coordinates have been defined.

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

The commutators involving two components of angular momentum are particularly interesting. Consider the commutator between and $\hat{L}_x$ and $\hat{L}_y$.

$$\left|\hat{L}_x, \hat{L}_y\right| = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x$$

Let's define each term separately and then take the difference.

$$\begin{aligned}\hat{L}_x\hat{L}_y &= (-i\hbar)^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\\ &= -\hbar^2\left(y\frac{\partial}{\partial z}z\frac{\partial}{\partial x} - y\frac{\partial}{\partial z}x\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}z\frac{\partial}{\partial x} + z\frac{\partial}{\partial y}x\frac{\partial}{\partial z}\right)\end{aligned}$$

The second, third and fourth terms are easy to simplify as the derivatives do not affect the $\mathbf{x}$ or $\mathbf{z}$ variables. The first term, however, requires some application of the chain rule.

$$\hat{L}_x\hat{L}_y = -\hbar^2\left(\left\{y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial x\partial z}\right\} - xy\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial x\partial y} + xz\frac{\partial^2}{\partial y\partial z}\right)$$

Similarly,

$$\begin{aligned}\hat{L}_y\hat{L}_x &= (-i\hbar)^2\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\\ &= -\hbar^2\left(z\frac{\partial}{\partial x}y\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}z\frac{\partial}{\partial y} - x\frac{\partial}{\partial z}y\frac{\partial}{\partial z} + x\frac{\partial}{\partial z}z\frac{\partial}{\partial y}\right)\\ &= -\hbar^2\left(zy\frac{\partial^2}{\partial x\partial z} - z^2\frac{\partial^2}{\partial x\partial y} - xy\frac{\partial^2}{\partial z^2} + \left\{x\frac{\partial}{\partial y} + xz\frac{\partial^2}{\partial z\partial y}\right\}\right)\end{aligned}$$

Taking the difference will cancel all of the second derivative terms, leaving only the first derivative terms behind.

$$\begin{aligned}\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x &= -\hbar^2\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)\\ &= i\hbar\hat{L}_z\end{aligned}$$

Similarly, it can be shown that

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

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3.17: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

Learning Objectives

- Understand how to measure the orbital angular momentum of an electron around a nucleus.
- Understand how the Heisenburgh Uncertainty Principle extends to orbital angular momenta.
- Manipulate the angular momenta cyclic permutations that allow two of the three projects to be simultaneous measured

Consider a particle described by the Cartesian coordinates $(x, y, z) \equiv \vec{r}$ and their conjugate momenta $(p_x, p_y, p_z) \equiv \vec{p}$. The classical definition of the *orbital angular momentum* of such a particle about the origin is (i.e., via the vector cross product):

$$\vec{L} = \vec{r} \times \vec{p}$$

which can be separated into projections into each of the primary axes :

Multiple \label

Extending this discussion to the quantum mechanics, we can assume that the operators $(\hat{L}_x, \hat{L}_y, \hat{L}_z) \equiv \vec{L}$ - that represent the components of orbital angular momentum in quantum mechanics - can be defined in an analogous manner to the corresponding components of classical angular momentum. In other words, we are going to assume that the above equations specify the angular momentum operators in terms of the position and linear momentum operators.

In Cartesian coordinates, the three operators for the orbital angular momentum components can be written as

$$\hat{L}_x = -\mathrm{i}\,\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \tag{3.17.1}$$

$$\hat{L}_y = -\mathrm{i}\,\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \tag{3.17.2}$$

$$\hat{L}_z = -\mathrm{i}\,\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \tag{3.17.3}$$

These can be transforming to operators in standard spherical polar coordinates,

Multiple \label

we obtain

Multiple \label

We can introduce a new operator $\hat{L}^2$:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{3.17.4}$$

$$= -\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \varphi^2} \right) \tag{3.17.5}$$

The eigenvalue problem for $\hat{L}^2$ takes the form

$$\hat{L}^2 \left| \psi \right\rangle = \lambda\, \hbar^2 \left| \psi \right\rangle \tag{3.17.6}$$

where $\psi(r, \theta, \varphi)$ is the wavefunction, and λ is a number. Let us write

$$\psi(r, \theta, \varphi) = R(r)\, Y(\theta, \varphi) \tag{3.17.7}$$

By definition,

$$\boxed{L^2 Y_l^{m_l} = l\,(l+1)\,\hbar^2\, Y_l^{m_l}} \tag{3.17.8}$$

where l is an integer. This is an important conclusion that argues the angular momentum is quantized with the square of the magnitude of the angular momentum only capable of assume one of the discrete set of values (Equation 3.17.8). From this, the **amplitude** of angular momentum can be expressed

$$\boxed{\left|\vec{L}\right| = \sqrt{L^2} = \sqrt{l(l+1)}\hbar} \tag{3.17.9}$$

Warning

We often refer to a particle in a state with angular momentum quantum number l as having angular momentum l, rather than saying that it has angular momentum of $\sqrt{l(l+1)}\hbar$ magnitude, primarily since it is awkward to say quickly.

The properties of spherical harmonics that the z-component of the angular momentum (L_z) is also quantized and can only assume a one of a discrete set of values

$$L_z Y_l^{m_l} = m\hbar Y_l^{m_l} \tag{3.17.10}$$

where m_l is an integer lying in the range $-l \leq m_l \leq l$.

- l is sometimes called "azimuthal quantum number" or "orbital quantum number"
- m_l is sometimes called "magnetic quantum number"

3.17.1: Simultaneous Measurements

Note that observables associated with $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ can, in principle, 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:

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\hbar\hat{L}_z \tag{3.17.11}$$

$$[\hat{L}_y, \hat{L}_z] = \mathrm{i}\hbar\hat{L}_x \tag{3.17.12}$$

$$[\hat{L}_z, \hat{L}_x] = \mathrm{i}\hbar\hat{L}_y \tag{3.17.13}$$

The three commutation relations (Equations 3.17.11 - 3.17.13) are the foundation for the whole theory of angular momentum in quantum mechanics. Whenever we encounter three operators having these commutation relations, we know that the dynamical variables that they represent have identical properties to those of the components of an angular momentum (which we are about to derive). In fact, we shall assume that any three operators that satisfy the commutation relations (Equations 3.17.11 - 3.17.13) represent the components of some sort of angular momentum.

> *Any three operators that satisfy the cyclic commutation relations represent the components of some sort of angular momentum.*

Example 6.3.1 : Commutators

Show that the $\hat{L}^2$ and $\hat{L}_x$ operators commute.

Solution

We want to confirm that $[\hat{L}^2, \hat{L}_x] = 0$ that from Equation 3.17.4 this can be expanded

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x]$$

from the properties of commutators, this can be expanded

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2, \hat{L}_x] + [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x]$$

However,

$$[\hat{L}_x^2, \hat{L}_x] = \hat{L}_x^2\hat{L}_x - \hat{L}_x\hat{L}_x^2 = \hat{L}_x\hat{L}_x\hat{L}_x - \hat{L}_x\hat{L}_x\hat{L}_x = 0$$

So

$$\begin{aligned}[\hat{L}^2, \hat{L}_x] &= [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\ &= \hat{L}_y^2\hat{L}_x - \hat{L}_x\hat{L}_y^2 + \hat{L}_z^2\hat{L}_x - \hat{L}_x\hat{L}_z^2 \\ &= \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z\end{aligned}$$

Lets look at some related forms which can be used to simplify the above expression. The first two terms can and final two terms can be rewritten as different commutators

$$\begin{aligned}[\hat{L}_y, \hat{L}_x] &= \hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] \\ &= (\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y)\hat{L}_y + \hat{L}_y(\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y) \\ &= \cancel{\hat{L}_y\hat{L}_x\hat{L}_y} - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_y\hat{L}_y\hat{L}_x - \cancel{\hat{L}_y\hat{L}_x\hat{L}_y}\end{aligned}$$

The first & fourth terms cancel, giving

$$[\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] = \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y$$

Similarly,

$$[Lz, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] = \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z$$

So,

$$\begin{aligned}[\hat{L}^2, \hat{L}_x] &= [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] \\ &= -i\hbar\hat{L}_z\hat{L}_y - i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_y\hat{L}_z + ih\hat{L}_z\hat{L}_y \\ &= 0\end{aligned}$$

One can also show similarly that

$$[\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0$$

Example 6.3.1 shows that while L_z can be known with certainty, L_x and L_y would **unknown**. This means that every vector with the appropriate length and z-component can drawn to represent $\vec{L}$, which forms a cone (Figure 6.3.1). The expected value of the angular momentum for a given ensemble of systems in the quantum state characterized by l and m_l could be somewhere on this cone while it cannot be defined for a single system (since the components of L do not commute with each other).

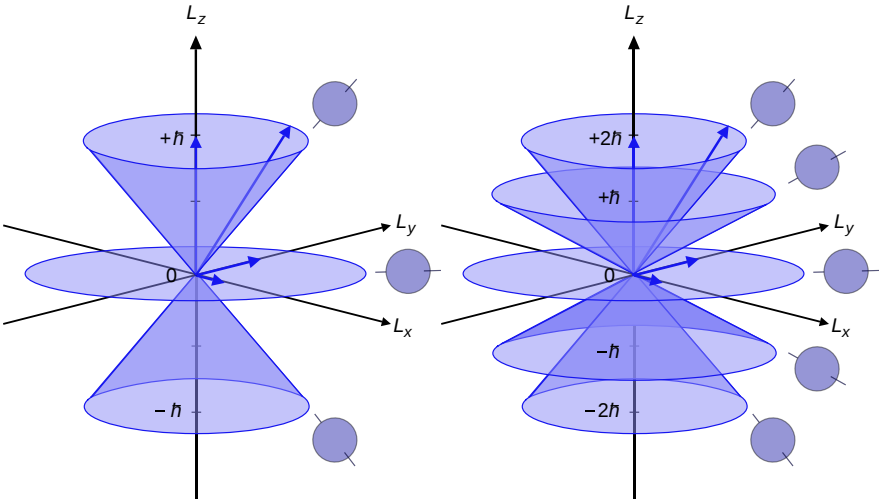


Figure 6.3.1 : Illustration of the vector model of orbital angular momentum. (left) A set of states with quantum numbers $l = 1$, and $m_l = -1, 0, +1,$. (right) A set of states with quantum numbers $l = 2$, and $m_l = -2, -1, 0, +1, +2$. (Public Domain; Maschen via Wikipedia)

The Meaning of Commutation of Two Operators

The mathematics of commutation relations is relatively straightforward, but what does it physically mean for an observable (Hermitian operator) to commute with another observable (Hermitian operator) in quantum mechanics?

If two operators $\hat{A}$ and $\hat{B}$ commute with each other then

$$\hat{A}\hat{B} - \hat{B}\hat{A} = 0,$$

which can be rearranged to

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

This is not a trivial statement and many operations do not commute and hence the end-result depends on how you have ordered the operations.

If you recall that operators act on quantum mechanical states and give you a new state in return, then this means that with $\hat{A}$ and $\hat{B}$ commuting, the state you obtain from letting first $\hat{A}$ act and then $\hat{B}$ act on some initial state is the same as if you let first $\hat{B}$ and then $\hat{A}$ act on that state, i.e.,

$$\hat{A}\hat{B}\left|\psi\right\rangle = \hat{B}\hat{A}\left|\psi\right\rangle.$$

Recall that when you perform a quantum mechanical measurement, you will always measure an eigenvalue of your operator, and after the measurement your state is left in the corresponding eigenstate. The eigenstates to the operator are precisely those states for which there is **no uncertainty** in the measurement: You will **always** measure the eigenvalue.

Therefore, $\hat{B}|a\rangle$ must be an eigenfunction of $\hat{A}$ with eigenvalue a just like $|a\rangle$ itself is. That is essentially saying that $|a\rangle$ is an eigenfunction of $\hat{B}$.

A key example of this is since $\hat{L}^2$ and $\hat{L}_x$ commute (Example 6.3.1) then both operators share the same eigenstates. Hence, we do no need to solve two eignevalue problems:

$$\hat{L}^2\left|\psi\right\rangle = \lambda\left|\psi\right\rangle$$

and

$$\hat{L}_x\left|\psi\right\rangle = \beta\left|\psi\right\rangle$$

If we solve one, we then know the eigenvalues ($|\psi\rangle$) for the other!

What does it mean when some observable $\hat{A}$ commutes with the Hamiltonian $\hat{H}$? First, we get all the result from above: There is a simultaneous eigenbasis of the energy-eigenstates and the eigenstates of $\hat{A}$. This can yield a tremendous simplification of the task of solving Schrödinger equations. For example, the Hamiltonian of the hydrogen atom commutes with $\hat{L}$, the angular momentum operator, and with $\hat{L}_z$, its z-component. This tells you that you can classify the eigenstates by an angular- and magnetic quantum number l and m.

3.17.2: Summary

In the quantum world, angular momentum is quantized. The square of the magnitude of the angular momentum (determined by the eigenvalues of the $\hat{L}^2$ operator) can only assume one of the discrete set of values

$$L^2 = l(l+1)\hbar^2$$

or the magnitude of the angular momentum

$$L = \sqrt{l(l+1)}\hbar$$

with $l = 0, 1, 2, ...$

The z-component of the angular momentum (i.e., projection of L onto the z-axis) is also quantized with

$$L_z = m_l\hbar$$

with $m_l = -l, 0-1, ..., 0, ... + l + 1, l$ for a given value of l. Hence, l and m_l are the *angular momentum quantum number* and the *magnetic quantum number*, respectively.

Contributors and Attributions

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3.18: Application to the Rotation of Real Molecules

While the spherical harmonics are the wavefunctions that describe the rotational motion of a rigid rotator, the names of the quantum numbers are changed to reflect the type of angular momentum encountered in the problem. The quantum number l and m_l should be familiar as these are the ones used in the hydrogen atom problem to describe the orbital angular momentum. However, for rotational motion, these are replaced by $\mathbf{J}$ and $\mathbf{M_J}$. The energy levels of the rigid rotator are therefore given by

$$E_J = J(J+1)\frac{\hbar^2}{2\mu r^2}$$

And since $\mathbf{M_J}$ does not appear in the energy level expression, each level has a $(\mathbf{2\ J+1})$ degeneracy. The spacings between energy levels increases with increasing $\mathbf{J}$ due to the $\mathbf{J(J+1)}$ dependence (which has a $\mathbf{J^2}$ term.) This pattern is shown in the diagram below.

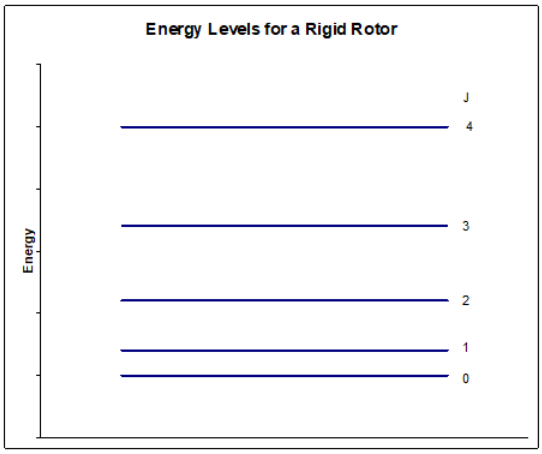


Figure **3.18.1**

For spectroscopic measurements, the rotational energy (given the symbol F_J) is often expressed in spectroscopic units, such as $\mathbf{cm^{-1}}$. Also, a spectroscopic constant, B, is used to describe the energy level stack.

$$F_J = \frac{E_J}{hc} = BJ(J+1)$$

where the spectroscopic constant B is given by

$$B = \frac{h}{8\pi^2 c\mu r^2}$$

Thus, by knowing the value of μ, the reduced mass, and measuring the value of B, the rotational constant, one can determine the value of $\mathbf{r}$, the bond length. This is the utility of rotational spectroscopy - it gives us detailed information about molecular structure!

Centrifugal Distortion

As we know, since they vibrate, real molecules do not have rigid bonds. So it is no surprise to learn that the Rigid Rotor is really just a limiting ideal model, much like the ideal gas law describes limiting ideal behavior.

Real molecules, especially when rotating with very high angular momentum, will tend to stretch. In other words, the average bond length will increase with increasing J. And given the inverse relationship between $\mathbf{B}$ and bond length(r), it is not surprising that the effective B value is smaller at higher levels of $\mathbf{J}$. In fact, this centrifugal distortion problem is well treated by introducing a "distortion constant" D such that

$$F_J = BJ(J+1) - D[J(J+1)]^2$$

Naturally, one would expect the distortion constant to be small in the case of a strong, inflexible bond, but larger if the bond is weaker. The approximation of Kraitzer suggests that the distortion constant is determined to a good approximation by

$$D \approx \frac{4B^3}{\omega_e^2}$$

For a well behaved molecule, he distortion constant **D** is always smaller in magnitude than **B**. Some molecules require several distortional constants to yield a reasonable description of their rotational energy level stack. If additional constants are needed, they are introduced as coefficients in a power series of $\mathbf{J(J+1)}$.

$$\mathbf{F_J = BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3 + ...}$$

The power series is truncated at a point that yields a good fit to experimental observations for a given molecule.

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CHAPTER OVERVIEW

4: The Hydrogen Atom

4.1: The Hydrogen Atomic Spectrum
4.2: The Rydberg Formula and the Hydrogen Atomic Spectrum
4.3: Bohr's Hydrogen Atom
4.4: The Schrödinger Equation
4.5: Other One-Electron Systems
4.6: The Wavefunctions
4.7: s-orbitals are Spherically Symmetric
4.8: Orbital Angular Momentum and the p-Orbitals

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4.1: 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.

4.1.1: Atomic Line Spectra

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

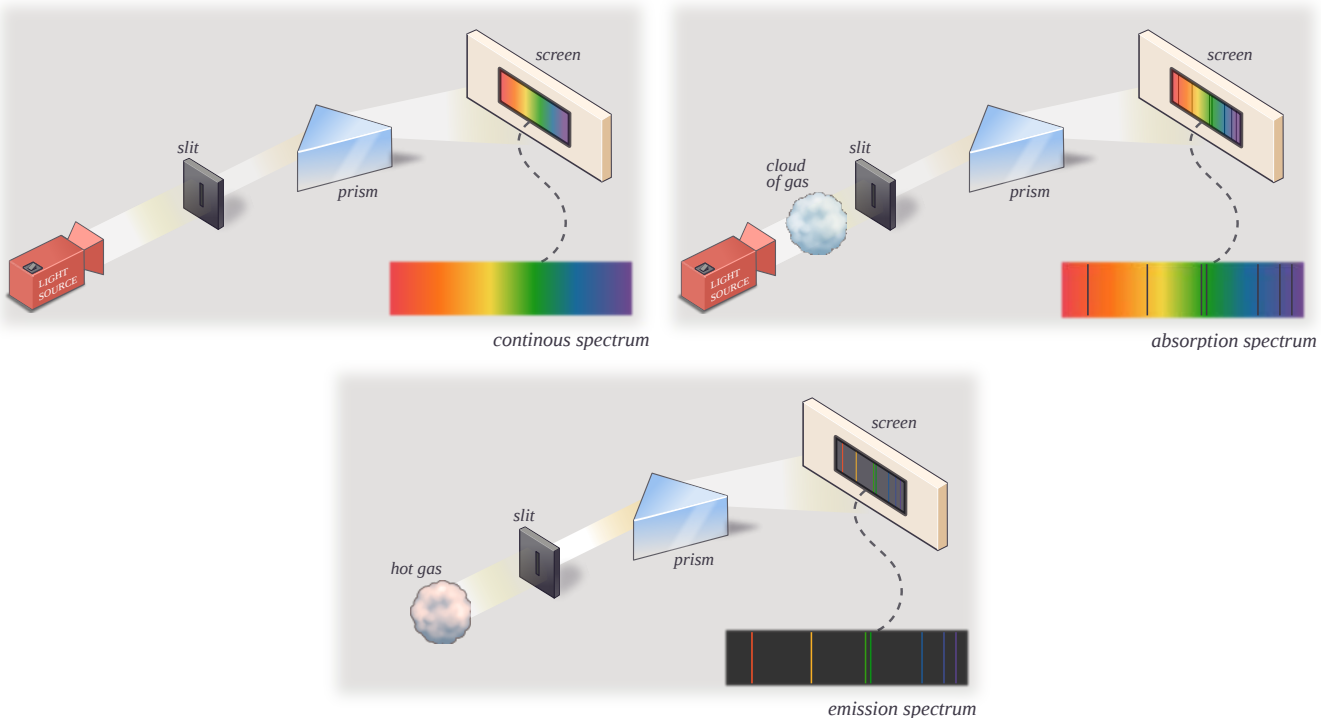


Figure 1.4.1 : Three Kinds of Spectra. When we see a lightbulb or other source of continuous radiation, all the colors are present. When the continuous spectrum is seen through a thinner gas cloud, the cloud's atoms produce absorption lines in the continuous spectrum. When the excited cloud is seen without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

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

Fraunhofer Lines

In 1802, William Wollaston in England had discovered that the solar spectrum had tiny gaps - there were many thin dark lines in the rainbow of colors. These were investigated much more systematically by Joseph von Fraunhofer, beginning in 1814. He increased the dispersion by using more than one prism. He found an "almost countless number" of lines. He labeled the strongest dark lines A, B, C, D, etc. Frauenhofer between 1814 and 1823 discovered nearly 600 dark lines in the solar spectrum viewed at high resolution and designated the principal features with the letters A through K, and weaker lines with other letters (Table 1.4.1). Modern observations of sunlight can detect many thousands of lines. It is now understood that these lines are caused by absorption by the outer layers of the Sun.

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

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

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

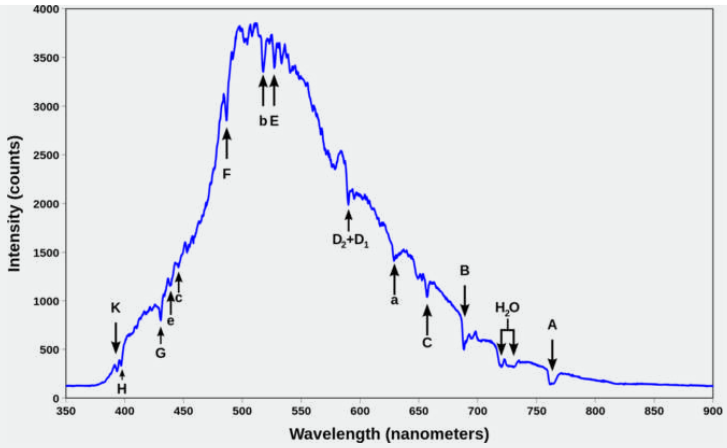


Figure 1.4.2 : Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. (CC BY-SA 4.0; Eric Bajart via Wikipedia).

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

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

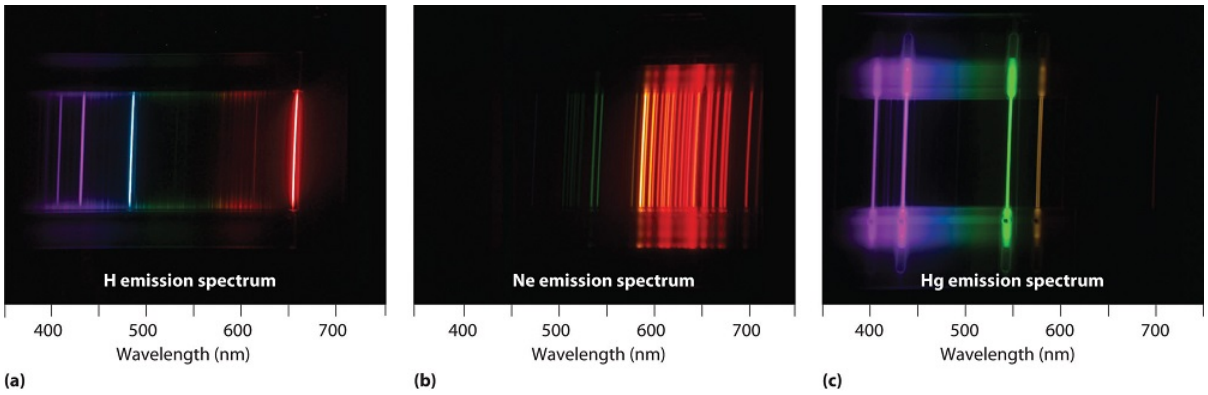


Figure 1.4.3 : The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The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

4.1.2: The Balmer Series of Hydrogen

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

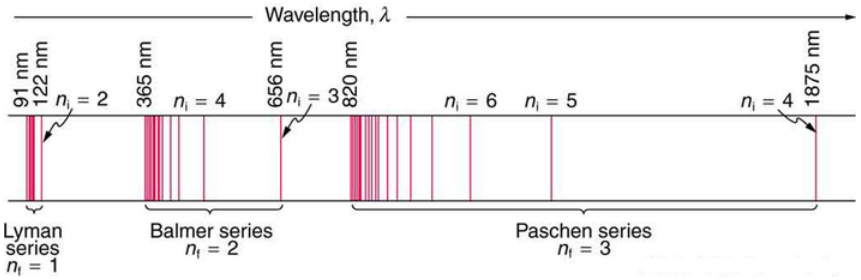


Figure 1.4.4 : A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of n_f and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

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

$$\lambda = b\left(\frac{n_2^2}{n_2^2 - 4}\right) \tag{4.1.1}$$

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

The first four wavelengths of Equation 4.1.1 (with n_2 = 3, 4, 5, 6) were in excellent agreement with the experimental lines from Ångström (Table 1.4.2). Balmer predicted that other lines exist in the ultraviolet that correspond to $n_2 \geq 7$ and in fact some of them had already been observed, unbeknown to Balmer.

Table 1.4.2 : The Balmer Series of Hydrogen Emission Lines

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

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

Balmer's general formula (Equation 4.1.1) can be rewritten in terms of the inverse wavelength typically called the *wavenumber* ($\tilde{\nu}$).

$$\tilde{\nu} = \frac{1}{\lambda} \tag{4.1.2}$$

$$= R_H\left(\frac{1}{4} - \frac{1}{n_2^2}\right) \tag{4.1.3}$$

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

$$\begin{aligned}\tilde{\nu} &= \frac{1}{\lambda} \\ &= \frac{\nu}{c}\end{aligned}$$

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

$$\begin{aligned}E &= \frac{hc}{\lambda} \\ &= hc \times \frac{1}{\lambda} \\ &= hc\tilde{\nu} \\ &\propto \tilde{\nu}\end{aligned}$$

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

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

This is also known as the H_α line of atomic hydrogen and is bright red (Figure **4.1.3***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 4.1.3) and simply solved:

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

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

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

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4.2: 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:

$$\tilde{\nu} = \frac{1}{\lambda} \tag{4.2.1}$$

$$= R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{4.2.2}$$

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

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

4.2.1: 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., $n_1 = 1$)?

$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \tag{4.2.3}$$

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

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

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

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

Other Series

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

- Lyman series with $n_1 = 1$

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

Example 1.5.1 : The Lyman Series

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

Given: lowest-energy orbit in the Lyman series

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

Strategy

A. Substitute the appropriate values into Equation 4.2.2 (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 4.2.2) to calculate the wavelength:

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

Solution A

For the Lyman series, $n_1 = 1$.

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

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

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

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

Solution B

his wavelength is in the ultraviolet region of the spectrum.

Exercise 1.5.1 : The Pfund Series

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

Answer

$4.65 \times 10^3\ nm$; 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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4.3: Bohr's Hydrogen Atom

Niels Bohr introduced the atomic Hydrogen model in 1913. He described it as a positively charged nucleus, comprised of protons and neutrons, surrounded by a negatively charged electron cloud. In the model, electrons orbit the nucleus in atomic shells. The atom is held together by electrostatic forces between the positive nucleus and negative surroundings.

Hydrogen Energy Levels

The Bohr model is used to describe the structure of hydrogen energy levels. The image below represents shell structure, where each shell is associated with principal quantum number *n*. The energy levels presented correspond with each shell. The amount of energy in each level is reported in eV, and the maxiumum energy is the ionization energy of 13.598eV.

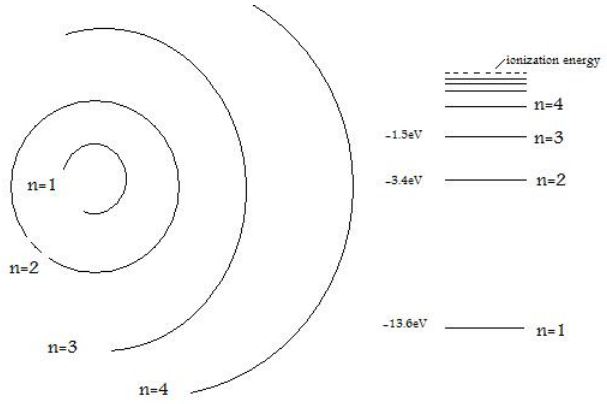


Figure 1: *Some of the orbital shells of a Hydrogen atom. The energy levels of the orbitals are shown to the right.*

Hydrogen Spectrum

The movement of electrons between these energy levels produces a spectrum. The Balmer equation is used to describe the four different wavelengths of Hydrogen which are present in the visible light spectrum. These wavelengths are at 656, 486, 434, and 410nm. These correspond to the emission of photons as an electron in an excited state transitions down to energy level n=2. The Rydberg formula, below, generalizes the Balmer series for all energy level transitions. To get the Balmer lines, the Rydberg formula is used with an n_f of 2.

Rydberg Formula

The Rydberg formula explains the different energies of transition that occur between energy levels. When an electron moves from a higher energy level to a lower one, a photon is emitted. The Hydrogen atom can emit different wavelengths of light depending on the initial and final energy levels of the transition. It emits a photon with energy equal to the difference of square of the final (n_f) and initial (n_i) energy levels.

$$\text{Energy} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{4.3.1}$$

The energy of a photon is equal to Planck's constant, h=6.626*$10^{-34}$$m^2$kg/s, times the speed of light in a vacuum, divided by the wavelength of emission.

$$E = \frac{hc}{\lambda} \tag{4.3.2}$$

Combining these two equations produces the Rydberg Formula.

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{4.3.3}$$

The Rydberg Constant (R) = $10,973,731.6\ m^{-1}$ or $1.097 \times 10^{7}\ m^{-1}$.

Limitations of the Bohr Model

The Bohr Model was an important step in the development of atomic theory. However, it has several limitations.

- It is in violation of the Heisenberg Uncertainty Principle. The Bohr Model considers electrons to have both a known radius and orbit, which is impossible according to Heisenberg.
- The Bohr Model is very limited in terms of size. Poor spectral predictions are obtained when larger atoms are in question.
- It cannot predict the relative intensities of spectral lines.
- It does not explain the Zeeman Effect, when the spectral line is split into several components in the presence of a magnetic field.
- The Bohr Model does not account for the fact that accelerating electrons do not emit electromagnetic radiation.

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Problems

1. An emission spectrum gives one of the lines in the Balmer series of the hydrogen atom at 410 nm. This wavelength results from a transition from an upper energy level to n=2. What is the principal quantum number of the upper level?

2. The Bohr model of the atom was able to explain the Balmer series because:

a. larger orbits required electrons to have more negative energy in order to match the angular momentum.
b. differences between the energy levels of the orbits matched the difference between energy levels of the line spectra.
c. electrons were allowed to exist only in allowed orbits and nowhere else.
d. none of the above

3. One reason the Bohr model of the atom failed was because it did not explain why

a. accelerating electrons do not emit electromagnetic radiation.
b. moving electrons have a greater mass.
c. electrons in the orbits of an atom have negative energies.
d. electrons in greater orbits of an atom have greater velocities.

Answers

1. $(1/\lambda) = R*[\ 1/(2^2) - 1/(n^2)\ ]$, $R=1.097x10^{7}\ m^{-1}$, $\lambda=410nm$

$(1/410nm) = (1.097x10^{7}\ m^{-1}) * [\ 1/(2^2) - 1/(n^2)\ ]$

$[\ (1/4.10x10^{-7}m) / (1.097x10^{7}\ m^{-1})\ ] - [\ (1/4)\ ] = [\ -1/(n^2)\ ]$

$-1/-0.02778 = n^2$

$36 = n^2$, n=6 --> The emission resulted from a transition from energy level 6 to energy level 2.

2. (B) differences between the energy levels of the orbits matched the difference between energy levels of the line spectra.

3. (A) accelerating electrons do not emit electromagnetic radiation.

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4.4: The Schrödinger Equation

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.

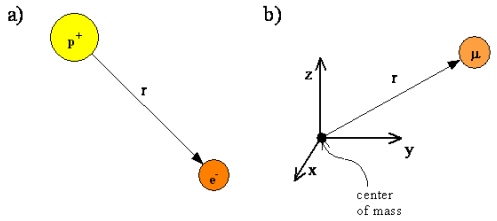


Figure 4.4.1: a) The proton (p^+) and electron (e^-) of the hydrogen atom. b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

Exercise 4.4.1

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 that we considered in Chapter 7. The Schrödinger Equation for the hydrogen atom

$$\hat{H}(r,\theta,\varphi)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{4.4.1}$$

employs the same kinetic energy operator, $\hat{T}$, written in spherical coordinates as developed in Chapter 7. 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,

$$\hat{V}(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{4.4.2}$$

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

$$\hat{H}(r,\theta,\varphi) = -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r} \tag{4.4.3}$$

The contributions from rotational and radial components of the motion become clearer if we write out the complete Schrödinger equation,

$$\left\{-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\right\}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{4.4.4}$$

multiply both sides of Equation 4.4.4 by $2\mu r$, and rearrange to obtain

$$\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right) + 2\mu r^2\left[E + \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(r,\theta,\varphi) = \tag{4.4.5}$$

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\varphi) \tag{4.4.6}$$

Manipulating the Schrödinger equation in this way helps us recognize the square of the angular momentum operator in Equation 4.4.6. The square of the angular momentum operator, which was defined in Chapter 7, is repeated here as Equation 4.4.7.

$$\hat{M}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{4.4.7}$$

Substituting Equation 4.4.7 into Equation 4.4.6 produces

$$\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right) + 2\mu r^2[E - \hat{V}]\psi(r,\theta,\varphi) = \hat{M}^2\psi(r,\theta,\varphi) \tag{4.4.8}$$

Exercise 4.4.1

Show the algebraic steps going from Equation 4.4.4 to Equation 4.4.6 and finally to Equation 4.4.8. Justify the statement that the rotational and radial motion are separated in Equation 4.4.8.

Since the angular momentum operator does not involve the radial variable, r, we can separate variables in Equation 4.4.8 by using a product wavefunction, as we did previously in Chapter 7. From our work on the rigid rotor, Chapter 7, we know that the eigenfunctions of the angular momentum operator are the Spherical Harmonic functions, $Y(\theta,\varphi)$, so a good choice for a product function is

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi) \tag{4.4.9}$$

The Spherical Harmonic functions table 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 4.4.9, into Equation 4.4.8, 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.

$$\frac{\hbar^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \frac{2\mu r^2}{R(r)}[E - V]R(r) = \lambda \tag{4.4.10}$$

$$\frac{1}{Y(\theta,\varphi)}\hat{M}^2 Y(\theta,\varphi) = \lambda \tag{4.4.11}$$

Equations 4.4.10 and 4.4.11 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 4.4.3

Complete the steps leading from Equation 4.4.8 to Equation 4.4.10 and Equation 4.4.11.

Rearranging Equation 4.4.11 yields

$$\hat{M}^2 Y_l^{m_l}(\theta,\varphi) = \lambda Y_l^{m_l}(\theta,\varphi) \tag{4.4.12}$$

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 in Chapter 7. 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 4.4.12 is

$$\hat{L}^2 Y_l^{m_l}(\theta,\varphi) = \lambda Y_l^{m_l}(\theta,\varphi) \tag{4.4.13}$$

Equation 4.4.13 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 4.4.13 becomes

$$\hat{L}^2 Y_l^{m_l}(\theta,\varphi) = l(l+1)\hbar^2 Y_l^{m_l}(\theta,\varphi) \tag{4.4.14}$$

Using this value for λ and rearranging Equation 4.4.10, we obtain

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) - E\right]R(r) = 0 \tag{4.4.15}$$

Exercise 4.4.4

Write the steps leading from Equation 4.4.10 to Equation 4.4.15.

The details for solving Equation 4.4.15 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.

The asymptotic solution is

$$R_{asymptotic}(r) = e^{-\frac{r}{n}a_0} \tag{4.4.16}$$

where n will turn out to be a quantum number and a_0 is the Bohr radius. 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 4.4.5

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?

ExercisE 4.4.6

Why is exp(-r/na0) used instead of exp(+r/na0) as the exponential component of the hydrogen atom radial function?

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 ci are constant coefficients.

$$L_{n,l}(r) = \sum_{r=0}^{n-l-1} c_i r^i \tag{4.4.17}$$

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 4.4.15.

The $R(r)$ functions, Equation ???, that solve the radial differential Equation 4.4.15, are products of the associated Laguerre polynomials times the exponential factor, multiplied by a normalization factor ($N_{n,l}$) and $\left(\frac{r}{a_0}\right)^l$.

$$R(r) = N_{n,l}\left(\frac{r}{a_0}\right)^l L_{n,l}(r)e^{-\frac{r}{na_0}} \tag{4.4.18}$$

As in Chapter 6, 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 **4.4.1**. 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 4.4.1: 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	$R_{n,l}(\rho)$
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	$\frac{1}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} (27-18\rho+2\rho^2)e^{-\rho/3}$
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 discussed in Chapter 2.

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2} \tag{4.4.19}$$

It is interesting to compare the results obtained by solving the Schrödinger equation with Bohr's model of the hydrogen atom. There are several ways in which the Schrödinger model and Bohr model differ. 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. 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 $\sqrt{(l(l+1)}\hbar$. 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 4.4.7

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.

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4.5: Other One-Electron Systems

The quantum mechanical treatment of the hydrogen atom can be extended easily to other one-electron systems such as $\mathbf{He^+}$, $\mathbf{Li^{2+}}$, etc. The Hamiltonian changes in two places. Most importantly, the potential energy term is changed to account for the charge of the nucleus, which is the atomic number of the atom or ion, Z, times the fundamental unit of charge, e. As shown in Equation 4.5.1, the energy of attraction between the electron and the nucleus increases (i.e., V gets more negative) as the nuclear charge increases.

$$\hat{V}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \tag{4.5.1}$$

The other effect is a very slight change in the reduced mass included in the kinetic energy operator. In fact, the larger the nucleus, the better the approximation that the reduced mass is given by the mass of the electron.

Exercise 4.5.1

Compare the reduced mass of the Li^{+2} ion to that of the hydrogen atom.

The effects of the change in V show up in the wavefunctions and the energy eigenvalues. The expression for the energy becomes

$$E_n = -\frac{Z^2\mu e^4}{8\epsilon_0^2 h^2 n^2} = Z^2 E_{n,H} \tag{4.5.2}$$

where $E_{n,H}$ is the energy of the hydrogen atom. The forms of the wavefunctions are identical to those of the hydrogen atom, except for the fact that Z in the radial functions is no longer equal to 1. The selection rules are unchanged, and the Zeeman effect still occurs.

Exercise 4.5.2

Use the orbital energy level expression in Equation 4.5.2 to predict quantitatively the relative energies (in cm^{-1}) of the spectral lines for H and Li^{2+}.

As the plots in Figure 4.5.1 reveal, the increased charge on the nucleus creates a stronger attraction for the electron and thus the electron charge density distributions shift to smaller values of r. These other systems look a lot like compressed hydrogen atoms.

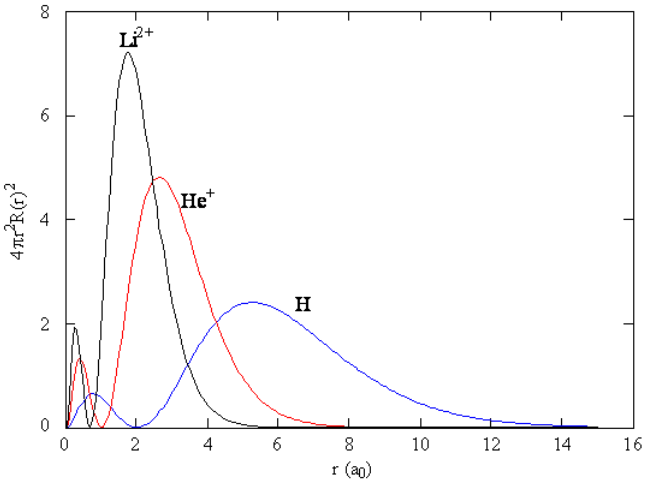


Figure 4.5.1: Radial distribution functions plotted for the 2s orbitals of H (blue), He^+ (red) and Li^{2+} (black) on the same axis, demonstrating compression of the orbital as Z is increased from 1 to 3.

Exercise 4.5.3

Determine whether or not the angular momentum values, the spherical harmonic functions, and the spectroscopic selection rules that describe the electron in $\hat{H}$ are the same or are different for $\mathbf{Li^{2+}}$. Write a paragraph to justify your answer.

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4.6: The Wavefunctions

The solutions to the hydrogen atom Schrödinger equation are functions that are products of a **spherical harmonic function** and a **radial function**.

$$\psi_{n,l,m_l}(r,\theta,\varphi) = R_{n,l}(r)Y_l^{m_l}(\theta,\varphi) \tag{4.6.1}$$

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 4.6.1

What is the value of the integral

$$\int_{\text{all space}} |\psi(r,\theta,\varphi)|^2 d\tau\,?$$

The quantum numbers have names: n is called the **principal quantum number**, l is called the **angular momentum quantum number**, and m_l is called the magnetic quantum number because (as we will see in Section 8.4) 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.

Exercise 4.6.2

Consider several values for n, and show that the number of orbitals for each n is n^2.

Exercise 4.6.3

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 4.6.4

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, $\psi(r,\theta,\varphi)$, are called **atomic orbitals**. An atomic orbital is a function that describes one electron in an atom. The wavefunction with n = 1, $l = 1$, and m_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 in Chapter 9 that these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

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 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 $\psi^*\psi$. Do not confuse such plots with polar plots, which look similar.

Probability densities also can be represented by contour maps, as shown in Figure **4.6.1**.

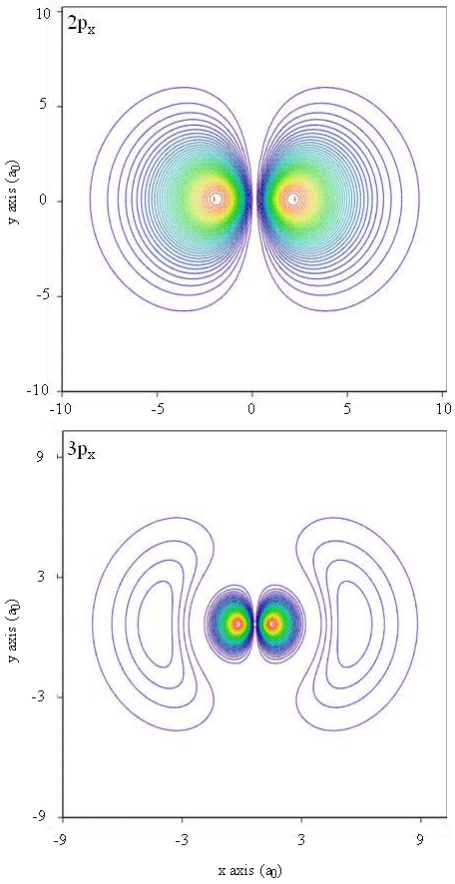


Figure **4.6.1**: Contour plots in the x-y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low \(R(r)^{\wedge}2\). The angular function used to create the figure was a linear combination of two Spherical Harmonic functions (see Problem 10 at the end of this chapter.)

Another representational technique, virtual reality modeling, holds a great deal of promise for representation of electron densities. Imagine, for instance, being able to experience electron density as a force or resistance on a wand that you move through three-dimensional space. Devices such as these, called haptic devices, already exist and are being used to represent scientific information. Similarly, wouldn't it be interesting to "fly" through an atomic orbital and experience changes in electron density as color changes or cloudiness changes? Specially designed rooms with 3D screens and "smart" glasses that provide feedback about the direction of the viewer's gaze are currently being developed to allow us to experience such sensations.

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 **4.6.2**.

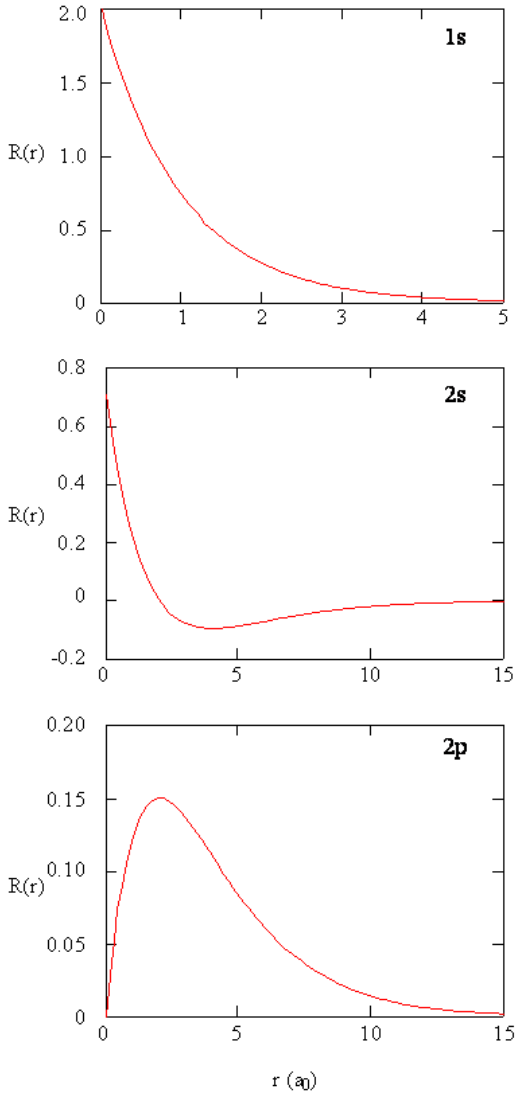


Figure **4.6.2**: Radial function, R(r), for the 1s, 2s, and 2p orbitals.

The 1s function in Figure **4.6.2** 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 **4.6.2**, 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 4.6.5

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 4.6.6

What mathematical feature of each of the radial functions controls the number of radial nodes?

Exercise 4.6.7

At what value of r does the 2s radial node occur?

Exercise 4.6.8

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, 2, and 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.

The quantity $R(r)^*R(r)$ gives the **radial probability density**; i.e., the probability density for the electron to be at a point located the distance r from the proton. Radial probability densities for three types of atomic orbitals are plotted in Figure (\PageIndex{3}\).

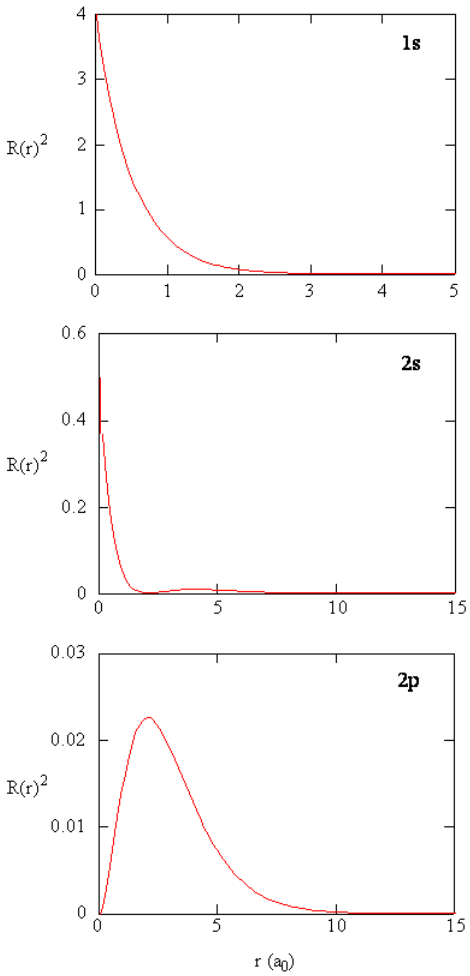


Figure 4.6.3: Radial probability densities for the 1s, 2s, and 2p orbitals.

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 $4\pi r^2 R(r)^*R(r)$.

Radial distribution functions are shown in Figure 4.6.4. 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.

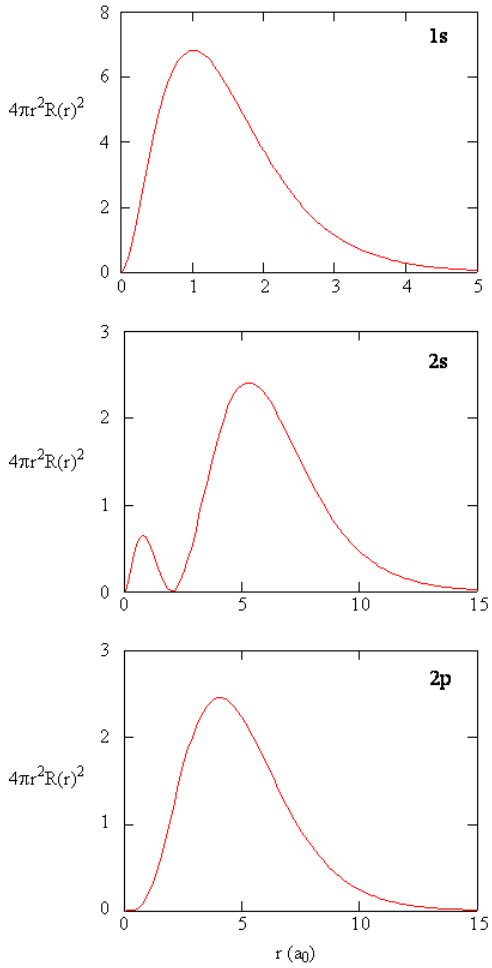


Figure 4.6.4: The radial distribution function for the 1s, 2s, and 2p orbitals.

Exercise 4.6.9

Write a quality comparison of the radial function and radial distribution function for the 2s orbital. See Figure (\PageIndex{5}\)

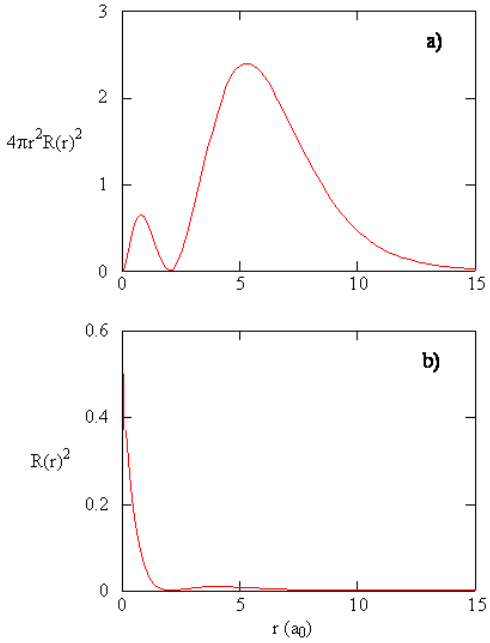


Figure **4.6.5**: Comparison of a) the radial distribution function and b) the radial probability density for the 2s orbital.

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4.7: s-orbitals are Spherically Symmetric

The hydrogen atom wavefunctions, $\psi(r,\theta,\varphi)$, are called atomic orbitals. An atomic orbital is a function that describes one electron in an atom. The wavefunction with $n = 1$, l = 0 is called the 1s orbital, and an electron that is described by this function is said to be "in" the ls orbital, i.e. have a 1s orbital state. The constraints on n, l, and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

Visualizing the variation of an electronic wavefunction with r, θ, and φ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron deficient part of one molecule is attracted to an electron rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

We can obtain an energy and one or more wavefunctions for every value of n, the principal quantum number, by solving Schrödinger's equation for the hydrogen atom. A knowledge of the wavefunctions, or probability amplitudes ψ_n, allows us to calculate the probability distributions for the electron in any given quantum level. When n = 1, the wavefunction and the derived probability function are independent of direction and depend only on the distance r between the electron and the nucleus. In Figure 6.5.1 , we plot both ψ_1 and P_1 versus r, showing the variation in these functions as the electron is moved further and further from the nucleus in any one direction. (These and all succeeding graphs are plotted in terms of the atomic unit of length, $a_0 = 0.529 \times 10^{-8}\,cm$.)

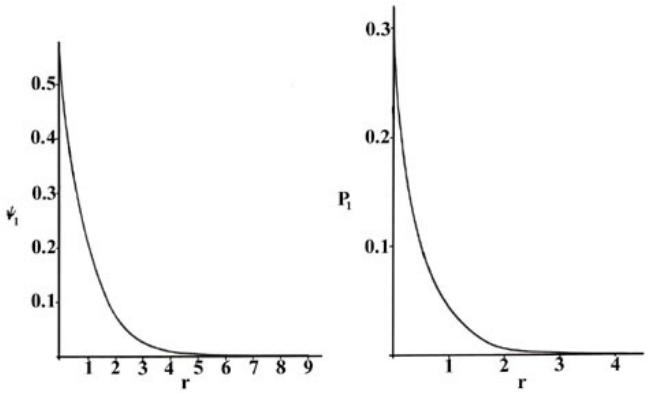


Figure 6.5.1 : The wavefunction and probability distribution as functions of r for the $n = 1$ level of the H atom. The functions and the radius r are in atomic units in this and succeeding figures.

Two interpretations can again be given to the P_1 curve. An experiment designed to detect the position of the electron with an uncertainty much less than the diameter of the atom itself (using light of short wavelength) will, if repeated a large number of times, result in Figure 6.5.1 for P_1. That is, the electron will be detected close to the nucleus most frequently and the probability of observing it at some distance from the nucleus will decrease rapidly with increasing r. The atom will be ionized in making each of these observations because the energy of the photons with a wavelength much less than 10^{-8} cm will be greater than K, the amount of energy required to ionize the hydrogen atom. If light with a wavelength comparable to the diameter of the atom is employed in the experiment, then the electron will not be excited but our knowledge of its position will be correspondingly less precise. In these experiments, in which the electron's energy is not changed, the electron will appear to be "smeared out" and we may interpret P_1 as giving the fraction of the total electronic charge to be found in every small volume element of space. (Recall that the addition of the value of P_n for every small volume element over all space adds up to unity, i.e., one electron and one electronic charge.)

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately does not reveal the shape of an orbital very well. The shape can be revealed better in

a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$.

We could also represent the distribution of negative charge in the hydrogen atom in the manner used previously for the electron confined to move on a plane (Figure 6.5.2), by displaying the charge density in a plane by means of a contour map. Imagine a plane through the atom including the nucleus. The density is calculated at every point in this plane. All points having the same value for the electron density in this plane are joined by a contour line (Figure 6.5.2). Since the electron density depends only on *r*, the distance from the nucleus, and not on the direction in space, the contours will be circular. A contour map is useful as it indicates the "shape" of the density distribution.

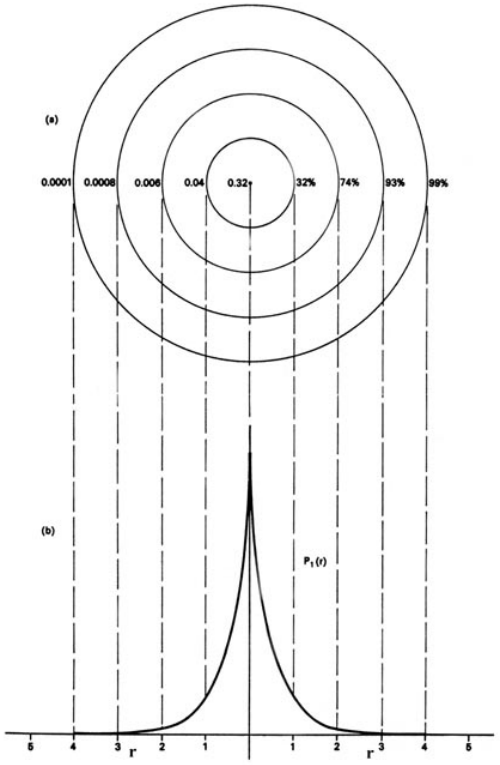


Figure 6.5.2 : (a) A contour map of the electron density distribution in a plane containing the nucleus for the $n = 1$ level of the H atom. The distance between adjacent contours is 1 au. The numbers on the left-hand side on each contour give the electron density in au. The numbers on the right-hand side give the fraction of the total electronic charge which lies within a sphere of that radius. Thus 99% of the single electronic charge of the H atom lies within a sphere of radius 4 au (or diameter = 4.2×10^{-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 **4.7.3**; 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.

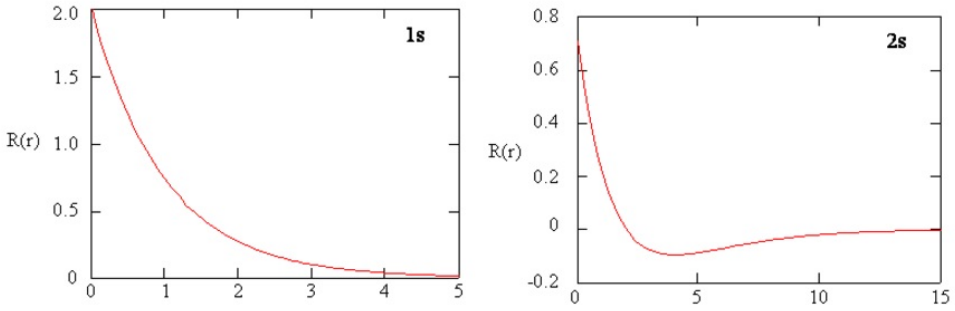


Figure 6.5.3 : Radial function, $R(r)$, for the 1s and 2s orbitals. For an interactive graph click here.

Next notice how the radial function for the 2s orbital, Figure **4.7.3**;, 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.

Answer

	Energy 1.Particle in a Box ($h^2n^2/8m_eL^2$) 2.Harmonic Oscillator($(n+0.5)\hbar\omega$) 3.Hydrogen ($-13.6eV/n^2$)	Number of Radial Nodes (n-l-1)	Number of Angular Nodes l = (n-1) l : s =0 p = 1 d = 2	Total Number of Nodes
n = 1	1. 6.02 *10^{-38} J/L^2 2. $1.5\hbar\omega$ 3. -13.6 eV	-	0	0
n = 2	1. 6.02 *10^{-38} J/L^2 2. $2.5\hbar\omega$ 3. -3.4 eV	for s: 1 for p: 0	for s: 0 for p: 1	1
n = 3	1. 6.02 *10^{-38} J/L^2 2. $3.5\hbar\omega$ 3. 1.51 eV	for s: 2 for p: 1 for d: 0	for s: 0 for p:1 for d: 2	2

For a particle in a box the energy is equivalent to $E_n = 6.02 \times 10^{-38} n^2 L^2$ where n is any value greater than and not equal to 0 and L is the length of the box.

Radial probability densities for the 1s and 2s atomic orbitals are plotted in Figure 6.5.4 .

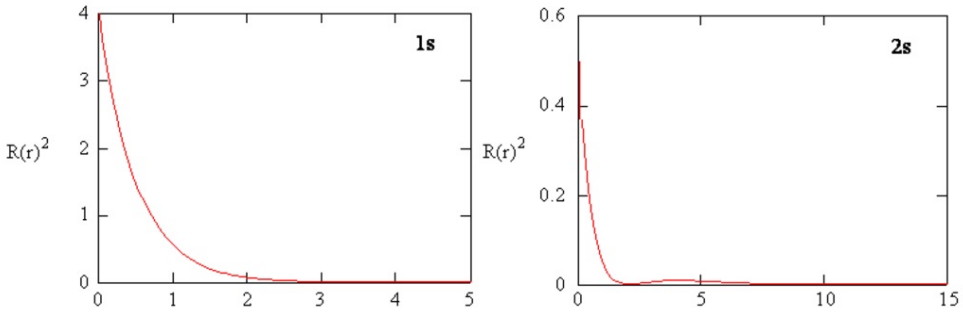


Figure 6.5.4 : Radial densities ($R(r)^*R(r)$) for the 1s and 2s orbitals.

4.7.1: Radial Distribution Functions

Rather than considering the amount of electronic charge in one particular small element of space, we may determine the total amount of charge lying within a thin spherical shell of space. Since the distribution is independent of direction, consider adding up all the charge density which lies within a volume of space bounded by an inner sphere of radius r and an outer concentric sphere with a radius only infinitesimally greater, say $r + \Delta r$. The area of the inner sphere is $4\pi r^2$ and the thickness of the shell is Δr. Thus the volume of the shell is $4\pi r^2 \Delta r$ and the product of this volume and the charge density $P_1(r)$, which is the charge or number of electrons per unit volume, is therefore the total amount of electronic charge lying between the spheres of radius r and $r + \Delta r$. The product $4\pi r^2 P_n$ is given a special name, the **radial distribution function**.

Volume Element for a Shell in Spherical Coordinates

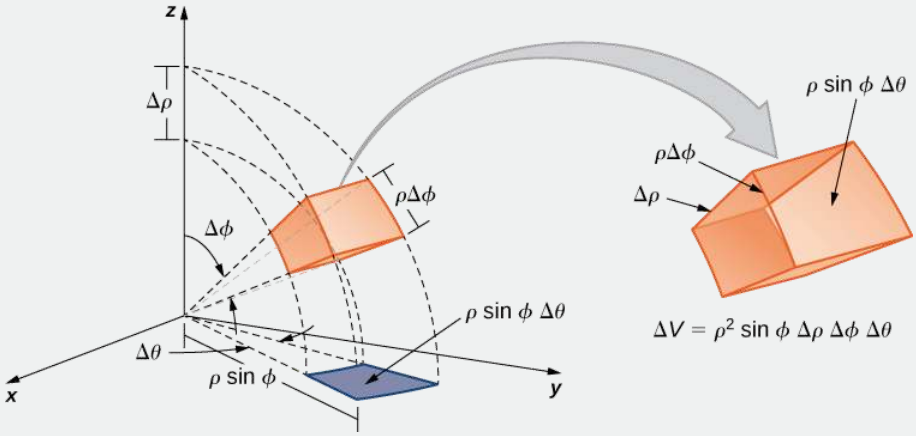
The reader may wonder why the volume of the shell is not taken as:

$$\frac{4}{3}\pi\left[(r+\Delta r)^3 - r^3\right]$$

the difference in volume between two concentric spheres. When this expression for the volume is expanded, we obtain

$$\frac{4}{3}\pi\left(3r^2\Delta r + 3r\Delta r^2 + \Delta r^3\right)$$

and for very small values of Δr the $3r\Delta r^2$ and Δr^3 terms are negligible in comparison with $3r^2\Delta r$. Thus for small values of Δr, the two expressions for the volume of the shell approach one another in value and when Δr represents an infinitesimal small increment in r they are identical.



The volume element of a box in spherical coordinates. (CC BY; OpenStax).

The radial distribution function is plotted in Figure 6.5.5 for the ground state of the hydrogen atom.

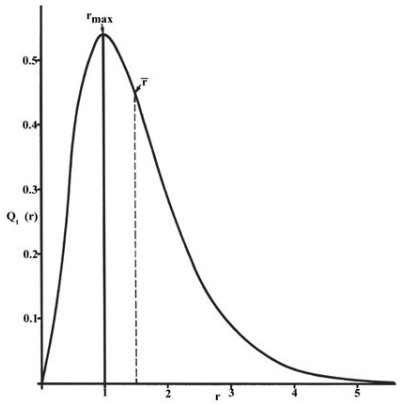


Figure 6.5.5 : The radial distribution function for an H atom. The value of this function at some value of r when multiplied by δr gives the number of electronic charges within the thin shell of space lying between spheres of radius r and $r + \delta r$.

The curve passes through zero at $r = 0$ since the surface area of a sphere of zero radius is zero. As the radius of the sphere is increased, the volume of space defined by $4\pi r^2 Dr$ increases. However, as shown in Figure 6.5.4 , the absolute value of the electron density at a given point decreases with r and the resulting curve must pass through a maximum. This maximum occurs at $r_{max} = a_0$. Thus more of the electronic charge is present at a distance a_o, out from the nucleus than at any other value of r. Since the curve is unsymmetrical, the average value of r, denoted by $\bar{r}$, is not equal to r_{max}. The average value of r is indicated on the figure by a dashed line. A "picture" of the electron density distribution for the electron in the $n = 1$ level of the hydrogen atom would be a spherical ball of charge, dense around the nucleus and becoming increasingly diffuse as the value of r is increased.

> *The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the proton. Since the area of a spherical surface is $4\pi r^2$, the radial distribution function is given by $4\pi r^2 R(r)^* R(r)$.*

Radial distribution functions are shown in Figure 6.5.6 . At small values of r, the radial distribution function is low because the small surface area for small radii modulates the high value of the radial probability density function near the nucleus. As we increase r, the surface area associated with a given value of r increases, and the r^2 term causes the radial distribution function to

increase even though the radial probability density is beginning to decrease. At large values of r, the exponential decay of the radial function outweighs the increase caused by the r^2 term and the radial distribution function decreases.

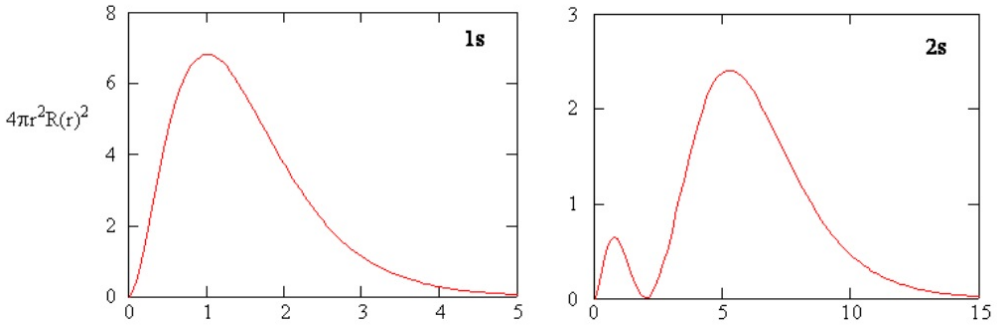


Figure 6.5.6 : The radial distribution function ($4\pi r^2 R(r)^* R(r)$) for the 1s and 2s orbitals. Compare to the radial functions in Figure 6.5.3 or the radial densities in Figure 6.5.4 . For an interactive graph click here.

Example 6.5.1 :

Calculate the probability of finding a 1s hydrogen electron being found within distance $2a_o$ from the nucleus.

Solution

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

$$\begin{aligned} prob &= 2 \times 2\pi \times \frac{1}{\pi a_0^3} \int_0^2 a_0(-a_0/2) r^2 de^{-2r/a_0} \\ &= \frac{4}{a_0^3}\left(-\frac{a_0}{2}\right)\left(r^2 e^{-2r/a_0}\Big|_0^{2a_0} - \int_0^{2a_0} 2re^{-2r/a_0} dr\right) \\ &= -\frac{2}{a_0^2}\left[(2a_0)^2 e^{-4} - 0 - 2\int_0^{2a_0} r\left(-\frac{a_0}{2}\right) de^{-2r/a_0}\right] \\ &= -\frac{2}{a_0^2} 4a_0^2 e^{-4} + \frac{4}{a_0^2}\left(-\frac{a_0}{2}\right)\left(re^{-2r/a_0}\Big|_0^{2a_0} - \int_0^{2a_0} e^{-2r/a_0} dr\right) \\ &= -8e^{-4} - \frac{2}{a_0}\left[2a_0 e^{-4} - 0 - \left(-\frac{a_0}{2}\right) e^{-2r/a_0}\Big|_0^{2a_0}\right] \\ &= -8e^{-4} - 4e^{-4} - e^{2r/a_0}\Big|_0^{2a_0} \\ &= -12e^{-4} - (e^{-4} - 1) = 1 - 13e^{-4} = 0.762 \end{aligned}$$

There is a 76.2% probability that the electrons will be within $2a_o$ of the nucleus in the 1s eigenstate.

4.7.2: Summary

This completes the description of the most stable state of the hydrogen atom, the state for which $n = 1$. Before proceeding with a discussion of the excited states of the hydrogen atom we must introduce a new term. When the energy of the electron is increased

to another of the allowed values, corresponding to a new value for n, y_n and P_n change as well. The wavefunctions y_n for the hydrogen atom are given a special name, ***atomic orbitals***, because they play such an important role in all of our future discussions of the electronic structure of atoms. In general the word orbital is the name given to a wavefunction which determines the motion of a single electron. If the one-electron wavefunction is for an atomic system, it is called an atomic orbital.

Do not confuse the word orbital with the classical word and notion of an orbit. First, an orbit implies the knowledge of a definite trajectory or path for a particle through space which in itself is not possible for an electron. Secondly, an orbital, like the wavefunction, has no physical reality but is a mathematical function which when squared gives the physically measurable electron density distribution.

Contributors and Attributions

- Dr. Richard F.W. Bader (Professor of Chemistry / McMaster University)
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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4.8: Orbital Angular Momentum and the p-Orbitals

Learning Objectives

- To relate the classical orbital angular momentum for an particle to the quantum equivalent
- Characterize the mangnitude and orientation of orbital angular momentum for an electron in terms of quantum numbers

4.8.1: Classical Orbital Angular Momentum

The physical quantity known as angular momentum plays a dominant role in the understanding of the electronic structure of atoms. To gain a physical picture and feeling for the angular momentum it is necessary to consider a model system from the classical point of view. The simplest classical model of the hydrogen atom is one in which the electron moves in a circular orbit with a constant speed or angular velocity (Figure 6.6.1). Just as the linear momentum $m\vec{v}$ plays a dominant role in the analysis of linear motion, so angular momentum (L) plays the central role in the analysis of a system with circular motion as found in the model of the hydrogen atom.

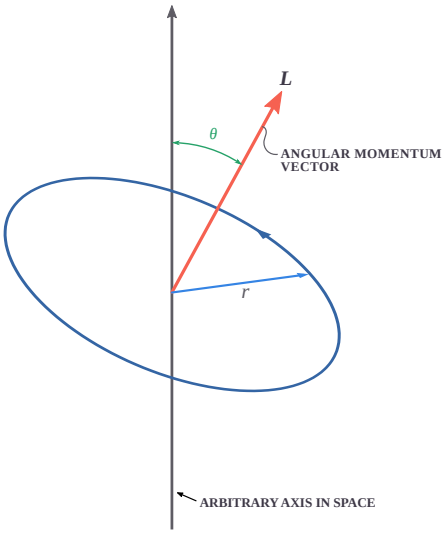


Figure 6.6.1 : The angular momentum vector for a classical model of the atom. (CC BY-NC; Ümit Kaya via LibreTexts)

In Figure 6.6.1 , m is the mass of the electron, $\vec{v}$ is the linear velocity (the velocity the electron would possess if it continued moving at a tangent to the orbit) and r is the radius of the orbit. The linear velocity $\vec{v}$ is a vector since it possesses at any instant both a magnitude and a direction in space. Obviously, as the electron rotates in the orbit the direction of $\vec{v}$ is constantly changing, and thus the linear momentum $m\vec{v}$ is ***not*** constant for the circular motion. This is so even though the speed of the electron (i.e, the magnitude of $\vec{v}$ which is denoted by $|\vec{v}|$) remains unchanged. According to Newton's second law, a force must be acting on the electron if its momentum changes with time. This is the force which prevents the electron from flying on tangent to its orbit. In an atom the attractive force which contains the electron is the electrostatic force of attraction between the nucleus and the electron, directed along the radius *r* at right angles to the direction of the electron's motion.

The angular momentum, like the linear momentum, is a vector and is defined as follows:

$$|\vec{L}| = mvr$$

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.

4.8.2: 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:

$$|L| = \sqrt{l(l+1)}\hbar \tag{4.8.1}$$

with $l = 0, 1, 2, 3, ...n-1$.

Furthermore, the value of *n* limits the maximum value of the angular momentum as the value of *l* cannot be greater than *n* - 1. For the state *n* = 1 discussed above, l may have the value of zero only. When *n* = 2, *l* may equal 0 or 1, and for *n* = 3, *l* = 0 or 1 or 2, etc. When *l* = 0, it is evident from Equation 4.8.1 that the angular momentum of the electron is zero. The atomic orbitals which describe these states of zero angular momentum are called *s* orbitals. The *s* orbitals are distinguished from one another by stating the value of *n*, the principal quantum number. They are referred to as the 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 .

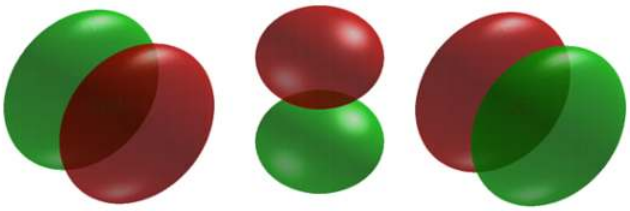


Figure 6.6.2 : The appearance of the three 2p orbitals in three-dimensional space. (CC BY-SA 3.0; I, Sarxos).

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 wavefunction is positive in value on one side and negative in value on the other side of a plane which is perpendicular to the axis of the orbital and passes through the nucleus. The orbital has a node in this plane, and consequently an electron in a 2*p* orbital does not place any electronic charge density at the nucleus. The electron density of a 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.*

4.8.3: The m_l Quantum Number and Magnetic Fields

The magnetic quantum number, designated by the letter m_l, is the third quantum numbers which describe the unique quantum state of an electron. The magnetic quantum number distinguishes the orbitals available within a subshell, and is used to calculate the azimuthal component of the orientation of the orbital in space. As with our discussion of rigid rotors, the quantum number m_l refers to the projection of the angular momentum in this arbitrarily chosen direction, conventionally called the z direction or quantization axis. L_z, the magnitude of the angular momentum in the z direction, is given by the formula

$$L_z = m_l \hbar$$

The quantum number m_l refers, loosely, to the direction of the angular momentum vector. The magnetic quantum number m_l only affects the electron's energy if it is in a magnetic field because in the absence of one, all spherical harmonics corresponding to the different arbitrary values of m_l are equivalent. The magnetic quantum number determines the energy shift of an atomic orbital due to an external magnetic field (this is called the Zeeman effect) - hence the name magnetic quantum number. However, the actual magnetic dipole moment of an electron in an atomic orbital arrives not only from the electron angular momentum, but also from the electron spin, expressed in the spin quantum number, which is the fourth quantum number. m_s and discussed in the next chapter.

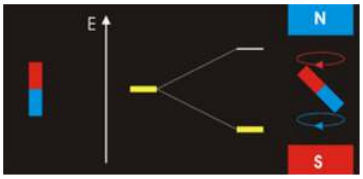


Figure 6.6.3 : The orbiting electron with a non-zero l value acts like a magnetic field with is no energetic difference for any particular orientation (only one energy state, on the left). However, in external magnetic field there is a high-energy state and a low-energy state depending on the relative orientations of the magnet to the external field. (CC SA-BY 3.0; Darekk2).

m_l Which Number Corresponds to which p-Orbital?

The answer is complicated; while $m_l = 0$ corresponds to the p_z, the orbitals for $m_l = +1$ and $m_l = -1$ lie in the xy-plane (see Spherical Harmonics), but not on the axes. The reason for this outcome is that the wavefunctions are usually formulated in spherical coordinates to make the math easier, but graphs in the Cartesian coordinates make more intuitive sense for humans. The p_x and p_y orbitals are constructed via a linear combination approach from radial and angular wavefunctions and converted into xy (this was discussed previously). Thus, it is not possible to directly correlate the values of $m_l = \pm 1$ with specific orbitals. The notion that we can do so is sometimes presented in introductory courses to make a complex mathematical model just a little bit simpler and more intuitive, but it is incorrect.

The three wavefunctions for $n = 2$ and $l = 1$ are as follows.

$$|\psi_{2,1,0}\rangle = r\cos\theta R(r) \tag{4.8.2}$$

$$|\psi_{2,1,+1}\rangle = -\frac{r}{2}\sin\theta e^{i\phi} R(r) \tag{4.8.3}$$

$$|\psi_{2,1,-1}\rangle = +\frac{r}{2}\sin\theta e^{-i\phi} R(r) \tag{4.8.4}$$

The notation is $|\psi_{n,l,m_l}\rangle$ with $R(r)$ is the radial component of this wavefuction, θ is the angle with respect to the z-axis and ϕ is the angle with respect to the xz-plane.

$$R(r) = \sqrt{\frac{Z^5}{32\pi a_0^5}} e^{-Zr/2a_0}$$

in which Z is the atomic number (or probably better nuclear charge) and a_0 is the Bohr radius.

In switching from spherical to Cartesian coordinates, we make the substitution $z = r\cos\theta$, so:

$$|\psi_{2,1,0}\rangle = zR(r)$$

This is ψ_{2p_z} since the value of ψ is dependent on z: when $z = 0$; $\psi = 0$, which is expected since $z = 0$ describes the xy-plane.

The other two wavefunctions are degenerate in the xy-plane. An equivalent statement is that these two orbitals do not lie on the x- and y-axes, but rather bisect them. Thus it is typical to take linear combinations of them to make the equation look prettier. If any set of wavefunctions is a solution to the Schrödinger equation, then any set of linear combinations of these wavefunctions must also be a solution (Section 2.4). We can do this because of the linearity of the Schrödinger equation.

In the equations below, we're going to make use of some trigonometry, notably Euler's formula:

$$e^{i\phi} = \cos\phi + i\sin\phi \tag{4.8.5}$$

$$\sin\phi = \frac{e^{i\phi} - e^{-i\phi}}{2i} \tag{4.8.6}$$

$$\cos\phi = \frac{e^{i\phi} + e^{-i\phi}}{2} \tag{4.8.7}$$

We're also going to use $x = \sin\theta\cos\phi$ and $y = \sin\theta\sin\phi$.

$$\begin{aligned}
\psi_{2p_x} &= \frac{1}{\sqrt{2}}\left(\psi_{2,1,+1} - \psi_{2,1,-1}\right) \\
&= \frac{1}{2}\left(e^{i\phi} + e^{-i\phi}\right) r\sin\theta f(r) \\
&= r\sin\theta\cos\phi f(r) = x f(r) \\
\psi_{2p_y} &= \frac{i}{\sqrt{2}}\left(\psi_{2,1,+1} + \psi_{2,1,-1}\right) \\
&= \frac{1}{2i}\left(e^{i\phi} - e^{-i\phi}\right) r\sin\theta f(r) \\
&= r\sin\theta\sin\phi f(r) = y f(r)
\end{aligned}$$

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 $(|p_x\rangle - |p_y\rangle)$.

4.8.4: d-Orbitals (even higher angular momenta wavefunctions)

When $l = 2$, the orbitals are called *d* orbitals and Figure 6.6.4 shows the contours in a plane for a 3*d* orbital and its density distribution. Notice that the density is again zero at the nucleus and that there are now two nodes in the orbital and in its density distribution. As the angular momentum of the electron increases, the density distribution becomes increasingly concentrated along an axis or in a plane in space. Only electrons in s orbitals with **zero angular momentum** give spherical density distributions and in addition place charge density at the position of the nucleus.



Figure 6.6.4 : The appearance of the 3d electron density distribution in three-dimensional space. (CC BY-SA 3.0; I, Sarxos)

As with the p-orbitals, the only d-orbital that a specific m_l can be ascribed is the d_{z^2} orbitals with $m_l = 0$. The rest are linear combinations of the hydrogen atom wavefunctions with complex spherical harmonic angular components.

There seems to be neither rhyme nor reason for the naming of the states corresponding to the different values of ℓ (s, *p*, *d*, *f* for *l* = 0, 1, 2, 3). This set of labels had its origin in the early work of experimental atomic spectroscopy. The letter *s* stood for

sharp, *p* for principal, *d* for diffuse and *f* for fundamental in characterizing spectral lines. From the letter *f* onwards the naming of the orbitals is alphabetical $l = 4, 5, 6 \rightarrow g, h, i, ...$

We have not as yet accounted for the full degeneracy of the hydrogen atom orbitals which we stated earlier to be n^2 for every value of n. For example, when $n = 2$, there are four distinct atomic orbitals. The remaining degeneracy is again determined by the angular momentum of the system. Since angular momentum like linear momentum is a vector quantity, we may refer to the component of the angular momentum vector which lies along some chosen axis. For reasons we shall investigate, the number of values a particular component can assume for a given value of l is $(2l + 1)$. Thus when $l = 0$, there is no angular momentum and there is but a single orbital, an s orbital. When $l = 1$, there are three possible values for the component $(2 \times 1 + 1)$ of the total angular momentum which are physically distinguishable from one another. There are, therefore, three p orbitals. Similarly there are five d orbitals, $(2 \times 2 + 1)$, seven f orbitals, $(2 \times 3 + 1)$, etc. All of the orbitals with the same value of n and l, the three 2p orbitals for example, are similar but differ in their spatial orientations.

To gain a better understanding of this final element of degeneracy, we must consider in more detail what quantum mechanics predicts concerning the angular momentum of an electron in an atom.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Dr. Richard F.W. Bader (Professor of Chemistry / McMaster University)
- Stack Exchange (Ben Norris and Loong)

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CHAPTER OVERVIEW

5: Many Electron Atoms

5.1: The Helium Atom Cannot Be Solved Exactly
5.2: Atomic and Molecular Calculations are Expressed in Atomic Units
5.3: The Variational Method Approximation
5.4: Single-electron Wavefunctions and Basis Functions
5.5: An Electron has an Intrinsic Spin Angular Momentum
5.6: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
5.7: Antisymmetric Wavefunctions can be Represented by Slater Determinants
5.8: Electron Configurations, The Pauli Exclusion Principle, The Aufbau Principle, and Slater Determinants
5.9: The Self-Consistent Field Approximation (Hartree-Fock Method)
5.10: Hartree-Fock Calculations Give Good Agreement with Experimental Data
5.11: Term Symbols Gives a Detailed Description of an Electron Configuration
5.12: The Allowed Values of J - the Total Angular Momentum Quantum Number
5.13: Hund's Rules Determine the Term Symbols of the Ground Electronic States

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5.1: 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).

5.1.1: 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.

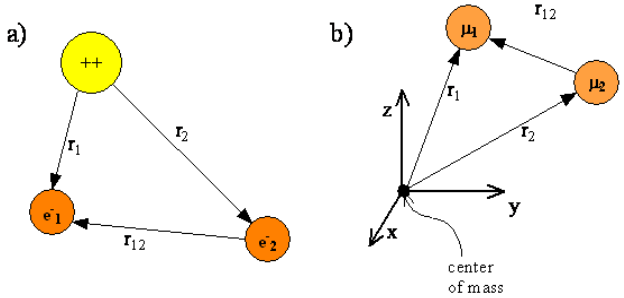


Figure 6.7.1 : (a) The nucleus (++) and electrons (e-) of the helium atom. (b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that $\boldsymbol{\mu_1}$ and $\boldsymbol{\mu_2 \approx m_e}$.

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

$$\hat{H} = \hat{T} + \hat{V} \tag{5.1.1}$$

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

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V_1(r_1) + V_2(r_2) + V_{12}(r_{12}) \tag{5.1.2}$$

where

$$V_1(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{5.1.3}$$

$$V_2(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{5.1.4}$$

$$V_{12}(r_{12}) = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{5.1.5}$$

The two-electron Hamiltonian in Equation 5.1.2 can be extended to any atom or ion by replacing the He nuclear charge of +2 with a general charge Z; e.g.

$$V_1(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{5.1.6}$$

and including terms for the additional electrons. The subsequent multi-electron atom with n electron is

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_i^n \nabla_i^2}_{\text{Kinetic Energy}} + \underbrace{\sum_i^n V_i(r_i)}_{\text{Coulombic Attraction}} + \underbrace{\sum_{i\neq j}^{n,n} V_{ij}(r_{ij})}_{\text{electron-electron Repulsion}} \tag{5.1.7}$$

This multi-electron Hamiltonian is qualitatively similar to the 2-electron Hamiltonian (Equation 5.1.1) with each electron having its own kinetic energy and nuclear potential energy terms (Equations 5.1.3 and 5.1.4). 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 5.1.7):

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.

$$\hat{H}_B(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\vec{r}_5) = -\frac{\hbar^2}{2m_e}\sum_i^5 \nabla_i^2 + \sum_i^5 \frac{-5e^2}{4\pi\epsilon_0 r_i} + \sum_{i\neq j}^{5,5} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

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

$$\hat{H}_{B^+}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4) = -\frac{\hbar^2}{2m_e}\sum_i^4 \nabla_i^2 + \sum_i^4 \frac{-5e^2}{4\pi\epsilon_0 r_i} + \sum_{i\neq j}^{4,4} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

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.

5.1.2: 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 5.1.7 would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their Coulomb repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends *simultaneously* upon the coordinates of all the electrons; i.e., **a multi-electron wavefunction**,

$$\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\cdots\vec{r}_n)$$

The modulus squared of such a wavefunction would describe the probability of finding the electrons (though not specific ones) at a designated volume (V) in the atom.

$$p(V) = \int_V \left|\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\cdots\vec{r}_n)\right|^2 d\tau$$

All of the electrons are described simultaneously by a multi-electron wavefunction, so the total amount of electron density represented by the wavefunction equals the number of electrons in the atom.

$$\int_{\text{all space}} \left|\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\cdots\vec{r}_i)\right|^2 d\tau = n$$

Unfortunately, the Coulomb repulsion terms (Equation 5.1.5) 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 5.1.7) involve writing a multi-electron wavefunction ($\psi(r_1,r_2,\cdots,r_n)$) as a simple product of single-electron wavefunctions ($\varphi_i(r_i)$):

$$\psi(r_1,r_2,\cdots,r_n) \approx \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_n(r_n) \tag{5.1.8}$$

or in Dirac notation

$$|\psi(r_1,r_2,\cdots,r_n)\rangle \approx |\varphi_1(r_1)\rangle\,|\varphi_2(r_2)\rangle\cdots|\,\varphi_n(r_n)\rangle \tag{5.1.9}$$

The energy of the atom in the state associated with a specific multi-electron wavefunction (E) is obtained from the multi-electron Schrödinger Equation

$$\hat{H}\psi(r_1,r_2,\cdots,r_n) = E\psi(r_1,r_2,\cdots,r_n)$$

Within the approximation in Equation 5.1.8, E can be expressed sum of the energies of the one-electron components (ϵ_i).

$$E \approx \sum_i \epsilon_i$$

This is called the **orbital approximation**.

By writing the multi-electron wavefunction as a product of single-electron functions (Equations 5.1.8 or 5.1.9), we conceptually transform a multi-electron atom into a collection of individual electrons located in individual orbitals whose spatial characteristics and energies can be separately identified. For atoms, these single-electron wavefunctions are called *atomic orbitals* and resemble the wavefunctions for hydrogen-like atoms. For molecules, as we will see in the following chapters, these are called *molecular orbitals*. While a great deal can be learned from such an analysis, it is important to keep in mind that such a discrete, compartmentalized picture of the electrons is an approximation, albeit a powerful one.

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5.2: Atomic and Molecular Calculations are Expressed in Atomic Units

Learning Objectives

- Demonstrate how solving electron structure problems are less cluttered by switching to atomic units instead of SI units.

Atomic units (au or a.u.) form a system of natural units which is especially convenient for atomic physics calculations. Atomic units, like SI units, have a unit of mass, a unit of length, and so on. However, the use and notation is somewhat different from SI. Suppose a particle with a mass of m has 3.4 times the mass of electron. The value of mass m can be written in three ways:

- $m = 3.4\ m_e$: This is the clearest notation (but least common), where the atomic unit is included explicitly as a symbol.
- $m = 3.4\ a.u.$: This notation is ambiguous, but is common. Here, it means that the mass m is 3.4 times the atomic unit of mass. If considering a length L of 3.4 times the atomic unit of length, the equation would look the same, $L = 3.4\ a.u.$ The dimension needs to be inferred from context, which is sloppy.
- $m = 3.4$: This notation is similar to the previous one, and has the same dimensional ambiguity. It comes from formally setting the atomic units to 1 (Table 8.1.1).

This article deals with "Hartree type" of atomic units, where the numerical values of the following four fundamental physical constants are all unity by definition:

Table 8.1.1 : Fundamental atomic units

Dimension	Name	Symbol/Definition	Value in SI units	Value in Atomic Units
mass	electron rest mass	m_e	9.109×10^{-31} kg	1
charge	elementary charge	e	1.602×10^{-19} C	1
action	reduced Planck's constant	$\hbar = \frac{h}{2\pi}$	1.054×10^{-34} J·s	1
electric constant^{-1}	Coulomb force constant	$k_e = \frac{1}{4\pi\epsilon_o}$	8.987 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 units were designed for atomic-scale calculations in the present-day universe, with units normalize the reduced Planck constant and also mass and charge of the electron are set to 1, and, as a result, the speed of light in atomic units is a large value, $1/\alpha \approx 137$. For example, the orbital velocity of an electron around a small atom is of the order of 1 in atomic units. Table 8.1.2 give a few derived units. Some of them have proper names and symbols assigned, as indicated in the table.

Table 8.1.2 : Derived atomic units

Dimension	Name	Symbol	Expression	Value in SI units	Value in more common units
length	bohr	a_o	$4\pi\epsilon_0\hbar^2/(m_e e^2) = \hbar/(m_e c\alpha)$	5.291×10^{-11} m	0.052 nm = 0.529 Å
energy	hartree	E_h	$m_e e^4/(4\pi\epsilon_0\hbar)^2 = \alpha^2 m_e c^2$	4.359×10^{-18} J	27.2 eV = 627.5 kcal·mol^{-1}
time			$\hbar/E_h$	2.418×10^{-17} s	
velocity			$a_0 E_h/\hbar = \alpha c$	2.187×10^6 m·s^{-1}	

5.2.1: Bohr model in atomic units

Atomic units are chosen to reflect the properties of electrons in atoms. This is particularly clear from the classical Bohr model of the hydrogen atom in its ground state. The ground state electron orbiting the hydrogen nucleus has (in the classical Bohr model):

- Orbital velocity = 1
- Orbital radius = 1
- Angular momentum = 1
- Orbital period = 2π
- Ionization energy = ½
- Electric field (due to nucleus) = 1
- Electrical attractive force (due to nucleus) = 1

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5.3: The Variational Method Approximation

Learning Objectives

- Appreciate the complexity of solving muliti-electron atoms
- Characterize multi-electron interactions within shielding and penetration concepts
- Use the variational method as an approximation to study insolvable problems
- User variational method to evaluate the effective nuclear charge for a specific atom

In this section we introduce the powerful and versatile variational method and use it to improve the approximate solutions we found for the helium atom using the independent electron approximation.

5.3.1: The True (Experimentally Determined) Energy of the Helium Atom

The helium atom has two electrons bound to a nucleus with charge $Z = 2$. The *successive* removal of the two electrons can be considered stepwise:

$$\mathrm{He} \xrightarrow{I_1} \mathrm{He}^+ + e^- \xrightarrow{I_2} \mathrm{He}^{++} + 2e^- \tag{5.3.1}$$

The *first ionization energy* I_1 is the minimum energy required to remove the first electron from helium gas and is experimentally determined:

$$I_1 = -E_{1s}(\mathrm{He}) = 24.59\ eV$$

While the second ionization energy, I_2 can be experimentally determined, it can also be calculated exactly from the hydrogen atom solutions since He^+ is a hydrogen-like ion with $Z = 2$. Hence, we have

$$\begin{aligned} I_2 &= -E_{1s}(\mathrm{He}^+) \\ &= \frac{Z^2}{2n^2} \\ &= 54.42\ \mathrm{eV} \end{aligned}$$

The energy of the three separated particles on the right side of Equation 5.3.1 is zero (by definition). Therefore the ground-state energy of helium atom is given by

$$\begin{aligned} E_{true} &= -(I_1 + I_2) \\ &= -79.02\ \mathrm{eV}. \end{aligned}$$

which can be expressed in terms of the ***Rydberg*** constant ($R_H = 13.6\ eV$) that also describes the lowest energy of the hydrogen atom

$$E_{true} = -5.8066\, R_H$$

We will attempt to reproduce this **true value**, as close as possible, by different theoretical approaches (all approximations).

5.3.2: The "Ignorance is Bliss" Approximation

The Hamiltonian for the Helium atom is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \cancel{\frac{e^2}{4\pi\epsilon_0 r_{12}}} \tag{5.3.2}$$

If we simply *ignore* the electron-electron repulsion term, then Equation 5.3.2 can be simplified to

$$\hat{H} \approx -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_2} \tag{5.3.3}$$

$$\approx h_1(r_1) + h_2(r_2) \tag{5.3.4}$$

where h_1 and h_2 are one electron Hamiltonians for electron 1 and 2, respectively, and are just the hydrogen-like Hamiltonians. The approximation in Equation 5.3.4 is convenient since electron 1 is *separable* from electron 2, so that the two-electron wavefunction is approximated as a product to two one-electron wavefunctions:

$$\Psi_{total} = \psi_{el_1}\psi_{el_2} \tag{5.3.5}$$

or in braket notation

$$|\Psi_{total}\rangle = \hat{H}\left|\psi_{el_1}\psi_{el_2}\right\rangle \tag{5.3.6}$$

With some operator algebra, something important arises - the one electron energies are **additive**:

$$\hat{H}\Psi_{total} = (\hat{H}_{el_1} + \hat{H}_{el_2})\psi_{n\ el_1}\psi_{n\ el_2} = (E_{n_1} + E_{n_2})\psi_{n\ el_1}\psi_{n\ el_2}$$

or in bra-ket notation

$$\begin{aligned}\hat{H}|\Psi_{total}\rangle &= \hat{H}|\psi_{el_1}\psi_{el_2}\rangle \\ &= (E_{n_1} + E_{n_2})|\psi_1\psi_2\rangle\end{aligned}$$

The energy for a ground state Helium atom (both electrons in lowest state) is then

$$\begin{aligned}E_{He_{1s}} &= \underbrace{E_{n_1}}_{\text{energy of single electron in helium}} + \underbrace{E_{n_2}}_{\text{energy of single electron in helium}} \\ &= -R_H\left(\frac{Z^2}{1}\right) - R_H\left(\frac{Z^2}{1}\right) \\ &= -8R_H\end{aligned}$$

This approximation significantly overestimates the true energy of the helium atom $E_{He_{1s}} = -5.8066\ R$. This is a poor approximation and we need to address electron-electron repulsion properly (or better at least).

5.3.3: Shielding and Penetration

One way to take electron-electron repulsion into account is to modify the form of the wavefunction. A logical modification is to change the nuclear charge, Z, in the wavefunctions to an effective nuclear charge (Z_{eff}), from +2 to a smaller value. The rationale for making this modification is that one electron partially shields the nuclear charge from the other electron, as shown in Figure 7.1.1 .

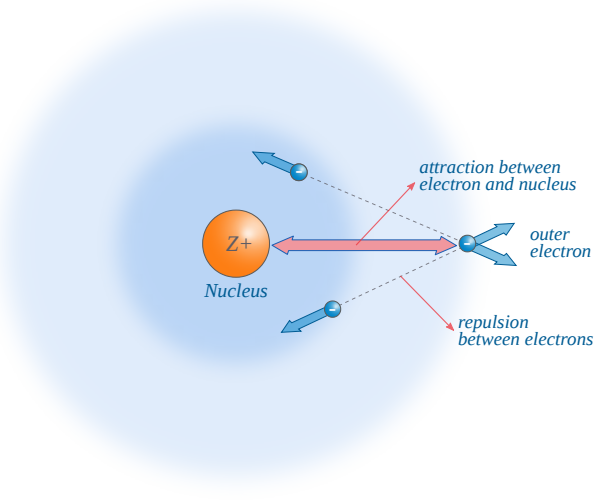


Figure 7.1.1 : Electron-electron shielding leading to a reduced effective nuclear charge. The attractive force of the nucleus on the outer electron is partially countered by the repulsive force between inner electrons and the outer electron. (CC BY-SA; Ümit Kaya via LibreTexts)

A region of negative charge density between one of the electrons and the +2 nucleus makes the potential energy between them more positive (decreases the attraction between them). We can effect this change mathematically by using $\zeta < 2$ in the wavefunction expression. If the shielding were complete, then Z_{eff} would equal 1. If there is no shielding, then $Z_{eff} = 2$. So a way to take into account the electron-electron interaction is by saying it produces a shielding effect. The shielding is not zero, and it is not complete, so the effective nuclear charge varies between one and two.

In general, a theory should be able to make predictions in advance of knowledge of the experimental result. Consequently, a principle and method for choosing the best value for Z_{eff} or any other adjustable parameter that is to be optimized in a calculation is needed. The Variational Principle provides the required criterion and method and says that the best value for any variable parameter in an approximate wavefunction is the value that gives the **lowest energy for the ground state**; i.e., the value that minimizes the energy. The variational method is the procedure that is used to find the lowest energy and the best values for the variable parameters.

5.3.4: 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

$$E_{trial} \geq E_{true} \tag{5.3.7}$$

where

$$E_{trial} = \frac{\langle \psi_{trial} \left| \hat{H} \right| \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{5.3.8}$$

$$= \frac{\int \psi^*_{trial} \hat{H} \psi_{trial} d\tau}{\int \psi^*_{trial} \psi_{trial} d\tau} \tag{5.3.9}$$

Equation 5.3.7 is called the variational theorem and states that for a time-independent Hamiltonian operator, any trial wavefunction will have an variational energy (i.e., expectation value) that is **greater than or equal** to the true ground state wavefunction corresponding to the given Hamiltonian (Equation 5.3.7). Because of this, the variational energy is an upper bound to the true ground state energy of a given molecule. The general approach of this method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible (Figure 7.1.2).

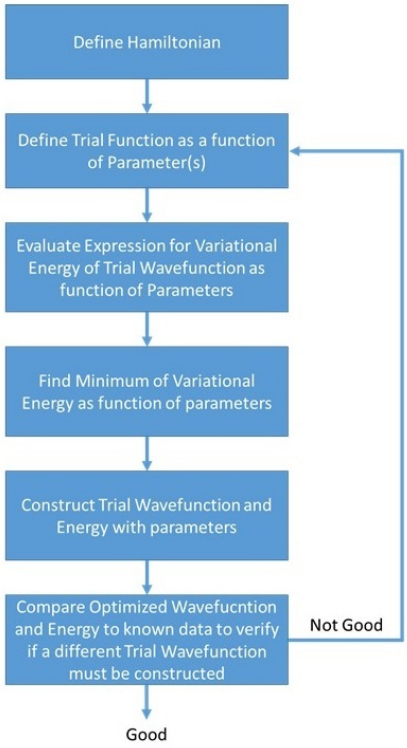


Figure 7.1.2 : Simplified algorithmic flowchart of the Variational Method approximation

> *The variational energy E_{trial} is only equal to the true energy E_{true} when the the corresponding trial wavefunction ψ_{trial} is equal to the true wavefunction ψ_{true}.*

5.3.5: Application to the Helium atom Ground State

Often the expectation values (numerator) and normalization integrals (denominator) in Equation 5.3.9 can be evaluated analytically. For the case of the He atom, let's consider the trial wavefunction as the product wavefunction given by Equation 5.3.10 (this is called the **orbital approximation**),

$$\psi(r_1, r_2) \approx \varphi(r_1)\varphi(r_2) \tag{5.3.10}$$

The adjustable or variable parameter in the trial wavefunction is the effective nuclear charge ζ, and the Hamiltonian is the complete form given below (Note: quantum calculations typically refer to effective nuclear charge as ζ rather than Z_{eff} as we used previously).

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{5.3.11}$$

the adjustable or variable parameter in the trial wavefunction is the effective nuclear charge ζ (would be equal to $\zeta = 2$ if fully unshielded), and the Hamiltonian is the complete form. When the expectation value for the trial energy (Equation 5.3.9) is evaluated for helium, the result is a variational energy that depends on the adjustable parameter, ζ.

$$E_{trial}(\zeta) = \frac{\mu e^4}{4\epsilon_0^2 h}\left(\zeta^2 - \frac{27}{8}\zeta\right) \tag{5.3.12}$$

This function is plotted in Figure 7.1.3 as a function of ζ. According to the variational principle (Equation 5.3.7), the minimum value of the energy on this graph is the best approximation of the true energy of the system, and the associated value of ζ is the best value for the adjustable parameter.

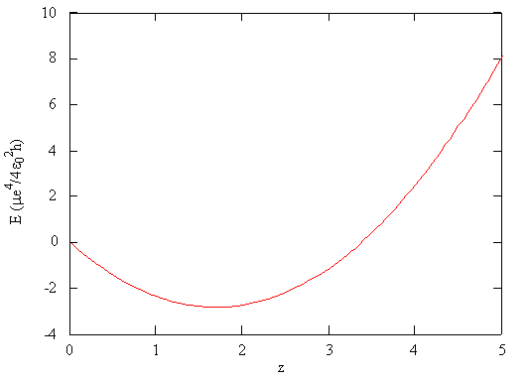


Figure 7.1.3 : Graph of trial energies for helium atom as a function of the adjustable parameter ζ in Equation 5.3.12 that represents the effective nuclear charge felt by the electrons.

Using the mathematical function for the energy of a system, the minimum energy with respect to the adjustable parameter can be found by taking the derivative of the energy with respect to that parameter, setting the resulting expression equal to zero, and solving for the parameter, in this case ζ. This is a standard method in calculus for finding maxima and minima.

? Exercise 7.1.1

Find the value for ζ that minimizes the helium binding energy for the product trial wavefunction in Equation 5.3.10 with the Hamiltonian in Equation 5.3.11. and compare the binding energy to the experimental value. What is the percent error in the calculated value?

Solution

The variational method requires following the workflow in Figure 7.1.2 .

- Step 1: Define the Hamiltonian - This is given by Equation 5.3.11.
- Step 2: Define the trial wavefunction as a function of at least one parameter - This is given by Equation 5.3.10.
- Step 3: Evaluate variational energy (E_{trial} integral (Equation 5.3.9) - This procedure was already above in Equation 5.3.12.
- Step 4: Minimize the variational energy as a function of the parameter(s) - Following the standard approach to find extrema in calculus, evaluate the derivative of E_{trial} with respect to ζ and set to zero:

$$\frac{dE_{trial}}{d\zeta} = \frac{\mu e^4}{4\epsilon_0^2 h}\left(2\zeta - \frac{27}{8}\right) = 0$$

then find solve for the roots of this polynomial

$$2\zeta - \frac{27}{8} = 0$$

or

$$\zeta = \frac{27}{16} \approx 1.6875$$

- Step 5-6: The question does not ask for the optimized wavefunction (Step 5) or to compare the result with the true value to evaluate the quality of the approximation (Step 6). We can skip these steps.

From Exercise 7.1.1 , the $\zeta = 1.6875$ and the approximate energy we calculate using this approximation method, E_{approx} = -77.483 eV. Table 7.1.1 show that a substantial improvement in the accuracy of the computed binding energy is obtained by using shielding to account for the electron-electron interaction. Including the effect of electron shielding in the wavefunction reduces the error in the binding energy to about 2%. This idea is very simple, elegant, and significant.

Table 7.1.1 : Comparison of the results of three approximation methods to experiment.

Method	He binding energy (eV)
"Ignorance is Bliss" Approximation (neglect repulsion between electrons)	-108.8
Variational method with variable effective charge	-77.483
Experimental	-79.0

The improvement we have seen in the total energy calculations using a variable parameter ζ indicates that an important contribution of electron-electron interaction or repulsion to the total binding energy arises from the fact that each electron shields the nuclear charge from the other electron. It is reasonable to assume the electrons are independent; i.e., that they move independently, but the shielding must be taken into account in order to fine-tune the wavefunctions. The inclusion of optimizable parameters in the wavefunction allows us to develop a clear physical image of the consequences of our variation calculation. Calculating energies correctly is important, and it is also important to be able to visualize electron densities for multi-electron systems. In the next two sections, we take a temporary break from our consideration of approximation methods in order to examine multi-electron wavefunctions more closely.

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5.4: Single-electron Wavefunctions and Basis Functions

Finding the most useful single-electron wavefunctions to serve as building blocks for a multi-electron wavefunction is one of the main challenges in finding approximate solutions to the multi-electron Schrödinger Equation. The functions must be different for different atoms because the nuclear charge and number of electrons are different. The attraction of an electron for the nucleus depends on the nuclear charge, and the electron-electron interaction depends upon the number of electrons.

As we saw in our initial approximation methods, the most straightforward place to start in finding reasonable single-electron wavefunctions for multi-electron atoms is with the atomic orbitals produced in the quantum treatment of hydrogen, the so-called "hydrogenic" spin-orbitals. These traditional atomic orbitals, with a few modifications, give quite reasonable calculated results and are still in wide use for conceptually understanding multi-electron atoms. In this section and in Chapter 10 we will explore some of the many other single-electron functions that also can be used as atomic orbitals.

Hydrogenic spin-orbitals used as components of multi-electron systems are identified in the same way as they are for the hydrogen atom. Each spin-orbital consists of a spatial wavefunction, specified by the quantum numbers (n, l, m_l) and denoted ls, 2s, 2p, 3s, 3p, 3d, etc, multiplied by a spin function, specified by the quantum number m_s and denoted α or β. In our initial approximation methods, we ignored the spin components of the hydrogenic orbitals, but they must be considered in order to develop a complete description of multi-electron systems. The subscript on the argument of the spatial function reveals which electron is being described (r_1 is a vector that refers to the coordinates of electron 1, for example.) No argument is given for the spin function. An example of a spin-orbital for electron 2 in a $3p_z$ orbital:

$$|\varphi_{3p_z}\alpha(r_2)\rangle = \varphi_{3,1,0}(r_2)\alpha \tag{5.4.1}$$

In the alternative shorthand notation for this spin-orbital shown below, the coordinates for electron 2 in the spatial function are abbreviated simply by the number "2," and the spatial function is represented by "$3p_z$" rather than "$\varphi_{3,1,0}$". The argument "2" given for the spin function refers to the unknown spin variable for electron 2. Many slight variations on these shorthand forms are in use in this and other texts, so flexibility and careful reading are important.

$$|\varphi_{3p_z}\alpha(2)\rangle = 3p_z(2)\alpha(2) \tag{5.4.2}$$

In this chapter we will continue the trend of moving away from writing specific mathematical functions and toward a more symbolic, condensed representation. Your understanding of the material in this and future chapters requires that you keep in mind the form and properties of the specific functions denoted by the symbols used in each equation.

Exercise 5.4.1

Write the full mathematical form of $\varphi_{3pz\alpha}$ using as much explicit functional detail as possible.

The basic mathematical functions and thus the general shapes and angular momenta for hydrogenic orbitals are the same as those for hydrogen orbitals. The differences between atomic orbitals for the hydrogen atom and those used as components in the wavefunctions for multi-electron systems lie in the radial parts of the wavefunctions and in the energies. Specifically, the differences arise from the replacement of the nuclear charge Z in the radial parts of the wavefunctions by an adjustable parameter ζ that is allowed to vary in approximation calculations in order to model the interactions between the electrons. We discussed such a procedure for helium The Variational Method previously. The result is that electrons in orbitals with different values for the angular momentum quantum number, l, have different energies. Figure **5.4.1** shows the results of a quantum mechanical calculation on argon in which the degeneracy of the 2s and 2p orbitals is found to be removed, as is the degeneracy of the 3s, 3p, and 3d orbitals.

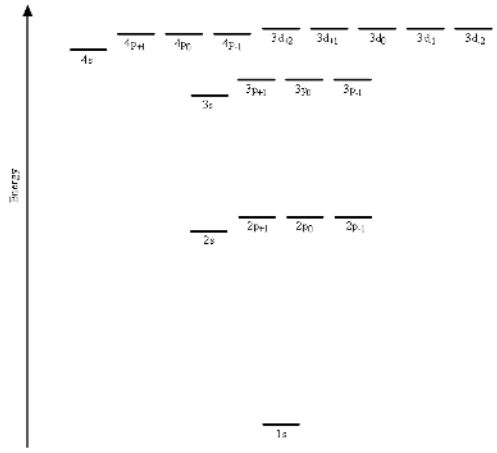


Figure 5.4.1: Ordering of energy levels for Ar. Energy level differences are not to scale.

The energy of each electron now depends not only on its principal quantum number, n, but also on its angular momentum quantum number, l.

The presence of ζ in the radial portions of the wavefunctions also means that the electron probability distributions associated with hydrogenic atomic orbitals in multi-electron systems are different from the exact atomic orbitals for hydrogen. Figure 5.4.2 compares the radial distribution functions for an electron in a 1s orbital of hydrogen (the ground state), a 2s orbital in hydrogen (an excited configuration of hydrogen) and a 1s orbital in helium that is described by the best variational value of ζ. Our use of hydrogen-like orbitals in quantum mechanical calculations for multi-electron atoms helps us to interpret our results for multi-electron atoms in terms of the properties of a system we can solve exactly.

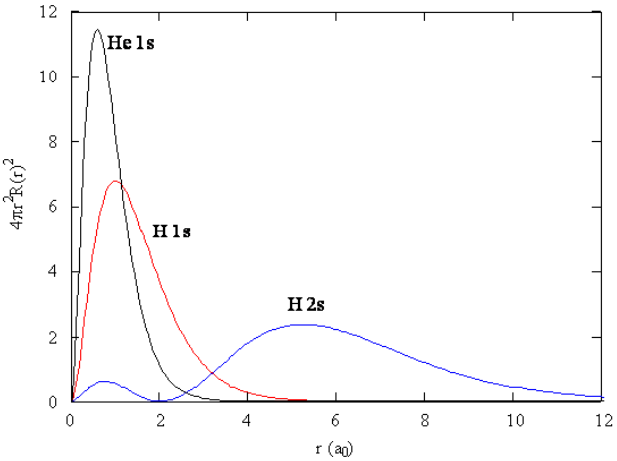


Figure 5.4.2: Radial distribution functions for 1s of hydrogen (red, $\zeta = 1$), 2s of hydrogen (blue, $\zeta = 1$) and 1s of helium (black, $\zeta = 1.6875$).

Exercise 5.4.2

Analyze Figure 5.4.2 and write a paragraph about what you can discern about the relative sizes of ground state hydrogen, excited state hydrogen and ground state helium atoms.

While they provide useful stepping off points for understanding computational results, nothing requires us to use the hydrogenic functions as the building blocks for multi-electrons wavefunctions. In practice, the radial part of the hydrogenic atomic orbital presents a computational difficulty because the radial function has nodes, positive and negative lobes, and steep variations that make accurate evaluation of integrals by a computer slow. Consequently other types of functions are generally used in building multi-electron functions. These usually are related to the hydrogenic orbitals to aid in the analysis of molecular electronic structure. For example, Slater-type atomic orbitals (STO's), designated below as $S_{nlm}(r,\theta,\varphi)$, avoid the difficulties imposed by the hydrogenic functions. The STO's, named after their creator, John Slater, were the first alternative functions that were used

extensively in computations. STO's do not have any radial nodes, but still contain a variational parameter ζ (zeta), that corresponds to the effective nuclear charge in the hydrogenic orbitals. In Equation 5.4.3 and elsewhere in this chapter, the distance, r, is measured in units of the Bohr radius, a_0.

$$S_{nlm}(r,\theta,\varphi) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} Y_l^m(\theta,\varphi) \tag{5.4.3}$$

Exercise 5.4.3

a. Write the radial parts of the 1s, 2s, and 2p atomic orbitals for hydrogen.
b. Write the radial parts of the n = 1 and n = 2 Slater–type orbitals (STO).
c. Check that the above five functions are normalized.
d. Graph these five functions, measuring r in units of the Bohr radius.
e. Graph the radial probability densities for these orbitals. Put the hydrogen orbital and the corresponding STO on the same graph so they can be compared easily.
f. Adjust the zeta parameter ζ in each case to give the best match of the radial probability density for the STO with that of the corresponding hydrogen orbital.
g. Comment on the similarities and differences between the hydrogen orbitals and the STOs and the corresponding radial probability densities.

Linear Variational Method

An alternative approach to the general problem of introducing variational parameters into wavefunctions is the construction of a single-electron wavefunction as a linear combination of other functions. 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

$$\varphi_{1s}(r_1) = \sum_j c_j e^{-\zeta_j r_j / a_o} \tag{5.4.4}$$

The linear combination permits weighting of the different exponentials through the adjustable coefficients (cj) 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 5.4.4 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 5.4.4 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 5.4.4

Make plots of φ in Equation 5.4.4 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 5.4.4 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 5.4.1, generally can be used in the STOs for other and larger systems.

Table 5.4.1: 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 5.4.5

Compare the value ζ_{1s} = 1.24 in Table 5.4.1 for hydrogen with the value you obtained in Exercise 5.4.3. 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?

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.

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5.5: An Electron has an Intrinsic Spin Angular Momentum

Learning Objectives

- Understand the forth quantum number for electrons - spin.
- Understand how spin is connected to magnetic properties of the electrons and atoms.
- Understand how to break degeneracy via externally applied magnetic fields in electrons and atoms.

Imagine doing a hypothetical experiment that would lead to the discovery of electron spin. Your laboratory has just purchased a microwave spectrometer with variable magnetic field capacity. We try the new instrument with hydrogen atoms using a magnetic field of 10^4 Gauss and look for the absorption of microwave radiation as we scan the frequency of our microwave generator (Figure 8.4.1).

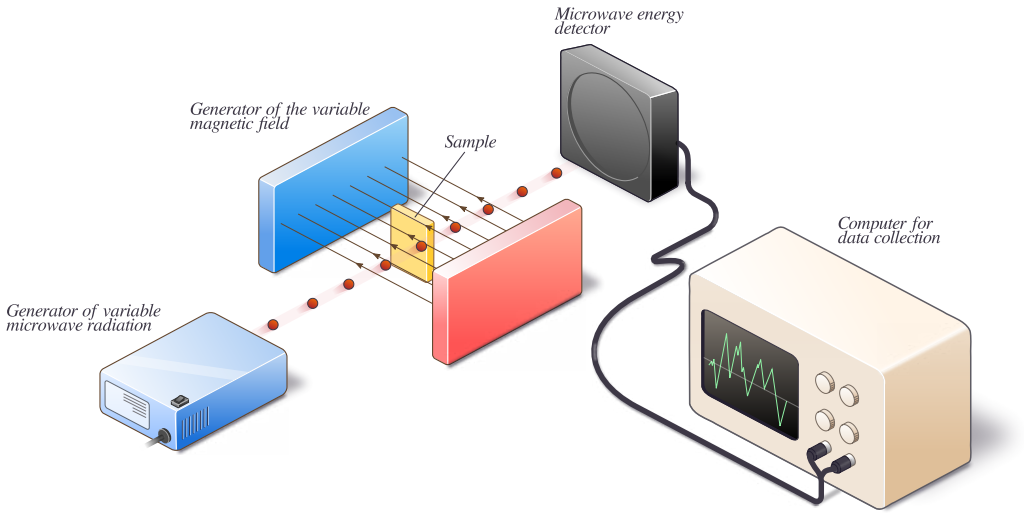


Figure 8.4.1 : Schematic diagram of a microwave spectrometer with the sample in a variable magnetic field. The strength of the magnetic field is set, and the sample's absorption of microwave photons is measured for a range of microwave photon energies (or frequencies). (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Finally we see absorption at a microwave photon frequency of $28 \times 10^9\ Hz$ (28 gigahertz). This result is really surprising from several perspectives. Each hydrogen atom is in its ground state, with the electron in a 1s orbital. The lowest energy electronic transition that we predict based on existing theory (the electronic transition from the ground state (ψ_{100} to ψ_{21m}) requires an energy that lies in the vacuum ultraviolet (the lower Lyman line at 121 nm), not the microwave, region of the spectrum. Furthermore, when we vary the magnetic field we note that the frequency at which the absorption occurs varies in proportion to the magnetic field.

5.5.1: The Zeeman Effect: Breaking Degeneracies with Magnetic Fields

Magnetism results from the circular motion of charged particles. This property is demonstrated on a macroscopic scale by making an electromagnet from a coil of wire and a battery. Electrons moving through the coil produce a magnetic field, which can be thought of as originating from a magnetic dipole or a bar magnet. Electrons in atoms also are moving charges with angular momentum so they too produce a magnetic dipole, which is why some materials are magnetic. A **magnetic dipole** interacts with a magnetic field, and the energy of this interaction is given by the scalar product of the magnetic dipole moment, and the magnetic field, $\vec{B}$.

$$E_B = -\vec{\mu}_m \cdot \vec{B} \tag{5.5.1}$$

Pieter Zeeman was one of the first to observe the splittings of spectral lines in a magnetic field caused by this interaction. Consequently such splittings are known as the Zeeman effect. (Figure 8.4.2). The expectation value calculated for the total energy in this case is the sum of the energy in the absence of the field, E_n, plus the Zeeman energy:

$$\langle E \rangle = E_n + \frac{e\hbar B_z m_l}{2m_e} \tag{5.5.2}$$

$$= E_n + \mu_B B_z m_l \tag{5.5.3}$$

The factor

$$\frac{e\hbar}{2m_e} = -\gamma_e \hbar = \mu_B \tag{5.5.4}$$

defines the constant μ_B, called the **Bohr magneton**, which is taken to be the fundamental magnetic moment. It has units of 9.2732×10^{-21} erg/Gauss or 9.2732×10^{-24} Joule/Tesla. This factor will help you to relate magnetic fields, measured in Gauss or Tesla, to energies, measured in ergs or Joules, for any particle with a charge and mass the same as an electron.

Equation 5.5.3 demonstrates that that m_l quantum number degeneracy of the hydrogen atom is removed by the externally applied magnetic field. For example, the three hydrogen atom eigenstates $|\psi_{211}\rangle$, $|\psi_{21-1}\rangle$, and $|\psi_{210}\rangle$ are degenerate in zero magnetic field, but have different energies in an externally applied magnetic field (Figure 8.4.2).

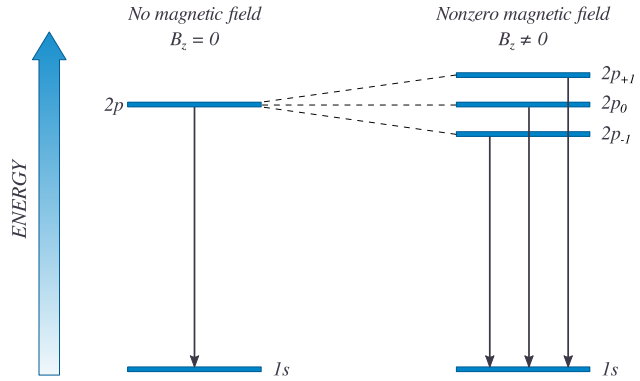


Figure 8.4.2 : The Zeeman effect for the $2s \rightarrow 1s$ transition. Emission when an electron switches from a 2p orbital to a 1s orbital occurs at only one energy in the absence of a magnetic field, but can occur at three different energies in the presence of a magnetic field. (CC BY-NC; Ümit Kaya via LibreTexts)

The $m_l = 0$ state, for which the component of angular momentum and hence also the magnetic moment in the external field direction is zero, experiences no interaction with the magnetic field. The $m_l = +1$ state, for which the angular momentum in the z-direction is +ħ and the magnetic moment is in the opposite direction, against the field, experiences a raising of energy in the presence of a field. Maintaining the magnetic dipole against the external field direction is like holding a small bar magnet with its poles aligned exactly opposite to the poles of a large magnet. It is a higher energy situation than when the magnetic moments are aligned with each other.

5.5.2: Electron Spin and the Stern-Gerlach Experiment

To discover new things, experimentalists sometimes must explore new areas in spite of contrary theoretical predictions. Our theory of the hydrogen atom at this point gives no reason to look for absorption in the microwave region of the spectrum. By doing the crazy experiment outlines above, we discovered that when an electron is in the $|1s\rangle$ orbital of the hydrogen atom, there are two different states that have the same energy. When a magnetic field is applied, this degeneracy is removed, and microwave radiation can cause transitions between the two states. In the rest of this section, we see what can be deduced from this experimental observation. This experiment actually could be done with electron spin resonance spectrometers available today (Figure 8.4.1). To explain our observations, a new model for the hydrogen atom. Our original model for the hydrogen atom accounted for the motion of the electron and proton in our three-dimensional world; the new model needs something else that can give rise to an additional Zeeman-like effect. We need a charged particle with angular momentum to produce a magnetic moment, just like that obtained by the orbital motion of the electron. We can postulate that our observation results from a motion of the electron that was not considered in the last section - electron spin. We have a charged particle spinning on its axis. We then have charge moving in a circle, angular momentum, and a magnetic moment, which interacts with the magnetic field and gives us the Zeeman-like effect that we observed (Figure 8.4.2).

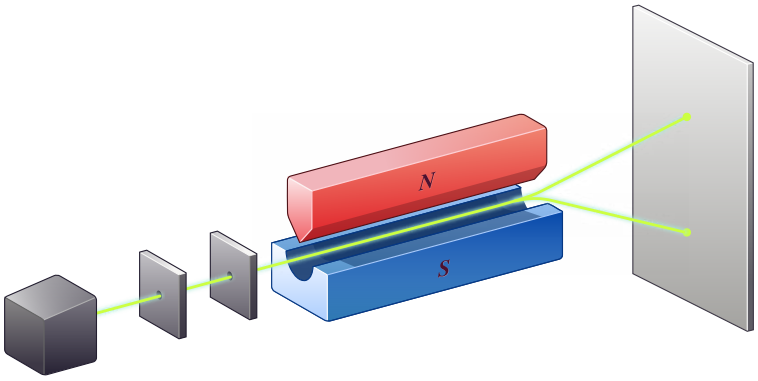


Figure 8.4.2 : Stern–Gerlach experiment: silver atoms travel through an inhomogeneous magnetic field and are deflected up or down depending on their spin. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

In 1920, Otto Stern and Walter Gerlach designed an experiment, which unintentionally led to the discovery that electrons have their own individual, continuous spin even as they move along their orbital of an atom. Today, this electron spin is indicated by the fourth quantum number, also known as the **Electron Spin Quantum Number** and denoted by m_s. In 1925, Samuel Goudsmit and George Uhlenbeck made the claim that features of the hydrogen spectrum that were unexamined might by explained by assuming electrons act as if it has a spin, which can be denoted by an arrow pointing up, which is +1/2, or an arrow pointing down, which is -1/2. The Stern and Gerlach experiment which demonstrated this was done with a beam of vaporized silver atoms that split into two beams after passing through a magnetic field (Figure 8.4.2). An explanation of this is that an electron has a magnetic field due to its spin. When electrons that have opposite spins are put together, there is no net magnetic field because the positive and negative spins cancel each other out. The silver atom used in the experiment has a total of 47 electrons, 23 of one spin type, and 24 of the opposite. Because electrons of the same spin cancel each other out, the *one unpaired electron* in the atom will determine the spin.

5.5.3: 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

$$\hat{L}^2 \left|Y_l^{m_l}\right\rangle = l(l+1)\hbar^2 \left|Y_l^{m_l}\right\rangle$$

so by analogy for the spin states, we must have

$$\hat{S}^2 \left|\sigma_s^{m_s}\right\rangle = s(s+1)\hbar^2 \left|\sigma_s^{m_s}\right\rangle$$

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

$$\hat{L}_z \left|Y_l^{m_l}\right\rangle = m_l\hbar \left|Y_l^{m_l}\right\rangle$$

so by analogy, we must have a similar projection for the spin angular momentum:

$$\hat{S}_z \left|\sigma_s^{m_s}\right\rangle = m_s\hbar \left|\sigma_s^{m_s}\right\rangle \tag{5.5.5}$$

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

$$\begin{aligned} m_{s,f} - m_{s,i} &= 1 \\ (+s) - (-s) &= 1 \\ 2s &= 1 \\ s &= \frac{1}{2} \end{aligned} \tag{5.5.6}$$

Therefore our conclusion is that the magnitude of the spin quantum number is 1/2 and the values for m_s are +1/2 and -1/2. The two spin states correspond to spinning clockwise and counter-clockwise with positive and negative projections of the spin angular momentum onto the z-axis (Figure 8.4.3). The state with a positive projection, m_s = +1/2, is called α; the other is called β. These spin states are arbitrarily labeled α and β, and the associated spin wavefunctions also are designated by $|\alpha\rangle$ and $|\beta\rangle$.

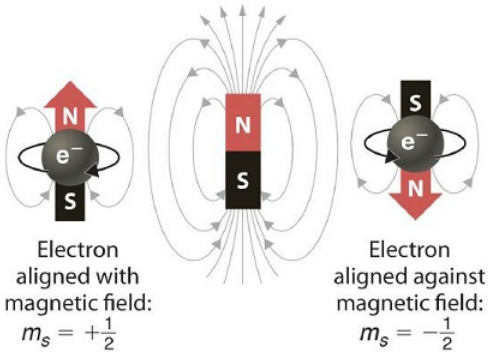


Figure 8.4.3 : Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden. (CC BY-SA-NC 3.0; Anonymous).

From Equation 5.5.5, the magnitude of the z-component of spin angular momentum, S_z, is given by

$$S_z = m_s \hbar \tag{5.5.7}$$

so the value of S_z is $+\hbar/2$ for spin state α and $-\hbar/2$ for spin state β. Hence, we conclude that the α spin state, where the magnetic moment is aligned against the external field direction, has a **greater energy** than the β spin state.

Electrons are not Actually Spinning

Electron's hypothetical surface would have to be moving *faster* than the speed of light for it to rotate quickly enough to produce the observed angular momentum. Hence, an electron is not simply a spinning ball or ring and electron spin appears to be an *intrinsic angular moment* of the particle rather than a consequence of the rotation of a charge particle like Figure 8.4.3 suggests. Despite this, the term "electron spin" persists in quantum vernacular.

Properties of Spin Eigenstates

Even though we do not know their functional forms, the spin wavefunctions are taken to be normalized and orthogonal to each other.

$$\int \alpha^* \alpha \, d\tau_s = \int \beta^* \beta \, d\tau_s = 1 \tag{5.5.8}$$

or in braket notation

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \tag{5.5.9}$$

and

$$\int \alpha^* \beta \, d\tau_s = \int \beta^* \alpha \, d\tau_s = 0 \tag{5.5.10}$$

or in braket notation

$$\langle\alpha|\beta\rangle = \langle\alpha|\beta\rangle = 0 \tag{5.5.11}$$

where the integral is over the spin variable τ_s.

Now let's apply these deductions to the experimental observations in our hypothetical microwave experiment in Figure 8.4.1 . We can account for the frequency of the transition (ν= 28 gigahertz) that was observed in this hypothetical experiment in terms of the magnetic moment of the spinning electron and the strength of the magnetic field. The photon energy, $h\nu$, is given by the difference between the energies of the two states, E_α and E_β

$$\Delta E = h\nu \tag{5.5.12}$$

$$= E_\alpha - E_\beta \tag{5.5.13}$$

The energies of these two states consist of the sum of the energy of an electron in a 1s orbital, E_{1s}, and the energy due to the interaction of the spin magnetic dipole moment of the electron, μ_s, with the magnetic field, B.

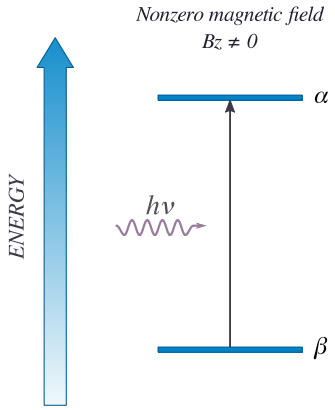


Figure 8.4.4 : Absorption of a photon to cause a transition from the β to the α state. (CC BY-NC; Ümit Kaya via LibreTexts)

The two states with distinct values for spin magnetic moment μ_s are denoted by the subscripts α and β (the spin version of Equation 5.5.1.

$$E_\alpha = E_{1s} - \mu_{s,\alpha} \cdot B$$

$$E_\beta = E_{1s} - \mu_{s,\beta} \cdot B$$

Substituting the two equations above into the expression for the photon (Equation 5.5.13) energy gives

$$h\nu = E_\alpha - E_\beta \tag{5.5.14}$$

$$= (E_{1s} - \mu_{s,\alpha} \cdot B) - (E_{1s} - \mu_{s,\beta} \cdot B) \tag{5.5.15}$$

$$= (\mu_{s,\beta} - \mu_{s,\alpha}) \cdot B \tag{5.5.16}$$

Again by analogy with the orbital angular momentum and magnetic moment discussed above, we take the spin magnetic dipole of each spin state, $\mu_{s,\alpha}$ and $\mu_{s,\beta}$, to be related to the total spin angular momentum of each state, S_α and S_β, by a constant **spin gyromagnetic ratio**, γ_s, as shown below.

$$\mu_s = \gamma_s S$$

or each of the two states

$$\mu_{s,\alpha} = \gamma_s S_\alpha$$

$$\mu_{s,\beta} = \gamma_s S_\beta$$

With the magnetic field direction defined as z, the scalar product in Equation 5.5.16 becomes a product of the z-components of the spin angular momenta, $S_{z,\alpha}$ and $S_{z,\beta}$, with the external magnetic field.

Inserting the values for $S_{z,\alpha} = +\frac{1}{2}\hbar$ and $S_{z,\alpha} = -\frac{1}{2}\hbar$ from Equation 5.5.7 and rearranging Equation 5.5.16 yields

$$\frac{h\nu}{B} = -\gamma_s\hbar$$

Calculating the ratio $\frac{h\nu}{B}$ from our experimental results, $\nu = 28 \times 10^9\ Hz$ when $B = 10^4\ gauss$, gives us a value for

$$-\gamma_s\hbar = 18.5464 \times 10^{-21}\ erg/gauss.$$

This value is about twice the Bohr magneton,$-\gamma_e\hbar$, found in Equation 5.5.4 i.e. $\gamma_s\hbar = 2.0023, \gamma_e\hbar$, or

$$\gamma_s = 2.0023\gamma_e \tag{5.5.17}$$

The factor of 2.0023 is called the **g-factor** and accounts for the deviation of the spin gyromagnetic ratio from the value expected for orbital motion of the electron. In other words, it accounts for the spin transition being observed where it is instead of where it would be if the same ratio between magnetic moment and angular momentum held for both orbital and spin motions. The value 2.0023 applies to a freely spinning electron; the coupling of the spin and orbital motion of electrons can produce other values for g.

? Exercise 8.4.1

Carry out the calculations that show that the g-factor for electron spin is 2.0023.

Interestingly, the concept of electron spin and the value g = 2.0023 follow logically from *Dirac's relativistic quantum theory*, which is beyond the scope of this discussion. Electron spin was introduced here as a postulate to explain experimental observations. Scientists often introduce such postulates parallel to developing the theory from which the property is naturally deduced.

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5.6: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

Learning Objectives

- Interprete the consequence of exchanging two electrons in a multi-electron atom on the wavelengths
- Connect the Pauli's Exclusion Principle to the permutation symmetry of multi-electron atoms

Quantum mechanics allows us to predict the results of experiments. If we conduct an experiment with indistinguishable particles a correct quantum description cannot allow anything which distinguishes between them. For example, if the wavefunctions of two particles overlap, and we detect a particle, which one is it? The answer to this is not only that we do not know, but that we cannot know. Quantum mechanics can only tell us the probability of finding a particle in a given region. The wavefunction must therefore describe both particles.

The Schrödinger equation for the helium atom is then:

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_1^2)-V(\mathbf{r}_1)-V(\mathbf{r}_2)+V_{12}(\mathbf{r}_1,\mathbf{r}_2)\right]\psi(\mathbf{r}_1,\mathbf{r}_2)=E\psi(\mathbf{r}_1,\mathbf{r}_2)$$

where the subscripts label each particle, and there are six coordinates, three for each particle. While $|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ is a six dimensional wavefunction (three for each electron) and contains all the information we can measure (a Postulate of Quantum Mechanics), it only provide the probability of finding the electron at a specific volume element, and does **not** tell us which particle is which (e.g., is it electon 1 or electron 2?).

What basis states would be appropriate for $|\psi\rangle$? If we consider the orbital approximation that uses a product wavefunction

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle=|\varphi_a(\mathbf{r}_1)\rangle|\varphi_b(\mathbf{r}_2)\rangle$$

where $|\varphi_a(\mathbf{r}_1)\rangle$ and $|\varphi_b(\mathbf{r}_2)\rangle$ are one-particle spin-orbitals (with both spin and spatial components) of atoms 1 and 2. This approximation allows us to separate the two particle equation into two one-electron equations:

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2+V(\mathbf{r}_1)\right]|\varphi_a(\mathbf{r}_1)\rangle=E|\,\varphi_a(\mathbf{r}_1)\rangle$$

$$\left[-\frac{\hbar^2}{2m}\nabla_2^2+V(\mathbf{r}_2)\right]|\varphi_b(\mathbf{r}_2)\rangle=E|\,\varphi_a(\mathbf{r}_2)\rangle$$

provided that the particles do not interact (e.g., ∇_1^2 does not act on $|\varphi_b(\mathbf{r}_2)\rangle$ and $V_{12}=0$).

Unfortunately, by doing this we have introduced unphysical *labels* to the indistinguishable particles. And this is wrong: the effect of it is that the particles do not interfere with each other because they are in different dimensions (six dimensional space - remember?). When we construct a two particle wavefunction out of two one-particle wavefunctions we must be ensure that the probability density (the measurable quantity $|\psi|^2$) is independent of the **artificial** labels.

5.6.1: 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

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = \psi(\mathbf{r}_2, \mathbf{r}_1)^*\psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{5.6.1}$$

since the probability density of the electrons in the atom does **not** change upon permutation of the electrons.

Exercise 8.5.1

Permute the electrons the product function for He wavefunction:

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = |\varphi_{1s}(\mathbf{r}_1)\rangle|\,\varphi_{1s}(\mathbf{r}_2)\rangle$$

Equation 5.6.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{5.6.2}$$

so that

$$\left(e^{-i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right)\left(e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{5.6.3}$$

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.,

$$e^{i\varphi}e^{i\varphi} = e^{i2\varphi} = 1 \tag{5.6.4}$$

which is true only if $\varphi = 0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature.

Exercise 8.5.2

Use Euler's Equality

$$e^{i\pi} + 1 = 0$$

to show that $e^{i2\varphi} = 1$ when $\varphi = 0$ or $n\pi$ and consequently $e^{i\varphi} = \pm 1$.

We can introduce the *exchange operator* $\hat{P}_{12}$: an operator which permutes the labels of the particles in a multi-particle wavefucntion. This is a rather strange operator, because it only changes the *unphysical* labels which we have attached to the one-particle wavefunctions in order to make the maths more easy. For a meaningful solution we must have a wavefunction which has a probability amplitude unchanged by $\hat{P}_{12}$: it must be either symmetric or antisymmetric with respect to exchange:

$$\hat{P}_{12}\,|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \pm|\,\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle \tag{5.6.5}$$

Bosons and femions

Physical solutions must be eigenfunctions of $\hat{P}_{12}$ (i.e., $\hat{H}$ and $\hat{P}_{12}$ commute). Moveover, Equation 5.6.5 argues that the eigenvalues of the Exchange Operator are either +1 (bosons) or −1 (fermions).

Bosons

Wavefunctions for which $e^{i\varphi} = +1$ are defined as symmetric with respect to permutation, because the wavefunction is identical before and after a single permutation. Wavefunctions that are symmetric with respect to interchange of the particles obey the following mathematical relationship,

$$\hat{P}_{12} |\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = +|\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle$$

The behavior of some particles requires that the wavefunction be symmetric with respect to permutation. These particles are called bosons and have integer spin such as deuterium nuclei, photons, and gluons.

Fermions

The behavior of other particles requires that the wavefunction be antisymmetric with respect to permutation ($e^{i\varphi} = -1$). A wavefunction that is antisymmetric with respect to electron interchange is one whose output changes sign when the electron coordinates are interchanged, as shown below.

$$\hat{P}_{12} |\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = -|\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle$$

These particles are called fermions and have half-integer spin and include electrons, protons, and neutrinos. Since electrons are fermion, any wavefunction used to describe multiple electrons **must** be antisymmetric with respect to permutation of the electrons. The requirement that the wavefunction be antisymmetric applies to all multi-electron functions $\psi(\mathbf{r}_1, \mathbf{r}_2, \cdots r_i)$, including those approximated as products of single electron functions

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \cdots r_i)\rangle \approx \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\cdots\varphi_i(r_i) \tag{5.6.6}$$

? Exercise 8.5.4

What is meant by the term permutation symmetry?

? Exercise 8.5.5

Explain why the product function $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ could describe two bosons (deuterium nuclei), but can not describe two fermions (e.g. electrons).

Answer

Because if we switch $\mathbf{r}_1$ and $\mathbf{r}_2$, the product function becomes $\varphi(r_2)\varphi(r_1)$, which is equal to $\varphi(r_1)\varphi(r_2)$, which is consistent with the wavefunctions of bosons, because boson wavefunctions are symmetric. However, fermion wavefunctions are antisymmetric, which means that if switch r_1 and r_2, the result should be -1×the original wavefunction. Therefore, the product function $\varphi(r_1)\varphi(r_2)$ **cannot** describe fermions.

5.6.2: 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 5.6.6 does **not** satisfy this (unless $\varphi_a = \varphi_b$). A **linear combination of all permutations** is required to satisfy indistinguishability constraints.

For a two particle system (e.g., Helium) there is the asymmetric combination

$$|\psi^-\rangle = \frac{1}{\sqrt{2}}\Big|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{5.6.7}$$

and symmetric combination

$$|\psi^+\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle + C_{aa}\,|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle + C_{bb}|\,\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{5.6.8}$$

where the C_{ab} terms are expansion and normalization parameters.

> *Note that the antisymmetric combination (Equation 5.6.7) **cannot** include terms where both particles are in the same state (spin-orbital), but there are three possibilities for the symmetric state (Equation 5.6.8).*

Although any linear combinations of C_{ab}, C_{bb}, and C_{aa} in Equation 5.6.8 is possible, there are three limiting expressions for possible symmetric combinations:

$$|\psi_1^{+i}\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{5.6.9}$$

$$|\psi_2^{+i}\rangle = C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle \tag{5.6.10}$$

$$|\psi_3^{+i}\rangle = C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{5.6.11}$$

If $\varphi_a(\mathbf{r}_1) = \varphi_a(\mathbf{r}_2)$, then $|\varphi^{-i}\rangle = 0$. Thus there is no possible antisymmetric combination involving electrons in the same state (spin-orbit). This is the **Pauli exclusion principle**.

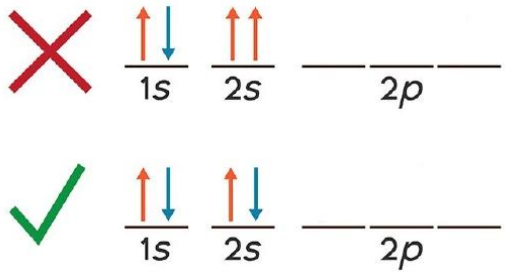


Figure 8.5.1 : The 1s and 2s subshells for beryllium atoms can hold only two electrons and when filled, since each electrons is described by a specific spin-orbital and each orbital (spatial) can hold either an α or a β electron (i.e., they must have opposite spins). Otherwise they will have the same four quantum numbers, in violation of the Pauli Exclusion Principle.

The Pauli Exclusion Principle argues that two electrons **could not** be described by the same spin-orbital. To see the relationship between this statement and the requirement that the wavefunction be antisymmetric for electrons, try to construct an anti-symmetric wavefunction for two electrons that are described by the same spin-orbital

$$|\varphi_b(\mathbf{r}_1)\rangle = \varphi_a(\mathbf{r}_2)\rangle$$

For example, if this were the case for the anti-symmetric combination for helium (Equation 5.6.7), then the wavefunction collapses to zero. We can only constructs wavefunctions that are antisymmetric with respect to permutation symmetry only if each electron is described by a different function.

> *The Pauli Exclusion Principle is simply the requirement that the wavefunction be antisymmetric for electrons, since they are fermions.*

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5.7: Antisymmetric Wavefunctions can be Represented by Slater Determinants

Learning Objectives

- Understand how the Pauli Exclusion principle affects the electronic configuration of mulit-electron atoms
- Understand how determinantal wavefunctions (Slater determinents) ensure the proper symmetry to electron permutation required by Pauli Exclusion Principle.
- Connect the electron permutation symmetry requirement to multi-electron wavefunctions to the Aufbau principle taught in general chemistry courses

Let's try to construct an antisymmetric function that describes the two electrons in the ground state of helium. Blindly following the first statement of the Pauli Exclusion Principle, then each electron in a multi-electron atom **must** be described by a different spin-orbital. For the ground-state helium atom, this gives a $1s^2 2s^0 2p^0$ configuration (Figure 8.6.1).

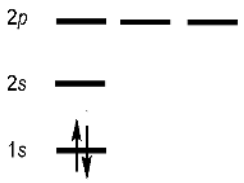


Figure 8.6.1 : Electron configuration for ground state of the helium atom.

We try constructing a simple product wavefunction for helium using two different spin-orbitals. Both have the 1s spatial component, but one has spin function α and the other has spin function β so the product wavefunction matches the form of the ground state electron configuration for He, $1s^2$.

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \varphi_{1s}\alpha(\mathbf{r}_1)\varphi_{1s}\beta(\mathbf{r}_2) \tag{5.7.1}$$

After permutation of the electrons, this becomes

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = \varphi_{1s}\alpha(\mathbf{r}_2)\varphi_{1s}\beta(\mathbf{r}_1) \tag{5.7.2}$$

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 5.7.1 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 5.7.2 from the right-hand side of Equation 5.7.1 has the desired antisymmetric behavior. The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s}\alpha(\mathbf{r}_1)\varphi_{1s}\beta(\mathbf{r}_2) - \varphi_{1s}\alpha(\mathbf{r}_2)\varphi_{1s}\beta(\mathbf{r}_1)] \tag{5.7.3}$$

In this orbital approximation, a single electron is held in a single s*pin-orbital* with an orbital component (e.g., the $1s$ orbital) determined by the n, l, m_l quantum numbers and a spin component determined by the m_s quantum number.

The wavefunction in Equation 5.7.3 can be decomposed into spatial and spin components:

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{1s}(2)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)-\alpha(2)\beta(1)]}_{\text{spin component}} \tag{5.7.4}$$

Example 8.6.1 : Symmetry to Electron Permutation

Show that the linear combination of spin-orbitals in Equation 5.7.3 is antisymmetric with respect to permutation of the two electrons.

Hint

Replace the minus sign with a plus sign (i.e. take the positive linear combination of the same two functions) and show that the resultant linear combination is symmetric.

Solution

First a reminder of permutation symmetries:

- If the wavefunction is symmetric with respect to permutation of the two electrons then

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = |\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$

- If the wavefunction is antisymmetric with respect to permutation of the two electrons then

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = -|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$

We start with the original wavefunction

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

and flip the position of electron 1 with electron 2 and vice versa

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1) - \varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)] \tag{5.7.5}$$

We then we ask if we can rearrange the left side of Equation 5.7.5 to either become $+|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ (symmetric to permutation) or $-|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ (antisymmetric to permutation).

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = \frac{1}{\sqrt{2}}[-\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) + \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

or

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = -\frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

This is just the negative of the original wavefunction, therefore

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = -|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$$

The wavefunction is antisymemtric.

Exercise 8.6.1 : Symmetry

Is this linear combination of spin-orbitals

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) + \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

symmetric or antisymmetric with respect to permutation of the two electrons?

Answer

Symmetric

The electronic configuration of the first excited state of He is $1s^1 2s^1 2p^0$ and we can envision four microstates for this configuration (Figure 8.6.2). As spected, the wavefunctions associated for of these microstate must satisfy indistinguishability requirement just like the ground state.

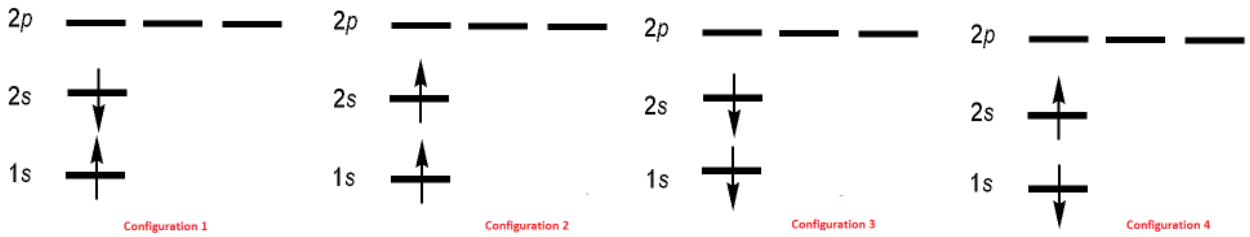


Figure 8.6.2 : Electron configurations for first-excited state of the helium atom.

These electron configurations are used to construct four possible excited-state two-electron wavefunctions (but not necessarily in a one-to-one correspondence):

$$|\psi_1(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)+\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)-\alpha(2)\beta(1)]}_{\text{spin component}} \tag{5.7.6}$$

$$|\psi_2(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\alpha(2)]}_{\text{spin component}} \tag{5.7.7}$$

$$|\psi_3(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)+\alpha(2)\beta(1)]}_{\text{spin component}} \tag{5.7.8}$$

$$|\psi_4(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\beta(1)\beta(2)]}_{\text{spin component}} \tag{5.7.9}$$

All four wavefunctions are antisymmetric as required for fermionic wavefunctions (which is left to an exercise). Wavefunctions $|\psi_2\rangle$ and $|\psi_4\rangle$ correspond to the two electrons both having spin up or both having spin down (Configurations 2 and 3 in Figure 8.6.2 , respectively). Wavefunctions $|\psi_1\rangle$ and $|\psi_3\rangle$ are more complicated and are antisymmetric (Configuration 1 - Configuration 4) and symmetric combinations (Configuration 1 + 4). That is, a single electron configuration does not describe the wavefunction. For many electrons, this ad hoc construction procedure would obviously become unwieldy. However, there is an elegant way to construct an antisymmetric wavefunction for a system of N identical particles.

5.7.1: 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

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2)\end{vmatrix} \tag{5.7.10}$$

A shorthand notation for the determinant in Equation 5.7.10 is then

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = 2^{-\frac{1}{2}}Det\left|\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)\right| \tag{5.7.11}$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is $(N!)^{-\frac{1}{2}}$ for N electrons.

The generalized Slater determinant for a multi-electrom atom with N electrons is then

$$\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\varphi_1(\mathbf{r}_1) & \varphi_2(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_1)\\ \varphi_1(\mathbf{r}_2) & \varphi_2(\mathbf{r}_2) & \cdots & \varphi_N(\mathbf{r}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \varphi_1(\mathbf{r}_N) & \varphi_2(\mathbf{r}_N) & \cdots & \varphi_N(\mathbf{r}_N)\end{vmatrix} \tag{5.7.12}$$

✔ Example 8.6.2 : Helium Atom

Expand the Slater determinant in Equation 5.7.10 for the **He** atom.

Solution

To expand the Slater determinant of the Helium atom, the wavefunction in the form of a two-electron system:

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2)\end{vmatrix}$$

This is a simple expansion exercise of a $\mathbf{2\times 2}$ determinant

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\left[\varphi_{1s}(1)\alpha(1)\varphi_{1s}(2)\beta(2)-\varphi_{1s}(2)\alpha(2)\varphi_{1s}(1)\beta(1)\right]$$

It is not unexpected that the determinant wavefunction in Equation 5.7.10 is the same as the form for the helium wavefunction that is given in Equation 5.7.3.

Exercise 8.6.2 : Lithium Atom

Write and expand the Slater determinant for the ground-state **Li** atom.

Answer

Slater determinant for **Li** atom:

$$\psi(1,2,3) = \frac{1}{\sqrt{6}}\det\begin{pmatrix} \varphi_{1s}\alpha(1) & \varphi_{1s}\beta(1) & \varphi_{2s}\alpha(1) \\ \varphi_{1s}\alpha(2) & \varphi_{1s}\beta(2) & \varphi_{2s}\alpha(2) \\ \varphi_{1s}\alpha(3) & \varphi_{1s}\beta(3) & \varphi_{2s}\alpha(3) \end{pmatrix}$$

Expansion of Slater determinant:

$$\psi(1,2,3) = \frac{1}{\sqrt{6}}[\varphi_{1s}\alpha(1)\varphi_{1s}\beta(2)\varphi_{2s}\alpha(3) - \varphi_{1s}\alpha(1)\varphi_{1s}\beta(3)\varphi_{2s}\alpha(2) + \varphi_{1s}\alpha(3)\varphi_{1s}\beta(1)\varphi_{2s}\alpha(2) - \varphi_{1s}\alpha(3)\varphi_{1s}\beta(2)\varphi_{1s}\alpha(1) + \varphi_{1s}\alpha(2)\varphi_{1s}\beta(3)\varphi_{2s}\alpha(3)]$$

Note that this is also a valid ground state wavefunction

$$\psi(1,2,3) = \frac{1}{\sqrt{6}}\det\begin{pmatrix} \varphi_{1s}\alpha(1) & \varphi_{1s}\beta(1) & \varphi_{2s}\beta(1) \\ \varphi_{1s}\alpha(2) & \varphi_{1s}\beta(2) & \varphi_{2s}\beta(2) \\ \varphi_{1s}\alpha(3) & \varphi_{1s}\beta(3) & \varphi_{2s}\beta(3) \end{pmatrix}$$

What is the difference between these two wavefunctions?

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

$$|\phi_a(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} \tag{5.7.13}$$

$$|\phi_b(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \tag{5.7.14}$$

$$|\phi_c(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \tag{5.7.15}$$

$$|\phi_d(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} \tag{5.7.16}$$

Slater determinants are constructed by arranging spinorbitals in columns and electron labels in rows and are normalized by dividing by $\sqrt{N!}$, where N is the number of occupied spinorbitals. As you can imagine, the algebra required to compute integrals involving Slater determinants is extremely difficult. It is therefore most important that you realize several things about these states so that you can avoid unnecessary algebra:

- A Slater determinant corresponds to a single electron configuration diagram (Figure 8.6.2). Furthermore, recall that for the excited states of helium we had a problem writing certain stick diagrams as a (space)x(spin) product and had to make linear combinations of certain states to force things to separate (Equation 5.7.7 and 5.7.9). Because of the direct correspondence of configuration diagrams and Slater determinants, the same pitfall arises here: Slater determinants sometimes may not be representable as a (space)x(spin) product, in which case a linear combination of Slater determinants must be used instead. This generally only happens for systems with unpaired electrons (like several of the Helium excited-states).
- A Slater determinant is anti-symmetric upon exchange of any two electrons. We recall that if we take a matrix and interchange two its rows, the determinant changes sign.

The wavefunctions in 5.7.6-5.7.9 can be expressed in term of the four determinants in Equations 5.7.13-5.7.16.

$$|\psi_2\rangle = |\phi_b\rangle$$
$$= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix}$$

$$|\psi_4\rangle = |\phi_d\rangle$$
$$= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix}$$

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 5.7.13-5.7.15)

$$|\psi_1\rangle = |\phi_a\rangle - |\phi_c\rangle$$
$$= \frac{1}{2}\left(\begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} - \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \right)$$

$$|\psi_3\rangle = |\phi_a\rangle + |\phi_c\rangle$$
$$= \frac{1}{2}\left(\begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} + \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \right)$$

Note the expected change in the normalization constants.

✔ Example 8.6.3 : Carbon Atom

Write the Slater determinant for the ground-state carbon atom. If you expanded this determinant, how many terms would be in the linear combination of functions?

Solution

Carbon has 6 electrons which occupy the 1s 2s and 2p orbitals. Each row in the determinant represents a different electron and each column a unique spin-obital where the electron could be found. There are 6 rows, 1 for each electron, and 6 columns, with the two possible p orbitals both alpha (spin up), in the determinate. There are two columns for each s orbital to account for the alpha and beta spin possibilities. There are two different p orbitals because the electrons in their ground state will be in the different p orbitals and both spin up. N=6 so the normalization constant out front is 1 divided by the square-root of 6!

$$\psi(1,2,3,4,5,6)$$
$$= \frac{1}{6!^{1/2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) & \varphi_{2px}(1)\alpha(1) & \varphi_{2py}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) & \varphi_{2px}(2)\alpha(2) & \varphi_{2py}(2)\alpha(2) \\ \varphi_{1s}(3)\alpha(3) & \varphi_{1s}(3)\beta(3) & \varphi_{2s}(3)\alpha(3) & \varphi_{2s}(3)\beta(3) & \varphi_{2px}(3)\alpha(3) & \varphi_{2py}(3)\alpha(3) \\ \varphi_{1s}(4)\alpha(4) & \varphi_{1s}(4)\beta(4) & \varphi_{2s}(4)\alpha(4) & \varphi_{2s}(4)\beta(4) & \varphi_{2px}(4)\alpha(4) & \varphi_{2py}(4)\alpha(4) \\ \varphi_{1s}(5)\alpha(5) & \varphi_{1s}(5)\beta(5) & \varphi_{2s}(5)\alpha(5) & \varphi_{2s}(5)\beta(5) & \varphi_{2px}(5)\alpha(5) & \varphi_{2py}(5)\alpha(5) \\ \varphi_{1s}(6)\alpha(6) & \varphi_{1s}(6)\beta(6) & \varphi_{2s}(6)\alpha(6) & \varphi_{2s}(6)\beta(6) & \varphi_{2px}(6)\alpha(6) & \varphi_{2py}(6)\alpha(6) \end{vmatrix}$$

Expanding this determinant would result in a linear combination of functions containing 720 terms. An expanded determinant will contain N! factorial terms, where N is the dimension of the matrix.

5.7.3A? Exercise : Excited-State of Helium Atom

Write the Slater determinant for the $1s^1 2s^1$ excited state orbital configuration of the helium atom.

Answer

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

$$\frac{1}{\sqrt{2}} \begin{bmatrix} \varphi 1_s(1)\alpha(1) & \varphi 2_s(1)\beta(1) \\ \varphi 1_s(2)\alpha(2) & \varphi 2_s(2)\beta(2) \end{bmatrix}$$

5.7.3B? Exercise

> 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!)

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5.8: Electron Configurations, The Pauli Exclusion Principle, The Aufbau Principle, and Slater Determinants

To discuss the electronic states of atoms we need a system of notation for multi-electron wavefunctions. As we saw in Chapter 8, the assignment of electrons to orbitals is called the electron configuration of the atom. One creates an electronic configuration representing the electronic structure of a multi-electron atom or ion in its ground or lowest-energy state as follows. First, obey the Pauli Exclusion Principle, which requires that each electron in an atom or molecule must be described by a different spin-orbital. Second, assign the electrons to the lowest energy spin-orbitals, then to those at higher energy. This procedure is called the Aufbau Principle (which translates from German as build-up principle). The mathematical analog of this process is the construction of the approximate multi-electron wavefunction as a product of the single-electron atomic orbitals.

For example, the configuration of the boron atom, shown schematically in the energy level diagram in Figure **5.8.1**, is written in shorthand form as $1s^2 2s^2 2p^1$. As we saw in previously, the degeneracy of the 2s and 2p orbitals is broken by the electron-electron interactions in multi-electron systems.

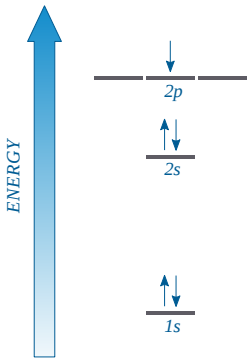


Figure **5.8.1**: Orbital energy level diagram that represents the electron configuration of the boron atom. Orbital energy differences are approximately to scale. (CC BY-SA; Ümit Kaya)

Rather than showing the individual spin-orbitals in the diagram or in the shorthand notation, we commonly say that up to two electrons can be described by each spatial orbital, one with spin function α (electron denoted by an arrow pointing up) and the other with spin function β (arrow pointing down). This restriction is a manifestation of the Pauli Exclusion Principle mentioned above. An equivalent statement of the Pauli Exclusion Principle is that each electron in an atom has a unique set of quantum numbers (n, l, m_l, m_s). Since the two spin functions are degenerate in the absence of a magnetic field, the energy of the two electrons with different spin functions in a given spatial orbital is the same, and they are shown on the same line in the energy diagram.

Exercise 5.8.1

Write the electronic configuration of the carbon atom and draw the corresponding energy level diagram.

Exercise 5.8.2

Write the values for the quantum numbers (n, l, m_l, m_s) for each of the six electrons in carbon.

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.

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 $\psi(r_1, r_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 (r_l) for the coordinates of particle 2 (r_2) and vice versa, to get the new wavefunction $\psi(r_1, r_2)$. This new wavefunction must have the property that

$$|\psi(r_1, r_2)|^2 = \psi(r_2, r_1)^*\psi(r_2, r_1) = \psi(r_1, r_2)^*\psi(r_1, r_2) \tag{5.8.1}$$

since the probability density of the electrons in the atom does not change upon permutation of the electrons.

Exercise 5.8.3

Permute the electrons in Equation ??? (the product function for He wavefunction.)

Equation 5.8.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(r_1, r_2) = e^{i\varphi}\psi(r_1, r_2) \tag{5.8.2}$$

so that

$$\left(e^{-i\varphi}\psi(r_1, r_2)^*\right)\left(e^{i\varphi}\psi(r_1, r_2)^*\right) = \psi(r_1, r_2)^*\psi(r_1, r_2) \tag{5.8.3}$$

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.,

$$e^{i\varphi}e^{i\varphi} = e^{i2\varphi} = 1 \tag{5.8.4}$$

which is true only if $\varphi = 0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature.

Exercise 5.8.4

Use Euler's Equality to show that $e^{12\varphi} = 1$ when $\varphi = 0$ or $n\pi$ and consequently $e^{i\varphi} = \pm 1$.

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:

$$e^{i\varphi}e^{i\varphi} = e^{i2\varphi} = 1 \tag{5.8.5}$$

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.

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:

$$\psi(r_2, r_1) = e^{i\varphi}\psi(r_1, r_2) = -\psi(r_1, r_2) \tag{5.8.6}$$

These particles, called fermions, have half-integer spin and include electrons, protons, and neutrinos.

Exercise 5.8.5

Explain without any equations why there are only two kinds of particles in the world: bosons and fermions.

In fact, an elegant statement of the Pauli Exclusion Principle is simply "electrons are fermions." This statement means that any wavefunction used to describe multiple electrons must be antisymmetric with respect to permutation of the electrons, providing yet another statement of the Pauli Exclusion Principle. The requirement that the wavefunction be antisymmetric applies to all multi-electron functions $\psi(r_1, r_2, \cdots r_i)$, including those written as products of single electron functions $\varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_i(r_i)$.

> *Another way to simply restate the Pauli Exclusion Principle is that "electrons are fermions."*

The first statement of the Pauli Exclusion Principle was 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 **antisymmetric wavefunction** for two electrons that are described by the same spin-orbital. We can try to do so for helium. Write the He approximate two-electron wavefunction as a product of identical 1s spin-orbitals for each electron,$\varphi_{1s_\alpha}(r_1)$ and $\varphi_{1s_\alpha}(r_2)$:

$$\psi(r_1, r_2) = \varphi_{1s\alpha}(r_1)\varphi_{1s\alpha}(r_2) \tag{5.8.7}$$

To permute the electrons in this two-electron wavefunction, we simply substitute the coordinates of electron 1 (r_l) for the coordinates of electron 2 (r_2) and vice versa, to get

$$\psi(r_2, r_1) = \varphi_{1s\alpha}(r_2)\varphi_{1s\alpha}(r_1) \tag{5.8.8}$$

This is identical to the original function (Equatin 5.8.7) since the two single-electron component functions **commute**. The two-electron function has not changed sign, as it must for fermions. We can construct a wavefunction that is antisymmetric with respect to permutation symmetry only if each electron is described by a different function.

Exercise 5.8.6

What is meant by the term permutation symmetry?

Exercise 5.8.7

Explain why the product function $\varphi(r_1)\varphi(r_2)$ could describe two bosons (deuterium nuclei) but can not describe two fermions (e.g. electrons).

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, 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, $1s^2$.

$$\psi(r_1, r_2) = \varphi_{1s\alpha}(r_1)\varphi_{1s\beta}(r_2) \tag{5.8.9}$$

After permutation of the electrons, this becomes

$$\psi(r_2, r_1) = \varphi_{1s\alpha}(r_2)\varphi_{1s\beta}(r_1) \tag{5.8.10}$$

which is different from the starting function (Equation 5.8.9) since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are **different** 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 5.8.10 from the right-hand side of Equation 5.8.9 has the desired antisymmetric behavior.

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(r_1)\varphi_{1s\beta}(r_2) - \varphi_{1s\alpha}(r_2)\varphi_{1s\beta}(r_1)] \tag{5.8.11}$$

The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

Exercise 5.8.8

Show that the linear combination in Equation 5.8.11 is antisymmetric with respect to permutation of the two electrons. 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.

Exercise 5.8.9

Write a similar linear combination to describe the $1s^1 2s^1$ excited configuration of helium.

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 of helium is

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) \end{vmatrix} \tag{5.8.12}$$

and a shorthand notation for this determinant is

$$\psi(r_1, r_2) = 2^{-\frac{1}{2}} Det|\varphi_{1s}(r_1)\varphi_{1s}(r_2)| \tag{5.8.13}$$

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.

Exercise 5.8.10

Show that the determinant form is the same as the form for the helium wavefunction that is given in Equation 5.8.11.

Exercise 5.8.11

Expand the Slater determinant in Equation 5.8.12 for the He atom.

Exercise 5.8.12

Write and expand the Slater determinant for the electronic wavefunction of the Li atom.

Exercise 5.8.13

Write the Slater determinant for the carbon atom. If you expanded this determinant, how many terms would be in the linear combination of functions?

Exercise 5.8.14

Write the Slater determinant for the $1s^1 2s^1$ excited state orbital configuration of the helium atom.

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 can't 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.

Exercise 5.8.13

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!)

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5.9: The Self-Consistent Field Approximation (Hartree-Fock Method)

In this section we consider a method for finding the best possible one-electron wavefunctions that was published by Hartree in 1948 and improved two years later by Fock. For the Schrödinger equation to be solvable, the variables must be separable. The variables are the coordinates of the electrons. In order to separate the variables in a way that retains information about electron-electron interactions, the Coulomb repulsion term, e.g. $\frac{e^2}{4\pi\epsilon_0 r_{12}}$ for helium, 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 best possible one-electron wavefunctions, by definition, will give the lowest possible total energy for a multi-electron system when combined into a Slater determinant and 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. Application of the variational method to the problem of minimizing the total energy leads to the following set of Schrödinger-like equations called Hartree-Fock equations,

$$\hat{F}\varphi_i = \epsilon_i \varphi_i \tag{5.9.1}$$

where $\hat{F}$ is called the Fock operator. 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 5.9.1. Since the spatial portion of an orbital can be used to describe two electrons, each of the energies and wavefunctions found by solving 5.9.1 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 atomic and molecular orbitals. The full antisymmetrized wavefunction written as a Slater determinant of spin-orbitals is necessary to derive the form of the Fock operator, which is

$$\hat{F} = \hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) \tag{5.9.2}$$

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. For electron 1 in helium, for example,

$$\hat{H}^0(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} \tag{5.9.3}$$

The second term in Equation 5.9.2, $\sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j)$, accounts for the potential energy of one electron in an average field created by all the other electrons in the system. The Fock operator is couched in terms of the coordinates of the one electron whose perspective we are taking (which we'll call electron 1 throughout the following discussion), and the average field created by all the other electrons in the system is built in terms of the coordinates of a generic "other electron" (which we'll call electron 2) that is considered to occupy each orbital in turn during the summation over the N spatial orbitals.

The operators $\hat{j}$ and $\hat{K}$ 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, $\frac{e^2}{4\pi\epsilon_0 r_{12}}$, which in atomic units simplifies to 1/r12. Atomic units are used in the rest of this discussion to simplify the notation by removing fundamental constants.

The operators $\hat{J}$ and $\hat{K}$ are most conveniently defined by examining how they operate on a wavefunction, φ_i, which describes electron 1.

$$\hat{J}_j(1)\varphi_i(1) = \left[\int \varphi_i^*(2)\frac{1}{r_{12}}\varphi_i(2)d\tau_2\right]\varphi_i(1) \tag{5.9.4}$$

$$\hat{K}_j(1)\varphi_i(1) = \left[\int \varphi_j^*(2)\frac{1}{r_{12}}\varphi_i(2)d\tau_2\right]\varphi_j(1) \tag{5.9.5}$$

$\hat{J}$ is called a Coulomb operator. As mentioned above, the specific coordinates 1 and 2 are used here to underline the fact that $\hat{J}$ operates on a function of one electron in an orbital (here, electron 1 in φ_i using the results of an expectation value integral over the coordinates of a different electron (electron 2 in φ_j. The second electron can be described by the same spatial orbital (if i = j) or by a different spatial orbital (if i ≠ j). $\hat{J}$ takes the complex conjugate of an orbital describing electron 2, $\varphi_j^*(2)\varphi_j(2)$, multiplies by 1/r12, and integrates over the coordinates of electron 2. The quantity $d\tau_2\varphi_j^*(2)\varphi_j(2)$ represents the charge distribution in space due to electron 2 in orbital j. The quantity $d\tau_2\varphi_j^*(2)\varphi_j(2)\frac{1}{r_{12}}$ thus represents the potential energy at r_1 due to the charge density at r_2 where r_{12} is the distance between r_1 and r_2. Evaluation of the integral gives the total potential energy at r1 due to the overall, or average, charge density produced by electron 2 in orbital j. Since the part of the Fock operator containing $\hat{J}$ involves a sum over all the orbitals, and a multiplicative factor of 2 to account for the presence of two electrons in each orbital, solution of the Hartree-Fock equation produces a spatial orbital φ_i that is determined by the average potential energy or Coulomb field of all the other electrons.

The other operator under the summation in the Fock operator is $\hat{K}$, the exchange operator. Equation 5.9.5 reveals that this operator involves a change in the labels on the orbitals. In analogy with the Coulomb operator, $d\tau_2\varphi_j^*(2)\varphi_i(2)\frac{1}{r_{12}}$ represents the potential energy at r_1 due to the overlap charge distribution at r_2 associated with orbitals i and j. The integral is the potential energy due to the total overlap charge density associated with electron 2. The term exchange operator is used because the electron is exchanged between the two orbitals i and j. This overlap contribution to the charge density and potential energy is a quantum mechanical effect. It is a consequence of the wave-like properties of electrons. Wave-like properties means the electrons are described by wavefunctions. While difficult to understand in a concrete physical way, the effects of the exchange operator are important contributors to the total energy of the orbitals and the system as a whole. There is no classical analog to this interaction energy, and a classical theory is unable to calculate correctly the energies of multi-electron systems.

For the ground state of helium, electrons 1 and 2 are both described by spatial orbital φ_i, so N = 1 and the sum in Equation 5.9.2 includes only j = 1. Furthermore, since i = j = 1, the exchange and Coulomb integrals are identical in this case. As a result, the summation in the Fock operator takes a very simple form and the complete Fock operator for electron 1 in helium is given by

$$\hat{F}(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} + \hat{U}(1) \tag{5.9.6}$$

where $\hat{U}(1)$ is given by the summation in the Fock operator.

$$\hat{U}(1) = \sum_{j=1}^{1}(2\hat{j}_j - \hat{K}_j) = \int \varphi_1(2)\frac{1}{r_{12}}\varphi_1(2)d\tau_2 \tag{5.9.7}$$

Exercise 5.9.30

Show that $\sum_{j=1}^{1}(2\hat{j}_j - \hat{K}_j) = \int \varphi_1(2)\frac{1}{r_{12}}\varphi_1(2)d\tau_2$ by substituting the definitions of $\hat{J}(1)$ and $\hat{K}(1)$ for helium into the summation and evaluating the summation over the only occupied spatial orbital.

The interaction of electron 1 with electron 2 is averaged over all positions of electron 2 to produce $\hat{U}(1)$. By integrating over the coordinates of electron 2, the explicit dependence of the potential energy on the coordinates of electron 2 is removed. This approach makes it possible to account for the electron-electron repulsion in terms of the spatial distribution of the two electrons using only single-electron terms in the Fock operator and one-electron wavefunctions.

Since both electrons in helium are described by the same spatial wavefunction, the Fock equation given by 5.9.8 and 5.9.6 describes either electron equally well. Solving the Fock equation therefore will give us the spatial wavefunction and the one-electron energy associated with either of the electrons.

The energy of an electron in the spatial orbital φ_1 can be calculated either by solving the Fock equation

$$\hat{F}(1)\varphi_1(1) = \epsilon_1(1)\varphi_1(1) \tag{5.9.8}$$

or by using an expectation value expression.

$$\epsilon_1(1) = \int \varphi_1^*(r_1)\hat{F}(r_1)\varphi_1(r_1)d\tau \tag{5.9.9}$$

In order to solve either of these equations for the energy ϵ_1, we need to evaluate the potential energy function $\hat{U}(1)$ that is part of the Fock operator $\hat{F}(1)$. In order to evaluate $\hat{U}(1)$, the forms of all of the occupied spatial orbitals, $\varphi_i(2)$ must be known. For the simple case of helium, only the $\varphi_1(2)$ function is required, but for larger multi-electron systems, the forms of occupied orbitals ϵ_1, ϵ_2 etc. will be needed to specify $\hat{U}(1)$. For helium, we know that $\varphi_1(2)$ will have the same form as $\varphi_1(1)$, and the φ_1 functions can be obtained by solving the Fock equation (9-58). However, we are now caught in a circle because the Fock operator depends upon the φ_1 function.

The problem with solving Equation 5.9.8 to obtain the Fock orbitals is that the Fock operator, as we have seen, depends on the Fock orbitals. In other words, we need to know the solution to this equation in order to solve the equation. We appear to be between a rock and a hard place. A procedure has been invented to wiggle out of this situation. One makes a guess at the orbitals, e.g. one inserts some adjustable parameters into hydrogenic wavefunctions, for example. These orbitals are used to construct the Fock operator that is used to solve for new orbitals. The new orbitals then are used to construct a new Fock operator, and the process is repeated until no significant change in the orbital energies or functions occurs. At this end point, the orbitals produced by the Fock operator are the same as the orbitals that are used in the Fock operator to describe the average Coulomb and overlap (or exchange) potentials due to the electron-electron interactions. The solution therefore is self-consistent, and the method therefore is called the self-consistent field (SCF) method.

The objective of the Hartree-Fock method is to produce the best possible one-electron wavefunctions for use in approximating the exact wavefunction for a multi-electron system, which can be an atom or a molecule. So what kind of guess functions should we write to get the best possible one-electron wavefunctions? Answers to this question have spawned a huge area of research in computation chemistry over the past 40 years, including a Nobel Prize in 1998. In Chapter 10 we examine in detail the various alternatives for constructing one-electron wavefunctions from basis functions.

Exercise 5.9.31

Write a paragraph without using any equations that describes the essential features of the Hartree-Fock method. Create a block diagram or flow chart that shows the steps involved in the Hartree-Fock method.

The expectation value of the Fock operator gives us the energy of an electron in a particular orbital.

$$\epsilon_i(1) = \int d\tau_1 \varphi_i^*(1)\hat{F}(1)\varphi_i(1) \tag{5.9.10}$$

Using the definition of the Fock operator and representing the integrals with bracket notation gives

$$\epsilon_i(1) = \langle H_i^0 \rangle + \sum_{j=1}^{N}(2J_{ij} - K_{ij}) \tag{5.9.11}$$

where

$$\langle H_i^0 \rangle = \left\langle \varphi_i \middle| -\frac{1}{2}\nabla_1^2 \middle| \varphi_i \right\rangle - \left\langle \varphi_i \middle| \frac{Z}{r_1} \middle| \varphi_i \right\rangle \tag{5.9.12}$$

The kinetic and potential energy terms in the operator $\hat{H}^0$, defined in Equation 5.9.3, are written here in atomic units for simplicity of notation. The sum involving the Coulomb and exchange integrals, J and K, accounts for the electron-electron interaction energy between the electron in orbital i and all the other electrons in the system. We now want to examine the meaning and the nature of the sum over all the orbitals in Equation 5.9.11.

Exercise 5.9.32

Describe the contributions to the orbital energy or single-electron energy *epsilon* in words as represented by Equation 5.9.11.

For the case j = k one has for $2J_{ik} - K_{ik}$

$$2\left\langle \varphi_i(1)\varphi_k(2)\left|\frac{1}{r_{12}}\right|\varphi_i(1)\varphi_k(2)\right\rangle - \left\langle \varphi_i(1)\varphi_k(2)\left|\frac{1}{r_{12}}\right|\varphi_k(1)\varphi_i(2)\right\rangle \tag{5.9.13}$$

The first term with the factor of 2 is the average potential energy due to the charge distribution caused by an electron in orbital i with the charge distribution caused by the two electrons in orbital k. The factor of 2 accounts for the two electrons in orbital k. The second term is the average potential energy due to the overlap charge distribution caused by electrons 1 and 2 in orbitals i and k. The second term appears only once, i.e. without a factor of 2, because only one of the electrons in orbital k has the same spin as the electron in orbital i and can exchange with it. The minus sign results from the wavefunction being antisymmetric with respect to electron exchange.

Exercise 5.9.33

Rewrite Equation 5.9.13 including the spin functions α and β explicitly for each electron. Since these two spin functions form an orthonormal set and factor out of the spatial integrals, show that that the exchange integral is zero if the two electrons have different spin.

For the case j = i one has

$$2\left\langle \varphi_i(1)\varphi_i(2)\left|\frac{1}{r_{12}}\right|\varphi_i(1)\varphi_i(2)\right\rangle - \left\langle \varphi_i(1)\varphi_i(2)\left|\frac{1}{r_{12}}\right|\varphi_i(1)\varphi_i(2)\right\rangle \tag{5.9.14}$$

revealing that $J_{ii} = K_{ii}$, and $2J_{ii} - K_{ii} = J_{ii}$, which corresponds to the *Coulomb repulsion* between the two electrons in orbital i. Because these electrons have opposite spin, there is no exchange energy. This was the case for our helium example, above.

If the single-electron orbital energies are summed to get the total electronic energy, the Coulomb and exchange energies for each pair of electrons are counted twice: once for each member of the pair. These additional $2J - K$ contributions to the single-electron energies must be subtracted from the sum of the single-electron energies to get the total electronic energy, as shown in Equation 5.9.15. The factor of 2 accounts for the fact that two electrons occupy each spatial orbital, and {\varepsilon }_{i}\, is the energy of a single electron in a spatial orbital.

$$E_{elec} = \sum_{i=1}^{N}\left[2\epsilon_i - \sum_{j=1}^{N}(2J_{ii} - K_{ij})\right] \tag{5.9.15}$$

Exercise 5.9.34

Use Equations 5.9.11 and 5.9.15 to show that the total electronic energy also can be expressed in the following

$$E_{elec} = \sum_{i=1}^{N}\left[2\left\langle H_i^0\right\rangle - \sum_{j=1}^{N}(2J_{ii} - K_{ij})\right] \tag{5.9.16}$$

$$E_{elec} = \sum_{i=1}^{N}\left(\epsilon_i + \left\langle H_i^0\right\rangle\right) \tag{5.9.17}$$

forms.

Exercise 5.9.35

Write out all the terms in Equation 5.9.15 for the case of 4 electrons in 2 orbitals with different energies.

As we increase the flexibility of wavefunctions by adding additional parameters to the guess orbitals used in Hartree-Fock calculations, we expect to get better and better energies. The variational principle says that any approximate energy calculated using the exact Hamiltonian is an upper bound to the exact energy of a system, so the lowest energy that we calculate using the Hartree-Fock method will be 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 Slater determinant wavefunction. This limit is called the Hartree-Fock limit, the energy is the Hartree-Fock energy, the orbitals producing this limit are by definition the best single-electron orbitals that can be constructed and are called Hartree-Fock orbitals, and the Slater determinant is the Hartree-Fock wavefunction.

Contributors and Attributions

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5.10: Hartree-Fock Calculations Give Good Agreement with Experimental Data

Learning Objectives

- Understand how the Hartree method is expanded to include symmetrized mulit-electron determential wavefunctions via the Hartree-Fock equations.
- Understand how to calculate the orbital energies from HF theory.
- Apply HF theory with Koopman's theory to estimate ionization energies and electron affinities.

The Hartree method discussed previously is useful as an introduction to the solution of many-particle system and to the concepts of self-consistency and of the self-consistent-field calculations, but its importance is confined to the history of physics. In fact the Hartree method is not just approximate, it is fundamentally wrong since its wavefunction is not antisymmetric to electron permutation! The Hartree-Fock approach discussed below is a better approach, which correctly takes into account the antisymmetric character of the trial wavefunctions.

Although the *Hartree equations* are numerically tractable via the self-consistent field method, it is not surprising that such a crude approximation fails to capture elements of the essential physics. The Pauli exclusion principle demands that the many-body wavefunction be antisymmetric with respect to interchange of any two electron coordinates, e.g.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) \tag{5.10.1}$$

which clearly cannot be satisfied by the multi-electron wavefunctions of the form used in the Hartree Approximation, i.e., the orbital approximation (Equation 5.10.2).

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_N(\mathbf{r}_N) \tag{5.10.2}$$

This indistinguishability condition can be satisfied by forming a Slater determinant of single-particle orbitals

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N}} |\psi(\mathbf{r}_1)\psi(\mathbf{r}_2)\dots\psi(\mathbf{r}_N)| \tag{5.10.3}$$

This decouples the electrons resulting in N single-particle **Hartree-Fock** equations:

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r})}_{\text{kinetic energy}} + \underbrace{V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{electron-nucleus potential}} + \underbrace{V_{electron}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{Hartree Term}} - \sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = \epsilon_i\psi_i(\mathbf{r}). \tag{5.10.4}$$

As with the *Hartree equations*, the first term is the kinetic energy of the i^{th} electron

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r})$$

and the second term is the electron-nucleus potential between the i^{th} electron and nucleus

$$V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r})$$

The third term (sometimes called the “Hartree” term) is the electrostatic potential between the i^{th} electron and the **average** charge distribution of the other $N-1$ electrons.

$$V_{electron}(\mathbf{r})\psi_i(\mathbf{r}) = J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr' \tag{5.10.5}$$

These three terms are identical to Hartree Equations with the product wavefunction ansatz (i.e., orbital approximation). The fourth term of Equation 5.10.4 is not in the Hartree Equations:

$$\sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

and is the *exchange* term. This term resembles the direct Coulomb term, but for the exchanged indices. It is a manifestation of the Pauli exclusion principle, and acts so as to separate electrons of the same spin. This "exchange" term acts only on electrons with the same spin and comes from the Slater determinant form of the wavefunction (Equation 5.10.3). Physically, the effect of exchange is for like-spin electrons to avoid each other. The exchange term adds considerably to the complexity of these equations.

The Hartree-Fock Equations in Equation 5.10.4 can be recast as series of Schrödinger-like equations:

$$\hat{F}\left|\varphi_i\right\rangle = \epsilon_i\left|\varphi_i\right\rangle \tag{5.10.6}$$

where $\hat{F}$ is called the **Fock operator** and $\{|\varphi_i\rangle\}$ are the Hatree-Fock orbitals with corresponding energies ϵ_i.

The Fock operator is a one-electron operator and solving a Hartree-Fock equation gives the energy and Hartree-Fock orbital for one electron. For a system with 2N electrons, the variable i will range from 1 to N; i.e there will be one equation for each orbital. The reason for this is that only the spatial wavefunctions are used in Equation 5.10.6. Since the spatial portion of an orbital can be used to describe two electrons, each of the energies and wavefunctions found by solving Equation 5.10.6 will be used to describe two electrons.

The nature of the Fock operator reveals how the Hartree-Fock (HF) or Self-Consistent Field (SCF) Method accounts for the electron-electron interaction in atoms and molecules while preserving the idea of **independent atomic orbitals**. The wavefunction written as a Slater determinant of spin-orbitals is necessary to derive the form of the Fock operator, which is

$$\begin{aligned}\hat{F} &= \hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) \\ &= -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j)\end{aligned} \tag{5.10.7}$$

As shown by the expanded version on the far right, the first term in this equation, $\hat{H}^0$, is the familiar hydrogen-like operator that accounts for the kinetic energy of an electron and the potential energy of this electron interacting with the nucleus. The next term accounts for the potential energy of one electron in an average field created by all the other electrons in the system. The $\hat{J}$ and $\hat{K}$ operators result from the electron-electron repulsion terms in the full Hamiltonian for a multi-electron system. These operators involve the one-electron orbitals as well as the electron-electron interaction energy.

The Fock operator (Equation 5.10.7) depends on **all occupied** orbitals (because of the exchange and Coulomb operators). Therefore, a specific orbital can only be determined if all the others are known. One must use iterative methods to solve the HF equations like the Self-consistent field method discussed previously for the Hartree Approximation.

Exchange Energy

The exchange interaction is a quantum mechanical effect that only occurs between identical particles. Despite sometimes being called an exchange force in analogy to classical force, **it is not a true force**, as it lacks a force carrier. The effect is due to the wavefunction of indistinguishable particles being subject to exchange symmetry, that is, either remaining unchanged (symmetric) or changing its sign (antisymmetric) when two particles are exchanged. Both bosons and fermions can experience the exchange interaction. For fermions, it is sometimes called Pauli repulsion and related to the Pauli exclusion principle. For bosons, the exchange interaction takes the form of an effective attraction that causes identical particles to be found closer together, as in Bose–Einstein condensation.

Example 8.7.1 : Hartree-Fock Energy of Helium

For example, the electron 1 in helium (with $Z = 2$), then

$$\hat{H}^0(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}$$

The Fock operator is couched in terms of the coordinates of the one electron whose perspective we are taking (which we will call electron 1 throughout the following discussion), and the **average field created by all the other electrons** in the system is built in

terms of the coordinates of a generic “other electron” (which we’ll call electron 2) that is considered to occupy each orbital in turn during the summation over the N spatial orbitals. The best possible one-electron wavefunctions, by definition, will give the **lowest possible total energy** for a multi-electron system used with the complete multielectron Hamiltonian to calculate the expectation value for the total energy of the system. These wavefunctions are called the **Hartree-Fock wavefunctions** and the calculated total energy is the Hartree-Fock energy of the system.

As with the Hartree Equations, solving the Hartree-Fock Equations is mathematically equivalent to assuming each electron interacts only with the average charge cloud of the other electrons. This is how the electron-electron repulsion is handled. This also why this approach is also called the **Self-Consistant Field (SCF)** approach.

5.10.1: 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:

Multiple \label

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

5.10.2: 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)

$$E_{N-1} - E_N = -\epsilon_k \tag{5.10.8}$$

- and for electron attachment (electron affinities)

$$E_N - E_{N+1} = -\epsilon_k. \tag{5.10.9}$$

The Hartree-Fock equations deal with exchange exactly; however, the equations neglect more detailed correlations due to many-body interactions. The effects of electronic correlations are not negligible; indeed the failure of Hartree-Fock theory to successfully incorporate correlation leads to one of its most celebrated failures.

Example 8.7.2 : Electron Affinity

Let's derive this result for the case in which an electron is added to the $N+1^{st}$ spin-orbital. The energy of the N-electron determinant with spin-orbitals ϕ_1 through f_N occupied is

$$E_N = \sum_{i=1}^{N} \langle \phi_i | T + V | \phi_i \rangle + \sum_{i=1}^{N} [J_{i,j} - K_{i,j}]$$

which can also be written as

$$E_N = \sum_{i=1}^{N} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N} [J_{i,j} - K_{i,j}].$$

Likewise, the energy of the $N+1$-electron determinant wavefunction is

$$E_{N+1} = \sum_{i=1}^{N+1} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N+1} [J_{i,j} - K_{i,j}].$$

The difference between these two energies is given by

$$\begin{aligned} E_N - E_{N+1} = & - \langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \frac{1}{2} \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ & - \frac{1}{2} \sum_{j=1}^{N+1} [J_{N+1,j} - K_{N+1,j}] \\ & = - \langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ & = -\epsilon_{N+1}. \end{aligned}$$

That is, the energy difference is equal to minus the expression for the energy of the $N+1^{st}$ spin-orbital, which was given earlier.

Advanced: Electron Correlation and the "Exchange Hole"

In the Copenhagen Interpretation, the squared modulus of the wavefunction gives the probability of finding a particle in a given place. The many-body wavefunction gives the N-particle distribution function, i.e. $|\Phi(r_1, ..., r_N)|^2$ is the probability density that particle 1 is at r_1, ..., and particle N is at r_N. However, when trying to work out the interaction between electrons, what we want to know is the probability of finding an electron at r, given the positions of all the other electrons $\{r_i\}$. This implies that the electron behaves quantum mechanically when we evaluate its wavefunction, but as a classical point particle when it contributes to the potential seen by the other electrons.

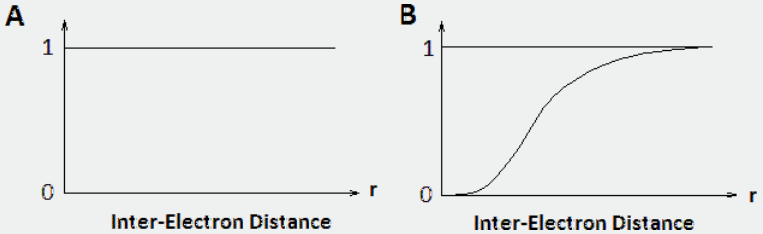


Figure 8.7.2 : Normalized Conditional Probability for from electron-electron interactions (excluding coulomb effects) in (A) the Hartree approximation and (B) the Hartree-Fock approximation.

The contributions of electron-electron interactions in N-electron systems within the Hartree and Hartree-Fock methods are shown in Figure 8.7.2 . The conditional electron probability distributions $n(r)$ of $N-1$ electrons around an electron with given spin situated at $r=0$. Within the Hartree approximation, all electrons are treated as independent, therefore $n(r)$ is structureless. However, within the Hartree-Fock approximation, the N-electron wavefunction reflects the Pauli exclusion principle and near the electron at $r=0$ the exchange hole can be seen where the the density of spins equal to that of the central electron is reduced. Electrons with opposite spins are **unaffected** (not shown).

5.10.3: 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 5.10.8) and Electron Affinities (Equation 5.10.9) and often yields results that are qualitatively correct (i.e., ± 0.5 eV). In general Hartree-Fock theory gives a great first order solution (99%) to describing multi-electron systems, but that last 1% is still too great for quantitatively describing many aspects of chemistry and more sophisticated approaches are necessary. These are discussed elsewhere.

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5.11: Term Symbols Gives a Detailed Description of an Electron Configuration

Learning Objectives

- Understand how electron configurations results in different manifestations of angular momenta (both oribital and spin)
- Describe the manifestations in atoms via atomic term symbols

Atoms have quantum numbers that are directly analogous to the electronic quantum numbers.

5.11.1: The Total Orbital Angular Momentum Quantum Number: L

One might naively think that you could get the total angular momentum of an atom (L) by simply adding up the l values of the individual electrons. The problem with this idea is that the angular momenta of the various electrons are not necessarily pointing in the same direction. Let's consider the case of adding two 2p-orbitals together (i.e., with $l = 1$ quantum numbers).

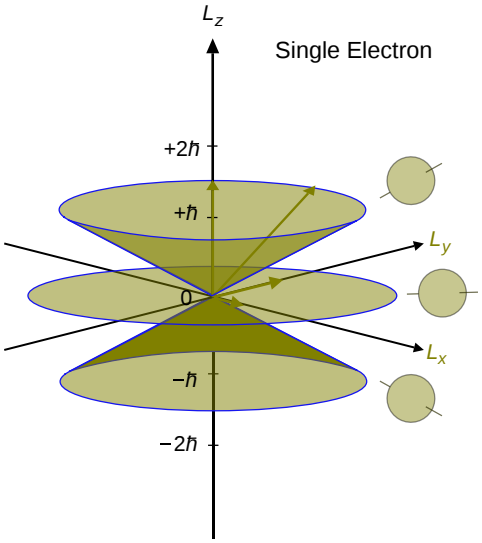


Figure 8.8.1 : The three possible angular momenta vectors for a p-orbital.

As discussed in Section 6.3, each of these electrons has $\sqrt{2}\hbar$ of angular momentum, but oriented in three different directions given by three different m_l values of 1, 0, and -1 (Figure 8.8.1).

$$L = \sum_{i}^{n} l_i \tag{5.11.1}$$

However, we must recognize that while the magnitude of angular momentum is a scalar (represented by l), angular momenta are really vector quantities and to add them together will require vector addition (vs. scalar addition) to do properly and must address all possible orientations of l for each electron.

For example, if two electrons are revolving in the same direction as each other (i.e., same m_l values), one would add just their l values together

$$L(\text{same direction}) = \sqrt{2}\hbar + \sqrt{2}\hbar = 2\hbar$$

If the two elections were revolving in opposites direction (e.., opposite m_l values, you subtract their values.

$$L(\text{same direction}) = \sqrt{2}\hbar - \sqrt{2}\hbar = 0$$

If they are revolving at some off-angle relative to each other (one revolving in a plane and one off plane), you would partially subtract them.

$$L(\text{same direction}) = \sqrt{2}\hbar + 0 = \sqrt{2}\hbar$$

To figure out all of the possible combinations of l for a pair of electrons, simply add them together to get the co-aligned case, subtract them to get the opposing case, and then fill in all the numbers in between to get the off-angle cases. For the two p-orbital case, there are no other possibilities (remember that l and hence L must be non-negative since they represent the magnitude of angular momenta (addressing the m_l values is a different story as we discuss below).

If you prefer to have a formula for the possibilities of L, you can use this:

$$L = |l_1 + l_2|, |l_1 + l_2\text{-}1|, \ldots, |l_1\text{-}l_2| \tag{5.11.2}$$

Technically, Equation 5.11.2 should include all electrons in a system, not just two, to account for all possible combinations of orbital angular momenta, however, there are some tricks that aid in applying this equations to address larger multi-electron atoms. First, electrons in s-orbitals have no orbital angular momentum, so they can be ignored. Second, if block of orbitals are completely filled (e.g., all six p-block spin-orbitals or all 10 d-block spin-orbitals), then the orbital angular momentum vector of each electron will be countered by another electron in the system; these are called **closed-shell** systems. Systems with partially unfilled blocks are called **open-shell** systems.

Hence, conveniently for chemists, an atom's electronic state depends entirely on its unfilled sub shells. Because electrons distribute themselves in a symmetric manner, the inner shell electrons end up canceling out each other's momenta. For an atom in the configuration $1s^2 2s^2 p^2$, only the two p-electrons matter. For an atom in the configuration $1s^2 2s^1 2p^1$, we have to examine only the 2s and 2p electrons (and can ignore the s electrons too).

Example 8.8.1 : Total Orbital Angular Momentum of Carbon

What are the possible L values for the electrons in the $1s^2 2s^2 2p^2$ configuration of carbon?

Solution

Both open-shell electrons (i.e., the 2p electrons) are $l = 1$. The possible combinations are 2, 1, 0.

Example 8.8.2 : Total Orbital Angular Momentum of Unknown Species

What are the possible L values for the electrons in the $[Xe]6s^2 4f^1 5d^1$?

Solution

We can ignore the electrons in the $[Xe]$ core and the electrons in the $6s$ block. So all we have to consider is the f electron $l = 3$ and d electron $l = 2$.

The two extremes possible (Equation 5.11.2) are

$$3 + 2 = 5$$

and

$$3\text{-}2 = 1$$

The possible combinations are thus 5, 4, 3, 2, and 1.

5.11.2: The Total Magnetic Quantum Number: M_l

The Total Magnetic Quantum Number M_l is the total z-component of all of the relevant electrons' orbital momentum. Where L told you how much total angular momentum there is in the system, M_l tells you which direction it is pointing. Like L, a given configuration can have several possible values of M_l, depending on the electrons' relative orientation. Unlike L, M_l is allowed to have negative values. To list the possible M_l values for a two electron system, take the case where both m_l are positive, then take the case where they are both negative, and then fill in the numbers in between (Figure 8.8.1).

$$M_l = m_{l1} + m_{l2}, m_{l1} + m_{l2}\text{-}1, \ldots, \text{-}m_{l1}\text{-}m_{l2} \tag{5.11.3}$$

Note that there is no absolute value function in Equation 5.11.3 like in Equation 5.11.2.

Example 8.8.3 : Total Magnetic Quantum Number of the Zirconium Ground State

What are the possible values M_l of a zirconium atom with the $[Kr]5s^24d^2$ electron configuration?

Solution

Both open-shell electrons (i.e., the 4d electrons) are $l = 2$, so the values are 4, 3, 2, 1, 0, -1, -2, -3, -4.

5.11.2.1: 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.

$$M_s = m_{s1} + m_{s2}, m_{s1} + m_{s2}\text{-}1, ..., m_{s1}\text{-}m_{s2} \tag{5.11.4}$$

Example 8.8.4 : Total Spin Magnetic Quantum Number of the Carbon Ground State

What are the M s values for $1s^22s^22p^2$?

Solution

$M_s = 1, 0, \text{-}1$

5.11.3: 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.

$$S = |s_1 + s_2|, |s_1 + s_2\text{-}1|, ..., |s_1\text{-}s_2| \tag{5.11.5}$$

Example 8.8.5 : The Hydrogen Ground State

Find S for $1s^1$.

Solution

S clearly has to be ½ since that's the spin of a single electron and there's only one electron to worry about.

Example 8.8.6 : The Beryllium Excited State

Find S for $1s^22s^12p^1$.

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 $S = 3/2, 1, 1/2$.

5.11.4: The Total Angular Momentum Quantum Number J

The total orbital angular momentum of an atom (measured in terms of l), and the total spin angular momentum of an atom (measure in S) combine to form total angular momentum, a number that is quantized by the number J. L and S do not necessarily have to be pointing in the same direction (Figure 8.8.1), so J can range from $L + S$ to $|L–S|$.

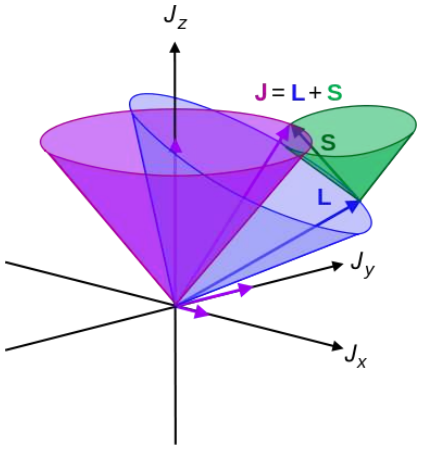


Figure 8.8.1 : Illustration of L-S coupling. Total angular momentum J is purple, orbital L is blue, and spin S is green.

Table 8.8.1 : Quantum Numbers and associated ranges

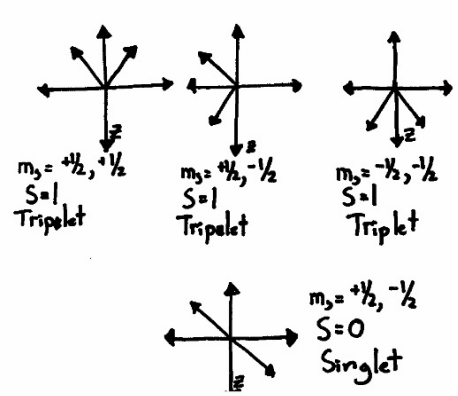
Symbol	Name	Allowed Range
l	Total orbital angular momentum	$\|l_1 + l_2\|, ..., \|l_1 - l_2\|$
M_l	Magnet Quantum number	$[m_{l1} + m_{l2}, ..., -m_{l1} - m_{l2}]$
M_s	Spin Magnetic Quantum Number	$\|m_{s1} + m_{s2}\|, ..., \|m_{s1} - m_{s2}\|$
S	Inherent Spin Number	$\|s_1 + s_2\|, ..., \|s_1 - s_2\|$
M	Multiplicity	2S+1
J	Total Angular Momentum	$L + S, ..., \|L - S\|$

5.11.5: Multiplicity

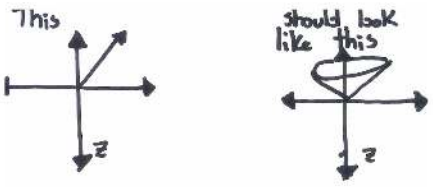
Multiplicity is a simple - sounding concept that defies simple explanations. You know from your first - year education that a singlet is when the net spin (S) is equal to zero (e.g. all the electrons are spin paired), and a triplet happens when the net spin is equal to 1 (e.g. two electrons are pointing 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:



5.11.6: Constructing Term Symbols

Atomic term symbols contain two pieces of information. They tell you the total orbital angular momentum of the atom (l), and they tell you the multiplicity (M). l is denoted by a simple code, similar to the code used to delineate the types of atomic orbitals:

- $L = 0 \rightarrow S$
- $L = 1 \rightarrow P$
- $L = 2 \rightarrow D$
- $L = 3 \rightarrow F$

Note that while the notation is similar, L does NOT say anything about what types of orbitals the electrons are in. A state that has the term symbol P does NOT necessarily have an open p-shell. The multiplicity is indicated by appending a number to the upper left of the symbol. A $L = 2$, $M = 3$ state would be represented by ^3D. The secret to writing the term symbols for an atom is to discover what combinations of l and M are possible for that atom with that specific electronic configuration. An atom that only has closed shells will always be $1S$.

Each term symbol represents a discrete energy level. We can place these levels in the correct order by using these simple rules:

- 1: High multiplicity values mean low energy
- 2: If there is a tie, high l values mean low energy
- 3a: If there is still a tie and the shell is less than half full, then low J means low energy
- 3b: If the shell is more than half full, then high J means low energy

These rules reliably predict the ground state. They have only erratic agreement with experiment when ordering the other levels.

Example 8.8.9 : Hydrogen Ground State

What are the term symbols for the microstates possible for $1s^1$ electronic configuration of hydrogen?

Solution

Since there is only one electron, this is a simple problem. $L = 0$ and $M = 1$, so the only possible term symbol is ^2S. With only one electron, $S = ½$, so $J = 0 + ½ = ½$. Only one microstate exists for this configuration and it has a term symbol of $^2S_{½}$.

Example 8.8.10 : Boron

What are the term symbols for the microstates possible for $1s^2 2s^2 2p^1$ electronic configuration of boron?

Solution

There still only one open shell electron, so $L = 1$, $M = 1$ and $S = ½$. We get a term symbol of the type ^2P, which gets split into separate symbols because $J = 3/2$ and $1/2$. Two possible microstates exist for this system with term symbols of $^2P_{3/2}$ and $^2P_{1/2}$.

Example 8.8.11 : Beryllium Excited State

What are the term symbols for the microstates possible for the $1s^2 2s^1 2p^1$ excited-state electronic configuration of Beryllium?

Solution

Now we have two electrons to worry about. Since $l_1 = 0$ and $l_2 = 1$, the only possible combination is $L = 1$. The possible combinations of S are: $S = 1, 0$. This means that $M = 3$ or $M = 1$. The term symbols will be of the form ^1P and ^3P. For the ^1P state, $L = 1$ and $S = 0$, so $J = 1$. For the second state, $L = 1$ and $S = 1$, so $J = 2, 1, 0$. There are four microstates for this configuration with term symbols of $^1P_1$ and $^3P_2$, $^3P_1$, and $^3P_0$.

Example 8.8.12 : Zirconium

What are the term symbols for the microstates possible for the $[Kr]5s^2 4d^2$ ground-state electronic configuration of zirconium?

Solution

This is a much harder problem. We will need to use a special technique to disentangle all of the possible combinations of l and M. Let's start be listing the relevant quantum numbers for the two open-shell electrons:

$l_1 = 2$	$l_2 = 2$
$m_{l1} = 2, 1, 0, -1, -2$	$m_{l2} = 2, 1, 0, -1, -2$
$m_{s1} = ½, -½$	$m_{s1} = ½, -½$

Let's combine these numbers to generate the atomic quantum numbers:

$$L = 4, 3, 2, 1, 0$$

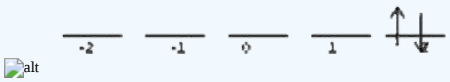
$$M_l = 4, 3, 2, 1, 0, -1, -2, -3, -4$$

$$M_s = 1, 0$$

We know that there will at least one each of S, P, D, F and G. It isn't immediately clear which of these will be singlets and which will be triplets. To figure this out, we need to systematically examine the possible microstates. It turns out that there are **45** possible ways to put distribute two electrons between 5 d orbitals. That's a lot! The easiest way to list the states is to organize them into a chart:

$M_s = -1$	$M_s = 0$	$M_s = +1$

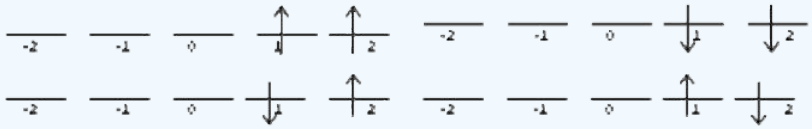
Attacking the chart one row at a time. Ask yourself, how many ways can I arrange the two electrons to give me $M_l = 4$? It turns out there is only one possible combination that does this:



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:

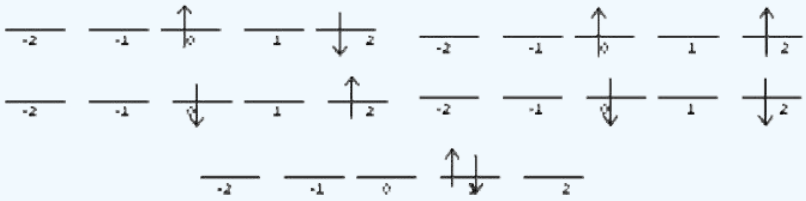
M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0

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.

5.11.7: 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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5.12: The Allowed Values of J - the Total Angular Momentum Quantum Number

Learning Objectives

- Compate two spin-orbit coupling schemes that couple the total spin angular momenta and total orbital angular momenta of a multi-electron spectra

We need to be able to identify the electronic states that result from a given electron configuration and determine their relative energies. An electronic state of an atom is characterized by a specific energy, wavefunction (including spin), electron configuration, total angular momentum, and the way the orbital and spin angular momenta of the different electrons are coupled together. There are two descriptions for the coupling of angular momentum. One is called **j-j coupling**, and the other is called **L-S coupling**. The j-j coupling scheme is used for heavy elements (z > 40) and the L-S coupling scheme is used for the lighter elements. Only L-S coupling is discussed below.

5.12.1: 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

$$L = \sum_i l_i \tag{5.12.1}$$

$$S = \sum_i s_i \tag{5.12.2}$$

The total angular momentum vector then is the sum of the total orbital angular momentum vector and the total spin angular momentum vector.

$$J = L + S \tag{5.12.3}$$

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.

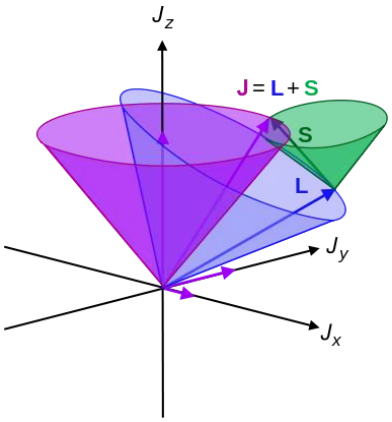


Figure 8.9.1 : "Vector cones" of total angular momentum $\boldsymbol{J}$ (purple), orbital $\boldsymbol{L}$ (blue), and spin $\boldsymbol{S}$ (green). The cones arise due to quantum uncertainty between measuring angular momentum components (see vector model of the atom). (Public Domain; Maschen).

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

$$|\vec{L}| = \hbar\sqrt{\ell(\ell+1)}$$

with its projection on the z-axis

$$L_z = m_\ell \hbar$$

Spin Angular Momentum

$$|\vec{S}| = \hbar\sqrt{s(s+1)}$$

with its projection on the z-axis

$$S_z = m_s \hbar$$

Total Angular Momentum

$$|\vec{J}| = \hbar\sqrt{j(j+1)}$$

with its projection on the z-axis

$$J_z = m_j \hbar$$

where

- l is the azimuthal quantum number of a single electron,
- s is the spin quantum number intrinsic to the electron,
- j is the total angular momentum quantum number of the electron,

The quantum numbers take the values:

$$m_\ell \in \{-\ell, -(\ell-1) \cdots \ell-1, \ell\}, \quad \ell \in \{0, 1 \cdots n-1\} \tag{5.12.4}$$
$$m_s \in \{-s, -(s-1) \cdots s-1, s\}, \tag{5.12.5}$$
$$m_j \in \{-j, -(j-1) \cdots j-1, j\}, \tag{5.12.6}$$
$$m_j = m_\ell + m_s, \quad j = |\ell + s| \tag{5.12.7}$$

and the magnitudes are:

$$|\mathbf{J}| = \hbar\sqrt{j(j+1)} \tag{5.12.8}$$
$$|\mathbf{J}_1| = \hbar\sqrt{j_1(j_1+1)} \tag{5.12.9}$$
$$|\mathbf{J}_2| = \hbar\sqrt{j_2(j_2+1)} \tag{5.12.10}$$

in which

$$j \in \{|j_1 - j_2|, |j_1 - j_2| - 1 \cdots j_1 + j_2 - 1, j_1 + j_2\}$$

This process may be repeated for a third electron, then the fourth etc. until the total angular momentum has been found.

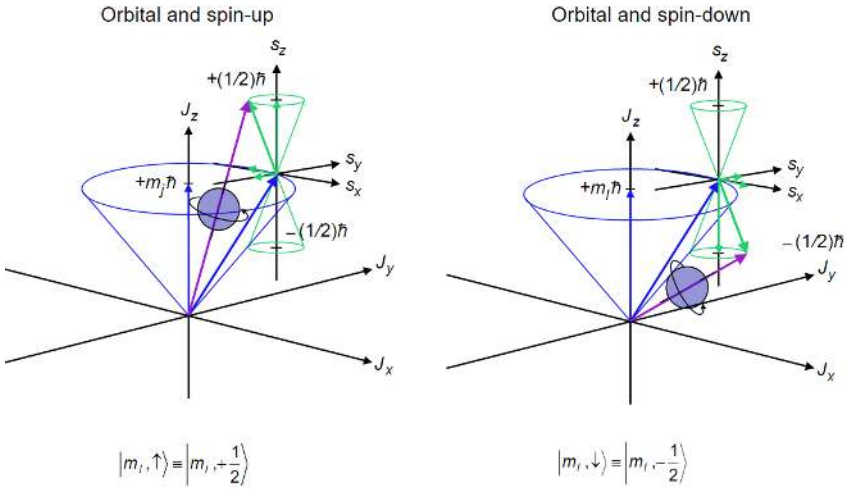


Figure 8.9.2 : Vector model of total angular momentum: spin and orbital coupling (spin-1/2 particles). (Public Domain; Maschen).

The result of these vector sums is specified in a code that is called a Russell-Saunders term symbol, and each term symbol identifies an energy level of the atom. Consequently, the energy levels also are called terms. A term symbol has the form ${}^{2s+1}L_J$ where the code letter that is used for the total orbital angular momentum quantum number L = 0, 1, 2, 3, 4, 5 is S, P, D, F, G, H, respectively. Note how this code matches that used for the atomic orbitals. The superscript $2S+1$ gives the spin multiplicity of the state, where S is the total spin angular momentum quantum number. The spin multiplicity is the number of spin states associated with a given electronic state. In order not to confuse the code letter S for the orbital angular momentum with the spin quantum number S, you must examine the context in which it is used carefully. In the term symbol, the subscript J gives the total angular momentum quantum number. Because of spin-orbit coupling, only J and M_j are valid quantum numbers, but because the spin-orbit coupling is weak L, M_l, S, and m_s still serve to identify and characterize the states for the lighter elements.

For example, the ground state, i.e. the lowest energy state, of the hydrogen atom corresponds to the electron configuration in which the electron occupies the 1s spatial orbital and can have either spin α or spin β. The term symbol for the ground state is ${}^2S_{1/2}$, which is read as “doublet S 1/2”. The spin quantum number is 1/2 so the superscript 2S+1 = 2, which gives the spin multiplicity of the state, i.e. the number of spin states equals 2 corresponding to α and β. The S in the term symbol indicates that the total orbital angular momentum quantum number is 0 (For the ground state of hydrogen, there is only one electron and it is in an s-orbital with $l = 0$). The subscript ½ refers to the total angular momentum quantum number. The total angular momentum is the sum of the spin and orbital angular momenta for the electrons in an atom. In this case, the total angular momentum quantum number is just the spin angular momentum quantum number, ½, since the orbital angular momentum is zero. The ground state has a degeneracy of two because the total angular momentum can have a z-axis projection of $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$, corresponding to m_J = +1/2 or -1/2 resulting from the two electron spin states α and β. We also can say, equivalently, that the ground state term or energy level is two-fold degenerate.

? Exercise 8.9.1

Write the term symbol for a state that has 0 for both the spin and orbital angular momentum quantum numbers.

? Exercise 8.9.2

Write the term symbol for a state that has 0 for the spin and 1 for the orbital angular momentum quantum numbers

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5.13: Hund's Rules Determine the Term Symbols of the Ground Electronic States

Learning Objectives

- Define Hund three rules
- Use Hunds three rules to predict the lowest energy configuration and term symbols for multi-electron systems

The Aufbau section discussed how that electrons fill the lowest energy orbitals first, and then move up to higher energy orbitals only after the lower energy orbitals are full. However, there a problem with this rule. Certainly, 1s orbitals should be filled before 2s orbitals, because the 1s orbitals have a lower value of n, and thus a lower energy. What about the three different 2p orbitals? In what order should they be filled? The answer to this question involves Hund's rule, which make a lot more sense in the context of generated term symbols that are used to combine the various L and S values represent vector additions of possible microstates.

5.13.1: 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):

$$^3D,\ ^3P,\ ^3S,\ ^1D,\ ^1P,\ ^1S$$

5.13.1.1: 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.

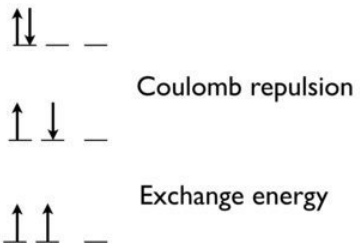


Figure 8.10.1 : Origin of Hund's First Rule. Hund's first rule is that for a given electron configuration, a state in which the spins are unpaired has lower total energy than one in which the spins are paired.

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.

5.13.1.2: 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.

5.13.1.3: 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.

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CHAPTER OVERVIEW

6: Molecular Structure and Bonding

6.1: The Born-Oppenheimer Approximation
6.2: The Orbital Approximation and Orbital Configurations
6.3: Linear Variational Method and the Secular Determinant
6.4: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters
6.5: The H_2^+ Prototypical Species
6.6: The Overlap Integral
6.7: Chemical Bond Stability
6.8: Bonding and Antibonding Orbitals
6.9: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital
6.10: Molecular Orbitals Can Be Ordered According to Their Energies
6.11: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule
6.12: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle
6.13: Diatomic Molecules of the First and Second Periods
6.14: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic
6.15: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules
6.16: Orbital ionization energies
6.17: Polar bonds
6.18: Molecular Term Symbols Describe Electronic States of Molecules
6.19: Molecular Term Symbols Designate Symmetry
6.20: The pi-Electron Approximation of Conjugation
6.21: Butadiene is Stabilized by a Delocalization Energy
6.22: Benzene and Aromaticity

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6.1: 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

$$\frac{Ze^2}{r^2} \tag{6.1.1}$$

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 1000. 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 1000 times greater than yours. That person could literally run circles around you. So a good approximation is to describe the electronic states of a molecule by thinking that the nuclei aren't 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

$$\hat{H}(r,R) = \hat{T}_{nuc}(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} + \hat{H}_{elec}(r,R) \tag{6.1.2}$$

where

$$T_{nuc}(R) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 \tag{6.1.3}$$

and

$$\hat{H}_{elec}(r,R) = \frac{-\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left(-\sum_i \frac{Z_A}{r_{Ai}} - \sum_i \frac{Z_B}{r_{Bi}} + \frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{r_{ij}}\right) \tag{6.1.4}$$

In Equation 6.1.2, 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. Bold-face type is used to represent that $\boldsymbol{r}$ and $\boldsymbol{R}$ are vectors specifying the positions of all the electrons and all the nuclei, respectively.

Exercise 6.1.1

Define all the symbols in Equations 6.1.2 through 6.1.4.

Exercise 6.1.2

Explain why the factor of 1/2 appears in the last term in Equation 6.1.4.

The Born-Oppenheimer approximation says that the nuclear kinetic energy terms in the complete Hamiltonian, Equation 6.1.2, 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:

$$\hat{H}_{elec}(r,R)\varphi_e(r,R) = E_e(R)\varphi_e(r,R) \tag{6.1.5}$$

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 the Born-Oppenheimer Approximation

$$\psi_{ne}(r,R) = X_{ne}(R)\varphi_e(r,R) \tag{6.1.6}$$

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 6.1.6 to give he complete molecular wavefunction when the translational and rotational motions are not coupled to the vibrational and electronic motion.

Crude Born-Oppenheimer Approximation

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.

The electronic energy, $E_e(R)$, in Equation 6.1.5 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 6.1.1.

$$V_e(R) = E_e(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} \tag{6.1.7}$$

Consequently the Schrödinger equation for the vibrational motion is

$$(\hat{T}_{nuc}(R) + V(R))_{X_{ne}}(R) = E_{ne}X_{ne}(R) \tag{6.1.8}$$

In Chapter 6, the potential energy was approximated as a harmonic potential depending on the displacement, Q, of the nuclei from their equilibrium positions.

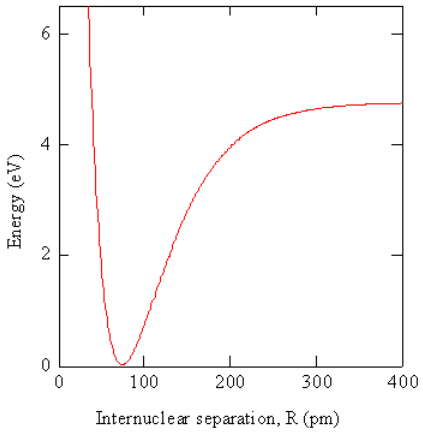


Figure 6.1.1: The potential energy function for a diatomic molecule.

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 6.1.1.

The graph in Figure **6.1.1** is the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When $\boldsymbol{R}$ is very large there are two atoms that are weakly interacting. As $\boldsymbol{R}$ 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 $\boldsymbol{R}$, 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 $\boldsymbol{R} = \boldsymbol{R_0}$. If we obtain the wavefunction at $\boldsymbol{R} = \boldsymbol{R_0}$, and use this function for all values of $\boldsymbol{R}$, we have employed the *Crude Born-Oppenheimer* approximation.

Exercise 6.1.3

Relate Equation 6.1.8 to the one previously used in our description of molecular vibrations in terms of the harmonic oscillator model.

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.

Exercise 6.1.4

Explain the difference between the Born-Oppenheimer approximation and the Crude Born-Oppenheimer approximation.

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6.2: The Orbital Approximation and Orbital Configurations

You should be able to recognize from the form of the electronic Hamiltonian, Equation that the electronic Schrödinger equation, Equation, cannot be solved. The problem, as for the case of atoms, is the electron-electron repulsion terms. Approximations must be made, and these approximations are based on the idea of using one-electron wavefunctions to describe multi-electron systems, in this case molecules just as is done for multi-electron atoms. Initially two different approaches were developed. Heitler and London originated one in 1927, called the **Valence Bond Method**, and Robert Mulliken and others developed the other somewhat later, called the **Molecular Orbital Method**. By using configuration interaction, both methods can provide equivalent electronic wavefunctions and descriptions of bonding in molecules, although the basic concepts of the two methods are different. We will develop only the molecular orbital method because this is the method that is predominantly employed now. The wavefunction for a single electron in a molecule is called a molecular orbital in analogy with the one-electron wavefunctions for atoms being called atomic orbitals.

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.

$$\psi_i = \sum_j c_{ij}\varphi_j \tag{6.2.1}$$

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.

Just as for atoms, each electron in a molecule can be described by a product of a spatial orbital and a spin function. These product functions are called 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,

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_A(r_1)\alpha(1) & \psi_B(r_1)\beta(1)\\ \psi_A(r_2)\alpha(2) & \psi_B(r_2)\beta(2)\end{vmatrix} \tag{6.2.2}$$

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, 2 electrons with different spins (α and β, consistent with the Pauli Exclusion Principle) 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 **6.2.1**. Higher energy configurations exist as well, and these configurations produce excited states of molecules. Some examples are shown in Figure **6.2.1**.

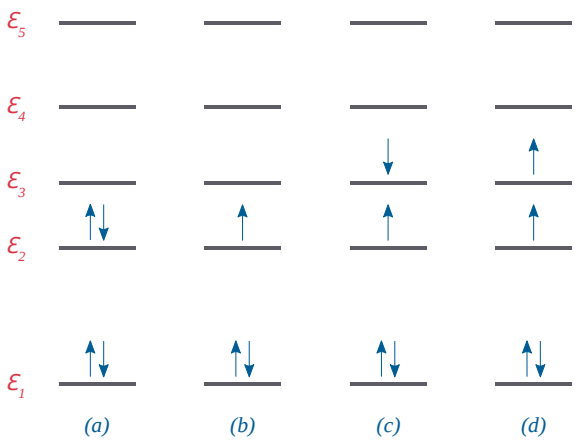


Figure **6.2.1**: a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration. (CC BY-SA 4.0; Ümit Kaya via LibreTexts)

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 $\mathbf{N_2}$ is

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$$

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6.3: 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

$$|\psi_{trial}\rangle = \sum_{j=1}^{N} a_j \Big| \phi_j \rangle \tag{6.3.1}$$

and

$$\langle \psi_{trial}| = \sum_{j=1}^{N} a_j^* \langle \phi_j| \tag{6.3.2}$$

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 6.3.1 and 6.3.2.

As discussed in Section 7.1, the variational energy for a generalized trial wavefunction is

$$E_{trial} = \frac{\langle \psi_{trial} \Big| \hat{H} \Big| \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{6.3.3}$$

Substituting Equations 6.3.1 and 6.3.2 into Equation 6.3.3 involves addressing the numerator and denominator individually. For the numerator, the integral can be expanded thusly:

$$\langle \psi_{trial} | H | \psi_{trial} \rangle = \sum_{i}^{N} \sum_{j}^{N} a_i^* a_j \langle \phi_i | H | \phi_j \rangle. \tag{6.3.4}$$

$$= \sum_{i,j}^{N,N} a_i^* a_j \langle \phi_i | H | \phi_j \rangle. \tag{6.3.5}$$

We can rewrite the following integral in Equation 6.3.5 as a function of the basis elements (not the trial wavefunction) as

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle$$

So the numerator of the right side of Equation 6.3.3 becomes

$$\langle \psi_{trial} | H | \psi_{trial} \rangle = \sum_{i,j}^{N,N} a_i^* a_j H_{ij} \tag{6.3.6}$$

Similarly, the denominator of the right side of Equation 6.3.3 can be expanded

$$\langle \psi_{trial} | \psi_{trial} \rangle = \sum_{i,j}^{N,N} a_i^* a_j \langle \phi_i | \phi_j \rangle \tag{6.3.7}$$

We often simplify the integrals on the right side of Equation 6.3.7 as

$$S_{ij} = \langle \phi_i | \phi_j \rangle$$

where S_{ij} are **overlap integrals** between the different $\{\phi_j\}$ basis functions. Equation 6.3.7 is thus expressed as

$$\langle \psi_{trial} | \psi_{trial} \rangle = \sum_{i,j}^{N,N} a_i^* a_j S_{ij} \tag{6.3.8}$$

Orthonormality of Basis Functions

There is no explicit rule that the $\{\phi_j\}$ functions have to be **orthogonal** or **normalized** functions, although they often are selected that way for convenience. Therefore, *a priori*, S_{ij} does not have to be δ_{ij}.

Substituting Equations 6.3.6 and 6.3.8 into the variational energy formula (Equation 6.3.3) results in

$$E_{trial} = \frac{\sum_{i,j}^{N,N} a_i^* a_j H_{ij}}{\sum_{i,j}^{N,N} a_i^* a_j S_{ij}} \tag{6.3.9}$$

For such a trial wavefunction as Equation 6.3.1, 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.

6.3.1: Minimizing the Variational Energy

The expression for variational energy (Equation 6.3.9) can be rearranged

$$E_{trial} \sum_{i,j}^{N,N} a_i^* a_j S_{ij} = \sum_{i,j}^{N,N} a_i^* a_j H_{ij} \tag{6.3.10}$$

The optimum coefficients are found by searching for minima in the variational energy landscape spanned by varying the $\{a_i\}$ coefficients (Figure 7.2.1).

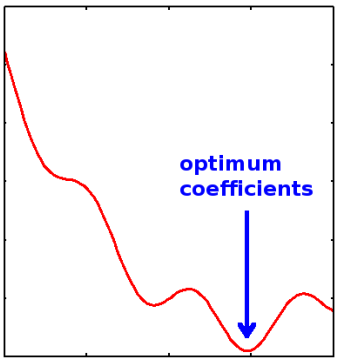


Figure 7.2.1 : Linear Variational Principle in action. Two (or more) wavefunctions are mixed by linear combination. The coefficients a_1, a_2 determine the weight each of them is given. The optimum coefficients are found by searching for minima in the potential landscape spanned by a_1 and a_2. (CC BY-SA-NC; Rudolf Winter; Aberystwyth University).

We want to minimize the energy with respect to the linear coefficients $\{a_i\}$, which requires that

$$\frac{\partial E_{trial}}{\partial a_i} = 0$$

for all i.

Differentiating both sides of Equation 6.3.10 for the k^{th} coefficient gives,

$$\frac{\partial E_{trial}}{\partial a_k} \sum_{i,j}^{N,N} a_i^* a_j S_{ij} + E_{trial} \sum_i \sum_j \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^* \right] S_{ij} \tag{6.3.11}$$
$$= \sum_{i,j}^{N,N} \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^* \right] H_{ij}$$

Since the coefficients are independent

$$\frac{\partial a_i^*}{\partial a_k} = \delta_{ik}$$

and

$$S_{ij} = S_{ji}$$

and also since the Hamiltonian is a Hermitian Operator (see below)

$$H_{ij} = H_{ji}$$

then Equation 6.3.11 simplifies to

$$\frac{\partial E_{trial}}{\partial a_k} \sum_i \sum_j a_i^* a_j S_{ij} + 2E_{trial} \sum_i a_i S_{ik} = 2 \sum_i a_i H_{ik} \tag{6.3.12}$$

At the minimum variational energy, when

$$\frac{\partial E_{trial}}{\partial a_k} = 0$$

then Equation 6.3.12 gives

$$\sum_i^N a_i (H_{ik} - E_{trial} S_{ik}) = 0 \tag{6.3.13}$$

for all k. The equations in 6.3.13 are called the **Secular Equations**.

Hermitian Operators

Hermitian operators are operators that satisfy the general formula

$$\langle \phi_i \left| \hat{A} \right| \phi_j \rangle = \langle \phi_j \left| \hat{A} \right| \phi_i \rangle \tag{6.3.14}$$

If that condition is met, then $\hat{A}$ is a Hermitian operator. For any operator that generates a real eigenvalue (e.g., observables), then that operator is Hermitian. The Hamiltonian $\hat{H}$ meets the condition of a Hermitian operator. Equation 6.3.14 can be rewriten as

$$A_{ij} = A^*_{ji}$$

where

$$A_{ij} = \langle \phi_i \left| \hat{A} \right| \phi_j \rangle$$

and

$$A_{ji} = \langle \phi_j \left| \hat{A} \right| \phi_i \rangle$$

Therefore, when applied to the Hamiltonian operator

$$H^*_{ij} = H_{ji}.$$

If the functions $\{|\phi_j\rangle\}$ are orthonormal, then the overlap matrix S reduces to the unit matrix (one on the diagonal and zero every where else) and the Secular Equations in Equation 6.3.13 reduces to the more familiar Eigenvalue form:

$$\sum_i^N H_{ij} a_j = E_{trial} a_i. \tag{6.3.15}$$

Hence, the secular equation, in either form, have as many eigenvalues E_i and eigenvectors $\{C_{ij}\}$ as the dimension of the H_{ij} matrix as the functions in $|\psi_{trail}\rangle$ (Example 6.3.1). 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*'.

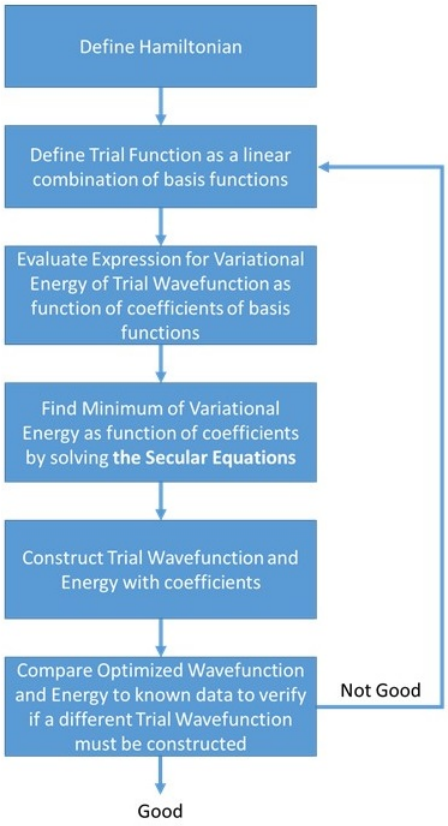


Figure 7.2.2 : Simplified algorithmic flowchart of the linear Variational Method approximation. Compared to the similar algorithmic flowchart for the "normal" Variational Method approximation.

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.

6.3.2: The Secular Determinant

From the secular equations with an orthonormal functions (Equation 6.3.15), we have k simultaneous secular equations in k unknowns. These equations can also be written in matrix notation, and for a non-trivial solution (i.e. $c_i \neq 0$ for all i), the determinant of the secular matrix must be equal to zero.

$$|H_{ik}-ES_{ik}| = 0 \tag{6.3.16}$$

Properties of Determinants

- The determinant is a **real** number, it is **not** a matrix.
- The determinant can be a negative number.
- It is **not** associated with absolute value at all except that they both use vertical lines.
- The determinant **only** exists for square matrices (2×2, 3×3, ..., $n \times n$). The determinant of a 1×1 matrix is that single value in the determinant.
- The inverse of a matrix will exist only if the determinant is not zero.

Expanding Determinants

The determinant can be evaluated using an expansion method involving minors and cofactors. Before we can use them, we need to define them. It is the product of the elements on the main diagonal minus the product of the elements off the main diagonal. In the case of a 2×2 matrix, the specific formula for the determinant is

$$|A| = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc.$$

Similarly, suppose we have a 3×3 matrix A, and we want the specific formula for its determinant $|A|$:

$$\begin{aligned} |A| = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} &= a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \begin{vmatrix} d & e \\ g & h \end{vmatrix} \\ &= aei + bfg + cdh - ceg - bdi - afh. \end{aligned}$$

To solve Equation 6.3.16, the determinate should be expanded and then set to zero. That generates a polynomial (called a **characteristic equation**) that can be directly solved with linear algebra methods or numerically.

Example 7.2.1 : A Simple Two Component Basis Set

If $|\psi_{trial}\rangle$ is a linear combination of two functions. In math terms,

$$|\psi_{trial}\rangle = \sum_{n=1}^{N=2} a_n \Big| f_n \rangle = a_1 |\phi_1\rangle + a_2 | \phi_2 \rangle$$

then the secular determinant (Equation 6.3.16), in matrix formulation would look like this

$$\begin{vmatrix} H_{11} - E_{trial} S_{11} & H_{12} - E_{trial} S_{12} \\ H_{12} - E_{trial} S_{12} & H_{22} - E_{trial} S_{22} \end{vmatrix} = 0$$

Solution

Solving the secular equations is done by finding E_{trial} and putting the value into the expansion of the secular determinant

$$a_1^2 H_{11} + 2 a_1 a_2 H_{12} + a_2^2 H_{22} = 0$$

and

$$a_1 (H_{12} - E_{trial} S_{12}) + a_2 (H_{22} - E_{trial} S_{22}) = 0$$

Equation 6.3.16 can be solved to obtain the energies E. When arranged in order of increasing energy, these provide approximations to the energies of the first k states (each having an energy higher than the true energy of the state by virtue of the variation theorem). To find the energies of a larger number of states we simply use a **greater number** of basis functions $\{\phi_i\}$ in the trial wavefunction (Example 6.3.1). 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 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.

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6.4: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters

Learning Objectives

- Demonstrate that variational problems can include changing parameters within the elements (normal variational method) and changing coefficients of a basis set (linear variational method)

An alternative approach to the general problem of introducing variational parameters into wavefunctions is the construction of a wavefunction as a linear combination of other functions each with one or multiple parameters that can be varied

For hydrogen, the radial function decays, or decreases in amplitude, exponentially as the distance from the nucleus increases. For helium and other multi-electron atoms, the radial dependence of the total probability density does not fall off as a simple exponential with increasing distance from the nucleus as it does for hydrogen. More complex single-electron functions therefore are needed in order to model the effects of electron-electron interactions on the total radial distribution function. One way to obtain more appropriate single-electron functions is to use a sum of exponential functions in place of the hydrogenic spin-orbitals.

An example of such a wavefunction created from a sum or linear combination of exponential functions is written as

$$\varphi_{1s}(r_1) = \sum_j c_j e^{-\zeta_j r_j / a_o} \tag{6.4.1}$$

The linear combination permits weighing of the different exponentials through the adjustable coefficients (c_j) for each term in the sum. Each exponential term has a different rate of decay through the zeta-parameter ζ_j. The exponential functions in Equation 6.4.1 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 6.4.1 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 6.4.1 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 6.4.1 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.

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6.5: 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 $\mathbf{H_2^+}$.

6.5.1: The Hydrogen Molecular Ion

The simplest conceivable molecule would be made of two protons and one electron, namely $\mathbf{H_2^+}$. 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 $\mathbf{H_2^+}$ 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.

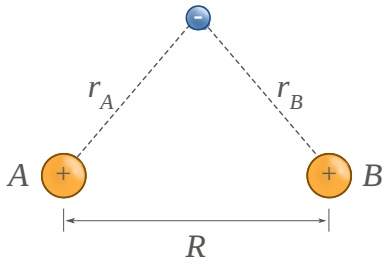


Figure 9.2.1 : Hydrogen molecular ion $\mathbf{H_2^+}$ with fixed nuclei $\boldsymbol{A}$ and $\boldsymbol{B}$, internuclear distance $\boldsymbol{R}$. (CC BY-NC; Ümit Kaya via LibreTexts)

The electronic Hamiltonian for $\mathbf{H_2^+}$ is

$$\hat{H}_{elec}(r,R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \tag{6.5.1}$$

where r_A and r_B are the distances electron from the $\boldsymbol{A}$ and $\boldsymbol{B}$ hydrogen nuclei, respectively and $\boldsymbol{R}$ is the distance between the two protons.

Although the Schrödinger equation for $\mathbf{H_2^+}$ 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.

6.5.2: 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 $\boldsymbol{A}$ or $\boldsymbol{B}$, the electron is near. Here $1s_A$ denotes a 1s hydrogen atomic orbital with proton A serving as the origin of the spherical polar coordinate system in which the position r of the electron is specified. Similarly $1s_B$ has proton B as the origin. A useful approximation for the molecular orbital when the protons are close together therefore is a linear combination of the two atomic orbitals. The general method of using

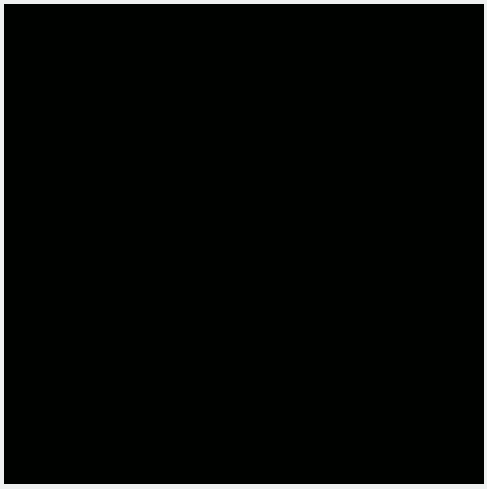
$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \tag{6.5.2}$$

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 6.5.2 with two atomic orbitals contributing result in two molecule orbitals.

This method yields a approximate picture of the molecular orbitals in a molecules. The figure below shows two atoms approaching along the axis of one of their $2p$ states. In the top row, the two lobes facing one another have the same sign; in the bottom row they have opposite sign. These are two different linear combinations of the same two atomic states, on different atoms and with difference phases (i.e., signs of C_A vs. C_B in the expansion). In the first example, the electron density increases between the nuclei and in the second example, a very steep-sided node between the two nuclei causes all the probability density to face away from the atom opposite.



For H_2^+, the simplest molecule, the starting function is given by Equation 6.5.2. 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:

$$\psi_+ = C_+(1s_A + 1s_B) \tag{6.5.3}$$

$$\psi_- = C_-(1s_A - 1s_B) \tag{6.5.4}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for ψ_+ is enhanced (Figure 9.2.2 (bottom) between the two protons, whereas it is diminished for ψ_- as shown in Figures 9.2.2 (top). ψ_- has a node in the middle while ψ_+ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons.

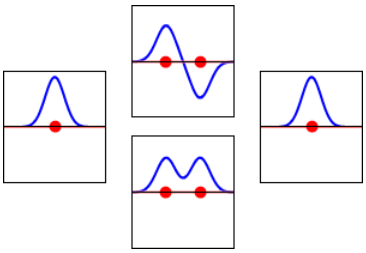


Figure 9.2.2 : Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H_2^+ ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red dots mark the locations of the nuclei. The electron wavefunction oscillates according to the Schrödinger wave equation, and orbitals are its standing waves. The standing wave frequency is proportional to the orbital's kinetic energy. (This plot is a one-dimensional slice through the three-dimensional .)

So ψ_+ is called a **bonding molecular orbital**. If the electron were described by ψ_-, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so ψ_- is called an **antibonding molecular orbital**.

Contributors and Attributions

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6.6: The Overlap Integral

For H_2^+, the simplest molecule, we must determine the values for the coefficients, C_A and C_B for the LCAO approximation for the molecular orbital as a linear combination of the two atomic orbitals

$$|\psi(r)\rangle = C_A 1s_A(r) + C_B 1s_B(r)$$

We could use the linear variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition

$$|C_A|^2 = |C_B|^2$$

so $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\underbrace{|\psi_+\rangle = C_+(1s_A + 1s_B)}_{\text{bonding molecular orbital}} \tag{6.6.1}$$

and

$$\underbrace{|\psi_-\rangle = C_-(1s_A - 1s_B)}_{\text{antibonding molecular orbital}} \tag{6.6.2}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for $|\psi_+\rangle$ is enhanced between the two protons, whereas it is diminished for $|\psi_-\rangle$ as shown in Figures 9.3.1 . ψ_- has a node in the middle while $|\psi_+\rangle$ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons. So $|\psi_+\rangle$ is called a *bonding molecular orbital*. If the electron were described by $|\psi_-\rangle$, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so $|\psi_-\rangle$ is called an *antibonding molecular orbital*.

Now we want to evaluate C_+ and C_- and then calculate the energy. The bonding and antibonding character of ψ_+ and ψ_- also should be reflected in the energy. If $|\psi_+\rangle$ indeed describes a bonding orbital, then the energy of this state should be less than that of a proton and hydrogen atom that are separated. The calculation of the energy will tell us whether this simple theory predicts H_2^+ to be stable or not and also how much energy is required to dissociate this molecule.

The constants C_+ and C_- are evaluated from the standard normalization condition:

$$\int \psi_\pm^* \psi_\pm d\tau = \langle \psi_\pm | \psi_\pm \rangle = 1 \tag{6.6.3}$$

$$\langle C_\pm(1s_A \pm 1s_B) | C_\pm(1s_A \pm 1s_B) \rangle = 1 \tag{6.6.4}$$

$$|C_\pm|^2[\underbrace{\langle 1s_A|1s_A\rangle}_{1} + \underbrace{\langle 1s_B|1s_B\rangle}_{1} \pm \underbrace{\langle 1s_B|1s_A\rangle}_{S} \pm \underbrace{\langle 1s_A|1s_B\rangle}_{S^*}] = 1 \tag{6.6.5}$$

Since the atomic orbitals are normalized, the first two integrals are just 1. The last two integrals are called *overlap integrals* and are symbolized by S and S^*, respectively, since one is the complex conjugate of the other.

The overlap integrals are telling us to take the value of $1s_B$ at a point multiply by the value of $1s_A$ at that point and sum (integrate) such a product over all of space (Figure 9.3.1). If the functions do not overlap, i.e. if one is zero when the other one is not and vice versa, these integrals then will be zero. It also is possible in general for such integrals to be zero even if the functions overlap because of the cancelation of positive and negative contributions.

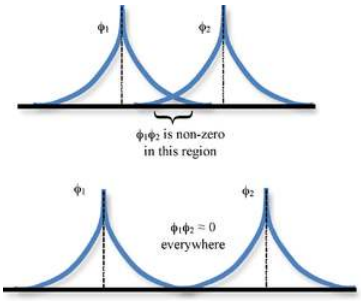


Figure 9.3.1 : The wavefunctions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case both S is close to zero.

If the overlap integral is zero, for whatever reason, the functions are said to be *orthogonal*. Notice that the overlap integral ranges from 0 to 1 as the separation between the protons varies from $R = \infty$ to $R = 0$. Clearly when the protons are infinite distance apart, there is no overlap, and when $R = 0$ both functions are centered on one nucleus and $\langle 1s_A | 1s_B \rangle$ becomes identical to $\langle 1s_B | 1s_A \rangle$, which is normalized to 1, because $1s_A = 1s_B$.

With these considerations and using the fact that $1s$ wavefunctions are real so

$$\langle 1s_A | 1s_B \rangle = \langle 1s_B | 1s_A \rangle = S \tag{6.6.6}$$

Equation 6.6.5 becomes

$$|C_{\pm}|^2 (2 \pm 2S) = 1 \tag{6.6.7}$$

The solution to Equation 6.6.7 is given by

$$C_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} \tag{6.6.8}$$

Hence, the normalized molecular orbitals in Equations 6.6.1 and 6.6.1 are

$$|\psi_+\rangle = \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B) \tag{6.6.9}$$

and

$$|\psi_-\rangle = \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B) \tag{6.6.10}$$

The energies associated with these wavefunctions requires a bit more effort to calculate though as demonstrated in the following section.

For the overlap integral of two 1s orbitals from the hydrogen dimer discussed above is difficult to evaluate analytically and is explained here. The final answer is:

$$S(R) = \langle 1s_A | 1s_B \rangle \tag{6.6.11}$$

$$= e^{-R/a_o} \left(1 + \frac{R}{a_o} + \frac{R^2}{3a_o^2} \right) \tag{6.6.12}$$

The overlap integral for two 1s atomic orbitals of hydrogen is graphically displayed below

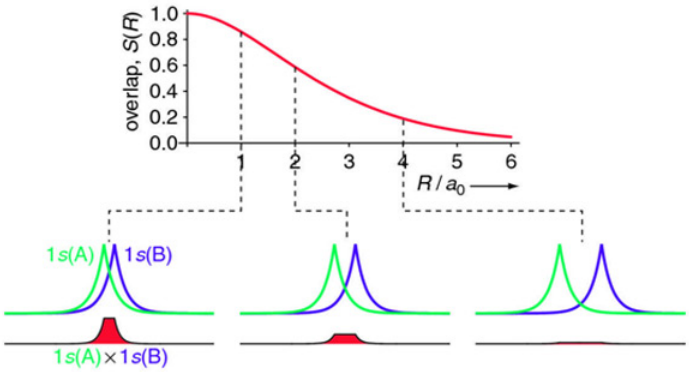


Figure 9.3.2 : The overlap integral at different proton separations.

Example 9.3.1

Calculate the difference in the electronic charge density (C/pm^3) at a point halfway between the two nuclei for $\mathbf{H_2^+}$ 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 6.6.9) gives us:

$$\begin{aligned}\psi_+^2 &= \frac{1}{2(1+S)}(1s_A + 1s_B)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3}\left(e^{-r_A/a_0} + e^{-r_B/a_0}\right)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3} \\ &= (0.561)^2 \times \left(\frac{1}{\pi \times (52.9\text{ pm})^3}\right) = 6.7672 \times 10^{-7}\text{ pm}^{-3}\end{aligned}$$

(Note: The value of C^2 is obtained from equation 9.3.12 and the value of S is from Equation 6.6.12)

To find the density at halfway between A and B for the bonding orbital evalulate at 1/2 R,

$$r_A = \frac{1}{2}R \text{ and } r_B = \frac{1}{2}R$$

$$\psi_+^2 = 3.7 \times 10^{-7}\text{ pm}^{-3}$$

Now multiply this answer by e to generate the electronic charge density,

$$P = \left(3.7 \times 10^{-7}\text{ pm}^{-3}\right) \times \left(1.602 \times 10^{-19}\right)\text{ C} = 5.93 \times 10^{-26} C/pm^3$$

b: Antibonding Molecular Orbital

To find the halfway between A and B for the anti-bonding orbital at $r_A = \frac{1}{2}R$ and $r_B = \frac{1}{2}R$. However, simple inspection of Equation 6.6.10 or Figure 9.3.1 shows this will be zero.

$$e\psi_-^2 = 0$$

Obviously, when multiplied by e, the answer is still zero. This makes logical sense as there would be no charge density between the two atoms as there lies a node with no probability of finding an electron.

Exercise 9.3.1

> Show that for two arbitrary functions $\langle\varphi_B|\varphi_A\rangle$ is the complex conjugate of $\langle\varphi_A|\varphi_B\rangle$ and that these two integrals are equal if the functions are real.

Contributors and Attributions

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

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6.7: Chemical Bond Stability

Learning Objectives

- Identify the nature of the energy of molecular orbitals of a diatomic as a function of intermolecular distance
- Identify the three integrals involved in calculation the total Molecular Orbital Energy: coulomb Integral, exchange integral, and overlap integral

As shown previously, we can construct two molecular orbitals for the H_2^+ system using the LCAO approximation with a basis set of two 1s atomic orbitals (i.e., the $1s$ orbitals on hydrogen A ($1s_A$) and hydrogen B ($1s_B$):

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}}(1s_A \pm 1s_B) \tag{6.7.1}$$

The energy of these two molecular orbitals can be calculated from the expectation value integral of the Hamiltonian,

$$E_{\pm} = \left\langle \psi_{\pm} \middle| \hat{H}_{elec} \middle| \psi_{\pm} \right\rangle \tag{6.7.2}$$

which can be expanded using the expanded molecular orbital wavefunctions in Equations 6.7.1 to give

$$E_{\pm} = \frac{1}{2(1 \pm S)} \tag{6.7.3}$$

$$\left[\underbrace{\left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A \middle| \hat{H}_{elec} \middle| 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B \middle| \hat{H}_{elec} \middle| 1s_A \right\rangle}_{H_{BA}} \right]$$

where S is the overlap integral between the two atomic orbitals of the basis. The four integrals in Equation 6.7.3 can be represented by H_{AA}, H_{BB}, H_{AB}, and H_{BA}, respectively.

$$E_{\pm} = \frac{1}{2(1 \pm S)} [H_{AA} + H_{BB} \pm H_{AB} \pm H_{BA}] \tag{6.7.4}$$

Exercise 9.4.1

Show that Equation 6.7.2 expands to give Equation 6.7.3 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 6.7.1).

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}} (1_{Sa} \pm 1_{Sb})$$

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 6.7.3 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 for H_2^+. This equivalence means that integrals involving $1s_A$ must be the same as corresponding integrals involving $1s_B$, i.e.

$$H_{AA} = H_{BB} \tag{6.7.5}$$

and since the wavefunctions are real

$$|A\rangle = \langle A|$$

so

$$H_{AB} = H_{BA} \tag{6.7.6}$$

These two equalities simplify Equation 6.7.4:

$$E_{\pm} = \frac{1}{1 \pm S}(H_{AA} \pm H_{AB}) \tag{6.7.7}$$

Now examine the details of H_{AA} after inserting the Hamiltonian operator for H_2^+ (Equation 9.2.1):

$$H_{AA} = \underbrace{\left\langle 1s_A \middle| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} \middle| 1s_A \right\rangle}_{E_H} + \frac{e^2}{4\pi\epsilon_0 R} \cancelto{1}{\langle 1s_A | 1s_A \rangle} \underbrace{- \left\langle 1s_A \middle| \frac{e^2}{4\pi\epsilon_0 r_B} \middle| 1s_A \right\rangle}_{J_{AB}} \tag{6.7.8}$$

- The first term is just the integral for the energy of the hydrogen atom of the 1s orbital, E_H.
- The second integral is equal to 1 by normalization; the prefactor is just the Coulomb repulsion of the two protons.
- The last integral, *including the minus sign*, is represented by J and is called the **Coulomb integral**.

Physically J_{AB} is the potential energy of interaction of the electron located around proton A with proton B. It is negative because it is an attractive interaction. It is the average interaction energy of an electron described by the $1s_A$ function with proton B.

J The Coulomb Integral ()

The **Coulomb Integral** is the potential energy of electrostatic repulsion between the electron with the electron density in $1S_A$ and the the electron with the electron density function $1S_B$

Now consider H_{AB}.

$$H_{AB} = \underbrace{\left\langle 1s_A \middle| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_B} \middle| 1s_B \right\rangle}_{E_H S} + \frac{e^2}{4\pi\epsilon_0 R} \cancelto{S}{\langle 1s_A | 1s_B \rangle} - \underbrace{\left\langle 1s_A \middle| \frac{e^2}{4\pi\epsilon_0 r_A} \middle| 1s_B \right\rangle}_{K_{AB}} \tag{6.7.9}$$

- In the first integral we have the hydrogen atom Hamiltonian and the H atom function $1s_B$. The function $1s_B$ is an eigenfunction of the operator with eigenvalue E_H. Since E_H is a constant it factors out of the integral, which then becomes the overlap integral, S. The first integral therefore reduces to $E_H S$.
- The second term is just the Coulombic energy of the two protons times the overlap integral.
- The third term, *including the minus sign*, is given the symbol K and is called the *exchange integral* because the electron is described by the $1s_A$ orbital on one side and by the $1s_B$ orbital on the other side of the operator. The electron changes or exchanges position in the molecule.

K The Exchange Integral ()

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 6.7.8) and H_{AB} (Equation 6.7.9) and substituting into Equation 6.7.7 produces:

$$E_{\pm} = \frac{1}{1 \pm S}\left[\left(E_H + \frac{e^2}{4\pi\epsilon_0 R}\right)(1 \pm S) + J \pm K\right] \tag{6.7.10}$$

$$= E_H + \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{6.7.11}$$

Equation 6.7.11 tells us that the energy of the H_2^+ molecule is the energy of a hydrogen atom plus the repulsive energy of two protons plus some additional electrostatic interactions of the electron with the protons. These additional interactions are given by the last term

$$\frac{J \pm K}{1 \pm S}.$$

If the protons are infinitely far apart then only E_H is nonzero, which we can set to zero by subtracting off:

$$\Delta E_{\pm} = E_{\pm} - E_H \tag{6.7.12}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{6.7.13}$$

To get a chemical bond and a stable H_2^+ molecule $\Delta E_{\pm}$ must be less than zero and have a minimum, i.e. $\frac{J \pm K}{1 \pm S}$ must be sufficiently negative to overcome the positive repulsive energy of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ for some value of R. For large R, these terms are zero, and for small R, the **Coulomb repulsion of the protons rises to infinity.**

? Exercise 9.4.2

Show that Equation 9.2.1 follows from Equation 6.7.7

6.7.1: 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

$$J_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_A}(r)\frac{e^2}{4\pi\epsilon_0 r_B}d\tau \tag{6.7.14}$$

$$K_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_B}(r)\frac{e^2}{4\pi\epsilon_0 r_A}d\tau \tag{6.7.15}$$

Figure 9.4.2 shows graphs of the four terms contributing to the energy of H_2^+ (Equation 6.7.13). In Figure 9.4.2 , you can see that as the internuclear distance R approaches zero,

- the Coulomb repulsion of the two protons goes from near zero to a large positive number,
- the overlap integral goes for zero to one, and
- J and K become increasingly negative.

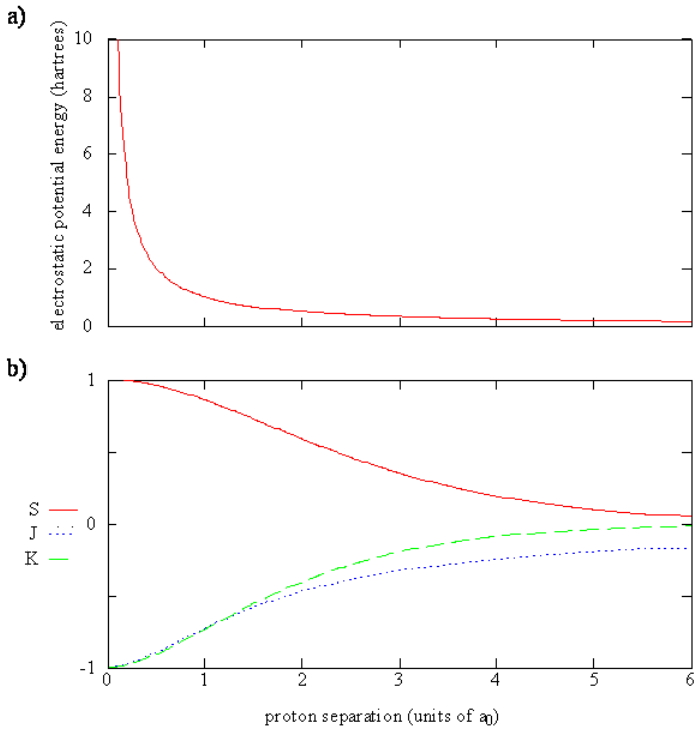


Figure 9.4.2 : (a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance R in units of the Bohr radius (52.92 pm). (b) The overlap (S), Coulomb (J), and exchange (K) integrals at different proton separations. The units for J and K are hartrees; S has no units. (CC BY-SA-NC; David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski via ChemEdDL)

Note that both J and K integrals are **negative** since all quantities in the integrands of Equation 6.7.14 and 6.7.15 are positive. In the Coulomb integral, $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the charge density of the electron around proton A, since **r** represents the coordinates of the electron relative to proton A. Since r_B is the distance of this electron to proton B, the Coulomb integral gives the potential energy of the charge density around proton A interacting with proton B. J can be interpreted as an average potential energy of this interaction because $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the probability density for the electron at point r, and $\frac{e^2}{4\pi\epsilon_0 r_B}$ is the potential energy of the electron at that point due to the interaction with proton B. Essentially, J accounts for the attraction of proton B to the electron density of hydrogen atom A. As the two protons get further apart, this integral goes to zero because all values for r_B become very large and all values for $1/r_B$ become very small.

In the **exchange integral**, K, the product of the two functions is nonzero **only** in the regions of space where the two functions overlap. If one function is zero or very small at some point then the product will be zero or small. The exchange integral also approaches zero as internuclear distances increase because the both the overlap and the $1/r$ values become zero. The product $e\varphi^*_{1s_A}(r)\varphi_{1a_B}(r)$ is called the *overlap charge density*. Since the overlap charge density is significant in the region of space between the two nuclei, it makes an important contribution to the chemical bond. The exchange integral, K, is the potential energy due to the interaction of the overlap charge density with one of the protons. While J accounts for the attraction of proton B to the electron density of hydrogen atom A, K accounts for the added attraction of the proton due the build-up of electron charge density between the two protons.

? Exercise 9.4.3

Write a paragraph describing in your own words the physical significance of the Coulomb and exchange integrals for H_2^+.

Figure 9.4.3 shows the energy of H_2^+ relative to the energy of a separated hydrogen atom and a proton as given by Equation 6.7.11. For the electron in the ψ_- orbital, the energy of the molecule, $E_{el}(R)$, **always** is greater than the energy of the separated atom and proton.

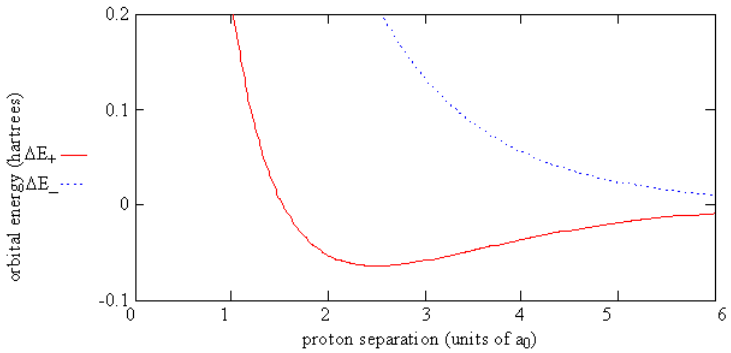


Figure 9.4.3 : Energy of the H_2^+ bonding molecular orbital ΔE_+ and the molecular orbital ΔE_-, relative to the energy of a separated hydrogen atom and proton.

For the electron in the ψ_+ orbital, you can see that the big effect for the energy of the bonding orbital, $E_+(R)$, is the balance between the repulsion of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ and J and K, which are both negative. J and K manage to compensate for the repulsion of the two protons until their separation is less than 100 pm (i.e the energy is negative up until this point), and a minimum in the energy is produced at 134 pm. This minimum represents the formation of a chemical bond. The effect of S is small. It only causes the denominator in Equation 6.7.11 to increase from 1 to 2 as R approaches 0.

For the antibonding orbital, $-K$ is a positive quantity and essentially cancels J so there is not sufficient compensation for the Coulomb repulsion of the protons. The effect of the -K in the expression, Equation 6.7.11, for E_- is to account for the absence of overlap charge density and the enhanced repulsion because the charge density between the protons for ψ_- is even lower than that given by the atomic orbitals.

Contributors and Attributions

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

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6.8: Bonding and Antibonding Orbitals

Learning Objectives

- Characterize the bonding and anti-bonding molecular orbitals in $\mathbf{H^+}$

The two molecular orbitals of the $\mathbf{H^+}$ ion were created via the linear combinations of atomic orbitals (LCAOs) approximation were created from the sum and the difference of two atomic orbitals. Within this approximation, the jth molecular orbital can be expressed as a linear combination of many atomic orbitals $\{\phi_i\}$:

$$|\psi_J\rangle = \sum_i^N c_{J,i} \Big| \phi_i \rangle \tag{6.8.1}$$

A molecule will have as many molecular orbitals as there are atomic orbitals used in the basis set (N in Equation 6.8.1). 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).

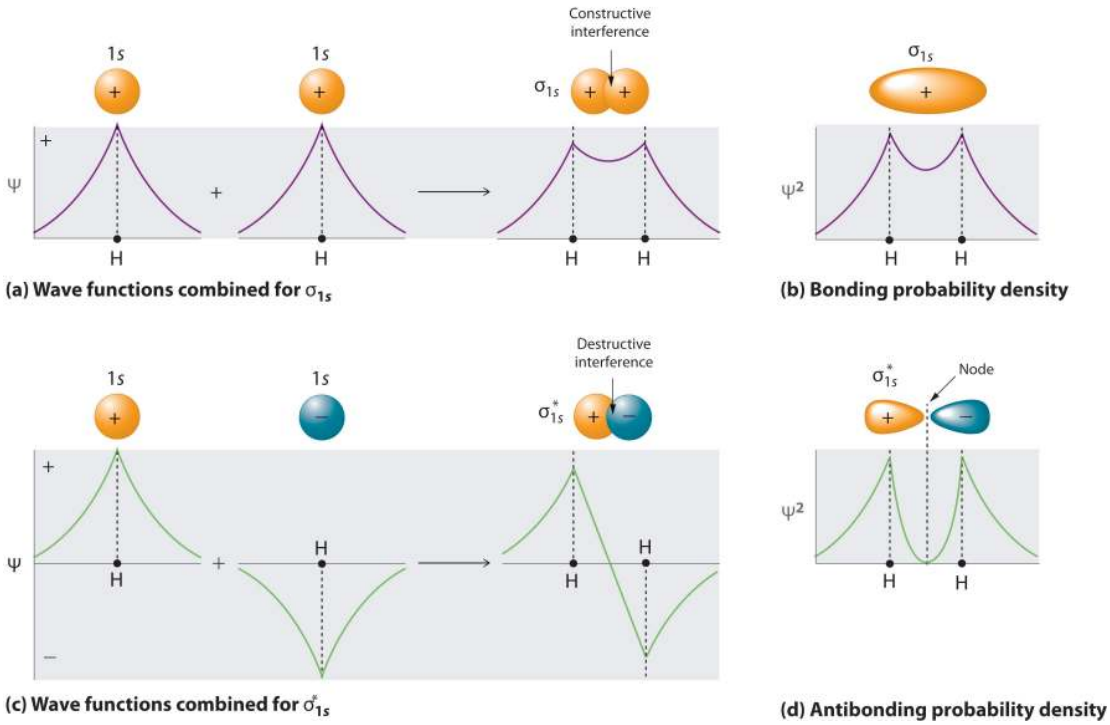


Figure 9.5.1 : Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wavefunctions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wavefunction (Ψ^2) for the bonding σ1s molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wavefunction.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the atomic orbital wavefunctions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wavefunction (Ψ2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei. (CC BY-SA-NC; anonymous).

In the sigma (σ) orbital, the electron density along the internuclear axis and between the nuclei has *cylindrical symmetry*; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived.

$$|\sigma_{1s}\rangle = \frac{1}{\sqrt{2(1+S)}} \left(|1s_A\rangle + |1s_B\rangle\right) \tag{6.8.2}$$

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:

$$|\sigma^*_{1s}\rangle = \frac{1}{\sqrt{2(1-S)}}\left(|1s_A\rangle - |1s_B\rangle\right) \tag{6.8.3}$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wavefunctions. In contrast, electrons in the 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 wavefunctions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 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

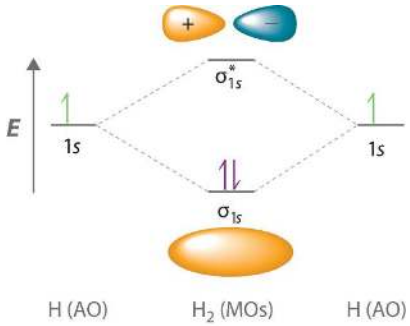


Figure 9.5.2 : Molecular Orbital Energy-Level Diagram for H2. The two available electrons (one from each H atom) in this diagram fill the bonding σ1s molecular orbital. Because the energy of the σ1s molecular orbital is lower than that of the two H 1s atomic orbitals, the H2 molecule is more stable (at 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).*

6.8.1: 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,

$$E_J = \frac{\left\langle \psi_J \middle| \hat{H}_{elec} \middle| \psi_J \right\rangle}{\langle \psi_J | \psi_J \rangle} \tag{6.8.4}$$

This is the variational energy using $|\psi_J\rangle$ as the trail wavefunction. After substituting the LCAO expansion for $|\psi_J\rangle$ (Equation 6.8.1) into the energy expression of Equation 6.8.4 results in:

$$E_J = \frac{\left\langle \sum_i c_{J,i}^* \phi_i \middle| \hat{H}_{elec} \middle| \sum_j c_{J,i} \phi_j \right\rangle}{\left\langle \sum_i c_{J,i}^* \phi_j \middle| \sum_j c_{J,j} \phi_j \right\rangle} \tag{6.8.5}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} \langle \phi_i | \hat{H}_{elec} | \phi_j \rangle}{\sum_{i,j} c_{J,i}^* c_{J,j} \langle \phi_i | \phi_j \rangle} \tag{6.8.6}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} H_{ij}}{\sum_{i,j} c_{J,i}^* c_{J,j} S_{ij}} \tag{6.8.7}$$

where H_{ij} is the Hamiltonian matrix element.

$$H_{ij} = \langle \phi_i \left| \hat{H}_{elec} \right| \phi_j \rangle$$

Following the variational theorem, to determine the coefficients of the LCAO expansion c_i, we need to minimize E_J

$$\frac{\partial E_J}{\partial c_k} = 0 \tag{6.8.8}$$

for all k. This requires solving N linear equations to hold true (where N is the number of atomic orbitals in the basis)

$$\sum_{i=1}^{N} c_i (H_{ki} - E S_{ki}) = 0 \tag{6.8.9}$$

These equations are the **secular equations** and were discussed previously in the context of the linear variational method approximation. For the two basis set expansion (N) in Figure 9.5.1 , these are

$$\begin{aligned} c_1(H_{11} - E S_{11}) + c_2(H_{12} - E S_{12}) &= 0 \\ c_1(H_{12} - E S_{12}) + c_2(H_{22} - E S_{22}) &= 0 \end{aligned} \tag{6.8.10}$$

where c_1 and c_2 are the coefficients in the linear combination of the atomic orbitals used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

$$\begin{pmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} \\ H_{12} - E S_{12} & H_{22} - E S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{6.8.11}$$

Solving these secular equations with N different atomic orbitals in the expansion (Equation 6.8.1) requires finding the N roots of an N order polynomial.

$$\begin{vmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} & \ldots \\ H_{12} - E S_{12} & H_{22} - E S_{22} & \ldots \\ \ldots & \ldots & \ldots \end{vmatrix} = 0 \tag{6.8.12}$$

Each molecular orbital ($|\psi_J\rangle$) from this treatment has an energy E_J that is given by a different set of coefficients, $\{c_{ij}\}$ where i runs over all N functions in the basis (i.e., number of the atomic orbitals in the LCAO approximation of Equation 6.8.1), 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 6.8.1), 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

$$|\psi_J\rangle = c_{J,1}1s_A + c_{J,2}1s_B + c_{J,3}2s_A + c_{J,4}2s_B + c_{J,5}2p_{z,A} + c_{J,6}2p_{z,B} \tag{6.8.13}$$

The reasons that only the p_z atomic orbitals are included in this expansion are discussed later.

Contributors and Attributions

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

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6.9: 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.

$$|\psi_i\rangle = \sum_j c_{ij}\varphi_j \tag{6.9.1}$$

where

- j is the index for the j^{th} basis function (e.g., atomic orbital)
- i is the i^{th} molecular orbitals and
- c_{ij} is the expansion coefficient of the j^{th} basis function for the i^{th} 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,

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_A(r_1)\alpha(1) & \psi_B(r_1)\beta(1)\\ \psi_A(r_2)\alpha(2) & \psi_B(r_2)\beta(2)\end{vmatrix} \tag{6.9.2}$$

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 .

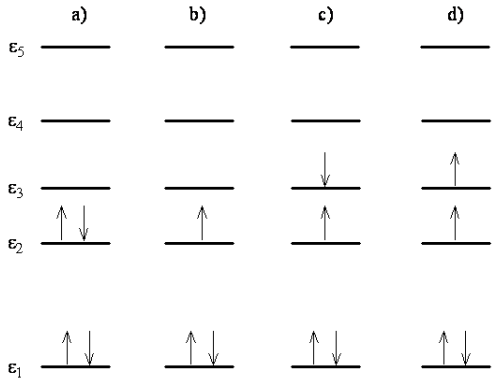


Figure 9.6.1 : a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration.

6.9.1: 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

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 \tag{6.9.3}$$

Contrasting LCAO with other Quantum Chemistry Methods

As we have already seen, the LCAO approach is very approximate, yielding only qualitative results. It should be noted that the Hartree-Fock method discussed earlier for atoms can also be used for molecules. For example, the molecule He_2^+ has three electrons, and the Li atom also has three electrons. As usual with Hartree-Fock, the idea is to optimize the shapes of the single-electron orbitals $\psi_1(r)$, $\psi_2(r)$ and $\psi_3(r)$ by minimizing the guess to the ground state energy E_g. Of course, we will not get the same answer as for Li because there is a different V_{en} energy for He_2^+ due to the presence of two positively charge nuclei $(charge = +2e)$ separated by a distance R in contrast to the single $+3e$ charged nucleus for Li. When the shapes of the orbitals are optimized, we also obtain three energy ε_1, ε_2 and ε_3. Not unexpectedly, we find that two of the HF orbitals resemble $1\sigma_g$ while the third resembles $1\sigma_u^*$ and the first two energies ε_1 and ε_2 will be nearly equal, while the third ε_3 will be noticeably higher. To contrast with the LCAO approach, in LCAO, we do not optimize the shapes of the orbitals (these are assumed *a priori* to be $1s$ shaped). All we do is choose the mixing coefficients so as to minimize the guess to the ground-state energy E_g.

We note, finally, that the density functional theory alluded to earlier can also be used for molecules. It is often the case that density functional theory yields a more accurate description than Hartree-Fock, but this depends on the molecule. In any case, both are more accurate than LCAO. There is also a hierarchy of methods called *post Hartree-Fock* methods, all of which are based on the wavefunction rather than the electron density, that can be used to improve upon the HF approximation systematically. The greater the accuracy that is desired for the calculation, the more costly computationally the post HF methods become, so quantum chemistry is often a trade-off between accuracy and efficiency, an issue that becomes more critical to take into account when calculations on large molecules must be carried out!

Contributors and Attributions

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

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6.10: 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.

6.10.1: Molecular Orbitals Formed from *ns* Orbitals

The molecular orbitals diagrams formatted for the dihydrogen species are similar to the diagrams to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 9.7.1 , where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

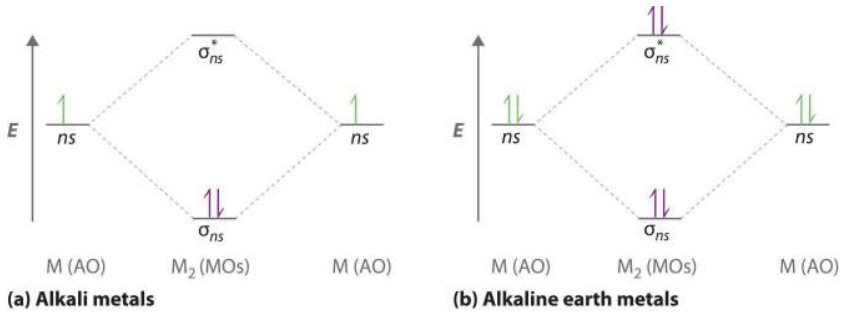


Figure 9.7.1 : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σns (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ^*_{ns} (nonbonding) levels, leading to a predicted bond order of 0. (CC BY-SA-NC; anonymous).

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule. As shown in Figure **6.10.1*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.

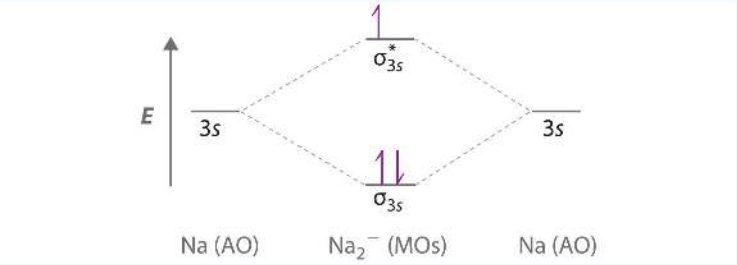
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

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.

6.10.2: 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.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{6.10.1}$$

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 wavefunctions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{6.10.2}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{6.10.3}$$

In this combination, shown in part (b) in Figure 9.7.2 , the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

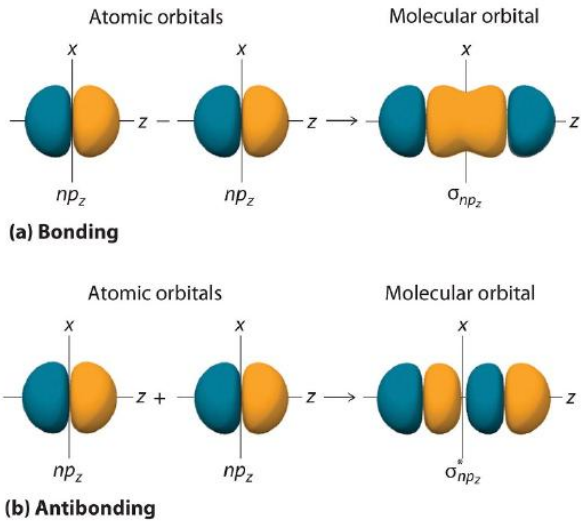


Figure 9.7.2 : Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the z-axis always corresponds to the internuclear axis, with +z to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 9.7.3 , we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_z} = np_x\,(A) + np_x\,(B) \tag{6.10.4}$$

$$\pi^*_{np_z} = np_x\,(A) - np_x\,(B) \tag{6.10.5}$$

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.

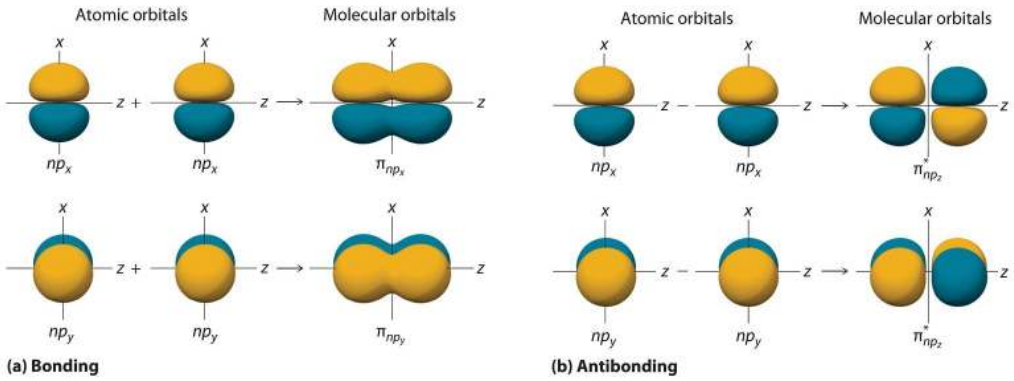


Figure 9.7.3 : Formation of π Molecular Orbitals from npx and npy Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the npx and the npy atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In 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).

6.10.3: Energies for Homonuclear Diatomic Molecules

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

Figure 9.7.4 is an energy-level diagram that can be applied to two *identical* interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

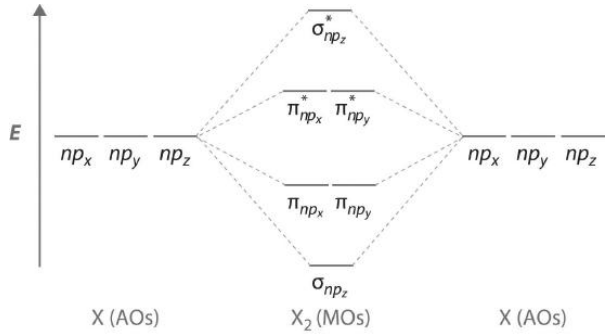


Figure 9.7.4 : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals. (CC BY-SA-NC; anonymous).

> *The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.*

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in Figure **6.10.5*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.

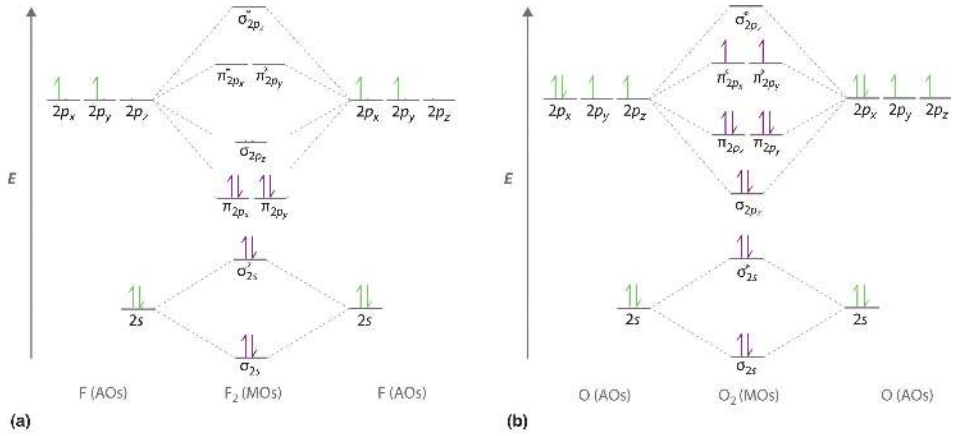


Figure 9.7.5 : Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For C_2, with 8 valence electrons (4 from each F atom). This diagram shows 6 electrons in bonding orbitals and 2 in antibonding orbitals, resulting in a bond order of 2. (b) For O_2, with 12 valence electrons (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).

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.

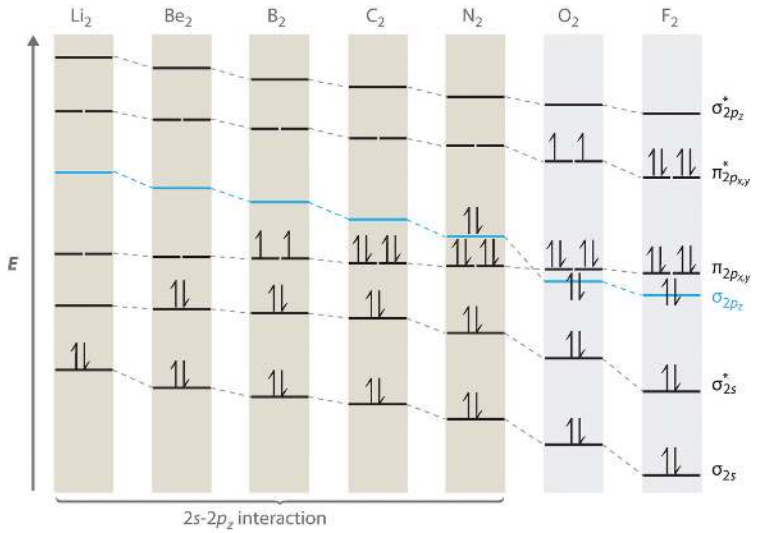


Figure 9.7.6 : Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For 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 2s and 2*p* atomic orbitals as the nuclear charge increases across the row. (CC BY-SA-NC; anonymous).

Example 9.7.2 : Diatomic Sulfur

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

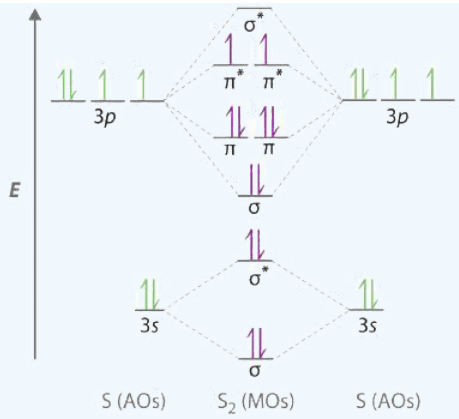
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^23p^4$ 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 $\pi_{3p_{z,y}}$ 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 $\pi_{3p_{z,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



(CC BY-SA-NC; anonymous).

Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_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) ÷ 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

6.10.4: Molecular Orbitals Formed from *ns* with n*p* Orbitals

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 9.7.7 , the sum of the two atomic wavefunctions (*ns* + np_z) produces a σ bonding molecular orbital. Their difference (*ns* − np_z) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

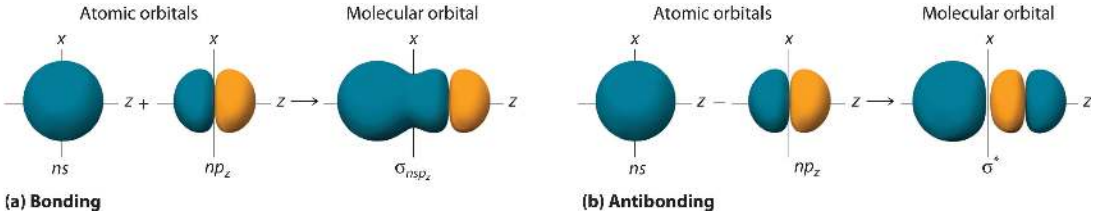


Figure 9.7.7 : Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous).

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6.11: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

Learning Objectives

- Using bond order as a metric for the existance of molecules

6.11.1: 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:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \tag{6.11.1}$$

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

$$\text{bond order} = \frac{2-0}{2} = 1 \tag{6.11.2}$$

This result corresponds to the single covalent bond; double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams to describe the bonding in other pairs of atoms and ions where n = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's Rules.

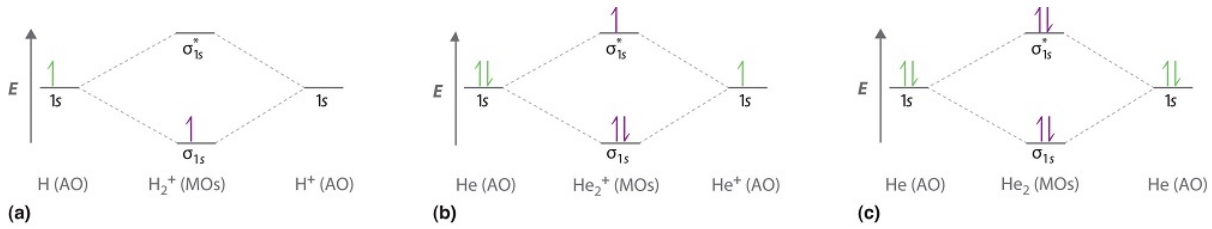


Figure 9.8.1 : Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here. (CC BY-SA-NC; anonymous)

Figure **6.11.1***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 6.11.1)

$$\text{bond order} = \frac{1-0}{2} = 1/2$$

Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 9.8.1 , these predictions agree with the experimental data.

Table 9.8.1 : Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Species	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma^*_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2$	0	5,500	4.6×10^{-5}

Figure 6.11.1*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 6.11.1) of

$$\text{bond order} = \frac{2-1}{2} = 1/2$$

As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 9.8.1).

He_2^{2+} ✔ Example 9.8.1 : The ion

Use a molecular orbital energy-level diagrams to predict the bond order and stability of the He_2^{2+} ion.

Given: chemical species

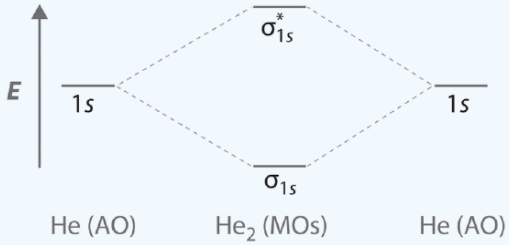
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

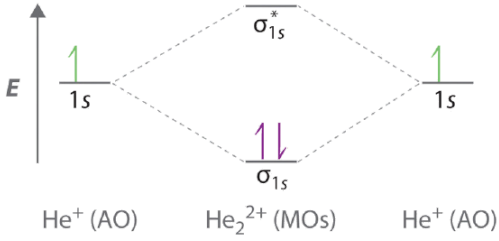
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning 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 6.11.1)

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

H_2^{2-}? Exercise 9.8.1 : The 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 $(\sigma_{1s})^2(\sigma_{1s}^\star)^2$ with a bond order of 0. It is therefore predicted to be unstable.

6.11.2: The Helium Dimer

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure 6.11.1*c* is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and $\sigma_{1s}^\star$ antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^\star)^1$ electron configuration, with a predicted bond order (via Equation 6.11.1) of

$$\text{bond order}=\frac{2-2}{2}=0 \tag{6.11.3}$$

which indicates that the He_2 molecule has no net covalent bond and is not a stable species.

The ability to track bond order to bond strength is due to the fact that the energy difference between the anti-bonding $\sigma_{1s}^\star$ molecular orbital and the original $1s$ atomic orbital is *larger* than the energy difference between the bonding σ_{1s} molecular orbital and the $1s$ atomic orbitals. This was derived previously where the stabilization energy (ΔE_+) of the σ_{1s} molecular orbital is less than the destabilization energy (ΔE_-) of the anti-bonding $\sigma_{1s}^\star$ molecular orbital:

$$\Delta E_\pm = E_\pm - E_H \tag{6.11.4}$$

$$= \frac{e^2}{4\pi\epsilon_0 R}+\frac{J\pm K}{1\pm S} \tag{6.11.5}$$

Hence, the anti-bonding $\sigma_{1s}^\star$ molecular orbital is more destabilized relative to the atomic orbitals than the bonding σ_{1s} molecular orbital is stabilized relative to the $1s$ atomic orbitals (E_H.

The fact that the anti-bonding MO energy difference is larger than the bonding σ_{1s} molecular orbital energy difference is the true reason that helium dimer is not predicted to exist with a covalent bond. Of the four valence electrons in helium dimer, two will fill the bonding σ_{1s} molecular orbital, and the other two will fill the anti-bonding $\sigma_{1s}^\star$ molecular orbital. The two electrons in the bonding σ_{1s} molecular orbital will achieve some stabilization relative to the $1s$ atomic orbitals, but the two electrons in the anti-bonding $\sigma_{1s}^\star$ molecular orbital will achieve *greater* de-stabilization relative to their position in the atomic orbitals. The net result is a less stable molecule than if the electrons remained in their respective $1s$ atomic orbitals.

> *The electrons in antibonding orbitals cancel (and exceed) the stabilization resulting from electrons in bonding orbitals. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature (at least as a covalently bonding complex).*

However, Van der Waals Helium Dimers do exist

Based on molecular orbital theory discussed above, the He_2 molecule should not exist since no covalent bond formed between the helium atoms (Equation 6.11.3). However, the molecular orbital description above neglects the van der Waals force that exists between the atoms as demonstrated by the existence of liquid helium (at 4 K). So a "molecule" composed of two helium atoms bound by the van der Waals force may exist by this attractive force instead - and it does.

A helium dimer molecule bound by Van der Waals forces was first proposed by John Clarke Slater in 1928 and observed in 1993 by Gentry and coworkers. Interestingly, $\mathbf{He_2}$ 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 $\mathbf{He—He}$ bond is 5,000 times weaker than the covalent bond in the hydrogen molecule (Table 9.8.1).

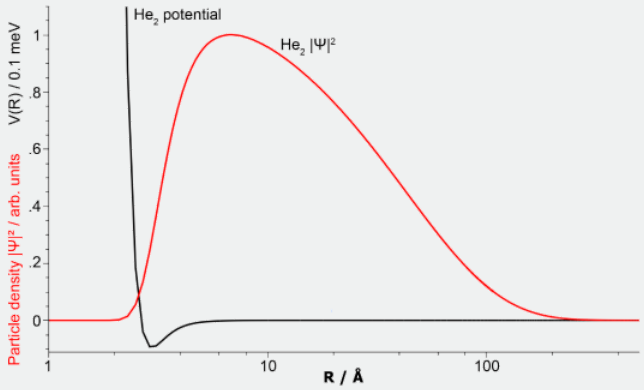


Figure 9.8.2 : The weak helium-helium Van der Waals potential decrease leads to the particle probability density distribution leaking more into the classically forbidden region (i..e, tunneling). This effect allows the wavefunction to extend to sizes of fullerenes, the diameter of DNA and even small viruses ($\mathbf{He_2}$ 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)

6.11.3: 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.

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6.12: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle

Just like with multielectron atoms, there are restrictions on how electrons occupy molecular orbitals. The most important of these rules is the Pauli exclusion principle, which we will not try to prove but will take as a fact. In general chemistry, you were told that the Pauli exclusion principle means that electrons in the same orbital must have opposite spin, and that only two electrons can be in each orbital. That is close, but not entirely accurate. The true statement of the Pauli exclusion principle is this: wavefunctions must be antisymmetric with respect to exchange of identical fermions, and symmetric with respect to exchange of identical bosons. A is a particle with half-integer spin, and a is a particle with integer spin. Recall that electrons are fermions (spin 1/2): we represent the two possible spin states as $|\alpha\rangle$ ($m_z = 1/2$) and $|\beta\rangle$ ($m_z = -1/2$), according to their spin projections.

Because all electrons are identical, the Pauli exclusion principle requires that the electronic wavefunction be antisymmetric with respect to exchanging any of them.[2] The word "antisymmetric" in this context means that if we swap two electrons (i.e., exchange their labels), the wavefunction must change sign. To denote both the orbital of an electron and its spin, we use a product of , each of the form $|\psi\sigma\rangle$, where ψ depends only on the spatial coordinates of the electrons, and σ depends only on their spins.

In the ground electronic state of , the electrons both occupy the $|1\sigma\rangle$ spatial orbital. Naively, we could write the following product of spin orbitals:

$$|\psi\rangle = |1\sigma^1\alpha^1\rangle|1\sigma^2\beta^2\rangle \tag{6.12.1}$$

where the superscript refers to the electron number. Note that since the spatial and spin coordinates are independent of one another, we can group them into kets in whichever way is most convenient for us at the time. Let us define the permutation operator $\hat{p}_{12}$, which swaps the labels of electrons 1 and 2, in order to test the wavefunction for asymmetry in accordance with the **Pauli Exclusion Principle**. It is clear that the electronic wavefunction we wrote above does not change sign under this permutation operation!

$$\hat{p}_{12}|\psi\rangle = |1\sigma^2\alpha^2\rangle|1\sigma^1\beta^1\rangle \neq -|\psi\rangle. \tag{6.12.2}$$

Instead, we can take a linear combination of spin functions to make a new wavefunction:

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle - |1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle\right) \tag{6.12.3}$$

Since the Hamiltonian did not contain any terms that depend on spin, the energy of this new wavefunction is equal to the energy of our original wavefunction.[3] We can use the permutation operator $\hat{p}_{12}$ to see that this wavefunction is in fact antisymmetric:

$$\begin{aligned}\hat{p}_{12}|\psi\rangle &= \frac{1}{\sqrt{2}}\left(|1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle - |1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle\right)\\ &= -\frac{1}{\sqrt{2}}\left(|1\sigma^1\alpha^1 1\sigma^2\beta^2\rangle - |1\sigma^2\alpha^2 1\sigma^1\beta^1\rangle\right)\\ &= -|\psi\rangle.\end{aligned} \tag{6.12.4}$$

We see here that the orbital is not occupied by one electron of each spin, but in fact it is occupied electrons in a superposition of spin states. In larger systems, antisymmetrized wavefunctions show that each orbital is occupied by a superposition of all electrons in the system in both spin states. Although that is difficult to conceptualize, in most practical cases the electrons can still be thought of as localized in one particular orbital with one particular spin.

There is a standard procedure to generate an appropriately antisymmetrized electronic wavefunction from any set of single-electron functions. Like in multi-electron atoms, the general method for doing this is by use of a Slater determinant: a determinant in which each column contains the product of one molecular orbital and spin function for each possible labeling of the electrons. For our system above (two electrons in $|1\sigma\rangle$, one with spin α, and the other with spin β), we would write

$$|\psi\rangle = \frac{1}{\sqrt{2!}}\begin{vmatrix} |1\sigma^1\alpha^1\rangle & |1\sigma^1\beta^1\rangle \\ |1\sigma^2\alpha^2\rangle & |1\sigma^2\beta^2\rangle \end{vmatrix}, \tag{6.12.5}$$

where once again the superscript indicated the label on the electron. The Slater determinant therefore contains all of the possible ways that we could assign numbers to the electrons in the system.

Note

A few things to know about Slater determinants:

- If two columns are swapped, the determinant changes sign (this is why it satisfies the exclusion principle!).
- If any two columns in a determinant are the same, the determinant is 0. This is why the Pauli exclusion principle only allows one electron of each spin to occupy a single orbital, which you learned way back in Gen Chem. It also directly leads to the "Aufbau" principle: when populating molecular orbitals, we fill up orbitals in order of increasing energy with two electrons each.
- The energy of a Slater determinant (in the independent particle approximation) is simply the sum of the orbitals that make it up (i.e., add up the energy of each electron in the MO diagram).
- The wavefunction described by a Slater determinant is normalized if the individual orbitals that make it up are normalized.
- Two Slater determinants are orthogonal if they differ in any single orbital.

Given an MO diagram, it is easy to generate a Slater determinant for the ground electronic state of a closed-shell molecule using general chemistry rules: the Aufbau principle and the Pauli exclusion principle. Each orbital can accommodate one electrons of each spin, and electrons are placed into orbitals from lowest to highest energy. A system with N electrons in the orbitals $|\phi_1\rangle$, $|\phi_2\rangle$, etc., will generate an $N \times N$ dimensional Slater determinant, and the general form is (if N is even):

$$|\psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\phi_1^1\alpha^1\rangle & |\phi_1^1\beta^1\rangle & |\phi_2^1\alpha^1\rangle & |\phi_2^1\beta^1\rangle & \cdots & |\phi_{N/2}^1\alpha^1\rangle & |\phi_{N/2}^1\beta^1\rangle \\ |\phi_1^2\alpha^2\rangle & |\phi_1^2\beta^2\rangle & |\phi_2^2\alpha^2\rangle & |\phi_2^2\beta^2\rangle & \cdots & |\phi_{N/2}^2\alpha^2\rangle & |\phi_{N/2}^2\beta^2\rangle \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ |\phi_1^N\alpha^N\rangle & |\phi_1^N\beta^N\rangle & |\phi_2^N\alpha^N\rangle & |\phi_2^N\beta^N\rangle & \cdots & |\phi_{N/2}^N\alpha^N\rangle & |\phi_{N/2}^N\beta^N\rangle \end{vmatrix} \tag{6.12.6}$$

Once again, each column contains the orbital and spin state of one of the electrons in the diagram, and each row in the column corresponds to a different choice of label (1, 2, 3, etc...). Evaluating the determinant yields a normalized, antisymmetrized wavefunction. Therefore, an MO diagram can stand as an effective substitute for an electronic wavefunction; it is implied that the true wavefunction used in calculations comes from the Slater determinant described by the diagram.

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6.13: Diatomic Molecules of the First and Second Periods

First Period Homonuclear Diatomic Molecules

In the first row of the periodic table, the valence atomic orbitals are $1s$. There are two possible homonuclear diatomic molecules of the first period:

Dihydrogen, H_2 [$\sigma_g^2(1s)$]: This is the simplest diatomic molecule. It has only two molecular orbitals (σ_g and σ_u^*), two electrons, a bond order of 1, and is diamagnetic. Its bond length is 74 pm. MO theory would lead us to expect bond order to decrease and bond length to increase if we either add or subtract one electron. The calculated bond length for the H_2^+ ion is approximately 105 pm.[1]

Dihelium, He_2 [$\sigma_g^2\sigma_u^{*2}(1s)$]: This molecule has a bond order of zero due to equal number of electrons in bonding and antibonding orbitals. Like other nobel gases, He exists in the atomic form and does not form bonds at ordinary temperatures and pressures.

Exercise 6.13.1

Draw the complete molecular orbital diagrams for H_2 and for He_2. Include sketches of the atomic and molecular orbitals.

Answer

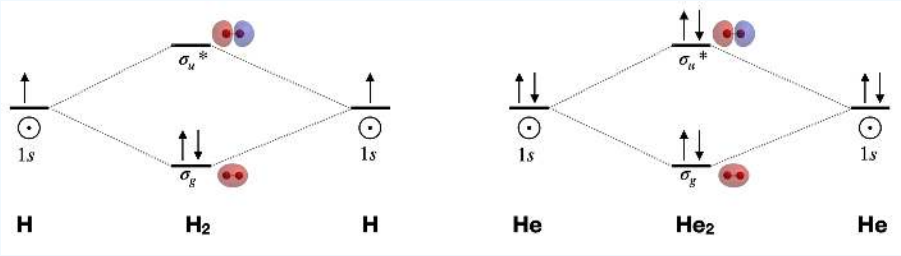


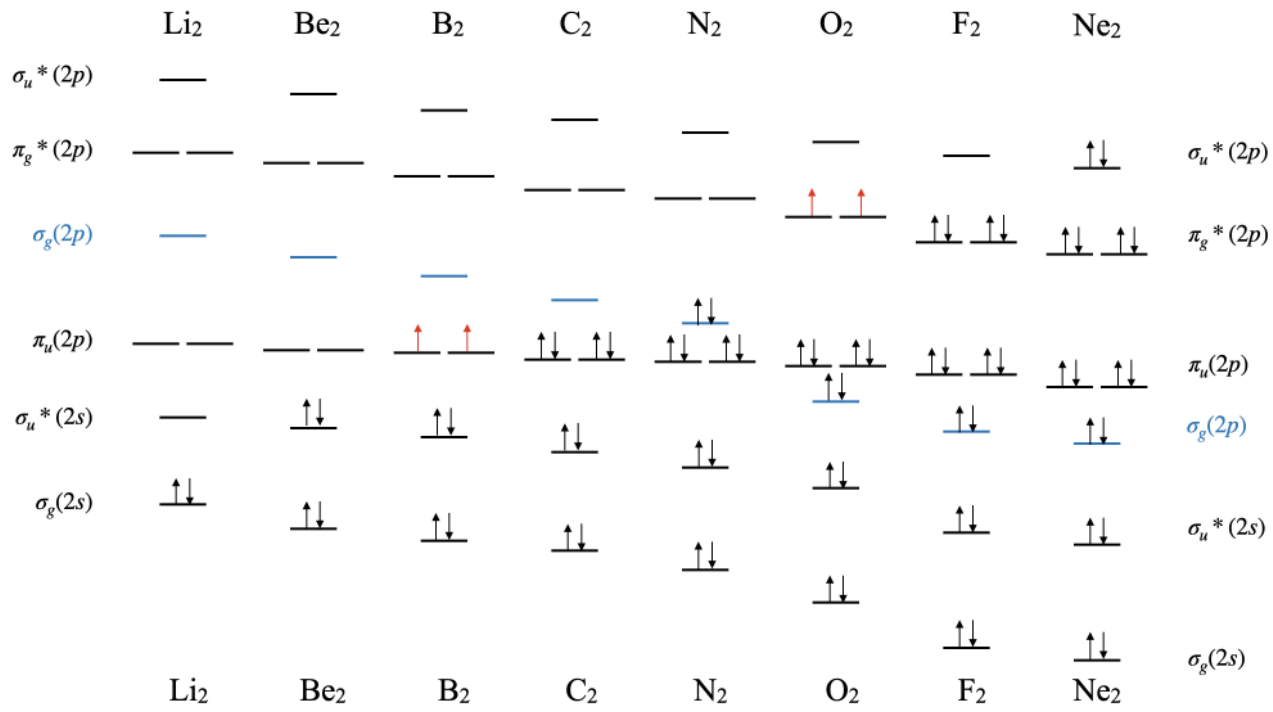
Figure for Exercise 6.13.1: Molecular orbital diagrams for dihydrogen and dihelium. Molecular orbital surfaces calculated using Spartan software. (CC-BY-NC-SA; Kathryn Haas)

A complete molecular orbital diagram includes all atomic orbitals and molecular orbitals, their symmetry labels, and electron filling.

Second Period Homonuclear Diatomic Molecules

The second period elements span from Li to Ne. The valence orbitals are 2s and 2p. In their molecular orbital diagrams, non-valence orbitals (1s in this case) are often disregarded in molecular orbital diagrams.

Orbital mixing has significant consequences for the magnetic and spectroscopic properties of second period homonuclear diatomic molecules because it affects the order of filling of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals. Early in period 2 (up to and including nitrogen), the $\pi_u(2p)$ orbitals are lower in energy than the $\sigma_g(2p)$ (see Figure 6.13.1). However, later in period 2, the $\sigma_g(2p)$ orbitals are pulled to a lower energy. This lowering in energy of $\sigma_g(2p)$ is not unique; all of the σ orbitals in the molecule are pulled to lower energy due to the increasing positive charge of the nucleus. The π orbitals in the molecule are also affected, but to a much lesser extent than σ orbitals. The reason has to do with the high penetration of s atomic orbitals compared to p atomic orbitals (recall our previous discussion on penetration and shielding, and its effect on periodic trends). The σ molecular orbitals have more s character and thus their energy is more influenced by increasing nuclear charge. As nuclear charge increases, the energy of the $\sigma_g(2p)$ orbital is lowered significantly more than the energy of the $\pi_u(2p)$ orbitals (Figure 6.13.1).



	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Unpaired e⁻	0	0	2	0	0	2	0	0
Bond Order	1	0	1	2	3	2	1	0
Experimental* Bond Length (pm)	267.3	246.0	159.0	124.3	109.8	120.8	141.2	310.0

*Experimental bond lengths from "List of Experimental Diatomic Bond Lengths", NIST, https://cccbdb.nist.gov/diatomicexpbondx.asp

Figure 6.13.1: Molecular orbital energy-level diagrams for the diatomic molecules of the period 2 elements. Unlike earlier diagrams, *only the valence molecular orbital energy levels for the **molecules** are shown here (atomic orbitals not shown for simplicity).* For Li_2 through N_2, the $\sigma_g(2p)$ orbital is higher in energy than the $\pi_u(2p)$ orbitals. In contrast, from O_2 onward, the $\sigma_g(2p)$ orbital is *lower* in energy than the $\pi_u(2p)$ orbitals because the nuclear charge increases across the row. The experimental bond lengths correlate with the calculated bond order. (CC-BY-NC-SA, Kathryn Haas)

Dilithium, Li_2 [$\sigma_g^2(2s)$]: This molecule has a bond order of one and is observed experimentally in the gas phase to have one Li-Li bond.

Diberylium, Be_2 [$\sigma_g^2\sigma_u^{*2}(2s)$]: This molecule has a bond order of zero due to the equal number of electrons in bonding and antibonding orbitals. Although Be_2 does not exist under ordinary conditions, it can be produced in a laboratory and its bond length measured (Figure 6.13.2). Although the bond is very weak, its bond length is surprisingly ordinary for a covalent bond of the second period elements.[2]

Diboron, B_2 [$\sigma_g^2\sigma_u^{*2}(2s)\pi_u^1\pi_u^1(2p)$]: The case of diboron is one that is much better described by molecular orbital theory than by Lewis structures or valence bond theory. This molecule has a bond order of one. The molecular orbital description of diboron also predicts, accurately, that diboron is paramagnetic. The paramagnetism is a consequence of orbital mixing, resulting in the σ_g orbital's being at a higher energy than the two degenerate π_u^* orbitals.

Dicarbon, C_2 [$\sigma_g^2\sigma_u^{*2}(2s)\pi_u^2\pi_u^2(2p)$]: This molecule has a bond order of two. Molecular orbital theory predicts two bonds with π symmetry, and no σ bonding. C_2 is rare in nature because its allotrope, diamond, is much more stable.

Dinitrogen, N_2 [$\sigma_g^2\sigma_u^{*2}(2s)\pi_u^2\pi_u^2\sigma_g^2(2p)$]: This molecule is predicted to have a triple bond. This prediction is consistent with its short bond length and bond dissociation energy. The energies of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals are very close, and their relative energy levels have been a subject of some debate (see next section for discussion).

Dioxygen, O_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*1}\pi_g^{*1}(2p)]$: This is another case where valence bond theory fails to predict actual properties. Molecular orbital theory correctly predicts that dioxygen is paramagnetic, with a bond order of two. Here, the molecular orbital diagram returns to its "normal" order of orbitals where orbital mixing could be somewhat ignored, and where $\sigma_g(2p)$ is lower in energy than $\pi_u(2p)$.

Difluorine, F_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*2}\pi_g^{*2}(2p)]$: This molecule has a bond order of one and like oxygen, the $\sigma_g(2p)$ is lower in energy than $\pi_u(2p)$.

Dineon, Ne_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*2}\pi_g^{*2}\sigma_u^{*2}(2p)]$: Like other noble gases, Ne exists in the atomic form and does not form bonds at ordinary temperatures and pressures. Like Be_2, Ne_2 is an unstable species that has been created in extreme laboratory conditions and its bond length has been measured (Figure **6.13.2**)

? Exercise 6.13.2

Draw the complete molecular orbital diagram for O_2. Show calculation of its bond order and tell whether it is diamagnetic or paramagnetic.

Answer

O_2 is paramagnetic with a bond order of 2. Its $\sigma_g(2p)$ molecular orbital is lower in energy that the set of $\pi_u(2p)$ orbitals.

$$\text{Bond order} = \frac{1}{2}\left[\left(\begin{array}{c}\textbf{8 electrons in}\\ \textbf{valence bonding orbitals}\end{array}\right) - \left(\begin{array}{c}\textbf{4 electrons in}\\ \textbf{valence antibonding orbitals}\end{array}\right)\right]$$

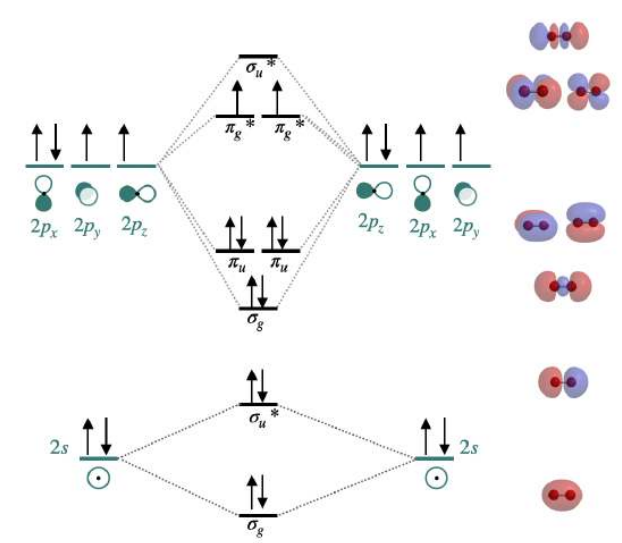


Figure for Exercise **6.13.2**. Molecular orbital diagram of O_2. (CC-BY-NC-SA, Kathryn Haas)

? Exercise 6.13.3: The Peroxide Ion

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

This diagram looks similar to that of $\mathbf{O_2}$, except that there are two additional electrons.
$(\sigma_g(2s))^2\,(\sigma_u^*(2s))^2\,(\sigma_g(2p))^2\,(\pi_u(2p))^4\,(\pi_g(2p))^4$; bond order of 1; no unpaired electrons.

Bond Lengths in Homonuclear Diatomic Molecules

The trends in experimental bond lengths are predicted by molecular orbital theory, specifically by the calculated bond order. The values of bond order and experimental bond lengths for the second period diatomic molecules are given in Figure **6.13.1**, and shown

in graphical format on the plot in Figure **6.13.2**. From the plot, we can see that bond length correlates well with bond order, with a minimum bond length occurring where the bond order is greatest ($\mathbf{N_2}$). The shortest bond distance is at $\mathbf{N_2}$ due to its high bond order of 3. From $\mathbf{N_2}$ to $\mathbf{F_2}$ the bond distance increases despite the fact that atomic radius decreases.

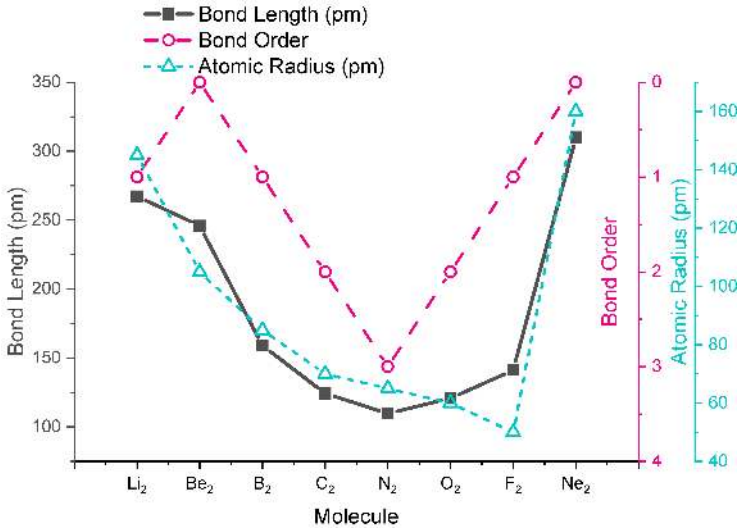


Figure **6.13.2**: Overlayed plots of bond length (black squares), bond order (pink circles), and atomic radius (teal triangles) versus atomic number for second period homonuclear diatomic molecules. (CC-BY-NC-SA; Kathryn Haas)

References

1. NIST, Calculated Geometries available for H_2^+ (Hydrogen cation) 2Σg+ D∞h, available at https://cccbdb.nist.gov/diatomicexpbondx.asp
2. Merritt, J. M.; Bondybey, V. E.; Heaven, M. C., Beryllium Dimer-Caught in the Act of Bonding. *Science* **2009,** *324* (5934), 1548-1551.

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6.14: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic

Learning Objectives

- To describe the connection between bond order, bond length and bond energy in diatomic molecules
- To explain the observed paramagnetic properties of molecular oxygen with Molecular Orbital theory

In general chemistry courses, students learn that covalent bonds can come as either single, double or triple bonds, which are identifies by their bond order. Both bond length and bond energy changes as the bond order increases and as the number of electrons shared between two atoms in a molecule increases, the bond order of a bond increases, the strength of the bond increases and the distance between nuclei decreases (Table 9.10.1).

Table 9.10.1 : General Correlation between Bond Strength, length and order in Covalent bonds

Bond	Bond Order	Bond Enthalpy (kJ/mol)	Bond Length (Å)
C–C	1	348	1.54
C=C	2	614	1.34
C≡C	3	839	1.20
N–N	1	163	1.47
N=N	2	418	1.24
N≡N	3	941	1.10

The above trend can be observed in the first row diatomics in Figure 9.10.1 . The bond order can be determined directly form the molecular orbital electron configurations. For diatomics, the occupations can correlate to bond length, bond energies (Figure 9.10.1).

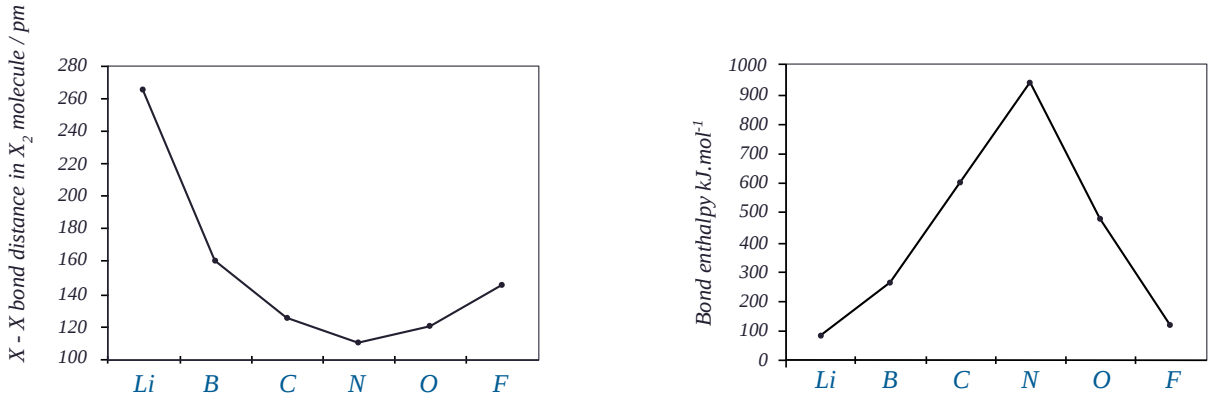


Figure 9.10.1 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

The trends in Figure 9.10.1 and Table 9.10.1 extend to molecular ions.

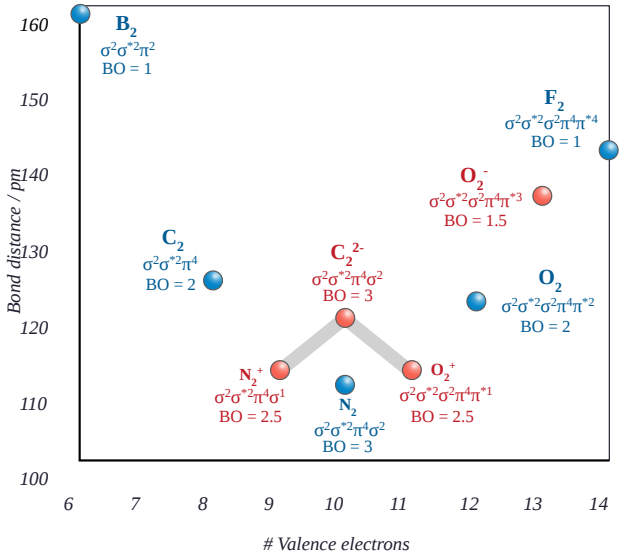


Figure 9.10.2 : Plot of bond length (left) and bond energy (right) for first row diatomics. (CC BY-NC; Ümit Kaya via LibreTexts)

Example 9.10.1 : Molecular Oxygen

Arrange the following four molecular oxygen species in order of increasing bond length: O_2^+, O_2, O_2^-, and O_2^{2-}.

Solution

The bond length in the oxygen species can be explained by the positions of the electrons in molecular orbital theory. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in Figure 9.10.1 . We again fill the orbitals according to Hund's rules and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, two more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. According to Hund's first rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving a multiplicity of 3 (a triplet state) with two unpaired electrons. This leads to a predicted bond order of

$$\frac{8-4}{2}=2$$

which corresponds to a double bond, in agreement with experimental data: the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

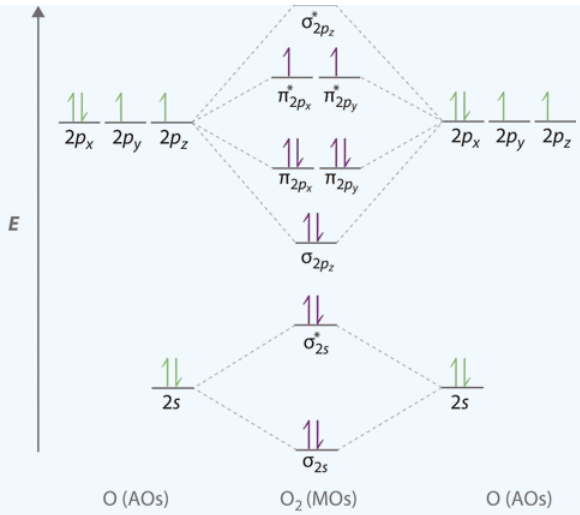


Figure 9.10.3 : Molecular Orbital Energy-Level Diagrams for O_2. With 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{np_z}, \pi^*_{np_y}\right)$ pair of orbitals. Hund's first rule dictates that one electron occupies each orbital, and their spins are 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. 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 ???, 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 ???, 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 ???, 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 ???, 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).

6.14.1: Molecular Oxygen is Paramagnetic

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. None of the other bonding models (e.g., Valence Bond theory or Lewis bonding) can predict the presence of two unpaired electrons in O_2.

Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Video 9.10.1 , it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches.



Video 9.10.1 : Liquid O_2 Suspended between the Poles of a Magnet. Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

Advanced: Spin Barriers

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*.

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6.15: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure **6.15.4**. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

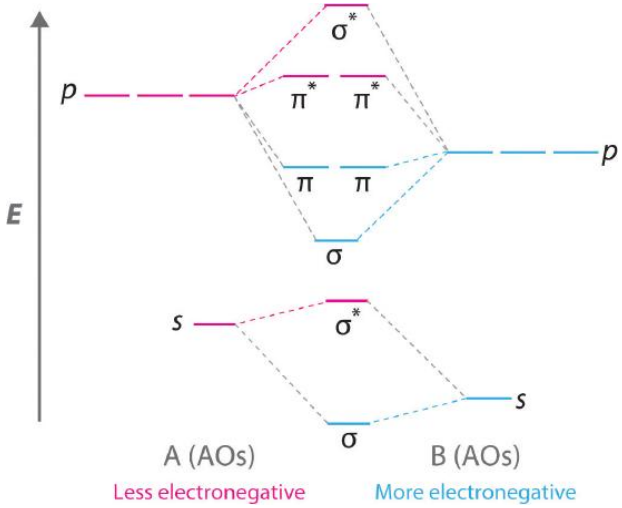


Figure **6.15.4**: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

> *A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.*

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure **6.15.13**) shows that the general pattern is similar to that for the O_2 molecule (Figure **6.15.11**). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

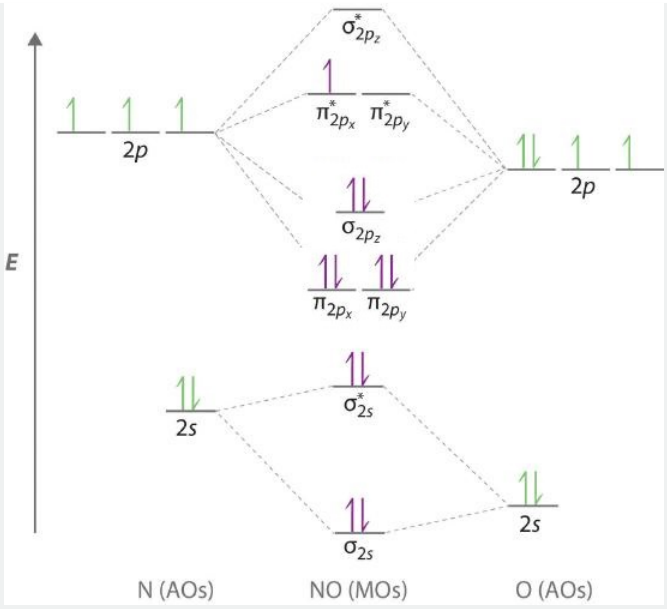


Figure **6.15.13**: Molecular Orbital Energy-Level Diagram for **NO**. Because **NO** has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_z}, \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of **NO** to be $(\sigma_{2s})^2 (\sigma^{\star}_{2s})^2 \left(\pi_{2p_{z,y}}\right)^4 (\sigma_{2p_z})^2 \left(\pi^{\star}_{2p_{z,y}}\right)^1$ in order of increasing energy. Hence, the $\pi_{2p_{z,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the **NO** molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure **6.15.11**).

Molecular orbital theory can also tell us something about the *chemistry* of ***NO***. As indicated in the energy-level diagram in Figure **6.15.13**, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, ***NO*** is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

6.15.1: Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure **6.15.6** that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+} - - Cl^{\delta-}$.

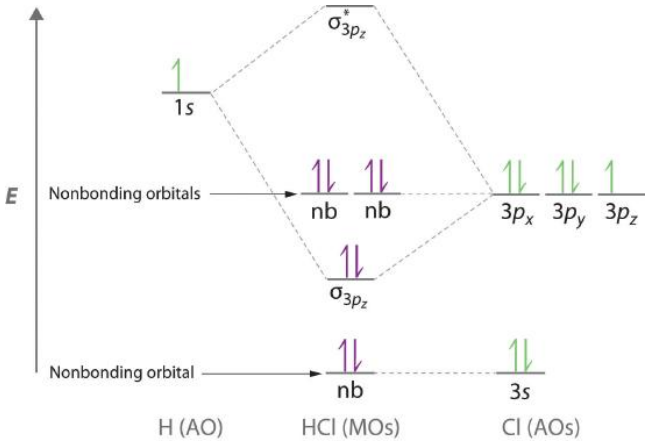


Figure **6.15.6**: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the 3p_z orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have no effect on bond order.*

Example 6.15.4: The Cyanide Ion

Use a "skewed" molecular orbital energy-level diagram like the one in Figure **6.15.4** to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

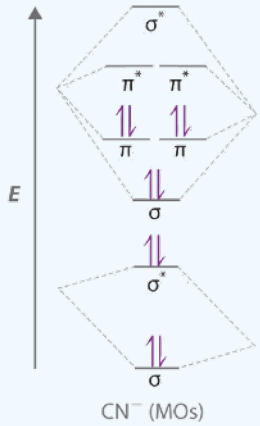
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure **6.15.4** in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure **6.15.4** fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C.

B The resulting valence electron configuration gives a predicted bond order of (8 − 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

? Exercise 6.15.4: The Hypochlorite Ion

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.



6.15.2: Summary

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

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6.16: Orbital ionization energies

To generate molecular orbital diagrams of heteronuclear diatomic molecules, we must start with a knowledge of the relative energies of electrons in different atomic orbitals. In other words, we need knowledge of the orbital potential energies (or orbital ionization energies).

Orbital Ionization Energies

There are two approaches you can use to "know" or estimate the atomic orbital energy levels.

1. Use a table of atomic orbital ionization energies, like those found in Table **6.16.1**.
2. When you do not have access to a table of values like the one below, use periodic trends in electronegativity and/or ionization energies as your guide to approximate relative values for different atoms.

Table **6.16.1**: These are one-electron ionization energies of the valence orbitals calculated by average energies of both the ground-state and ionized-state configurations. (From Harry Gray, "Electrons and Chemical Bonding," Benjamin, 1964, Appendix) Values are expressed in eV.

Atom	1*s*	2*s*	2*p*	3*s*	3*p*	4*s*	4*p*	*Atom*	3*d*	4*s*	4*p*
H	−13.64							*Sc*	−4.71	−5.70	−3.22
He	−24.55							*Ti*	−5.58	−6.08	−3.35
Li		−5.46						*V*	−6.32	−6.32	−3.47
Be		−9.30						*Cr*	−7.19	−6.57	−3.47
B		−14.01	−8.31					*Mn*	−7.93	−6.82	−3.60
C		−19.47	−10.66					*Fe*	−8.68	−7.07	−3.72
N		−25.54	−13.14					*Ni*	−10.04	−7.56	−3.84
O		−32.36	−15.87					*Cu*	−10.66	−7.69	−3.97
F		−46.37	−18.72								
Ne		−48.48	−21.57								
Na				−5.21							
Mg				−7.69							
Al				−11.28	−5.95						
Si				−15.00	−7.81						
P				−18.72	−10.17						
S				−20.71	−11.65						
Cl				−25.29	−13.76						
Ar				−29.26	−15.87						
K						−4.34					
Ca						−6.08					
Zn						−9.42					
Ga						−12.65	−5.95				
Ge						−15.62	−7.56				
As						−17.61	−9.05				
Se						−20.83	−10.79				
Br						−24.05	−12.52				
Kr						−27.52	−14.26				

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6.17: Polar bonds

Molecular orbital diagrams for heteronuclear diatomic molecules

The molecular orbital diagram of a heteronuclear diatomic molecule is approached in a way similar to that of a homonuclear diatomic molecule. The orbital diagrams may also look similar. A major difference is that the more electronegative atom will have orbitals at a lower energy level. Two examples of heteronuclear diatomic molecules will be explored below as illustrative examples.

Carbon monoxide MO diagram

Carbon monoxide is an example of a heteronuclear diatomic molecule where both atoms are second-row elements. The valence molecular orbitals in both atoms are the $2s$ and $2p$ orbitals. The molecular orbital diagram for carbon monoxide (Figure **6.17.1**) is constructed in a way similar to how you would construct dicarbon or dioxygen, except that the oxygen orbitals have a lower potential energy than analogous carbon orbitals. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial labels according to type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher energy orbitals of the same type are assigned by increasing intervals (..2, 3, 4...). The orbital labeling system described previously is inappropriate for heteronuclear diatomic molecules that cannot be assigned g and u subscripts.

A consequence of unequal atomic orbital energy levels is that orbital mixing is significant. Notice the order of the molecular orbitals labeled 1π and 3σ in Figure **6.17.1**. This is a similar order of π and σ orbitals to the one we saw in the case of the σ_g and π_u orbitals of N_2 and lighter diatomics of the second period. Because the oxygen $2p_z$ orbital is close in energy to both the carbon $2p_z$ and carbon $2s$, these three orbitals will have significant interaction (mixing). The result is an increase in the energy of the 3σ orbital and a decrease in energy of the $2\sigma^*$ orbital, resulting in the diagram shown in Figure **6.17.1**.

In the case of carbon monoxide (Figure **6.17.1**), atomic orbitals contribute unequally to each molecular orbital. For example, because the $2s$ orbital of oxygen is very close in energy to the 2σ moelcular orbital, it contributes to that molecular orbital more than the $2s$ orbital from carbon. Notice the shape of this 2σ orbital and how it is unevenly distributed over the two atoms; it is more heavily distributed on the oxygen because it is most like the oxygen $2s$. This is in line with the assumption that electron density is distributed more on oxygen because it is more electronegative than carbon. Likewise, the 1π orbitals are unevenly distributed, with more distribution close to the oxygen.

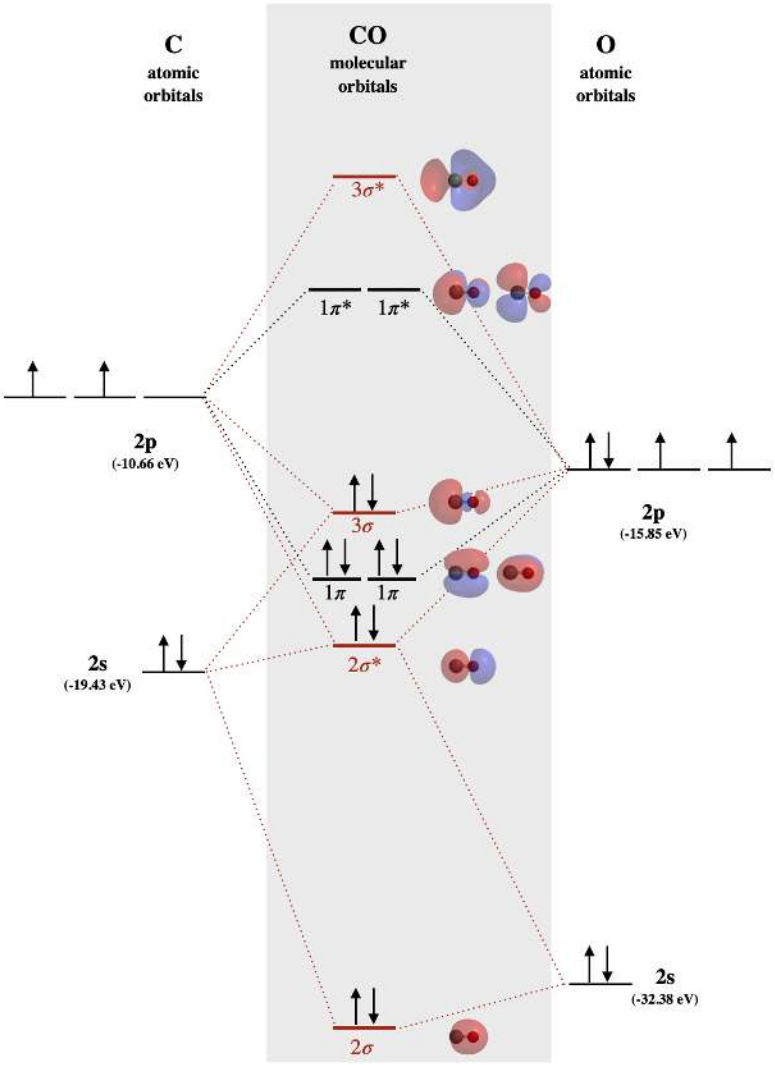
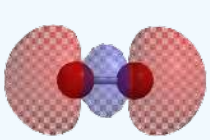


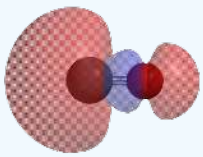
Figure 6.17.1: Molecular orbital diagram of carbon monoxide. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial names according to the type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher energy orbitals of the same type are assigned by increasing intervals (..2, 3, 4...). The orbital labeling system described previously is inappropriate for heteronuclear diatomic molecules that cannot be assigned g and u subscripts. Molecular orbital surfaces were calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

? Exercise 6.17.1

Examine the shape of the 3σ orbital of carbon monoxide in Figure 6.17.1. Describe what ways this shape is different from the shape of the σ_g orbitals from second period homonuclear diatomic molecules (see Fig. 5.2.1.1). Rationalize these differences. Both orbitals are re-created below for convenience.



σ_g of homonuclear diatomic



3σ of CO

Answer

The 3σ orbital is like the σ_g in that it has three lobes and two nodes distributed along the internuclear bond. They are different in their distribution. The two external lobes of σ_g are evenly distributed because they are an equal combination of two p_z orbitals (one from each atom). The 3σ orbital is more heavily distributed toward the carbon atom, the less electronegative atom, than toward the oxygen. The unequal distribution of 3σ is apparent in the unequal sizes of its exterior lobes and the uneven shape of the interior lobe. The heavier distribution within the exterior lobe on carbon is caused by the mixing of the carbon $2s$ orbital with carbon and oxygen $2p_z$ orbitals. The uneven shape of the interior lobe, where it leans toward oxygen, is best explained by the fact that the 3σ orbital is closer in energy to the oxygen $2p_z$ than the carbon $2p_z$.

Hydrogen fluoride MO diagram

Hydrogen fluoride is an example of a heteronuclear diatomic molecule in which the two atoms are from different periods. In this case, the valence orbital of H is $1s$ while those of F are $2s$ and $2p$. The molecular orbital diagram for HF is shown in Figure 6.17.2.

Three of these orbitals have compatible symmetry for mixing; these are the hydrogen $1s$, fluorine $2s$, and fluorine $2p$. However, the extent to which they will interact depends on their relative energies. Fluorine is more electronegative than H, and the fluorine atom has a higher first ionization energy than does hydrogen. From these trends, we can expect that the fluorine valence orbitals are lower in energy than that of hydrogen. From Table 5.3.1, we find that the 1s orbital of H (-13.6 eV) is higher in energy than both fluorine orbitals (-18.7 and -40.2 eV, respectively for $2p$ and $2s$). The energies of hydrogen $1s$ and fluorine $2p$ are a good match for combination; however, the fluorine $2s$ orbital is much too different to create a productive interaction. Therefore, we expect that the fluorine $2s$ will create a non-bonding molecular orbital, while the $1s$ and $2p_z$ orbitals combine to make σ bonding and σ^* antibonding molecular orbitals. The remaining $2p_x$ and $2p_y$ orbitals do not have compatible symmetry for bonding with hydrogen, and they will form non-bonding π molecular orbitals. The non-bonding orbitals will have similar energy and character as their component atomic orbitals.

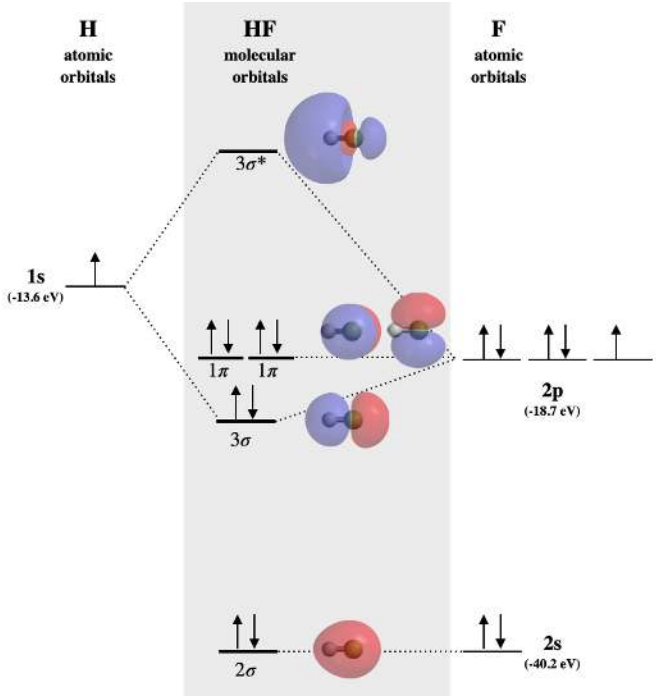


Figure 6.17.2: Molecular Orbital diagram of hydrogen fluoride. Molecular orbitals calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

Chemical reactions take place at the HOMO and LUMO orbitals

Knowledge of molecular orbital diagrams, and the shapes of molecular orbitals, can be used to accurately explain and predict chemical reactivity. Chemical reactions take place using the highest occupied molecular orbitals (HOMO) of a nucleophile or Lewis base, and the lowest unoccupied molecular orbital (LUMO) of an electrophile or Lewis acid.

> *Lewis bases react using electrons in the HOMO, while Lewis acids react using the empty LUMO.*

Example: Reactivity of CO with metal ions

CO is an excellent ligand for many metal ions. In fact, the strong affinity between CO and the heme iron (Fe) ions in hemoglobin can explain the mechanism of carbon monoxide poisoning. When CO binds in place of O_2 to hemoglobin, that hemoglobin can no longer carry O_2 to tissue cells. CO binding to hemoglobin is strong and practically irreversible. When CO binds to metal ions, it does so through the carbon atom. This is contrary to expectations based on the Lewis structure and the known bond polarity, where electron density is polarized toward oxygen. The distribution of the electron density of the HOMO of CO can explain this observation!

? Exercise 6.17.2

Refer to the MO diagram for CO. Identify the HOMO and explain why CO bonds to metal ions through the carbon atom rather than through the oxygen atom.

Answer

In the interaction between CO and a metal ion, CO would act as a Lewis base; thus it will react using electrons in its HOMO. The MO diagram for CO is shown in Figure 6.17.1: the HOMO is the 3σ orbital (also discussed in ? Exercise 6.17.1). The electron density of that MO is centered around the carbon atom, thus the carbon atom will be a better Lewis base than the O atom.

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6.18: 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.

6.18.1: 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.

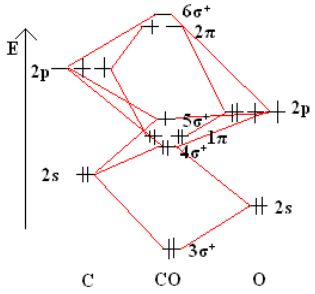
For homonuclear diatomics, the term symbol has the following form:

$$^{2S+1}\Lambda^{(+/-)}_{\Omega,(g/u)} \tag{6.18.1}$$

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.

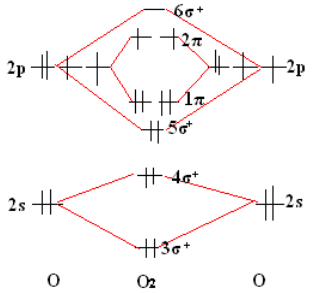
6.18.2: Determining term symbols of diatomics

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.

6.18.3: 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 $\Omega = 0 \ddagger \Omega' = 0$

6.18.4: References

1. Harris, Daniel C. (republished in 1989). *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy.* Dover Publications. pp. 421-478. ISBN 0-486-66144-X
2. D. J. Willock (2009). *Molecular Symmetry*. John Wiley & Sons Ltd. ISBN 0-470-85348-4

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6.19: 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:

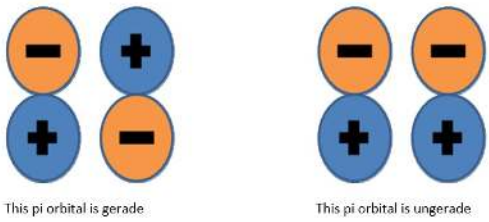
- $\Lambda = 0 \rightarrow \Sigma$
- $\Lambda = 1 \rightarrow \Pi$
- $\Lambda = 2 \rightarrow \Delta$
- $\Lambda = 3 \rightarrow \Phi$

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}.

6.19.1: Two New Symmetries: Parity and Reflection

Molecular orbitals are more complex than atomic ones and require more modifiers to completely define. **Parity** (sometimes called "inversion") tells you if the orbital is *symmetric* or *anti-symmetric* when an inversion operation is performed. The symmetry notation **u** and **g** are sometimes used when describing molecular orbitals. This refers to the operation of inversion, which requires starting at an arbitrary point in the orbital, traveling straight through the center, and then continuing outwards an equal distance from the center. The orbital is designated **g** (for gerade, even) if the phase is the same, and **u** (for ungerade, uneven) if the phase changes sign.



This pi orbital is gerade

This pi orbital is ungerade

To determine whether or not a given state is g or u, find the parity of each individual open-shell electron and uses these simple (Laporte rules):

- $g + g \rightarrow g$
- $g + u \rightarrow u$
- $u + u \rightarrow g$

Example 9.15.1: Closed Shell Configuration

What is the parity of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

Solution

Since both open shell electrons are ungerade, the overall parity is g. Helpful hint: bonding sigma orbitals and anti - bonding pi orbitals are always gerade. Anti - bonding sigmas and bonding pis are always ungerade. Draw them and see for yourself.

Reflection determines if a given orbital is symmetric or anti-symmetric upon reflection through a plane that contains both nuclei. The choice of symmetry planes is arbitrary. As long as you pick a plane and stick with it, you will always get the right answer.

When an orbital is symmetric, it is labeled +. When an orbital is anti - symmetric, it is labeled - . To find the overall reflection of a state, use these rules:

- (+)(+) \rightarrow +
- (+)(-) \rightarrow -
- (-)(-) \rightarrow +

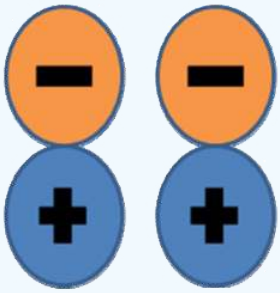
Reflection only applies to Σ states! For Λ > 0, there are no reflection labels! If you experiment with the rules, you will quickly realize why this is the case.

Example 9.15.2

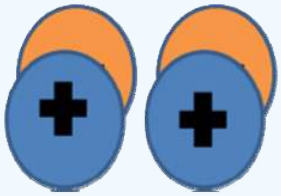
What is the reflection of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

Solution

You need to know what the orbitals look like. Draw a picture and then pick a plane. For this example, the plane of the page is selcted, but the orthogonal plane would have worked just as well.



The “vertical” orbital is +



The “horizontal” orbital is -

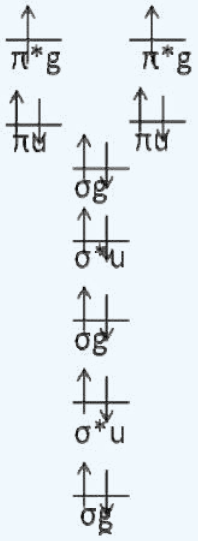
The “vertical” orbital is + The “horizontal” orbital is - Since one is + and one is - , the overall reflection is - . Try using the orthogonal plane and convince yourself that you still get the same answer.

Example 9.15.3: Oxygen

What are the term symbols for O_2 ?

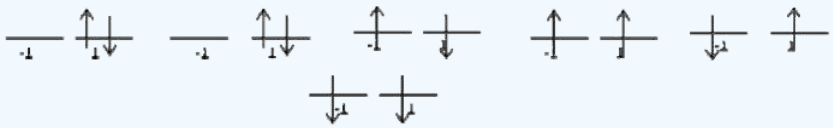
Solution

The molecular orbital diagram for O_2 is



Where I chose arbitrary configurations for the last two electrons.

There are two open - shell electrons occupying the anti-bonding π_g orbitals. These are the only electrons that matter. It is easiest to simply draw all of the permutations and figure out the bounds on Λ and M_L by inspection. If we do this, it is easy to see that $\Lambda = 2, 0$ and that $M_L = 2, 0, -2$



$M_s = -1$	$M_s = 0$	$M_s = 2$
0	**1**	0
1	2	1
0	1	0

The top row is a $\Lambda = 2\ M_S = 0$ state, so it is $^1\Delta$. Both electrons are in the rightmost orbital. This orbital is gerade, and (g)(g) = g, so the parity label is g. We do not assign reflection labels to non Σ states, so the term symbol is $^1\Delta_g$. After removing the used up microstates, the chart becomes

$M_s = -1$	$M_s = 0$	$M_s = 2$
1	**1**	0

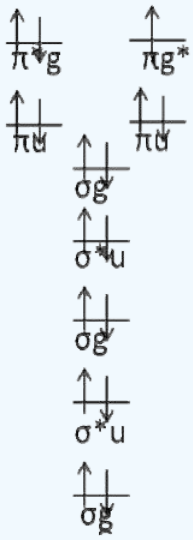
This is a Λ =0 state with three possible spin configurations, so it is $^3\Sigma$. We know that the electrons are in different sub-orbitals (if you cannot see this, try drawing all of the possible combinations that give $\Lambda = 0$). Both of the orbitals are gerade, so the overall parity is gerade. One of the orbitals will be +, the other will be - . The final answer is $^1\Delta_g$\($^3\Sigma_g^+$

? Exercise 9.15.1

Write the term symbols for O_2^-

Solution

First draw the electron configuration diagram.



There are only two possible configurations. It should be easy to see that the term symbol is $^2\Pi_g$.

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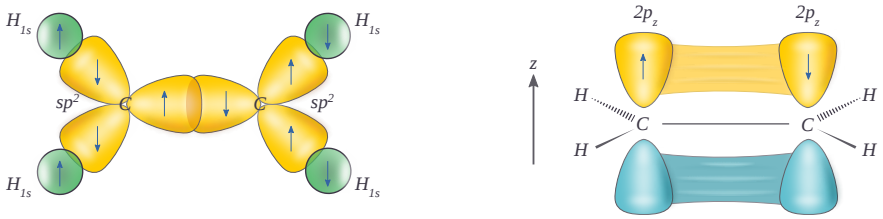
6.20: The pi-Electron Approximation of Conjugation

Learning Objectives

- Demonstrate how Hückel's theory approximates the full molecular orbital picture of molecules by treating the σ-bonding and π-bonding networks independently.

Molecular orbital theory has been very successfully applied to large conjugated systems, especially those containing chains of carbon atoms with alternating single and double bonds. An approximation introduced by Hückel in 1931 considers only the delocalized *p* electrons moving in a framework of π-bonds. This is, in fact, a more sophisticated version of a free-electron model.

The simplest hydrocarbon to consider that exhibits π bonding is ethylene (ethene), which is made up of four hydrogen atoms and two carbon atoms. Experimentally, we know that the $\mathbf{H–C–H}$ and $\mathbf{H–C–C}$ angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied *s* orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H (sp^2 + *s*) and one C–C (sp^2 + sp^2) (part a of Figure 10.5.1).



(a) C_2H_4 σ - bonded framework *(b) C_2H_4 π bonding*

Figure 10.5.1 : (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the *z*-axis.) (CC BY-NC; Ümit Kaya via LibreTexts)

The Hückel approximation is used to determine the energies and shapes of the π molecular orbitals in conjugated systems. Within the Hückel approximation, the covalent bonding in these hydrocarbones can be separated into two independent "frameworks": the σ -bonding framework and the the σ-bonding framework. The wavefunctions used to describe the bonding orbitals in each framework results from different combinations of atomic orbitals. The method limits itself to addressing conjugated hydrocarbons and specifically only π electron molecular orbitals are included because these determine the general properties of these molecules; the sigma electrons are ignored. This is referred to as *sigma-pi separability* and is justified by the orthogonality of σ and π orbitals in planar molecules. For this reason, the Hückel method is limited to planar systems. Hückel approximation assumes that the electrons in the π bonds “feel” an electrostatic potential due to the entire σ-bonding framework in the molecule (i.e. it focuses only on the formation of π bonds, given that the σ bonding framework has already been formed).

Conjugated Systems

A conjugated system has a region of overlapping p-orbitals, bridging the interjacent single bonds, that allow a *delocalization* of π electrons across all the adjacent aligned p-orbitals. These π electrons do not belong to a single bond or atom, but rather to a group of atoms.

6.20.1: Ethylene

Before considering the Hückel treatment for ethylene ($\mathbf{C_2H_4}$), it is beneficial to review the general bonding picture of the molecule. Bonding in ethylene involves the $\boldsymbol{sp^2}$ hybridization of the $\boldsymbol{2s}$, $\boldsymbol{2p_x}$, and $\boldsymbol{2p_y}$ atomic orbitals on each carbon atom; leaving the $\boldsymbol{2p_z}$ orbitals untouched (Figure 10.5.2).

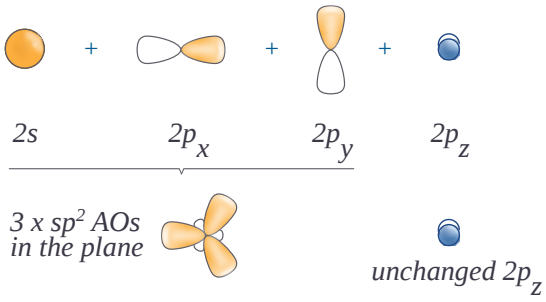


Figure 10.5.2 : Hybridizing of the carbon atomic orbitals to give sp^2 hybrid orbitals for bonding to hydrogen atoms in ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

The use of hybrid orbitals in the molecular orbital approach describe here is merely a convenience and not invoking valence bond theory (directly). An identical description can be extracted using exclusively atomic orbitals on carbon, but the interpretation of the resulting wavefunctions is less intuitive. For example, the i[th] molecular orbital can be described via hybrid orbitals

$$|\psi_1\rangle = c_1|sp_1^2\rangle + c_2|1s_a\rangle$$

or via atomic orbitals.

$$|\psi_1\rangle = a_1|2s\rangle + a_1\,|2p_x\rangle + a_1|\,2p_y\rangle + a_4|1s_a\rangle$$

where $\{a_i\}$ and $\{c_i\}$ are coefficients of the expansion. Either describe will work and both are identical approaches since

$$|sp_1^2\rangle = b_1|2s\rangle + b_1\,|2p_x\rangle + b_1|\,2p_y\rangle$$

where $\{c_i\}$ are coefficients describing the hybridized orbital.

The bonding occurs via the mixing of the electrons in the sp^2 hybrid orbitals on carbon and the electrons in the $1s$ atomic orbitals of the four hydrogen atoms (Figure 10.5.1 ; left) resulting in the σ-bonding framework. The π-bonding framework results from the unhybridized $2p_z$ orbitals (Figure 10.5.2 ; right). The independence of these two frameworks is demonstrated in the resulting molecular orbital diagram in Figure 10.5.3 ; Hückel theory is concerned only with describing the molecular orbitals and energies of the π bonding framework.

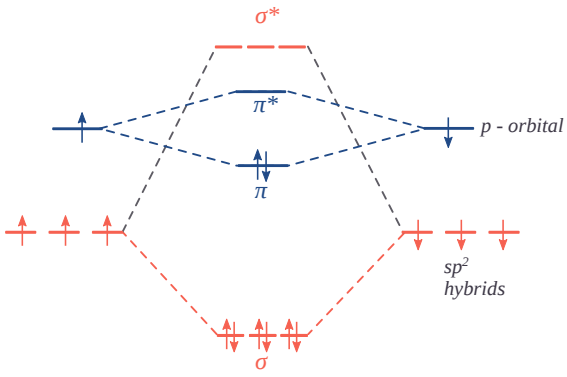


Figure 10.5.3 : Molecular orbitals demonstrating the sigma-pi separability of the π-bonding framework (blue) and the σ-bonding frameworks (red) of ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

> *Hückel treatment is concerned only with describing the molecular orbitals and energies of the π bonding framework.*

Since Hückel theory is a special consideration of molecular orbital theory, the molecular orbitals $|\psi_i\rangle$ can be described as a linear combination of the $2p_z$ atomic orbitals ϕ at carbon with their corresponding $\{c_i\}$ coefficients:

$$|\psi_i\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \tag{6.20.1}$$

This equation is substituted in the Schrödinger equation:

$$\hat{H}\left|\psi_i\right\rangle = E_i\left|\psi_i\right\rangle$$

with $\hat{H}$ the Hamiltonian and E_i the energy corresponding to the molecular orbital to give:

$$\hat{H}c_1\left|\phi_1\right\rangle + \hat{H}c_2\left|\phi_2\right\rangle = Ec_1\left|\phi_1\right\rangle + Ec_2\left|\phi_2\right\rangle \tag{6.20.2}$$

If Equation 6.20.2 is multiplied by $\langle\phi_1|$ (and integrated), then

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{6.20.3}$$

where H_{ij} are the Hamiltonian matrix elements (see note below)

$$H_{ij} = \langle\phi_i\left|\hat{H}\right|\phi_j\rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle\phi_i|\phi_j\rangle = \int \phi_i\phi_j \mathrm{d}v$$

If Equation 6.20.2 is multiplied by $\langle\phi_2|$ (and integrated), then

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \tag{6.20.4}$$

Both Equations 6.20.3 and 6.20.4 can better represented in matrix notation,

$$\begin{bmatrix} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) \\ c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) \end{bmatrix} = 0$$

or more simply as a product of matrices.

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{6.20.5}$$

All diagonal Hamiltonian integrals H_{ii} are called **Coulomb integrals** and those of type H_{ij} are called **resonance integrals**. Both integrals are negative and the resonance integrals determines the strength of the bonding interactions. The equations described by Equation 6.20.5 are called the ***secular equations*** and will also have the trivial solution of

$$c_1 = c_2 = 0$$

Within linear algebra, the secular equations in Equation 6.20.5 will also have a non-trivial solution, if and only if, the secular determinant is zero

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{6.20.6}$$

or in shorthand notation

$$\det(H - ES) = 0$$

Everything in Equation 6.20.6 is a known number except E. Since the secular determinant for ethylene is a 2×2 matrix, finding E, requires solving a quadratic equation (after expanding the determinant)

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{21} - ES_{21})(H_{12} - ES_{12}) = 0$$

There will be two values of E which satisfy this equation and they are the molecular orbital energies. For ethylene, one will be the bonding energy and the other the antibonding energy for the π-orbitals formed by the combination of the two carbon $2p_z$ orbitals (Equation 6.20.1). However, if more than two $|\phi\rangle$ atomic orbitals were used, e.g., in a bigger molecule, then more energies would be estimated by solving the secular determinant.

Solving the secular determinant is simplified within Hückel method via the following four assumptions:

1. All overlap integrals S_{ij} are set equal to zero. This is quite reasonable since the $\pi-$ orbitals are directed perpendicular to the direction of their bonds (Figure 10.5.1). This assumption is often call neglect of differential overlap (NDO).

2. All resonance integrals H_{ij} between non-neighboring atoms are set equal to zero.
3. All resonance integrals H_{ij} between neighboring atoms are equal and set to β.
4. All coulomb integrals H_{ii} are set equal to α.

These assumptions are mathematically expressed as

$$H_{11} = H_{22} = \alpha$$

$$H_{12} = H_{21} = \beta$$

Assumptions 1 means that the overlap integral between the two atomic orbitals is 0

$$S_{11} = S_{22} = 1$$

$$S_{12} = S_{21} = 0$$

Matrix Representation of the Hamiltonian

The Coulomb integrals

$$H_{ii} = \langle \phi_i | H | \phi_i \rangle$$

and resonance integrals.

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \ \ (i \neq i)$$

are often described within the matrix representation of the Hamiltonian (specifically within the $|\phi\rangle$ basis):

$$\hat{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}$$

or within the Hückel assumptions

$$\hat{H} = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix}$$

The Hückel assumptions reduces Equation 6.20.5 in two homogeneous equations:

$$\begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{6.20.7}$$

if Equation 6.20.7 is divided by β:

$$\begin{bmatrix} \frac{\alpha - E}{\beta} & 1 \\ 1 & \frac{\alpha - E}{\beta} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

and then a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{6.20.8}$$

then Equation 6.20.7 simplifies to

$$\begin{bmatrix} x & 1 \\ 1 & x \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{6.20.9}$$

The trivial solution gives both wavefunction coefficients equal to zero and the other (non-trivial) solution is determined by solving the secular determinant

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

which when expanded is $x^2 - 1 = 0$ so $x = \pm 1$.

Knowing that $E = \alpha - x\beta$ from Equation 6.20.8, the energy levels can be found to be

$$E = \alpha - \pm 1 \times \beta$$

or

$$E = \alpha \mp \beta$$

Since β is negative, the two energies are ordered (Figure 10.5.4)

- For π_1: $E_1 = \alpha + \beta$
- For π_2: $E_2 = \alpha - \beta$

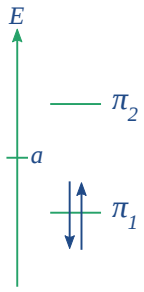


Figure 10.5.4 : π energies of ethylene with occupation. (CC BY-NC; Ümit Kaya via LibreTexts)

To extract the coefficients attributed to these energies, the corresponding x values can be substituted back into the Secular Equations (Equation 6.20.9). For the lower energy state ($x = -1$)

$$\begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 6.20.1):

$$|\psi_1\rangle = N_1(|\phi_1\rangle + |\phi_2\rangle) \tag{6.20.10}$$

where N_1 is the normalization constant for this molecular orbital; this is the **bonding** molecular orbital.

For the higher energy molecular orbital ($x = -1$) and then

$$\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = -c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 6.20.1):

$$\psi_2\rangle = N_2(|\phi_1\rangle - |\phi_2\rangle) \tag{6.20.11}$$

where N_2 is the normalization constant for this molecular orbital; this is the **anti-bonding** molecular orbital.

The normalization constants for both molecular orbitals can obtained via the standard normalization approach (i.e., $\langle\psi_i|\psi_i\rangle = 1$) to obtain

$$N_1 = N_2 = \frac{1}{\sqrt{2}}$$

These molecular orbitals form the π-bonding framework and since each carbon contributes one electron to this framework, only the lowest molecular orbital ($|\psi_1\rangle$) is occupied (Figure 10.5.5) in the ground state. The corresponding electron configuration is then π_1^2.

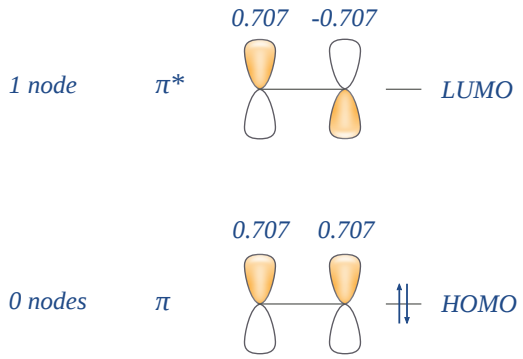


Figure 10.5.5 : Schemetic representation of the π molecular orbitals framework for ethylene . Notice that the antibonding molecular orbital has one more node than the bonding molecular orbital as expected since it is higher in energy. (CC BY-NC; Ümit Kaya via LibreTexts)

> *HOMO and LUMO are acronyms for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively and are often referred to as frontier orbitals. The energy difference between the HOMO and LUMO is termed the HOMO–LUMO gap.*

The 3-D calculated π molecular orbitals are shown in Figure 10.5.6 .

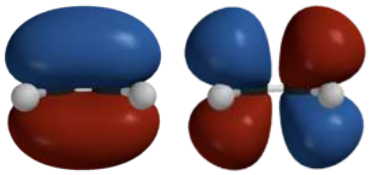


Figure 10.5.6 : Calculated π molecular orbitals for ethylene . (left) the bonding orbital (|\psi_1 \rangle\) and (right) the antibonding ($|\psi_2\rangle$ orbital.

Limitations of Hückel Theory

Hückel theory was developed in the 1930's when computers were unavailable and a simple mathematical approaches were very important for understanding experiment. Although the assumptions in Hückel theory are drastic they enabled the early calculations of molecular orbitals to be performed with mechanical calculators or by hand. Hückel Theory can be extended to address other types of atoms in conjugated molecules (e.g., nitrogen and oxygen). Moreover, it can be extended to also treat σ orbitals and this "Extended Hückel Theory" is still used today. Despite the utility of Hückel Theory, it is highly qualitative and we should remember the limitations of Hückel Theory:

- Hückel Theory is very approximate
- Hückel Theory cannot calculate energies accurately (electron-electron repulsion is not calculated)
- Hückel Theory typically overestimates predicted dipole moments

Hückel Theory is best used to provide simplified models for understanding chemistry and for a detailed understanding modern *ab initio* molecular methods discussed in Chapter 11 are needed.

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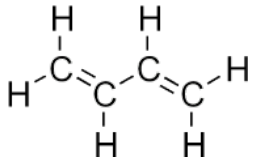
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6.21: Butadiene is Stabilized by a Delocalization Energy

Learning Objectives

- Apply Hückel theory to an extended π-bonding network
- Identify the origin of delocalization energy from Hückel theory and relate it to resonances structures in valence bond theory

1,3-Butadiene is a simple conjugated diene with the formula $\mathbf{C_4H_6}$ and can be viewed structurally as two vinyl groups ($\mathbf{CH_2{=}CH_2}$) joined together with a single bond. Butadiene can occupy either a cis or trans conformers and at room temperature, 96% of butadiene exists as the trans conformer, which is 2.3 kcal/mole more stable than the cis structure.



trans-1,3-Butadiene

For the simple application of applying Hückel theory for understanding the electronic structure of butadiene, we will ignore the energetic differences between the two conformers. As discussed previously, the molecular orbitals are linear combination of the four $|p\rangle$ atomic orbitals on the carbon atoms that are not participating in the σ bonding network:

$$|\psi_i\rangle = \sum_j^4 c_{ij} \Big| p_i \rangle$$

or explicitly

$$|\psi_i\rangle = c_{i1}|p_1\rangle + c_{i2}\,|p_2\rangle + c_{i3}|\,p_3\rangle + c_{i4}|p_4\rangle \tag{6.21.1}$$

for the ith molecular orbital $|\psi_i\rangle$. The secular equations that need to be solved are

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{6.21.2}$$

If the standard Hückel theory approximations were used

$$H_{ii} - ES_{ii} = \alpha$$

and

$$H_{ij} - ES_{ij} = \beta$$

when $i = j \pm 1$, otherwise

$$H_{ij} - ES_{ij} = 0$$

then the secular equations for butadiene in Equation 6.21.2 become

$$\begin{bmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{6.21.3}$$

Solving Equation 6.21.3 for $\{c_i\}$ coefficients and energy secular equation requires extracting the roots of the secular determinant:

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0 \tag{6.21.4}$$

If both sides of Equation 6.21.4 were divided by β^4 and a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{6.21.5}$$

then Equation 6.21.4 simplifies further to

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{6.21.6}$$

This is essentially the connection matrix for the butadiene molecule. Each pair of connected atoms is represented by 1, each non-connected pair by 0 and each diagonal element by x. Expansion of the determinant in Equation 6.21.6 gives the 4th order polynomial equation

$$x^4 - 3x^2 + 1 = 0 \tag{6.21.7}$$

While solving 4th order equations typically require numerical estimation, Equation 6.21.7 can be further simplified by recognizing that it is a quadratic equation in terms of x^2. Therefore, the roots are

$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

or $x = \pm\ 0.618$ and $x = \pm\ 1.618$. Since α and β are negative, these molecular orbital energies can ordered in terms of energy (from lowest to highest):

$$E_1 = \alpha + 1.618\beta \tag{6.21.8}$$

$$E_2 = \alpha + 0.618\beta \tag{6.21.9}$$

$$E_3 = \alpha - 0.618\beta \tag{6.21.10}$$

$$E_4 = \alpha - 1.618\beta \tag{6.21.11}$$

This sequence of energies is displayed in the energy diagram of Figure 10.6.1 .

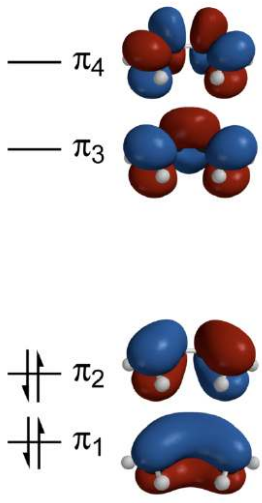


Figure 10.6.1 : The π molecular orbital energies from Hückel theory for butadiene with ground-state configuration. Structures calculated and images produced using HF/6-31G* (Public Domain; Ben Mills).

Each p atomic orbital of carbon contributes a single electron to the π manifold, so the ground-state occupation of the resulting four π electrons have a $\pi_1^2\pi_2^2$ configuration (Figure 10.6.1). The the total π-electron energy is then determined by adding up the energies in Equations 6.21.8-6.21.11 and scaling by their occupations to get

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_1 + 2\times E_2 + 0\times E_3 + 0\times E_4 \\ &= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) \\ &= 4\alpha + 4.472\beta \end{aligned} \tag{6.21.12}$$

If the bonding of butadiene were described only as two localized double bond as in its dominant valence-bond structure (Figure 10.6.1), then its π-electron energy would be given by twice the E_π predicted for the ethlyene molecule:

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_\pi(\text{ethylene}) \\ &= 2\times 2(\alpha+\beta) \\ &= 4\alpha + 4\beta \end{aligned} \tag{6.21.13}$$

Comparing Equation 6.21.12 with Equation 6.21.12, the total π energy of butadiene lies lower than the total π energy of two double bonds by 0.48β (the σ bond does not contribute). This difference is known as the **delocalization energy**; a typical estimate of β is around -75 kJ/mol, which results in a *delocalization energy* for butadiene of -35 kJ/mol.

> *The delocalization energy is the extra stabilization resulting from the electrons extending over the whole molecule.*

Delocalization Energy in Valence Bond Theory

Delocalization energy is intrinsic to molecular orbital theory, since it results from breaking the two-center bond concept with the molecular orbitals that spread over more that just one pair of atoms. However, within the two-center theory of valence bond theory, the delocalization energy results from a stabilization energy attributed to resonance. Several conventional valence bond resonance structures that can be written for 1,3-butadiene, four of which are shown in Figure 10.6.2 . However, while structure **2a** dominates, the other resonance structures also contribute to describing the total molecule and hence predict a corresponding stabilization energy akin to the delocalization energy in molecular orbital theory.

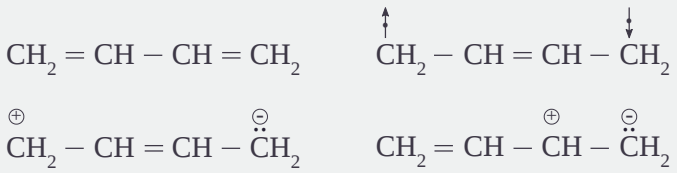


Figure 10.6.2 : Several resonance structures that can be written for 1,3-butadiene. The resonance structure in the upper left dominates, but does not exclusively describe the system since a delocalization energy is experimentally observed compared to two ethylene molecules. (CC BY-NC; Ümit Kaya via LibreTexts)

In general, the true description of the bonding within the valence bond theory is a superposition of resonance structures with amplitudes that are determined via a variational optimization to find the lowest possible energy for the valence bond wavefunctions.

The solving the secular equations (Equation 6.21.2) gives the $\{c_{ij}\}$ coefficients for the molecular orbitals in Equation 6.21.1 (not demonstrated):

$$|\psi_1\rangle = 0.37|p_1\rangle + 0.60\,|p_2\rangle + 0.60|\,p_3\rangle + 0.37|p_4\rangle \tag{6.21.14}$$

$$|\psi_3\rangle = 0.60|p_1\rangle + 0.37\,|p_2\rangle - 0.37|\,p_3\rangle - 0.60|p_4\rangle \tag{6.21.15}$$

$$|\psi_3\rangle = 0.60|p_1\rangle - 0.37\,|p_2\rangle - 0.37|\,p_3\rangle + 0.60|p_4\rangle \tag{6.21.16}$$

$$|\psi_4\rangle = 0.37|p_1\rangle - 0.60\,|p_2\rangle + 0.60|\,p_3\rangle - 0.37|p_4\rangle \tag{6.21.17}$$

These are depicted in Figure 10.6.3 .

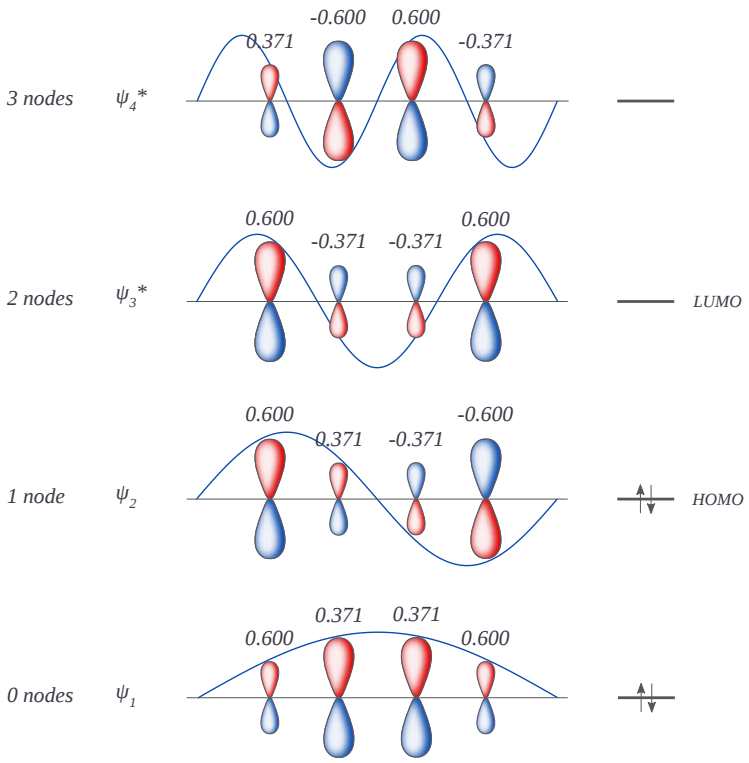


Figure 10.6.3 : Energy level diagram and decomposition of the π molecular orbitals of butadiene. This is view three-dimensionally in Figure 10.6.1 . (CC BY-NC; Ümit Kaya via LibreTexts)

Note the correlation of the energy of the π molecular orbitals of butadiene to the number of nodes in the wavefunction; this is the general trend observed in previous systems like the particle in the box and atomic orbitals. The four 3-D calculated molecular orbitals are contrasted in Figure 10.6.1 .

Exercise 10.6.1

What would Hückel theory predict for the energy levels and π molecular orbitals of cis-butadiene? Do you believe this approach adequately describes the energy levels of the cis-trans isomerization reaction of butadiene?

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6.22: Benzene and Aromaticity

Learning Objectives

- Apply Hückel theory to describing the pi bonding in cyclical conjugated system
- Identify the origin of aromaticity within Hückel theory to describe extra stabilization in certain cyclical conjugated systems

The previous sections addressed the π orbitals of linear conjugated system. Here we address conjugated systems of **cyclic conjugated hydrocarbons** with the general formula of 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).

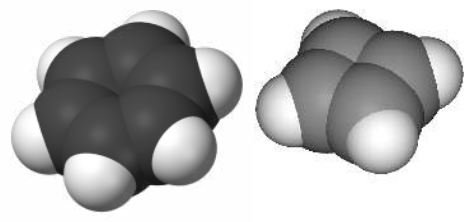


Figure 10.7.1 : Space-filling model of benzene (left) and cyclobutadiene (right). Carbon atoms are indicated in black, while hydrogen atoms are indicated in white. (Public domain; Benjah-bmm27 and Edgar181, respectively).

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.

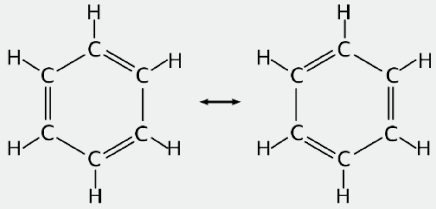


Figure 10.7.2 : Resonance structures of benzene.

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 of the structures in Figure 10.7.2 are correct and the true 'structure' of benzene is a mixture of the two. As discussed previously, that such a valence bond perspective results in a **delocalization energy** within a molecular orbital approach.

Aromatic systems provide the most significant applications of Hückel theory. For benzene, we find the secular determinant

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{6.22.1}$$

with the six roots $x = \pm 2, \pm 1, \pm 1$. This corresponds to the following energies (ordered from most stable to least since $\beta < 0$):

- $E_1 = \alpha + 2\beta$
- $E_2 = \alpha + \beta$

- $E_3 = \alpha + \beta$
- $E_4 = \alpha - \beta$
- $E_5 = \alpha - \beta$
- $E_6 = \alpha - 2\beta$

The two pairs of $E = \alpha \pm \beta$ energy levels are two-fold degenerate (Figure 10.7.3).

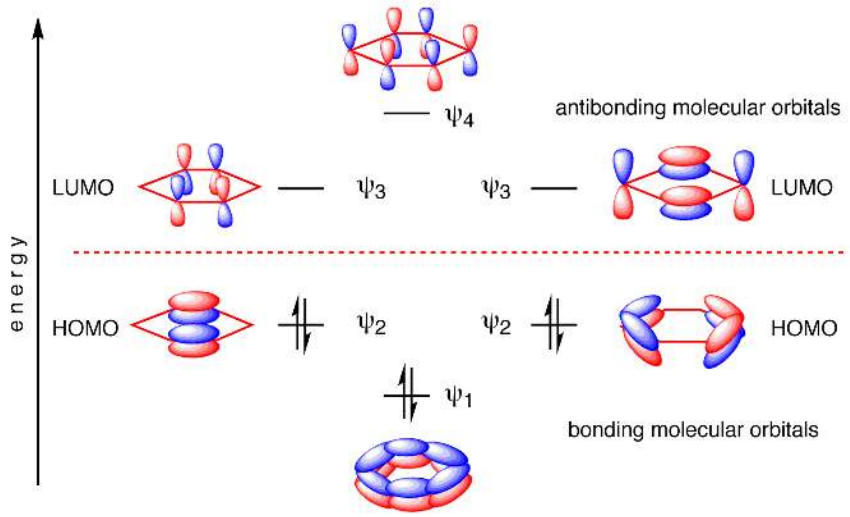


Figure 10.7.3 : The π molecular orbitals for benzene. The dashed lines represent the energy of an isolated p orbitals and all orbitals below this line are bonding. All orbitals above it are antibonding. (CC BY-NC-SA 4.0; Nick Greeves via ChemTube3D)

The resulting wavefunctions are below (expanded in terms of carbon $|2p\rangle$ atomic orbitals).

$$|\psi_1\rangle = \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle\right]$$

$$|\psi_2\rangle = \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle\right]$$

$$|\psi_3\rangle = \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle + \frac{1}{2}\left|2p_{z2}\right\rangle - \frac{1}{2}\left|2p_{z3}\right\rangle - \left|2p_{z4}\right\rangle - \frac{1}{2}\left|2p_{z5}\right\rangle + \frac{1}{2}|2p_{z6}\rangle\right]$$

$$|\psi_4\rangle = \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle\right]$$

$$|\psi_5\rangle = \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle - \frac{1}{2}\left|2p_{z2}\right\rangle - \frac{1}{2}\left|2p_{z3}\right\rangle + \left|2p_{z4}\right\rangle - \frac{1}{2}\left|2p_{z5}\right\rangle - \frac{1}{2}|2p_{z6}\rangle\right]$$

$$|\psi_6\rangle = \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle\right]$$

Each of the carbons in benzene contributes one electron to the π-bonding framework (Figure 10.7.3). This means that all bonding molecular orbitals are fully occupied and benzene then has an electron configuration of $\pi_1^2\pi_2^2\pi_3^2$. With the three lowest molecular orbitals occupied, the total π-bonding energy is

$$\begin{aligned} E_{tot}(\text{benzene}) &= 2(\alpha + 2\beta) + 4(\alpha + \beta) \\ &= 6\alpha + 8\beta \end{aligned} \tag{6.22.2}$$

Since the energy of a localized double bond is $2(\alpha + \beta)$, as determined from the analysis of ethylene, the delocalization energy of benzene is

$$\begin{aligned} \Delta E &= E_{tot}(\text{benzene}) - 3E_{tot}(\text{ethylene}) \\ &= (6\alpha + 8\beta) - 3 \times 2(\alpha + \beta) \\ &= 2\beta \end{aligned}$$

The experimental thermochemical value is -152 kJ mol^{-1}.

6.22.1: Aromaticity

In general, cyclic polyenes are only closed shell (i.e., each electron paired up) and extra stable for with $(4n+2)\pi$ electrons (n=0,1,2…). These special molecules have the highest delocalization energies and are said to be “aromatic”. For benzene this is 2β (Equation 6.22.2), which is the energy by which the delocalized π electrons in benzene are more stable than those in three isolated double bonds.

Hückel's Rule

A stable, closed-shell conjugated cyclic structure is obtained for molecules with $(4n+2)\pi$ electrons with n=2, 6, 10, ... electrons.

Evidence for the enhanced thermodynamic stability of benzene was obtained from measurements of the heat released when double bonds in a six-carbon ring are hydrogenated (hydrogen is added catalytically) to give cyclohexane as a common product.

$$C_6H_6 + 3\,H_2 \longrightarrow C_6H_{12}$$

In the following diagram cyclohexane represents a low-energy reference point. Addition of hydrogen to cyclohexene produces cyclohexane and releases heat amounting to 11.9 kJ mol^{-1}. If we take this value to represent the energy cost of introducing one double bond into a six-carbon ring, we would expect a cyclohexadiene to release 23.9 kJ mol^{-1} on complete hydrogenation, and 1,3,5-cyclohexatriene to release 35.9 kJ mol^{-1}. These heats of hydrogenation ΔH_{hyd} reflect the relative thermodynamic stability of the compounds (Figure 10.7.4).

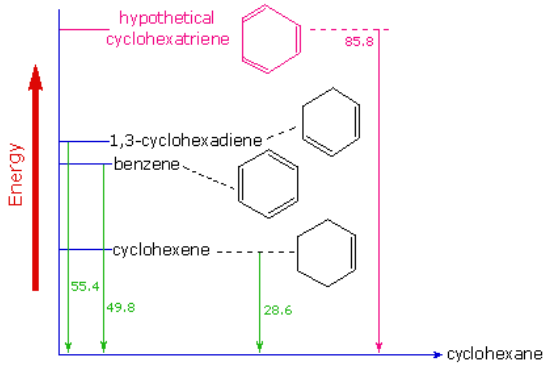


Figure 10.7.4 : Experimental evidence for aromatic stabilization energy in benzene from the heat of hydrogenation. Energies are in kcal/mol. (CC BY-NC-SA 4.0; William Resuch);

In practice, 1,3-cyclohexadiene is slightly more stable than expected, by about 8.1 kJ mol^{-1}, presumably due to conjugation of the double bonds. Benzene, however, is an extraordinary 15 kJ mol-1 more stable than expected. This additional stability is a characteristic of all aromatic compounds.

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CHAPTER OVERVIEW

10: Group Theory and Symmetry

10.1: Symmetry Elements and Operations Define the Point Groups
10.2: Symmetry Operations Define Groups
10.3: Symmetry Operations as Matrices
10.4: Molecules can be Represented by Reducible Representations
10.5: Character Tables Summarize the Properties of a Point Group
10.6: Characters of Irreducible Representations
10.7: Molecular Orbitals can be Constructed on the Basis of Symmetry
10.8: H_2O
10.9: The Exploitation of Symmetry Can Help Simplify Numerical Calculations

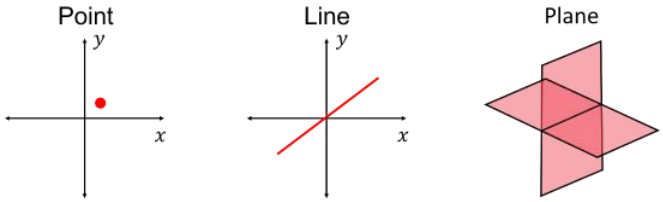
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10.1: Symmetry Elements and Operations Define the Point Groups

10.1.1: 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 (2-dimensional), line (1-dimensional) or point (0-dimensional) 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 of a molecule or ion can be described in terms of the complete collection of symmetry operations it possesses. The symmetry elements that a molecule (and any other 3-D object) may possess are discussed below.

10.1.2: Symmetry Operations

The symmetry of a molecule or ion can be described in terms of the complete collection of symmetry operations it possesses. There are five types of operations:

1. Identity, E
2. Rotation, C_n
3. Reflection, σ
4. Inversion, i
5. Improper Rotation, S_n

Symmetry Operations

A symmetry operation is a permutation of atoms such that the molecule is transformed into a state **indistinguishable** from the starting state.

10.1.2.1: Identity Symmetry, E

The identity operator, E, consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule possesses at least this operation. For example, the $\mathrm{CHFClBr}$ molecule in Figure 12.2.1 . The identify symmetry operation is not indicated since all molecule exhibit this symmetry.

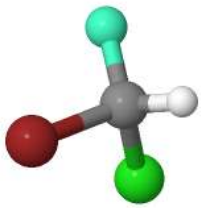


Figure 12.2.1 : Example of Identify Symmetry: The $\mathrm{CHFClBr}$ molecule contain no other symmetry other than identity. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

10.1.2.2: n-fold Axis of Rotation, C_n

The rotation operation (sometimes called proper rotation), C_n, rotates an object about an axis by $2\pi/n$ radians or $360°/n$. Rotation by C_n leaves the molecule unchanged. The H_2O molecule has a C_2 axis (Figure 12.2.2). Molecules can have more than one C_n

axis, in which case the one with the highest value of n is called the *principal axis*. In some high symmetry systems, there may be more than one principal axis. Note that by convention, rotations are *counterclockwise* about the axis. C_n rotations are indicated via vectors with labels as indicated below.

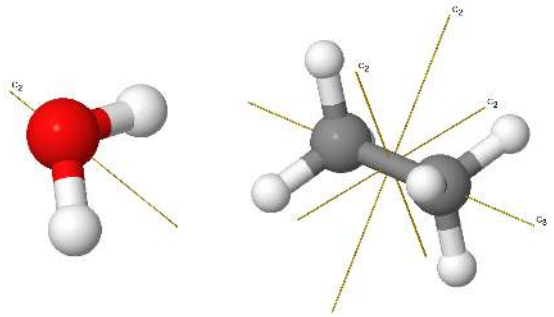


Figure 12.2.2 : Examples of n-fold Axis of Rotation: (left) The water molecule contains a C_2 axis. (right) Ethane contains both C_2 and C_3 axes. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

We always want to express rotations in their simplest equivalent fractions of m/n:

$$C_4^2 = C_2$$

$$C_6^4 = C_3^2$$

$$C_8^6 = C_4^3$$

Rotating an object n times brings the object back to the original object and is equivalent to the identity operation, E:

$$C_n^n = E$$

Linear molecules have a very high rotational symmetry: C_∞. Examples include diatomics such as CO, NO, and $\mathrm{CO_2}$.

10.1.2.3: Reflection, σ

Reflection, σ, defines the bilateral symmetry about a plane (mirror plane / reflection plane). 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. If no principal axis exist, σ_h is defined as the plane of the molecule. σ symmetry is indicated as a plane on molecules; since they often bisect atoms, which should be clearly indicated.

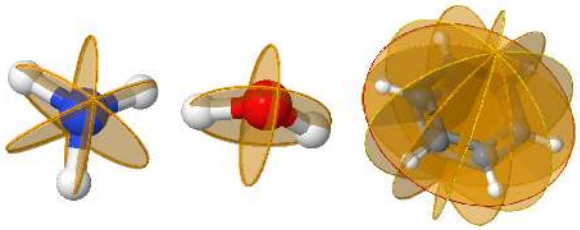


Figure 12.2.3 : Examples of reflection symmetry. (left) The ammonia molecule contains three identical reflection planes. All are designated as vertical symmetry planes (σ_v) because they contain the principle rotation axis.(middle) The water molecule contains two different reflection planes. (right) 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.

For any mirror plane, performing two successive reflections about the same plane brings objects back to their original configuration:

$$\sigma\sigma = \sigma^2 = E$$

10.1.2.4: Inversion, i

Inversion, i, 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. If inversion symmetry exists, a line drawn from

any atom through the center will connect with an equivalent atom at an equivalent distance from the center. 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 inversion center is always located at the central point of the molecule and there can only be one inversion center in any system. The centers of inversion in the examples below do not overlap with atoms.

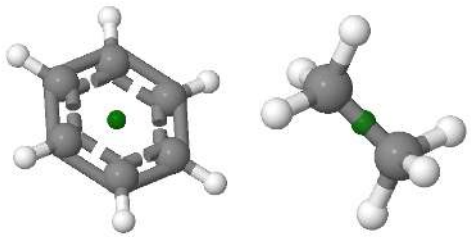


Figure 12.2.4 : Examples of Center of Inversion Symmetry. (left) Benzene and (right) staggard ethane have centers of inversion (green balls). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

Performing inversion twice in succession brings every point back to its original position:

$$ii = i^2 = E$$

Molecules with no inversion symmetry are said to be centrosymmetric.

10.1.2.5: n-fold Axis of Improper Rotation, S_n

Improper rotations, S_n, are also called rotation-reflections. The rotation-reflection operation consists of rotating by C_n about an axis, followed by reflecting in a plane perpendicular to the same axis. Improper rotation symmetry is indicated with both an axis and a plan as demonstrated in the examples in Figure 12.2.5 .

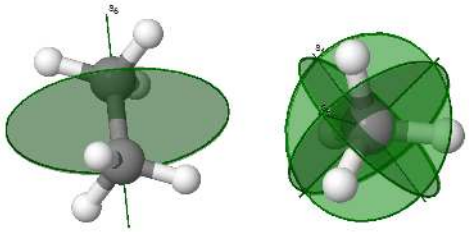


Figure 12.2.5 : Examples of Improper axis of rotation. (left) Staggered ethane contains an S_6 axis of improper rotation. (right) Methane contains three S_4 axes of improper rotation. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

Note

S_1 is the same as reflection and S_2 is the same as inversion.

The lowest-order improper rotation that is not a simpler operation is S_3. The pattern of successive operations depends on if n is even or odd. The general relationships for S_n operations are:

- If n is even, $S_n^n = E$
  - Molecule returns to original orientation configuration after each full rotation
  - There are an even number of rotation operators and reflection operators
- If n is odd, $S_n^n = \sigma$ and $S_n^{2n} = E$
  - First full rotation:
    - Molecular does not return to original configuration after first rotation
    - There are an odd number of rotation operators and reflection operators
  - Second full rotation:
    - Molecule returns to original orientation configuration
    - There are an even number of rotation operators and reflection operators
- When m is even, there is always a corresponding proper rotation (C_n):

- $S_n^m = C_n^m$ when $m < n$
- $S_n^m = C_n^{m-n}$ when $m > n$ (2nd rotation)

- If S_n with even n exists, $C_{n/2}$ exists
- If S_n with odd n exists, then both C_n and σ perpendicular to C_n exist

10.1.2.6: Summary of Symmetry Operations

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 operations are tabulated in Table 12.2.1 .

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.

10.1.3: Defining the Coordinate System

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.

Generally, the following conventions are observed to define the coordinate system:

1. The origin of the coordinate system is located at the central atom or the center of the molecule.
2. The z-axis is collinear with the highest-order rotational axis (principal axis).
3. For planar molecules, if the z-axis is perpendicular to the molecular plane:
   - The x-axis lies in the plane of the molecule and passes through the greatest number of atoms.

   If the z-axis lies in the plane of the molecule:
   - The x-axis stands perpendicular to the plane
4. For non-planar molecules, once the z-axis has been defined, the x-axis is the usually chosen so that the xz plane contains as many atoms as possible.

10.1.4: 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 Schönflies and Hermann-Mauguin (or International) systems. Schönflies notation is used by chemists and spectroscopists, while Crystallographers prefer Hermann-Mauguin notation.The symmetry of individual molecules is usually described using the **Schönflies** notation, which is used below. The common point groups can be categorized into the following:

- Nonrotational groups
- Single-axis rotationa groups
- Dihedral groups
- Cubic groups

Shared Names

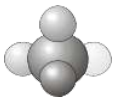
Some of the point groups share their names with symmetry operations, so be careful you do not mix up the two. It is usually clear from the context which one is being referred to.

10.1.4.1: Nonrotational groups

Nonrotational groups represent the lowest symmetry groups. They include:

C_1 - Contains only the identity (a C_1 rotation is a rotation by 360° and is the same as the identity operation, E). Molecules that belongs to the C_1 group have no symmetry and are therefore asymmetric.

- Example: CHDFCl



C_i - Contains the identity E and a center of inversion i.

- Example: $C_2H_2F_2Cl_2$



C_S - Contains the identity E and a plane of reflection σ.



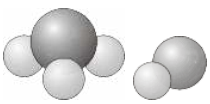
10.1.4.2: Single-axis rotation groups

Single-axis rotation groups are examples of cyclic groups. In cyclic groups, all of the operators commute (Abelian). In their multiplication tables, elements appear along right-to-left diagonals. Knowing this pattern makes it easy to construct multiplication tables! Single-axis rotational groups include:

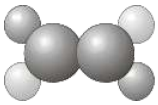
C_n - Contains the identity and an n-fold axis of rotation.



C_{nv} - Contains the identity, an n-fold axis of rotation, and n vertical mirror planes σ_v.



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).



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).

10.1.4.3: Dihedral groups

The dihedral groups have n two-fold axes perpendicular to the principal n-fold axis. These C_2 axis are called dihedral axes. Dihedral groups groups include:

D_n - Contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.

D_{nd} - Contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.



D_{nh} - Contains the same symmetry elements as D_n with the addition of a horizontal mirror plane.

- There are n-fold vertical mirror places (σ_v)
- Includes n-fold improper axis when $n > 2$
- They are centrosymmetric when n is even

$D_{\infty h}$ - Same as D_{nh}, except the principal rotational axis is an infinite-fold C_∞.

- This is the point group for all linear centrosymmetric linear molecules (e.g. H_2, CO_2)

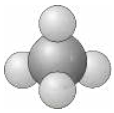


10.1.4.4: Cubic groups

The following groups are the cubic groups, which contain more than one principal axis. The cubic groups are associated with polyhedra that are geometrically related to the cube. All are characterized by the presence of multiple, intersecting, high-order rotational axes. They separate into the tetrahedral groups (T_d, T_h and T) and the octahedral groups (O and O_h).

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.

- Example: Methane, C_4

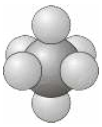


T - Same as for T_d but no planes of reflection.

T_h - Same as for T but contains a center of inversion.

O_h - The group of the regular octahedron.

- Example: Sulfur hexafluoride, SF_6



O - Same as for O_h, but with no planes of reflection.

I_h - Icoshedral, a geometric shape with 20 faces.

- Example: Buckminsterfullerene, (C_{60})

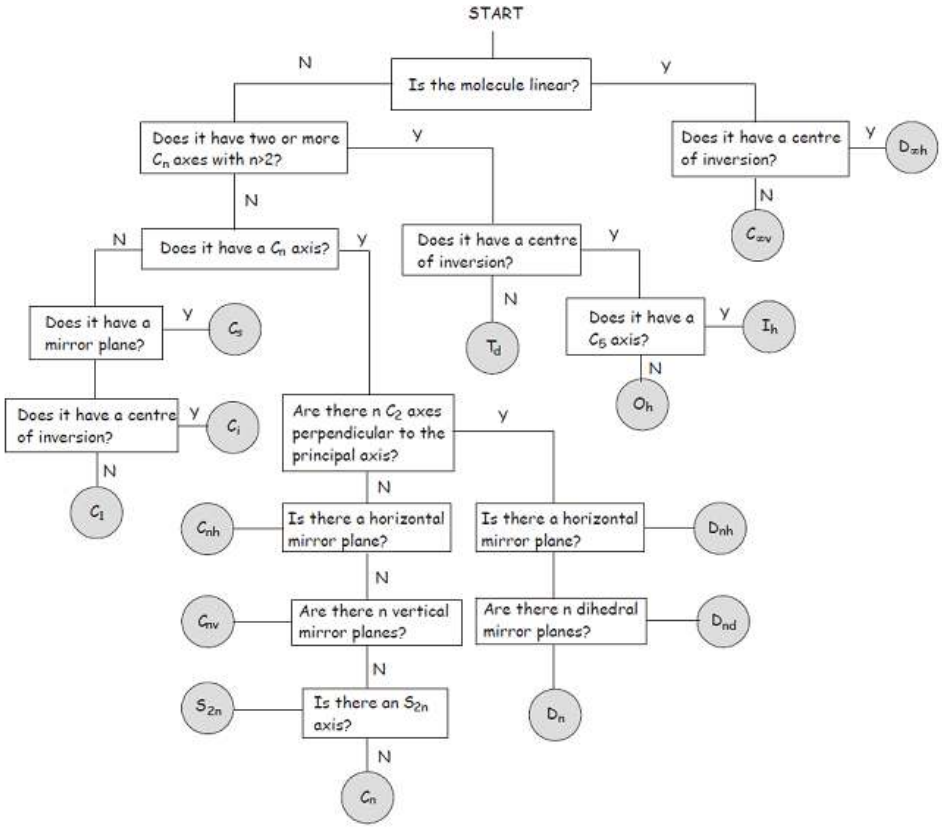
10.1.4.5: Summary of groups

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.

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	$C_{\infty v}$	$D_{\infty h}$	-	-	-	-	-	-	-

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*.

10.1.5: 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 ($\chi\epsilon\rho\iota$, 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.

10.1.6: Summary

All molecules can be described in terms of their symmetry or lack thereof, which may contain symmetry elements (point, line, plane). Identity, rotation, reflection, 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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10.2: Symmetry Operations Define Groups

10.2.1: Properties of 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. Identity
2. Closure
3. Associativity
4. Reciprocality

These criteria are explained below.

10.2.1.1: Identity

The group must include the **identity**, E. E commutes with any other elements of the group, g_i, such that:

$$Eg_i = g_iE = g_i \tag{10.2.1}$$

This requirement explains the need to define the symmetry operation of identity.

10.2.1.2: Closure

The elements must satisfy the group property of **closure**, meaning that the combination of any pair of elements is also an element of the group.

Closure is a mathematical definition. In mathematics, a group has closure under an operation if performance of that operation on members of the group always produces a member of the same group:

If A and B are elements of the group G, and if $AB = g_i$, then g_i is also in the group G

10.2.1.3: Reciprocality

To satisfy reciprocality, each element g_i must have an inverse g_i^{-1}, which is also an element of the group, such that:

$$g_ig_i^{-1} = g_i^{-1}g_i = E \tag{10.2.2}$$

Some symmetry operations are their own inverses:

- $C_2C_2 = E$
- $\sigma\sigma = E$
- $ii = E$
- $EE = E$

The inverse of each of these operations effectively 'undoes' the effect of the symmetry operation. Most other operations are not the inverse of themselves. For example, in C_{3v} the inverse of C_3 is C_3^{-1}.

10.2.1.4: Associativity

The **associative law** of combination states that all combinations of elements of a group must be associative:

$$(g_ig_j)(g_k) = g_i(g_jg_k) \tag{10.2.3}$$

The above definition **does not** require the elements to commute, which would require:

$$g_ig_k = g_kg_i \tag{10.2.4}$$

10.2.2: Group Multiplication

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.

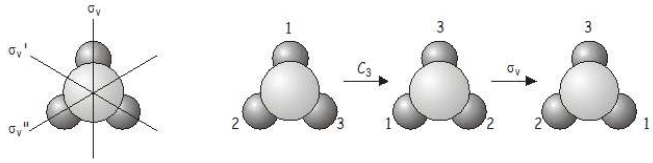
Commuting is not a Requirement of Group Elements

Groups for which the elements do not commute are called **non-Abelian** groups; those for which they elements do commute are *Abelian*.

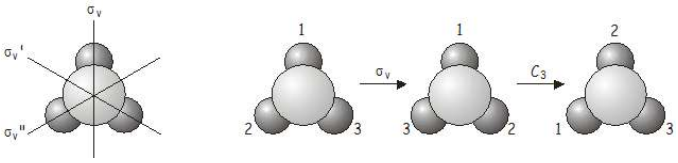
Group theory is an important area in mathematics, and luckily for chemists the mathematicians have already done most of the work for us. Along with the formal definition of a group comes a comprehensive mathematical framework that allows us to carry out a rigorous treatment of symmetry in molecular systems 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.

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

(10.2.5)

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10.3: 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*. 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. The basis we will use are unit vectors pointing in the x, y, and z directions.

The transformation matrix for any operation in a group has a form that is unique from the matrices of the other members of the same group; however, the character of the transformation matrix for a given operation is the same as that for any other operation in the same class. Each symmetry operation below will operate on an arbitrary vector, $\mathbf{u}$:

$$\mathbf{u} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

10.3.1: The Identity Operation, E

The first rule is that the group must include the identity operation E (the 'do nothing' operation). The matrix representative of the identity operation is simply the identity matrix and leaves the vector unchanged:

$$E\mathbf{u} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{10.3.1}$$

Every matrix representation includes the appropriate identity matrix.

10.3.2: The Reflection Operation, σ

The reflection operation reflects the vector $\mathbf{u}$ over a plane. This can be the xy, xz, or yz plane. The matrix is similar to the identity matrix, with the exception that there is a sign change for the appropriate element. The reflect matrix in the xy plane is:

$$\sigma(xy)\mathbf{u} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ -z \end{pmatrix} \tag{10.3.2}$$

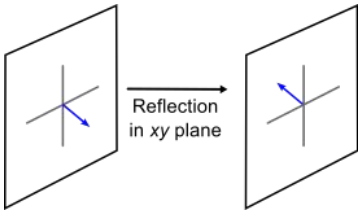


Figure 12.4.1 : Reflection in the xy plane.

Notice that the element for the dimension being reflected is the on that is negative. In the above case, since z is being reflected over the xy plane, the z element in the matrix is negative. If we were to reflect over the xz plane instead, the y element would be the one that is negative:

$$\sigma(xz)\mathbf{u} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

10.3.3: The n-fold Rotation Operation, C_n

The C_n operator rotates the molecule about an axis. The counterclockwise rotation of vector $\mathbf{u}$ about the z axis is:

$$C_n\mathbf{u} = \begin{pmatrix} \cos\frac{2\pi}{n} & -\sin\frac{2\pi}{n} & 0 \\ \sin\frac{2\pi}{n} & \cos\frac{2\pi}{n} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z \end{pmatrix}$$

For clockwise rotation, the sign on the $\sin\theta$ terms are reversed. This matrix simplifies dramatically for the C_2 rotation:

$$C_2\mathbf{u} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

Rotation matrices operating about the x, y and z axes are given by:

$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \tag{10.3.3}$$

$$R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \tag{10.3.4}$$

$$R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{10.3.5}$$

10.3.4: The Inversion operation, I

The inversion operation inverts every point:

$$I\mathbf{u} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$

10.3.5: C_{2v} Point Group

Now that we have seen the matrix form of our operators, we can see how the multiplication of each operator leads to another operations in the group. The C_{2v} multiplication table is:

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

For multiplication tables, the standard order of operation is the row elements (top) first, following by the column element (side). Every row or column includes every operation once and is different from any other row or column.

Let's look at $C_2\sigma_v$ multiplication, where σ_v is a reflection across the xz plane:

$$C_2\sigma_v = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \sigma_v'$$

where σ_v' is the reflection across the yz plane.

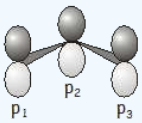
10.3.6: Matrix Representations and Groups

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. **Identity**.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. **Closure**. 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_{2v} point group, we showed that the combined symmetry operation $C_2\sigma_v$ is equivalent to σ_v'. In a matrix representation of the group, if the matrix representatives of C_2 and σ_v are multiplied together, the result will be the representative of σ_v'.
3. **Associativity**. The third 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.
3. **Reciprocality**. The final 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.

C_{2v}✔ Example 12.4.1 : Matrix Representation of the Point Group (the allyl radical)

We often use sets of atomic orbitals as basis functions for matrix representations. 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:

$$E \quad \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} \rightarrow \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$$

$$C_2 \quad \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} \rightarrow \begin{pmatrix} -p_3 \\ -p_2 \\ -p_1 \end{pmatrix}$$

$$\sigma_v \quad \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} \rightarrow \begin{pmatrix} -p_1 \\ -p_2 \\ -p_3 \end{pmatrix}$$

$$\sigma_v' \quad \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} \rightarrow \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$$

The matrices that carry out the transformation are

$$\Gamma(E) \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$$

$$\Gamma(C_2) \quad \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} -p_3 \\ -p_2 \\ -p_1 \end{pmatrix}$$

$$\Gamma(\sigma_v) \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} -p_1 \\ -p_2 \\ -p_3 \end{pmatrix}$$

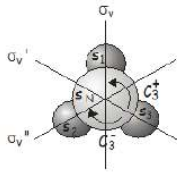
$$\Gamma(\sigma_v') \quad \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$$

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10.4: Molecules can be Represented by Reducible Representations

In addition to operators, we can define properties of molecules using a matrix representation. Before making the matrix, we need to carefully choose a basis set that defines the information we want to extract For example, let's say we want to know the symmetry of the valence s orbitals in ammonia, NH_3, which is in the C_{3v} point group. 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:

$$\begin{array}{ll} E & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3) \\ C_3^+ & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1) \\ C_3^- & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2) \\ \sigma_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2) \\ \sigma_v' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3) \\ \sigma_v'' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1) \end{array} \tag{10.4.1}$$

By inspection, the matrices that carry out the same transformations are:

$$\begin{array}{lll} \Gamma(E) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_1, s_2, s_3) \\ \Gamma(C_3^+) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_2, s_3, s_1) \\ \Gamma(C_3^-) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_1, s_2) \\ \Gamma(\sigma_v) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_1, s_3, s_2) \\ \Gamma(\sigma_v') & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_2, s_1, s_3) \\ \Gamma(\sigma_v'') & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_2, s_1) \end{array} \tag{10.4.2}$$

These six matrices therefore form a **reducible representation** for the C_{3v} point group in the (s_N, s_1, s_2, s_3) basis as we will see in the next chapter that these matrices reduce down to the irreducible representations found in the character tables. These reducible representations multiply together according to the group multiplication table and satisfy all the requirements for a mathematical group.

We choose different basis sets to extract different properties of molecules. For example, we could include representations of the valence p orbitals in N in our basis set to obtain the structure and symmetry of the molecular orbitals for ammonia. To understand understand the molecular motions of ammonia (translates, rotates, and vibrates), we could place a x, y, and z unit vectors on each atom to represent the their motion, and then construct our matrices.

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10.5: Character Tables Summarize the Properties of a Point Group

Now that we've learned 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.

10.5.1: Similarity Transforms

Suppose we have a basis set $(x_1, x_2, x_3, ...x_n)$, where x_i represents so position in x of each atom, and we have determined the matrix reducible 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). Consider an additional 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 $\mathbf{x'} = C\mathbf{x}$:

$$\begin{pmatrix} x'_1 \\ x'_2 \\ ... \\ x'_n \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & ... & c_{1n} \\ c_{21} & c_{22} & ... & c_{2n} \\ ... & ... & ... & ... \\ c_{n1} & c_{n2} & ... & c_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ ... \\ x_n \end{pmatrix} \tag{11.2}$$

where C is the transformation matrix. 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*. Now we look at what happens when we apply a symmetry operation g to our two basis sets. If $\mathbf{\Gamma}(g)$ and $\mathbf{\Gamma'}(g)$ are matrix representatives of the symmetry operation in the $\mathbf{x}$ and $\mathbf{x'}$ bases, then we have:

$$\begin{aligned} g\mathbf{x'} &= \mathbf{x'}\mathbf{\Gamma'}(g) \\ g\mathbf{x}C &= \mathbf{x}C\mathbf{\Gamma'}(g) && \text{since } \mathbf{x'} = \mathbf{x}C \\ g\mathbf{x} &= \mathbf{x}C\mathbf{\Gamma'}(g)C^{-1} && \text{multiplying on the right by } C^{-1} \text{and using } CC^{-1} = I \\ &= \mathbf{x}\mathbf{\Gamma}(g) \end{aligned} \tag{11.3}$$

We can therefore identify the similarity transform relating $\mathbf{\Gamma}(g)$, the matrix representative in our original basis, to $\mathbf{\Gamma'}(g)$, the representative in the transformed basis. The transform depends only on the matrix of coefficients used to transform the basis functions:

$$\mathbf{\Gamma}(g) = C\mathbf{\Gamma'}(g)C^{-1} \tag{11.4}$$

Also:

$$\mathbf{\Gamma'}(g) = C^{-1}\mathbf{\Gamma}(g)C \tag{11.5}$$

Characters of Representations

The trace of a matrix representative $\mathbf{\Gamma}(g)$ 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.

10.5.2: 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. All operations in the character table are contained in the first row of the character table, in this case E, C_3, & σ_v, these are all of the operations that can be preformed on the molecule that return the original structure. The first column contains the three irreducible representations A_1, A_2 & E. The character of the irreducible representation denotes what the operation does. A value of 1 represents no change, -1 opposite change and 0 is a combination of 1 & -1 (0's are found in degenerate molecules. The final two columns Rotation and Translation represented by R_x,R_y, R_z & x, y, z respectively. Each R_x, R_y, R_z & x, y, z term is the irreducible symmetry of a rotation or translation operation. Like wise the final column the orbital symmetries relates the orbital wave function to a irreducible representation.

C_{3v}	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	$(x, y), (xy, x^2 + y^2), (xz, yz), (R_x, R_y)$

(10.5.1)

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.

10.5.3: 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:

$$\begin{aligned} x' &= \cos\theta\, x + \sin\theta\, y \\ y' &= -\sin\theta\, x + \cos\theta\, y \end{aligned} \tag{10.5.2}$$

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 $\cos\theta$.*

10.5: Character Tables Summarize the Properties of a Point Group is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Jerry LaRue.

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10.6: Characters of Irreducible Representations

10.6.1: Symbols 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:

A	Nondegenerate ($d_i = 1$) representation that is symmetric (character 1) with respect to rotation about the principal axis in finite-order ($h \neq \infty$) groups.
B	Nondegenerate ($d_i = 1$) representation that is antisymmetric (character -1) with respect to rotation about the principal axis in finite-order ($h \neq \infty$) groups.
E	Doubly-degenerate ($d_i = 2$) representation in finite-order ($h \neq \infty$) groups.
T	Triply-degenerate ($d_i = 3$) representation in finite-order ($h \neq \infty$) groups.
Σ	Nondegenerate ($d_i = 1$) representation in infinite-order ($h = \infty$) groups.
Π, Δ, Φ	Doubly-degenerate ($d_i = 2$) representation in infinite-order ($h = \infty$) groups.

1. 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)
2. 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.
3. 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

10.6.2: 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	$\begin{Bmatrix}1 & \epsilon & \epsilon* \\ 1 & \epsilon* & \epsilon\end{Bmatrix}$		

(10.6.1)

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

(10.6.2)

10.6.3: Groups and subgroups have well-defined relationships as they descend or ascend in symmetry

Molecules can undergo structural changes through conformations or chemical reactions. Remember that the order of the subgroup must be an integer divisor from the order of the group. If the basic geometry of the molecule is preserved, the structure after the change may be a subgroup of the structure before the change, or vice versa. If the basic geometry does change, there may not be a relationship between the groups before and after. When point groups are related as group and subgroup, their irreducible representations are also related. A property that transforms as one representation in a group will transform as its correlated representation in a subgroup. **Correlation diagrams** show the relationships between subgroups and groups. Often, to or more bases of separate representations of a group yield the same set of $\chi(R)$ values for those operations that are carried over into the subgroup. In many cases, degenerate representations of a group (E or T) may become two or three distinguishable bases in a subgroup.

10.6.4: Reduce representations of infinite groups by approximating them as finite groups

We cannot use the tabular method for infinite-order groups since we cannot divide an infinite quantity by h. We will use group-subgroup relations to use the tabular method:

- Set up the reducible representation in any convenient subgroup
  - For $C_{\infty v}$, use C_{2v}
  - For $D_{\infty h}$, use D_{2h}
- Correlate the component irreducible representations with the species for the infinite-order group.

While somewhat limiting, this method is fairly effective.

10.6.5: The direct product of two irreducible representations give either a reducible or irreducible representation of the same group

The last column in the character table shows the direct product between any two linear vectors. Direct products can also be taken between any number of irreducible representations:

$$\Gamma_a \Gamma_b \Gamma_c = \Gamma_{abc}$$

The characters of the direct product representation Γ_{abc} for each operator R of the group are given by:

$$\chi_a(R)\chi_b(R)\chi_c(R) = \chi_{abc}(R)$$

The resulting representation may be reducible or irreducible. The dimension of the product, D_p, is the product of the dimensions of all the component representations:

$$d_p = \prod_i d_i$$

These properties will become useful later, so we will reference them as needed. Briefly:

1. If all the combined irreducible representations are nondegenerate, then the product will be a nondegenerate representation too.
2. The product of a nondegenerate representation and a degenerate representation is a degenerate representation.
3. The direct product of any representation with the totally symmetric representation is the representation itself.
4. The direct product of degenerate representations is a reducible representation.

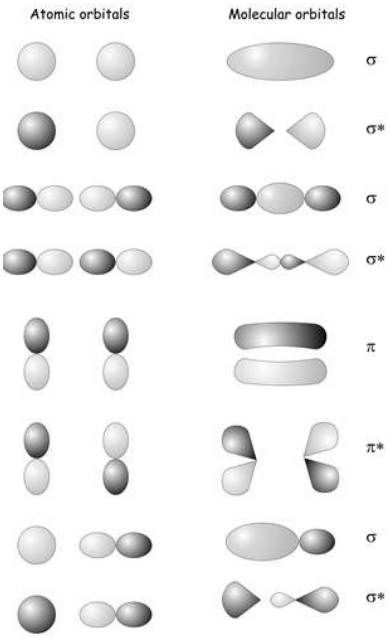
5. The direct product of an irreducible representation with itself is or contains the totally symmetry representation.
6. Only the direct product of a representation with itself is or contains the totally symmetric representation.

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10.7: Molecular Orbitals can be Constructed on the Basis of Symmetry

10.7.1: Bonding in Diatomics



You will already be familiar with the idea of constructing molecular orbitals from linear combinations of atomic orbitals from previous courses covering bonding in diatomic molecules. By considering the symmetries of s and p orbitals on two atoms, we can form **bonding** and **antibonding** combinations labeled as having either σ or π symmetry depending on whether they resemble s or p orbitals when viewed along the bond axis (see diagram below). In all of the cases shown, only atomic orbitals that have the same symmetry when viewed along the bond axis z can form a chemical bond e.g. two s orbitals, two p_z orbitals , or an s and a p_z can form a bond, but a p_z and a p_x or an s and a p_x or a p_y cannot. It turns out that the rule that determines whether or not two atomic orbitals can bond is that *they must belong to the same symmetry species within the point group of the molecule*.

We can prove this mathematically for two atomic orbitals ϕ_i and ϕ_j by looking at the overlap integral between the two orbitals.

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \int \phi_i^* \phi_j d\tau \qquad (18.1)$$

In order for bonding to be possible, this integral must be non-zero. The product of the two functions ϕ_1 and ϕ_2 transforms as the direct product of their symmetry species i.e. $\Gamma_{12} = \Gamma_1 \otimes \Gamma_2$. As explained above, for the overlap integral to be non-zero, Γ_{12} must contain the totally symmetric irreducible representation (A_{1g} for a homonuclear diatomic, which belongs to the point group $D_{\infty h}$). As it happens, this is only possible if ϕ_1 andϕ_2 belong to the same irreducible representation. These ideas are summarized for a diatomic in the table below.

First Atomic Orbital	Second Atomic Orbital	$\Gamma_1 \otimes \Gamma_2$	Overlap Integral	Bonding?
$s\ (A_{1g})$	$s\ (A_{1g})$	A_{1g}	Non-zero	Yes
$s\ (A_{1g})$	$p_x\ (E_{1u})$	E_{1u}	Zero	No
$s\ (A_{1g})$	$p_z\ (A_{1u})$	A_{1u}	Zero	No
$p_x\ (E_{1u})$	$p_x\ (E_{1u})$	$A_{1g} + A_{2g} + E_{2g}$	Non-zero	Yes
$p_X\ (E_{1u})$	$p_z\ (A_{1u})$	E_{1g}	Zero	No
$p_z\ (A_{1u})$	$p_z\ (A_{1u})$	A_{1g}	Non-zero	Yes

(18.2)

10.7.2: Bonding in Polyatomics- Constructing Molecular Orbitals from SALCs

In the previous section we showed how to use symmetry to determine whether two atomic orbitals can form a chemical bond. How do we carry out the same procedure for a polyatomic molecule, in which many atomic orbitals may combine to form a bond? Any SALCs of the same symmetry could potentially form a bond, so all we need to do to construct a molecular orbital is take a linear combination of all the SALCs of the same symmetry species. The general procedure is:

1. Use a basis set consisting of valence atomic orbitals on each atom in the system.
2. Determine which irreducible representations are spanned by the basis set and construct the SALCs that transform as each irreducible representation.
3. Take linear combinations of irreducible representations of the same symmetry species to form the molecular orbitals. E.g. in our NH_3 example we could form a molecular orbital of A_1 symmetry from the two SALCs that transform as A_1,

$$\begin{aligned} \Psi(A_1) &= c_1\phi_1 + c_2\phi_2 \\ &= c_1 s_N + c_2 \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3) \end{aligned} \qquad (19.1)$$

Unfortunately, this is as far as group theory can take us. It can give us the functional form of the molecular orbitals but it cannot determine the coefficients c_1 and c_2. To go further and obtain the expansion coefficients and orbital energies, we must turn to quantum mechanics. The material we are about to cover will be repeated in greater detail in later courses on quantum mechanics

and valence, but they are included here to provide you with a complete reference on how to construct molecular orbitals and determine their energies.

10.7.3: 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 k^{th} irreducible representation appears in the representation.

$$a_k = \frac{1}{h}\sum_C n_C \chi(g)\chi_k(g) \tag{10.7.1}$$

3. Construct the SALCs ϕ_i that transform as each irreducible representation using Equation 16.1

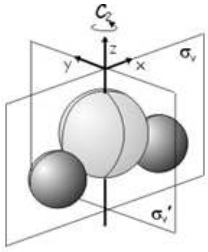
$$\phi_i = \sum_g \chi_k(g) g f_i \tag{10.7.2}$$

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.

10.7.4: A more complicated bonding example

As another example, we will use group theory to construct the molecular orbitals of H_2O (point group C_{2v}) using a basis set consisting of all the valence orbitals. The valence orbitals are a $1s$ orbital on each hydrogen, which we will label s_H and s'_H, and a $2s$ and three $2p$ orbitals on the oxygen, which we will label s_O, p_x, p_y, p_z giving a complete basis $(s_H, s'_H, s_O, p_x, p_y, p_z)$.

The first thing to do is to determine how each orbital transforms under the symmetry operations of the C_{2v} point group (E, C_2, σ_v and σ'_v), construct a matrix representation and determine the characters of each operation. The symmetry operations and axis system we will be using are shown below.



The orbitals transform in the following way

$$\begin{array}{lllll} E & (s_H, s'_H, s_O, p_x, p_y, p_z) & \rightarrow & (s_H, s'_H, s_O, p_x, p_y, p_z) \\ C_2 & (s_H, s'_H, s_O, p_x, p_y, p_z) & \rightarrow & (s'_H, s_H, s_O, -p_x, -p_y, p_z) \\ \sigma_v(xz) & (s_H, s'_H, s_O, p_x, p_y, p_z) & \rightarrow & (s_H, s'_H, s_O, p_x, -p_y, p_z) \\ \sigma'_v(yz) & (s_H, s'_H, s_O, p_x, p_y, p_z) & \rightarrow & (s'_H, s_H, s_O, -p_x, p_y, p_z) \end{array} \tag{10.7.3}$$

10.7.5: A short aside on constructing matrix representatives

After a little practice, you will probably be able to write matrix representatives straight away just by looking at the effect of the symmetry operations on the basis. However, if you are struggling a little the following procedure might help.

Remember that the matrix representatives are just the matrices we would have to multiply the left hand side of the above equations by to give the right hand side. In most cases they are very easy to work out. Probably the most straightforward way to think about it

is that each column of the matrix shows where one of the original basis functions ends up. For example, the first column transforms the basis function s_H to its new position. The first column of the matrix can be found by taking the result on the right hand side of the above expressions, replacing every function that *isn't* s_H with a zero, putting the coefficient of s_H (1 or -1 in this example) in the position at which it occurs, and taking the transpose to give a column vector.

Rotation

Consider the representative for the C_2 operation. The original basis $(s_H, s'_H, s_O, p_x, p_y, p_z)$ transforms into $(s'_H, s_H, s_O, -p_x, -p_y, p_z)$. The first column of the matrix therefore transforms s_H into s'_H. Taking the result and replacing all the other functions with zeroes gives $(0, s_H, 0, 0, 0, 0)$. The coefficient of s_H is 1, so the first column of the C_2 matrix representative is

$$\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{10.7.4}$$

10.7.6: Matrix representation, characters and SALCs

The matrix representatives and their characters are

$$\begin{array}{cccc} E & C_2 & \sigma_v & \sigma'_v \\ \begin{pmatrix} 1&0&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&1&0&0 \\ 0&0&0&0&1&0 \\ 0&0&0&0&0&1 \end{pmatrix} & \begin{pmatrix} 0&1&0&0&0&0 \\ 1&0&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&-1&0&0 \\ 0&0&0&0&-1&0 \\ 0&0&0&0&0&1 \end{pmatrix} & \begin{pmatrix} 1&0&0&0&0&0 \\ 0&1&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&1&0&0 \\ 0&0&0&0&-1&0 \\ 0&0&0&0&0&1 \end{pmatrix} & \begin{pmatrix} 0&1&0&0&0&0 \\ 1&0&0&0&0&0 \\ 0&0&1&0&0&0 \\ 0&0&0&-1&0&0 \\ 0&0&0&0&1&0 \\ 0&0&0&0&0&1 \end{pmatrix} \\ \chi(E) = 6 & \chi(C_2) = 0 & \chi(\sigma_v) = 4 & \chi(\sigma'_v) = 2 \end{array} \tag{10.7.5}$$

Now we are ready to work out which irreducible representations are spanned by the basis we have chosen. The character table for C_{2v} is:

C_{2v}	E	C_2	σ_v	σ'_v	$h = 4$
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	−1	−1	xy, R_z
B_1	1	−1	1	−1	x, xz, R_y
B_2	1	−1	−1	1	y, yz, R_x

As before, we use Equation (15.20) to find out the number of times each irreducible representation appears.

$$a_k = \frac{1}{h} \sum_C n_C \chi(g) \chi_k(g) \tag{10.7.6}$$

We have

$$\begin{aligned} a(A_1) &= \frac{1}{4}(1 \times 6 \times 1 + 1 \times 0 \times 1 + 1 \times 4 \times 1 + 1 \times 2 \times 1) &= 3 \\ a(A_2) &= \frac{1}{4}(1 \times 6 \times 1 + 1 \times 0 \times 1 + 1 \times 4 \times -1 + 1 \times 2 \times -1) &= 0 \\ a(B_1) &= \frac{1}{4}(1 \times 6 \times 1 + 1 \times 0 \times -1 + 1 \times 4 \times 1 + 1 \times 2 \times -1) &= 2 \\ a(B_2) &= \frac{1}{4}(1 \times 6 \times 1 + 1 \times 0 \times -1 + 1 \times 4 \times -1 + 1 \times 2 \times 1) &= 1 \end{aligned} \tag{10.7.7}$$

so the basis spans $3A_1 + 2B_1 + B_2$. Now we use the projection operators applied to each basis function f_i in turn to determine the SALCs $\phi_i = \Sigma_g \chi_k(g) g f_i$

The SALCs of A_1 symmetry are:

$$\begin{array}{lcll} \phi(s_H) & = & s_H + s'_H + s_H + s'_H & = & 2(s_H + s'_H) \\ \phi(s'_H) & = & s'_H + s_H + s'_H + s_H & = & 2(s_H + s'_H) \\ \phi(s_O) & = & s_O + s_O + s_O + s_O & = & 4s_O \\ \phi(p_x) & = & p_x - p_x + p_x - p_x & = & 0 \\ \phi(p_y) & = & p_y - p_y + p_y - p_y & = & 0 \\ \phi(p_z) & = & p_z + p_z + p_z + p_z & = & 4p_z \end{array} \tag{10.7.8}$$

The SALCs of B_1 symmetry are:

$$\begin{array}{lcll} \phi(s_H) & = & s_H - s'_H + s_H - s'_H & = & 2(s_H - s'_H) \\ \phi(s'_H) & = & s'_H - s_H + s'_H - s_H & = & 2(s'_H - s_H) \\ \phi(s_O) & = & s_O - s_O + s_O - s_O & = & 0 \\ \phi(p_x) & = & p_x + p_x + p_x + p_x & = & 4p_x \\ \phi(p_y) & = & p_y + p_y - p_y - p_y & = & 0 \\ \phi(p_z) & = & p_z - p_z + p_z - p_z & = & 0 \end{array} \tag{10.7.9}$$

The SALCs of B_2 symmetry are:

$$\begin{array}{lcll} \phi(s_H) & = & s_H - s'_H - s_H = s'_H & = & 0 \\ \phi(s'_H) & = & s'_H - s_H - s'_H + s_H & = & 0 \\ \phi(s_O) & = & s_O - s_O - s_O + s_O & = & 0 \\ \phi(p_x) & = & p_x + p_x - p_x - p_x & = & 0 \\ \phi(p_y) & = & p_y + p_y + p_y + p_y & = & 4p_y \\ \phi(p_z) & = & p_z - p_z - p_z + p_z & = & 0 \end{array} \tag{10.7.10}$$

After normalization, our SALCs are therefore:

A_1 symmetry

$$\begin{array}{lcl} \phi_1 & = & \frac{1}{\sqrt{2}}(s_H + s'_H) \\ \phi_2 & = & s_O \\ \phi_3 & = & p_z \end{array} \tag{10.7.11}$$

B_1 symmetry

$$\begin{array}{lcl} \phi_4 & = & \frac{1}{\sqrt{2}}(s_H - s'_H) \\ \phi_5 & = & p_x \end{array} \tag{10.7.12}$$

B_2 symmetry

$$\phi_6 = p_y \tag{10.7.13}$$

Note that we only take one of the first two SALCs generated by the B_1 projection operator since one is a simple multiple of the other (i.e. they are not linearly independent). We can therefore construct three molecular orbitals of A_1 symmetry, with the general form

$$\begin{array}{rcl} \Psi(A_1) & = & c_1\phi_1 + c_2\phi_2 + c_3\phi_3 \\ & = & c'_1(s_H + s'_H) + c_2 s_O + c_3 p_z \quad \text{where } c'_1 = \frac{c_1}{\sqrt{2}} \end{array} \tag{10.7.14}$$

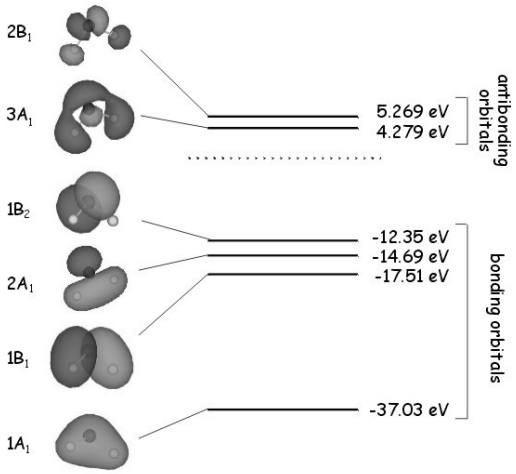
two molecular orbitals of B_1 symmetry, of the form

$$\begin{array}{rcl} \Psi(B_1) & = & c_4\phi_4 + c_5\phi_5 \\ & = & c'_4(s_H - s'_H) + c_5 p_z \end{array} \tag{10.7.15}$$

and one molecular orbital of B_2 symmetry

$$\begin{aligned} \Psi(B_2) &= \phi_6 \\ &= p_y \end{aligned} \tag{10.7.16}$$

To work out the coefficients c_1 - c_5 and determine the orbital energies, we would have to solve the secular equations for each set of orbitals in turn. We are not dealing with a conjugated p system, so in this case Hückel theory cannot be used and the various H_{ij} and S_{ij} integrals would have to be calculated numerically and substituted into the secular equations. This involves a lot of tedious algebra, which we will leave out for the moment. The LCAO orbitals determined above are an approximation of the true molecular orbitals of water, which are shown on the right. As we have shown using group theory, the A_1 molecular orbitals involve the oxygen $2s$ and $2p_z$ atomic orbitals and the sum $s_H + s'_H$ of the hydrogen $1s$ orbitals. The B_1 molecular orbitals involve the oxygen $2p_x$ orbital and the difference $s_H - s'_H$ of the two hydrogen $1s$ orbitals, and the B_2 molecular orbital is essentially an oxygen $2p_y$ atomic orbital.



10.7.7: Electronic transitions in molecules

When an electron is excited from one electronic state to another, this is what is called an electronic transition. A clear example of this is part C in the energy level diagram shown above. Just as in a vibrational transition the selection rules for electronic transitions are dictated by the transition moment integral. However we now must consider both the electronic state symmetries and the vibration state symmetries since the electron will still be coupled between two vibrational states that are between two electronic states. This gives us this modified transition moment integral:

$$\langle \psi_{el}\psi_{vib}|\mu|\psi_{el}\psi_{vib}\rangle$$

Where you can see that the symmetry of the initial electronic state & vibrational state are in the Bra and the final electronic and vibrational states are in the Ket. Though this appears to be a modified version of the transition moment integral, the same equation holds true for a vibrational transition. The only difference would be the electronic state would be the same in both the initial and final states. Which the dot product of yields the totally symmetric representation, making the electronic state irrelevant for purely vibrational spectroscopy.

10.7.7.1: Raman

In Resonance Raman spectroscopy transition that occurs is the excitation from one electronic state to another and the selection rules are dictated by the transition moment integral discussed in the electronic spectroscopy segment. However mechanically Raman does produce a vibration like IR, but the selection rules for Raman state there must be a change in the polarization, that is the volume occupied by the molecule must change. But as far as group theory to determine whether or not a transition is allowed one can use the transition moment integral presented in the electronic transition portion. Where one enters the starting electronic state symmetry and vibrational symmetry and final electronic state symmetry and vibrational state, perform the direct product with the different M's or polarizing operators For more information about this topic please explore the Raman spectroscopy portion of the Chemwiki

10.7.7.2: Fluorescence

For the purposes of Group Theory Raman and Fluorescence are indistinguishable. They can be treated as the same process and in reality they are quantum mechanically but differ only in how Raman photons scatter versus those of fluorescence.

10.7.7.3: Phosphorescence

Phosphorescence is the same as fluorescence except upon excitation to a singlet state there is an interconversion step that converts the initial singlet state to a triplet state upon relaxation. This process is longer than fluorescence and can last microseconds to several minutes. However despite the singlet to triplet conversion the transition moment integral still holds true and the symmetry of ground state and final state still need to contain the totally symmetric representation.

10.7.7.4: Symmetry

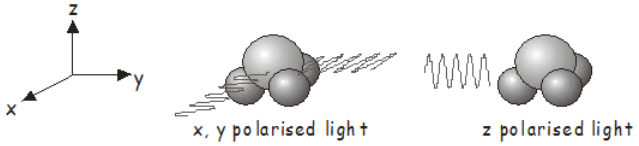
Assume that we have a molecule in some initial state Ψ_i. We want to determine which final states Ψ_f can be accessed by absorption of a photon. Recall that for an integral to be non-zero, the representation for the integrand must contain the totally symmetric irreducible representation. The integral we want to evaluate is

$$\hat{\mu}_{fi} = \int \Psi_f^* \hat{\mu} \Psi_i d\tau \tag{27.4}$$

so we need to determine the symmetry of the function $\Psi_f^* \hat{\mu} \Psi_i$. As we learned in Section 18, the product of two functions transforms as the direct product of their symmetry species, so all we need to do to see if a transition between two chosen states is allowed is work out the symmetry species of Ψ_f, $\hat{\mu}$ and Ψ_i , take their direct product, and see if it contains the totally symmetric irreducible representation for the point group of interest. Equivalently (as explained in Section 18), we can take the direct product of the irreducible representations for $\hat{\mu}$ and Ψ_i and see if it contains the irreducible representation for Ψ_f. This is best illustrated using a couple of examples.

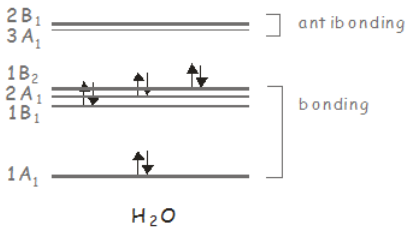
Earlier in the course, we learned how to determine the symmetry molecular orbitals. The symmetry of an electronic state is found by identifying any unpaired electrons and taking the direct product of the irreducible representations of the molecular orbitals in which they are located. The ground state of a closed-shell molecule, in which all electrons are paired, always belongs to the totally symmetric irreducible representation[7]. As an example, the electronic ground state of NH_3, which belongs to the C_{3v} point group, has A_1 symmetry. To find out which electronic states may be accessed by absorption of a photon, we need to determine the irreducible representations for the electric dipole operator $\hat{\mu}$. Light that is linearly polarized along the x, y, and z axes transforms in the same way as the functions x, y, and z in the character table[8]. From the C_{3v} character table, we see that x- and y-polarized light transforms as E, while z-polarized light transforms as A_1. Therefore:

i. For x- or y-polarized light, $\Gamma_{\hat{\mu}} \otimes \Gamma_{\Psi 1}$ transforms as $E \otimes A_1 = E$. This means that absorption of x- or y-polarized light by ground-state NH_3 (see figure below left) will excite the molecule to a state of E symmetry.
ii. For z-polarized light, $\Gamma_{\hat{\mu}} \otimes \Gamma_{\Psi 1}$ transforms as $A_1 \otimes A_1 = A_1$. Absorption of z-polarized light by ground state NH_3 (see figure below right) will excite the molecule to a state of A_1 symmetry.



Of course, the photons must also have the appropriate energy, in addition to having the correct polarization to induce a transition.

We can carry out the same analysis for H_2O, which belongs to the C_{2v} point group. We showed previously that H_2O has three molecular orbitals of A_1 symmetry, two of B_1 symmetry, and one of B_2 symmetry, with the ground state having A_1 symmetry. In the C_{2v} point group, x-polarized light has B_1 symmetry, and can therefore be used to excite electronic states of this symmetry; y-polarized light has B_2 symmetry, and may be used to access the B_2 excited state; and z-polarized light has A_1 symmetry, and may be used to access higher lying A_1 states. Consider our previous molecular orbital diagram for H_2O.



The electronic ground state has two electrons in a B_2 orbital, giving a state of A_1 symmetry ($B_2 \otimes B_2 = A_1$). The first excited electronic state has the configuration $(1B_2)^1(3A_1)^1$ and its symmetry is $B_2 \otimes A_1 = B_2$. It may be accessed from the ground state by a y-polarized photon. The second excited state is accessed from the ground state by exciting an electron to the $2B_1$ orbital. It has the configuration $(1B_2)^1(2B_1)^1$, its symmetry is $B_2 \otimes B_1 = A_2$. Since neither x-, y- or z-polarized light transforms as A_2, this state may not be excited from the ground state by absorption of a single photon.

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10.8: H_2O

Construct SALCs and the molecular orbital diagram for H_2O.

This is the first example so far that is not a linear molecule. Water is a bent molecule, and so it is important to remember that interactions of pendant ligands are dependent on their positions in space. You should consider the positions of the three atoms in water to be essentially fixed in relation to each other. The process for constructing the molecular orbital diagram *for a non-linear molecule*, like water, is similar to the process for linear molecules. We will walk through the steps below to construct the molecular orbital diagram of water.

Preliminary Steps

Step 1. Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.

The H_2O molecule is bent and its point group is C_{2v}. The z axis is collinear with the principal axis, the C_2 axis. There is no need to simplify this problem, as we had done for previous examples. The C_{2v} point group is simple enough.

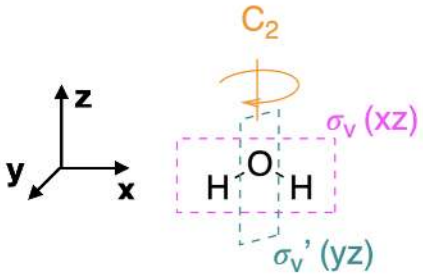


Figure **10.8.1**: The water molecular is in the C_{2v} point group. (CC-BY-NC-SA; Kathryn Haas)

Step 2. Identify and count the pendant atoms' valence orbitals.

Each of the two pendant hydrogen atoms has one valence orbital, the $1s$. Thus, we can expect a total of two SALCs from these two atoms.

Generate SALCs

The SALCs for H_2O are quite simple, yet we will systematically derive the SALCs here to demonstrate the process.

Step 3. Generate the Γ's

Use the C_{2v} character table to generate one reducible representation (Γ); in this case we need only one Γ because there is only one type of valence orbital (the $1s$). For each s orbital, assign a value of 1 if it remains in place during the operation or zero if it moves out of its original place. The Γ is given below:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Γ_{1s}	2	0	2	0

Step 4. Break Γ's into irreducible representations for individual SALCs

Reduce each Γ into its component irreducible representations. Using either of the processes described previously, we find that the Γ reduces to the two irreducible representations A_1 and B_1 under the C_{2v} point group.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Γ_{1s}	**2**	**0**	**2**	**0**
A_1	1	1	1	1
B_1	1	−1	1	−1

Step 5. Sketch the SALCs

From the systematic process above, you have found the symmetries (the irreducible representations) of both SALCs under the C_{2v} point group. To sketch the SALC that corresponds to each irreducible representation, again we use the C_{2v} character table, and

specifically the functions listed on the right side columns of the table.

One A_1 SALC: The A_1 SALC is singly degenerate and symmetric with respect to both the principle axis (z) and the inversion center (i) (based on its Mulliken Label). We can look at the functions in the C_{2v} character table that correspond to A_1 and see that it is completely symmetric under the group (because the combination of x^2, y^2, z^2 shows that it is totally symmetric). This would be the same symmetry as an s orbital on the central oxygen atom. From this information, we know that this SALC must have symmetry compatible with an s orbital on the central atom. We can also see from the character table that the z axis, and thus a p_z orbital on oxygen, also possesses A_1 symmetry. This tells us that in addition to being compatible with the oxygen s orbital, it should also be compatible with the oxygen p_z orbital. From this information we can draw the A_1 SALC shown in Figure 10.8.2. *If it is not obvious how the A_1 sketch in Fig. 10.8.2 is compatible with the s and p_z orbitals of oxygen, inspect the drawings corresponding to molecular orbitals $2a_1$ and $3a_1$ in Fig. 10.8.3.*

One B_1 SALC: The Mulliken Label tells us that the B_1 SALC is singly degenerate and antisymmetric with respect to both the principal axis and the inversion center. The function, x, appearing with B_1 in the character table tells us that this SALC has the same symmetry as the x axis, or a p_x orbital on the central oxygen atom. From this information, we know that this SALC should be compatible with a p_x orbital on the central atom, and we can draw the B_1 SALCs shown in Figure 10.8.2. *If it is not obvious how the B_1 sketch in Fig. 10.8.2 is compatible with the p_x orbital of oxygen, inspect the drawing corresponding to molecular orbital $1b_1$ in Fig. 10.8.3.*

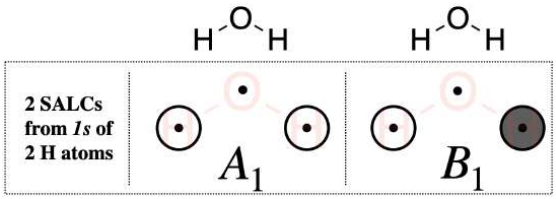


Figure 10.8.2: Sketch of the A_1 and B_1 hydrogen SALCs of water. (CC-BY-NC-SA; Kathryn Haas)

Not convinced about the sketches of these SALCs? You can convince yourself by putting them to the test. Try the exercise below.

? Exercise 10.8.1

Perform all operations of the C_{2v} point group on the two sketches of H SALCs shown in Figure 10.8.2, and convince yourself that each sketch does possess the A_1 and B_1 symmetries assigned to them, respectively, under the C_{2v} point group.

Answer

Add texts here. Do not delete this text first.

Draw the MO diagram for H_2O

Step 6. Combine SALCs with AO's of like symmetry.

First we must identify the valence orbitals on the central oxygen: there are four including $2s$, $2p_x$, $2p_y$, and $2p_z$. Now we identify the symmetry of each using the C_{2v} character table. The symmetry of a central $2s$ orbital corresponds to the combination of functions x^2, y^2, and z^2 in the character table; this is A_1. The p_z orbital also corresponds to A_1. And so on... The symmetries of oxygen valence orbitals are listed below.

$$2s = A_1$$
$$2p_x = B_1$$
$$2p_y = B_2$$
$$2p_z = A_1$$

Now that we have identified the symmetries of the two hydrogen SALCs and the four valence orbitals on oxygen, we know which atomic orbitals and SALCs may combine based on compatible symmetries. We also need to know the relative orbital energy levels so that we can predict the relative strength of orbital interactions. The orbital ionization energies are listed in Section 5.3.1.

With knowledge of both orbital symmetries and energies, we can construct the molecular orbital diagram. The valence orbitals of oxygen go on one side of the diagram while the hydrogen group orbitals are drawn on the opposite side. Molecular orbitals are

drawn in the center column of the diagram, as shown in Figure 10.8.3:

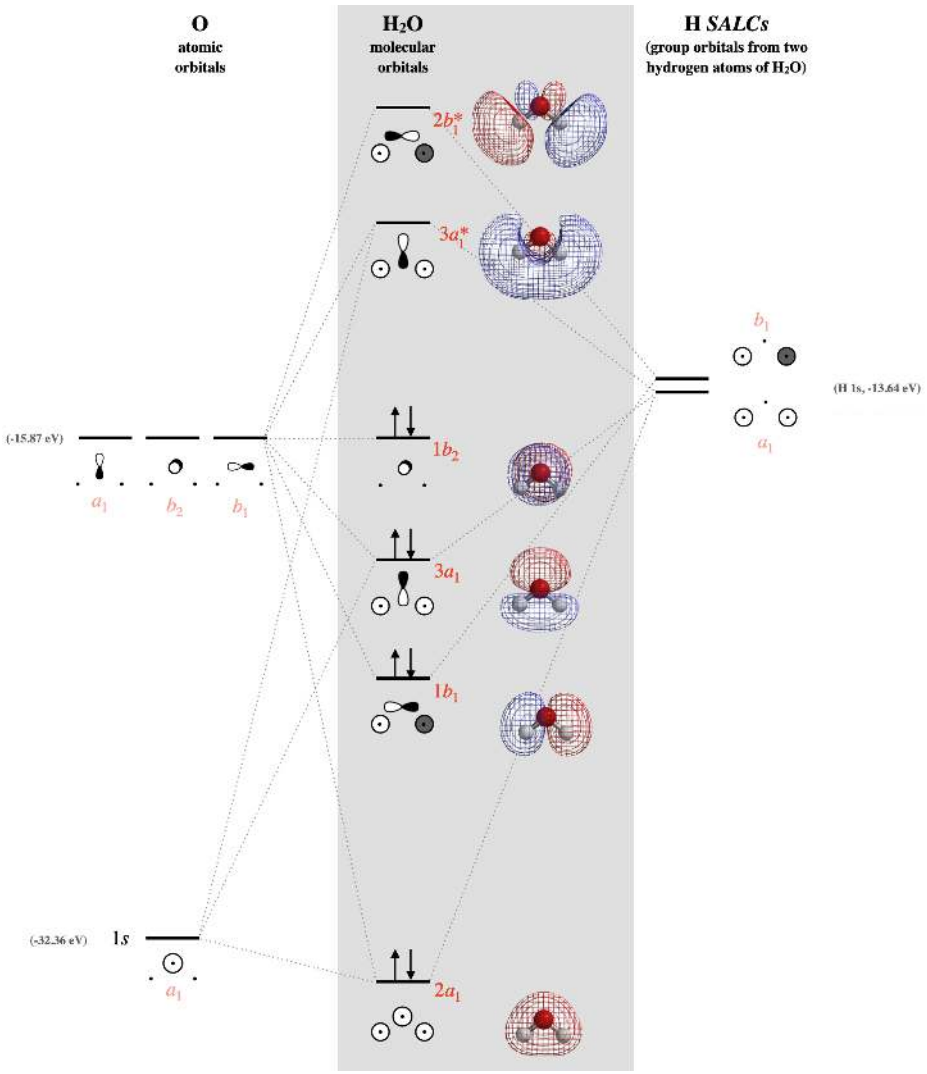


Figure 10.8.3: The molecular orbital diagram of water. Molecular orbital surfaces calculated using Spartan software. The surface of the $3a_1^*$ orbital has been trimmed. (CC-BY-NC-SA; Kathryn Haas)

Example 10.8.1

In the previous examples shown for the molecular orbital diagrams of the bifluoride anion and carbon dioxide, we discussed differences in the understanding of those molecules from molecular orbital theory compared to Lewis structures. Water contains two lone pairs in its Lewis structure. Compare the predictions about water's lone pairs of electrons and its reactivity based on (1) the combination of elementary models (Lewis, Valence Bond, and Hybridized Orbital theories) and (2) Molecular Orbital theory. Specifically address and explain how the elementary models differ from molecular orbital theory in the following respects:

a. Where are the lone pairs in water?
b. Are the two lone pairs equivalent or are they different?
c. Where are sites on the molecule that will undergo reaction with electrophiles and nucleophiles?

Solution

1) Elementary models: The Lewis structure predicts that two lone pairs are (a) localized on the oxygen atom of water and that (b) both lone pairs are equivalent. The Lewis structure, combined with Valence Bond Theory, would predict that lone pairs occupy two equivalent hybridized sp^3 atomic orbitals on oxygen. (c) Lewis theory would predict that the oxygen lone pairs are

nucleophiles; thus an electrophile would react with the oxygen atom lone pairs. The polarized O-H bond leaves the H atoms as the most electrophilic locations on the water molecule; thus nucleophiles would react at the H atoms of water.

2) Molecular orbital theory: The molecular orbitals predict that (a) the two lone pairs of water are not equivalent, and that (b) each is distributed over the entire molecule. One lone pair is in the truly non-bonding $1b_2$ orbital (Figure **10.8.3**), which is also the HOMO. There is not another truly non-bonding orbital in the molecule, but the lowest-energy $2a_1$ orbital could be considered mostly non-bonding due to the large energy difference between it and other valence orbitals. (c) Although the $2a_1$ orbital can be considered mostly non-bonding, we cannot expect the electrons in $2a_1$ to react readily, as they are in the lowest-energy molecular orbital. Molecular orbital theory predicts that reactions occur at the HOMO and LUMO orbitals. The HOMO reacts with electrophiles, and in this case, the HOMO is distributed over the top and bottom faces of the molecule, and is centered on the oxygen atom. The LUMO would react with nucleophiles. The LUMO is the orbital labeled $3a_1^*$ in Figure **10.8.3**, and has a major lobe that is distributed more heavily over the H atoms, and from this we should predict H atoms to be the preferred site of reaction for nucleophiles.

Expressing molecular orbitals in terms of Ψ

The general expression for a molecular orbital, or the linear combination of atomic orbitals (LCAO), was given previously as $\Psi = c_a\psi_a + c_b\psi_b$. In this expression, the wavefunction of two atoms (ψ_a and ψ_b) is combined to form the wavefunction of the molecular orbital. The coefficients c_a and c_b quantify the contribution of each atomic ψ to the molecular Ψ.

$$\Psi = c_a\psi_a + c_b\psi_b$$

In the case of polyatomic orbitals, each LCAO is constructed of atomic orbitals from a central atom and group orbitals (SALCs) from the pendent atoms. In the case of water, the expression above could be modified to give the expression below.

$$\Psi = c_{oxygen}\,(\psi_{oxygen}) + c_{SALCs}\,(N(\psi_{H_a} \pm \psi_{H_b}))$$

N represents the normalizing requirement that was mentioned previously in reference to the requirements for electron wavefunctions and probability functions. The normalizing requirement simply stated is the requirement that the probability of finding the electron in any orbital, including group orbitals, is 1. In general, the value of N for a group orbital is...

$$N = \frac{1}{\sum c_i^2}$$

...where c_i is the coefficient of each unique atomic orbital that contributes to the group. For the hydrogen SALCs of water, there are two atomic orbitals that contribute to equally to each SALC, and so the coefficient on each of the two orbitals is 1. This gives $N = \left(\frac{1}{\sqrt{1^2+1^2}}\right) = \frac{1}{\sqrt{2}}$ for the H SALCs of water.

There are only two hydrogen SALCs: the one in which the hydrogen wavefunctions are added ($N(\psi_{H_a} + \psi_{H_b})$) has A_1 symmetry, and the one in which the hydrogen wavefunctions are subtracted ($N(\psi_{H_a} - \psi_{H_b})$) has B_1 symmetry.

The molecular orbitals from Figure **10.8.3** are expressed below in terms of their LCAO of individual wavefunctions. Yet, note that these expressions are simplifications that ignore orbital mixing. For example, as expressed below, they ignore contributions of oxygen $2s$ to the higher energy moelcular orbitals with A_1 symmetry (the $3a_1$ and $3a_1^*$ in Figure **10.8.3**).

MO		*OxygenAO*		*HydrogenSALC*	*Description*
Ψ_{2a_1}	$=$	$c_{(ox1)}\psi_{(2s)}$	$+$	$c_{(hy1)}[N(\psi_{H_a} + \psi_{H_b})]$	$c_{(hy1)}$ is positive; bonding, slightly nonbonding
Ψ_{1b_1}	$=$	$c_{(ox2)}\psi_{(2p_x)}$	$+$	$c_{(hy2)}[N(\psi_{H_a} - \psi_{H_b})]$	$c_{(hy2)}$ is positive; bonding
Ψ_{3a_1}	$=$	$c_{(ox3)}\psi_{(2p_z)}$	$+$	$c_{(hy3)}[N(\psi_{H_a} + \psi_{H_b})]$	$c_{(hy3)}$ is positive; bonding
Ψ_{1b_2}	$=$	$\psi_{(2p_y)}$			nonbonding
$\Psi^*_{3a_1}$	$=$	$c_{(ox4)}\psi_{(2p_z)}$	$+$	$c_{(hy4)}[N(\psi_{H_a} + \psi_{H_b})]$	$c_{(hy4)}$ is negative; antibonding
$\Psi^*_{1b_1}$	$=$	$c_{(ox5)}\psi_{(2p_x)}$	$+$	$c_{(hy5)}[N(\psi_{H_a} - \psi_{H_b})]$	$c_{(hy5)}$ is negative; antibonding

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10.9: The Exploitation of Symmetry Can Help Simplify Numerical Calculations

To a fully understand the math behind group theory one needs to take a look at the theory portion of the Group Theory topic or refer to one of the reference text listed at the bottom of the page. Never the less as Chemist the object in question we are examining is usually a molecule. Though we live in the 21st century and much is known about the physical aspects that give rise to molecular and atomic properties. The number of high level calculations that need to be performed can be both time consuming and tedious. To most experimentalist this task is takes away time and is usually not the integral part of their work. When one thinks of group theory applications one doesn't necessarily associated it with everyday life or a simple toy like a Rubik's cube. A Rubik's cube is an a cube that has a $\mathbf{3 \times 3}$ array of different colored tiles on each of its six surfaces, for a total of 54 tiles. Since the cube exist in 3D space, the three axis are x, y, z. Since the rubik's cube only allows rotation which are called operations, there are three such operations around each of the x, y, z axis.

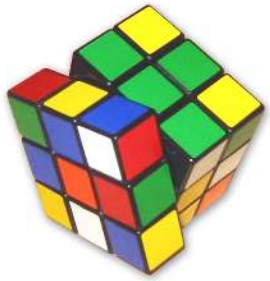


Figure: Reubik's cube. Use with permission from Wikipedia

Of course the ultimate challenge of a Rubik's cube is to place all six colors on each of the six faces. By performing a series of such operations on the Rubik's cube one can arrive at a solution (A link of a person solving a Rubik's cube[1] in 10.4s with operations performed noted, the operations performed will not translate to chemistry applications but it is a good example of how symmetry operations arrive at a solution). The operations shown in the Rubik's cube case are inherent to the make up of the cube, i.e., the only operations allowed are the rotations along the x, y, z axis. Therefore the Rubik's cube only has x,y,z rotation operations. Similarly the operations that are specific to a molecule are dependent on its symmetry.

Using group theory, we can exploit the symmetry of molecules to give us a rich amount of information on the molecular orbitals, rotations, and vibrations of bonds, to name a few. Making symmetry arguments, we can skip complicated quantum calculations to gain qualitatively accurate information.

In section 10.7, 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 $\mathbf{6 \times 6}$ secular determinant.

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{10.9.1}$$

Since the secular determinant is a $\mathbf{6 \times 6}$ matrix, there are six solutions or values of x that can be determined after expanding the determinant into the resulting (6th-order) polynomial.

$$x^6 - 6x^4 + 9x^2 - 4 = 0 \tag{10.9.2}$$

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 10.9.1, 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:

$$
\begin{aligned}
\left|\phi_1\right\rangle &= \frac{1}{\sqrt{6}}\left[\left|2p_{z1}\right\rangle + \left|2p_{z2}\right\rangle + \left|2p_{z3}\right\rangle + \left|2p_{z4}\right\rangle + \left|2p_{z5}\right\rangle + \left|2p_{z6}\right\rangle\right] \\
\left|\phi_2\right\rangle &= \frac{1}{\sqrt{4}}\left[\left|2p_{z2}\right\rangle + \left|2p_{z3}\right\rangle - \left|2p_{z4}\right\rangle - \left|2p_{z5}\right\rangle\right] \\
\left|\phi_3\right\rangle &= \frac{1}{\sqrt{3}}\left[\left|2p_{z1}\right\rangle + \frac{1}{2}\left|2p_{z2}\right\rangle - \frac{1}{2}\left|2p_{z3}\right\rangle - \left|2p_{z4}\right\rangle - \frac{1}{2}\left|2p_{z5}\right\rangle + \frac{1}{2}\left|2p_{z6}\right\rangle\right] \\
\left|\phi_4\right\rangle &= \frac{1}{\sqrt{4}}\left[\left|2p_{z2}\right\rangle - \left|2p_{z3}\right\rangle + \left|2p_{z4}\right\rangle - \left|2p_{z5}\right\rangle\right] \\
\left|\phi_5\right\rangle &= \frac{1}{\sqrt{3}}\left[\left|2p_{z1}\right\rangle - \frac{1}{2}\left|2p_{z2}\right\rangle - \frac{1}{2}\left|2p_{z3}\right\rangle + \left|2p_{z4}\right\rangle - \frac{1}{2}\left|2p_{z5}\right\rangle - \frac{1}{2}\left|2p_{z6}\right\rangle\right] \\
\left|\phi_6\right\rangle &= \frac{1}{\sqrt{6}}\left[\left|2p_{z1}\right\rangle - \left|2p_{z2}\right\rangle + \left|2p_{z3}\right\rangle - \left|2p_{z4}\right\rangle + \left|2p_{z5}\right\rangle - \left|2p_{z6}\right\rangle\right]
\end{aligned}
$$

In this new basis set $\{\phi\rangle\}$, the secular determinant Equation 10.9.1 is represented as

$$
\begin{vmatrix}
x+2 & 0 & 0 & 0 & 0 & 0 \\
0 & x-2 & 0 & 0 & 0 & 0 \\
0 & 0 & x+1 & \frac{x+1}{2} & 0 & 0 \\
0 & 0 & \frac{x+1}{2} & x+1 & 0 & 0 \\
0 & 0 & 0 & 0 & x-1 & \frac{x-1}{2} \\
0 & 0 & 0 & 0 & \frac{x-1}{2} & x-1
\end{vmatrix} = 0 \tag{10.9.3}
$$

This is the determinant into a bock diagonal form; which can be expanded into a product of smaller determinants to give the polynomial

$$\frac{9}{16}(x+2)(x-2)(x+1)^2(x-1)^2 = 0$$

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 10.9.2). 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)

$$
\begin{vmatrix}
H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} & H_{15}-ES_{15} & H_{16}-ES_{16} \\
H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} & H_{25}-ES_{25} & H_{26}-ES_{26} \\
H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} & H_{35}-ES_{35} & H_{36}-ES_{36} \\
H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} & H_{45}-ES_{45} & H_{46}-ES_{46} \\
H_{51}-ES_{51} & H_{52}-ES_{52} & H_{53}-ES_{53} & H_{54}-ES_{54} & H_{55}-ES_{55} & H_{56}-ES_{56} \\
H_{61}-ES_{61} & H_{62}-ES_{62} & H_{63}-ES_{63} & H_{64}-ES_{64} & H_{65}-ES_{65} & H_{66}-ES_{6}
\end{vmatrix} = 0 \tag{10.9.4}
$$

where H_{ij} are the Hamiltonian matrix elements

$$H_{ij} = \left\langle \phi_i \middle| \hat{H} \middle| \phi_j \right\rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \int \phi_i \phi_j \mathrm{d}v$$

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 10.9.4 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. Group

theory is used to exploit the symmetry of molecules to quickly gain insights into their properties, such as vibrations and molecular orbitals.

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CHAPTER OVERVIEW

7: Statistical Mechanics

7.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System
7.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution
7.3: Translational Partition Functions of Monotonic Gases
7.4: Most Atoms are in the Ground Electronic State
7.5: Pressure can be Expressed in Terms of the Canonical Partition Function
7.6: Most Molecules are Rotationally Excited at Ordinary Temperatures
7.7: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number
7.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule
7.9: Most Molecules are in the Ground Vibrational State
7.10: Vibrational Partition Functions of Polyatomic Molecules Include the Partition Function for Each Normal Coordinate
7.11: The Partition Function of Distinguishable, Independent Molecules is the Product of the Molecular Partition Functions
7.12: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom
7.13: The Average Ensemble Energy is Equal to the Observed Energy of a System
7.14: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms
7.15: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature
7.16: Molar Heat Capacities
7.17: The Equipartition Principle
7.18: The Famous Equation of Statistical Thermodynamics is S=k ln W
7.19: Entropy Can Be Expressed in Terms of a Partition Function
7.20: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition
7.21: Practical Absolute Entropies of Gases Can Be Calculated from Partition Functions
7.22: Standard Entropies Depend Upon Molecular Mass and Structure
7.23: Spectroscopic Entropies sometimes disgree with Calorimetric Entropies

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7.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System

Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc.

7.1.0.1: The Microscopic Laws of Motion

Consider a system of N classical particles. The particles are confined to a particular region of space by a container of volume V. In classical mechanics, the state of each particle is specified by giving its position and its velocity, i.e., by telling where it is and where it is going. The position of particle i is simply a vector of three coordinates $r_i = (x_i, y_i, z_i)$, and its velocity $\mathbf{v}_i$ is also a vector $(v_{x_i}, v_{y_i}, v_{z_i})$ of the three velocity components. Thus, if we specify, at any instant in time, these six numbers, we know everything there is to know about the state of particle i.

The particles in our system have a finite kinetic energy and are therefore in constant motion, driven by the forces they exert on each other (and any external forces which may be present). At a given instant in time t, the Cartesian positions of the particles are $\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t)$, and the velocities at t are related to the positions by differentiation:

$$\mathbf{v}_i(t) = \frac{d\mathbf{r}_i}{dt} = \dot{\mathbf{r}}_i \tag{7.1.1}$$

In order to determine the positions and velocities as function of time, we need the classical laws of motion, particularly, Newton's second law. Newton's second law states that the particles move under the action of the forces the particles exert on each other and under any forces present due to external fields. Let these forces be denoted $\mathbf{F}_1, \mathbf{F}_2, \ldots, \mathbf{F}_N$. Note that these forces are functions of the particle positions:

$$\mathbf{F}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{7.1.2}$$

which is known as a force field (because it is a function of positions). Given these forces, the time evolution of the positions of the particles is then given by Newton's second law of motion:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

where $\mathbf{F}_1, \ldots, \mathbf{F}_N$ are the forces on each of the N particles due to all the other particles in the system. The notation $\ddot{\mathbf{r}}_i = d^2\mathbf{r}_i/dt^2$.

N Newton's equations of motion constitute a set of $3N$ coupled second order differential equations. In order to solve these, it is necessary to specify a set of appropriate initial conditions on the coordinates and their first time derivatives, $\{\mathbf{r}_1(0), \ldots, \mathbf{r}_N(0), \dot{\mathbf{r}}_1(0), \ldots, \dot{\mathbf{r}}_N(0)\}$. Then, the solution of Newton's equations gives the complete set of coordinates and velocities for all time t.

7.1.1: The Ensemble Concept (Heuristic Definition)

For a typical macroscopic system, the total number of particles is $N \sim 10^{23}$. Since an essentially infinite amount of precision is needed in order to specify the initial conditions (due to exponentially rapid growth of errors in this specification), the amount of information required to specify a trajectory is essentially infinite. Even if we content ourselves with quadrupole precision, however, the amount of memory needed to hold just one phase space point would be about 128 bytes $= 2^7 \sim 10^2$ bytes for each number or $10^2 \times 6 \times 10^{23} \sim 10^{17}$ gigabytes which is also 10^2 yottabytes! The largest computers we have today have perhaps 10^6 gigabytes of memory, so we are off by 11 orders of magnitude just to specify 1 classical state.

Fortunately, we do not need all of this detail. There are enormous numbers of microscopic states that give rise to the same macroscopic observable. Let us again return to the connection between temperature and kinetic energy:

$$\frac{3}{2}NkT = \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2 \tag{7.1.3}$$

which can be solved to give:

$$T = \frac{2}{3k}\left(\frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}m_i v_i^2\right) \tag{7.1.4}$$

Here we see that T is related to the average kinetic energy of all of the particles. We can imagine many ways of choosing the particle velocities so that we obtain the same average. One is to take a set of velocities and simply assign them in different ways to the N particles, which can be done in $N!$ ways. Apart from this, there will be many different choices of the velocities, themselves, all of which give the same average.

Since, from the point of view of macroscopic properties, precise microscopic details are largely unimportant, we might imagine employing a construct known as the *ensemble concept* in which a large number of systems with different microscopic characteristics but similar macroscopic characteristics is used to "wash out" the microscopic details via an averaging procedure. This is an idea developed by individuals such as Gibbs, Maxwell, and Boltzmann.

Consider a large number of systems each described by the same set of microscopic forces and sharing a common set of macroscopic thermodynamic variables (e.g. the same total energy, number of moles, and volume). Each system is assumed to evolve under the microscopic laws of motion from a different initial condition so that the time evolution of each system will be different from all the others. Such a collection of systems is called an *ensemble*. The ensemble concept then states that macroscopic observables can be calculated by performing averages over the systems in the ensemble. For many properties, such as temperature and pressure, which are time-independent, the fact that the systems are evolving in time will not affect their values, and we may perform averages at a particular instant in time.

The questions that naturally arise are:

1. How do we construct an ensemble?
2. How do we perform averages over an ensemble?
3. How do we determine which thermodynamic properties characterize an ensemble?
4. How many different types of ensembles can we construct, and what distinguishes them?

These questions will be addresses in the sections ahead.

7.1.2: Thermal energy

A confined monatomic gas can be seen as a box with a whole bunch of atoms in it. Each of these particles can be in one of the states given by the last formula. If all of them have large n values there is obviously a lot of kinetic energy in the system. The lowest energy is when all atoms have 1,1,1 as quantum numbers. Boltzmann realized that this should relate to temperature. When we add energy to the system (by heating it up without changing the volume of the box), the temperature goes up. At higher temperatures we would expect higher quantum numbers, and at lower T, lower ones. But how exactly are the atoms distributed over the various states?

This is a good example of a problem involving a discrete probability distribution. The probability that a certain level (e.g., $n = (n_1, n_2, n_3)$ with energy E_i) is occupied should be a function of temperature: $P_i(T)$. Boltzmann postulated that you could look at temperature as a form of energy. The thermal energy of a system is directly proportional to an absolute temperature.

$$E_{thermal} = kT$$

The proportionality constant k (or k_B) is named after him: the Boltzmann constant. It plays a central role in all statistical thermodynamics. The Boltzmann factor is used to approximate the fraction of particles in a large system. The Boltzmann factor is given by:

$$e^{-\beta E_i} \tag{7.1.5}$$

where:

- E_i is the energy in the state i,
- T is the kelvin temperature, and
- k is Boltzmann constant.

As the following section demonstrates, the term β in Equation 7.1.5 is expressed as:

$$\beta = \frac{1}{kT}$$

The rates of many physical processes are also determined by the Boltzmann factor. For a random particle, its thermal energy of a particle is a small multiple of the energy kT. An increase in temperature results in more particles crossing the energy barrier characteristic of activation processes. If this is to occur, particles need to carry sufficient energy. This energy is needed for the particles to successfully cross the energy barrier and is usually called activation energy. The fraction of molecules that have sufficient energy to escape the original material surface is approximately proportional to the Boltzmann factor.

7.1.3: References

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7.1.4: Problems

1. How are temperature and the average energy per particle for a system related?
2. What does the Boltzmann factor tell you? Why is it important?
3. When is it possible for particles to get extra energy?
4. Give three examples of activation processes.
5. What do "separate arrangements" mean? What are the differences between these arrangements?

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7.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution

Consider a N-particle ensemble. The particles are not necessarily indistinguishable and possibly have mutual potential energy. Since this is a large system, there are many different ways to arrange its particles and yet yield the same thermodynamic state. Only one arrangement can occur at a time. The sum of the probabilities of each separate arrangement equals the total number of separate arrangements. Then the probability of a system is:

$$p_N = W_N p_i$$

where p_N is the probability of the system, W_N is the total number of different possible arrangements of the N particles in the system, and p_i is the probability of each separate arrangement. Heisenberg's uncertainty principle states that it is impossible to simultaneously know the momentum and the position of an object with complete precision. In agreement with the uncertainty principle, the total possible number of combinations can be defined as the total number of distinguishable rearrangements of the N particles.

The most practical ensemble is the canonical ensemble with N, V, and T fixed. We can imagine a collection of boxes with equal volumes and number of particles with the entire collection kept in thermal equilibrium. Based on the Boltzmann factor, we know that for a system that has states with energies e_1, e_2, e_3..., the probability p_j that the system will be in the state j with energy E_j is exponentially proportional to the energy of state j. The partition functions of the state places a very important role in calculating the properties of a system, for example, it can be used to calculate the probability, as well as the energy, heat capacity, and pressure.

7.2.1: The Boltzmann Distribution

We are ultimately interested in the probability that a given distribution will occur. The reason for this is that we must have this information in order to obtain useful thermodynamic averages. Let's consider an ensemble of A systems. We will define a_j as the number of systems in the ensemble that are in the quantum state j. For example, a_1 represents the number of systems in the quantum state 1. The total number of possible microstates is:

$$W(a_1, a_2, ...) = \frac{A!}{a_1! a_2! ...}$$

The overall probability that P_j that a system is in the jth quantum state is obtained by averaging a_j/A over all the allowed distributions. Thus, P_j is given by:

$$P_j = \frac{\langle a_j \rangle}{A}$$
$$= \frac{1}{A} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)}$$

where the angle brackets indicate an ensemble average. Using this definition we can calculate any average property (i.e. any thermodynamic property):

$$\langle M \rangle = \sum_j M_j P_j \tag{7.2.1}$$

The method of the most probable distribution is based on the idea that the average over P_j is **identical** to the most probable distribution. Physically, this results from the fact that we have so many particles in a typical system that the fluctuations from the mean are extremely (immeasurably) small. The equivalence of the average probability of an occupation number and the most probable distribution is expressed as follows:

$$P_j = \frac{\langle a_j \rangle}{A} = \frac{a_j}{A}$$

The probability function is subject to the following constraints:

- Constraint 1: Conservation of energy requires:

$$E_{total} = \sum_j a_j e_j \tag{7.2.2}$$

where e_j is the energy of the jth quantum state.

- Constraint 2: Conservation of mass requires:

$$A = \sum_j a_j \tag{7.2.3}$$

which says only that the total number of all of the systems in the ensemble is A.

As we will learn in later chapters, the system will tend towards the distribution of a_j that maximizes the total number of microstates. This can be expressed as:

$$\sum_j \left(\frac{\partial \ln W}{\partial a_j} \right) = 0$$

Our constraints becomes:

$$\sum_j e_j da_j = 0$$

$$\sum_j da_j = 0$$

The method of Lagrange multipliers (named after Joseph Louis Lagrange is a strategy for finding the local maxima and minima of a function subject to equality constraints. Using the method of LaGrange undetermined multipliers we have:

$$\sum_j \left[\left(\frac{\partial \ln W}{\partial a_j} \right) da_j + \alpha da_j - \beta e_j da_j \right] = 0$$

We can use Stirling's approximation:

$$\ln x! \approx x \ln x – x$$

to evaluate:

$$\left(\frac{\partial \ln W}{\partial a_j} \right)$$

to get:

$$\left(\frac{\partial A!}{\partial a_j} \right) - \sum_i \left(\frac{\partial \ln a_i}{\partial a_j} \right) = 0$$

as outlined below.

7.2.2: Application of Stirling's Approximation

First step is to note that:

$$\ln W = \ln A! - \sum_j \ln a_j ! a \approx A \ln A – A - \sum_j a_j \ln a_j - \sum_j a_j$$

Since (from Equation 7.2.3):

$$A = \sum_j a_j$$

these two cancel to give:

$$\ln W = A \ln A - \sum_j a_j \ln a_j$$

The derivative is:

$$\left(\frac{\partial \ln W}{\partial a_j}\right) = \frac{\partial A \ln A}{\partial a_j} - \sum_i \frac{\partial a_i \ln a_i}{\partial a_j}$$

Therefore we have:

$$\left(\frac{\partial A \ln A}{\partial a_j}\right) = \frac{\partial A}{\partial a_j}\ln A - \frac{\partial A}{\partial a_j} = \ln A - 1$$

$$\left(\frac{\partial a_i \ln a_i}{\partial a_j}\right) = \frac{\partial a_i}{\partial a_j}\ln a_i - \frac{\partial a_i}{\partial a_j} = \ln a_j + 1$$

These latter derivatives result from the fact that:

$$\left(\frac{\partial a_i}{\partial a_i}\right) = 1$$

$$\left(\frac{\partial a_j}{\partial a_i}\right) = 0$$

The simple expression that results from these manipulations is:

$$-\ln\left(\frac{a_j}{A}\right) + \alpha - \beta e_j = 0$$

The most probable distribution is:

$$\frac{a_j}{A} = e^{\alpha}\sum_j e^{-\beta e_j} \tag{7.2.4}$$

Now we need to find the undetermined multipliers α and β.

The left hand side of Equation 7.2.4 is 1. Thus, we have:

$$P_j = \frac{a_j}{A} = \frac{e^{-\beta e_j}}{\sum_j e^{-\beta e_j}}$$

This determines α and defines the Boltzmann distribution. We will show that β from the optimization procedure of method of Lagrange multipliers is:

$$\beta = \frac{1}{kT}$$

This identification will show the importance of temperature in the Boltzmann distribution. The distribution represents a thermally equilibrated most probable distribution over all energy levels (Figure 17.2.1).

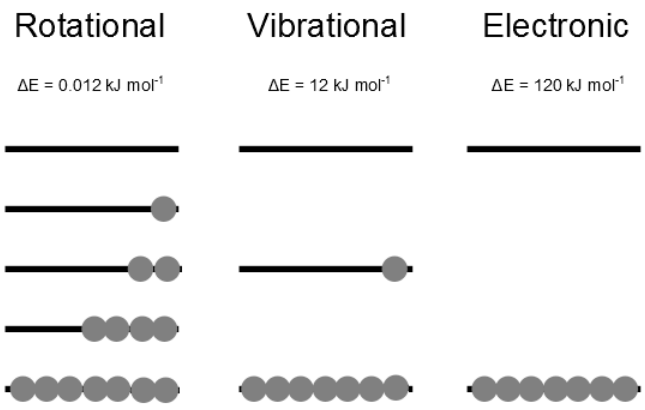


Figure 17.2.1 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. k_BT 2.5 $kJ\ mol^{-1}$ at 300 K. (CC SA-BY 3.0; Mysterioso via Wikiversity).

Boltzmann Distribution

The Boltzmann distribution represents a thermally equilibrated **most probable** distribution over all energy levels. There is always a **higher** population in a state of lower energy than in one of higher energy.

Once we know the probability distribution for energy, we can calculate thermodynamic properties like the energy, entropy, free energies and heat capacities, which are all average quantities (Equation 7.2.1). To calculate P_j, we need the energy levels of a system (i.e., $\{e_i\}$). The energy ("levels") of a system can be built up from the quantum energy levels

> *It must always be remembered that no matter how large the energy spacing is, there is always a non-zero probability of the upper level being populated. The only exception is a system that is at absolute zero. This situation is however hypothetical as absolute zero can be approached but not reached.*

7.2.3: Partition Function

The sum over all factors $e^{-\beta e_j}$ is given a name. It is called the molecular partition function, q:

$$q = \sum_j e^{-\beta e_j}$$

The molecular partition function q gives an indication of the average number of states that are thermally accessible to a molecule at the temperature of the system. The partition function is a sum over states (of course with the Boltzmann factor β multiplying the energy in the exponent) and is a number. Larger the value of q, larger the number of states which are available for the molecular system to occupy (Figure 17.2.2).

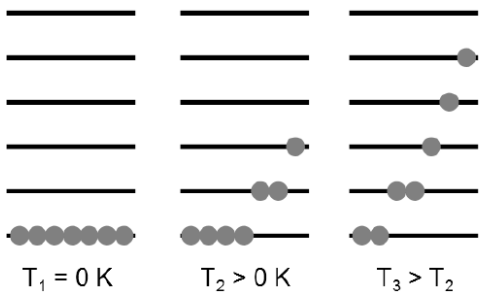


Figure 17.2.2 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. (CC SA-BY 3.0; Mysterioso via Wikiversity).

We distinguish here between the partition function of the ensemble, Q and that of an individual molecule, q. Since Q represents a sum over all states accessible to the system it can written as:

$$Q(N,V,T) = \sum_{i,j,k\ldots} e^{-\beta(e_i+e_j+e_k\ldots)}$$

where the indices i, j, k represent energy levels of **different** particles.

Regardless of the type of particle the molecular partition function, q represents the energy levels of one individual molecule. We can rewrite the above sum as:

$$Q = q_i q_j q_k \ldots$$

or:

$$Q = q^N$$

for N particles. Note that q_i means a sum over states or energy levels accessible to molecule i and q_j means the same for molecule j. The molecular partition function, q counts the energy levels accessible to molecule i only. Q counts not only the states of all of the

molecules, but all of the possible combinations of occupations of those states. However, if the particles are not distinguishable then we will have counted $N!$ states too many. The factor of $N!$ is exactly how many times we can swap the indices in $Q(N,V,T)$ and get the same value (again provided that the particles are not distinguishable). See this video for more information.

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7.2.5: Problems

1. Complete the justification of Boltzmann's distribution law by computing the proportionality constant a.
2. A system contains two energy levels E_1, E_2. Using Boltzmann statistics, express the average energy of the system in terms of E_1, E_2.
3. Consider a system contains N energy levels. Redo problem #2.
4. Use the property of exponential function, derive equation (17.9).
5. What are the uses of partition functions?

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7.3: Translational Partition Functions of Monotonic Gases

Let us consider the translational partition function of a monatomic gas particle confined to a cubic box of length L. The particle inside the box has translational energy levels given by:

$$E_{\text{trans}} = \frac{h^2\left(n_x^2 + n_y^2 + n_z^2\right)}{8mL^2}$$

where n_x, n_y and n_z are the quantum numbers in the three directions. The translational partition function is given by:

$$q_{\text{trans}} = \sum_i e^{-\epsilon_i/kT}$$

which is the product of translational partition functions in the three dimensions. We can write the translation partition function as the product of the translation partition function for each direction:

$$q_{\text{trans}} = q_x q_y q_z \tag{7.3.1}$$

$$= \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \sum_{n_y=1}^{\infty} e^{-\epsilon_y/kT} \sum_{n_z=1}^{\infty} e^{-\epsilon_z/kT} \tag{7.3.2}$$

Since the levels are very closely spaced (continuous), we can replace each sum in Equation 7.3.2 with an integral. For example:

$$q_x = \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{7.3.3}$$

$$\approx \int_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{7.3.4}$$

and after substituting the energy for the relevant dimension:

$$\epsilon_x = \frac{h^2 n_x^2}{8mL^2}$$

we can extend the lower limit of integration in the approximation of Equation 7.3.4:

$$q_x = \int_1^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2kT}} \approx \int_0^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2kT}}$$

We then use the following solved Gaussian integral:

$$\int_o^{\infty} e^{-an^2} dn = \sqrt{\frac{\pi}{4a}}$$

with the following substitution:

$$a = \frac{h^2}{8mL^2kT}$$

we get:

$$q_x = \frac{1}{2}\sqrt{\frac{\pi}{a}} = \frac{1}{2}\sqrt{\frac{\pi 8mkT}{h^2}}L$$

or more commonly presented as:

$$q_x = \frac{L}{\Lambda}$$

where Λ is the **de Broglie wavelength** and is given by

$$\Lambda = \frac{h}{\sqrt{2\pi 8mkT}}$$

Multiplying the expressions for q_x, q_y and q_z (Equation 7.3.1) and using V as the volume of the box L^3, we arrive at:

$$q_{trans} = \left(\frac{\sqrt{2\pi 8mkT}}{h} \right)^{3/2} V = \frac{V}{\Lambda^3} \tag{7.3.5}$$

This is usually a very large number (10^{20}) for volumes of 1 cm^3 for small molecular masses. This means that such a large number of translational states are accessible and available for occupation by the molecules of a gas. This result is very similar to the result of the classical kinetic gas theory that said that the observed energy of an ideal gas is:

$$U = \frac{3}{2} nRT$$

We postulate therefore that the observed energy of a macroscopic system should equal the statistical average over the partition function as shown above. In other words: if you know the particles your system is composed of and their energy states you can use statistics to calculate what you should observe on the whole ensemble.

Example

Calculate the translational partition function of an I_2 molecule at 300K. Assume V to be 1 liter.

Solution

Mass of I_2 is $2 \times 127 \times 1.6606 \times 10^{-27} kg$

$$\begin{aligned} 2\pi mkT &= 2 \times 3.1415 \times (2 \times 127 \times 1.6606 \times 10^{-27}\, kg) \times 1.3807 \times 10^{-23}\, J/K \times 300K \\ &= 1.0969 \times 10^{-44}\, J\, kg \end{aligned}$$

$$\begin{aligned} \Lambda &= \frac{h}{\sqrt{2\pi mkT}} \\ &= \frac{6.6262 \times 10^{-34}\, J\, s}{\sqrt{1.0969 \times 10^{-44}\, J\, kg}} = 6.326 \times 10^{-12}\, m \end{aligned}$$

The via Equation 7.3.5

$$q_{trans} = \frac{V}{\Lambda^3} = \frac{1000 \times 10^{-6} m^3}{(6.326 \times 10^{-12}\, m)^3} = 3.95 \times 10^{30}$$

This means that 3.95×10^{30} quantum states are thermally accessible to the molecular system

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7.4: Most Atoms are in the Ground Electronic State

Writing the electronic energies as $E_1, E_2, E_3, ...$ with corresponding degeneracies $g_1, g_2, g_3, ...$ The electronic partition function is then given by the following summation:

$$q_{el}(T) = g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + ... \tag{7.4.1}$$

Usually, the differences in electronic energies are significantly greater than thermal energy kT:

$$kT \ll E_1 < E_2 < E_3$$

If we treat the lowest energy electronic state E_1 as the reference value of zero of energy, the electronic partition function (Equation 7.4.1) can be approximated as:

$$q_{elec}(T) = g_1 + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + ... \tag{7.4.2}$$

Typically electronic states are tens of thousands of wave numbers above the ground state. For example, the first excited electronic state of nitric oxide (NO) is ~40,000 cm^{-1}. Using this value:

$$\frac{E_2}{kT} = \frac{40000 \text{ cm}^{-1}}{kT} = \frac{10^4 \text{ K}}{T}$$

That means, that even at 1,000 K, the value of the second term in {\reference{3.24}} is:

$$g_2 e^{-10} = g_2 4.5 \times 10^{-5}$$

The result is that the higher electronic states are not accessible under ordinary temperatures. There are some cases, however, where the first excited state lies much closer to the ground state, but these are the exception rather than the rule.

Example 18.2.1

Find the electronic partition of H_2 at 300 K.

Solution

The lowest electronic energy level of H_2 is near $-32\ eV$ and the next level is about $5\ eV$ higher. Taking -32 eV as the zero (or reference value of energy), then

$$q_{el} = e_0 + e^{-5eV/kT} + ...$$

At 300 K, T = 0.02\; eV and

$$q_{el} = 1 + e^{-200} + ...$$
$$\approx 1.0$$

Where all terms other than the first are essentially 0. This implies that $q_{el} = 1$.

The physical meaning of the result from Example 18.2.1 is that only the ground electronic state is generally thermally accessible at room temperature.

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7.5: Pressure can be Expressed in Terms of the Canonical Partition Function

Pressure can also be derived from the canonical partition function. The average pressure is the sum of the probability times the pressure:

$$\langle P \rangle = \sum_i P_i(N,V,T) P_i(N,V)$$

The pressure of a macroscopic system is:

$$P(N,V) = -\left(\frac{\partial E_i}{\partial V}\right)_N$$

So we can write the average pressure as:

$$\begin{aligned}\langle P \rangle &= \sum_i P_i(N,V,\beta)\left(-\frac{\partial E_i}{\partial V}\right)_N \\ &= \sum_i \left(-\frac{\partial E_i}{\partial V}\right)_N \frac{e^{-E_i(N,V)/kT}}{Q(N,V,T)}\end{aligned}$$

In a few steps we can show that the temperature can be expressed in terms of the partition function:

$$Q(N,V,T) = \sum_i e^{-E_i(N,V)/kT}$$

Writing in terms of β instead of temperature:

$$Q(N,V,\beta) = \sum_i e^{-\beta E_i(N,V)}$$

The derivative of the partition function with respect to volume is:

$$\left(\frac{\partial Q}{\partial V}\right)_{N,\beta} = -\beta \sum_i \left(\frac{\partial E_i}{\partial V}\right)_N e^{-\beta E_i(N,V)}$$

The average pressure can then be written as:

$$\langle P \rangle = \frac{kT}{Q(N,V,\beta)}\left(\frac{\partial Q}{\partial V}\right)_{N,\beta}$$

Which shows that the pressure can be expressed solely terms of the partition function:

$$\langle P \rangle = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

We can use this result to derive the ideal gas law. For N particles of an ideal gas:

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!}$$

where:

$$q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V$$

is the translational partition function. The utility of expressing the pressure as a logarithm is clear from the fact that we can write:

$$\begin{aligned}\ln Q &= N \ln q - \ln N! \\ &= -\frac{3N}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right) + N \ln V - \ln N!\end{aligned}$$

We have used the property of logarithms that $\ln(AB) = \ln(A) + \ln(B)$ and $\ln(X^Y) = Y \ln(X)$. Only one term in the ln Q depends on V. Taking the derivative of $N \ln V$ with respect to V gives:

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N}{V}$$

Substituting this into the above equation for the pressure gives:

$$P = \frac{NkT}{V}$$

which is the ideal gas law. Recall that $Nk = nR$ where N is the number of molecules and n is the number of moles. R is the universal gas constant (8.314 J/mol-K) which is nothing more than k multiplied by Avagadro's number. $N_A k = R$ converts the constant from a "per molecule" to a "per mole" basis.

7.5.1: Gas Compressed by a Piston

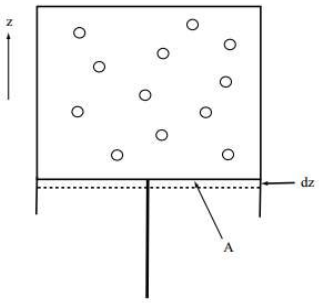


Figure 17.5.1 : Illustration of a thought experiment in which a system is compressed via a piston pushed into the system along the positive z axis.

Let us consider a simple thought experiment, which is illustrated in the figure above: A system of N particles is compressed by a piston pushing in the positive z direction. Since this is a classical thought experiment, we think in terms of forces. The piston exerts a constant force of magnitude F on the system. The direction of the force is purely in the positive z direction, so that we can write the force vector $\mathbf{F}$ as $\mathbf{F} = (0, 0, F)$. At equilibrium (the piston is not moving), the system exerts an equal and opposite force on the piston of the form $(0, 0, -F)$. If the energy of the system is E, then the force exerted by the system on the piston will be given by the negative change in E with respect to z:

$$-F = -\frac{dE}{dz} \tag{7.5.1}$$

or:

$$F = \frac{dE}{dz} \tag{7.5.2}$$

The force exerted by the system on the piston is manifest as an observable pressure P equal to the force F divided by the area A of the piston, $P = F/A$. Given this, the observed pressure is just:

$$P = \frac{dE}{Adz} \tag{7.5.3}$$

Since the volume decreases when the system is compressed, we see that $Adz = -dV$. Hence, we can write the pressure as $P = -dE/dV$.

Of course, the relation $P = -dE/dV$ is a thermodynamic one, but we need a function of x that we can average over the ensemble. The most natural choice is:

$$p(x) = -\frac{d\mathcal{E}(x)}{dV} \tag{7.5.4}$$

so that $P = \langle p(x) \rangle$. Setting up the average, we obtain:

$$P = -\frac{C_N}{Q(N,V,T)} \int \frac{\partial \mathcal{E}}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{7.5.5}$$

$$= \frac{C_N}{Q(N,V,T)} \frac{1}{\beta} \int \frac{\partial}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{7.5.6}$$

$$= \frac{kT}{Q(N,V,T} \frac{\partial}{\partial V} C_N \int e^{-\beta \mathcal{E}(x)} \tag{7.5.7}$$

$$= kT \left(\frac{\partial \ln Q(N,V,T)}{\partial V} \right) \tag{7.5.8}$$

7.5.2: Ideal Gas in the Canonical Ensemble

Recall that the mechanical energy for an ideal gas is:

$$\mathcal{E}(x) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \tag{7.5.9}$$

where all particles are identical and have mass m. Thus, the expression for the canonical partition function $Q(N,V,T)$ is:

$$Q(N,V,T) = \frac{1}{N! h^{3N}} \int dx \, e^{-\beta \sum_{i=1}^{N} \mathbf{p}_i^2 / 2m}$$

Note that this can be expressed as:

$$Q(N,V,T) = \frac{1}{N! h^{3N}} V^N \left[\int dp \, e^{-\beta p^2 / 2m} \right]^{3N}$$

Evaluating the Gaussian integral gives us the final result immediately:

$$Q(N,V,T) = \frac{1}{N!} \left[\frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} \right]^N$$

The expressions for the energy:

$$E = -\frac{\partial}{\partial \beta} \ln Q(N,V,T)$$

which gives:

$$E = \frac{3}{2} NkT = \frac{3}{2} nRT \tag{7.5.10}$$

and pressure:

$$P = kT \left(\frac{\partial \ln Q(N,V,T)}{\partial V} \right)$$

giving:

$$P = \frac{NkT}{V} = \frac{nRT}{V} \tag{7.5.11}$$

which is the ideal gas law.

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7.6: Most Molecules are Rotationally Excited at Ordinary Temperatures

The rotational quantum number is J and the energy of the rotations is:

$$E(J) = \tilde{B}J(J+1)$$

Where $\tilde{B}$ is in units of cm^{-1} and is equivalent to:

$$\frac{h}{8\pi^2 Ic}$$

Where c is the speed of light in units of cm^{-1}. However, with the exception of the ground state (i.e., $J = 0$), multiple eigenstates exist for a given value of J. This is a form of **degeneracy**, (g), and the number of levels per energy goes as 1, 3, 5, 7, 9 etc or:

$$g(J) = 2J + 1$$

Therefore, the summation to find the partition function $q_{rot}(T)$ contains an extra factor $g = 2J + 1$. This factor is mathematically very handy, because it is the derivative of:

$$g(J) = J(J+1)$$

This makes it possible to change variables to $X = J(J+1)$ and the integration becomes very easy. Notice that just like in the translation partition function, we approximate the summation with an integral. However, because we are dealing with far fewer levels, this is less justified in the rotational case. How justified it is depends on the gas and the temperature we consider. Roughly speaking we should be at a temperature $T >> \Theta_{rot}$.

? Exercise 18.5.1

Look at table 18.2. When do we need to actually work out the (discrete) summation instead of making a (continuous) integration out of it?

Answer

Only for the lightest gases like $\mathbf{He}$ and $\mathbf{H_2}$ do we need to worry and then only at pretty low cryogenic circumstances. At room temperature, we can take the rotational levels as a continuous set and use an integral. Notice that the vibrational Θ values are much larger! At $T = 300\,\mathrm{K}$, usually only a single level is occupied and we are in the discrete limit. On the surface of the sun that would be a different matter of course.

The rotational constant B is directly linked to the moment of inertia:

$$I = \mu r^2$$

Where μ is the reduced mass of the molecule:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

and r is the bond length. Again we can scale the behavior of different systems to one and the same picture by introducing a characteristic temperature:

$$\Theta_{rot} = \frac{hb}{k} = \frac{\hbar^2}{2Ik_b}$$

As we did for the translations, we can calculate the moment $\langle\epsilon\rangle$. For vibrations we get a relatively complicated function of temperature. However, for rotations, the moment is simply equal to NkT and this means that the rotational contribution to the molar C_v of a diatomic is simply R. As the vibrational and electronic contributions to the heat capacity are typically negligible at room temperature, we get:

- monatomic gas

$$C_v = C_v^{trans} = \frac{3}{2}nR$$

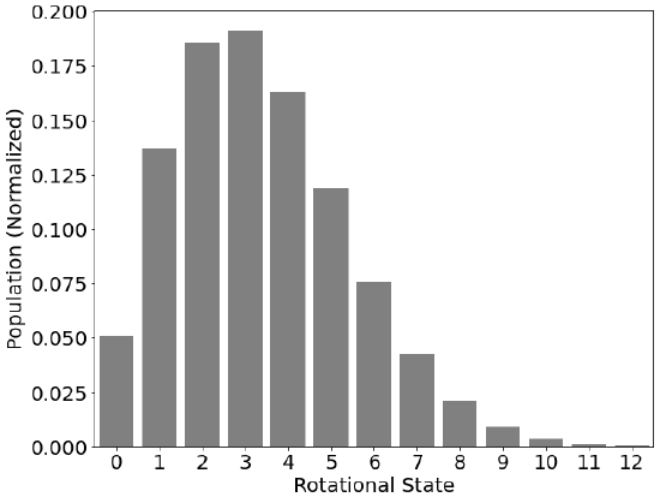
- diatomic

$$C_v = C_v^{trans} + C_v^{rot} \tag{7.6.1}$$

$$= \frac{3}{2}nR + nR \tag{7.6.2}$$

$$= \frac{5}{2}nR \tag{7.6.3}$$

Rotational energies are less than vibrational and electronic energies and, at room temperature, many rotational states will be populated.



The normalized rotational population of HCl at room temperature.

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7.7: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number

The rotational energy levels of a **diatomic molecule** are given by:

$$E_{\text{rot}}(J) = \tilde{B}J(J+1) \tag{7.7.1}$$

where:

$$\tilde{B} = \frac{h}{8\pi^2 Ic}$$

Here, $\tilde{B}$ is the rotational constant expressed in cm^{-1}. The rotational energy levels are given by:

$$E_j = \frac{J(J+1)h^2}{8\pi I}$$

where I is the moment of inertia of the molecule given by μr^2 for a diatomic, and μ is the reduced mass, and r the bond length (assuming rigid rotor approximation). The energies can be also expressed in terms of the rotational temperature, Θ_{rot}, defined as:

$$\Theta_{\text{rot}} = \frac{r^2}{8\pi^2 Ik} \tag{7.7.2}$$

The interpretation of θ_{rot} is as an estimate of the temperature at which thermal energy ($\approx kT$) is comparable to the spacing between rotational energy levels. At about this temperature the population of excited rotational levels becomes important. See Table 1.

Table 1: Select Rotational Temperatures. In each case the value refers to the most common isotopic species.

Molecule	H_2	N_2	O_2	F_2	HF	HCl	CO_2	HBr	CO
Θ_{rot}	87.6	2.88	2.08	1.27	30.2	15.2	0.561	12.2	2.78

In the summation for the expression for rotational partition function (q_{rot}), Equation 7.7.3, we can do an explicit summation:

$$q_{\text{rot}} = \sum_{j=0} (2J+1)e^{-E_J/kT} \tag{7.7.3}$$

if only a finite number of terms contribute. The factor $(2J+1)$ for each term in the expansion accounts for the degeneracy of a rotational state J. For each allowed energy E_J from Equation 7.7.1 there are $(2J+1)$ eigenstates. The Boltzmann factor must be multiplied by $(2J+1)$ to properly account for the degeneracy these states:

$$(2J+1)e^{-E_J/kT}$$

If the rotational energy levels are lying very close to one another, we can integrate similar to what we did for q_{trans} previously to get:

$$q_{\text{rot}} = \int_0^\infty (2J+1)R^{-\tilde{B}J(J+1)/kT}dJ$$

This integration can easily be done by substituting $x = J(J+1)$ and $dx = (2J+1)dJ$:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}} \tag{7.7.4}$$

For a homonuclear diatomic molecule, rotating the molecule by 180° brings the molecule into a configuration which is *indistinguishable* from the original configuration. This leads to an overcounting of the accessible states. To correct for this, we divide the partition function by σ, which is called the **symmetry number** and is equal to the distinct number of ways by which a molecule can be brought into identical configurations by rotations. The rotational partition function becomes:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}\sigma} \tag{7.7.5}$$

or commonly expressed in terms of Θ_{rot}:

$$q_{rot} = \frac{T}{\Theta_{rot}\sigma} \tag{7.7.6}$$

Example 18.6.1

What is the rotational partition function of H_2 at 300 K?

Solution

The value of $\tilde{B}$ for H_2 is 60.864 cm^{-1}. The value of kT in cm^{-1} can be obtained by dividing it by hc, i.e., which is $kT/hc = 209.7\ cm^{-1}$ at 300 K. $\sigma = 2$ for a homonuclear molecule. Therefore from Equation 7.7.5,

$$\begin{aligned} q_{rot} &= \frac{kT}{\tilde{B}\sigma} \\ &= \frac{209.7\ cm^{-1}}{(2)(60.864\ cm^{-1})} \\ &= 1.723 \end{aligned}$$

Since the rotational frequency of H_2 is quite large, only the first few rotational states are accessible at 300 K

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7.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule

For a polyatomic molecule containing N atoms, the total number of degrees of freedom is $3N$. Out of these, three degrees of freedom are taken up for the translational motion of the molecule as a whole. For nonlinear molecules, there are three rotational degrees of freedom and the $3N–6$ vibrational degrees. For linear molecules, the rotational motion along the molecular axis is quantum mechanically not meaningful as the rotated configuration is indistinguishable from the original configuration. Therefore, linear molecules have two rotational degrees of freedom and $3N–5$ vibrational degrees of freedom.

To investigate the rotational motion, we need to fix the center of mass of the molecule and calculate the three principal moments of inertia I_A, I_B, and I_C of the ellipsoid of inertia. The center of mass is defined as the point for which the following identities hold:

$$\sum_i m_i x_i = \sum_i m_i y_i = \sum_i m_i z_i$$

The inertia products are defined by:

$$I_{xx} = \sum_i m_i \left(y_i^2 + z_i^2\right)$$

$$I_{xy} = \sum_i m_i \left(x_i y_i\right)$$

The other components I_{yy}, I_{xz},.. are defined analogously. To find the direction cosines $\alpha_i, \beta_o, \gamma_i$ of the three principle moments of inertia, we need to solve the following matrix equations:

$$\alpha(I_{xx} - \eta) - \beta I_{xy} - \gamma I_{xz} = 0$$

$$\alpha I_{xy} - \beta(I_{yy} - \eta) - \gamma I_{yz} = 0$$

$$-\alpha I_{xz} - \beta I_{yz} + \gamma(I_{zz} - \eta) = 0$$

If the off diagonal terms I_{xy} are zero in the above equations, then the x, y, z axis will be the principal axis. The energy of a rotor with the three moments of inertia I_A, I_B. and I_C is given by:

$$\epsilon = \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2$$
$$= \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C}$$

Each of the rotational degrees of freedom will have a characteristic rotational temperature in terms of the moment of inertia:

$$\Theta_{rot,i} = \frac{hbar^2}{2 I_i k} \qquad i = A, B, C$$

There are many different shapes of molecules and these shapes affect the rotational behavior of the molecules. Molecules are therefore classified according to symmetry into different groups called tops. The three different tops are:

Spherical top	$\Theta_{rot,A} = \Theta_{rot,B} = \Theta_{rot,C}$
Symmetric top	$\Theta_{rot,A} = \Theta_{rot,B} \neq \Theta_{rot,C}$
Asymmetric top	$\Theta_{rot,A} \neq \Theta_{rot,B} \neq \Theta_{rot,C}$

7.8.1: Spherical Tops

The spherical top can be solved exactly to give:

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

$$g_J = (2J + 1^2) \qquad J = 0, 1, 2, \ldots$$

The rotational partition function is:

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)^2 e^{\hbar^2 J(J+1)/2IkT}$$
$$= \sum_{J=0}^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T}$$

For almost all spherical top molecules:

$$\Theta_{\text{rot}} \gg T$$

Therefore, we can convert the sum to an integral:

$$q_{\text{rot}} = \frac{1}{\sigma} \int_0^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T}$$

where we have now included the symmetry term, σ. Solving for this integral, we get:

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{q_{\text{rot}}} \right)^{3/2}$$

7.8.2: Symmetric Tops

Here, ω_A, ω_B, and ω_C are the three angular speeds and L_A, L_B, and L_C are the three angular momenta. For a symmetric top molecule such as ammonia, or chloromethane, two components of the moments of inertia are equal, i.e., $I_B = I_C$. The rotational energy levels of such a molecule are specified by two quantum numbers J and K. The total angular momentum is determined by J and the component of this angular momentum along the unique molecular axis is determined by K. The energy levels are given by:

$$\epsilon_{J,K} = \tilde{B} J(J+1) + (\tilde{A} - \tilde{B}) K^2$$

with rotational constants in units of wavenumbers:

$$\tilde{B} = \frac{h}{8\pi^2 c I_B}$$

and:

$$\tilde{A} = \frac{h}{8\pi^2 c I_A}$$

where

- J takes on values $0, 1, 2, ...\infty$ and
- $K = -J, -J+1, -J+2, ...0, 1, 2, ...J$.

The rotational partition function is given by:

$$q_{rot} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\tilde{B}J(J+1)/kT} \sum_{K=-J}^{J} (2J+1) e^{\tilde{A}-\tilde{B})K^2/kT}$$

This can be converted to an integral and the result is:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi I_B kT}{h^2} \right) \left(\frac{8\pi I_A kT}{h^2} \right)^{1/2}$$

7.8.3: Asymmetric Tops

For asymmetric tops, the expressions for rotational energies are more complex and the conversions to integrations are not easy. One can actually calculate the sum of terms using a computer. An intuitive answer can be obtained by integrating over the angular momenta L_A, L_B and L_C as:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{H(p,q)/kT} \, dL_A \, dL_B \, dL_C = \sqrt{2\pi I_A kT} \sqrt{2\pi I_B kT} \sqrt{2\pi I_C kT}$$

And then multiplying by a factor of $8\pi^2/\sigma h^3$, we get the rotational partition function. The factor of $8\pi^2$ accounts for the angular integration. For any axis chosen in a molecule, a complete rotation contributes a factor of 2π. Integration over all possible orientations of this axis contribute another factor of 4π. The factor of h^3 is for the conversion from the classical phase space to the quantum mechanical phase space.

Symmetry Number

As discussed previously, the **symmetry number** σ corrects for overcounting of rotational configurations. If the molecule has no center of symmetry (e.g. HCN) $\sigma = 1$ whereas if the molecule has a center of symmetry (e.g. CO_2) then $\sigma = 2$.

The final result is:

$$q_{rot} = \frac{\pi^2}{\sigma}\sqrt{\frac{8\pi I_A kT}{h^2}}\sqrt{\frac{8\pi I_B kT}{h^2}}\sqrt{\frac{8\pi I_C kT}{h^2}} \tag{7.8.1}$$

Classical Derivation (Optional)

We can explicitly obtain the classical rotational partition function of an asymmetric top by writing the classical expression for the rotational energy in terms of the Euler angles. The orientation of a rigid rotor can be specified by there Euler angles θ, φ, and ψ with the ranges of angles 0 to π, 0 to 2π and 0 to 2π respectively. The rotational Hamiltonian for the kinetic energy can be written in terms of the angles and their conjugate momenta (p_θ, p_ϕ, p_ψ)

$$H = \frac{\sin^2\psi}{2I_A}\left(p_\theta - \frac{\cos\psi}{\sin\theta\sin\psi}(p_\phi - \cos\theta p_\psi)\right)^2$$

$$+\frac{\cos^2\psi}{2I_B}\left(p_\theta - \frac{\sin\psi}{\cos\theta\cos\psi}(p_\phi - \cos\theta p_\psi)\right)^2 + \frac{1}{2I_C}p_\psi^2$$

The classical rotational partition function is given by

$$q_{rot} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}\frac{1}{h^3}e^{-H(p,q)/kT}\,dp_\theta\,dp_\phi\,dp_\psi\,d\theta\,d\phi\,d\psi$$

The integrations can be simplified by rewriting $H(p,q)/kT$ as

$$\frac{H}{kT} = \frac{1}{2I_A kT}\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)\left(p_\theta + \left(\frac{1}{I_B} - \frac{1}{I_A}\right)\frac{\sin\psi\cos\psi}{\sin\theta\left(\frac{\sin^\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)}(p_\phi - \cos\theta p_\psi)\right)^2$$

$$+\frac{1}{2kTI_A I_B\sin^2\theta}\left(\frac{1}{\sin\theta\left(\frac{\sin^\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)}(p_\phi - \cos\theta p_\psi)\right)^2 + \frac{1}{2KTI_c}p_\psi^2$$

Using the following integral,

$$\int_{-\infty}^{\infty}e^{-a(x+b)^2}dx = \int_{-\infty}^{\infty}e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$$

Integration over p_θ gives using the above expression

$$\sqrt{2\pi kT}\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)^{-1/2} \tag{7.8.2}$$

Integration over p_φ gives the factor,

$$\sqrt{2\pi kTI_A I_B}\sin\theta\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)^{1/2}$$

This cancels partly the second square root in Equation 7.8.2. Integration over p_ψ gives the factor

$$\sqrt{2\pi kTI_c}$$

Integration over θ, φ and ψ gives a factor of $8\pi^2$.

$$\int_0^\pi \sin\theta\, d\theta = 2$$

$$\int_0^{2\pi} d\phi = 2\pi$$

$$\int_0^{2\pi} d\psi = 2\pi$$

Combining all the integrals, we finally get Equation 7.8.1 after reintroduced the symmetry number σ as before with diatomic molecular rotation.

We can simplify calculations by defining **characteristic rotational temperatures** for each axis of rotational:

$$\Theta_A = \frac{h^2}{8\pi^2 I_A k}$$

$$\Theta_B = \frac{h^2}{8\pi^2 I_B k}$$

$$\Theta_C = \frac{h^2}{8\pi^2 I_C k}$$

The polyatomic rotational partition function expressed in Equation 7.8.1 can then be re-expressed as:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}} \tag{7.8.3}$$

or alternatively:

$$\ln q_{rot} = \frac{1}{2}\ln\frac{\pi T}{\Theta_A\Theta_B\Theta_C\sigma^2}$$

Example: Nitrogen Dioxide

The three characteristic rotational temperatures for NO_2 are $111.5\ K$, $0.624\ K$ and $0.590\ K$. Calculate the rotational partition function at 300 K.

Solution

The rotational temperature is given by Equation 7.8.3:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}}$$

The rotational partition function becomes,

$$q_{rot} = \frac{1.772}{2}\sqrt{\frac{300\ K}{(11.5\ K)(0.624\ K)(22.55\ K)}} = 2242.4$$

7.8.4: Thermodynamics Properties

The molar thermodynamic functions can be readily calculated including average rotation energy and molar heat capacity:

$$E_{rot} = \frac{3}{2}RT$$

and:

$$\bar{C}_V = \frac{3}{2}R$$

Improvements over the classical approximation for the rotational partition function derived above have been obtained. One of the improved versions (with no derivation) is:

$$q_{rot} = q^0_{rot}\left[1 + \frac{h^2}{96\pi^2 kT}\left(\frac{2}{I_A} + \frac{2}{I_C} + \frac{2}{I_C} + \frac{I_C}{I_B I_B} - \frac{I_A}{I_B I_C} - \frac{I_B}{I_A I_C}\right)\right]$$

where q^0_{rot} is the classical approximation in Equation 7.8.1.

Comparing this result with the vibrational partition function calculation before ($q_{vib} = 1.0035$), give the implication that while multiple rotational states are accessible at room temperature, very few vibrational states (other than the ground vibrational state) are accessible.

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7.9: Most Molecules are in the Ground Vibrational State

The vibrational energy levels of a diatomic are given by:

$$E_v = (v + 1/2)h\nu$$

where is ν the vibrational frequency and v is the vibrational quantum number. In this case, it is easy to sum the geometric series shown below:

$$\begin{aligned} q_{\text{vib}} &= \sum_{v=0}^{\infty} e^{-(v+1/2)h\nu/kT} \\ &= e^{-h\nu/2kT}\left(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + ...\right) \end{aligned}$$

or rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(1 + x + x^2 + x^3 + ...\right) \tag{7.9.1}$$

where $x = e^{-h\nu/kT}$. Given the following power series expansion:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + ...$$

Equation 7.9.1 can be rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(\frac{1}{1-x}\right)$$

or:

$$q_{\text{vib}} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \tag{7.9.2}$$

If the zero of energy scale is at $h\nu/2kT$, then Equation 7.9.2 can be rewritten as:

$$q_{\text{vib}} \approx \frac{1}{1 - e^{-h\nu/kT}} \tag{7.9.3}$$

A vibrational temperature Θ_{vib} may be defined as:

$$\Theta_{\text{vib}} = \frac{hc\tilde{\nu}}{k}$$

where $\tilde{\nu}$ is the vibrational frequency in cm^{-1}. Θ_{vib} is a good way to express the *stiffness* of the vibrating bond in units of the Boltzmann constant. Because the stiffness obviously depends on what bond your are talking about, this is a good way to do the same thing we did for the critical temperature of the non-ideal gases.

Table **7.9.1** : Representative molecular data for a few diatomics

Molecule	g	Bond Length (pm)	ω (cm^{-1})	Θ_{vib} (K)	$\tilde{B}$ (cm^{-1})	Θ_{rot} (K)	Force constant k (dynes/cm)	D_0 (kcal/mol)
H_2	1	0.7474	4400	6332	60.9	87.6	5.749	103.2
D_2	1	0.7415	3118	4487	30.45	43.8	5.77	104.6
N_2	1	1.097	2358	3393	2.001	2.99	22.94	225.1
O_2	3	1.207	1580	2274	1.446	2.08	11.76	118.0
Cl_2	1	1.987	560	805	0.244	0.351	3.2	57.0
CO	1	1.128	2170	3122	1.931	2.78	19.03	255.8
NO	2	1.15	190	2719	1.695	2.45	15.7	150.0
HCl	1	1.275	2938	4227	10.44	15.02	4.9	102.2
HI	1	1.609	2270	3266	6.46	9.06	3.0	70.5
Na_2	1	3.096	159	229	0.154	0.221	0.17	17.3
K_2	1	3.979	92.3	133	0.0561	0.081	0.10	11.8

Example 18.4.1

The vibrational frequency of of I_2 is $214.57\ cm^{-1}$. Calculate the vibrational partition function of I_2 at 300 K.

Solution:

$$\frac{h\nu}{kT} = \frac{214.57}{209.7} = 1.0232$$

so

$$e^{-h\nu/kT} = 0.3595$$

and

$$q_{vib} = \frac{1}{1-0.3595} = 1.561$$

This implies, as before, that very few vibrational states are accessible and much less than rotation states and many orders less than translation states.

7.9.1: Vibrational Heat Capacity

The vibrational energy is given by the above expression and the molar heat capacity at constant volume, $\bar{C}_V$ is given by:

$$\bar{C}_V = \left(\frac{\partial E}{\partial T}\right)_V$$

We have:

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta} \tag{7.9.4}$$

$$= \frac{-1}{kT^2}\frac{\partial}{\partial \beta} \tag{7.9.5}$$

$$= (-k\beta^2)\left(\frac{\partial}{\partial \beta}\right) \tag{7.9.6}$$

Therefore:

$$\bar{C}_V = (-k\beta^2)\left(\frac{\partial \varepsilon_{\text{vib}}}{\partial \beta}\right)$$

and when the vibrational partition function (Equation 7.9.3) is introduced:

$$q_{\text{vib}} = -k\beta^2 \frac{\left[(1-e^{-hc\nu/kT})(-hc\tilde{\nu}) - e^{-hc\nu/kT}(+hc\tilde{\nu})\right] e^{-hc\nu/kT}}{(1-e^{-hc\nu/kT})^2} h\nu\tilde{\nu} \tag{7.9.7}$$

$$= k\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left(1-e^{-\Theta_{\text{vib}}/T}\right)^2} \tag{7.9.8}$$

For large T, the $\bar{C}_V$ becomes:

$$N_A k = R$$

and for small T, $\bar{C}_V$ goes to zero as demonstrated in Figure 18.4.1 .

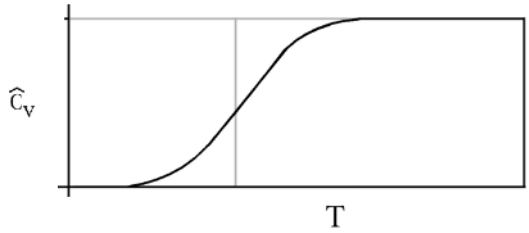


Figure 18.4.1 : Vibrational heat capacity of a diatomic

The vibrational heat capacity is shown as function of the reduced temperature T/Θ to get a general picture valid for all diatomic gases. Compare the parameters on Table 18.4.1 to see on what different absolute scales we have to think for different gases. Clearly the vibrational contribution to the heat capacity *depends on temperature*. For many molecules (especially light ones), the vibrational contribution only kicks in at quite high temperatures.

The value of Θ_{vib} is determined mostly by

1. the strength of a bond (the stronger the higher Θ_{vib})
2. the (effective) mass of the molecule (the lighter the higher Θ_{vib})

Molecules with low Θ_{vib} often dissociate at lower temperatures, although the *harmonic* oscillator model is not sufficient to describe that phenomenon.

7.9.2: Vibrational Populations

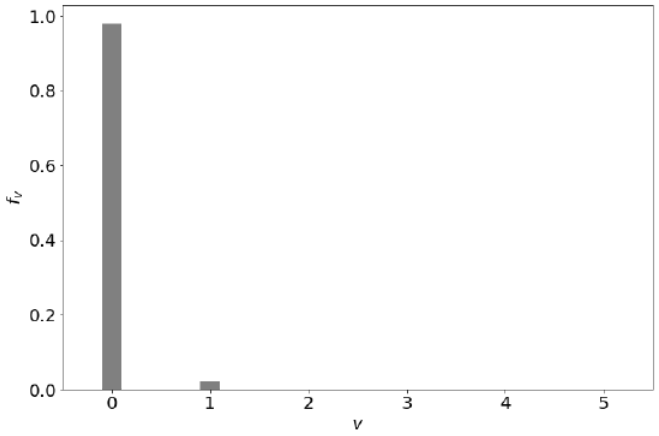
We can calculate the fraction of molecules in each vibrational state. The fraction of molecules in the vth vibrational state is given by:

$$f_v = \frac{e^{-h\nu(v+\frac{1}{2})/kT}}{q_{\text{vib}}}$$

Substituting in Equation 7.9.2, we get:

$$f_v = \left(1-e^{-h\nu/kT}\right) e^{-h\nu v/kT} = \left(1-e^{-\Theta_{\text{vib}}/T}\right) e^{-\Theta_{\text{vib}} v/T} \tag{7.9.9}$$

We can plot the fraction molecules in each vibrational state.



The vibrational population of Cl_2 at 300 K. Most of the molecules are in the ground vibrational state, $v = 0$.

From the figure, we can see that most of the Cl_2 molecules are in the ground vibrational state at room temperature (300 K). This is true for most molecules. Only molecules with very weak bonds and low vibrational temperatures will populate a significant fraction of molecules in excited vibrational states.

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7.10: Vibrational Partition Functions of Polyatomic Molecules Include the Partition Function for Each Normal Coordinate

As with diatomic molecules, the energies of polyatomic molecules can be approximated by the sum of its individual degrees of freedom. Therefore, we can write the partition function as:

$$Q(N,V,T) = \frac{[q(V,T)]^2}{N!}$$

We can write the polyatomic analog to diatomic molecules:

$$Q(N,V,T) = \frac{(q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}})^N}{N!}$$

When derived for diatomic molecules, we assumed the rigid rotor model for rotations and the harmonic oscillator for vibrations. This allowed us to separate the rotational motion from the vibrational motion of the molecule. Polyatomic molecules are a bit more complicated, but we will still make use of these approximations.

The number of translational states available to any given molecule is far greater than the number of molecules in the system. q_{trans} is given by:

$$q_{\text{trans}} = \left[\frac{2\pi MkT}{h^2}\right]^{3/2} V$$

where M is the mass of the particle. Moving to the electronic partition function:

$$q_{\text{elec}} = \sum_i g_i e^{-E_i/kT}$$

where E_i is the energy of the electronic state i and {g_i} is its degeneracy. Electronic states are typically spaced far apart from each other. The probability of the system being in any state but the ground state is extremely small. We can therefore simplify the electronic partition function to include only the ground electronic state:

$$q_{\text{elec}} = g_{e1}e^{D_e/kT}$$

where $-D_e$ is the energy of the ground electronic state. To complete the polyatomic partition function, we still need q_{vib} and q_{rot}. We will finish this section with q_{vib} and talk about q_{rot} in the next.

The vibrational motion of diatomic molecules can be expressed as a set of independent harmonic oscillators. For polyatomic molecules, the independent vibrational motions are referred to as normal modes of vibration. The vibrational energy is then the sum of the energies for each normal mode:

$$E_{\text{vib}} = \sum_i^{\alpha}\left(v_i + \frac{1}{2}\right)h\nu$$

where ν_i is the vibrational frequency for the ith normal mode and α is the number of vibration degrees of freedom. A linear molecule has $3n-5$ vibrational degrees of freedom and a nonlinear molecule has $3n-6$ vibrational degrees of freedom. Because the normal modes are independent of each other, we can take out results from previous sections:

$$q_{\text{vib}} = \prod_i^{\alpha}\frac{e^{-\theta_{\text{vib},i}/2T}}{1-e^{-\theta_{\text{vib},i}/T}}$$

$$E_{\text{vib}} = Nk\sum_i^{\alpha}\left(\frac{\theta_{\text{vib},i}}{2} + \theta_{\text{vib},i}\frac{e^{-\theta_{\text{vib},i}/T}}{1-e^{-\theta_{\text{vib},i}/T}}\right)$$

$$C_{V,\text{vib}} = Nk\sum_i^{\alpha}\left(\left(\frac{\theta_{\text{vib},i}}{2}\right)^2 + \frac{e^{-\theta_{\text{vib},i}/T}}{(1-e^{-\theta_{\text{vib},i}/T})^2}\right)$$

where $\theta_{\text{vib},i}$ is the characteristic vibrational temperature defined by:

$$\theta_{vib,i} = \frac{h\nu_i}{k}$$

7.10.1: Vibrational Entropy

There is a great deal of utility for thermodynamic functions calculated from the vibrational normal modes of a molecule. The vibrational energy and entropy depend on the shape a multidimensional potential energy surface. If one performs a conformational search of macromolecule it is one obtains energies and structures but little direct information concerning the shape of the potential energy surface for each conformation. The vibrational entropy gives a means determining whether there are significant entropic differences in the structures and therefore whether certain conformations will be favored based on the entropy.

However, it is possible to take appropriate linear combinations of the coordinates so that the cross terms are eliminated and the classical Hamiltonian as well as the operator corresponding to it contains no cross terms and in terms of the new coordinates, the Hamiltonian can be written as,

$$H = \sum_{i=1}^{f} \frac{h^2}{2\mu_i} \frac{\partial}{\partial q_i^2} + \sum_{i=1}^{f} \frac{k_i}{2} q_i^2 \tag{7.10.1}$$

Here, the degrees of freedom f is $3N-5$ for a linear molecule and $3N-6$ for a nonlinear molecule. Here, k_i is the force constant and μ_i is the reduced mass for that particular vibrational mode which is referred to as a **normal mode**.

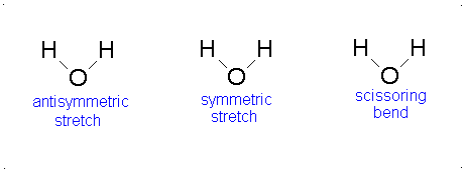


Figure 18.7.1 : The three vibrational modes of water, the symmetric stretch (3656.7 cm^{-1}, 5160 K), the asymmetric stretch (3755.8 cm^{-1} , 5360 K) and the bending mode (1594.8 cm^{-1} ,2290 K) are shown. The vibrational frequencies and the characteristic temperature for each mode are shown in parenthesis. Although not shown in the animation, the oxygen atom also moves with each of these normal modes.

The Equation 7.10.1 represents f linearly independent harmonic oscillators and the total energy for such a system is

$$\epsilon_{vib} = \sum_{i=1}^{f} \left(v_i + \frac{1}{2}\right) h\nu_i$$

The vibrational frequencies are given by

$$\nu_i = \frac{1}{2\pi}\sqrt{\frac{k_i}{\mu_i}}$$

The vibrational partition function is given by the product of f vibrational functions for each frequency.

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1 - e^{-\Theta_{vib,i}/T}} \tag{7.10.2}$$

with

$$\Theta_{vib,i} = \frac{h\nu_i}{k_B}$$

As with the previous discussion regarding simple diatomics, $\Theta_{vib,i}$ is called the **characteristic vibrational temperature**. The molar energies and the heat capacities are given by

$$\langle E_{vib} \rangle = Nk \sum_{i=1}^{f} \left[\frac{\Theta_{vib,i}}{2} + \frac{\Theta_{vib,i} e^{-\Theta_{vib,i}/T}}{1 - e^{-\Theta_{vib,i}/T}} \right]$$

and

$$\bar{C}_V = Nk_B \sum_{i=1}^{f} \left(\frac{\Theta_{vib,i}}{T} \right)^2 \frac{e^{-\Theta_{vib,i}/T}}{\left(1-e^{-\Theta_{vib,i}/T}\right)^2}$$

NO_2 Example

The three characteristic vibrational temperatures for $\mathbf{NO_2}$ are 1900 K, 1980 K and 2330 K. Calculate the vibrational partition function at 300 K.

Solution

The vibrational partition is (Equation 7.10.2)

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1-e^{-\Theta_{vib,i}/T}}$$

If we calculate q_{vib} by taking the zero point energies as the reference points with respect to which the other energies are measured

$$q_{vib} = \prod_{i=1}^{f} \frac{1}{1-e^{-\Theta_{vib,i}/T}} = \left(\frac{1}{1-e^{-1900/300}} \right) \left(\frac{1}{1-e^{-1980/300}} \right) \left(\frac{1}{1-e^{-2330/300}} \right)$$
$$= (1.0018)(1.0014)(1.0004) = 1.0035$$

The implication is that very few vibrational states of $\mathbf{NO_2}$ (other than the ground vibrational state) are accessible at 300 K. This is standard of the vibrations of most molecules.

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7.11: The Partition Function of Distinguishable, Independent Molecules is the Product of the Molecular Partition Functions

A system, such as a container of gas, can consist of a large number of subsystems. How is the partition function of the system built up from those of the subsystems? This depends on whether the subsystems are distinguishable or indistinguishable. Let's start with energy. Energy is additive so that:

$$E_{tot}(N,V) = \epsilon_1(V) + \epsilon_2(V) + \epsilon_3(V) + \cdots$$

Each of the molecules can have their energy distributed over their respective energy states (e.g., vibrations, rotations, etc.). This means that each ϵ_i is already a summation over the states of the molecule. Let us assume that we can somehow distinguish all the molecules as: a, b, c, d… and denote the energy state they are in by i, j, k:

$$E_l(N,V) = \epsilon_i^a(V) + \epsilon_j^b(V) + \epsilon_k^c(V) + \cdots$$

A good example would be the molecules in a molecular crystal. They only move around a fixed site and so we can distinguish by how far molecule 'a' is from a given corner of the crystal. The systems partition function becomes:

$$Q(N,V,\beta) = \sum_i e^{-\beta E_l} = \sum_{i,j,k,\ldots} e^{-\beta(\epsilon_i^a + \epsilon_j^b + \epsilon_k^c)}$$

So far, we have done little effort to distinguish between the partition function of a molecular system q and the whole ensemble Q (e.g. the gas). If the entities that we called systems are **distinguishable** and independent, the whole ensemble partition function is the product of the molecular system partition functions. We get:

$$Q(N,V,\beta) = \prod_i q_i$$

for N distinguishable systems. We can split up the summation into a product of molecular partition functions:

$$Q(N,V,\beta) = \prod_i^N q_i(V,\beta) = q_a(V,\beta)q_b(V,\beta)q_c(V,\beta)\cdots$$

This results in each molecular system partition function being summed over independently:

$$Q(N,V,\beta) = \sum_i e^{-\beta\epsilon_i^a} \sum_j e^{-\beta\epsilon_i^b} \sum_k e^{-\beta\epsilon_i^c} \ldots$$

If the energy states of all the particles are the same, then the equation simplifies to:

$$Q(N,V,\beta) = [q(V,\beta)]^N$$

We can do this if, for example, the particles are embedded in a crystal where we can distinguish them by their location. We will see in the next chapter that for indistinguishable particles, such as those in a gas, we get a different result.

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7.12: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom

From the previous sections, the partition function for a system of N indistinguishable and independent molecules is:

$$Q(N,V,\beta) = \frac{\sum_i e^{-\beta E_i}}{N!} \tag{7.12.1}$$

And the average energy of the system is:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \tag{7.12.2}$$

We can combine these two equations to obtain:

$$\begin{aligned} \langle E \rangle &= kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \\ &= NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \\ &= N \sum_i \epsilon_i \frac{e^{-\epsilon_i / kT}}{q(V,T)} \end{aligned} \tag{7.12.3}$$

The average energy is equal to:

$$\langle E \rangle = N \langle \epsilon \rangle \tag{7.12.4}$$

where $\langle \epsilon \rangle$ is the average energy of a single particle. If we compare Equation 7.12.2 with Equation 7.12.2, we can see:

$$\langle \epsilon \rangle = \sum_i \epsilon_i \frac{e^{-\epsilon_i / kT}}{q(V,T)}$$

The probability that a particle is in state i, π_i, is given by:

$$\langle \epsilon \rangle = \frac{e^{-\epsilon_i / kT}}{q(V,T)} = \frac{e^{-\epsilon_i / kT}}{\sum_i e^{-\epsilon_i / kT}}$$

The energy of a particle is a sum of the energy of each degree of freedom for that particle. In the case of a molecule, the energy is:

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elec}}$$

The molecular partition function is the product of the degree of freedom partition functions:

$$q(V,T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

The partition function for each degree of freedom follows the same is related to the Boltzmann distribution. For example, the vibrational partition function is:

$$q_{\text{vib}} = \sum_i e^{-\epsilon_i / kT}$$

The average energy of each degree of freedom follows the same pattern as before. For example, the average vibrational energy is:

$$\langle \epsilon_{\text{vib}} \rangle = kT^2 \frac{\partial \ln q_{\text{vib}}}{\partial t} = -\frac{\partial \ln q_{\text{vib}}}{\partial \beta}$$

7.12: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jerry LaRue.

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7.13: The Average Ensemble Energy is Equal to the Observed Energy of a System

We will be restricting ourselves to the canonical ensemble (constant temperature and constant pressure). Consider a collection of N molecules. The probability of finding a molecule with energy E_i is equal to the fraction of the molecules with energy E_i. That is, in a collection of N molecules, the probability of the molecules having energy E_i:

$$P_i = \frac{n_i}{N}$$

This is the directly obtained from the Boltzmann distribution, where the fraction of molecules n_i/N having energy E_i is:

$$P_i = \frac{n_i}{N} = \frac{e^{-E_i/kT}}{Q} \tag{7.13.1}$$

The average energy is obtained by multiplying E_i with its probability and summing over all i:

$$\langle E \rangle = \sum_i E_i P_i \tag{7.13.2}$$

Equation 7.13.2 is the standard average over a distribution commonly found in quantum mechanics as expectation values. The quantum mechanical version of this Equation is

$$\langle \psi \left| \hat{H} \right| \psi \rangle$$

where Ψ^2 is the distribution function that the Hamiltonian operator (e.g., energy) is averaged over; this equation is also the starting point in the Variational method approximation.

Equation 7.13.2 can be solved by plugging in the Boltzmann distribution (Equation 7.13.1):

$$\langle E \rangle = \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{7.13.3}$$

Where Q is the partition function:

$$Q = \sum_i e^{-\frac{E_i}{kT}}$$

We can take the derivative of $\ln Q$ with respect to temperature, T:

$$\left(\frac{\partial \ln Q}{\partial T}\right) = \frac{1}{kT^2} \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{7.13.4}$$

Comparing Equation 7.13.3 with 7.13.4, we obtain:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)$$

It is common to write these equations in terms of β, where:

$$\beta = \frac{1}{kT}$$

The partition function becomes:

$$Q = \sum_i e^{-\beta E_i}$$

We can take the derivative of $\ln Q$ with respect to β:

$$\left(\frac{\partial \ln Q}{\partial \beta}\right) = -\sum_i \frac{E_i e^{-\beta E_i}}{Q}$$

And obtain:

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

Replacing $1/kT$ with β often simplifies the math and is easier to use.

> It is not uncommon to find the notation changes: Z instead of Q and $\bar{E}$ instead of $\langle E \rangle$.

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7.14: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms

A monatomic gas has three degrees of freedom per molecule, all of them translational:

1. movement in x-direction
2. movement in y-direction
3. movement in z-direction

A polyatomic gas, including diatomic molecules, has other levels that you can 'stuff' energy into. Polyatomic molecules can rotate and vibrate, and if enough energy is available you could also excite the electrons involved in the σ and π bonds. A reasonable approximation of the partition function of the molecule would become:

$$q_{\text{tot}}(V,T) = q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}$$

The partition function of a molecular idea gas is then:

$$Q(N,V,T) = \frac{(q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}})^N}{N!}$$

The total energy of the molecule is then the sum of the translation, vibrational, rotational, and electronic energies:

$$E_{tot} = E_{\text{trans}} E_{\text{vib}} E_{\text{rot}} E_{\text{elec}}$$

We will only scratch the surface of the additional degrees of freedom and their partition functions.

7.14.1: Electronic

At room temperature the system is usually in its ground electronic state. This means that the **electronic partition function** $q_{\text{elec}} = 1$. Usually we do not have to worry about these degrees of freedom. If we do, there are usually just a few levels to worry about. This includes their **degeneracy g**. If there is a single state at a certain energy ($g = 1$), two states ($g = 2$), or more states, we must multiply the Boltzmann factor by this degeneracy number.

If there are more than one state to worry about, we could follow the same procedure as we did for the translational states:

1. Define the energy states and their degeneracies
2. Compose the partition function q for the molecule and Q for the gas
3. Use the (β or T) derivative of $\ln Q$ to determine $\langle E \rangle$
4. Use the T derivative of $U \approx \langle E \rangle$ to find the contribution to the heat capacity

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7.15: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature

The heat capacity at constant volume (C_V) is defined to be the change in internal energy with respect to temperature:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{7.15.1}$$

Since:

$$E = -\frac{\partial \ln Q(N,V,\beta)}{\partial \beta} \tag{7.15.2}$$

We see that:

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T} \\ &= \frac{\partial U}{\partial \beta}\frac{\partial \beta}{\partial T} \\ &= \frac{1}{kT^2}\frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \\ &= k\beta^2\frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \end{aligned} \tag{7.15.3}$$

where k is the Boltzmann constant. Energy can be stored in materials/gases via populating the specific degrees of freedom that exist in the sample. Understanding how this occurs requires the usage of Quantum Mechanics.

Dulong-Petit Law on the Heat Capacities of Solids

Pierre Louis Dulong and Alexis Thèrèse Petit conducted experiments in 1819 on three dimensional solid crystals to determine the heat capacities of a variety of these solids (Heat capacity is the solids ability to absorb and retain heat). Dulong and Petit discovered that all investigated solids had a heat capacity of approximately 2.49 x 10^4 J kilomole^{-1} K^{-1} at around 298 K or room temperature. The result from their experiment was explained by considering every atom inside the solid as an oscillator with six degrees of freedom (an oscillator can be thought of as a spring connecting all the atoms in the solid lattice). These springs extend into three dimensional space. The more energy that is added to the solid the more these springs vibrate. Each atom has an energy of $\frac{1}{2}kT$, where k is the Boltzmann constant and T is the absolute temperature. Thus,

$$C_V = \frac{6R}{2} = 3R \qquad \text{(Dulong-Petit Law)}$$

The number 6 in this equation is the number of degrees of freedom for the molecule. Petit and Dulong suggested that these results supported their foundation for the heat capacity of solids. The explanation for Petit and Dulong's experiment was not sufficient when it was discovered that heat capacity decreased as temperature approached absolute zero. The degrees of freedom do not slow down or cease to move when the solid reaches a sufficiently cold temperature. An additional model was proposed to explain this deviance. Two main theories were developed to explain this puzzling deviance in the heat capacity experiments. The first was constructed by Einstein and the second was authored by Debye.

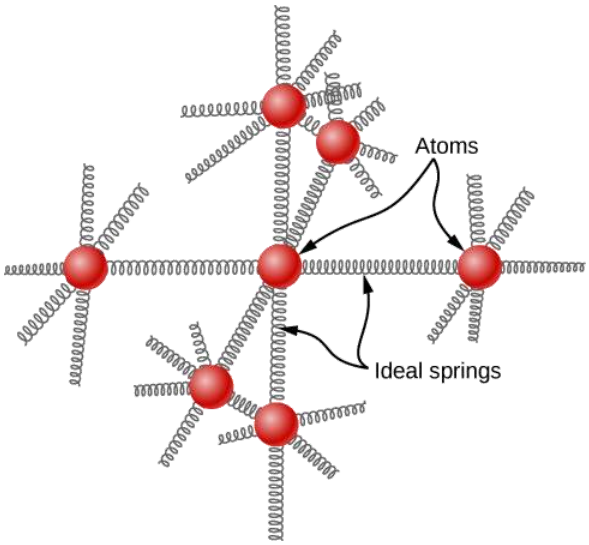


Figure 17.4.1 : In a simple model of a solid element, each atom is attached to others by six springs, two for each possible motion: x, y, and z. Each of the three motions corresponds to two degrees of freedom, one for kinetic energy and one for potential energy. (CC BY-SA 4.0; OpenStax).

Einstein's Theory on the Heat Capacities of Solids

Einstein assumed three things when he investigated the heat capacity of solids. First, he assumed that each solid was composed of a lattice structure consisting of N atoms. Each atom was treated as moving independently in three dimensions within the lattice (3 degrees of freedom). This meant that the entire lattice's vibrational motion could be described by a total of $3N$ motions, or degrees of freedom. Secondly, he assumed that the atoms inside the solid lattice did not interact with each other and thirdly, all of the atoms inside the solid vibrated at the same frequency. The third point highlights the main difference in Einstein's and Debye's two models.

Einstein's first point is accurate because the experimental data supported his hypothesis, however his second point is not because if atoms inside a solid could not interact, sound could not propagate through it. For example, a tuning fork's atoms, when struck, interact with one another to create sound which travels through air to the listener's ear. Atoms also interact in a solid when they are heated. Take for example a frying pan. If the pan is heated on one side, the heat transfers throughout the metal effectively warming the entire pan. Molecules that make up the frying pan interact to transfer heat. Much in the same way the oscillators in a solid interact when energy is added to the system. The extent of these interactions lead to the physically observed heat capacity.

The heat capacity of a solid at a constant volume is

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= 3Nk\left(\frac{\theta_E}{T}\right)^2 \\ &= \frac{\exp\left(\frac{\theta_E}{T}\right)}{\left(\exp\frac{\theta_E}{T}-1\right)^2} \end{aligned}$$

where

- $\theta_E = \frac{h\nu}{k}$ is the **Einstein temperature**,
- h is Planck's constant,
- k is Boltzmann's constant, and
- ν is the oscillator frequency of the atoms inside the solid.

The Einstein temperature's accessibility of the vibrational energy inside of a solid molecule determines the heat capacity of that solid. The greater the accessibility the greater the heat capacity. If the vibrational energy is easily accessible the collisions in the molecule have a greater probability of exciting the atom into an upper vibrational level. This is displayed below.

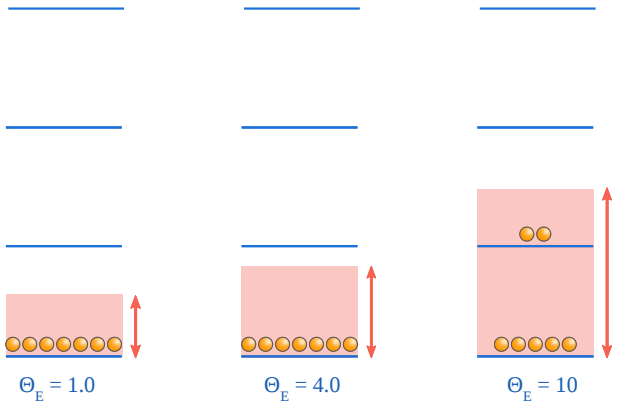


Figure 17.4.2 : This Figure illustrates the effect of the Einstein temperature on the likelihood of an oscillator absorbing energy from a collision and transferring that energy into stored heat or heat capacity. As the Einstein temperature increases, the greater the probability of an oscillator being excited to the next vibrational state. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

So the Einstein temperature specifically indicates the probability that a molecule has in its degrees of freedom to store energy in its atomic oscillators (or bonds). Comparing the Einstein temperature to the traditional classical values of Heat capacity will illustrate the differences the specific strengths (high temperature) and weaknesses (low temperature) of the Einstein model.

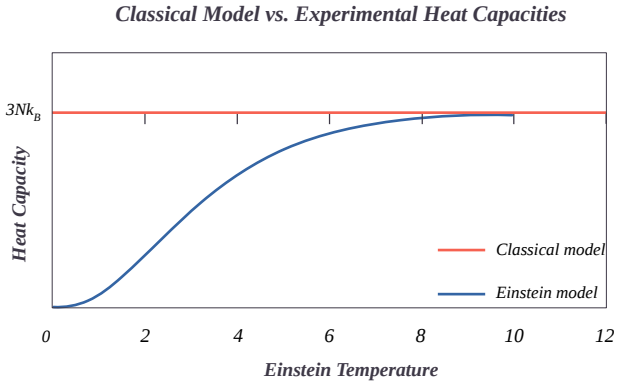


Figure 17.4.3 :This graph shows the accuracy of the of the Einstein temperature at low temperatures. The classical model is effective at temperatures above 10 Einstein Temperatures. (Cc BY-NC; Ümit Kaya via LibreTexts)

Thus, in the high temperature limit ($\frac{\theta_E}{T} \ll 1$) (i.e., the temperature is very large compared to the Einstein temperature) then

$$C_V \approx 3Nk = 3nR. \tag{7.15.4}$$

Einstein's model reveals the accuracy of the Petit and Dulong model and models high temperatures accurately. However, just as Petit and Dulong's model decreased in accuracy as the temperature decreased, so followed Einstein's.

When examining the extremely low temperature limit: $\frac{\theta_E}{T} \gg 1$, it can be seen:

$$C_V = 3Nk\left(\frac{\theta_E}{T}\right)^2 e^{\frac{-\theta_E}{T}} \tag{7.15.5}$$

As temperature (T) goes to zero, the exponential portion of the above equation goes to zero and therefore C_V also approaches zero. This supports the experimental values as temperature approaches zero the heat capacity of the solid likewise decreases to zero.

Einstein's theory also explains solids that exhibit a low heat capacity even at relatively high temperatures. An example of such a solid is diamond. The heat capacity of diamond approaches $3Nk$ as temperature greatly increases. Einstein's model supports this through the definition of an Einstein temperature. As the Einstein temperature increases, ν must increase likewise. This is the

equivalent of each atom possessing more energy and therefore vibrating more rapidly within the solid itself. The oscillator frequency, ν, can be written as:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}} \tag{7.15.6}$$

where κ is the force constant and μ is the reduced mass. This formula better predicts solids with high force constants or low reduced masses. This corrects deviations from the Petit and Dulong model.

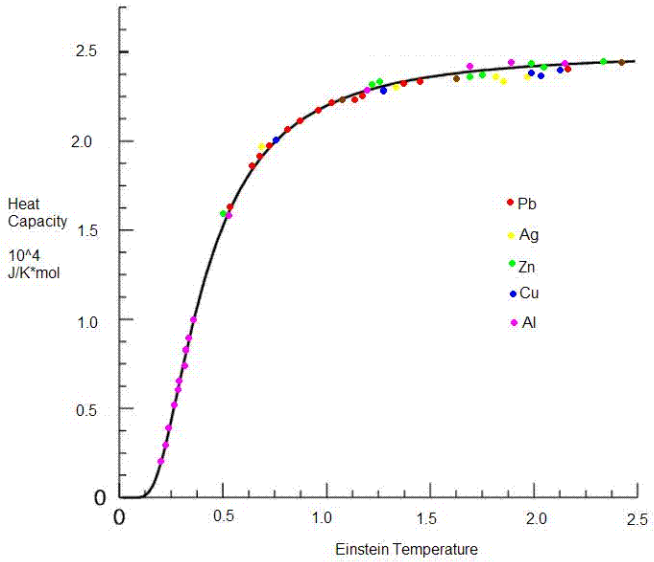


Figure 17.4.4 . This graph indicates the heat capacity of several solid metals as a function of the Einstein temperature: $\theta_E = \frac{h\nu}{k_B}$.

Essentially the Einstein temperature allows for the heat capacity equation and the vibrational frequencies in the solid to change as the temperature changes. This effectively adjusts for the deviations seen in the Petit/Dulong model. As the temperature increases or decreases, the Einstein temperature increases or decreases likewise to mirror the actual physical activity within the solid.

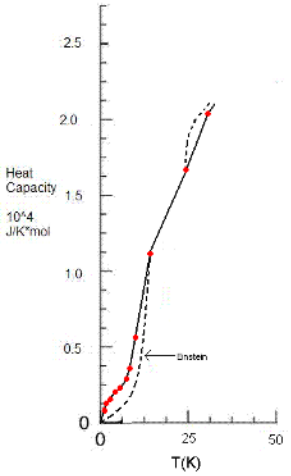


Figure 17.4.5 . This plot shows the heat capacity of lead compared to the expected values calculated from Einstein's model.

Einstein's model predicts relatively low temperatures well. However, when decreasing from approximately 15 K, Einstein's model deviates from experimental values. Also, this can be observed, although not as dramatically, for temperatures from 25 K to 30 K. Clearly a term or correction is still missing from Einstein's model to increase its accuracy.

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7.16: Molar Heat Capacities

Learning Objectives

- **Goal**: Specific heat capacity data for a wide range of elements are used to assess the accuracy and limitations of the Dulong-Petit Law.
- **Prerequisites**: An introductory knowledge of statistical thermodynamics including the derivation of the vibrational (harmonic oscillator) contributions to the heat capacity are recommended.
- **Resources you will need**: This exercise should be carried out within a data analysis software environment which is capable of graphing and generating a best-fit line for an x-y data set.

The heat capacity (C) of a substance is a measure of how much heat is required to raise the temperature of that substance by one degree Kelvin. For a simple molecular gas, the molecules can simultaneously store kinetic energy in the translational, vibrational, and rotational motions associated with the individual molecules. In this case, the heat capacity of the substance can be broken down into translational, vibrational, and rotational contributions;

$$C = C_{trans} + C_{vib} + C_{rot} \tag{7.16.1}$$

Monoatomic crystalline solids represent a much simpler case. Einstein proposed a simple model for such substances whereby the atoms only have vibrational energy (each atom can vibrate in three perpendicular directions around its lattice position). Specifically, the 'Einstein Solid Model' assumes that the atoms act like three-dimensional harmonic oscillators (with the vibrational motion of each atom in each perpendicular dimension entirely independent). Statistical mechanics provides a relatively simple expression for the constant volume molar heat capacity ($C_{V,m}$) of a one-dimensional harmonic oscillator

$$C_{V,m}^{1-D} = R\left(\frac{\Theta_v}{T}\right)^2 \left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{7.16.2}$$

where R is the universal gas constant, T is absolute temperature, and Θ_v is called the 'characteristic vibrational temperature' of the oscillator and depends on the vibrational frequency (ν) according to

$$\Theta_v = \frac{h\nu}{k} \tag{7.16.3}$$

with h representing Plank's constant and k representing Boltzmann's constant.

Since the vibrations in each dimension are assumed to be independent, the expression for the constant volume molar heat capacity of a 'three-dimensional' Einstein Solid is obtained by simply multiplying Equation 7.16.2 by three;

$$C_{V,m}^{3-D} = 3R\left(\frac{\Theta_v}{T}\right)^2 \left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{7.16.4}$$

The temperature variation of the heat capacity of most metallic solids is well described by Equation 7.16.4. Furthermore, plots of Equation 7.16.4 as a function of temperature for metals with widely varying vibrational frequencies reveal that the heat capacity always approaches the same asymptotic limit of $3R$ at high temperatures. Stated another way, at high temperatures

$$\lim_{T\to\infty}\left[\left(\frac{\Theta_v}{T}\right)^2 \left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2\right] = 1 \tag{7.16.5}$$

and Equation 7.16.4 reduces to

$$\lim_{T\to\infty}\left[C_{V,m}^{3D}\right] = 3R \tag{7.16.6}$$

(You will be asked to verify this result in the exercise below). According to Equation 7.16.6, the molar heat capacities of metallic solids should approach 24.9 J/(K mol) at high temperatures, regardless of the identity of the metal.

The vibrational frequencies of most metallic solids are usually small enough so that Θ_v lies considerably below room temperature ($\Theta_v \ll 298\ K$). For these substances, the limits implied by Equations 7.16.5 and 7.16.6 are well approximated even at room temperature, leading to the result that $C_{v,m} = 24.9\ J/(K \cdot mol)$ for most metals at room temperature.

In the early 1800s, two French scientists by the names of Pierre Louis Dulong and Alexis Therese Petit empirically discovered the same remarkable result. The Dulong-Petit Law is normally expressed in terms of the specific heat capacity (C_s) and the molar mass (M) of the metal

$$C_s M = C_{V,m} \approx 25 (J\,K^{-1}\,mol^{-1}) \tag{7.16.7}$$

where C_s represents how much heat is required to raise the temperature of 'one gram' of that substance by one degree Kelvin. Dulong and Petit, as well as other scientists of their time, used this famous relationship as a means of establishing more accurate values for the atomic weight of metallic elements (by instead measuring the specific heat capacity of the element and using the Dulong-Petit relationship, which is a relatively simple method of establishing weights in comparison to the more disputable gravimetric methods that were being used at the time to establish the equivalent weights of elements).

In the exercise below, you will look up the specific heat capacities of a number of elements that exist as simple monoatomic solids at room temperature and assess the accuracy of the Dulong-Petit law.

7.16.1: Experimental Data

Consult the CRC Handbook of Chemistry and Physics (CRC Press: Boca Raton, FL) and compile a table of specific heat capacities for a large number of elements that are known to exist as monoatomic solids at room temperature. Also look up and record the molar mass of these elements. The elements that you consider should be restricted to those appearing in groups 1-14 of the periodic table. Make sure you generate a fairly large list which includes a number of elements that are normally considered as metallic in character (such as copper, iron, sodium, lithium, gold, platinum, barium, and aluminum), but also some non-metallic elements that are nonetheless monoatomic isotropic solids (such as carbon-diamond, beryllium, boron, and silicon). Heat capacities that are usually reported in the literature are not actual constant volume heat capacities (C_v), but are instead constant pressure heat capacities (C_p). Fortunately, C_p and C_v are essentially equal for simple solids (within the level of precision that we consider in this exercise), and you can assume that the values from the CRC Handbook represent C_s.

7.16.2: Exercises

1. Enter the element name, the specific heat capacity, and the molar mass of each element in a spreadsheet. Calculate the product of specific heat and molar mass for each element and calculate how much this product differs from the Dulong-Petit prediction (express your result as a percent difference relative to $3R$).
2. Assess the generality of the Dulong-Petit law in an alternate way by generating a plot of specific heat as a function of reciprocal Molar Mass (C_s versus $1/M$), which should be linear with a slope equal to 3R if the data behave according to Equation 7.16.7.
3. Inspect your results from 1 and 2 above and identify any elements that significantly deviate from the Dulong-Petit law. When they occur, do deviations tend to be smaller or larger than 3R? Does the degree of deviation from the Dulong-Petit law seem to correlate with periodic trends in metallic (or covalent) bonding for these elements? Do deviations tend to occur more readily for elements of smaller or higher atomic weight? Explain how the type of bonding and the magnitude of the atomic weight can lead to deviations from the arguments made in Equations 7.16.5-7.16.7 above.
4. Use the plotting method that you employed in step 2 above as a means of determining a value for the universal gas constant (R) - but make sure you throw-out any specific heat data for elements that you suspect do not fall within the limit $\Theta_v \ll 298\,K$. Calculate the percent error in the value of R that you determine.
5. Verify that the limit expressed in Equation 7.16.5 above is true (HINT: expand each of the exponential terms in a power series and note that higher-order terms are negligible in the limit $T \gg \Theta_v$).

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7.17: The Equipartition Principle

The equipartition theorem, also known as the law of equipartition, equipartition of energy or simply equipartition, states that every degree of freedom that appears only quadratically in the total energy has an average energy of $\frac{1}{2}k_BT$ in thermal equilibrium and contributes $\frac{1}{2}k_B$ to the system's heat capacity. Here, k_B is the Boltzmann constant, and T is the temperature in Kelvin. The law of equipartition of energy states that each quadratic term in the classical expression for the energy contributes ½kBT to the average energy. For instance, the motion of an atom has three degrees of freedom (number of ways of absorbing energy), corresponding to the x, y and z components of its momentum. Since these momenta appear quadratically in the kinetic energy, every atom has an average kinetic energy of $3/2k_BT$ in thermal equilibrium. The number of degrees of freedom of a polyatomic gas molecule is $3N$ where N is the number of atoms in the molecule. This is equal to number of coordinates for the system; e.g. for two atoms you would have x, y, z for each atom.

7.17.1: Translations

The translational contribution to the average energy is derived in terms of the derivative of the translational partition:

$$\langle E_{trans} \rangle = -\frac{1}{q_{trans}} \frac{\partial q_{trans}}{\partial \beta} \tag{7.17.1}$$

Introducing the translational partition function derived earlier, Equation 7.17.1 becomes

$$= -\frac{\Lambda^3}{V} \frac{\partial}{\partial \beta} \frac{V}{\Lambda^3} = -\frac{3}{\Lambda} \frac{\partial \Lambda}{\partial \beta} = \frac{3}{2} k_B T$$

Thus, the three translational degrees of freedom in three dimensions satisfy the equipartition theorem with each translational degree providing $\frac{1}{2}k_BT$ of energy.

7.17.2: Rotations

Consider the molecular partition functions. The average rotational energy to the average energy is derived in terms of the derivative of the translational partition:

$$\langle E_{rot} \rangle = -\frac{1}{q_{rot}} \frac{\partial q_{rot}}{\partial \beta} \tag{7.17.2}$$

which when you introduce the rotational partition function, Equation 7.17.2 becomes

$$\langle E_{rot} \rangle = -\sigma \beta \tilde{B} \frac{1}{\sigma \tilde{B}} \frac{\partial}{\partial \beta} \frac{1}{\beta} = \frac{1}{\beta} = k_B T$$

The classical expression for the rotational energy of a diatomic molecule is

$$E_{rot}^{(classical)} = \frac{1}{2} I(\omega_x^2 + \omega_y^2)$$

where I is the moment of inertia and ω_x and ω_y are the angular velocities in the x and y directions. The rotation along the molecular axis (the z axis here) has no meaning in quantum mechanics because the rotations along the molecular axis lead to configurations which are indistinguishable from the original configuration. The two rotational degrees of freedom have thus given a value of kT with with each rotational degree providing $\frac{1}{2}k_BT$ of energy.

7.17.3: Vibrations

Consider vibrational motions. The average vibrational energy to the average energy is derived in terms of the derivative of the translational partition:

$$\langle E_{vib} \rangle = -\frac{1}{q_{vib}} \frac{\partial q_{vib}}{\partial \beta} \tag{7.17.3}$$

which when you introduce the partition function for vibration, Equation 7.17.3 becomes

$$\langle E_{vib} \rangle = \frac{-1}{q_{vib}} \left(-hc\tilde{\nu} \frac{e^{-hc\tilde{\nu}/k_BT}}{(1-e^{-hc\tilde{\nu}/k_BT})^2} \right) = hc\tilde{\nu} \frac{e^{-hc\tilde{\nu}/k_BT}}{(1-e^{-hc\tilde{\nu}/k_BT})} \tag{7.17.4}$$

This can be simplified by dividing both numerator and denominator of Equation 7.17.4 by $e^{-hc\tilde{\nu}/k_BT}$

$$\langle E_{vib} \rangle = hc\tilde{\nu} \left(\frac{1}{e^{hc\tilde{\nu}/k_BT} - 1} \right) \tag{7.17.5}$$

Equation 7.17.5 is applicable at all temperatures, but if $hc\tilde{\nu}/k_BT \ll 1$ (i.e., the high temperature limit), then the exponential in the denominator can be expanded

$$e^{hc\tilde{\nu}/k_BT} - 1 \approx 1 + hc\tilde{\nu}/k_BT - 1 = hc\tilde{\nu}/k_BT \tag{7.17.6}$$

and Equation 7.17.5 becomes

$$\langle E_{vib} \rangle \approx \cancel{hc\tilde{\nu}} \left(\frac{1}{\cancel{hc\tilde{\nu}}/k_BT} \right)$$

$$\langle E_{vib} \rangle \approx k_BT \tag{7.17.7}$$

with each vibrational degree providing k_BT of energy (since there ar two quadratic terms in the Hamiltonian for a harmonic oscillator (kinetics energy and potential energy).

Compare Equation 7.17.7 with the classical expression for the vibrational energy

$$E_{vib}^{(classical)} = ½kx^2 + ½\mu v_x^2$$

At high temperature the equipartition theorem is valid, but at low temperature, the expansion in Equation 7.17.6 fails (or more terms are required). In this case, only a few vibrational states are occupied and the equipartition principle is not typically applicable.

7.17.4: Heat Capacity

Heat capacity at constant volume C_v, is defined as

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

The equipartition theorem requires that each degree of freedom that appears only quadratically in the total energy has an average energy of ½k_BT in thermal equilibrium and, thus, contributes ½kB to the system's heat capacity. Thus the three translational degrees of freedom each contribute ½R to (3/2 R). The contribution of rotational kinetic energy will be R for the linear, and 3/2R for the nonlinear molecules. For the vibration, an oscillator has quadratic kinetic and potential terms, making the contribution of each vibrational mode R. However, k_BT has to be much greater than the spacing between the quantum energy levels. If this is not satisfied, the heat capacity will be reduced and which drop to zero at low temperatures. The corresponding degree of freedom is said to be **frozen out**; this is the situation for the vibrational degrees of freedom at room temperature and that is why the usual assumption is that they will not contribute.

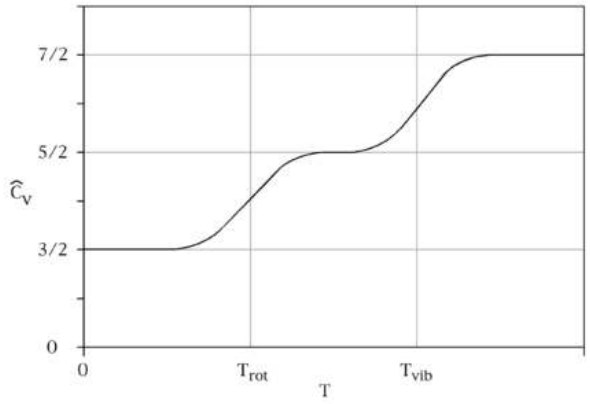


Figure 18.11.1 : Idealized plot of the molar specific heat of a diatomic gas against temperature. It agrees with the value (7/2)R predicted by equipartition at high temperatures (where R is the gas constant), but decreases to (5/2)R and then (3/2)R at lower temperatures, as the vibrational and rotational modes of motion are "frozen out". The failure of the equipartition theorem led to a paradox that was only resolved by quantum mechanics. For most molecules, the transitional temperature T_{rot} is much less than room temperature, whereas T_{vib} can be ten times larger or more. A typical example is carbon monoxide, CO, for which $T_{rot} \approx 2.8$ K and $T_{vib} \approx 3103$ K. For molecules with very large or weakly bound atoms, T_{vib} can be close to room temperature (about 300 K); for example, $T_{vib} \approx 308$ K for iodine gas, I_2. (Public domain; PD-Self)

22✔ Example: CO vs. NO

For comparing the molar heat capacities of nitrogen dioxide and carbon dioxide at constant volume (at room temperature), let us use the law of equipartition and assume the vibrations to be frozen out at room temperature. The predicted molar for the linear CO_2 (with three translational and two rotational degrees of freedom) is $5/2R$ $20.8\,JK^{-1}mo'^{-1}$).

The estimated molar for NO_2 (a bent molecule, with three translational and three rotational degrees of freedom) is $3R$ ($25.0\,JK^{-1}mol^{-1}$). These estimations are close to the experimental values:

- 30.1 JK^{-1} mol^{-1} for CO_2
- 29.5 JK^{-1} mol^{-1} for NO_2

Especially for CO_2, the deviation is significant. This suggests that, although not all vibrational degrees of freedom are available, they cannot be totally ignored. The bigger deviation in the prediction of molar heat capacities is probably due to the existence of the lower frequency-bending vibration in carbon dioxide.

7.17.5: References

1. Thermodynamics and Statistical Mechanics, Greiner W., Neise, Stocker, Springer, 2001
2. Physical Chemistry, 5th ed., Atkins P., W. H. Freeman and Company, 1994.

Contributors and Attributions

- Zane Sterkewolf (UC Davis)
- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf
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7.18: The Famous Equation of Statistical Thermodynamics is S=k ln W

A common interpretation of entropy is that it is somehow a measure of chaos or randomness. There is some utility in that concept. Given that entropy is a measure of the dispersal of energy in a system, the more chaotic a system is, the greater the dispersal of energy will be, and thus the greater the entropy will be. Ludwig Boltzmann (1844 – 1906) (O'Connor & Robertson, 1998) understood this concept well, and used it to derive a statistical approach to calculating entropy. Boltzmann proposed a method for calculating the entropy of a system based on the number of energetically equivalent ways a system can be constructed.

Boltzmann proposed an expression, which in its modern form is:

$$S = k_b \ln(W) \tag{7.18.1}$$

W is the number of available microstates in a macrostate (ensemble of systems) and can be taken as the quantitative measure of energy dispersal in a macrostate:

$$W = \frac{A!}{\prod_j a_j!}$$

Where a_j is the number of systems in the ensemble that are in state j and A represents the total number of systems in the ensemble:

$$A = \sum_j a_j$$

Equation 20.5.1 is a rather famous equation etched on Boltzmann's grave marker in commemoration of his profound contributions to the science of thermodynamics (Figure 7.18.1).



Figure 7.18.1: Ludwig Boltzmann (1844 - 1906)

Example 7.18.1:

Calculate the entropy of a carbon monoxide crystal, containing 1.00 mol of CO, and assuming that the molecules are randomly oriented in one of two equivalent orientations.

Solution:

Using the Boltzmann formula (Equation 7.18.1):

$$S = nK \ln(W)$$

And using $W = 2$, the calculation is straightforward.

$$S = \left(1.00\,mol \cot \frac{6.022 \times 10^{23}}{1\,mol}\right)(1.38 \times 10^{-23} J/K) \ln 2$$
$$= 5.76\,J/K$$

7.18.1: Contributors and Attributions

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7.19: Entropy Can Be Expressed in Terms of a Partition Function

We have seen that the partition function of a system gives us the key to calculate thermodynamic functions like energy or pressure as a moment of the energy distribution. We can extend this formulism to calculate the entropy of a system once its Q is known. We can start with Boltzmann's (statistical) definition of entropy:

$$S = k\ln(W) \tag{7.19.1}$$

with

$$W = \frac{A!}{\prod_j a_j!}$$

Combining these equations, we obtain:

$$S_{ensemble} = k\ln\frac{A!}{\prod_j a_j!}$$

Rearranging:

$$S_{ensemble} = k\ln A! - k\sum_j \ln a_j!$$

Using Sterling's approximation:

$$\begin{aligned} S_{ensemble} &= kA\ln A - kA - k\sum_j a_j \ln a_j + k\sum_j a_j \\ &= kA\ln A - k\sum_j a_j \ln a_j \end{aligned}$$

Since:

$$\sum_j a_j = A$$

The probability of finding the system in state a_j is:

$$p_j = \frac{a_j}{A}$$

Rearranging:

$$a_j = p_j A$$

Plugging in:

$$S_{ensemble} = kA\ln A - k\sum_j p_j A \ln p_j A$$

Rearranging:

$$S_{ensemble} = kA\ln A - k\sum_j p_j A\ln p_j - k\sum_j p_j A\ln A$$

If A is constant, then:

$$k\sum_j p_j A\ln A = kA\ln A\sum_j p_j$$

Since:

$$\textstyle\sum_j p_j = 1$$

We get:

$$S_{ensemble} = kA \ln A - k \sum_j p_j A \ln p_j - kA \ln A$$

The first and last term cancel out:

$$S_{ensemble} = -k \sum_j p_j A \ln p_j$$

We can divide by A to get the entropy of the system:

$$S_{system} = -k \sum_j p_j \ln p_j \tag{7.19.2}$$

If all the p_j are zero except for the for one, then the system is perfectly ordered and the entropy of the system is zero. The probability of being in state j is

$$p_j = \frac{e^{-\beta E_j}}{Q} \tag{7.19.3}$$

Plugging Equation 7.19.3 into Equation 7.19.2 results in

$$\begin{aligned} S &= -k \sum_j \frac{e^{-\beta E_j}}{Q} \ln \frac{e^{-\beta E_j}}{Q} \\ &= -k \sum_j \frac{e^{-\beta E_j}}{Q} (-\beta E_j - \ln Q) \\ &= -\beta k \sum_j \frac{E_j e^{-\beta E_j}}{Q} + \frac{k \ln Q}{Q} \sum_j e^{-\beta E_j} \end{aligned}$$

Making use of:

$$\beta k = \frac{1}{T}$$

And:

$$\sum \frac{e^{-\beta E_j}}{Q} = \sum p_j = 1$$

We obtain:

$$S = \frac{U}{T} + k \ln Q \tag{7.19.4}$$

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7.20: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition

The laws of thermodynamics can be understood in two ways: by looking at large-scale properties like temperature and pressure, or by examining how countless tiny atoms move and interact. Both perspectives lead to the same laws, even though the reasoning behind them is quite different.

We learned earlier that entropy, S, is related to the number of microstates, W, in an ensemble with A systems:

$$S_{ensemble} = k_B \ln W \tag{7.20.1}$$

and

$$W = \frac{A!}{\prod_j a_j!} \tag{7.20.2}$$

Combining Equations 7.20.1 and 7.20.2 to get:

$$\begin{aligned} S_{ensemble} &= k_B \ln \frac{A!}{\prod_j a_j!} \\ &= k_B \ln A! - k_B \sum_j \ln a_j! \end{aligned}$$

Using Sterling's approximation:

$$\ln A! \approx A \ln A - A$$

We obtain:

$$S_{ensemble} = k_B A \ln A - k_B A - k_B \sum_j a_j \ln a_j + k_B \sum a_j$$

Since:

$$A = \sum a_j$$

The expression simplifies to:

$$S_{ensemble} = k_B A \ln A - k_B \sum_j a_j \ln a_j$$

We can make use of the fact that the number of microstates in state j is equal to the total number of microstates multiplied by the probability of finding the system in state j, p_j:

$$a_j = p_j A$$

Plugging in, we obtain

$$\begin{aligned} S_{ensemble} &= k_B A \ln A - k_B \sum_j p_j A \ln p_j A \\ &= k_B A \ln A - k_B \sum_j p_j A \ln p_j - k_B \sum_j p_j A \ln A \end{aligned}$$

Since A is a constant and the sum of the probabilities of finding the system in state j is always 1:

$$\sum p_j = 1$$

The first and last term cancel out:

$$S_{ensemble} = -k_B A \sum_j p_j \ln p_j$$

We can use that the entropy of the system is the entropy of the ensemble divided by the number of systems:

$$S_{system} = S_{ensemble}/A$$

Dividing by A, we obtain:

$$S_{system} = -k_B \sum_j p_j \ln p_j$$

We can differentiate this equation and dropping the subscript:

$$dS = -k_B \sum_j (dp_j + \ln p_j dp_j)$$

Since $\sum_j p_j = 1$, the derivative $\sum_j dp_j = 0$:

$$dS = -k_B \sum_j \ln p_j dp_j$$

In short:

$$\sum_j \ln p_j dp_j = -\frac{\delta q_{rev}}{k_B T}$$

Plugging in:

$$dS = \frac{\delta q_{rev}}{T} \tag{7.20.3}$$

The thermodynamic definition of entropy comes from macroscopic observations. In classical thermodynamics, entropy is defined as the measure of energy dispersal in a system (Equation 7.20.3). It tells us how much heat is spread out or distributed in a system at temperature. This definition is practical and works well at the bulk level but does not say why entropy behaves this way.

The statistical definition of entropy in Equation 7.20.1, developed by Boltzmann, defines entropy in terms of the number of possible microstates that correspond to the same overall macroscopic state (macrostate). This shows that entropy measures the degree of microscopic disorder or multiplicity of arrangements consistent with what we see at the macroscopic level.

Both definitions describe the same underlying concept:

- The thermodynamic view says entropy measures the spread of energy in terms of heat and temperature.
- The statistical view says entropy measures the spread of possible microstates that energy can occupy.

They are equivalent because a system with more accessible microstates (higher disorder) will also tend to have greater energy dispersal, and thus higher entropy. In fact, the statistical definition explains why the thermodynamic definition works: macroscopic energy dispersal arises from the overwhelming number of microscopic ways energy can be arranged.

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7.21: Practical Absolute Entropies of Gases Can Be Calculated from Partition Functions

Recall that the entropy of a system, S, can be calculated if the partition function, Q, is known:

$$S = \frac{U}{T} + k_B \ln Q$$

where Q is:

$$Q = \sum_j e^{-\frac{E_j}{kT}}$$

The internal energy of the system can also be calculated from the partition function:

$$U = k_B T^2 \left(\frac{\delta \ln Q}{\delta T} \right)$$

Combining these equations, we obtain:

$$S = k_B \ln Q + k_B T \left(\frac{\delta \ln Q}{\delta T} \right)$$

The third law of thermodynamics states that entropy of a perfect crystal at absolute zero is zero. We can show that our equation for entropy in terms of the partition function is consistent with the third law. Plugging in our equation for the partition function into our equation for entropy, we obtain:

$$S = k_B \ln \sum_j e^{-\frac{E_j}{kT}} + k_B T \left(\frac{\delta \ln \sum_j e^{-\frac{E_j}{kT}}}{\delta T} \right)$$

As T goes to zero, all the states will be in their lowest energy configuration. If the ground state is n degenerate, then n states will be in the ground state:

$$E_1 = E_2 = ... = E_m$$

This is true for all the next states. For example, if the next state is m degenerate, then:

$$E_{n+1} = E_{n+2} = ... = E_{n+m}$$

This gives us the result:

$$\sum_j e^{-\frac{E_j}{kT}} = ne^{-\frac{E_1}{kT}} + me^{-\frac{E_{n+1}}{kT}} + ...$$

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7.22: Standard Entropies Depend Upon Molecular Mass and Structure

Entropy is related to the number of microstates a collection of particles can occupy. As both the molecular mass and molecular structure of the particles will affect the number of available microstates, they also affect the entropy of the collection of particles. So why does $S°$ depend on molecular mass and molecular structure?

Standard molar entropies depend strongly on both molecular mass and molecular structure. Heavier molecules generally have higher entropies because their greater mass leads to more accessible translational and vibrational energy states at a given temperature. Molecular complexity also plays a key role: larger or more structurally intricate molecules have more ways to store energy through rotations and vibrations, giving rise to a greater number of microstates. For example, methane (CH_4) has a higher standard entropy than carbon dioxide (CO_2) because it possesses more rotational and vibrational modes, while oxygen (O_2) has a higher entropy than nitrogen (N_2) due to its larger molecular mass. In essence, both increased mass and increased structural complexity expand the possible distributions of molecular energy, leading to higher entropy values.

From quantum theory, we know that increasing the molecular mass of a particle decreases the energy spacing between states. For a given temperature, more states are available to be occupied, increasing the number of available microstates the system may occupy, and hence the entropy of the system. Heavier molecules have more closely spaced translational and vibrational energy levels, so at room temperature a larger number of these quantum states can be populated, giving rise to higher entropy. Molecular structure also determines how many distinct types of motion are possible: nonlinear and polyatomic molecules possess more rotational and vibrational modes than simpler, linear, or diatomic molecules. Each additional degree of freedom increases the total number of accessible quantum states. Thus, as molecular mass increases or as structure becomes more complex, the system gains a vastly greater multiplicity of microstates, and the entropy correspondingly increases.

The table below shows the molar entropies for the noble gases. As the mass of increases, so does the molar entropy.

Table: Molar entropies for the noble gases

Noble Gas	He	Ne	Ar	Kr	Xe	Rn
Mass $\left(\frac{g}{mol}\right)$	4.0	20.2	39.9	84.8	131.3	222.0
$S°_{g,1\ bar}$ $\left(\frac{J}{mol \cdot K}\right)$	**126.15**[1]	**146.33**[1]	**154.84**[1]	**164.08**[1]	**169.68**[1]	**176.2**[1]

The same is true for the number of atoms in a molecule. A molecule with more atoms will, in general, have a more degrees of freedom to take up energy, increasing its number of available microstates and entropy.

7.22.1: References

1. Chase, M.W., Jr., *NIST-JANAF Themochemical Tables*, *Fourth Edition*, **J. Phys. Chem. Ref. Data, Monograph 9**, 1998, 1-1951.

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7.23: Spectroscopic Entropies sometimes disgree with Calorimetric Entropies

The entropy of gases can be experimentally measured using calorimetry (S°_{exp}) or calculated using spectroscopic methods (S°_{calc}). For most molecules, the experiment and calculated values are in a good agreement, however, this is not true for all molecules. The discrepancy is referred to as residual entropy:

$$\bar{S}_{\text{calc}} - \bar{S}_{\text{exp}}$$

Residual entropy arises from a material that can have many different states a 0 K. The third law of thermodynamics states that at zero kelvin, a substance will have an entropy of zero. In substances, such as glass, ice, and carbon monoxide, the substance can exist in many different configurations; it is not a perfect crystal, but must still have zero entropy according to third law. The material has residual entropy.

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CHAPTER OVERVIEW

8: Molecular Spectroscopy

8.1: The Electromagnetic Spectrum
8.2: Introduction to Spectroscopy
8.3: Rotation of Linear Molecules
8.4: Microwave Rotational Spectroscopy
8.5: The Selection Rule for the Rigid Rotor
8.6: Rotational Spectra of Polyatomic Molecules
8.7: The Harmonic Oscillator and Infrared Spectra
8.8: The Harmonic Oscillator Selection Rule
8.9: Vibrational Overtones
8.10: Vibrational Spectroscopy Techniques
8.11: Rotations Accompany Vibrational Transitions
8.12: Unequal Spacings in Vibration-Rotation Spectra
8.13: Unequal Spacings in Pure Rotational Spectra
10.10: Normal Modes in Polyatomic Molecules
10.11: Irreducible Representation of Point Groups
10.12: Group Theory Determines Infrared Activity
10.13: Raman- Application
10.14: Raman- Theory

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8.1: 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.

8.1.1: Electromagnetic Radiation

Electromagnetic radiation—light—is a form of energy whose behavior is described by the properties of both waves and particles. Some properties of electromagnetic radiation, such as its refraction when it passes from one medium to another are explained best by describing light as a wave. Other properties, such as absorption and emission, are better described by treating light as a particle. The exact nature of electromagnetic radiation remains unclear, as it has since the development of quantum mechanics in the first quarter of the 20th century. Nevertheless, the dual models of wave and particle behavior provide a useful description for electromagnetic radiation.

Electromagnetic radiation consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity. In a vacuum electromagnetic radiation travels at the speed of light, c, which is $2.99792 \times 10^8\ m/s$. When electromagnetic radiation moves through a medium other than a vacuum its velocity, v, is less than the speed of light in a vacuum. The difference between v and c is sufficiently small (<0.1%) that the speed of light to three significant figures, $3.00 \times 10^8\ m/s$, is accurate enough for most purposes.

The oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave's propagation. Figure 13.1.1 shows an example of plane-polarized electromagnetic radiation, consisting of a single oscillating electric field and a single oscillating magnetic field.

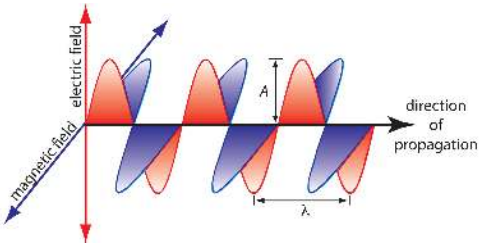


Figure 13.1.1 : Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, A, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation.[2] For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_t = A_e \sin(2\pi\nu t + \phi)$$

where A_t is the magnitude of the electric field at time t, A_e is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and ϕ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at $t = 0$. The identical equation for the magnetic field is

$$A_t = A_m \sin(2\pi\nu t + \phi)$$

where A_m is the magnetic field's maximum amplitude.

The frequency and wavelength of electromagnetic radiation vary over many orders of magnitude. For convenience, we divide electromagnetic radiation into different regions—the **electromagnetic spectrum**—based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons (Figure 13.1.2). The boundaries between the regions of the electromagnetic spectrum are not rigid, and overlap between spectral regions is possible.

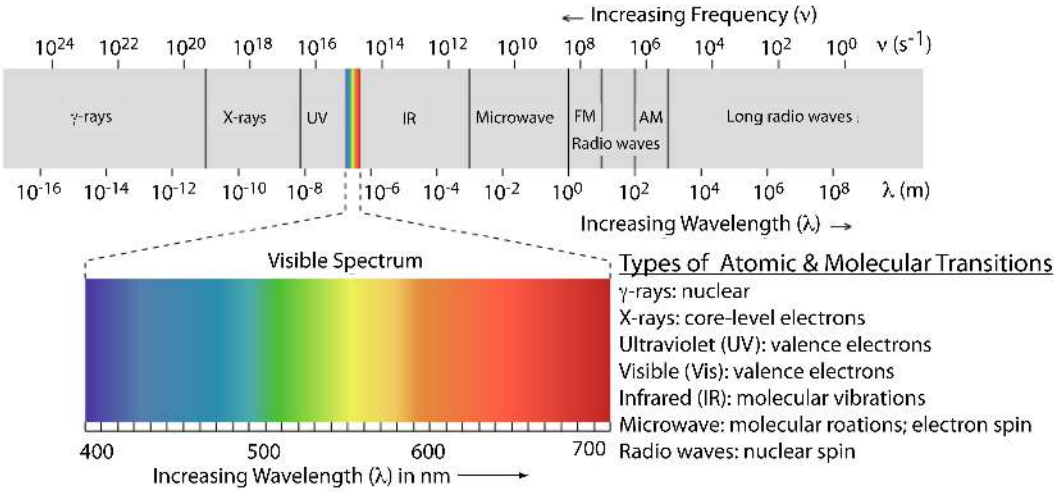


Figure 13.1.2 : The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.Wikipedia.org).

8.1.2: Other Units

Other properties also are useful for characterizing the wave behavior of electromagnetic radiation. The **wavelength**, λ, is defined as the distance between successive maxima (Figure 13.1.1). For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (1 nm = 10^{-9} m), and for infrared radiation it is given in microns (1 μm = 10^{-6} m). The relationship between wavelength and frequency is

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

Another unit useful unit is the **wavenumber**, $\tilde{\nu}$, which is the reciprocal of wavelength

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

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

Example 13.1.1

In 1817, Josef Fraunhofer studied the spectrum of solar radiation, observing a continuous spectrum with numerous dark lines. Fraunhofer labeled the most prominent of the dark lines with letters. In 1859, Gustav Kirchhoff showed that the D line in the sun's spectrum was due to the absorption of solar radiation by sodium atoms. The wavelength of the sodium D line is 589 nm. What are the frequency and the wavenumber for this line?

Solution

The frequency and wavenumber of the sodium D line are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{589 \times 10^{-9} \text{ m}} = 5.09 \times 10^{14} \text{ s}^{-1}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{589 \times 10^{-9} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 1.70 \times 10^4 \text{ cm}^{-1}$$

Exercise 13.1.1

Another historically important series of spectral lines is the Balmer series of emission lines form hydrogen. One of the lines has a wavelength of 656.3 nm. What are the frequency and the wavenumber for this line?

Above, we defined several characteristic properties of electromagnetic radiation, including its energy, velocity, amplitude, frequency, phase angle, polarization, and direction of propagation. A spectroscopic measurement is possible only if the photon's interaction with the sample leads to a change in one or more of these characteristic properties. We can divide spectroscopy into two broad classes of techniques. In one class of techniques there is a transfer of energy between the photon and the sample. Table 13.1.1 provides a list of several representative examples.

Table 13.1.1 : Examples of Spectroscopic Techniques Involving an Exchange of Energy Between a Photon and the Sample

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Technique
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis	UV/Vis spectroscopy atomic absorption spectroscopy
	IR	infrared spectroscopy raman spectroscopy
	Microwave	microwave spectroscopy
	Radio wave	electron spin resonance spectroscopy nuclear magnetic resonance spectroscopy
emission (thermal excitation)	UV/Vis	atomic emission spectroscopy
photoluminescence	X-ray	X-ray fluorescence
	UV/Vis	fluorescence spectroscopy phosphorescence spectroscopy atomic fluorescence spectroscopy
chemiluminescence	UV/Vis	chemiluminescence spectroscopy

Electromagnetic spectrum provides clearly information of molecules if they are rotational transitions, vibrational transitions, or electronic transitions. A molecule or a set of molecules can be read by the absorption of microwave radiation which provides transitions between rotational energy levels. In addition, if the molecules absorbs infrared radiation provides the transitions between vibrational levels follows by transitions between rotational energy levels. Finally, when molecules absorbs visible and ultraviolet radiation gives transitions between electronic energy levels follows by simultaneous transitions between vibrational and rotational levels.

When given the energy level of the molecules along with wavelength, we can easily figure the frequency of the molecules where they fall in the electromagnetic spectrum regions:

$$\Delta E = E_u - E_l = h\nu$$

The above equation describes the energy change between upper state and lower state of energy.

- Frequency falls between 10^9 - 10^{11} which is in the microwave range correlates to the rotation of polyatomic molecules.
- Frequency falls between 10^{11} - 10^{13} which is in the far infrared range correlates to the rotation of small molecules.
- Frequency falls between 10^{13} - 10^{14} which is in the infrared range correlates to the vibrations of flexible bonds.
- Frequency falls between 10^{14} - 10^{16} which is in the visible and ultraviolet range correlates to the electronic transitions.

The powerful technique of figuring out the the frequency of the molecules can help us determine the bond length, temperature, probability distribution as you will learn later on from the degree of freedoms and how the process is undergo in specific a reaction.

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8.2: Introduction to Spectroscopy

Realizing that light may be considered to have both wave-like and particle-like characteristics, it is useful to consider that a given frequency or wavelength of light is associated with a "light quanta" of energy we now call a **photon**. As noted in the following equations, frequency and energy change proportionally, but wavelength has an inverse relationship to these quantities.

$$\nu = \frac{c}{\lambda} \tag{8.2.1}$$

and

$$\Delta E = h\nu \tag{8.2.2}$$

with

- ν is the frequency of light
- λ is the wavelength of ligt
- c is the speed of light ($3 \times 10^8\ m/sec$)
- ΔE is the transition energy (difference of energies between the initial and final states)
- h is Planck's constant ($h = 6.626069 \times 10^{-34}\ J\,s$)

To "see" a molecule, we must use light having a wavelength smaller than the molecule itself (roughly 1 to 15 angstroms). Such radiation is found in the X-ray region of the spectrum, and the field of **X-ray crystallography** yields remarkably detailed pictures of molecular structures amenable to examination. The chief limiting factor here is the need for high quality crystals of the compound being studied. The methods of X-ray crystallography are too complex to be described here; nevertheless, as automatic instrumentation and data handling techniques improve, it will undoubtedly prove to be the procedure of choice for structure determination. The spectroscopic techniques described below do not provide a three-dimensional picture of a molecule, but instead yield information about certain characteristic features. A brief summary of this information follows:

- **Ultraviolet-Visible Spectroscopy**: Absorption of this relatively high-energy light causes electronic excitation. The easily accessible part of this region (wavelengths of 200 to 800 nm) shows absorption only if conjugated π electron systems are present.
- **Infrared Spectroscopy**: Absorption of this lower energy radiation causes vibrational and rotational excitation of groups of atoms. within the molecule. Because of their characteristic absorptions, identification of functional groups is easily accomplished.
- **Nuclear Magnetic Resonance (NMR) Spectroscopy**: Absorption in the low-energy radio-frequency part of the spectrum causes excitation of nuclear spin states. NMR spectrometers are tuned to certain nuclei (e.g. ^{1}H, ^{13}C, ^{19}F & ^{31}P). For a given type of nucleus, high-resolution spectroscopy distinguishes and counts atoms in different locations in the molecule.

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8.3: Rotation of Linear Molecules

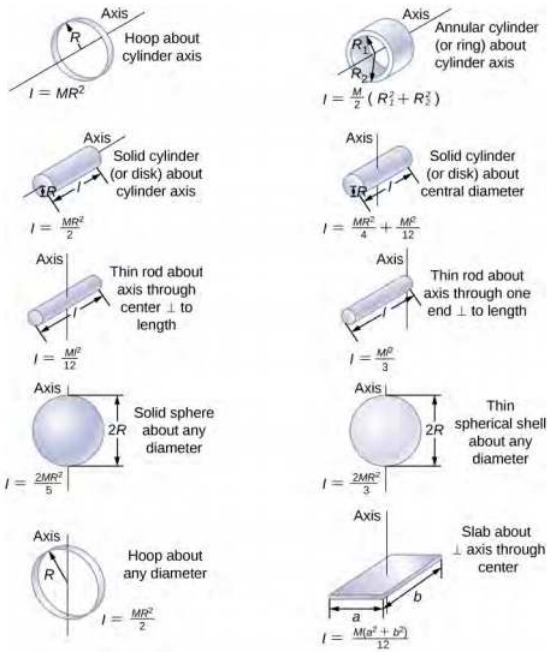
The rotational energy levels of a diatomic molecule in 3D space is given by the quantum mechanical solution to the rotating rigid rotor:

$$E = J(J+1)\frac{\hbar^2}{2I} \tag{8.3.1}$$

where

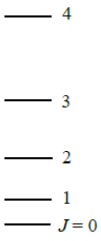
- J is a rotational quantum number ranging from $J = 0$ to $J = \infty$.
- I is the moment of inertia and is the rotational equivalent to mass in translation.

The moment of inertia of a molecule is very sensitive to the geometry to the the molecule (see below).



Values of rotational inertia for common shapes of objects.

In general, any three-dimension species (e.g., a molecule) will have three degrees of rotational energy since it can rotation in the x, y and z axis (i.e., the angular momentum vector can lie in each axis). This energy spacing for rotation in each degree is given by Equation 8.3.1 and is shown geometrically below.



Energy spacing for a rigid rotor (in 3D) as a function of \(J) quantum number.

The lowest energy transition is the $J = 0$ to $J = 1$ transition and corresponds to

$$E_{J=0\rightarrow J=1} = [1(1+1) - 0(0+1)]\frac{\hbar^2}{2I} = \frac{\hbar^2}{I} \tag{8.3.2}$$

Most of the mass of the molecule is in the nuclei, so when calculating the moment of inertia I we can ignore the electrons and just use the nuclei. But the size of the nuclei is around 10^{-5} times smaller than the bond length. This means the moment of inertia

around an axis along the bond is going to be about 10^{10} smaller than the moment of inertia around an axis normal to the bond. Therefore the energy level spacings will be around 10^{10} times bigger along the bond than normal to it.

It is common to argue that linear molecules do not rotate perpendicular to the axis of symmetry and often justified in terms of **symmetry** of the molecule (see Group Theory). Therefore, out of three possible rotational degrees of freedom for a three dimensional object, only two are applicable to linear molecules and the third rotation is often ignored. This is calipalized in terms of justifying how many vibrational degrees of freedom a molecule has:

- **Non-linear** molecules have 3N degrees of freedom in total: 3 are translational and 3 are rotational (all are allowed for non-linear molecules) so the remaining 3N-6 are vibrational.
- In contrast, **linear** molecules have 3 translational and only 2 rotational, and to keep a total of 3N degrees of freedom, they have 3N-5 vibrational degrees.

These equations are justified since rotation around the axis along the bond of the molecule requires huge energies (Equation **8.3.2**) since I due to the much smaller moment of inertia. To excited these rotations, gamma ray photons are required and is the topic of high energy physics. Moreover, the temperature at which energy levels above the ground level are important is extremely high (e.g., it can be higher than the temperature of dissociation of the molecule). Therefore, at temperatures of practical interest, rotation around the axis of the linear molecule is not important for thermodynamic properties.

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8.4: Microwave Rotational Spectroscopy

Microwave rotational spectroscopy uses microwave radiation to measure the energies of rotational transitions for molecules in the gas phase. It accomplishes this through the interaction of the electric dipole moment of the molecules with the electromagnetic field of the exciting microwave photon.

Introduction

To probe the pure rotational transitions for molecules, scientists use microwave rotational spectroscopy. This spectroscopy utilizes photons in the microwave range to cause transitions between the quantum rotational energy levels of a gas molecule. The reason why the sample must be in the gas phase is due to intermolecular interactions hindering rotations in the liquid and solid phases of the molecule. For microwave spectroscopy, molecules can be broken down into 5 categories based on their shape and the inertia around their 3 orthogonal rotational axes. These 5 categories include diatomic molecules, linear molecules, spherical tops, symmetric tops and asymmetric tops.

Classical Mechanics

The **Hamiltonian solution** to the rigid rotor is

$$H = T \tag{8.4.1}$$

since,

$$H = T + V \tag{8.4.2}$$

Where T is kinetic energy and V is potential energy. Potential energy, V, is 0 because there is no resistance to the rotation (similar to a particle in a box model).

Since $H = T$, we can also say that:

$$T = \frac{1}{2}\sum m_i v_i^2 \tag{8.4.3}$$

However, we have to determine v_i in terms of rotation since we are dealing with rotation. Since,

$$\omega = \frac{v}{r} \tag{8.4.4}$$

where ω = angular velocity, we can say that:

$$v_i = \omega X r_i \tag{8.4.5}$$

Thus we can rewrite the T equation as:

$$T = \frac{1}{2}\sum m_i v_i \left(\omega X r_i\right) \tag{8.4.6}$$

Since ω is a scalar constant, we can rewrite the T equation as:

$$T = \frac{\omega}{2}\sum m_i \left(v_i X r_i\right) = \frac{\omega}{2}\sum l_i = \omega\frac{L}{2} \tag{8.4.7}$$

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,

$$L = I\omega \tag{8.4.8}$$

where **I** is the moment of inertia of the rigid body relative to the axis of rotation. We can rewrite the T equation as,

$$T = \omega\frac{I\omega}{2} = \frac{1}{2}I\omega^2 \tag{8.4.9}$$

Quantum Mechanics

The internal Hamiltonian, H, is:

$$H = \frac{i^2\hbar^2}{2I} \tag{8.4.10}$$

and the Schrödinger Equation for rigid rotor is:

$$\frac{i^2\hbar^2}{2I}\psi = E\psi \tag{8.4.11}$$

Thus, we get:

$$E_n = \frac{J(J+1)h^2}{8\pi^2 I} \tag{8.4.12}$$

where J is a rotational quantum number and $\hbar$ is the reduced Planck's constant. However, if we let:

$$B = \frac{h}{8\pi^2 I} \tag{8.4.13}$$

where B is a rotational constant, then we can substitute it into the E_n equation and get:

$$E_n = J(J+1)Bh \tag{8.4.14}$$

Considering the transition energy between two energy levels, the difference is a multiple of 2. That is, from $J = 0$ to $J = 1$, the $\Delta E_{0\to1}$ is 2Bh and from J = 1 to J = 2, the $\Delta E_{1\to2}$ is 4Bh.

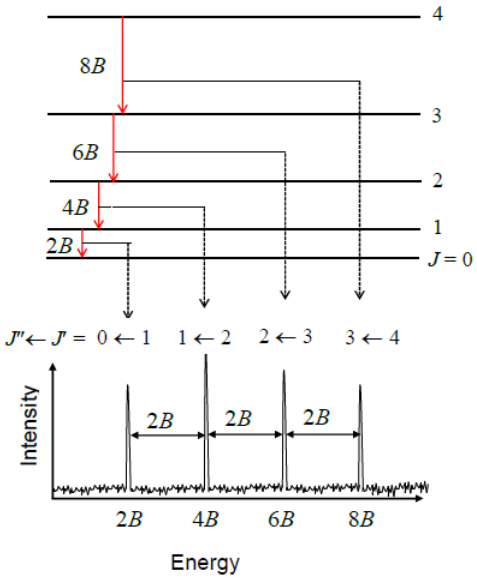


Figure **8.4.1**: Energy levels and line positions calculated in the rigid rotor approximation. This diagram illustrates how transitions between the rotational energy levels of molecules map onto the energies at which these transitions are observed during laboratory experiments. (CC CS-BY 3.0; Nnrw).

Theory

When a gas molecule is irradiated with microwave radiation, a photon can be absorbed through the interaction of the photon's electronic field with the electrons in the molecules. For the microwave region this energy absorption is in the range needed to cause transitions between rotational states of the molecule. However, only molecules with a permanent dipole that changes upon rotation can be investigated using microwave spectroscopy. This is due to the fact that their must be a charge difference across the molecule for the oscillating electric field of the photon to impart a torque upon the molecule around an axis that is perpendicular to this dipole and that passes through the molecules center of mass.

This interaction can be expressed by the transition dipole moment for the transition between two rotational states

$$\text{Probability of Transition} = \int \psi_{rot}(F)\hat{\mu}\psi_{rot}(I)d\tau \tag{8.4.15}$$

Where $\Psi_{rot(F)}$ is the complex conjugate of the wave function for the final rotational state, $\Psi_{rot(I)}$ is the wave function of the initial rotational state , and μ is the dipole moment operator with Cartesian coordinates of μ_x, μ_y, μ_z. For this integral to be nonzero the integrand must be an even function. This is due to the fact that any odd function integrated from negative infinity to positive infinity, or any other symmetric limits, is always zero.

In addition to the constraints imposed by the transition moment integral, transitions between rotational states are also limited by the nature of the photon itself. A photon contains one unit of angular momentum, so when it interacts with a molecule it can only impart one unit of angular momentum to the molecule. This leads to the selection rule that a transition can only occur between rotational energy levels that are only one quantum rotation level (J) away from another[1].

$$\Delta J = \pm 1 \tag{8.4.16}$$

The transition moment integral and the selection rule for rotational transitions tell if a transition from one rotational state to another is allowed. However, what these do not take into account is whether or not the state being transitioned from is actually populated, meaning that the molecule is in that energy state. This leads to the concept of the Boltzmann distribution of states. The Boltzmann distribution is a statistical distribution of energy states for an ensemble of molecules based on the temperature of the sample[2].

$$\frac{n_J}{n_0} = \frac{e^{(-E_{rot}(J)/RT)}}{\sum_{J=1}^{J=n} e^{(-E_{rot}(J)/RT)}} \tag{8.4.17}$$

where $E_{rot(J)}$ is the molar energy of the J rotational energy state of the molecule,

- R is the gas constant,
- T is the temperature of the sample.
- n(J) is the number of molecules in the J rotational level, and
- n_0 is the total number of molecules in the sample.

This distribution of energy states is the main contributing factor for the observed absorption intensity distributions seen in the microwave spectrum. This distribution makes it so that the absorption peaks that correspond to the transition from the energy state with the largest population based on the Boltzmann equation will have the largest absorption peak, with the peaks on either side steadily decreasing.

Degrees of Freedom

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 3 categories[3].

- **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.

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.

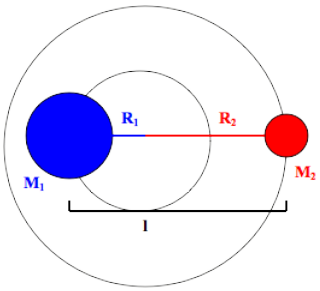
Rotational Symmetries

To analyze molecules for rotational spectroscopy, we can break molecules down into 5 categories based on their shapes and their moments of inertia around their 3 orthogonal rotational axes:[4]

1. Diatomic Molecules
2. Linear Molecules
3. Spherical Tops
4. Symmetrical Tops
5. Asymmetrical Tops

Diatomic Molecules

The rotations of a diatomic molecule can be modeled as a rigid rotor. This rigid rotor model has two masses attached to each other with a fixed distance between the two masses.



It has an inertia (I) that is equal to the square of the fixed distance between the two masses multiplied by the reduced mass of the rigid rotor.

$$I_e = \mu r_e^2 \tag{8.4.18}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{8.4.19}$$

Using quantum mechanical calculations it can be shown that the energy levels of the rigid rotator depend on the inertia of the rigid rotator and the quantum rotational number J[2].

$$E(J) = B_e J(J+1) \tag{8.4.20}$$

$$B_e = \frac{h}{8\pi^2 c I_e} \tag{8.4.21}$$

However, this rigid rotor model fails to take into account that bonds do not act like a rod with a fixed distance, but like a spring. This means that as the angular velocity of the molecule increases so does the distance between the atoms. This leads us to the **nonrigid rotor model** in which a centrifugal distortion term (D_e) is added to the energy equation to account for this stretching during rotation.

$$E(J)(cm^{-1}) = B_e J(J+1) – D_e J^2 (J+1)^2 \tag{8.4.22}$$

This means that for a diatomic molecule the transitional energy between two rotational states equals

$$E = B_e[J'(J'+1) - J''(J''+1)] - D_e[J'^2(J'+1)^2 - J''^2(J'+1)^2] \tag{8.4.23}$$

Where J' is the quantum number of the final rotational energy state and J'' is the quantum number of the initial rotational energy state. Using the selection rule of $\Delta J = \pm 1$ the spacing between peaks in the microwave absorption spectrum of a diatomic molecule will equal

$$E_R = (2B_e - 4D_e) + (2B_e - 12D_e)J'' - 4D_e J''^3 \tag{8.4.24}$$

Linear Molecules

Linear molecules behave in the same way as diatomic molecules when it comes to rotations. For this reason they can be modeled as a non-rigid rotor just like diatomic molecules. This means that linear molecule have the same equation for their rotational energy levels. The only difference is there are now more masses along the rotor. This means that the inertia is now the sum of the distance between each mass and the center of mass of the rotor multiplied by the square of the distance between them[2].

$$I_e = \sum_{j=1}^{n} m_j r_{ej}^2 \tag{8.4.25}$$

Where m_j is the mass of the jth mass on the rotor and r_{ej} is the equilibrium distance between the j^{th} mass and the center of mass of the rotor.

Spherical Tops

Spherical tops are molecules in which all three orthogonal rotations have equal inertia and they are highly symmetrical. This means that the molecule has no dipole and for this reason spherical tops do not give a microwave rotational spectrum.

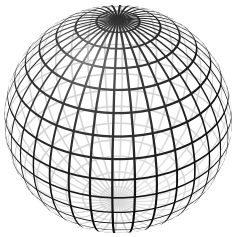
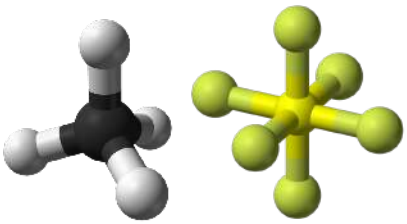


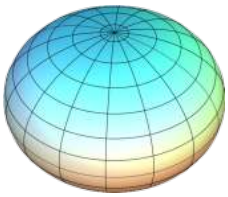
Figure 8.4.2: Geometrical example of a spherical top

Examples:



Symmetrical 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. 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.



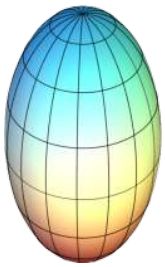


***Figure* 8.4.3:** *Symmetric Tops: (Left) Geometrical example of an oblate top and (right) a prolate top. Images used with permission from Wikipedia.com.*

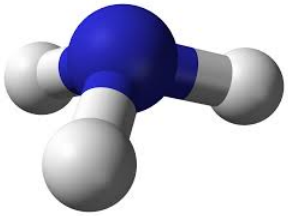


Figure 8.4.4: Examples of symmetric tops. Benzene (oblate) XeF_4 (oblate) $ClCH_3$ (prolate) NH_3 (prolate)

In the case of linear molecules there is one degenerate rotational axis which in turn has a single rotational constant. With symmetrical tops now there is one unique axis and two degenerate axes. This means an additional rotational constant is needed to describe the energy levels of a symmetrical top. In addition to the rotational constant an additional quantum number must be introduced to describe the rotational energy levels of the symmetric top. These two additions give us the following rotational energy levels of a prolate and oblate symmetric top

$$E_{(J,K)}(cm^{-1}) = B_e * J(J+1) + (A_e - B_e)K^2 \tag{8.4.26}$$

Where B_e is the rotational constant of the unique axis, A_e is the rotational constant of the degenerate axes, J is the total rotational angular momentum quantum number and K is the quantum number that represents the portion of the total angular momentum that lies along the unique rotational axis. This leads to the property that K is always equal to or less than J. Thus we get the two selection rules for symmetric tops

$$\Delta J = 0, \pm 1 \tag{8.4.27}$$

$$\Delta K = 0 \tag{8.4.28}$$

when $K \neq 0$

$$\Delta J = \pm 1 \tag{8.4.29}$$

$$\Delta K = 0 \tag{8.4.30}$$

when $K = 0$

However, like the rigid rotor approximation for linear molecules, we must also take into account the elasticity of the bonds in symmetric tops. Therefore, in a similar manner to the rigid rotor we add a centrifugal coupling term, but this time we have one for each quantum number and one for the coupling between the two.

$$E_{(J,K)}(cm^{-1}) = B_e J(J+1) - D_{eJ}J^2(J+1)^2 + (A_e - B_e) * K^2 \tag{8.4.31}$$

$$-D_{ek}K^4 - D_{ejk}J(J+1)K^2 \tag{8.4.32}$$

Asymmetrical Tops

Asymmetrical tops have three orthogonal rotational axes that all have different moments of inertia and most molecules fall into this category. Unlike linear molecules and symmetric tops these types of molecules do not have a simplified energy equation to determine the energy levels of the rotations. These types of molecules do not follow a specific pattern and usually have very complex microwave spectra.

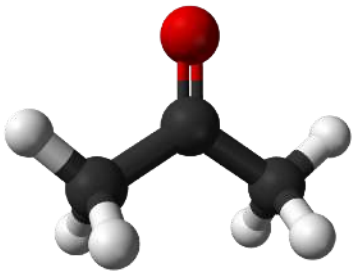


Figure 8.4.5: Molecular examples of asymmetrical tops. (left) water and (right) acetone

Additional Rotationally Sensitive Spectroscopies

In addition to microwave spectroscopy, IR spectroscopy can also be used to probe rotational transitions in a molecule. However, in the case of IR spectroscopy the rotational transitions are coupled to the vibrational transitions of the molecule. One other spectroscopy that can probe the rotational transitions in a molecule is Raman spectroscopy, which uses UV-visible light scattering to determine energy levels in a molecule. However, a very high sensitivity detector must be used to analyze rotational energy levels of a molecule.

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8.5: The Selection Rule for the Rigid Rotor

A **selection rule** describes how the probability of transitioning from one level to another cannot be **zero**. It has two sub-pieces: a **gross selection rule** and a **specific selection rule**. A gross selection rule illustrates characteristic requirements for atoms or molecules to display a spectrum of a given kind, such as an IR spectroscopy or a microwave spectroscopy. Once the atom or molecules follow the gross selection rule, the specific selection rule must be applied to the atom or molecules to determine whether a certain transition in quantum number may happen or not.

Selection rules specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation. Incident electromagnetic radiation presents an oscillating electric field $E_0 \cos(\omega t)$ that interacts with a transition dipole. The dipole operator is $\mu = e \cdot r$ where r is a vector pointing in a direction of space.

A dipole moment of a given state is

$$\mu_z = \int \Psi_1{}^* \mu_z \Psi_1 \, d\tau$$

A transition dipole moment is a transient dipolar polarization created by an interaction of electromagnetic radiation with a molecule

$$(\mu_z)_{12} = \int \Psi_1{}^* \mu_z \Psi_2 \, d\tau$$

In an experiment we present an electric field along the z axis (in the laboratory frame) and we may consider specifically the interaction between the transition dipole along the x, y, or z axis of the molecule with this radiation. If μ_z is zero then a transition is forbidden. The selection rule is a statement of when μ_z is non-zero.

> *The selection rule is a statement of when μ_z is non-zero.*

8.5.1: Rotational transitions

We can use the definition of the transition moment and the spherical harmonics to derive selection rules for a rigid rotator. Once again we assume that radiation is along the z axis.

$$(\mu_z)_{J,M,J',M'} = \int_0^{2\pi} \int_0^{\pi} Y_{J'}^{M'}(\theta,\phi) \mu_z Y_J^M(\theta,\phi) \sin\theta \, d\phi, d\theta$$

Notice that m must be non-zero in order for the transition moment to be non-zero. This proves that a molecule must have a permanent dipole moment in order to have a rotational spectrum. The spherical harmonics can be written as

$$Y_J^M(\theta,\phi) = N_{JM} P_J^{|M|}(\cos\theta) e^{iM\phi}$$

where N_{JM} is a normalization constant. Using the standard substitution of $x = \cos q$ we can express the rotational transition moment as

$$(\mu_z)_{J,M,J',M'} = \mu N_{JM} N_{J'M'} \int_0^{2\pi} e^{I(M-M')\phi} \, d\phi \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

The integral over f is zero unless M = M' so $\Delta M = 0$ is part of the rigid rotator selection rule. Integration over ϕ for $M = M'$ gives 2π so we have

$$(\mu_z)_{J,M,J',M'} = 2\pi\mu N_{JM} N_{J'M'} \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

We can evaluate this integral using the identity

$$(2J+1)x \, P_J^{|M|}(x) = (J - |M| + 1) P_{J+1}^{|M|}(x) + (J - |M|) P_{J-1}^{|M|}(x)$$

Substituting into the integral one obtains an integral which will vanish unless $J' = J+1$ or $J' = J-1$.

$$\int_{-1}^{1} P_{J'}^{|M'|}(x) \left(\frac{(J - |M| + 1)}{(2J+1)} P_{J+1}^{|M|}(x) + \frac{(J - |M|)}{(2J+1)} P_{J-1}^{|M|}(x) \right) dx$$

This leads to the selection rule $\Delta J = \pm 1$ for absorptive rotational transitions. Keep in mind the physical interpretation of the quantum numbers J and M as the total angular momentum and z-component of angular momentum, respectively. As stated above in the section on electronic transitions, these selection rules also apply to the orbital angular momentum ($\Delta l = \pm 1$, $\Delta m = 0$).

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8.6: Rotational Spectra of Polyatomic Molecules

Quick Review of Diatomic Rotation

As discussed previously, the Schrödinger equation for the angular motion of a rigid (i.e., having fixed bond length R) diatomic molecule is

$$\frac{\hbar^2}{2\mu}\left[\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{R^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\psi\rangle = E|\psi\rangle$$

or

$$\frac{L^2}{2\mu R^2}|\psi\rangle = E|\psi\rangle$$

The Hamiltonian in this problem contains only the kinetic energy of rotation; no potential energy is present because the molecule is undergoing unhindered "free rotation". The angles θ and φ describe the orientation of the diatomic molecule's axis relative to a laboratory-fixed coordinate system, and μ is the reduced mass of the diatomic molecule

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The eigenvalues corresponding to each eigenfunction are straightforward to find because H_{rot} is proportional to the L^2 operator whose eigenvalues have already been determined. The resultant rotational energies are given as:

$$E_J = \frac{\hbar^2 J(J+1)}{2\mu R^2} = BJ(J+1) \tag{8.6.1}$$

and are independent of M. B is the rotational constant. Thus each energy level is labeled by J and is $2J+1$-fold degenerate (because M ranges from $-J$ to J). The rotational energy in Equation 8.6.1 can be expressed in terms of the moment of inertia I

$$I = \sum_i m_i R_i^2 \tag{8.6.2}$$

where m_i is the mass of the i^{th} 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 8.6.1:

$$E_J = \frac{\hbar^2 J(J+1)}{2I} = BJ(J+1) \tag{8.6.3}$$

8.6.1: Rotation of Polyatomic Molecules

In contrast to diatomic molecules (Equation 8.6.2), the rotational motions of polyatomic molecules in three dimensions are characterized by multiple moments of inertia. typically reflected in an 3×3 inertia tensor. It is common in rigid body mechanics to express in these moments of inertia in *lab-based Cartesian coordinates* via a notation that explicitly identifies the x, y, and z axes such as I_{xx} and I_{xy}, for the components of the inertia tensor.

$$I = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{xx} & I_{xy} & I_{zz} \end{bmatrix} \tag{8.6.4}$$

The components of this tensor can be assembled into a matrix given by

$$I_{xx} = \sum_{k=1}^{N} m_k(y_k^2 + z_k^2)$$

$$I_{yy} = \sum_{k=1}^{N} m_k(x_k^2 + z_k^2)$$

$$I_{zz} = \sum_{k=1}^{N} m_k (x_k^2 + y_k^2)$$

$$I_{yx} = I_{xy} = -\sum_{k=1}^{N} m_k x_k y_k$$

$$I_{zx} = I_{xz} = -\sum_{k=1}^{N} m_k x_k z_k$$

$$I_{zy} = I_{yz} = -\sum_{k=1}^{N} m_k y_k z_k.$$

The rotational motions of polyatomic molecules are characterized by moments of inertia that are defined in a *molecule based coordinates* with axes that are labeled a, b, and c. Measured in the body frame the inertia matrix (Equation 8.6.4) is a constant real symmetric matrix, which can be decomposed into a diagonal matrix, given by

$$I = \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix}$$

These labels are assigned so that I_c is the **largest** principal moment of inertia with an order of the three moments set as

$$I_a < I_b < I_c$$

The rotational kinetic energy operator for a rigid non-linear polyatomic molecule is then expressed as

$$H_{rot} = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} \tag{8.6.5}$$

The components of the quantum mechanical angular momentum operators along the three principal axes are:

$$J_a = -i\hbar \cos\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \sin\chi \frac{\partial}{\partial\theta} \tag{8.6.6}$$

$$J_b = i\hbar \sin\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \cos\chi \frac{\partial}{\partial\theta} \tag{8.6.7}$$

$$J_c = -\frac{ih\partial}{\partial\chi} \tag{8.6.8}$$

The angles θ, φ, and χ are the **Euler angles** needed to specify the orientation of the rigid molecule relative to a laboratory-fixed coordinate system. The corresponding square of the total angular momentum operator J^2 can be obtained as

$$J^2 = J_a^2 + J_b^2 + J_c^2 \tag{8.6.9}$$

$$= -\frac{\partial^2}{\partial\theta^2} - \cot\theta \frac{\partial}{\partial\theta} - \left(\frac{1}{\sin\theta} \right) \left(\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial\chi^2} - 2\cos\theta \frac{\partial^2}{\partial\varphi\partial\chi} \right) \tag{8.6.10}$$

and the component along the lab-fixed Z axis is

$$J_Z = -ih \frac{\partial}{\partial\varphi}.$$

8.6.2: 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 8.6.5 can be expressed in terms of the total angular momentum operator J^2

$$H_{rot} = \frac{J^2}{2I}$$

As a result, the eigenfunctions of H_{rot} are those of J^2 (and J_a as well as J_Z both of which commute with J_2 and with one another; J_Z is the component of J along the lab-fixed Z-axis and commutes with J_a because

$$J_Z = -ih\frac{\partial}{\partial\varphi}$$

and

$$J_a = -ih\frac{\partial}{\partial\chi}$$

act on different angles. The energies associated with such eigenfunctions are

$$E(J,K,M) = \frac{\hbar^2 J(J+1)}{2I^2}$$

for all K (i.e., J a quantum numbers) ranging from -J to J in unit steps and for all M (i.e., J Z quantum numbers) ranging from -J to J. Each energy level is therefore $(2J+1)^2$ degenarate because there are $2J+1$ possible K values and $2J+1$ possible M values for each J. The eigenfunctions of J^2, J_Z and J_a, $|J,M,K>$ are given in terms of the set of rotation matrices $D_{J,M,K}$:

$$|J,M,K\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D^*_{J,M,K}(\theta,\varphi,\chi)$$

which obey

$$J^2\,|J,M,K\rangle = \hbar^2 J(J+1)|\,J,M,K\rangle$$

$$J_a\,|J,M,K\rangle = \hbar K|\,J,M,K\rangle$$

$$J_Z\,|J,M,K\rangle = \hbar M|\,J,M,K\rangle$$

8.6.3: 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.

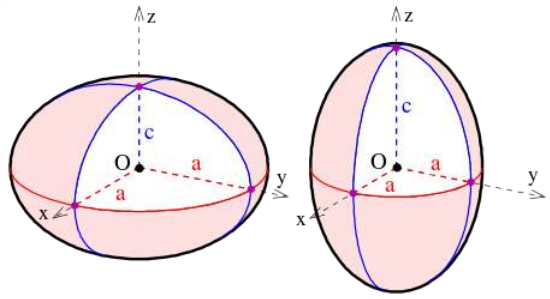


Figure 13.8.1 : The assignment of semi-axes on a spheroid. It is oblate if $c < a$ (left) and prolate if $c > a$ (right). (CC BY-SA 4.0; Ag2gaeh)

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 8.6.5 becomes

$$H_{rot} = \frac{J^2}{2I} + J_a^2\left(\frac{1}{2I_a} - \frac{1}{2I}\right)$$

For oblate tops, Equation 8.6.5 becomes

$$H_{rot} = \frac{J^2}{2I} + J_c^2\left(\frac{1}{2I_c} - \frac{1}{2I}\right)$$

As a result, the eigenfunctions of H_{rot} are those of J^2 and J_a or J_c (and of J_Z), and the corresponding energy levels.

The energies for prolate tops are

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I^2} + h^2 K^2 \left(\frac{1}{2I_a} - \frac{1}{2I}\right)$$

and the energies for oblate tops are

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I2} + h^2 K^2 \left(\frac{1}{2I_c} - \frac{1}{2I}\right)$$

again for K and M (i.e., J_a or J_c and J_Z quantum numbers, respectively) ranging from $-J$ to J in unit steps. Since the energy now depends on K, these levels are only $2J+1$ degenerate due to the $2J+1$ different M values that arise for each J value. The eigenfunctions $|J,M,K>$ are the same rotation matrix functions as arise for the spherical-top case.

8.6.4: 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 8.6.5 can be formed within a basis set of the $\{|J,M,K\rangle\}$ rotation matrix functions. This matrix will **not** be diagonal because the $|J,M,K\rangle$ functions are not eigenfunctions of the asymmetric top H_{rot}. However, the matrix can be formed in this basis and subsequently brought to diagonal form by finding its eigenvectors {C n, J,M,K } and its eigenvalues $\{E_n\}$. The vector coefficients express the asymmetric top eigenstates as

$$\psi_n(\theta,\varphi,\chi) = \sum_{J,M,K} C_{n,J,M,K}|J,M,K\rangle$$

Because the total angular momentum J^2 still commutes with H_{rot}, each such eigenstate will contain only one J-value, and hence Ψ_n can also be labeled by a J quantum number:

$$\psi_{n,J}(\theta,\varphi,\chi) = \sum_{M,K} C_{n,J,M,K}|J,M,K\rangle$$

To form the only non-zero matrix elements of H_{rot} within the $|J,M,K\rangle$ basis, one can use the following properties of the rotation-matrix functions:

$$\langle j,\rangle = \langle j,\rangle = 1/2 < j,\rangle = h2[J(J+1) - K2],$$

$$\langle j,\rangle = h^2K^2$$

$$\langle j\rangle = -\langle j\rangle = h^2[J(J+1) - K(K\pm1)]1/2[J(J+1) - (K\pm1)(K\pm2)]1/2\langle j\rangle = 0$$

Each of the elements of J_c^2, J_a^2, and J_b^2 must, of course, be multiplied, respectively, by $1/2I_c$, $1/2I_a$, and $1/2I_b$ and summed together to form the matrix representation of H_{rot}. The diagonalization of this matrix then provides the asymmetric top energies and wavefunctions.

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8.7: 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.

8.7.1: 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 v^{th} eigenstate of a harmonic oscillator can be written as

$$E_v = \left(v + \frac{1}{2}\right) \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{8.7.1}$$

where h is Planck's constant and v is the vibrational quantum number and ranges from 0, 1, 2, 3,..., ∞. Equation 8.7.1 is often rewritten as

$$E_v = \left(v + \frac{1}{2}\right) h\nu_m \tag{8.7.2}$$

where ν_m is the vibrational frequency of the vibration. Equation 8.7.2 is often written as

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega$$

where ω is the angular frequency (i.e., $2\pi\nu$).

Transitions in vibrational energy levels can be brought about by absorption of radiation, provided the energy of the radiation ($h\nu_{photon}$) **exactly** matches the difference in energy ($\Delta E_{vv'}$) between the vibrational quantum state v to quantum state v'. This can be expressed as

$$\begin{aligned} h\nu_{photon} &= \Delta E_{vv'} \\ &= E_{v'} - E_v \\ &= \left(v' + \frac{1}{2}\right) h\nu_m - \left(v + \frac{1}{2}\right) h\nu_m \\ &= (v' - v)\, h\nu_m \end{aligned} \tag{8.7.3}$$

Let's consider only transitions between adjacent eigenstates (discussed in more details below) so

$$v' - v = \pm 1$$

which is positive if an IR photon is absorbed and negative if it is emitted. For the absorption of a IR photon, Equation 8.7.3 simplifies to

$$h\nu_{photon} = h\nu_m$$

$$= \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{8.7.4}$$

The frequency of radiation ν_{photon} that will bring about this change is **identical** to the classical vibrational frequency of the bond ν.

The Wavenumber as a Unit of Energy

The cm^{-1} is the wavenumber scale and it can also be defined as 1/wavelength in cm. A wavenumber is often used due to its direct relationship with both frequency and energy. The frequency of the absorbed radiation causes the molecular vibrational frequency for the absorption process:

$$\bar{\nu}(cm^{-1}) = \frac{1}{\lambda(\mu m)} \times 10^4 \left(\frac{\mu m}{cm}\right) \tag{8.7.5}$$

$$= \frac{\nu\,(Hz)}{c\,(cm/s)} \tag{8.7.6}$$

Equation 8.7.3 can be modified so that the radiation can be expressed in wavenumbers

$$\tilde{\nu}_m = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{8.7.7}$$

where c is the velocity of light (cm/s) and $\tilde{\nu}$ is the wavenumber of an absorption maximum (cm^{-1}).

Example 5.5.1: Hydrogen Halides

The force constants for typical diatomic molecules are in the range between 400 to 2000 $N \cdot m^{-1}$.

Molecule	HF	HCl	HBr	HI	CO	NO
Force constant, k ($N.m^{-1}$)	970	480	410	320	1860	1530

For the diatomic molecules listed above, calculate the following:

a. angular frequency ($rad \cdot s^{-1}$)
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

$$\omega = 5.45 \times 10^{14} rad \cdot s^{-1}$$

b. natural frequency:

$$\nu = \frac{\omega}{2\pi} = 8.68 \times 10^{13}$$

c. period (s):

$$T = \frac{1}{\nu} = 1.15 \times 10^{-14}$$

d. separation between energy levels:

$$\Delta E = E_{v=1} - E_{v=0} = \hbar\omega = 5.75 \times 10^{-20}\ J$$

e. wavelength λ of the electromagnetic radiation absorbed in the transition $v = 0 \rightarrow v = 1$:

$$3.46 \times 10^{-6}\, m$$

The electromagnetic radiation released (and absorbed) for vibrations is primarily in the infrared (IR) part of the spectrum. Calculating the above properties for the other molecules remains as an exercise.

Note: We did not designate the specific isotopes in the hydrogen halides above because that information was not required to solve these questions.

IR deals with the interaction between a molecule and radiation from the electromagnetic region ranging (4000- 40 cm^{-1}). The IR region of the electromagnetic spectrum ranges in wavelength from 2 -15 μm. Conventionally the IR region is subdivided into three regions (Table 5.5.1): near IR, mid IR and far IR. Most of the IR used originates from the mid IR region.

Table 5.5.1: Regions of the IR Spectrum

Region	Wavelength	Wavenumbers ($\tilde{\nu}$), cm^{-1}	Frequencies (v), HZ
Near	0.78 -2.5	12800 - 4000	3.8 x 10^{14} - 1.2 x 10^{14}
Middle	2.5 - 50	4000 - 200	3.8 x 10^{14} - 1.2 x 10^{14}
Far	50 -100	200 -10	3.8 x 10^{14} - 1.2 x 10^{14}
Most Used	2.5 -15	4000 -670	3.8 x 10^{14} - 1.2 x 10^{14}

? Example 5.5.2: Hydrogen Chloride

The $H^{35}Cl$ equilibrium bond length is 0.127 nm and the $v = 0$ to $v = 1$ transition is observed in the infrared at 2,886 cm^{-1}. Compute the vibrational energy of $H^{35}Cl$ in its lowest state.

a. Compute the classical limit for the stretching of the HCl bond from its equilibrium length in this state.
b. What percent of the equilibrium bond length is this extension?

Solution

The H–Cl bond length is $0.127\,nm = 1.27 \times 10^{-10} m$ and the IR transition is observed at $2886\,cm^{-1}$. We first convert this to Hertz

$$2886\,cm^{-1}(3 \times 10^{10} cm/s) = 8.646 \times 10^{13} s^{-1} = 8.646 \times 10^{13}\,Hz$$

The equations for the energy of the v^{th} eigenstate of a harmonic oscillator is

$$E_v = (v + 1/2)\hbar\omega$$

So the ground state ($v = 0$) energy is

$$E_0 = \frac{1}{2}\hbar\omega$$

with

$$\begin{aligned}\omega &= 2\pi\nu \\ &= 5.54 \times 10^{14}\, rad/s\end{aligned}$$

We can then extra the ground state vibrational energy (aka zero-point energy) from

$$\begin{aligned}E_o &= \frac{1}{2}\hbar\omega \\ &= \frac{1}{2}\hbar(5.54 \times 10^{14} rad/s) \\ &= 2.916 \times 10^{-20}\ J\end{aligned}$$

The classical limit of the stretch is denoted as Q_0, this can be equated as potential energy in relation to the total E_0 found above as, at E_0, all of the energy would be potential energy in the form of the stretch. In comparison to the classic spring potential

$$V = \frac{1}{2}kQ_0^2$$

As described above, we can relate the two as

$$\frac{1}{2}\hbar\omega = \frac{1}{2}kQ_0^2$$

or,

$$2.916 \times 10^{-20} J = \frac{1}{2}481 Q_0^2$$

where $Q_0 = 1.10 \times 10^{-11} m = 0.0110\, nm$.

Lastly, this classical limit to length can be compared to the equilibrium bond length by a simple relation of

$$\begin{aligned} \text{Percent bond length} &= \frac{Q_0}{x_{eq}} \times 100\% \\ &= \frac{0.0110\, nm}{0.127\, nm} \times 100\% \\ &= 8.66\% \end{aligned}$$

8.7.2: Selection Rules for IR Transitions

Photons can be absorbed or emitted, and the harmonic oscillator can transition from one vibrational energy state to another. Which transitions between vibrational states are allowed? When discussing the Bohr hydrogen atom in Chapter 1, we identified multiple transitions between different states as being responsible for the line spectra emission of the hydrogen atom. No limitations were identified so that any transition between any starting state and ending state was possible and this resulted in a complex pattern in the spectra. As we will identify later on, when considering mulit-electron atoms, there are **selection rules** that limits which transitions will be observed (i.e., are allowed).

A similar situation exist for the harmonic oscillator and IR transitions and a set of selection rules must be satisfied to ensure a particular transition is allowed. Selection rules result from evaluating a **transition moment integral** that expresses the probability of a transition from the v to the v' eigenstates:

$$\mu_T = \langle \psi_{v'} \left| \hat{\mu}(x) \right| \psi_v \rangle \tag{8.7.8}$$

$$= \int_{-\infty}^{\infty} \psi_{v'}^*(x) \hat{\mu}(x) \psi_v(x) dx \tag{8.7.9}$$

When the transition moment integral is zero for two specific eigenstates (i.e., $\psi_v(x)$ and $\psi_v'(x)$), then the probability of observing that transition is zero. In this case, this transition is called a **forbidden transition** (i.e., it will not be obversed). Transitions with low probabilities are call "weakly allowed transitions" since they will have small amplitudes in spectra and transitions with high probabilities are "strongly allowed transitions" and will exhibit high amplitudes in spectra.

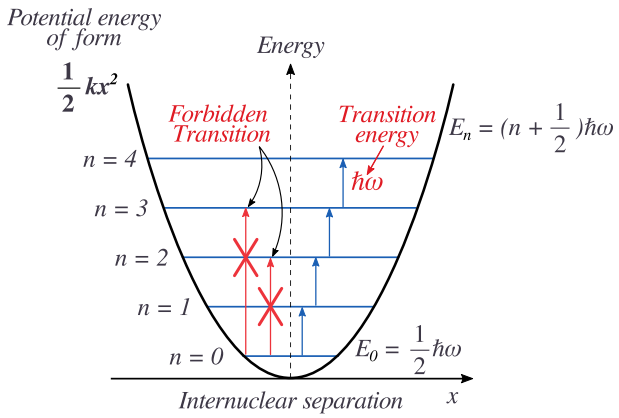


Figure 5.5.1: Possible transitions for a harmonic oscillator. Allowed transitions are labeled with blue arrows and forbidden transitions are labeled with red arrows. (CC BY-NC; Ümit Kaya via LibreTexts)

To evaluate Equation 8.7.9, we need to express the dipole moment operator, $\hat{\mu}$, in terms of the magnitude of the vibration x. The dipole moment operator is defined as

$$\hat{\mu} = \sum_{electrons} e\vec{r} + \sum_{nuclei} q\vec{R} \tag{8.7.10}$$

where the two sums are over all the electrons and nuclei and involve the particle charge ($-e$ or q) multiplying the position vector ($\vec{r}$ or $\vec{R}$, respectively). We can obtain this dipole moment operator in terms of the magnitude of the displacement coordinate, x, in a simple way by using a **Taylor series expansion** for the dipole moment around the equlibrium position ($x = 0$).

$$\hat{\mu}(x) = \mu_{x=0} + \left.\frac{d\mu(x)}{dx}\right|_{x=0} x + \left.\frac{d^2\mu(x)}{dx^2}\right|_{x=0} x^2 + \cdots \tag{8.7.11}$$

Retaining only the first two terms and substituting into Equation 8.7.9 produces

$$\mu_T = \mu_{x=0} \int_{-\infty}^{\infty} \psi_{v'}(x)\psi_v(x)dx + \left.\frac{d\mu(x)}{dx}\right|_{x=0} \int_{-\infty}^{\infty} x\psi_{v'}^*(x)\psi_v(x)dx \tag{8.7.12}$$

where $\mu_{x=0}$ is the **dipole moment** of the molecule when the nuclei are at their equilibrium positions, and

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0}$$

is the *linear* change in the dipole moment due to the displacement of the nuclei in the normal mode. The derivative is the linear change because it multiplies x and not a higher power of x in Equation 8.7.11. Both μ and

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0}$$

are moved outside of the integral because they are constants that no longer depend on x because they are evaluated at $x = 0$.

The integral in the first term in Equation 8.7.12 is 0 because any two harmonic oscillator wavefunctions are *orthogonal*. The integral in the second term of Equation 8.7.12 is zero except when $v' = v \pm 1$ as demonstrated in Exercise 5.5.1 . Also note that the second term is zero if

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0} = 0 \tag{8.7.13}$$

Hence we can identify two "rules" that need to be satisfied for an IR photon to be absorb (or emitted) by a vibrating molecule.

Rules for IR Absorption

For IR absorption to occur two conditions must be met:

1. There must be a **change** in the dipole moment of the molecule as a result of a molecular vibration (or rotation). The change (or oscillation) in the dipole moment allows interaction with the alternating electrical component of the IR radiation. Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment.
2. If the frequency of the radiation ν_{photon} matches the natural frequency of the vibration (ν_m), the IR photon can be absorbed and the amplitude of the vibration increases.

Exercise 5.5.1

Use one of the Hermite polynomial recursion relations to verify that the second integral in Equation 8.7.12 is 0 unless $v' = v \pm 1$.

If we are to observe absorption of infrared radiation due to a vibrational transition in a molecule, the transition moment cannot be zero. This condition requires that the dipole moment derivative Equation 8.7.13 **cannot** be zero and that the vibrational quantum number change by one unit. The normal coordinate motion must cause the dipole moment of the molecule to change in order for a molecule to absorb infrared radiation. If the normal coordinate oscillation does not cause the dipole moment to change then $\mu_T = 0$ and no infrared absorption is observed. So we can

$$\underbrace{\Delta v = \pm 1}_{\text{For allowed transitions}} \tag{8.7.14}$$

Consider oxygen and nitrogen molecules. Because they are symmetrical, their dipole moments are zero, $\mu = 0$. Since the vibrational motion (only bond stretching for a diatomic molecule) preserves this symmetry, the change in the dipole moment due to the vibrational motion also is zero, $\frac{d\mu(x)}{dx} = 0$. Consequently, oxygen and nitrogen do not absorb infrared radiation as a result of vibrational motion.

Exercise 5.5.2

Explain why the molar absorptivity or molar extinction coefficients (ϵ) in Beer's Law for the IR absorption of some vibrations are greater than others.

Answer

Qualitatively, if the probability of transition is large, then the molar absorptivity is large. And similar if the transition were not allowed, then there will be no intensity and no observed peak in the spectrum. Transitions can be "partially allowed" as well, and these bands appear with a lower intensity than the full allowed transitions.

When looking at the Beer's Law

$$A = \epsilon\, c\, l$$

where A is absorbance. ϵ is the molar absorptivity, c is the molar concentration and l is the optical path length

We are only looking at the change in the molar absorptivity as the IR absorptions of vibrations vary. To do this we have to look at the transition moment integral

$$\mu_T = \langle \psi_{v'} \,|\, \hat{\mu}(x) \,|\, \psi_v \rangle$$

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 $h\nu$. The case $v' = v - 1$ corresponds to a transition that emits a photon with energy $h\nu$. In the harmonic oscillator model infrared spectra are very simple; only the fundamental transitions, $\Delta = \pm 1$, are allowed. The associated transition energy is $\hbar\omega$, according to

Equation 8.7.4. The transition energy is the change in energy of the oscillator as it moves from one vibrational state to another, and it equals the photon energy.

$$\begin{aligned}\Delta E &= E_{final} - E_{initial} \\ &= h\nu_{photon} \\ &= \hbar\omega_{oscillator}\end{aligned}$$

For perfect harmonic oscillators, the only possible allowed transitions are $\Delta = \pm 1$ with all other transitions forbidden (Figure 5.5.1). This conclusion predicts that the vibrational absorption spectrum of a diatomic molecule consists of a single line since the energy levels are equally spaced in the harmonic oscillator model (Figure 5.5.1). If the vibration were anharmonic, then the levels would not be equally spaced and then transitions from $v = 0$ to $v = 1$ and from $v = 1$ to $v = 2$, etc. would occur at different frequencies.

> *Only the fundamental transitions, $\Delta = \pm 1$, are observed in infrared spectra within harmonic oscillator model.*

The actual IR spectrum is more complex, especially at high resolution. There is a fine structure due to the rotational states of the molecule. These states will be discussed in the next chapter. The spectrum is enriched further by the appearance of lines due to transitions corresponding to $\Delta = \pm n$ where $n > 1$. These transitions are called **overtone** transitions and their appearance in spectra despite being forbidden in the harmonic oscillator model is due to the anharmonicity of molecular vibrations. Anharmonicity means the potential energy function is not strictly the harmonic potential. The first overtone, $\Delta v = 2$, 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: Hydrogen Chloride

Compute the approximate transition frequencies in wavenumber units for the first and second overtone transitions in HCl given that the fundamental is at 2,886 cm^{-1}.

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8.8: The Harmonic Oscillator Selection Rule

Selection rules are a very important concept in spectroscopy and physical chemistry, as they directly complement the concept that systems on the atomic level are quantized. Quantization tells us how electrons, neutrons, and protons are set up, and selection rules tell us how, energetically speaking, they may move about. For example, the principal quantum number, n, determines the energy state of particles in the Particle in a Box model. With respect to real systems, the quantum number n describes electronic transitions, such as the excitation of an electron. There are other transitions, such as the rotational transition, which applies to the rigid rotator model and occurs where there are spherical harmonics. Vibrational transitions occur where there is a system that can be visualized as two masses connected by a spring, such as a diatomic molecule.

Selection rules can be very useful in spectroscopy for obtaining information about an unknown substance; any given substance has properties and behaviors that operate within the selection rules and determine the wavelengths of electromagnetic radiation (light) that cause transitions. By tracking these properties, chemists can use techniques like IR spectroscopy to determine the chemical structure of a molecule. For example, a selection rule might govern how a quantum number changes during a transition. That quantum number appears in equations that determine the energy transition based on the mass and other structural properties of a molecule. Thus, if one knows the selection rules and the energy transition, he or she can determine other properties about the molecule, such as its mass or its bond strength.

Example: Evaluating vibrational transitions using a transition moment integral.

Vibrational systems are described by the harmonic oscillator wavefunctions, which look like

$$\Psi_v(x) = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

A transition dipole moment can be written to describe a transition along the z-axis.

$$\mu_z = \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}\mu_z(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

μ is the dipole moment, so we pull it out of the integral.

$$\mu_z = \mu_z \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

Using the idea that the transition moment μ_z changes on x, we express it as a derivative.

$$\mu_z = \frac{d\mu}{dx} \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

To evaluate the integral, we take advantage of a special Hermite relationship: $\sqrt{\alpha}xH_v(\sqrt{\alpha}x) = vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)$

$$\mu_z = \frac{N_v N_{v+1}}{\sqrt{\alpha}}\left(\frac{d\mu}{dx}\right) \int_{-\infty}^{\infty} H_{v+1}(\sqrt{\alpha}x)e^{(}-\alpha x^2/2)[vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)]dx$$

By inspection, it is clear that the integral only allows transitions of $\Delta v = \pm 1$, because for any other value, the integral will be zero.

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8.9: Vibrational Overtones

Although the harmonic oscillator proves useful for modeling lower energy levels, like $v = 0, 1$, it fails at higher numbers of v. It not only fails to properly model atomic bonds and dissociations, but also is unable to match spectra showing additional lines that are not accounted for in the harmonic oscillator model.

8.9.1: Anharmonicity

Until this point, we have been using the harmonic oscillator to describe the internuclear potential energy of the vibrational motion. Fundamental vibrational frequencies of a molecule corresponds to a transition of $\Delta v = \pm 1$. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator approximation (Figure **8.9.1**). For example, the parabolic potential of the Harmonic Oscillator approximation means that the vibrations can hold any amount of energy and bonds can stretch to any length, while in real molecules if the atoms are too far apart the bond will dissociate.

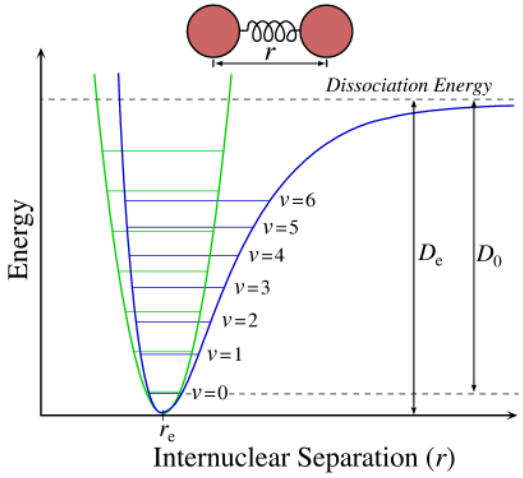


Figure **8.9.1** : Pictured above is the Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left 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 **8.9.1** , the harmonic oscillator potential well (in green) only roughly fits over the more accurate anharmonic oscillator well (in blue). The blue curve accounts for dissociation at large R values, which the green curve does not even remotely cover. However, this is just one important difference between the harmonic and anharmonic (real) oscillators.

The real potential energy can be expanded in the Taylor series.

$$V(R) = V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}(R-R_e)^4 + \ldots \tag{8.9.1}$$

This expansion was discussed in detail previously. The first term in the expansion is ignored since the derivative of the potential at R_e is zero (i.e., at the bottom of the well). The Harmonic Oscillator approximation only uses the next term, the quadratic term, in the series

$$V_{HO}(R) \approx V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2$$

or in terms of a spring constant, ignoring the absolute energy term($V(R_e)$) and defining r to equal the displacement from equilibrium ($r = R - R_e$), then we get the "standard" harmonic oscillator potential:

$$V_{HO}(R) = \frac{1}{2}kr^2$$

Alternatively, the expansion in Equation 8.9.1 can be shortened to the cubic term

$$V(x) = \frac{1}{2}kr^2 + \frac{1}{6}\gamma r^3 \tag{8.9.2}$$

where

- $V(x_0) = 0$, and $r = R - R_0$.
- k is the harmonic force constant, and
- γ is the first (i.e., cubic) *anharmonic* term

It is important to note that this approximation is only good for R near R_0.

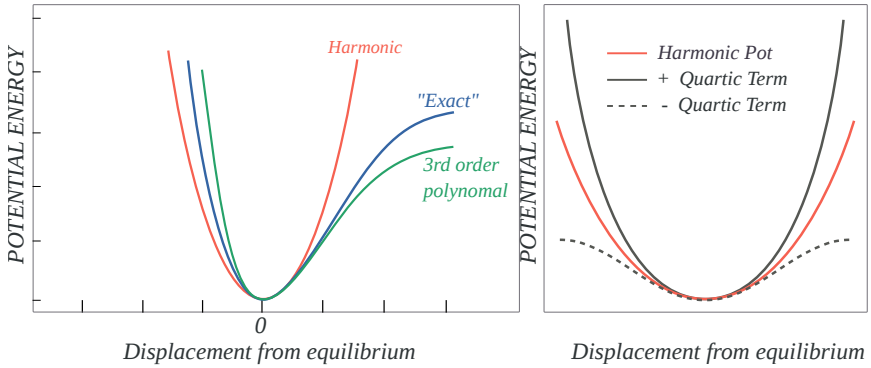


Figure 8.9.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

The harmonic oscillator approximation gives by the following energies:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right)$$

When the cubic term in the expansion (Equation 8.9.2) is included, and the Schrödinger equation is solved using perturbation theory this gives:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right) - \tilde{\chi_e}\tilde{\nu}\left(v + \frac{1}{2}\right)^2$$

where $\tilde{\chi_e}$ is the **anharmonicity constant**. It is much smaller than 1, which makes sense because the terms in the Taylor series approach zero. This is why, although E_v technically includes all of the Taylor series, we only concern ourselves with the first and second terms. The rest are so small and barely add to the total and thus can be ignored. To get a more accurate approximation, more terms can be included, but otherwise, can be ignored. Almost all diatomics have experimentally determined $\frac{d^2V}{dx^2}$ for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 have had terms up to $n < 10$ determined of Equation 8.9.1.

8.9.2: Overtones

The Harmonic Oscillator approximation predicts that there will be only one line in the spectrum of a diatomic molecule, while experimental data shows there is in fact one dominant line--**the fundamental**--and other weaker lines. How can we account for these extra lines?

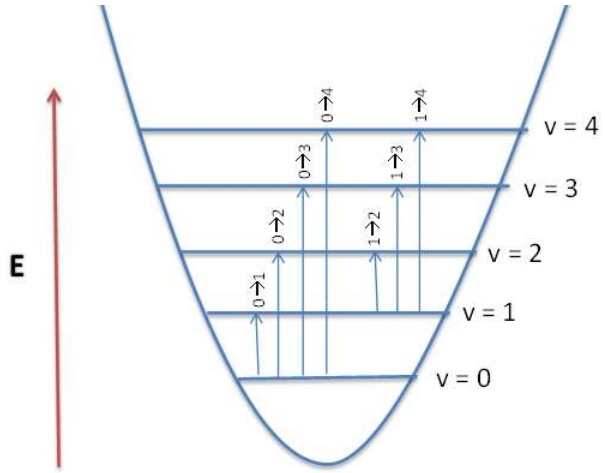


Figure 8.9.3 : A diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potential energy for the harmonic (quadratic) oscillator. The transition $0 \rightarrow 1$ is the fundamental, transitions $0 \rightarrow n$ (n>1) are called overtones, and transitions $1 \rightarrow n$ (n > 1) are called hot transitions (hot bands).

Any resonant frequency above the fundamental frequency is referred to as an *overtone*. In the IR spectrum, overtone bands are multiples of the fundamental absorption frequency. As you can recall, the energy levels in the Harmonic Oscillator approximation are evenly spaced apart. Energy is proportional to the frequency absorbed, which in turn is proportional to the wavenumber, the first overtone that appears in the spectrum will be twice the wavenumber of the fundamental. That is, first overtone $v = 0 \rightarrow 2$ is (approximately) twice the energy of the fundamental, $v = 0 \rightarrow 1$.

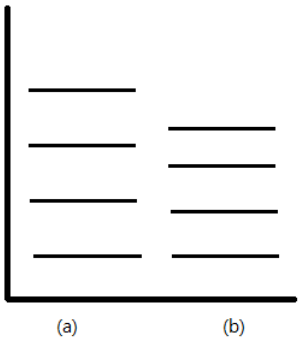


Figure 8.9.4 : An exaggerated view of the energy levels. (a) would be the harmonic oscillator, with the evenly spaced out energy levels. (b) would be the anharmonic, with the energy levels compressing until they converge.

The levels are not equally spaced, like in the harmonic oscillator, but decrease as v increases, until it ultimately converges, as implied by Figure 8.9.4. Also as a result of anharmonicity, the $\Delta v = \pm 1$ selection rule is no longer valid and v can be any number. This leads to the observation of higher order transitions, or **overtones**, which result from the transition of the ground state to higher energy levels.

Anharmonic Oscillator Selection Rules

For the anharmonic oscillator, the selection rule is $\Delta V = \text{any number}$. That is, there are no selection rules (for state to state transitions)

Overtones occur when a vibrational mode is excited from $v = 0$ to $v = 2$ (the first overtone) or $v = 0$ to $v = 3$ (the second overtone). The fundamental transitions, $v = \pm 1$, are the most commonly occurring, and the probability of overtones rapidly decreases as $\Delta v > \pm 1$ gets bigger. Based on the harmonic oscillator approximation, the energy of the overtone transition will be approximately v times the fundamental associated with that particular transition. The anharmonic oscillator calculations show that the overtones are usually less than a multiple of the fundamental frequency. Overtones are generally not detected in larger molecules.

This is demonstrated with the vibrations of the diatomic **HCl** in the gas phase:

Table **8.9.1** : HCl vibrational spectrum.

Transition	$\tilde{\nu}_{obs}$ [cm^{-1}]	$\tilde{\nu}_{obs}$ Harmonic [cm^{-1}]	$\tilde{\nu}_{obs}$ Anharmonic [cm^{-1}]
$0 \rightarrow 1$ (fundamental)	2885.9	2885.9	2,885.3
$0 \rightarrow 2$ (first overtone)	5668.0	5771.8	5,665.0
$0 \rightarrow 3$ (second overtone)	8347.0	8657.7	8,339.0
$0 \rightarrow 4$ (third overtone)	10 923.1	11 543.6	10,907.4
$0 \rightarrow 5$ (fourth overtone)	13 396.5	14 429.5	13,370

We can see from Table **8.9.1** that the anharmonic frequencies correspond much better with the observed frequencies, especially as the vibrational levels increase. Because the energy levels and overtones are closer together in the anharmonic model, they are also more easily reached. This means that there is a higher chance of that level possibly being occupied, meaning it can show up as additional, albeit weaker intensity lines (the weaker intensity indicates a smaller probability of the transition occuring).

? Exercise 13.5.1

HCl has a fundamental band at 2885.9 cm^{-1} and an overtone at 5668.1 cm^{-1} Calculate $\tilde{\nu}$ and $\tilde{\chi_e}$.

? Exercise 13.5.2

Write out the Taylor series, and comment on the trend in the increasing terms. Using a test number x, please add terms 3, 4, and 5, then compare this to term 2. How do they compare? We have seen that the anharmonic terms increase the accuracy of our oscillator approximation. Why don't we care so much about terms past the second?

8.9.3: References

1. Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry; Part B: Application in Coordination, Organometallic, and Bioinorganic Chemistry, 5th Edition (Nakamoto, Kazuo)
2. Lyle McAfee Journal of Chemical Education 2000 77 (9), 1122
3. Stuart, Barbara. *Infrared Spectroscopy: Fundamentals and Applications*. Wiley, 2004. Print.

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8.10: Vibrational Spectroscopy Techniques

Infrared and Raman spectroscopy are two experimental methods that are commonly used by chemists to measure vibrational frequencies (ω_e). Infrared spectroscopy generally involves direct absorption whereas Raman spectroscopy involves scattering of light.

Infrared Spectra

Infrared spectroscopy is a commonly used technique in the identification of molecular compounds. It is also a very convenient technique to use in determining molecular force constants, since the spectrum records vibrational frequencies.

Based on the results of the harmonic oscillator problem, the selection rules for an infrared spectrum are determined to be

$$\Delta v = \pm 1$$

That means that as a molecule absorbs or emits a single infrared photon (meaning the electronic state of the molecule does not change) the vibrational quantum number can go up or down (depending on absorption or emission) by one quantum. For a typical experiment, the theory predicts a single band in the spectrum of a molecule, and that band will be centered at a frequency equal to ω_e for the molecule.

A schematic diagram of a typical infrared absorption spectroscopy experiment is shown below. The light is produced at the source (typically an incandescent light bulb or a glowbar), passes through the sample where some of the light can be absorbed, and then the monochrometer (which is typically either a grating or an interferometer) which is used to distinguish between the various frequencies of light, and finally the light is detected by a detector. Plotting detected intensity as a function of frequency produces the spectrum.

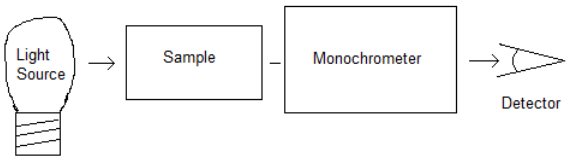


Figure 8.10.1

Determining a Force Constant

Consider the experimentally determined we value for carbon monoxide (CO.) The spectrum shows a strong absorption at $2143\ cm^{-1}$ due to CO. Using this value for ω_e (it is actually a little off due to anharmonicity), the force constant can be determined for the molecule.

$$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Using a value of 1.14×10^{-26} kg for the reduced mass of the molecule, the force constant is found to be 1856 N/m. The literature value for this force constant is $1860\ cm^{-1}$. Given that this calculation did not treat anharmonicity, the agreement is pretty good!

Progressions in Electronic Spectra

Electronic transition in diatomic molecules which can be observed in the visible and ultraviolet regions of the spectrum can have a great deal of vibrational structure as the molecule is free to vibrate in both the upper and lower states. Figure 8.10.2 shows vibrational progressions in the emission spectrum of AlBr near 2800 Å (Fleming & Mathews, 1996).

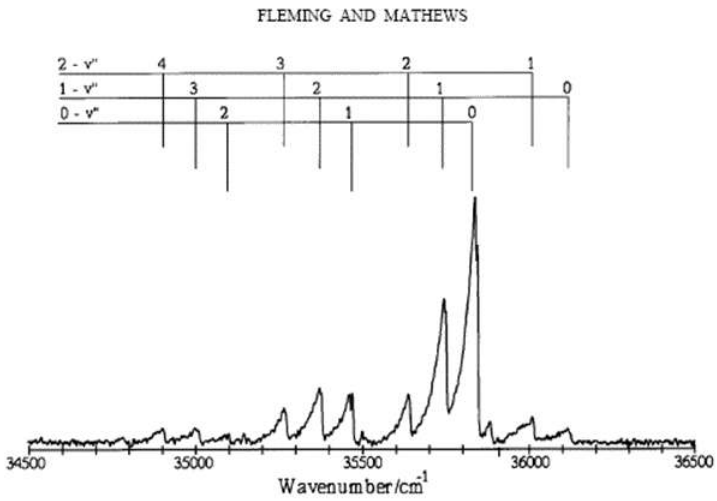


Figure 8.10.2: A-X transition of AlBr near 2800 Å.

These progressions can be analyzed to provide dissociation energies for the electronic states involved in the transition.

If the vibrational energy function is truncated at the $\omega_e x_e$ level (as predicted by the Morse potential) the vibrational term value will reach a maximum value at some value of v. Any further vibrational excitation is predicted to lower the molecular energy. This is actually the **dissociation limit**. Therefore, the maximum value of v for a bound state (v_{max}) is the largest value of v for which the vibrational energy spacing is positive. The dissociation energy of the molecule is then given by the sum of vibrational energy spacings from $v = 0$ to $v = v_{max}$.

Determining a Dissociation Energy

To find the value of the dissociation energy, it is convenient to define the difference between successive vibrational terms as

$$\Delta G_{v+1/2} \equiv G_{v+1} - G_v$$

Using the expression for G_v as predicted by the Morse potential,

$$\begin{aligned} \Delta G_{v+1/2} =& \omega_e(v+3/2) - \omega_e x_e(v+3/2)^2 - \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 \\ &= \omega_e(v+3/2-v-1/2) - \omega_e x_e\left(v^2+3v+9/4-v^2-v-1/4\right) \\ &= \omega_e - \omega_e x_e(2v+2) \\ &= \omega_e - 2\omega_e x_e(v+1) \end{aligned} \tag{8.10.1}$$

This suggests that a set of values of $\Delta G_{v+1/2}$ vs. $(v+1)$ should yield a straight line with a slope equal to -2ω_e x_e and an intercept equal to ω_e. And v_{max} is determined by setting $\Delta G_{v+\frac{1}{2}}$ to zero and solving for v (Figure 8.10.3).

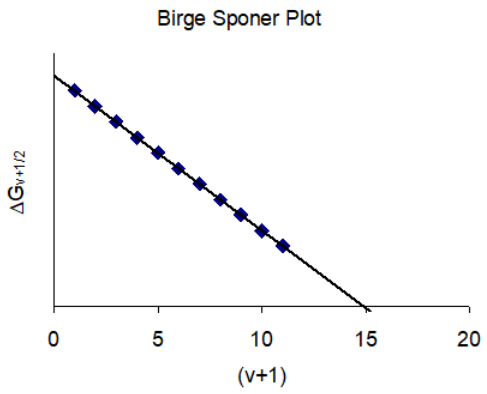


Figure 8.10.3: Birge-Sponer method to determine the dissociation energy of a molecule from the vibrational spacings.

The **Birge-Sponer method** (Gaydon, 1946) can be used to determine the sum of vibrational spacings, and thus the dissociation of a molecule. The method involves plotting $\Delta G_{v+\frac{1}{2}}$ vs. $(v+1)$. The dissociation energy is taken as the area under the curve.

Vibrations of Polyatomic Molecules

Nonlinear molecules have $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the molecule. Thus, a triatomic molecule such as water has three vibrational degrees of freedom. These account for the three vibrational modes of water (symmetric stretch, bend and antisymmetric stretch.)

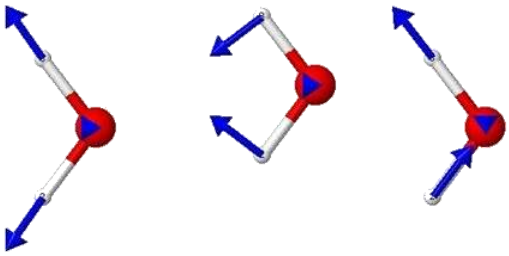


Figure 8.10.4

Each mode will have a characteristic frequency. If each mode is treated as a harmonic oscillator, the total vibrational energy is given by

$$G = \sum_{i=1}^{3N-6} \omega_i (v_i + 1/2)$$

where ω_i is the frequency of the i^{th} vibrational mode, and v_i is the quantum number indicating the number of quanta of the i^{th} mode excited. If anharmonicity is to be included, the expression becomes

$$G = \sum_{i=1}^{3N-6} \omega_i (v_i + 1/2) - \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} x_{ij} \, (v_i + 1/2) \, (v_j + 1/2)$$

where x_{ij} is the anharmonicity term that couples the vibrational modes.

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8.11: 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.

8.11.1: Selection Rules

Rotational and Vibration transitions (also known as rigid rotor and harmonic oscillator) of molecules help us identify how molecules interact with each other, their bond length as mentioned in previous section. In order to know each transitions, we have to consider other terms like wavenumber, force constant, quantum number, etc. There are rotational energy levels associated with all vibrational levels. From this, vibrational transitions can couple with rotational transitions to give **rovibrational spectra**. Rovibrational spectra can be analyzed to determine average bond length.

We treat the molecule's **vibrations** as those of a harmonic oscillator (ignoring anharmonicity). The energy of a vibration is quantized in discrete levels and given by

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$

Where v is the vibrational quantum number and can have integer values 0, 1, 2..., and ν is the frequency of the vibration given by:

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

where k is the force constant and μ is the reduced mass of a diatomic molecule with atom masses m_1 and m_2, given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{8.11.1}$$

We treat the molecule's **rotations** as those of a rigid rotor (ignoring centrifugal distortion from non-rigid rotor aspects). The energy of a rotation is also quantized in discrete levels given by

$$E_r = \frac{h^2}{8\pi^2 I}J(J+1)$$

In which I is the moment of inertia, given by

$$I = \mu r^2$$

where μ is the reduced mass (Equation 8.11.1) and r is the equilibrium bond length.

Experimentally, frequencies or wavenumbers are measured rather than energies, and dividing by h or hc gives more commonly seen term symbols, $F(J)$ using the rotational quantum number J and the rotational constant B in either frequency

$$F(J) = \frac{E_r}{h} = \frac{h}{8\pi^2 I}J(J+1) = BJ(J+1)$$

or wavenumbers

$$\tilde{F}(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 cI}J(J+1) = \tilde{B}J(J+1)$$

> It is important to note in which units one is working since the rotational constant is always represented as B, whether in frequency or wavenumbers.

- **Vibrational Transition Selection Rules**: At room temperature, typically only the lowest energy vibrational state v= 0 is populated, so typically $v_0 = 0$ and $\Delta v = +1$. 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).

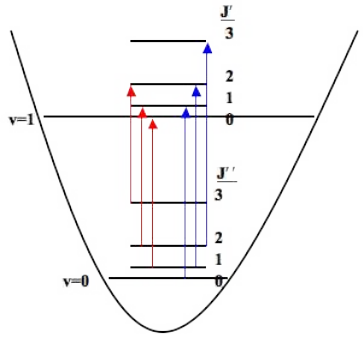


Figure 13.2.1 : Rotation-Vibration Transitions. Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels.

8.11.1.1: 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:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{8.11.2}$$
$$= h\nu_0 + hB\left[(J+1)(J+2) - J(J+1)\right] \tag{8.11.3}$$
$$= h\nu_0 + 2hB(J+1) \tag{8.11.4}$$

8.11.1.2: 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:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{8.11.5}$$
$$= h\nu_0 + hB\left[J(J-1) - J(J+1)\right] \tag{8.11.6}$$
$$= h\nu_0 - 2hBJ \tag{8.11.7}$$

8.11.1.3: 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:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \tag{8.11.8}$$
$$= h\nu_0 \tag{8.11.9}$$

The Q-branch can be observed in polyatomic molecules and diatomic molecules with electronic angular momentum in the ground electronic state, e.g. nitric oxide, NO. Most diatomics, such as O_2, have a small moment of inertia and thus very small angular momentum and yield no Q-branch.

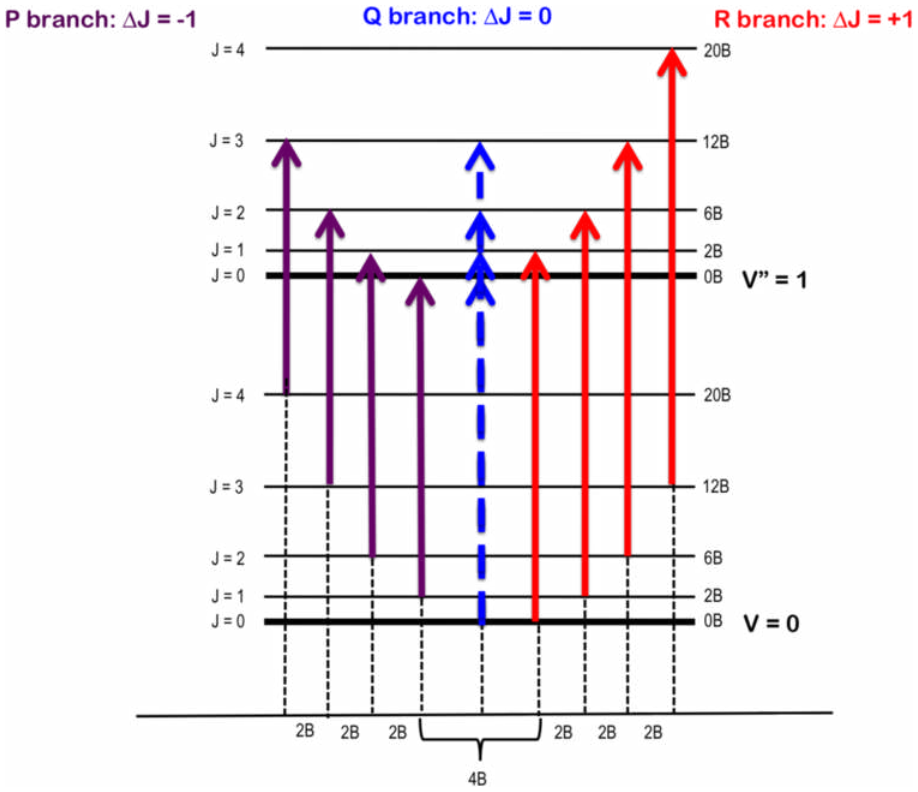


Figure 13.2.3 : Cartoon depiction of rotational energy levels, J, imposed on vibrational energy levels, v. The transitions between levels that would result in the P- and R-branches are depicted in purple and red, respectively, in addition to the theoretical Q-branch line in blue.

As seen in Figure 13.2.2 , the lines of the P-branch (represented by purple arrows) and R-branch (represented by red arrows) are separated by specific multiples of B (i.e, $2B$), thus the bond length can be deduced without the need for pure rotational spectroscopy.

The total nuclear energy of the combined rotation-vibration terms, $S(v, J)$, can be written as the sum of the vibrational energy and the rotational energy

$$S(v, J) = G(v) + F(J)$$

where $G(v)$ represents the energy of the harmonic oscillator, ignoring anharmonic components and $S(J)$ represents the energy of a rigid rotor, ignoring centrifugal distortion.

From this, we can derive

$$S(v, J) = \nu_0 \left(v + \frac{1}{2}\right) + BJ(J+1)$$

The spectrum we expect, based on the conditions described above, consists of lines equidistant in energy from one another, separated by a value of $2B$. The *relative* intensity of the lines is a function of the rotational populations of the ground states, i.e. the intensity is proportional to the number of molecules that have made the transition. The *overall* intensity of the lines depends on the vibrational transition dipole moment.

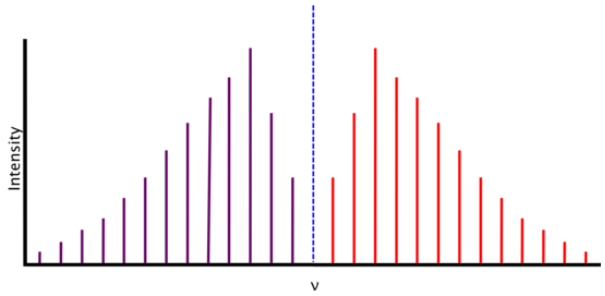


Figure 13.2.3 : A cartoon depiction of an ideal rovibrational spectrum.

In Figure 13.2.2 , between $P(1)$ and $R(0)$ lies the zero gap, where the the first lines of both the P- and R-branch are separated by $4B$, assuming that the rotational constant B is equal for both energy levels. The zero gap is also where we would expect the Q-branch, depicted as the dotted line, if it is allowed.

Advanced Concept: Occupations (Peak Intensities)

The relative intensity of the P- and R-branch lines depends on the thermal distribution of electrons; more specifically, they depend on the population of the lower J state. If we represent the population of the Jth upper level as N_J and the population of the lower state as N_0, we can find the population of the upper state relative to the lower state using the Boltzmann distribution:

$$\frac{N_J}{N_0} = (2J+1)e^{\left(-\frac{E_r}{kT}\right)}$$

(2J+1) gives the degeneracy of the Jth upper level arising from the allowed values of M_J (+J to –J). As J increases, the degeneracy factor increases and the exponential factor decreases until at high J, the exponential factor wins out and N_J/N_0 approaches zero at a certain level, J_{max}. Thus, when

$$\frac{d}{dJ}\left(\frac{N_J}{N_0}\right) = 0$$

by differentiation, we obtain

$$J_{max} = \left(\frac{kT}{2hB}\right)^{\frac{1}{2}} - \frac{1}{2}$$

This is the reason that rovibrational spectral lines increase in energy to a maximum as J increases, then decrease to zero as J continues to increase, as seen in Figure 13.2.2 .

From this relationship, we can also deduce that in heavier molecules, B will decrease because the moment of inertia will increase, and the decrease in the exponential factor is less pronounced. This results in the population distribution shifting to higher values of J. Similarly, as temperature increases, the population distribution will shift towards higher values of J.

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8.12: 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*.

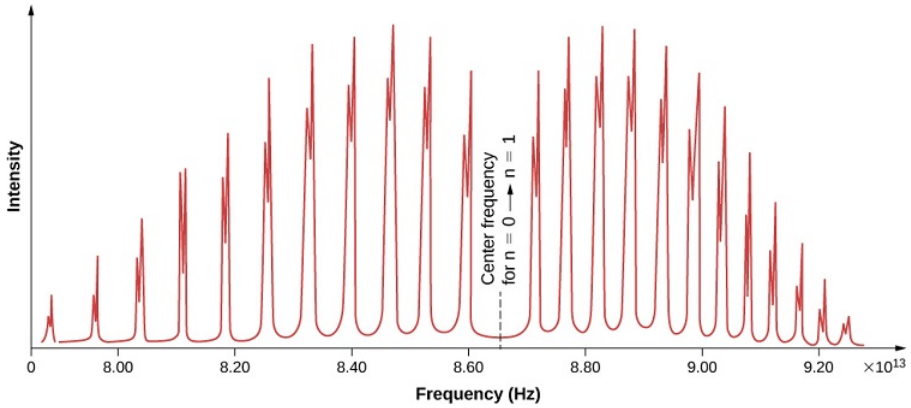


Figure 13.3.1 : Absorption spectrum of hydrogen chloride (**HCl**) from the $n = 0$ to $n = 1$ vibrational levels. The discrete peaks indicate a quantization of the angular momentum of the molecule. The bands to the left indicate a decrease in angular momentum, whereas those to the right indicate an 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.

8.12.1: Vibration-Rotation Interaction

Consider the rotational constant for a rigid rotator $\tilde{B} = h/8\pi^2 c\mu R_e^2$ where $\tilde{B}$ is the rotational constant, and R_e^2 is the bond length. It is clear from the equation that $\tilde{B}$ depends on R_e^2 in a inverse manner, so $\tilde{B}$ will decrease as R_e^2 increase, and vice versa.

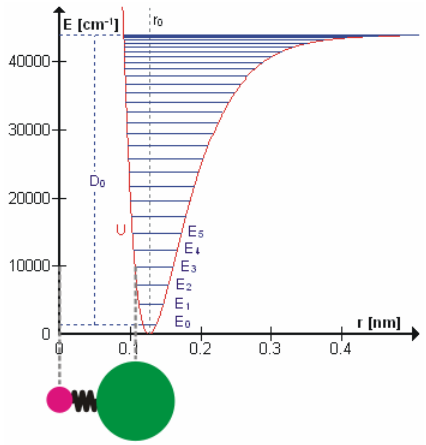


Figure 13.3.2 : Anharmonic Oscillator and Bond Length. Figure used with permission from Wikipedia.

Vibrational state and the bond length also possess a relationship, and that is bond length, R_e^2, will increase as the vibrational state, v increases. High vibrational states have large vibrational amplitudes (the amplitude can be visualized as the distance from one side to the other on the harmonic-oscillator parabola, and higher states has greater distance). On a potential graph, imagine a diatomic molecule with one of the atom fixed at the origin, the bond is along the x-axis, and the molecule vibrate toward and away from the origin along x-axis. The range at how much the bond can stretch or squeeze depend on the vibrational amplitude. So, at high vibrational state (thus high amplitude), the bond can squeeze in and stretch out more (just a little more) on the regular harmonic-

oscillator potential, but it can stretch out greatly on an anharmonic oscillator. That's why bond length increase with vibrational state.

> **Note**
>
> The two relationship established above
>
> - $\tilde{B} \propto R_e^2$ (inversely proportional)
>
> and
>
> - $R_e^2 \propto v$ (directly proportional)
>
> Therefore,
>
> - $\tilde{B} \propto v$ (inversely proportional)
>
> The rotational constant dependent on the vibrational state is denoted as $\tilde{B}_v$, and the dependence of $\tilde{B}$ on v is the vibrational-rotational interaction.

Let's calculate the frequencies of R and P Branches with vibrational dependent rotational constants. The energies of the rigid rotator-harmonic oscillator is

$$\tilde{E}_{v,J} = G(v) + F(J) = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}J(J+1)$$

or in term of $\tilde{B}_v$

$$\tilde{E}_{v,J} = \tilde{\nu}\left(v + \frac{1}{2}\right) + \tilde{B}_v J(J+1)$$

According to the vibration-rotation interaction, $\tilde{B}_1 < \tilde{B}_0$ because $R_e^2(v=1) > R_e^2(v=0)$. Hence, the frequencies of rovibrational transitions from $v = 0 \rightarrow 1$ can be calculated as the following:

For R branch, allowed $J = 0, 1, 2, ...$

$$\tilde{\nu}_R(\Delta J = +1) = \tilde{E}_{1,J+1} - \tilde{E}_{0,J}$$

$$= \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1)$$

$$= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

For P branch, allowed $J = 1, 2, 3, ...$

$$\tilde{\nu}_P(\Delta J = -1) = \tilde{E}_{1,J-1} - \tilde{E}_{0,J}$$

$$= \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

8.12.1.1: Decrease in Spacing of Lines in the R Branch with Increasing J

A closer look at

$$\tilde{\nu}_R = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value for increasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$+(smaller and smaller value) as J increase. Because the rotational frequencies keep getting smaller, the spacing between lines in R branch decreases as J increases.

8.12.1.2: Increasing in Spacing of Lines in the P Branch with Decreasing J

Using the same analysis as above,

$$\tilde{\nu}_P = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value even for decreasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}$–(smaller and smaller value) as J decreases. Because the rotational frequencies keep getting larger, the spacing between lines in P branch increase as J decreases.

8.12.2: References

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8.13: 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.

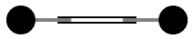


Figure 8.13.1: This animation can serve as an illustration of one of the aspects of the conservation of angular momentum. The animation is a schematic representation of two weights that are connected to each other. The two weights are circling around their common center of mass, the center of mass is 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,

$$F_c = \mu r_c \omega^2 = L^2/\mu {r_c}^3 \tag{8.13.1}$$

Equating the restoring force to the centrifugal force, one gets

$$k(r_c - r_e) = \frac{L^2}{\mu {r_c}^3} \tag{8.13.2}$$

$$r_c - r_e = \frac{L^2}{k\mu {r_c}^3} \cong \frac{L^2}{k\mu {r_e}^3} \tag{8.13.3}$$

Total energy, on adding kinetic energy, as expressed in Equation 8.13.3 to the potential energy,

$$\frac{1}{2}k(r_c - r_e)^2 \tag{8.13.4}$$

is given by

$$E_r = \frac{L^2}{2\mu {r_c}^2} + \frac{1}{2}k\,(r_c - r_e)^2 \tag{8.13.5}$$

Using $(r_c - r_e) = \Delta r$ and eliminating r_c from equation 8.13.5, one gets

$$E_r = \frac{L^2}{2\mu\ {r_e}^2(1 + \Delta r/r_e)^2} + \frac{1}{2}k\Delta r^2 \tag{8.13.6}$$

$$= \frac{L^2(1 - 2\Delta r/r_e)}{2\mu\ {r_e}^2} + \frac{1}{2}k\Delta r^2 \tag{8.13.7}$$

using

$$(1 + \Delta r/r_e)^{-2} \approx (1 - 2\Delta r/r_e) \tag{8.13.8}$$

$$E_r = \frac{L^2}{2\mu {r_e}^2} - \frac{L^4}{k\mu^2 {r_e}^6} + \frac{1}{2}k\frac{L^4}{k^{2\mu 2}{r_e}^6} \tag{8.13.9}$$

$$= \frac{L^2}{2\mu {r_e}^2} - \frac{1}{2}\frac{L^4}{k\mu^2 {r_e}^6} \tag{8.13.10}$$

$$= \frac{\hbar^2\, J(J+1)}{2\mu {r_e}^2} - \frac{\hbar^4\, J^2(J+1)^2}{2k\mu^2 {r_e}^6} \tag{8.13.11}$$

Use of Equation 8.13.3 and of the relation regarding angular momentum of a rotor

$$L = \hbar\sqrt{J(J+1)} \tag{8.13.12}$$

has been made to obtain relation in Equation 8.13.11, which may be expressed in cm^{-1} as

$$F(J) = \underbrace{\tilde{B}J(J+1)}_{\text{rigid rotator term}} - \underbrace{\tilde{D}J^2(J+1)^2 cm^{-1}}_{\text{centrifugal stretching}} \tag{8.13.13}$$

where

$$\tilde{B} = \frac{\hbar}{4\pi\,\mu\, {r_e}^2 c}\ (\text{in cm}^{-1}) \tag{8.13.14}$$

and

$$\tilde{D} = \frac{\hbar^3}{4\pi k\,\mu^2\, {r_e}^6\, c}\ (\text{in cm}^{-1}) \tag{8.13.15}$$

First term in the Equation 8.13.13 is same as for the rigid rotator; second term is the consequence of the centrifugal stretching. Recall Equation 8.13.3 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 8.13.13 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 8.13.2.

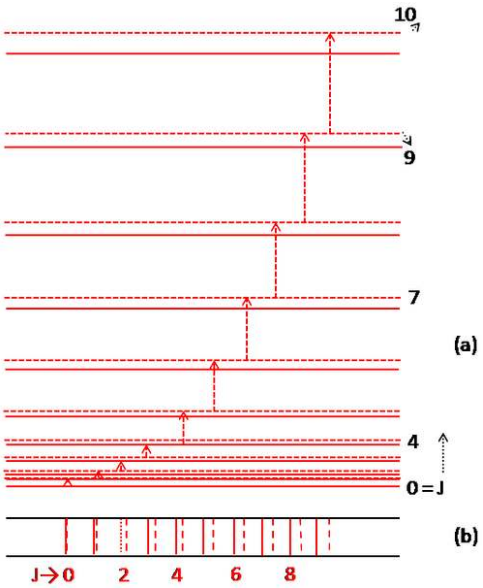


Figure 8.13.2: Energy levels and the transitions of rigid rotator (broken red lines) & of non-rigid rotator (solid red lines). (b) resulting spectra from both the models

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 **8.13.2**. 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 **8.13.2** 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.

8.13.1: Contributors and Attributions

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10.10: 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.

10.10.1: Degrees of Freedom

In general, a normal mode is an independent motion of atoms in a molecule that occurs without causing movement to any of the other modes. Normal modes, as implied by their name, are orthogonal to each other. In order to discuss the quantum-mechanical equations that govern molecular vibrations it is convenient to convert Cartesian coordinates into so called normal coordinates. Vibrations in polyatomic molecules are represented by these normal coordinates.

A molecule can have three types of degrees of freedom and a total of 3N degrees of freedom, where N equals the number of atoms in the molecule. These degrees of freedom can be broken down into three categories.

- **Translational**: These are the simplest of the degrees of freedom. These entail the movement of the entire molecule's center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.
- **Rotational**: These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational**: These are any other types of movement not assigned to rotational or translational movement and thus there are 3N – 6 degrees of vibrational freedom for a nonlinear molecule and 3N – 5 for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Table 13.9.1 : Overview of degrees of freedom

	Total Degrees of Freedom	Translational degrees of freedom	Rotational degrees of freedom	Vibrational degrees of freedom
Nonlinear Molecules	3N	3	3	3N **-6**
Linear Molecules	3N	3	2	3N - 5

Each of these degrees of freedom is able to store energy. However, In the case of rotational and vibrational degrees of freedom, energy can only be stored in discrete amounts. This is due to the quantized break down of energy levels in a molecule described by quantum mechanics. In the case of rotations the energy stored is dependent on the rotational inertia of the gas along with the corresponding quantum number describing the energy level.

Example 13.9.1 : Ethane vs. Carbon Dioxide

Ethane, C_2H_6 has eight atoms ($N = 8$) and is a nonlinear molecule so of the $3N = 24$ degrees of freedom, three are translational and three are rotational. The remaining 18 degrees of freedom are internal (vibrational). This is consistent with:

$$3N - 6 = 3(8) - 6 = 18$$

Carbon Dioxide, CO_2 has three atoms ($N = 3$ and is a linear molecule so of the $3N = 9$ degrees of freedom, three are translational and two are rotational. The remaining 4 degrees of freedom are vibrational. This is consistent with:

$$3N - 5 = 3(3) - 5 = 4$$

The normal modes of vibration are: asymmetric, symmetric, wagging, twisting, scissoring, and rocking for polyatomic molecules.

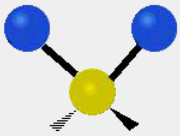
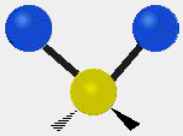
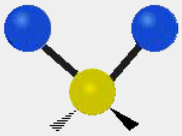
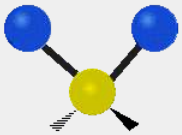
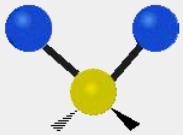
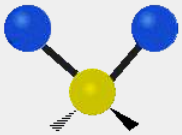
Symmetricical Stretching	Asymmetrical Stretching	Wagging
		
Twisting	**Scissoring**	**Rocking**
		

Figure 13.9.1 : *Six types of Vibrational Modes. Taken from publisher en.Wikipedia.org/wiki/Infrared_spectroscopy with permission from copyright holder.*

10.10.2: 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:

$$\Delta V = V(q_1, q_2, q_3, ..., q_n) - V(0, 0, 0, ..., 0) \tag{10.10.1}$$

$$= \frac{1}{2}\sum_{i=1}^{N_{vib}}\sum_{j=1}^{N_{vib}}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right) q_i q_j \tag{10.10.2}$$

$$= \frac{1}{2}\sum_{i=1}^{N_{vib}}\sum_{j=1}^{N_{vib}} f_{ij} q_i q_j \tag{10.10.3}$$

where q represents the equilibrium displacement and N_{vib} the number of vibrational degrees of freedom.

For simplicity, the *anharmonic* terms are neglected in this equation (i.e., higher order terms are ignore). A theorem of classical mechanics states that the cross terms can be eliminated from the above equation (the details of the theorem are very complex and will not be discussed in detail). By using matrix algebra a new set of coordinates $\{Q_j\}$ can be found such that

$$\Delta V = \frac{1}{2}\sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{10.10.4}$$

Note that there are no cross terms in this new expression. These new coordinates are called **normal coordinates** or **normal modes**. With these new normal coordinates in hand, the Hamiltonian operator for vibrations can be written as follows:

$$\hat{H}_{vib} = -\sum_{j=1}^{N_{vib}} \frac{\hbar^2}{2\mu_i}\frac{d^2}{dQ_j^2} + \frac{1}{2}\sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{10.10.5}$$

The total wavefunction is a product of the individual wavefunctions and the energy is the sum of independent energies. This leads to:

$$\hat{H}_{vib} = \sum_{j=1}^{N_{vib}} \hat{H}_{vib,j} = \sum_{j=1}^{N_{vib}} \left(\frac{-\hbar^2}{2\mu_j}\frac{d^2}{dQ_i^2} + \frac{1}{2}\sum_{j=1}^{N_{vib}} F_j Q_j^2\right) \tag{10.10.6}$$

and the wavefunction is then

$$\psi_{vib} = Q_1, Q_2, Q_3 ..., Q_{vib}$$
$$= \psi_{vib,1}(Q_1)\psi_{vib,2}(Q_2)\psi_{vib,3}(Q_3), ..., \psi_{vib,N_{vib}}(Q_{N_{vib}})$$

and the total vibrational energy of the molecule is

$$E_{vib} = \sum_{j=1}^{N_{vin}} h\nu_j \left(v_j + \frac{1}{2}\right) \tag{10.10.7}$$

where $v_j = 0, 1, 2, 3....$

The consequence of the result stated in the above equations is that each vibrational mode can be treated as a harmonic oscillator approximation. There are N_{vib} harmonic oscillators corresponding to the total number of vibrational modes present in the molecule.

10.10.3: Pictorial description of normal coordinates using CO

The normal coordinate q is used to follow the path of a normal mode of vibration. As shown in Figure 13.9.2 the displacement of the C atom, denoted by $\Delta r_o(\mathrm{C})$, and the displacement of the O atom, denoted by $\Delta r_o(\mathrm{O})$, occur at the same frequency. The displacement of atoms is measured from the equilibrium distance in ground vibrational state, r_o.

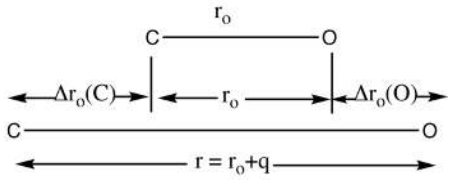


Figure 13.9.2 : The Normal coordinate for CO is equation to $\Delta r(C) + \Delta r(O)$

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10.11: 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.

10.11.1: 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 $\mathbf{XY_2}$, 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:

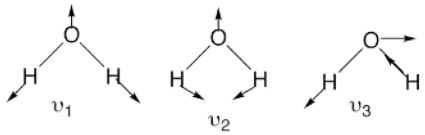


Figure 13.10.1 : Three normal modes of water

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 $\boldsymbol{\nu_2}$ 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:

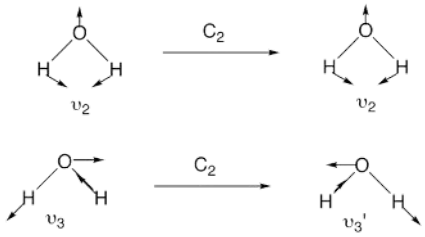


Figure 13.10.2 : Symmetry operations on the symmetric and asymmetric stretches of water

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)	
$\mathbf{v_1}$	1	1	1	1	= $\mathbf{a_1}$
$\mathbf{v_2}$	1	1	1	1	= $\mathbf{a_1}$
$\mathbf{v_3}$	1	-1	-1	1	= $\mathbf{b_2}$

Water has three normal modes that can be grouped together as the reducible representation

$$\boldsymbol{\Gamma_{vib} = 2a_1 + b_2.}$$

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).

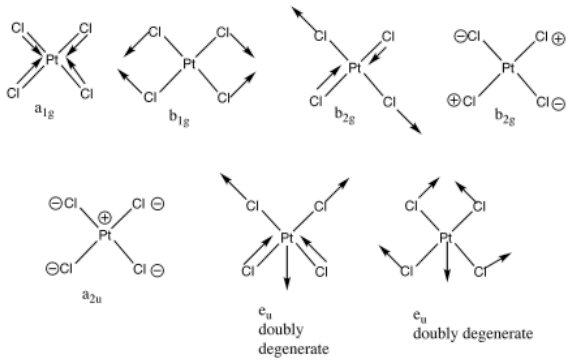


Figure 13.10.3 : A_{1g}, b_{1g} and e_u are stretching vibrations whereas b_{2g}, a_{2u}, b_{2u} and e_u are bending vibrations.

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10.12: Group Theory Determines Infrared Activity

10.12.1: Determining if a Normal Modes is IR or Raman Active

A transition from $v \rightarrow v'$ is IR active if the **transition moment integral** contains the totally symmetric irreducible representation of the point group the molecule belongs to. The transition moment integral is derived from the one-dimensional harmonic oscillator. Using the definition of electric dipole moment μ, the integral is:

$$M(v \rightarrow v') = \langle \textbf{final wavefunction} \left|\vec{\mu}\right| \textbf{initial wavefunction} \rangle$$

or in terms of vibrational wavefunctions for a specific normal mode $|\phi(v)\rangle$

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) \left|\vec{\mu}\right| \phi(v = 0) \rangle \tag{10.12.1}$$

assuming the transition from the $v = 0$ wavefunction to the $v' \neq 0$ wavefunction.

Now, consider the case that $\vec{\mu}$, is a constant and therefore independent of the vibration (i.e., the electric dipole moment does not change during the vibration). This it could be taken outside the integral in Equation 10.12.1 becomes

$$M(v \rightarrow v') = \vec{\mu} \langle \phi(v' \neq 0) | \phi(v = 0) \rangle \tag{10.12.2}$$

Since $|\phi(v = 0)\rangle$ and $|\phi(v =\neq 0)\rangle$ are mutually orthogonal to each other, the integral in Equation 10.12.1 will equal zero and the transition will **not** be allowed (i.e., it is forbidden). For the M to be nonzero, $\vec{\mu}$ must change during a vibration. This selection rule explains why homonuclear diatomic molecules do not produce an IR spectrum. There is no change in dipole moment resulting in a transition moment integral of zero and a transition that is forbidden.

For a transition to be Raman active, the same rules apply. The transition moment integral must contain the totally symmetric irreducible representation of the point group. The integral contains the polarizability tensor α (usually represented by a square matrix):

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) \left|\alpha\right| \phi(v = 0) \rangle \tag{10.12.3}$$

Following a similar argument as above, α must be nonzero for the transition to be allowed and exhibits Raman scattering.

10.12.1.1: 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 $\mathbf{\Gamma}_{tot}$ - $\mathbf{\Gamma}_{trans}$ - $\mathbf{\Gamma}_{rot}$.

$$\mathbf{\Gamma}_{vib}(H_2O) = (3a_1 + a_2 + 2b_1 + 3b_2) - (a_1 + b_1 + b_2) - (a_2 + b_1 + b_2) = 2a_1 + b_2$$

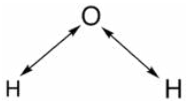
In order to determine which modes are IR active, a simple check of the irreducible representation that corresponds to x,y and z and a cross check with the reducible representation Γ_{vib} is necessary. If they contain the same irreducible representation, the mode is IR active.

For H_2O, z transforms as a_1, x as b_1 and y as b_2. The modes a1 and b2 are IR active since Γvib contains $2a_1 + b_2$.

In order to determine which modes are Raman active, the irreducible representation that corresponds to z^2, x^2-y^2, xy, xz and yz is used and again cross checked with Γvib. For H_2O, z^2 and x^2-y^2 transform as a_1, xy as a_2, xz as b_1 and yz as b_2.The modes a_1 and b_2 are also Raman active since Γ_{vib} contains both these modes.

The IR spectrum of H2O does indeed have three bands as predicted by Group Theory. The two symmetric stretches v1 and v2 occur at 3756 and 3657 cm-1 whereas the bending v3 motion occurs at 1595 cm-1.

In order to determine which normal modes are stretching vibrations and which one are bending vibrations, a stretching analysis can be performed. Then the stretching vibrations can be deducted from the total vibrations in order to obtain the bending vibrations. A double-headed arrow is drawn between the atom as depicted below:



Then a determination of how the arrows transform under each symmetry operation in C2v symmetry will yield the following results:

C_{2v}	E	C_2	σ (xz)	σ (yz)	
$\Gamma_{stretch}$	2	0	0	2	$= a_1 + b_2$

$$\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch} = 2a_1 + b_2 - a_1 - b_2 = a_1$$

H_2O has two stretching vibrations as well as one bending vibration. This concept can be expanded to complex molecules such as $PtCl4^-$. Four double headed arrows can be drawn between the atoms of the molecule and determine how these transform in D_{4h} symmetry. Once the irreducible representation for $\Gamma_{stretch}$ has been worked out, Γ_{bend} can be determined by $\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch}$.

Most molecules are in their zero point energy at room temperature. Therefore, most transitions do originate from the v=0 state. Some molecules do have a significant population of the v=1 state at room temperature and transitions from this thermally excited state are called **hot** bands.

10.12.2: References

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10.13: Raman- Application

If one can extract all of the vibrational information corresponds a molecule, its molecular structure can then be determined. In the field of spectroscopy, two main techniques are applied in order to detect molecular vibrational motions: Infrared spectroscopy (IR) and Raman spectroscopy. Raman Spectroscopy has its unique properties which have been used very commonly and widely in Inorganic, Organic, Biological systems [1] and Material Science [2], [3], etc.

Introduction

Generally speaking, vibrational and rotational motions are unique for every molecule. The uniqueness to molecules are in analogous to fingerprint identification of people hence the term molecular fingerprint. Study the nature of molecular vibration and rotation is particularly important in structure identification and molecular dynamics. Two of the most important techniques in studying vibration/rotation information are IR spectroscopy and Raman spectroscopy. IR is an absorption spectroscopy which measures the transmitted light. Coupling with other techniques, such as Fourier Transform, IR has been highly successful in both organic and inorganic chemistry.

Unlike IR, Raman spectroscopy measures the scattered light (Figure 2). There are three types of scattered lights: Rayleigh scattering, Stokes scattering, and anti-stokes scattering. Rayleigh scattering is elastic scattering where there is no energy exchange between the incident light and the molecule. Stokes scattering happens when there is an energy absorption from the incident light, while anti-stokes scattering happens when the molecule emites energy to the incident light. Thus, Stokes scattering results in a red shift, while anti-stokes scattering results in a blue shift. (Figure 1) Stokes and Anti-Stokes scattering are called Raman scattering which can provide the vibration/rotation information

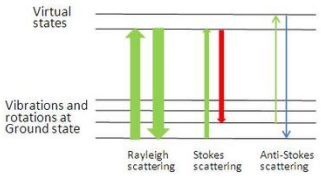


Figure 1: Scattered lights (The line thickness represents the intensity of the signal)

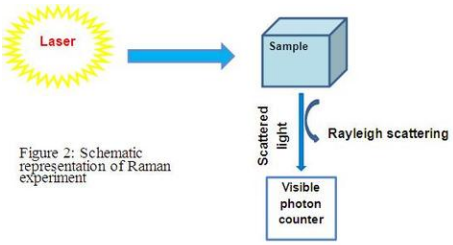


Figure 2: Schematic representation of Raman experiment

The intensity of Rayleigh scattering is around 10^7 times that of Stokes scattering. [4]According to the Boltzmann distribution, anti-Stokes is weaker than Stokes scattering. Thus, the main difficulty of Raman spectroscopy is to detect the Raman scattering by filtering out the strong Rayleigh scattering. In order to reduce the intensity of the Rayleigh scattering, multiple monochromators are applied to selectively transmit the needed wave range. An alternative way is to use Rayleigh filters. There are many types of Rayleigh filters. One common way to filter the Rayleigh light is by interference.

Because of the weakness of Raman scattering, the resolving power of a Raman spectrometer is much higher than an IR specctrometer. A resolution of 10^5 is needed in Raman while 10^3 is sufficient in IR. [5] In order to achieve high resolving power, prisms, grating spectrometers or interferometers are applied in Raman instruments.

Despite the limitations above, Raman spectroscopy has some advantages over IR spectroscopy as follows:

1. Raman Spectroscopy can be used in aqueous solutions (while water can absorb the infrared light strongly and affect the IR spectrum).
2. Because of the different selection rules, vibrations inactive in IR spectroscopy may be seen in Raman spectroscopy. This helps to complement IR spectroscopy.
3. There is no destruction to the sample in Raman Spectroscopy. In IR spectroscopy, samples need to disperse in transparent matrix. For example grind the sample in solid KBr. In RS, no such destructions are needed.
4. Glass vials can be used in RS *(this should only work in the visible region. If in UV region, glass is not applicable because it can strongly absorb light too.)*
5. Raman Spectroscopy needs relative short time. So we can do Raman Spectroscopy detection very quickly.

After analysis of the advantages and disadvantages of Raman Spectroscopy technique, we can begin to consider the application of Raman Spectroscopy in inorganic, organic, biological systems and Material Science, etc.

Applications

Raman Spectroscopy application in inorganic systems

X-ray diffraction (XRD) has been developed into a standard method of determining structure of solids in inorganic systems. Compared to XRD, it is usually necessary to obtain other information (NMR, electron diffraction, or UV-Visible) besides vibrational information from IR/Raman in order to elucidate the structure. Nevertheless, vibrational spectroscopy still plays an important role in inorganic systems. For example, some small reactive molecules only exist in gas phase and XRD can only be applied for solid state. Also, XRD cannot distinguish between the following bonds: –CN vs. –NC, –OCN vs. –NCO,–CNO vs. –ONC, -SCN vs. –NCS. [7] Furthermore, IR and Raman are fast and simple analytical method, and are commonly used for the first approximation analysis of an unknown compound.

Raman spectroscopy has considerable advantages over IR in inorganic systems due to two reasons. First, since the laser beam used in RS and the Raman-scattered light are both in the visible region, glass (Pyrex) tubes can be used in RS. On the other hand, glass absorbs infrared radiation and cannot be used in IR. However, some glass tubes, which contain rare earth salts, will gives rises to fluorescence or spikes. Thus, using of glass tubes in RS still need to be careful. Secondly, since water is a very weak Raman scatter but has a very broad signal in IR, aqueous solution can be directly analyzed using RS.

Raman Spectroscopy and IR have different selection rules. RS detects the polarizability change of a molecule, while IR detects the dipole momentum change of a molecule. Principle about the RS and IR can be found at Chemwiki Infrared Theory and Raman Theory. Thus, some vibration modes that are active in Raman may not be active IR, vice versa. As a result, both of Raman and IR spectrum are provided in the stucture study. As an example, in the study of Xenon Tetrafluoride. There are 3 strong bands in IR and solid Raman shows 2 strong bands and 2 weaker bands. These information indicates that Xenon Tetrafluoride is a planar molecule and has a symmetry of D4h. [8] Another example is the application of Raman Spectroscopy in homonuclear diatomic molecules. Homonuclear diatomic molecules are all IR inactive, fortunately, the vibration modes for all the homonuclear diatomic molecules are always Raman Spectroscopy active.

Raman Spectroscopy Application in Organic Systems

Unlike inorganic compounds, organic compounds have less elements mainly carbons, hydrogens and oxygens. And only a certain function groups are expected in organic specturm. Thus, Raman and IR spectroscopy are widely used in organic systems. Characteristic vibrations of many organic compounds both in Raman and IR are widely studied and summarized in many literature. [5] Qualitative analysis of organic compounds can be done base on the characteristic vibrations table.

Table 1: Characteristic frequencies of some organic function group in Raman and IR

Vibration	Region(cm^{-1})	Raman intensity	IR intensity
v(O-H)	3650~3000	weak	strong
v(N-H)	3500~3300	medium	medium
v(C=O)	1820~1680	strong~weak	very strong
v(C=C)	1900~1500	very strong~medium	0~weak

“RS is similar to IR in that they have regions that are useful for functional group detection and fingerprint regions that permit the identification of specific compounds.”[1] While from the different selection rules of Raman Spectroscopy and IR, we can get the Mutual Exclusion rule [5], which says that for a molecule with a center of symmetry, no mode can be both IR and Raman Spectroscopy active. So, if we find a strong bond which is both IR and Raman Spectroscopy active, the molecule doesn't have a center of symmetry.

Non-classical Raman Spectroscopy

Although classical Raman Spectroscopy has been successfully applied in chemistry, this technique has some major limitations as follows[5]:

1. The probability for photon to undergo Raman Scattering is much lower than that of Rayleigh scattering, which causes low sensitivity of Raman Spectroscopy technique. Thus, for low concentration samples, we have to choose other kinds of techniques.
2. For some samples which are very easily to generate fluorescence, the fluorescence signal may totally obscure the Raman signal. We should consider the competition between the Raman Scattering and fluorescence.
3. In some point groups, such as C_6 , D_6 , D_{6h} , C_{4h} , D_{2h}, there are some vibrational modes that is neither Raman or IR active.
4. The resolution of the classical Raman Spectroscopy is limited by the resolution of the monochromator.

In order to overcome the limitations, special techniques are used to modify the classical Raman Spectroscopy. These non-classical Raman Spectroscopy includes: Resonance Raman Spectroscopy, surface enhanced Raman Spectroscopy, and nonlinear coherent Raman techniques, such as hyper Raman spectroscopy

Resonance Raman Scattering (RRS)

The resonance effect is observed when the photon energy of the exciting laser beam is equal to the energy of the allowed electronic transition. Since only the allowed transition is affected, (in terms of group theory, these are the totally symmetric vibrational ones.), only a few Raman bands are enhanced (by a factor of 10^6). As a result, RRS can increase the resolution of the classical Raman Spectroscopy, which makes the detection of dilution solution possible (concentrations as low as 10^{-3} M). RRS is extensively used for biological molecules because of its ability to selectively study the local environment. As an example, the Resonance Raman labels are used to study the biologically active sites on the bond ligand. RRS can also be used to study the electronic excited state. For example, the excitation profile which is the Raman intensity as a function of incident laser intensity can tell the interaction between the electronic states and the vibrational modes. Also, it can be used to measure the atomic displacement between the ground state and the excited state.

Surface Enhanced Raman Scattering (SERS)

At 1974, Fleischmann discovered that pyridine adsorbed onto silver electrodes showed enhanced Raman signals. This phenomenon is now called surface enhanced Raman Scattering (SERS). Although the mechanism of SERS is not yet fully understood, it is believed to result from an enhancement either of transition polarizability, α,or the electric field, E, by the interaction with the rough metallic support.

Unlike RRS, SERS enhances every band in the Raman spectrum and has a high sensitivity. Due to the high enhancement (by a factor of $10^{10\sim11}$), the SERS results in a rich spectrum and is an ideal tool for trace analysis and in situ study of interfacial process. Also, it is a better tool to study highly diluted solutions. A concentration of $4x10^{-12}$ M was reported by Kneipp using SERS. [5]

Nonlinear Raman Spectroscopy

In a nonlinear process, the output is not linearly proportional to its input. This happens when the perturbation become large enough that the response to the perturbation doesn’t follows the perturbation’s magnitude. Nonlinear Raman Spectroscopy includes: Hyper Raman spectroscopy, coherent anti-Stokes Raman Spectroscopy, coherent Stokes Raman spectroscopy, stimulated Raman gain and inverse Ramen spectroscopy. Nonlinear Raman spectroscopy is more sensitive than classical Raman spectroscopy and can effectively reduce/remove the influence of fluorescence. The following paragraph will focus on the most useful nonlinear Raman spectroscopy---coherent anti-Stokes Raman Spectroscopy (CARS):

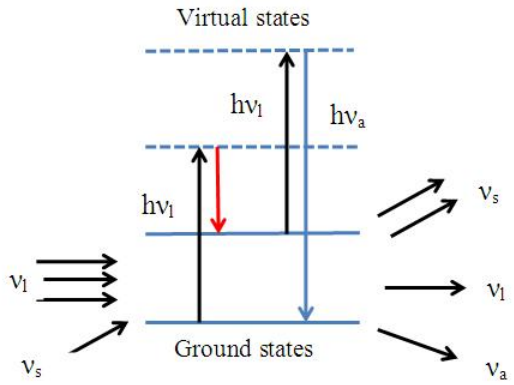


Figure 3: Schematic representation of coherent anti-Stoke Raman. ν is the frequency of the light. The subscript1 represents laser light; s represents Stoke scattering light; a represents anti-Stoke scattering light.

Figure 3) The two laser sources generate a coherent beam at frequency ν_3. There is a signal enhancement when ν_3 equal the anti-Stokes scattering (ν_a), and the vibrational transition equals to the energy difference between two light sources. Since CARS signal is at anti-Stoke region (a higher energy region than fluorescence), the influence of fluorescence is eliminated. Thus, CARS is very useful for molecules with high fluorescence effect, for example, some biological molecules. Another important advantage of CARS is that the resolution is no longer limited by the monochromator as in classical Raman because only the anti-Stokes frequency is studied in CARS. High-resolution CARS has been developed as a tool for small-time scale process, such as photochemical analysis and chemical kinetics studies. [6]

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Problems

1. What are the advantages and disadvantages for Raman spectroscopy, comparing with IR spectroscopy?
2. Please briefly explain the mutual exclusive principle in Raman and IR spectroscopy.

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10.14: Raman- Theory

The phenomenon of Raman scattering of light was first postulated by Smekai in 1923 and first observed experimentally in 1928 by Raman and Krishnan. Raman scattering is most easily seen as the change in frequency for a small percentage of the intensity in a monochromatic beam as the result of coupling between the incident radiation and vibrational energy levels of molecules. A vibrational mode will be Raman active only when it changes the polariazbility of the molecule.

Introduction

When monochromatic radiation with a wavenumber $\tilde{\nu}_0$ is incident on systems, most of it is transmitted without change, but, in addition, some scattering of the radiation occurs. If the frequency content of the scattered radiation is analyzed, there will be observed to be present not only the wavenumber $\tilde{\nu}_0$ associated with the incident radiation but also, in general, pairs of new wavenumbers of the type $\tilde{\nu}' = \tilde{\nu}_0 + \tilde{\nu}_M$. In molecular systems, the wavenumbers $\tilde{\nu}_M$ are found to lie principally in the ranges associated with transitions between rotational, vibrational, and electronic levels.

Such scattering of radiation with change of wavenumber is called Raman Scattering, after the Indian scientist C. V. Raman who, with K. S. Krishnan, first observed this phenomenon in liquids in 1928. The effect had been predicted on theoretical grounds in 1923 by A. Smekal. Due to its very low scattering efficiency, Raman spectroscopy did not become popular until powerful laser systems were available after the 1960s. Now, Raman spectroscopy has become one of the most popular approaches to study the vibrational structures of molecules together with infrared spectrum.

The origin of the modified frequencies found in Raman scattering is explained in terms of energy transfer between the scattering system and the incident radiation. When a system interacts with radiation of wavenumber $\tilde{\nu}_0$, it makes an upward transition from a lower energy level E_1 to an upper energy level E_2. It must then acquire the necessary energy, $\Delta E = E_2 - E_1$, from the incident radiation. The energy ΔE is expressed in terms of a wavenumber $\tilde{\nu}_M$ associated with the two levels involved, where

$$\Delta E = hc\tilde{\nu}_M \tag{10.14.1}$$

This energy requirement is regarded as being provided by the absorption of one photon of the incident radiation of energy $hc\tilde{\nu}_0$ and the simultaneous emission of a photon of smaller energy $hc(\tilde{\nu}_0 - \tilde{\nu}_M)$, so that scattering of radiation of lower wavenumber, $\tilde{\nu}_0 - \tilde{\nu}_M$, occurs. Alternatively, the interaction of the radiation with the system may cause a downward transition from a higher energy level E_2 to a lower energy level E_1, in which case it makes available energy

$$E_2 - E_1 = hc\tilde{\nu}_M \tag{10.14.2}$$

Again a photon of the incident radiation of energy $hc\tilde{\nu}_0$ and the simultaneous emission of a photon of higher energy $hc(\tilde{\nu}_0 + \tilde{\nu}_M)$, so that scattering of radiation of higher wavenumber, $\tilde{\nu}_0 + \tilde{\nu}_M$, occurs.

In the case of Rayleigh scattering, although there is no resultant change in the energy state of the system, the system still participates directly in the scattering act, causing one photon of incident radiation $hc\tilde{\nu}_0$ to be absorbed and a photon of the same energy to be emitted simultaneously, so that scattering of radiation of unchanged wavenumber, $\tilde{\nu}_0$, occurs.

It is clear that, as far as wavenumber is concerned, a Raman band is to be characterized not by its absolute wavenumber, $\tilde{\nu}' = \tilde{\nu}_0 \pm \tilde{\nu}_M$, but by the magnitude of its wavenumber shift $\tilde{\nu}_M$ from the incident wavenumber. Such wavenumber shifts are often referred to as Raman wavenumbers. Where it is necessary to distinguish Stokes and anti-Stokes Raman scattering we shall define $\Delta\tilde{\nu}$ to be positive for Stokes scattering and negative for anti-Stokes scattering, that is $\Delta\tilde{\nu} = \tilde{\nu}_0 + \tilde{\nu}'$ (see Fig. 1).

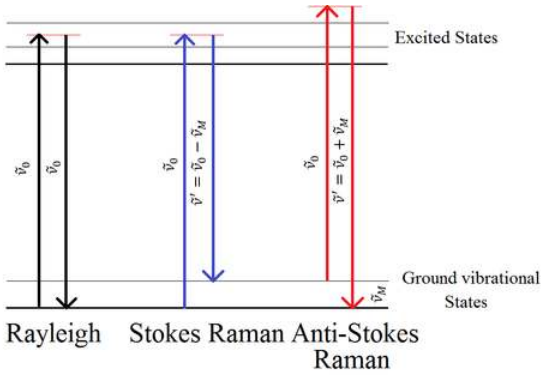


Figure 1. Diagrammatic representation of an energy transfer model of Rayleigh scattering, Stokes Raman and anti-Stokes Raman scattering.

The intensity of anti-Stokes relative to Stokes Raman scattering decreases rapidly with increase in the wavenumber shift. This is because anti-Stokes Raman scattering involves transitions to a lower energy state from a populated higher energy states.

Classical theory

According to the classical theory of electromagnetic radiation, electric and magnetic fields oscillating at a given frequency are able to give out electromagnetic radiation of the same frequency. One could use electromagnetic radiation theory to explain light scattering phenomena.

For a majority of systems, only an induced electric dipole moment $\boldsymbol{\mu}$ is taken into consideration. This dipole moment which is induced by the electric field $\boldsymbol{E}$ could be expressed by the power series

$$\mu = \mu^{(1)} + \mu^{(2)} + \mu^{(3)} + \cdots \tag{10.14.3}$$

where

$$\mu^{(1)} = \alpha \cdot \mathbf{E} \tag{10.14.4}$$

$$\mu^{(2)} = \tfrac{1}{2}\beta \cdot \mathbf{EE}$$

$$\mu^{(3)} = \tfrac{1}{6}\gamma \cdot \mathbf{EEE}$$

$\boldsymbol{\alpha}$ is termed the polarizability tensor. It is a second-rank tensor with all the components in the unit of $CV^{-1}m^2$. Typically, orders of magnitude for components in $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, and $\boldsymbol{\gamma}$ are as follows, $\boldsymbol{\alpha}$, 10^{-40} $CV^{-1}m^2$; $\boldsymbol{\beta}$, 10^{-50} $CV^{-2}m^3$; and $\boldsymbol{\gamma}$, 10^{-61} $CV^{-3}m^4$. According to the values, the contributions of $\boldsymbol{\mu}^{(2)}$and $\boldsymbol{\mu}^{(3)}$ are quite small unless electric field is very high. Since Rayleigh and Raman scattering are observed quite readily with very much lower electric field intensities, one may expect to explain Rayleigh and Raman scattering in terms of $\boldsymbol{\mu}^{(1)}$ only.

We shall now consider the interaction of a molecular system with the harmonically oscillating electric field in the frequency ω_0. To make the explanation easily, we shall ignore the rotation but just consider the vibration part. It is to be expected that the polarizability will be a function of the nuclear coordinates. The variation of components in polarizability tensor with vibrational coordinates is expressed in a Taylor series

$$\alpha_{ij} = (\alpha_{ij})_0 + \sum_k \left(\frac{\partial \alpha_{ij}}{\partial Q_k}\right)_0 Q_k + \frac{1}{2}\sum_{k,l}\left(\frac{\partial^2 \alpha_{ij}}{\partial Q_k \partial Q_l}\right)_0 Q_k Q_l + \cdots$$

where $(\alpha_{ij})_0$ is the α_{ij} value at the equilibrium configuration, Q_k, Q_l are normal coordinates of vibration at frequencies ω_k, ω_l. We shall make a harmonic approximation to neglect the terms which involve powers of Q higher than first. After initially fixing our attention on one normal mode, Q_k, we could get

$$\alpha_{ij} = (\alpha_{ij})_0 + \left(\frac{\partial \alpha_{ij}}{\partial Q_k}\right)_0 Q_k$$

As for a harmonic vibration,

$$Q_k = Q_{k0}\cos(\omega_k t + \delta_k) \tag{10.14.5}$$

Then we could get the expression of $\boldsymbol{\alpha}$ tensor resulting from k-th vibration,

$$\alpha_k = \alpha_0 + \left(\frac{\partial \alpha_k}{\partial Q_k}\right)_0 Q_{k0} \cos\left(\omega_k t + \delta_k\right)$$

Now, under the influence of electromagnetic radiation at frequency ω_0, the induced electric dipole moment $\boldsymbol{\mu}^{(1)}$ is expressed,

$$\mu^{(1)} = \alpha_k \cdot \mathbf{E}_0 \cos \omega_0 t \tag{10.14.6}$$

$$= \alpha_0 \cdot \mathbf{E}_0 \cos \omega_0 t + \left(\frac{\partial \alpha_k}{\partial Q_k}\right)_0 \cdot \mathbf{E}_0 Q_{k0} \cos \omega_0 t \cos\left(\omega_k t + \delta_k\right) t =$$

$$\alpha_0 \cdot \mathbf{E}_0 \cos \omega_0 t + \frac{1}{2}\left(\frac{\partial \alpha_k}{\partial Q_k}\right)_0 \cdot \mathbf{E}_0 Q_{k0} \cos\left(\omega_0 t + \omega_k t + \delta_k\right) \tag{10.14.7}$$

$$+ \frac{1}{2}\left(\frac{\partial \alpha_k}{\partial Q_k}\right)_0 \cdot \mathbf{E}_0 Q_{k0} \cos\left(\omega_0 t - \omega_k t - \delta_k\right)$$

We see that the linear induced dipole moment $\boldsymbol{\mu}^{(1)}$ has three components with different frequencies,

$\boldsymbol{\alpha}_0 \cdot \mathbf{E}_0 \cos \omega_0 t$ which gives rise to radiation at ω_0 and accounts for the Rayleigh scattering;

$$\tfrac{1}{2}\left(\tfrac{\partial \alpha_k}{\partial Q_k}\right)_0 \cdot \mathbf{E}_0 Q_{k0} \cos\left(\omega_0 t + \omega_k t + \delta_k\right)$$

which gives rise to radiation at ω_0+ω_k and accounts for the anti-Stokes Raman scattering; and

$$\frac{1}{2}\left(\frac{\partial \alpha_k}{\partial Q_k}\right)_0 \cdot \mathbf{E}_0 Q_{k0} \cos\left(\omega_0 t \omega_k t \delta_k\right) \tag{10.14.8}$$

which gives rise to radiation at ω_0-ω_k and accounts for the Stokes Raman scattering.

From these mathematical manipulations, there emerges a useful qualitative picture of the mechanisms of Rayleigh and Raman scattering in terms of classical radiation theory. Rayleigh scattering comes from the dipole oscillating at ω_0 induced in the molecule by the electric field of the incident radiation at frequency ω_0. Raman scattering arises from the dipole moment oscillating at $\omega_0 \pm \omega_k$ produced by the modulation of dipole oscillating at ω_0 with molecular vibration at frequency ω_k. In other words, the frequencies we observe in Raman scattering are beat frequencies of the radiation frequency ω_0 and the molecular vibrational frequency ω_k.

Quantum mechanical treatment

According to the quantum theory, radiation is emitted or absorbed as a result of a system making a downward or upward transition between two discrete energy levels. A quantum theory of spectroscopic processes should, therefore, treat the radiation and molecule together as a complete system, and explore how energy is transferred between the radiation and the molecule as a result of their interaction.

A transition between energy levels of the molecular systems takes place with the emission or absorption of radiation, provided a transition moment associated with the initial and final molecular states is non-zero. The transition moment could be defined as

$$\mathbf{M}_{fi} = \langle \Psi_f \mid \mu \mid \Psi_i \rangle$$

in the Dirac bracket notation, where Ψ_i and Ψ_f are the wave function of initial and final states, respectively, and $\boldsymbol{\mu}$ is the dipole moment operator.

As we have discussed in the classical part, the linear induced dipole moment could be expressed by

$$\mu^{(1)} = \alpha \cdot \mathbf{E} \tag{10.14.9}$$

Therefore, in quantum mechanical treatment, if a transition from an initial state to a final state is induced by incident radiation at frequency ω_0, the transition moment is given by

$$\mu_{fi}^{(1)} = \langle \Psi_f \mid \alpha \mid \Psi_i \rangle \cdot \mathbf{E} \tag{10.14.10}$$

Now we will examine in more detail the nature of a typical matrix element of the polarizability tensor, like $[\alpha_{xy}]_{fi}$, for Raman scattering. Just like in the classical theory, we will ignore the rotational wave function and consider the vibrational part only.

$$[\alpha_{xy}]_{fi} = \langle \Phi_f \mid \alpha_{xy} \mid \Phi_i \rangle \tag{10.14.11}$$

where Φ is the vibrational wave function.

In classical theory,

$$\alpha_{xy} = (\alpha_{xy})_0 + \sum_k \left(\frac{\partial \alpha_{xy}}{\partial Q_k}\right)_0 Q_k + \frac{1}{2}\sum_{k,l}\left(\frac{\partial^2 \alpha_{ij}}{\partial Q_k \partial Q_l}\right)_0 Q_k Q_l + \cdots \tag{10.14.12}$$

Introducing the quantum part, we obtain (just consider the first order term)

$$[\alpha_{xy}]_{fi} = (\alpha_{xy})_0 \langle \Phi_f \mid \Phi_i \rangle + \sum_k \left(\frac{\partial \alpha_{xy}}{\partial Q_k}\right)_0 \langle \Phi_f \mid Q_k \mid \Phi_i \rangle$$

In the harmonic oscillator model, the total vibrational wave function is product of the harmonic oscillator wave functions for each of the normal modes of vibration. Thus, for Φ,

$$\Phi_i = \prod_k \Phi_{v_k^i}(Q_k) \tag{10.14.13}$$

where $\Phi_{v_k^i}(Q_k)$ is the harmonic oscillator wave function associated with the normal coordinate Q_k, which has a vibrational quantum number v_k^i in a certain state. For harmonic oscillator functions, we have

$$\left\langle \Phi_{v_k^f}(Q_k) \mid \Phi_{v_k^i}(Q_k) \right\rangle = \begin{cases} 0 & \text{for } v_k^f \neq v_k^i \\ 1 & \text{for } v_k^f = v_k^i \end{cases} \tag{10.14.14}$$

and

$$\left\langle \Phi_{v_k^f}(Q_k) \mid Q_k \mid \Phi_{v_k^i}(Q_k) \right\rangle = \begin{cases} 0 & for\ v_k^f = v_k^i \\ (v_k^i+1)^{\frac{1}{2}} b_{v_k} & for\ v_k^f = v_k^i + 1 \\ (v_k^i)^{\frac{1}{2}} b_{v_k} & for\ v_k^f = v_k^i - 1 \end{cases} \tag{10.14.15}$$

where

$$b_{v_k} = \sqrt{\frac{h}{8\pi^2 v_k}} \tag{10.14.16}$$

Selection rules

We are now able to find out the conditions which have to be satisfied if the transition moment is non-zero. We will consider the zero order term which accounts for the Rayleigh scattering part first. This term is none-zero only if $v_k^f = v_k^i$ which means none of the vibrational quantum numbers change during this transition from initial state *i* to final state *f*. Thus, for Rayleigh scattering, the quantum mechanical treatment and the classical theory give the same results.

Then we could go to the first order term $\sum_k \left(\frac{\partial \alpha_{xy}}{\partial Q_k}\right)_0 \langle \Phi_f \mid Q_k \mid \Phi_i \rangle$ which accounts for the Raman scattering part. For the *k*-th summand, it is zero unless every term in the product is non-zero, and to achieve this the following conditions must be satisfied, for all modes except the *k*-th: the vibrational quantum numbers must be the same during the transition, i.e. $v_j^f = v_j^i$ where j≠k; and, for the *k*-th mode, and the vibrational quantum number must change by one unit, i.e. $v_k^f = v_k^i \pm 1$. The transition moment is associated with Stokes Raman scattering for Δv_k=1, and with anti-Stokes Raman scattering for Δv_k=-1. These conditions are a result of the properties of harmonic oscillator wave functions.

It follows from these arguments that, in the harmonic approximation, only vibrational fundamentals, i.e., transitions with only one vibrational quantum number changes by one unit, can be observed in the Raman scattering. However, this Δv_k=±1 restriction is only a necessary but not a sufficient condition for the occurrence of Raman scattering at the *k*-th vibrational mode. The vibrational mode should be Raman active, i.e., at least one of the elements of the derived polarizability tensor should be non-zero.

It can be rigorously established by group theory that the elements of the derived polarizability will be non-zero only if they have the same symmetry with the second order terms, i.e., x^2, y^2, z^2, xy, yz, xz. In other words, the irreducible representation of a certain vibrational mode should have a basis in x^2, y^2, z^2, xy, yz or xz.

Finally, we could establish a much better basis for determining selection rules for vibrational transitions in the Raman effect, if we consider the properties of the vibrational transition polarizability components, rather than the derived prolarizability tensor components. For fundamental vibrational transitions, where in the initial state all vibrational quantum numbers are zero and in the final state only the *k*-th vibrational quantum number has changed to unity,

$$[\alpha_{xy}]_{fi} = \langle \Phi_1 \mid \alpha_{xy} \mid \Phi_0 \rangle$$

According to the group theory, this integral will be non-zero, only if α_{xy} and $\Phi_1(Q_k)$ belong to the same symmetry species, which implies that, under each symmetry operation of the molecule in question, α_{xy} and $\Phi_1(Q_k)$ transform in the same way. This constitutes a general selection rule for the Raman activity of a fundamental transition.

In its most general way, covering all types of transitions, the selection rule is as follows: a transition between two states, $\Psi_i$and Ψ_f, is Raman forbidden unless at least one of the triple products of the type $\Psi_i\alpha_{xy}\Psi_f$ belongs to a representation whose structure contains the totally symmetric species.

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CHAPTER OVERVIEW

9: Electronic Spectroscopy

9.1: Using Atomic Term Symbols to Interpret Atomic Spectra
9.2: The Dynamics of Transitions can be Modeled by Rate Equations
9.3: A Two-Level System Cannot Achieve a Population Inversion
9.4: Population Inversion can be Achieved in a Three-Level System
9.5: What is Inside a Laser?
9.6: The Helium-Neon Laser
9.7: Modern Applications of Laser Spectroscopy
9.8: The Beer-Lambert Law
9.9: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
9.10: The Franck-Condon Principle
9.11: Electronically Excited Molecules can Relax by a Number of Processes

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9.1: Using Atomic Term Symbols to Interpret Atomic Spectra

Learning Objectives

- Demonstrate how spin-orbit coupling is experimentally observed in atomic spectra
- Use atomic terms symbols to ascribe transitions to specific angular momenta states described by atomic term symbols

Around 1930, several spectroscopists using high resolution instruments found that lines in the hydrogen atom spectrum actually are not single lines but they are multiplets as shown for an isotopic mixture of hydrogen,(H_α^1) and deuterium, (H_α^2), in Figure 8.11.1 . A multiplet consists of two or more closely spaced lines. Two lines together form a doublet, three a triplet, etc. Multiplets also are called fine structure. The term fine structure means the lines are spaced close together, i.e. finely spaced. Such fine structure also was found in spectra of one-electron ions such as $\mathbf{He^+}$.

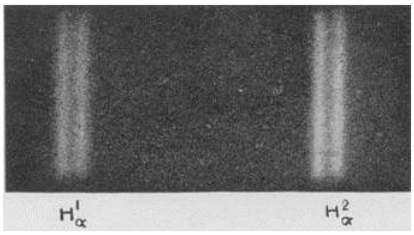


Figure 8.11.1 : Photograph of the first line in the Balmer series for atomic hydrogen and deuterium. These lines are identified as H_α^1 (hydrogen) and H_α^2 (deuterium), respectively. From H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) p. 132 and G.N. Lewis and F.H. Spedding, 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.

9.1.1: Spin-Orbit Coupling

Specifying the orbital configuration of an atom does not uniquely identify the electronic state of the atom because the orbital angular momentum, the spin angular momentum, and the total angular momentum are not precisely specified. For example in the hydrogen $2p^1$ configuration, the electron can be in any of the three p-orbitals, m_l = +1, 0, and –1, and have spins with m_s = +1/2 or –1/2. Thus, there are 3 times 2 different possibilities or states. Also, the orbital and spin angular momentum of the electrons combine in multiple ways to produce angular momentum vectors that are characteristic of the entire atom not just individual electrons, and these different combinations can have different energies. This coupling of orbital and spin angular momentum occurs because both the electron spin and orbital motion produce magnetic dipole moments. As we have seen previously, the relationship between the angular momentum and the magnetic moment is given by the gyromagnetic ratio. These magnetic dipoles interact just like two tiny bar magnets attracting and repelling each other. This interaction is called **spin-orbit interaction**. The interaction energy is proportional to the scalar product of the magnetic dipole moments, which are proportional to the angular momentum vectors.

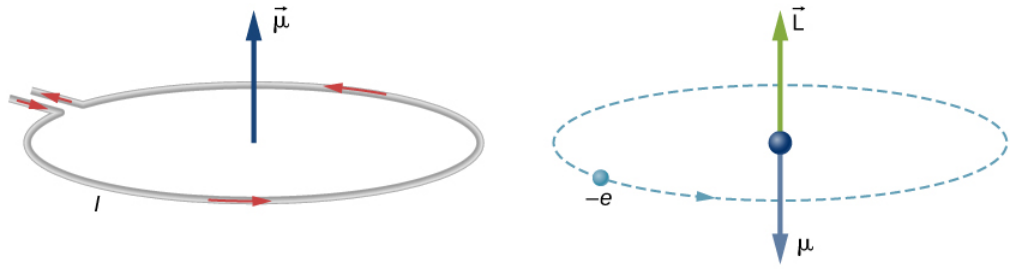
$$E_{s-o} \propto S \cdot L$$

with the following terms added to the Hamiltonian

$$\hat{H}_{s-o} \propto \hat{S} \cdot \hat{L}$$

where the constant of proportionality is called the spin-orbit coupling constant. The spin-orbit interaction couples the spin motion and orbital motion of all the electrons together. This coupling means that exact wavefunctions are not eigenfunctions of the spin and orbital angular momentum operators separately. Rather the total angular momentum $J = L + S$, the vector sum of the spin and orbital angular momentum, is required to be coupled for a completely accurate description of the system. Trying to describe the

coupled system in terms of spin and orbital angular momentum separately is analogous to trying to describe the positions of two coupled bar magnets independently. It cannot be done; their interaction must be taken into account (Figure 8.11.1).



(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).

9.1.2: Atomic Spectroscopy

Higher energy or excited orbital configurations also exist. The hydrogen atom can absorb energy, and the electron can be promoted to a higher energy orbital. The electronic states that result from these excited orbital configurations also are characterized or labeled by term symbols. The details of how to determine the term symbols for multi-electron atoms and for cases where both the orbital and spin angular momentum differ from zero are given elsewhere, along with rules for determining the relative energies of the terms.

We have found that the selection rules for promoting a single electron moving from one atomic orbital to another via the absorption or emission of light are

$$\Delta l = \pm 1$$
$$\Delta m_l = 0, \pm 1$$

These selection rules arise from the conservation fo angular momentum during a spectroscopic transition and the fact that a photon has a spin 1. Within the limits of L-S coupling, these rules can be expressed in terms of atomic term symbols resulting in the resulting Russell-Saunders selection rules:

$$\Delta S = 0 \tag{9.1.1}$$
$$\Delta L = 0, \pm 1 \tag{9.1.2}$$
$$\Delta J = 0, \pm 1, \tag{9.1.3}$$

but the $J = 0$ to $J = 0$ transition is forbidden

$$\Delta m_J = 0, \pm 1 \tag{9.1.4}$$

but the $m_J = 0$ to $m_J = 0$ transition is forbidden if $\Delta J = 0$.

These selection rules result from the general properties of angular momentum such as the conservation of angular momentum and commutation relations. The $\Delta L = 0$ option in Equation 9.1.2 does not violate the conservation of angular momentum discussed previously, since $\Delta l = \pm 1$ is still required. The orbital angular momentum of an electron must change upon absorption, but this does not necessarily affect the overall momentum of the state given by Equation 9.1.2.

The selection rules apply only to atoms that can be described with Russell-Saunders (LS) coupling. These rules fail as the atomic number increases because the S and L quantum numbers become "bad" quantum numbers; this occurs when the jj-coupling coupling approach is more applicable. For example, the transition between single ($S = 1/2$ and triplet $S = 1$ states (violation of selection rule in Equation 9.1.1) are allowed and experimentally observed, in heavy atoms.

Example 8.11.1 : Sodium Atoms

An example of this fine structure is the emission of sodium atoms.



Figure above does not show this splitting).

616.07 nm	615.42 nm	589.00 nm	589.59 nm	568.82 nm	568.26 nm

How can these transitions be described in terms of transitions between microstates

Solution

We need to discussed states in terms of not only electron configurations, but in terms of microstates (i.e., term symbols) and the principal quantum number of the valence electron, n:

- The ground state has a $(Ne]ns^1$ configuration, which has only one microstate $^2S_{1/2}$
- The excited state with the valence electron in the p-orbitals has an electron configuration of $[Ne]np^1$, which has two microstates: $^2P_{3/2}$ and $^2P_{1/2}$
- The excited state with the valence electron in the p-orbitals has an electron configuration of $[Ne]nd^1$, which has two microstates of $^2D_{5/2}$ and $^2D_{3/2}$

Observed lines can be explained:

- $5S \rightarrow 3P$ gives two lines since the initial configuration has two microstates: 616.07, 615.42 nm
- $3P \rightarrow 3S$ gives two lines since the terminal configuration has two microstates: 589.00, 589.59 nm
- $4D \rightarrow 3P$ gives two lines since the terminal configuration has two microstates: 568.82, 568.26 nm

Splitting of the Sodium D Line

One notable atomic spectral line of sodium vapor is the so-called D-line, which may be observed directly as the sodium flame-test line and also the major light output of low -pressure sodium lamps (these produce pressure sodium lamps (these produce an unnatural yellow). The D-line is one of the classified Fraunhofer lines in Sodium vapor in the upper layers of lines. Sodium vapor in the upper layers of the sun creates a dark line in the emitted spectrum of electromagnetic radiation by absorbing visible light in a band of wavelengths around 589.5 nm. This wavelength corresponds to transitions in atomic sodium in which the valence-electron transitions from a 3s to 3p electronic state.

Closer examination of the visible spectrum of atomic sodium reveals that the D-line actually consists of two lines called the D_1 and D_2 lines at 589 6 nm and 589.0 nm, respectively. The splitting between these lines arises because of spin-orbit coupling. Na has one unpaired electron ($S = ½$). If we consider the $S \rightarrow P$ transition, then for the excited state, P, we have $L = 1$. Thus, $J = 3/2$ or $J = 1/2$.

Now we want to apply these ideas to understand why multiplet structure is found in the luminescence spectrum of hydrogen and single electron ions. As we have said, the H_α line in the Balmer series at 656.279 nm can be understood via a transition of an electron in a n = 3 atomic orbital to a n = 2 atomic orbital. When this spectral line was examined using high-resolution instruments, it was found actually to be a doublet, i.e. two lines separated by 0.326 cm^{-1}.

There are 9 degenerate orbitals associated with the n = 3 level, and 4 associated with the n = 2 level. Since an electron can be in any orbital with any one of two spins, we expect the total number of states to be twice the number of orbitals. The number of orbitals is given by n^2 so there should be 8 states associated with n = 2 and 18 states associated with n = 3. Using the ideas of vector addition of angular momentum, the terms that result from having an electron in any one of these orbitals are given in Table 8.11.1 .

Table 8.11.1 : H Atom Terms Originating from n = 1, 2, and 3

Orbital Configuration	Term Symbols	Degeneracy
$1s^1$	$^2S_{1/2}$	2
$2s^1$	$^2S_{1/2}$	2
$2p^1$	$^2P_{1/2}$, $^2P_{3/2}$	2, 4
$3s^1$	$^2S_{1/2}$	2
$3p^1$	$^2P_{1/2}$, $^2P_{3/2}$	2, 4
$3d^1$	$^2D_{3/2}$, $^2D_{5/2}$	4, 6

Table 8.11.1 shows that there are three terms associated with n = 2, and 5 terms associated with n = 3. In principle, each term can have a different energy. The degeneracy of each term is determined by the number of projections that the total angular momentum vector has on the z-axis. These projections depend on the m_J quantum number, which ranges from $+J$ to $-J$ in integer steps. J is the total angular momentum quantum number, which is given by the subscript in the term symbol. This relationship between m_J and J (m_J varies from $+J$ to $-J$ in integer steps) is true for any angular momentum vector.

? Exercise 8.11.3

Confirm that the nine term symbols in Table 8.11.1 are correct.

? Exercise 8.11.4

Confirm that the values for the degeneracy in Table 8.11.1 are correct and that the total number of states add up to 8 for n = 2 and 18 for n = 3.

The energies of the terms depend upon spin-orbit coupling and relativistic corrections that need to be included in the Hamiltonian operator in order to provide a more complete description of the hydrogen atom. As a consequence of these effects, all terms with the same n and (J\) quantum numbers have the **same energy,** while terms with different values for n or J have different energies. The theoretical term splittings as given by H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) pp. 132-137 and are shown in Figure 8.11.2 .

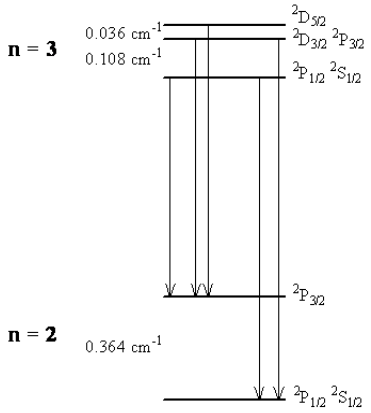


Figure 8.11.2 : Energy level diagram for the electronic states of hydrogen corresponding to an electron with the principal quantum number n = 3 and n = 2. While the relative energies of the terms are drawn to scale, the energy of n = 3 relative to n = 2 is not. Transitions to the $2P_{3/2}$ and ($2P_{1/2}$ and $2S_{1/2}$) levels correspond to the two lines in the H_α^1 band, which have a measured separation of 0.326 cm^{-1}.

Figure 8.11.2 shows 5 allowed transitions for the electron in the states associated with n = 3 to the states associated with n = 2. Of these five, two are most intense and are responsible for the doublet structure. These two transitions are indicated by the wide black lines at the bottom of the figure to correspond to the lines observed in the photographic spectrum shown in Figure 8.11.2 . The

other transitions contribute to the width of these lines or are not observed. The theoretical value for the doublet splitting is 0.328 cm^{-1}, which is in excellent agreement with the measured value of 0.326 cm^{-1}. The value of 0.328 cm^{-1} is obtained by taking the difference, 0.364 – 0.036 cm^{-1},in the term splittings.

As we have just seen, the electronic states, as identified by the term symbols, are essential in understanding the spectra and energy level structure of atoms, but it also is important to associate the term symbols and states with the orbital electron configurations. The orbital configurations help us understand many of the general or coarse features of spectra and are necessary to produce a physical picture of how the electron density changes because of a spectroscopic transition.

? Exercise 8.11.5

Use the Russell-Saunders selection rules to determine which transitions contribute to the H_α line in the hydrogen spectrum.

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9.2: The Dynamics of Transitions can be Modeled by Rate Equations

9.2.1: The Interaction of Light with Atoms

In 1916, Albert Einstein proposed that there are three processes occurring in the formation of an atomic spectral line. The three processes are referred to as spontaneous emission, stimulated emission, and absorption (figure **9.2.1**).

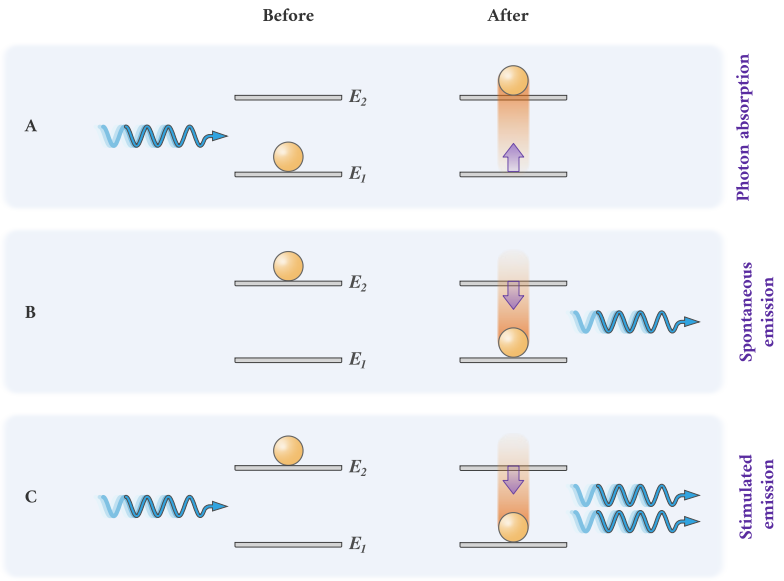


Figure **9.2.1**: The three processes that can occur during the formation of a spectral line. A) Absorption of a photon, leading to the promotion of an electron to a higher electronic energy level. B) The spontaneous emission of a photon created by the relaxation of an electron back to the ground state. C) The stimulated emission of a photon created by the influence of a passing photon, accompanied by the relaxation of an electron back to the ground state. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

For now, let's make our discussion as simple as possible, by assuming we are talking about the interaction of light with an atom that has only two energy levels. There is a collection of these atoms present, and they are in an assortment of states, some in the ground state, and some in "the" excited state. Our discussion of photon emission to this point has generally centered around *spontaneous emission*, the triggering of which we attributed to a perturbation in the hamiltonian that comes from (if nothing else) vacuum fluctuations.

Suppose some of these atoms spontaneously emit photons, and now the collection of atoms is not sitting in a total vacuum, but is in the presence of many photons as well. We now consider what effects these present photons can have on the atoms. The answer depends upon which state the atom is in when it encounters the photon. If the atom is in the ground state, then it can absorb the photon and go to the excited state. If the atom is in its excited state, it can't absorb the photon, but the time-varying EM fields of the photon present a nice perturbation to the electron's hamiltonian (at just the right frequency!) to induce the emission of a photon. This is called *stimulated emission*. The photon that induces the emission is unaffected by the interaction, and continues on its merry way. The emitted photon naturally has the same frequency as the passing photon (the energy gap assured this), but it also emerges moving in the same direction as, *and in phase with* the stimulating photon. This completes the acronym - **L**ight **A**mplification by the **S**timulated **E**mission of **R**adiation.

It turns out that if a photon happens by two of these atoms, the first in the ground state and the second in the excited state, the probability that it will be absorbed by the first is equal to the probability that it will stimulate emission in the other – neither of these results is preferred over the other. Now consider a collection of these atoms in a state of some fixed total energy. This total energy comes from the number of atoms in the ground state multiplied by the energy of that state, plus the number of atoms in the excited state multiplied by the number of atoms in that state. As we will discuss in a future chapter, the populations of these two states subject to the constraint of the total energy can be shown to be a function that depends upon the energy difference of the two

states and the temperature of the collection of atoms. Specifically, if N_1 is the number of atoms in the ground state, N_2 is the number of atoms in the excited state, and the energy difference is ΔE, then the following relation holds:

$$N_1 = N_2 e^{\frac{\Delta E}{k_B T}}$$

where T is the temperature and k_B is Boltzmann's constant. Clearly N_1 is greater than N_2, but how much greater? We can do a very quick calculation of this using an approximation that at room temperature, the constant $k_B T$ is about 140 eV. Let's assume that the energy difference between two energy states of an atom is on the order of 1eV. Then the number of ground state atoms would exceed the number of excited state atoms by a factor of $e^{40} = 2.4\times10^{17}$!

Thus, a photon passing through this collection has an equal probability of being absorbed or stimulating emission if it happens by an atom prepared for one of those actions. But there are so many more atoms available to absorb the photon, that this has a much greater chance of happening. While waiting for a photon to stimulate emission, an atom in an excited state will impatiently emit a photon spontaneously, which will then be much more likely to be absorbed than stimulate emission, and things continue like this, with some atoms spontaneously sending out photons while others absorb them... no laser.

9.2.2: Einstein Coefficients

Einstein proposed a separate rate equation for each of the three processes described above. The rate of each process is proportional to the number of particles in either the ground state (absorption) or the excited state (emission). Each rate is also proportional to the spectral radiant energy density, ρ_ν, which is a measure of the radiant energy density (ρ) per unit frequency of the light associated with the transition. Thus, $\rho_\nu = \frac{d\rho}{d\nu}$, and has units of $\frac{J \cdot s}{m^3}$. With each process there is also an associated Einstein coefficient, which is a proportionality constant.

9.2.2.1: Photon absorption

Absorption is the process by which a photon is absorbed by the atom, causing an electron to jump from a lower energy level to a higher one (figure **9.2.1***a*). The process is described by the Einstein coefficient $B_{12}\left(\frac{m^3}{J \cdot s^2}\right)$, which gives the probability per unit time per unit spectral radiance of the radiation field that an electron in state 1 with energy E_1 will absorb a photon with an energy $E_2 - E_1 = h\nu_{12}$ and jump to state 2 with energy E_2. If $N_1(t)$ is the number density of atoms in state 1, then the change in the number density of atoms in state 1 per unit time due to absorption will be

$$-\frac{dN_1(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t)$$

If only absorption occurred, the increase of the excited state population as a function of time is equal to the decrease of the ground state population as a function of time.

9.2.2.2: Spontaneous emission

Spontaneous emission is the process by which an electron "spontaneously" (i.e. without any outside influence) decays from a higher energy level to a lower one (figure **9.2.1***b*). The process is described by the Einstein coefficient $A_{21}(s^{-1})$, which gives the probability per unit time that an electron in state 2 with energy E_2 will decay spontaneously to state 1 with energy E_1, emitting a photon with an energy $E_2 - E_1 = h\nu_{21}$. Due to the energy-time uncertainty principle, the transition actually produces photons within a narrow range of frequencies called the spectral linewidth. If $N_2(t)$ is the number density of atoms in state 2, then the change in the number density of atoms in state 2 per unit time due to spontaneous emission will be

$$-\frac{dN_2(t)}{dt} = A_{21}N_2(t)$$

The same process results in increasing of the population of the state 1:

$$\frac{dN_1(t)}{dt} = A_{21}N_2(t)$$

9.2.2.3: Stimulated emission

Stimulated emission (also known as induced emission) is the process by which an electron is induced to jump from a higher energy level to a lower one by the presence of electromagnetic radiation at (or near) the frequency of the transition (figure **9.2.1***c*). From the

thermodynamic viewpoint, this process must be regarded as negative absorption. The process is described by the Einstein coefficient $B_{21}\left(\frac{m^3}{J\cdot s^2}\right)$, which gives the probability per unit time per unit spectral radiance of the radiation field that an electron in state 2 with energy E_2will decay to state 1 with energy E_1, emitting a photon with an energy $E_2 - E_1 = h\nu_{21}$. The change in the number density of atoms in state 1 per unit time due to induced emission will be

$$\frac{dN_1(t)}{dt} = B_{21}\rho_\nu(\nu_{21})N_2(t)$$

9.2.3: The Relationship between A_{21}, B_{12}, and B_{21}

In 1900, Max Planck derived a formula for the energy density per unit bandwidth of a blackbody radiator by making the assumption that only discrete energies are allowed. His work agreed with known experimental data, and it is one of the fundamental ideas of quantum mechanics. More specifically, the spectral energy density per unit bandwidth, $\rho_\nu(\nu_{12})$ in units $\frac{J\cdot s}{m^3}$, is given by

$$\rho_\nu(\nu_{12}) = \frac{8\pi h}{c^3}\frac{\nu_{12}^3}{e^{(h\nu_{12})/(k_BT)} - 1} \tag{9.2.1}$$

In a given sample of atoms exposed to radiation of the correct frequency all three processes will be occurring simultaneously. Thus the rate of change of the populations of the two states will be

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) - A_{21}N_2(t) - B_{21}\rho_\nu(\nu_{21})N_2(t) \tag{9.2.2}$$

If we assume that the two energy states are in thermal equilibrium, then N_1 and N_2 are constant, and thus

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) - A_{21}N_2(t) - B_{21}\rho_\nu(\nu_{21})N_2(t) = 0 \tag{9.2.3}$$

Upon solving for $\rho_\nu(\nu_{12})$, we get

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{(N_1(t)/N_2(t))B_{12} - B_{21}} \tag{9.2.4}$$

Recall that in this equation N_1/N_2 represents the electron density in the lower energy state divided by the electron density in the upper state at equilibrium. This quantity is a function of temperature. Assuming many allowed energy states, the number of occupied states decreases exponentially with temperature, as per Boltzmann statistics.

$$N_2/N_1 = \frac{g_2}{g_1}e^{(-h\nu_{12})/(k_BT)} \tag{9.2.5}$$

The quantity $\frac{g_2}{g_1}$ represents the degeneracy level, which is the number of allowed electrons in the upper state over the number of allowed electrons in the lower state. In this expression, g_1 and $g2$ are unitless measures of the number of ways electrons can occupy an energy states. Upon rearrangement, equation 9.2.5 becomes

$$N_1/N_2 = \frac{g_1}{g_2}e^{(h\nu_{12})/(k_BT)} \tag{9.2.6}$$

Equations 9.2.6 and 9.2.4 can be combined to get

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{\left(\frac{g_1}{g_2}e^{(h\nu_{12})/(k_BT)}\right)B_{12} - B_{21}} \tag{9.2.7}$$

which can be rearranged to

$$\rho_\nu(\nu_{12}) = \frac{\frac{A_{21}}{B_{21}}}{\left(\frac{g_1B_{12}}{g_2B_{21}}e^{(h\nu_{12})/(k_BT)}\right) - 1} \tag{9.2.8}$$

One expression for the energy density per unit bandwidth of this system is given by Equation 9.2.1. Equation 9.2.8 gives a second expression for the energy density per unit bandwidth, and it was found by considering the relative rates of absorption, spontaneous emission, and stimulated emission. These equations can be combined to relate the rates of the different processes.

$$\frac{8\pi h}{c^3}\frac{\nu_{12}^3}{e^{(h\nu_{12})/(k_BT)}-1}=\frac{\frac{A_{21}}{B_{21}}}{\left(\frac{g_1B_{12}}{g_2B_{21}}e^{(h\nu_{12})/(k_BT)}\right)-1} \tag{9.2.9}$$

The above equation is true for the conditions

$$\frac{A_{21}}{B_{21}}=\frac{8\pi h\nu_{12}^3}{c^3} \tag{9.2.10}$$

and

$$\frac{g_1B_{12}}{g_2B_{21}}=1 \tag{9.2.11}$$

If we know one of the Einstein coefficients, we can quickly calculate the other two Einstein coefficients using equations 9.2.10 and 9.2.11.

These equations also provide further insight into the operation of lasers and other devices based on stimulated emission. The overall nonequilibrium upper state population rate is given by

$$\frac{dN_2(t)}{dt}=-A_{21}N_2-B_{21}\rho_\nu(\nu_{21})N_2+B_{21}\frac{g_2}{g_1}\rho_\nu(\nu_{12})N_1 \tag{9.2.12}$$

which can be simplified with some algebra.

$$\frac{dN_2(t)}{dt}=-A_{21}N_2-B_{21}\rho_\nu(\nu_{12})\left(N_2-\frac{g_2}{g_1}N_1\right) \tag{9.2.13}$$

The term in parenthesis is the net upper state population. Optical amplification and lasing can only occur when the term in parenthesis is positive. The condition

$$N_2-\frac{g_2}{g_1}N_1>0 \tag{9.2.14}$$

is called a population inversion. It only occurs when enough energy is being supplied to the system, by optical, electrical, or thermal means, so that there are more electrons in the upper energy level than the lower energy level. This situation cannot be achieved for a two-level system, as will be shown in the next section. However, in section 15.4, it will be shown that this situation can be achieved if the system has more than two levels.

9.2.4: Contributors

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- Wikipedia (https://en.Wikipedia.org/wiki/Einstein_coefficients)
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9.3: A Two-Level System Cannot Achieve a Population Inversion

9.3.1: Lasing in Two-Level Systems

For the sake of our studies, let's first consider a laser medium whose atoms have only two energy states: a ground state and one excited state. In such an idealized atom the only possible transitions are excitation from the ground state to the excited state and de-excitation from the excited state back into ground state. Could such an atom be used to make a laser?

There are several important conditions that our laser must satisfy. First of all, the light that it produces must be coherent. That is to say, it must emit photons that are in-phase with one another. Secondly, it should emit monochromatic light, i.e. photons of the same frequency (or wavelength). Thirdly, it would be desirable if our laser's output were collimated, producing a sharply defined "pencil-like" beam of light (this is not crucial, but clearly a desirable condition). Lastly, it would also be desirable for our laser to be efficient, i.e. the higher the ratio of output energy - to - input energy, the better.

Let us begin by examining the requirements for our first condition for lasing, coherence. This condition is satisfied only when the lasing transition occurs through stimulated emission. As we have already seen, stimulated emission produces identical photons that are of equal energy and phase and travel in the same direction. But for stimulated emission to take place a "passer-by" photon whose energy is just equal to the de-excitation energy must approach the excited atom before it de-excites via spontaneous emission. Typically, a photon emitted by the spontaneous emission serves as the seed to trigger a collection of stimulated emissions. Still, if the lifetime of the excited state is too short, then there will not be enough excited atoms around to undergo stimulated emission. So, the first criteria that we need to satisfy is that the upper lasing state must have a relatively long lifetime, otherwise known as a meta-stable state, with typical lifetimes in the milliseconds range. In addition to the requirement of a long lifetime, we need to ensure that the likelihood of absorption of the "passer-by" photons is minimized. This likelihood is directly related to the ratio of the atoms in their ground state versus those in the excited state. The smaller this ratio, the more likely that the "passer-by" photon will cause a stimulated emission rather than get absorbed. So, to satisfy this requirement, we need to produce a **population inversion**: create more atoms in the excited state than those in the ground state.

Another way of stating the above set of conditions is that the rate of absorption must be less than the rate of stimulated emission

$$\underbrace{B_{21}\rho_\nu(\nu_{21})N_2}_{\text{rate of stimulated emission}} > \underbrace{B_{12}\rho_\nu(\nu_{12})N_1}_{\text{rate of absorption}} \tag{9.3.1}$$

As shown in the previous section, $B_{21} = B_{12}$ and $\rho_\nu(\nu_{12}) = \rho_\nu(\nu_{21})$, thus Equation 9.3.1 becomes

$$N_2 > N_1.$$

Hence, if $N_2 > N_1$ then there is a population inversion.

Achieving population inversion in a two-level atom is not very practical. Such a task would require a very strong pumping transition that would send any decaying atom back into its excited state. This would be similar to reversing the flow of water in a waterfall. It can be done but is very energy costly and inefficient. In a sense, the pumping transition would have to work against the lasing transition.

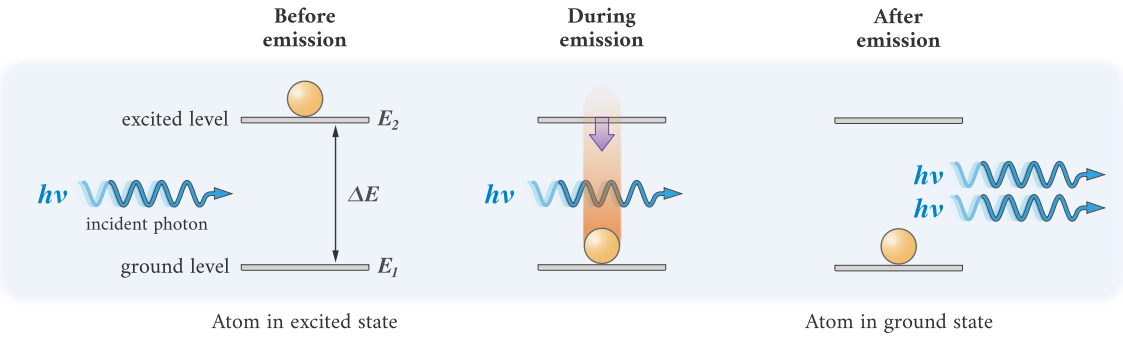


Figure **9.3.1**: A two-level lasing system. (CC BY-NC; Ümit Kaya via LibreTexts)

It is clear, from figure **9.3.1**, that in the two-level atom the pump is, in a way, the laser itself! Such a two-level laser would work only in jolts. That is to say, once the population inversion is achieved the laser would lase. But immediately it would end up with more atoms in the lower level. Such two-level lasers involve a more complicated process. We will see, in later material, examples of these in the context of excimer lasers, which are pulsed lasers. For continuous lasing action, we need to consider other possibilities, such as a three-level atom.

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9.4: Population Inversion can be Achieved in a Three-Level System

Optical pumping will at most achieve only an equal population in a two-level system. This is because the probabilities for raising an electron to the upper level and inducing the decay of an electron to the lower level (stimulated emission) are exactly the same! In other words, when both levels are equally populated, the numbers of electrons "going up" and "down" will be the same, so you cannot achieve population inversion which is required for lasers. The solution is to involve a third, metastable level of intermediate energy. The pumping will occur between the two levels with the greatest energy difference, creating a highly populated upper energy level. Two lasing processes are possible once this situation has been obtained. Lasing occurs between the upper level and the intermediate level if the electrons in the upper energy level decay slowly to the intermediate, metastable level, and if the electrons in the intermediate level decay rapidly to the ground state. However, if the electrons in the upper energy level quickly decay into the intermediate level, and the transition from the intermediate level to the ground level is slow, then lasing occurs between the intermediate level and the ground state. In both cases, the lasing frequency has a frequency different than that of the pumping frequency between the ground level and the upper level, so the pumping is off-resonant to the laser transition and will not trigger stimulated emission.

9.4.1: Lasing in Three-Level Systems

The first laser that was demonstrated to operate was a three-level laser, known as **Maiman's ruby laser**.

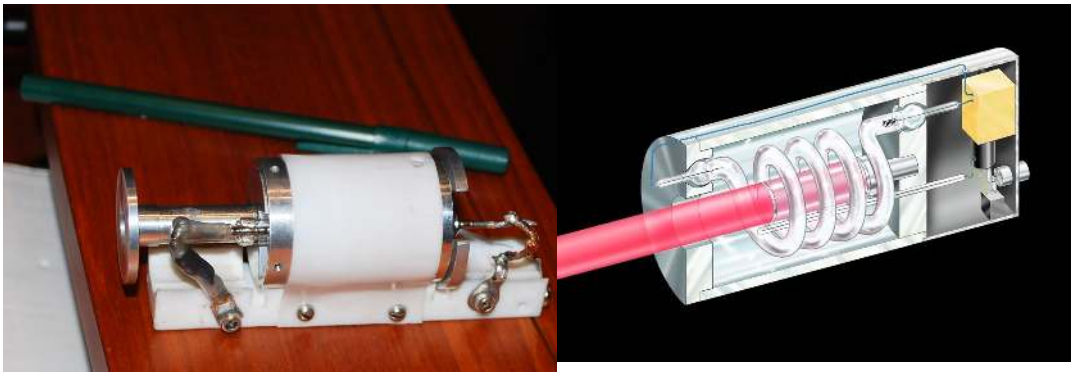


Figure 9.4.1: (left) A copy of a Maiman laser (CC 0; Guy Immega) (right) Internal view of a Maiman laser (https://commons.wikimedia.org/w/inde...ldid=42317741)

Figure 9.4.1 shows the outside and inside of a three-level laser. A pump causes an excitation from the ground state to the second excited state. This state is a rather short-lived state so that the atom quickly decays into the first excited level. (Atoms in the second excited state may also decay directly back to the ground state, but these atoms can be pumped back to the second excited state again.) The first excited state is a long-lived (i.e. metastable) state which allows the atom to "wait" for the "passer-by" photon while building up a large population of atoms in this state. The lasing transition, in this laser, is due to the decay of the atom from this first excited metastable state to the ground state. If the number of atoms in the ground state exceeds the number of atoms that are pumped into the excited state, then there is a high likelihood that the "lasing photon" will be absorbed and we will not get sustained laser light. The fact that the lower lasing transition is the ground state makes it rather difficult to achieve efficient population inversion. In a ruby laser, this task is accomplished by providing the ruby crystal with a very strong pulsating light source, called a flash lamp. The flash lamp produces a very strong pulse of light that is designed to excite the atoms from their ground state into a short-lived upper level. In this way, the ground state is depopulated and population inversion is achieved until a pulse of laser light is emitted. In the ruby laser, the flash lamp light lasts for about 1/1000 of a second (1 ms) and can be repeated about every second. The duration of the laser pulse is shorter than this, typically 0.1 ms. In some pulsed lasers, the pulse duration can be tailored using special methods to be much shorter than this, down to about 10 fs (where 1 fs = 10^{-15} s or one thousandth of a millionth of a millionth of a second). So, the output of a three-level laser is not continuous but consists of pulses of laser light.

9.4.2: Transition Rates in Three-level Systems

In a three-level system, there are nine (9) events that can occur (Figure 9.4.2):

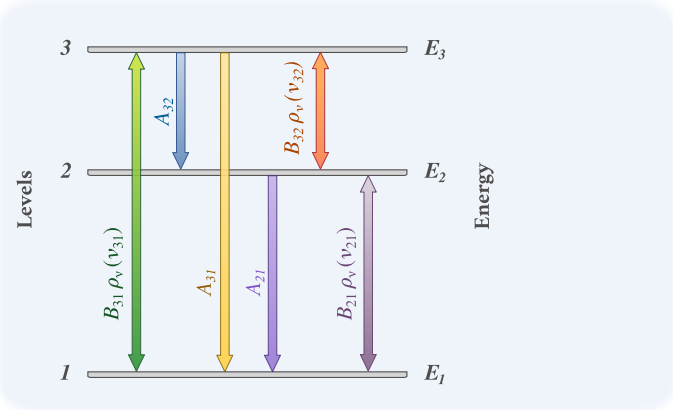


Figure **9.4.2**: The nine possible events in a three-level system. (CC BY-NC; Ümit Kaya via LibreTexts)

a. absorption from level 1 to level 3, as described by $\rho_\nu(\nu_{13})B_{13}N_1$
b. spontaneous emission from level 3 to level 1, as described by $A_{31}N_3$
c. stimulated emission from level 3 to level 1, as described by $\rho_\nu(\nu_{31})B_{31}N_3$
d. spontaneous emission from level 3 to level 2, as described by $A_{32}N_3$
e. stimulated emission from level 3 to level 2 (possible lasing), as described by $\rho_\nu(\nu_{32})B_{32}N_3$
f. absorption from level 2 to level 3, as described by $\rho_\nu(\nu_{23})B_{23}N_2$
g. absorption from level 1 to level 2, as described by $\rho_\nu(\nu_{12})B_{12}N_1$
h. spontaneous emission from level 2 to level 1, as described by $A_{21}N_2$
i. stimulated emission from level 2 to level 1 (possible lasing), as described by $\rho_\nu(\nu_{21})B_{21}N_2$

In most three-level lasers, neither the spontaneous emission from level 3 to level 1, nor the stimulated emission from level 3 to level 1 occur to any significant extent, and so these events are ignored in terms of the kinetics of the lasing process. It is also true that there is no excitation source to cause absorption from level 1 to level 2 other than the possible reabsorption of light emitted from a level 2 to level 1 transition, but this event is unlikely because most atoms in the ground state are pumped up to level 3. Because the pump will be used to drive the absorption from level 1 to level 3, this event is essentially under the control of the experimenter. This leaves a maximum of five events that we need to take into consideration when studying the lasing process.

9.4.2.1: A Ruby Laser

In a three-level system ruby laser such as that described above, the flash lamp will serve as the pump to repeatedly excite most of the atoms from the ground state to the second excited state. In this laser, lasing occurs due to the stimulated emission from level 2 to level 1 (Figure **9.4.3**.)

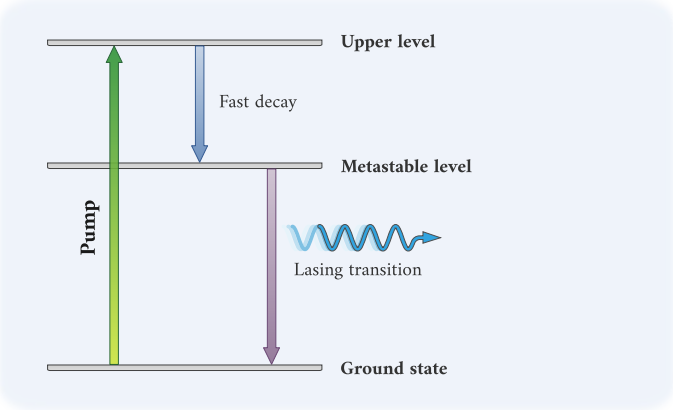


Figure **9.4.3**: Lasing from level 2 to level 1 in a three-level laser. (CC BY-NC; Ümit Kaya via LibreTexts)

Because the lasing will occur from the intermediate, metastable energy level 2, we will focus on the five events that affect its population:

a. absorption from level 2 to level 3, as described by $\rho_\nu(\nu_{32})B_{32}N_2$
b. spontaneous emission from level 3 to level 2, as described by $A_{32}N_3$
c. stimulated emission from level 3 to level 2, as described by $\rho_\nu(\nu_{32})B_{32}N_3$
d. spontaneous emission from level 2 to level 1, as described by $A_{21}N_2$
e. stimulated emission from level 2 to level 1 (lasing), as described by $\rho_\nu(\nu_{21})B_{21}N_2$

In this system, the rate of spontaneous emission from level 3 to level 2 is much more rapid than the rate of absorption from level 2 to level 3, and also much more rapid than the rate of stimulated emission from level 3 to level 2. Thus, any electrons pumped into the upper level are most likely to transition between level 2 and level 3 by spontaneous emission. This means that N_2 is greater than N_1 and thus, population inversion between states 2 and 1 can be achieved. A system of atoms that are able to attain such a population inversion is called a gain medium, and can lase.

9.4.2.2: A Copper Vapor Laser

In this three-level system, the flash lamp will again, serve as the pump to repeatedly excite most of the atoms from the ground state to the second excited state. However, in this laser, lasing occurs due to the stimulated emission from level 3 to level 2 (Figure **9.4.4**).

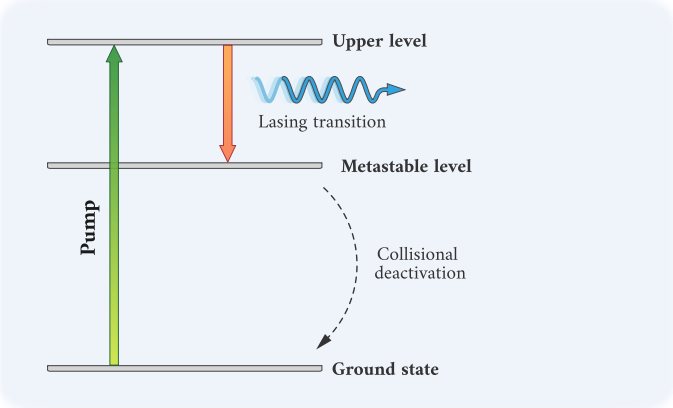


Figure **9.4.4**: Lasing from level 3 to level 2 in a three-level laser. (CC BY-NC; Ümit Kaya via LibreTexts)

Because the lasing will occur from the higher energy excited state, we focus on the four events that affect the population ratio between level 3 and level 2:

a. absorption from level 2 to level 3, as described by $\rho_\nu(\nu_{32})B_{32}N_2$
b. spontaneous emission from level 3 to level 2, as described by $A_{32}N_3$
c. stimulated emission from level 3 to level 2 (lasing), as described by $\rho_\nu(\nu_{32})B_{32}N_3$
d. spontaneous emission from level 2 to level 1, as described by $A_{21}N_2$

If we assume that the atoms in the total population will be distributed between the three energy levels, then

$$N_1(t) + N_2(t) + N_3(t) = N_{total}$$

At equilibrium, the population of each level will remain constant, and so

$$0 = \frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = \frac{dN_3(t)}{dt}.$$

Thus,

$$\frac{N_2(t)}{dt} = -\rho_\nu(\nu_{32})B_{32}N_2 + A_{32}N_3 - A_{21}N_2 + \rho_\nu(\nu_{32})B_{32}N_3 = 0 \tag{9.4.1}$$

Rearranging Equation 9.4.1 gives

$$N_2(A_{21} + \rho_\nu(\nu_{32})B_{32}) = N_3(A_{32} + \rho_\nu(\nu_{32})B_{32}) \tag{9.4.2}$$

which rearranges to

$$\frac{N_3}{N_2} = \frac{A_{21} + \rho_\nu(\nu_{32})B_{32}}{A_{32} + \rho_\nu(\nu_{32})B_{32}} \tag{9.4.3}$$

From Equation 9.4.3 we can see that if A_{21} is greater than A_{32}, then N_3 can be greater than N_2. If N_3 is greater than N_2, then population inversion between states 3 and 2 can be achieved. In other words, if atoms in state 2 decay to the ground state more rapidly than atoms in state 3 decay to state 2, there will be a population inversion between states 3 and 2, and the system can lase.

9.4.3: Four-Level Lasers

There are also lasers based on transitions between four energy levels. These lasers can be more efficiently pumped, because the lower level of the lasing transition is not the ground state. Only four-level lasers can provide a continuous lasing output. He-Ne and Nd:YAG lasers are common four-level lasers and will be described in section 15.6.

9.4.4: References

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9.5: What is Inside a Laser?

Most lasers consist of three basic components:

1. the gain medium from which light of a specific frequency is emitted
2. the pump source which provides energy to the gain medium to create the light
3. the laser optical cavity in which the light is amplified by repeatedly passing through the gain medium

9.5.1: The Gain Medium

The gain medium, or active medium, is a collection of atoms or molecules that can undergo stimulated emission. The active medium can be in a gaseous, liquid, or solid form. It can be a pure substance or a solution. Because the emitted light of a laser is created by the transition between two quantized states of the gain medium, laser light is always monochromatic. Laser light is also always coherent, meaning that the light waves emitted by the laser are all in phase.

9.5.1.1: Solids

The first laser, Maiman's ruby laser, described in section 15.4, used a solid rod of synthetic ruby as the gain medium (Figure **9.5.1**).

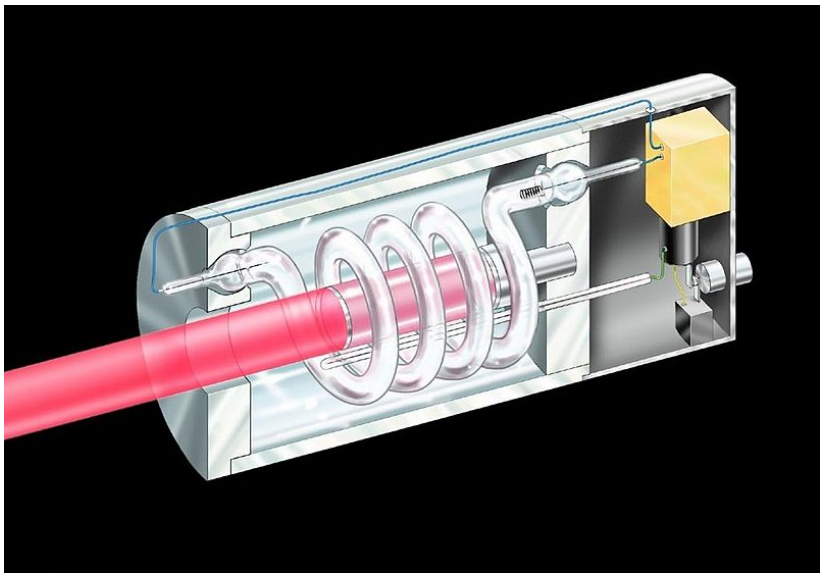


Figure **9.5.1**: Internal view of a Maiman laser (Public Domain; United States Department of Energy via Wikipedia)

Ruby is a gem variety of the mineral corundum, Al_2O_3, in which Cr^{3+} ions replace roughly 0.05% (by mass) of the Al^{3+} ions. The electronic structure of the Cr^{3+} impurities enables to ruby to act as a gain medium. However, synthetic ruby must be used because natural rubies have too many crystal defects. Other solid-state gain media are shown in Table **9.5.1**.

Table **9.5.1**: Solid-phase gain media

Solid-state Host	Active Ion	Wavelength (nm)	Output	Lifetime
Al_2O_3	Ti^{3+}	780	continuous and pulsed	10 fs - 5 ps
Al_2O_3	Cr^{3+}	694.3	pulsed	10 ps
Glass (SiO_2)	Nd^{3+}	1059	pulsed	1 ps
YAG $Y_3Al_5O_{15}$	Nd^{3+}	1064.1	continuous and pulsed	10-150 ps
YLF Y_3LixFy	Nd^{3+}	1054.3	continuous and pulsed	10-100 ps

9.5.1.2: Gases

A basic He-Ne laser is shown in figure **9.5.2**. The gain medium is the gas mixture through which the laser beam passes.

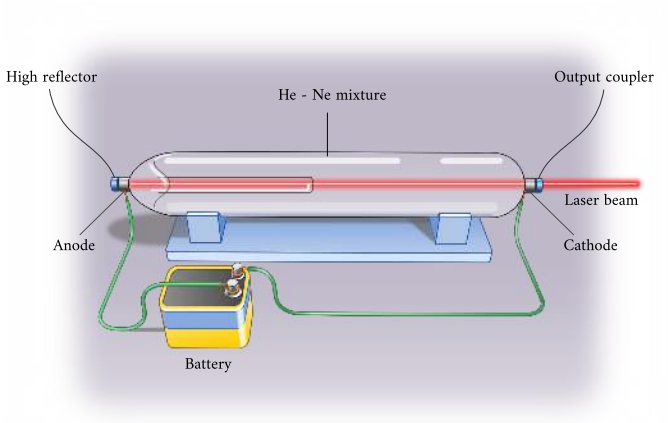


Figure **9.5.2**: Internal view of a He-Ne laser. (CC BY-NC; Ümit Kaya via LibreTexts)

Other common gas-phase media include noble gases and molecules, but also metal cations, and metal atoms as shown in Table **9.5.2**.

Table **9.5.2**: Gas-phase gain media

Gaseous Gain Medium	Wavelength (nm)	Output	Pulse Duration
N_2	337	pulsed	1 ns
Cu	510	pulsed	30 ns
CO_2, He, N_2	tunable near 10,000	pulsed	> 100 ns
He, Ne	3391, 1152, 632, 544	continuous	continuous
He, Cd	441, 325	continuous	continuous
Ar^+	488, 515	continuous	continuous
K^+	647	continuous	continuous.

9.5.1.3: Exciplex Lasers

Exciplex lasers involve the formation of an exciplex, a gaseous species that forms and exists only in an excited state. Because only the upper, excited state can exist, there is no population in the lower, dissociated state, thus a population inversion is obtained. The lasing transition occurs as the excited state exciplex emits its excitation energy and simultaneously falls apart. Two common exciplex lasers are XeCl* (308 nm) and KrF* ((249 nm). These lasers are often referred to as excimer laser, but the term "excimer" refers to an excited dimer, AA*, and so should not be used to describe an exciplex, AB*.

9.5.1.4: Liquid Solutions

Many dye lasers use an organic dye, usually dissolved in a solution, as the gain medium. One advantage of using a dye solution as the gain medium is that it can create a tunable laser, which allows for continuous tuning over a wide range of wavelengths. For example, rhodamine 6G is a dye that can be tuned from 635 nm to 560 nm. The dye solution enters the laser cavity by passing through a cell or by streaming through the air using a dye jet. (Figure **9.5.3**).



Figure **9.5.3**: A dye laser in use. The dye is entering the dye cell through the yellow tube in the left foreground. (CC BY-SA 4.0, By Zaereth - Own work, https://commons.wikimedia.org/w/inde...curid=55762750)

Some common laser dyes other than rhodamine 6G and the rhodamines, include various coumarins, stilbenes, and fluorescein. There are solid state dye lasers (SSDL), in which the dye is dispersed uniformly within a solid polymer matrix.

9.5.2: The Pump Source

For lasing to take place, the gain medium must be pumped into an *excited state* capable of undergoing stimulated emission. The energy required for excitation is often supplied by an electric current or an intense light source, such as a flashlamp or an excitation laser. Diode lasers, excimer lasers, and YAG lasers have all been used as pump sources.

Lasers are categorized as having either a continuous beam or a pulsed beam. In theory, any laser could be run as a pulsed beam laser if the pump source is set to deliver the excitation energy in regularly repeated bursts. Not all lasers can operate as continuous-wave (CW) lasers, though, because there are gain media in which it is not possible to maintain a continuous population inversion. The ruby laser is an example of a laser that cannot produce a continuous wave.

9.5.3: The Laser Optical Cavity

Figure **9.5.4** shows the main components of a generic laser optical (or resonator) cavity. The optical cavity is formed by a pair of mirrors that surround the gain medium and enable feedback of light into the medium. This feedback is critical to the operation of a laser because it is where the amplification of the signal occurs. The gain medium is excited by an external pump source, such as a flash lamp, electric current, or another laser. The output coupler is a partially reflective mirror that allows a portion of the laser radiation to leave the cavity but reflects a majority of the light back through the gain medium. The light trapped between the mirrors forms standing wave structures called modes. Although beyond the scope of this discussion, the reader interested in cavity modes can consult the "Laser Radiation Properties" module.

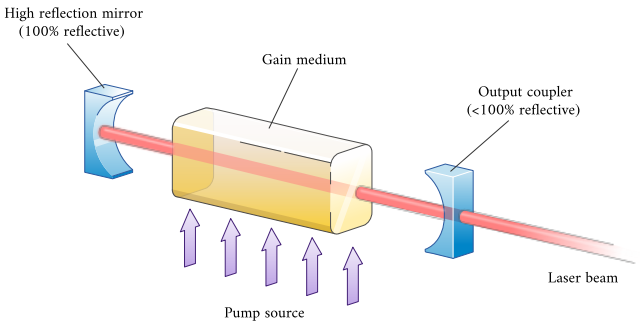


Figure **9.5.4**: A schematic of a generic laser cavity. (CC BY-NC; Ümit Kaya via LibreTexts)

Figure **9.5.5** shows the laser cavity of a tunable dye laser. The laser is tunable because the pump source provides several excitation energies, which result in the creation of several possible energies for the lasing beam. The user chooses the desired lasing energy by means of a tuning element, which is often a movable diffraction grating.

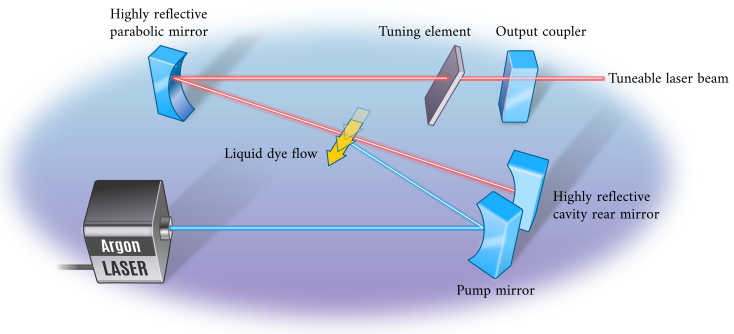


Figure **9.5.5**: A schematic of a dye laser cavity with a dye jet. (CC BY-NC; Ümit Kaya via LibreTexts)

9.5.4: Diode Lasers

Diode lasers do not lase in the same manner as the lasers described above. There is no laser optical cavity, and thus there is no stimulated emission. Diodes made of materials such as GaAs emit light when the recombination of an electron and a hole in a semiconductor releases energy in the form of photons. A population inversion is maintained by rapidly removing the electrons that are falling into the holes of the p-type semiconductor. A pseudo-optical cavity is formed because the semiconductor materials generally have a very high refractive index, causing the photons to be trapped in the crystal of the semiconductor due to the large and abrupt difference in the refractive indices at the surfaces of the crystal. GaAs emits infrared light, but it can be doped to create a material that emits at another wavelength. For example, $GaAs_{0.6}P_{0.4}$ emits red light.

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9.6: The Helium-Neon Laser

The He-Ne laser was the first continuous-wave (cw) laser invented. A few months after Maiman announced his invention of the pulsed ruby laser, Ali Javan and his associates W. R. Bennet and D. R. Herriott announced their creation of a cw He-Ne laser. This gas laser is a four-level laser that uses helium atoms to excite neon atoms. The atomic transitions in the neon produce the laser light. The most commonly used neon transition in these lasers produces red light at 632.8 nm. These lasers can also produce green and yellow light in the visible region, as well as several UV and IR wavelengths (Javan's first He-Ne operated in the IR at 1152.3 nm). By using highly reflective mirrors designed for one of these many possible lasing transitions, a given He-Ne's output is made to operate at a single wavelength.

He-Ne lasers are not sources of high-power laser light, typically producing a few to tens of mW (milli-Watt, or 10^{-3} W) of power. Probably one of the most important features of these lasers is that they are highly stable, both in terms of their wavelength (mode stability) and intensity of their output light (low jitter in power level). For these reasons, He-Ne lasers are often used to stabilize other lasers. They are also used in applications, such as holography, where mode stability is important. Until the mid-1990's, He-Ne lasers were the dominant type of lasers produced for low-power applications - from range finding to scanning to optical transmission, to laser pointers, etc. Recently, however, other types of lasers, most notably the semiconductor lasers, seem to have won the competition because of reduced costs.

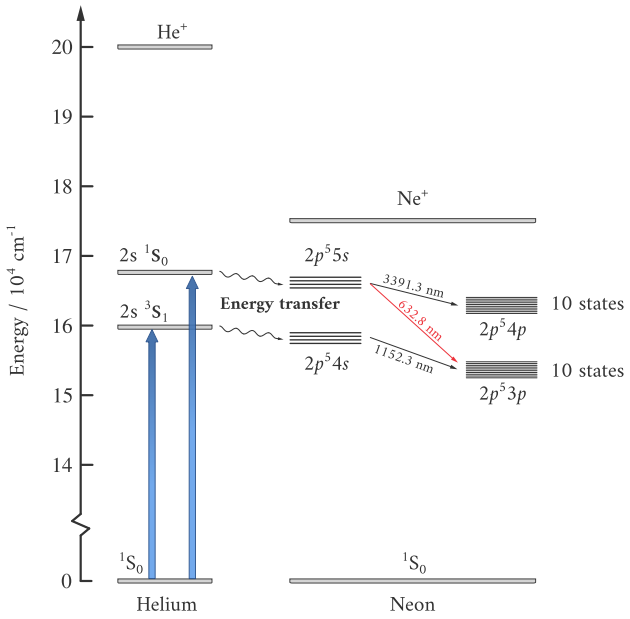


Figure **9.6.1**: An energy level diagram for He and Ne in a He-Ne laser. The pumping creates helium atoms in two excited states. These excited states have energies similar to two sets of four excited states in the Ne atoms. Thus, collisions between the excited He atoms and Ne atoms can lead to nonradiative energy transfer. The excited state Ne atoms have lifetimes that enable a population inversion and lasing. (CC BY-NC; Ümit Kaya via LibreTexts)

The energy level diagram in figure **9.6.1** shows the two excited states of a helium atom, the 2 ^{3}S and 2 ^{1}S, that get populated as a result of electromagnetic pumping. Both of these states are metastable and do not allow de-excitations via radiative transitions. Instead, the helium atoms give off their energy to neon atoms through collisional excitation. In this way, the 4s and 5s levels in neon get populated.

$$He^*(2s^3\,S_1) + Ne(g) \rightarrow He(g) + Ne^*(2p^5 4s)$$

$$He^*(2s^1\,S_0) + Ne(g) \rightarrow He(g) + Ne^*(2p^5 5s)$$

These are the two upper lasing levels, each for a separate set of lasing transitions. Each of these upper lasing levels contains 4 states ($^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$). Radiative decay from the 5s to the 4s levels is forbidden. So, ten states associated with the 4p and 3p levels

serve as the lower lasing levels and rapidly decay into the metastable 3s level. In this way, population inversion is easily achieved in the He-Ne mixture. The 632.8 nm laser transition, for example, involves the 5s and 3p levels, as shown above. Table **9.6.1** lists parameters of several of the Ne transitions.

Table **9.6.1**: Several Lasing Transitions for an Excited State Ne Atom

Transition	λ (nm)	Einstein Coefficient A (s^{-1})	Relative Intensity
$5s^1\ P_1 \rightarrow 3p^3\ P_1$	640.1	0.60×10^6	100
$5s^1\ P_1 \rightarrow 3p^3\ P0$	635.2	0.70×10^6	100
$5s^1\ P_1 \rightarrow 3p^3\ P2$	632.8	6.56×10^6	300
$5s^1\ P_1 \rightarrow 3p^1\ P_1$	629.4	1.35×10^6	100
$5s^1\ P_1 \rightarrow 3p^1\ D_2$	611.8	1.28×10^6	100

In most He-Ne lasers the gas, a mixture of 5 parts helium to 1 part neon, is contained in a sealed glass tube with a narrow (2 to 3 mm diameter) bore as shown above in figure **9.6.2**. Typically the laser's optical cavity mirrors, the high reflector and the output coupler form the two sealing caps for the narrow bore tube. High voltage electrodes create a narrow electric discharge along the length of this tube, which then leads to the narrow beam of laser light.

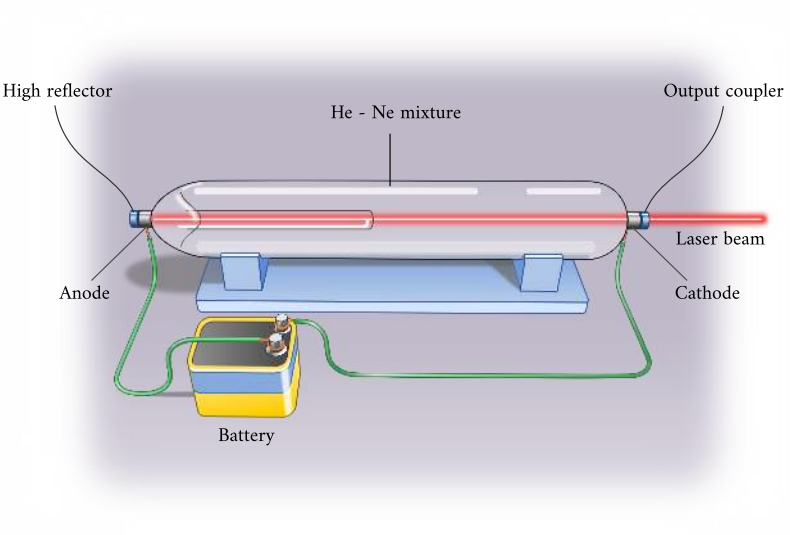


Figure **9.6.2**: A He-Ne laser cavity. (CC BY-NC; Ümit Kaya via LibreTexts)

Many He-Ne lasers also contain a ballast which serves to maintain the desired gas mixture. Since some of the atoms may get embedded in the glass and/or the electrodes as they accelerate within the discharge, in the absence of a ballast the lasing mixture would not last very long. To further prolong the useable life of the laser, some of these lasers also use "getters", often metals such as titanium, that absorb impurities in the gas. Figure **9.6.3** below shows a He-Ne laser with a ballast.

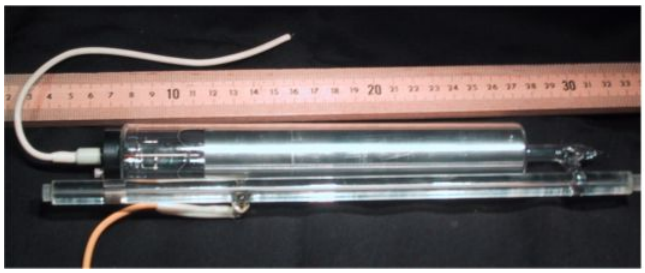


Figure 9.6.3: A commercial He-Ne tube. The thicker cylinder closest to the meter-stick (shown for scale) is the ballast. The thinner tube houses the resonant cavity where the lasing occurs. Notice the two mirrors that seal the two ends of the bore. For mode stability reasons, these mirrors are concave; they serve as the output coupler and the high reflector. (Copyright; author via source)

A typical commercially available He-Ne produces about a few mW of 632.8 nm light with a beam width of a few millimeters at an overall efficiency of near 0.1%. This means that for every 1 Watt of input power from the power supply, 1 mW of laser light is produced. Still, because of their long operating lifetime of 20,000 hours or more and their relatively low manufacturing cost, He-Ne lasers are among the most popular gas lasers.

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9.7: Modern Applications of Laser Spectroscopy

9.7.1: A Quick Overview

Laser light offers valuable tools to researchers who wish to use the interaction of light with matter to interrogate atomic and molecular systems. Most laser light is characterized by its near monochromaticity (relative to light from other sources), directionality, and coherence [1]. Those characteristics are used in modern laser spectroscopy. The monochromaticity of laser light allows it to be used to probe specific energy changes in atoms and molecules. This ability to select specific wavelengths allows scientists to focus on chosen components in mixtures, including complex reaction mixtures. For example, Park et. al. tracked the dynamics of the reaction of ground state oxygen with ethyl radical by using a 355 nm laser beam to track one of the products of this reaction [2]. Parsons et. al. used near monochromatic laser light sources to achieve state-selective ionization for the study of the products of a photodissociation reaction of atmospheric relevance [3]. Laser monochromaticity can be used to quantify the amount of greenhouse gases in the atmosphere [4]. Even when the samples are not mixtures, monochromaticity allows researchers to gather detailed information about atomic and/or molecular structure. Applications of this type are extremely numerous, including detailed studies of atomic systems [5], semiconductor materials [6], single molecules [7], and biological molecules [8]. Lasers find research applications in art and archeology, where the property of monochromaticity allows specific energies to be probed and laser beam directionality and small spot size curtail destruction of samples [9,10].

Other laser applications focus on the ability of pulsed lasers to provide short pulses. Short-pulsed lasers offer myriad tools for exploring chemical kinetics at a range of timescales, including very short ones. Short-pulse lasers open the opportunity for time-resolved studies of molecular processes such as reaction processes [2,11] and biological processes [12 - 15], and the properties of excited states [16]. Some research applications take advantage of the ability of certain lasers to produce high intensity light. One such application is laser-induced break down spectroscopy (LIBS), in which the high intensity of the laser creates a plasma from solid or liquid samples; that plasma can subsequently be probed [17]. Other techniques that exploit high laser intensities are the nonlinear spectroscopies, where the high intensities of some lasers can produce behaviors in samples that lower-power sources cannot sufficiently stimulate [18,19]. Although most lasers are monochromatic and coherent, some researchers have modified laser light to obtain information from broadband, incoherent laser light [20 – 22], which allows them to probe the response of samples to light that more resembles sunlight (incoherent) than do traditional laser sources [22, 23]. Another possibility is to probe multiple wavelengths with broadband laser sources that are coherent [24].

9.7.2: Conclusion

This brief overview has only skimmed the surface of the vast field of laser spectroscopy. The examples given here are a very small, somewhat arbitrary, and significantly biased subset of the enormous library of published laser-based experiments. References have been chosen to give examples of the topics covered here and have not been extensively reviewed by the author.

Overall, lasers are especially useful as light sources when one or more of the following properties are desired for light in an experiment:

1. A high degree of monochromaticity
2. A well-known central wavelength for a light source
3. A tunable light source
4. Spatial coherence
5. Phase coherence
6. Directionality
7. High intensity
8. Tight focus
9. Short pulses

A particular laser type will not necessarily have all the properties in the list above; however, the menu of available laser types allows a researcher to choose a laser system or systems with the characteristics needed for a particular experiment. New applications of laser spectroscopy and new spectroscopic techniques employing laser light continue to be invented.

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9.7.4: Contributor

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(Thank you to Tom Neils (Grand Rapids Community College) for editing the references)

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9.8: The Beer-Lambert Law

The Beer-Lambert law relates the attenuation of light to the properties of the material through which the light is traveling. This page takes a brief look at the Beer-Lambert Law and explains the use of the terms absorbance and molar absorptivity relating to UV-visible absorption spectrometry.

The Absorbance of a Solution

For each wavelength of light passing through the spectrometer, the intensity of the light passing through the reference cell is measured. This is usually referred to as I_o - that's I for Intensity.

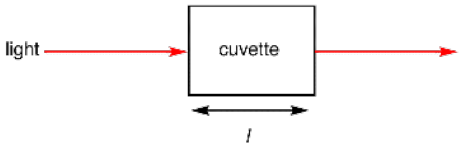


Figure 9.8.1: Light absorbed by sample in a cuvette

The intensity of the light passing through the sample cell is also measured for that wavelength - given the symbol, I. If I is less than I_o, then the sample has absorbed some of the light (neglecting reflection of light off the cuvette surface). A simple bit of math is then done in the computer to convert this into something called the absorbance of the sample - given the symbol, A. The absorbance of a transition depends on two external assumptions.

1. The absorbance is directly proportional to the concentration (c) of the solution of the sample used in the experiment.
2. The absorbance is directly proportional to the length of the light path (l), which is equal to the width of the cuvette.

Assumption one relates the absorbance to concentration and can be expressed as

$$A \propto c \tag{9.8.1}$$

The absorbance (A) is defined via the incident intensity I_o and transmitted intensity I by

$$A = \log_{10}\left(\frac{I_o}{I}\right) \tag{9.8.2}$$

Assumption two can be expressed as

$$A \propto l \tag{9.8.3}$$

Combining Equations 9.8.1 and 9.8.3:

$$A \propto cl \tag{9.8.4}$$

This proportionality can be converted into an equality by including a proportionality constant (ϵ).

$$A = \epsilon cl \tag{9.8.5}$$

This formula is the common form of the *Beer-Lambert Law*, although it can be also written in terms of intensities:

$$A = \log_{10}\left(\frac{I_o}{I}\right) = \epsilon lc \tag{9.8.6}$$

The constant ϵ is called **molar absorptivity** or **molar extinction coefficient** and is a measure of the probability of the electronic transition. On most of the diagrams you will come across, the absorbance ranges from 0 to 1, but it can go higher than that. An absorbance of 0 at some wavelength means that no light of that particular wavelength has been absorbed. The intensities of the sample and reference beam are both the same, so the ratio I_o/I is 1 and the $\log_{10}$ of 1 is zero.

Example 9.8.1

In a sample with an absorbance of 1 at a specific wavelength, what is the relative amount of light that was absorbed by the sample?

Solution

This question does not need Beer-Lambert Law (Equation 9.8.5) to solve, but only the definition of absorbance (Equation 9.8.2)

$$A = \log_{10}\left(\frac{I_o}{I}\right)$$

The relative loss of intensity is

$$\frac{I - I_o}{I_o} = 1 - \frac{I}{I_o}$$

Equation 9.8.2 can be rearranged using the properties of logarithms to solved for the relative loss of intensity:

$$10^A = \frac{I_o}{I}$$

$$10^{-A} = \frac{I}{I_o}$$

$$1 - 10^{-A} = 1 - \frac{I}{I_o}$$

Substituting in $A = 1$

$$1 - \frac{I}{I_o} = 1 - 10^{-1} = 1 - \frac{1}{10} = 0.9$$

Hence 90% of the light at that wavelength has been absorbed and that the transmitted intensity is 10% of the incident intensity. To confirm, substituting these values into Equation 9.8.2 to get the absorbance back:

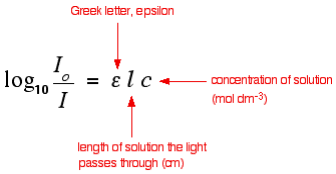
$$\frac{I_o}{I} = \frac{100}{10} = 10 \tag{9.8.7}$$

and

$$\log_{10} 10 = 1 \tag{9.8.8}$$

The Beer-Lambert Law

You will find that various different symbols are given for some of the terms in the equation - particularly for the concentration and the solution length.



The Greek letter epsilon in these equations is called the **molar absorptivity** - or sometimes the molar absorption coefficient. The larger the molar absorptivity, the more probable the electronic transition. In uv spectroscopy, the concentration of the sample solution is measured in mol L^{-1} and the length of the light path in cm. Thus, given that absorbance is unitless, the units of molar absorptivity are L mol^{-1} cm^{-1}. However, since the units of molar absorptivity is always the above, it is customarily reported without units.

Example 9.8.2: Guanosine

Guanosine has a maximum absorbance of 275 nm. $\epsilon_{275} = 8400 M^{-1} cm^{-1}$ and the path length is 1 cm. Using a spectrophotometer, you find the that $A_{275} = 0.70$. What is the concentration of guanosine?

Solution

To solve this problem, you must use Beer's Law.

$$A = \epsilon l c \tag{9.8.9}$$

$$0.70 = (8400\ M^{-1}\ cm^{-1})(1\ cm)(c)$$

Next, divide both side by [(8400 M^{-1} cm^{-1})(1 cm)]

$$c = 8.33x10^{-5}\ mol/L$$

Example 9.8.3

There is a substance in a solution (4 g/liter). The length of cuvette is 2 cm and only 50% of the certain light beam is transmitted. What is the extinction coefficient?

Solution

Using Beer-Lambert Law, we can compute the absorption coefficient. Thus,

$$-\log\left(\frac{I_t}{I_o}\right) = -\log(\frac{0.5}{1.0}) = A = 8\epsilon$$

Then we obtain that

$$\epsilon = 0.0376$$

Example 9.8.4

In Example 3 above, what is the molar absorption coefficient if the molecular weight is 100?

Solution

It can simply obtained by multiplying the absorption coefficient by the molecular weight. Thus,

$$\epsilon = 0.0376 \text{ x } 100 = 3.76\ L{\cdot}mol^{-1}{\cdot}cm^{-1}$$

The Importance of Concentration

The proportion of the light absorbed will depend on how many molecules it interacts with. Suppose you have got a strongly colored organic dye. If it is in a reasonably concentrated solution, it will have a very high absorbance because there are lots of molecules to interact with the light. However, in an incredibly dilute solution, it may be very difficult to see that it is colored at all. The absorbance is going to be very low. Suppose then that you wanted to compare this dye with a different compound. Unless you took care to make allowance for the concentration, you couldn't make any sensible comparisons about which one absorbed the most light.

Example 9.8.4

In Example **9.8.3** above, how much is the beam of light is transmitted when 8 g/liter ?

Solution

Since we know ϵ, we can calculate the transmission using Beer-Lambert Law. Thus,

$$log(1) - log(I_t) = 0 - log(I_t) = 0.0376 \text{ x } 8 \text{ x } 2 = 0.6016$$

$$log(I_t) = -0.6016$$

Therefore, $I_t = 0.2503 = 25\%$

Example 9.8.5

The absorption coefficient of a glycogen-iodine complex is 0.20 at light of 450 nm. What is the concentration when the transmission is 40 % in a cuvette of 2 cm?

Solution

It can also be solved using Beer-Lambert Law. Therefore,

$$-\log(I_t) = -\log_{10}(0.4) = 0.20 \times c \times 2 \tag{9.8.10}$$

Then c = 0.9948

The importance of the container shape

Suppose this time that you had a very dilute solution of the dye in a cube-shaped container so that the light traveled 1 cm through it. The absorbance is not likely to be very high. On the other hand, suppose you passed the light through a tube 100 cm long containing the same solution. More light would be absorbed because it interacts with more molecules. Again, if you want to draw sensible comparisons between solutions, you have to allow for the length of the solution the light is passing through. Both concentration and solution length are allowed for in the Beer-Lambert Law.

Molar Absorptivity

The Beer-Lambert law (Equation 9.8.5) can be rearranged to obtain an expression for ϵ (the molar absorptivity):

$$\epsilon = \frac{A}{lc} \tag{9.8.11}$$

Remember that the absorbance of a solution will vary as the concentration or the size of the container varies. Molar absorptivity compensates for this by dividing by both the concentration and the length of the solution that the light passes through. Essentially, it works out a value for what the absorbance would be under a standard set of conditions - the light traveling 1 cm through a solution of 1 mol dm^{-3}. That means that you can then make comparisons between one compound and another without having to worry about the concentration or solution length.

Values for molar absorptivity can vary hugely. For example, ethanal has two absorption peaks in its UV-visible spectrum - both in the ultra-violet. One of these corresponds to an electron being promoted from a lone pair on the oxygen into a pi anti-bonding orbital; the other from a π bonding orbital into a π anti-bonding orbital. Table 1 gives values for the molar absorptivity of a solution of ethanal in hexane. Notice that there are no units given for absorptivity. That's quite common since it assumes the length is in cm and the concentration is mol dm^{-3}, the units are mol^{-1} dm^3 cm^{-1}.

Table **9.8.1**

electron jump	wavelength of maximum absorption (nm)	molar absorptivity
lone pair to π anti-bonding orbital	290	15
π bonding to π anti-bonding orbital	180	10,000

The ethanal obviously absorbs much more strongly at 180 nm than it does at 290 nm. (Although, in fact, the 180 nm absorption peak is outside the range of most spectrometers.) You may come across diagrams of absorption spectra plotting absorptivity on the vertical axis rather than absorbance. However, if you look at the figures above and the scales that are going to be involved, you aren't really going to be able to spot the absorption at 290 nm. It will be a tiny little peak compared to the one at 180 nm. To get around this, you may also come across diagrams in which the vertical axis is plotted as $\log_{10}$(molar absorptivity).

If you take the logs of the two numbers in the table, 15 becomes 1.18, while 10,000 becomes 4. That makes it possible to plot both values easily, but produces strangely squashed-looking spectra!

Contributors and Attributions

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9.9: 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.

9.9.1: 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.

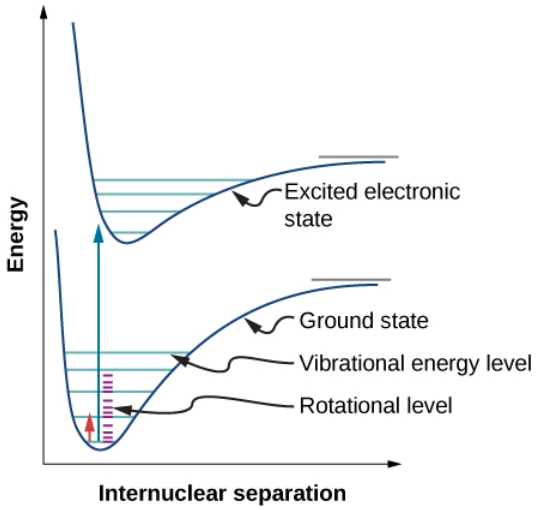


Figure **9.9.1** : Three types of energy levels in a diatomic molecule: electronic, vibrational, and rotational. If the vibrational quantum number (n) changes by one unit, then the rotational quantum number (l) changes by one unit. (CC BY 3.0; OpenStax).

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:

$$\tilde{E}_{total} = \tilde{\nu}_{el} + G(v) + F(J) \tag{9.9.1}$$

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 9.9.1 can be expanded accordingly:

$$\tilde{E}_{total} = \underbrace{\tilde{\nu}_{el}}_{\text{electronic}} + \underbrace{\tilde{\nu}_e\left(v+\frac{1}{2}\right) - \tilde{\chi}_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^2}_{\text{vibrational}} + \underbrace{\tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2}_{\text{rotational}} \tag{9.9.2}$$

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.

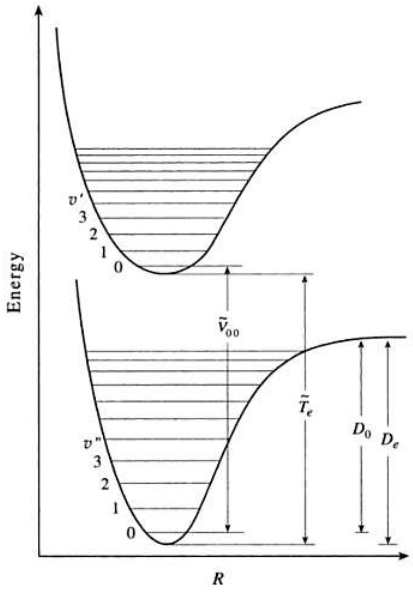


Figure **9.9.2** : As you can see, electronic transitions involve two energy potential wells! The vibrational levels are included, but rotational levels are excluded.

The eigenstate-to-eigenstate transitions (e.g., $\mathbf{1 \rightarrow 2}$) possible are numerous and have absorption lines at

$$\tilde{\nu}_{obs} = \tilde{E}_2 - \tilde{E}_1 \tag{9.9.3}$$

and for simplification, we refer to constants associated with these states as $|'\rangle$ and $|''\rangle$, respectively. So Equation 9.9.3 is

$$\tilde{\nu}_{obs} = E''\tilde{(v'')} - E'\tilde{(v')}$$

Also important to note that typically vibronic transitions are usually the result of the vibrational $v' = 0$ vibratonal state. Within this assumption and excluding the rotational contributions (due to their low energies), Equation 9.9.2 can be used with Equation 9.9.3 to get

$$\tilde{\nu}_{obs} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right) + \tilde{\nu}'_e v'' - \tilde{\chi}'_e\tilde{\nu}'_e v''(v''+1) \tag{9.9.4}$$

A common transition of importance is the $\tilde{\nu}_{00}$, which is the $\mathbf{0 \rightarrow 0}$ transition and include no vibrational change. For this case, equation 9.9.4 is then

$$\tilde{\nu}_{00} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right)$$

This is the lowest energy possible to observe in an electronic transition although it may be of low intensity as discussed in the following section.

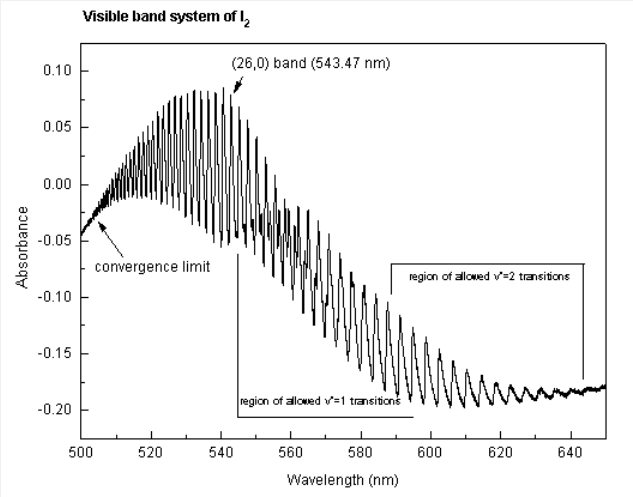
Iodine

The absorption spectrum of iodine yields information about the excited state well rather than the ground state well (notice that equation 9.9.4 depends primarily on excited state parameters). In this experiment you will characterize the excited state well by extracting values for the following excited state parameters.

Recall that as v' increases, the vibrational energy spacing decreases. At the upper edge of the well, the vibrational energy spacing decreases to 0, which means that the energies form a continuum rather than being quantized. It is at this limit that **bond dissociation occurs**. The energy required to dissociate the bond is actually D'_o rather than D'_e because the molecule cannot have less than **the zero point energy**.

The vibrational-electronic spectrum of I_2 in the region from 500-650 nm displays a large number of well-defined bands which, for the most part, correspond to v'<-- 0 transitions connecting the v" = 0 vibrational level of the ground electronic state (denoted as $X^1\Sigma^+$) to many different vibrational levels v' of the excited $B^3\Pi$ electronic state. Under the conditions of this

experiment (i.e., low resolution), the rotational lines within each band are not resolved. However, the peaks may be identified as R-branch band heads (1). For a molecule as heavy as I_2, the position of each band head is within a few tenths of one cm^{-1} of the band origin (2), and for the purposes of this experiment, the distinction between the two may be ignored. The general features of the absorption spectrum are shown below:



Each small bump, or peak, such as the (26,0) band labelled on the spectrum, corresponds to a transition between two vibrational levels and is called a *band*. Each band is comprised of several hundred *lines*, each of which involves different upper and lower rotational quantum numbers; as mentioned, these lines are not resolved in the present experiment. The region of maximum absorption in each band is caused by many of these lines falling together; it is called the *band head*. The set of all of these bands is referred to as the *visible band system* of I_2.

If the sample is hot, then excited vibrational levels of the ground state may be populated, and these also will absorb light. The *hot bands* arising from absorption from v"=1 and v"=2 are shown very approximately on the absorption spectrum above.

At a point called the *convergence limit*, the spacing between bands decreases to zero. Beyond this convergence limit, the spectrum is continuous because the excited state of the I_2 molecule is not bound. One of the purposes of this experiment is to identify this convergence limit accurately.

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9.10: The Franck-Condon Principle

Learning Objectives

- To explain the vibrational fine structure in electronic spectroscopy for bound excited states in terms of the Franck-Condon approximation
- To calculate the vibrational progressions (Franck-Condon factors) in a single displaced harmonic oscillator vibronic system.

The **Franck-Condon Principle** describes the intensities of vibronic transitions, or the absorption or emission of a photon. It states that when a molecule is undergoing an electronic transition, such as ionization, the nuclear configuration of the molecule experiences no significant change. This is due in fact that nuclei are much more massive than electrons and the electronic transition takes place faster than the nuclei can respond. When the nucleus realigns itself with the new electronic configuration, the theory states that it must undergo a vibration.

If we picture the vertical transition from ground to excited electronic state as occurring from a vibrational wavefunction that gives a probability distribution of finding the nuclei in a give region of space we can determine the probability of a given vibrational level from the overlap integral $S_{v',v}$ which gives the overlap of the vibrational wavefunction in the ground and excited state. The v' quantum numbers refer to the ground state and the v quantum numbers refer to the excited state. The transition probability can be separated into electronic and nuclear parts using the Condon approximation.

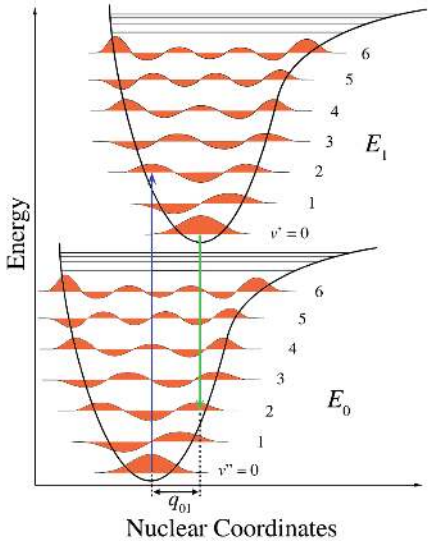


Figure 9.10.1 : Franck–Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v' = 2$. (CC-SA-BY-3.0; Samoza).

In Figure 9.10.1 , the nuclear axis shows a consequence of the internuclear separation and the vibronic transition is indicated by the blue and green vertical arrows. This figure demonstrates three things:

1. An absorption leads to a higher energy state,
2. fluorescence leads to a lower energy state, and
3. the shift in nuclear coordinates between the ground and excited state is indicative of a new equilibrium position for nuclear interaction potential. The fact that the fluorescence arrow is shorter than the absorption indicates that it has less energy, or that its wavelength is longer.

The Classical Condon approximation

Condon approximation is the assumption that the electronic transition occurs on a time scale short compared to nuclear motion so that the transition probability can be calculated at a fixed nuclear position.

This change in vibration is maintained during a state termed the **rapid electronic excitation**. The resulting Coulombic forces produce an equilibrium as shown in the figure for the nuclei termed a turning point. The turning point can be mapped by drawing a vertical line from the minimum of the lower curve to the intersection of the higher electronic state. This procedure is termed a **vertical transition** and was discussed before in the context of photoelectron spectroscopy (another electronic spectroscoy).

The Franck-Condon Principle explains the relative intensities of vibronic transitions by relating the probability of a vibrational transition to the overlap of the vibrational wavefunctions. It states that the probability of a vibrational transition occurring is weighted by the Franck-Condon overlap integral:

$$\begin{aligned} _{i\rightarrow f} &= \left|\langle \psi^*_{final} \left|\mu\right| \psi_{initial}\rangle\right|^2 \\ &= \left|\int \psi^*_{final} \mu \psi_{initial} d\tau\right|^2 \end{aligned}$$

Within the Franck-Condon approximation, the nuclei are considered "fixed" during electronic transitions. Thus, electronic transitions can be considered vertical transitions on electronic potential energy curves (vierical transitions in Figure **9.10.1**).

The Quantum Franck-Condon Principle

The Franck-Condon Principle has both a Classical and Quantum application. Classically, the Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

The Franck-Condon principle is based on the Born-Oppenheimer approximation, which allows separation of the electronic q and nuclear Q wavefunctions given the total wavefunction.

$$|\psi_{total}(Q,q) = |\psi_{nuc}(Q)\rangle\psi_{el}(Q;q)\rangle$$

Since the transition operator, $\hat{\mu}(q)$, is dependent only on the electronic component, the nuclear components can be separated from the transition moment integral that dictates the probability of the transition occurring:

$$\langle \psi^*_{total,f} \left|\hat{\mu}\right| \psi_{total,i}\rangle = \langle \psi^*_{nuc,f} \left|\langle \psi^*_{el,f} \left|\mu\right| \psi_{el,i}\rangle\right| \psi_{nuc,i}\rangle \tag{9.10.1}$$

$$= \underbrace{\langle \psi^*_{nuc,f} | \psi_{nuc,i}\rangle}_{\text{nuclear overlap}} \langle \psi^*_{el,f} \left|\mu\right| \psi_{el,i}\rangle \tag{9.10.2}$$

If the nuclear overlap integral is zero for this transition, then the transition will not be observed, irrespective of the magnitude of the electronic factor.

9.10.1: 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

$$|\psi(R)\rangle = \left|\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2}\right\rangle$$

The zero-point wavefunction in the excited electronic state is

$$|\psi(R)\rangle = \left|\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-Q_e)^2/2}\right\rangle$$

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

$$S_{00} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} e^{-\alpha(R-Q_e)^2/2} dR \tag{9.10.3}$$

The exponent in Equation 9.10.3 can be expanded as

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(2R^2 - RR_e - 2RQ_e + R_e^2 + Q_e^2)/2} dR \tag{9.10.4}$$

and we use

$$(R_e + Q_e)^2 = R_e^2 + Q_e^2 + 2R_eQ_e$$

and

$$(R_e - Q_e)^2 = R_e^2 + Q_e^2 - 2R_eQ_e$$

to substitute and complete the square inside the integral. We can express

$$R_e^2 + Q_e^2 = \frac{1}{2}[(R_e + Q_e)^2 + (R_e - Q_e)^2].$$

Thus, the integral in Equation 9.10.4 is

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \int_{-\infty}^{\infty} e^{-\alpha\{R - 1/2(R_e + Q_e)\}^2} dR$$

The integral is a **Gaussian integral**. You can show that if we let $z = \sqrt{\alpha}\{R - 1/2(R_e + Q_e)\}$ then $dz = \sqrt{\alpha} dR$ and the integral becomes

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \frac{1}{\sqrt{\alpha}} \int_{-\infty}^{\infty} e^{z^2} dz \tag{9.10.5}$$

this integral has been solved already, from a table of integrals, Equation 9.10.5 becomes

$$S_{00} = e^{-\alpha(R_e - Q_e)^2/4}$$

We would follow the same procedure to calculate that overlap of the zeroth level vibration in the ground to the first excited vibrational level of the excited state: S_{01}.

9.10.2: 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 $x = \sqrt{\alpha}(R - Q_e)$.

$$S_{01} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle \tag{9.10.6}$$

with the zero-point wavefunction in the ground electronic state is

$$|\psi(R)\rangle = \left| \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2} \right\rangle$$

The first excited-state wavefunction in the excited electronic state is

$$|\psi(R)\rangle = \left| \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{\alpha} 2(R - Q_e) e^{-\alpha(R-Q_e)^2/2} \right\rangle$$

The overlap of zeroth ground state level with the first excited state level (Equation 9.10.6) is then

$$S_{01} = \frac{1}{\sqrt{2}} \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} \sqrt{\alpha} 2(R - Q_e) e^{-\alpha(R-Q_e)^2/2}$$

and

$$S_{01} = \sqrt{\frac{2\alpha^2}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \int_{-\infty}^{\infty} (R - Q_e) e^{-\alpha\{R - 1/2(R_e + Q_e)^2\}}$$

The same substitutions can be made as above so that the integral can be written as (not shown and to be demonstrated in a homework exercises) and the final result is

$$S_{01} = \sqrt{\frac{\alpha^2}{2}} (R_e - Q_e) e^{-\alpha(R_e - Q_e)^2/4}$$

We could continue and calculate that overlap of the zeroth level in the ground state with all the higher light vibrational levels: S_{02}, S_{03}, etc. Each term corresponds to a transition with a different energy since the vibrational levels have different energies. The absorption band then has the appearance of a progression (a Franck-Condon progression) of transitions between different levels each with its own probability.

9.10.3: 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.

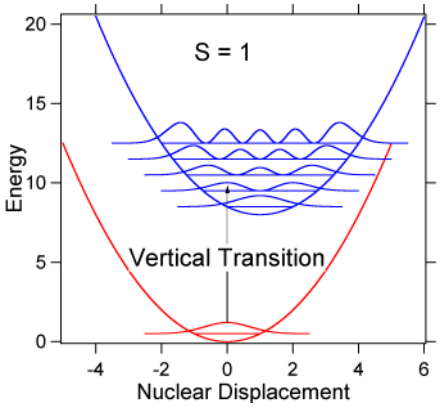


Figure **9.10.2** : Wavefunctions transitions for a harmonic oscillator model system with moderate displacement (S=1).

According to the above model for the Franck-Condon factor we would generate a "stick" spectrum (Figure **9.10.3**) 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.

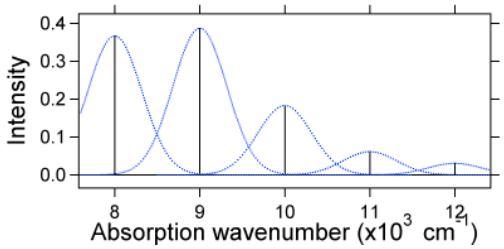


Figure **9.10.3** : Stick spectrum, dressed with Gaussians, for the moderate displacement (S=1) harmonic oscillator system from Figure **9.10.2** .

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:

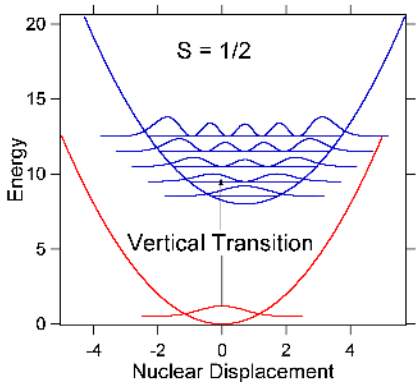


Figure **9.10.4** : Wavefunctions transitions for a harmonic oscillator model system with small displacement (S=1/2).

For this case the "stick" spectrum has the appearance in Figure **9.10.5**

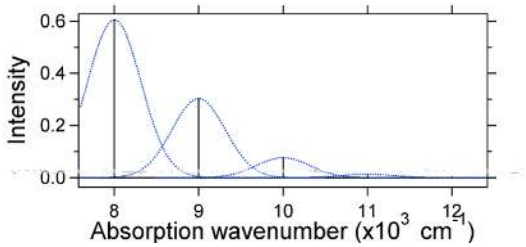


Figure **9.10.5** : Stick spectrum, dressed with Gaussians, for the small displacement (S=1/2) harmonic oscillator system from Figure **9.10.4**.

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.

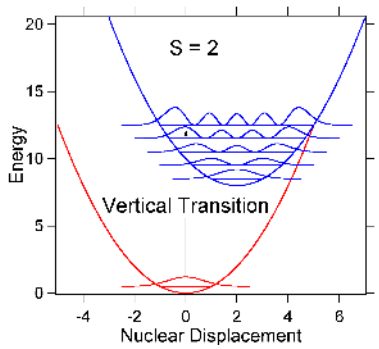


Figure **9.10.6** : Wavefunctions transitions for a harmonic oscillator model system with strong displacement (S=2).

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.

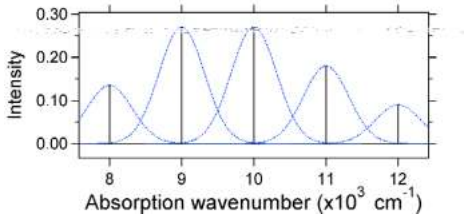


Figure **9.10.7** : Stick spectrum, dressed with Gaussians, for the large displacement (S=2) harmonic oscillator system from Figure **9.10.6**.

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.

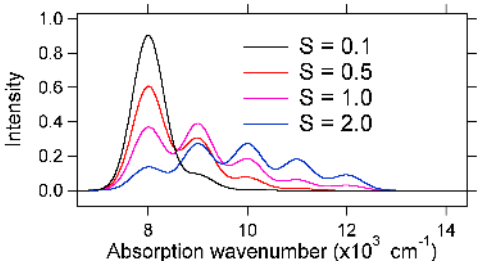


Figure **9.10.8** : Stick spectra, dressed with Gaussians, for the small to large displacements in harmonic oscillator system described above.

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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9.11: Electronically Excited Molecules can Relax by a Number of Processes

To understand how lasers work we must first describe how a molecule in an excited state can relax back to the ground state because the light emitted by a laser is influenced by these relaxation processes. The two radiative decay pathways for an excited molecule are fluorescence and phosphorescence. Fluorescence differs from phosphorescence in that the energy transition that is responsible for fluorescence does not involve a change in electron spin multiplicity. Thus fluorescence lifetimes are short (10^{-9} - 10^{-6} s). In phosphorescence, there is a change in electron spin multiplicity, resulting in a longer lifetime of the excited state (second to minutes). A description of electron spin and the differences between singlet and triplet states will clarify the difference between fluorescence and phosphorescence.

9.11.1: Spin Multiplicity - Singlet and Triplet Excited States

The Pauli Exclusion principle states that two electrons in an atom cannot have the same four quantum numbers (n, l, m_l, m_s). Therefore, because two electrons can occupy each orbital, these two electrons must have opposite spin states. These opposite spin states are called spin pairing. Because of this spin pairing, most molecules are diamagnetic, and are not attracted or repelled by an external magnetic or electric field. Molecules that contain unpaired electrons (free radicals) do have magnetic moments that are attracted to an external magnetic or electric field.

A molecule is said to be in a singlet state when all the electron spins are paired in the molecular electronic state, and the electronic energy levels do not split when the molecule is exposed to a magnetic field. A doublet state occurs when there is an unpaired electron that gives two possible orientations when exposed to a magnetic field and imparts different energies to the system. A singlet or a triplet state can form when one electron is excited to a higher energy level. In an excited singlet state, the promoted electron retains the spin orientation it had in the ground state (i.e., paired). In a triplet excited state, the promoted electron undergoes a change in spin, and so has the same spin orientation (parallel) to the unpaired electron that remains in the ground state orbital. The difference between the spins of ground singlet, excited singlet, and excited triplet is shown in Figure 9.11.1. The terms singlet, doublet and triplet are derived using the equation for multiplicity, 2S+1, where S is the total spin angular momentum (sum of all the electron spins). Individual spins are denoted as spin up (s = +1/2) or spin down (s = -1/2). If we were to calculate the multiplicity for the singlet ground state or the singlet excited state, the equation would be

$$2(+1/2 + -1/2) + 1 = 2(0) + 1 = 1$$

In a similar fashion, the spin multiplicity for the triplet excited state can be calculated as

$$2(+1/2 + +1/2) + 1 = 2(1) + 1 = 3$$

which gives a triplet state as expected.

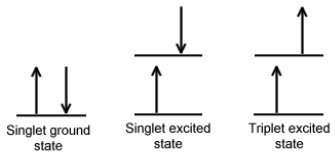


Figure 9.11.1: Spin in the ground and excited states (Tyler Matthews - Paint Shop Pro, Public Domain, https://commons.wikimedia.org/w/inde...curid=64926546)

The difference between a molecule in the ground and the triplet excited state is that the molecule is diamagnetic in the ground state and paramagnetic in the triplet excited state. This difference in spin state makes the transition from singlet to triplet (or triplet to singlet) less likely than the singlet-to-singlet transitions. For this reason, the lifetime of the triplet state is longer than the lifetime of the singlet state by a factor of roughly 10^4 seconds. The transition from ground to excited triplet state has a low probability of occurring, thus these absorption bands are less intense than singlet-singlet state absorption bands. However, an excited triplet state can be populated from an excited singlet state of certain molecules. Jablonski diagrams can be used to explain transitions such as this that occur in photoluminescence molecules.

9.11.2: Jablonski Diagrams

Aleksander Jablonski was a Polish academic who devoted his life to the study of molecular absorbance and emission of light. He developed a graphic representation that shows the possible consequences of applying photons from the visible spectrum of light to a particular molecule. These schematics are referred to as Jablonski diagrams.

A Jablonski diagram is an energy diagram, arranged with energy on a vertical axis. The energy levels can be quantitatively denoted, but most of these diagrams use energy levels schematically. The rest of the diagram is arranged into columns. Every column usually represents a specific spin multiplicity for a particular species. However, some diagrams divide energy levels within the same spin multiplicity into different columns. Within each column, horizontal lines represent eigenstates for that particular molecule. Bold horizontal lines are representations of the limits of electronic energy states. Within each electronic energy state are multiple vibrational energy states that may be coupled with the electronic state. Usually only a portion of these vibrational eigenstates are represented due to the massive number of possible vibrations in a molecule. Each of these vibrational energy states can be subdivided even further into rotational energy levels; however, typical Jablonski diagrams omit such intense levels of detail.

Through the use of straight and wavy lines, these figures show transitions between eigenstates that occur from the exposure of a molecule to a particular wavelength of light. Straight lines show the conversion between a photon of light and the energy of an electron. Wavy lines show nonradiative transitions of electrons. Within a Jablonski diagram several different pathways show how an electron may accept and then dissipate the energy from a photon. Thus, most diagrams start with arrows originating from the ground electronic state and finish with arrows returning to the ground electronic state.

The Jablonski diagram that drawn below is a partial energy diagram that represents the energy of a photoluminescent molecule in its different energy states. The lowest and darkest horizontal line represents the ground-state electronic energy of the molecule which is the singlet state labeled as S_0. At room temperature, a majority of the molecules are in this state. The thicker lines on the left labeled S_1, S_2 , and S_3 represent the excited electronic states for the molecule in the singlet state. The thicker lines on the right labeled T_1, T_2, and T_3 represent excited triplet states.

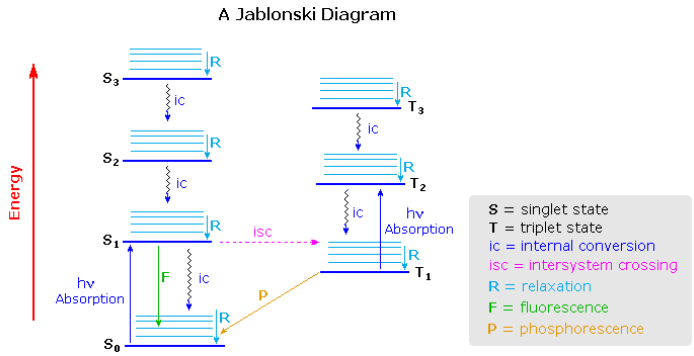


Figure **9.11.2**: Partial Jablonski Diagram for Absorption, Fluorescence, and Phosphorescence. (Bill Reusch, Michigan State University).

9.11.3: 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 **9.11.2**.The deactivation process of fluorescence and phosphorescence involve an emission of a photon radiation as shown by the straight arrow in Figure **9.11.2**. The wiggly arrows in Figure **9.11.2** are deactivation processes without the use of radiation. The favored deactivation process is the route that is most rapid and spends the least time in the excited state. If the rate constant for relaxation is more favorable in the radiationless path, the fluorescence will be less intense or absent.

9.11.3.1: Relaxation and Fluorescence

Often, when an excited state species relaxes, giving off a photon, the wavelength of the photon is different from the one that initially led to excitation. When this happens, the photon is invariably red-shifted; its wavelength is longer than the initial one. This situation is called "fluorescence" (Figure **9.11.3**).

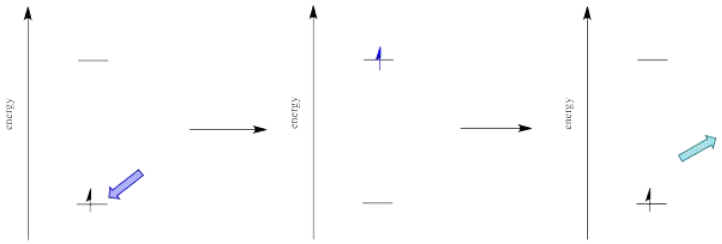


Figure 9.11.3: The absorption of purple light by a ground state particle, leading to the creation of an excited state particle. This excited state particle then emits blue light as it returns to the ground state.

How can that be? Isn't energy quantized? How is the molecule suddenly losing some of the energy that the original photon brought with it? This energy discrepancy is related to the Franck-Condon principle from the previous page. When an electron is promoted to an electronic excited state, it often ends up in an excited vibrational state as well (Figure 9.11.4). Vibrational energy, however, is not exchanged exclusively by means of photons. It can be gained or lost through molecular collisions and heat transfer.

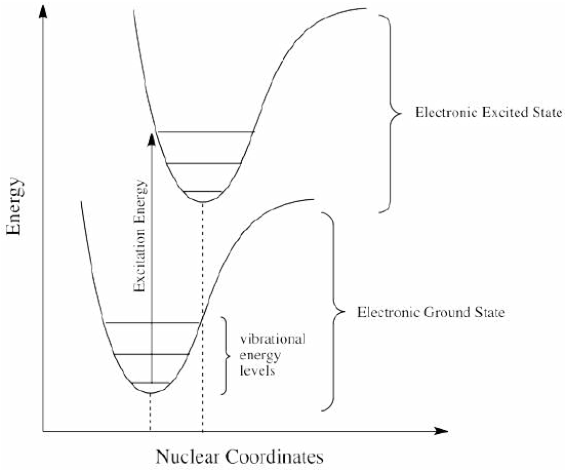


Figure 9.11.4: Transition from the ground state to an excited vibrational state within the excited electronic state.

Thus, an excited state molecule with an electron in a high-energy vibrational level within an excited electronic state might simply re-emit a photon of exactly the same wavelength as the one that was absorbed. But the excited electron is much more likely to relax into the lowest vibrational state within the excited electronic state, losing some of that initial excitation energy as heat. When the electron relaxes to this lower vibrational state, the energy gap between this excited state and the ground state is a little smaller. The photon that is emitted upon fluorescence will have lower energy and longer wavelength than a photon emitted from the original, higher vibrational level, excited state. See Figure 9.11.5.

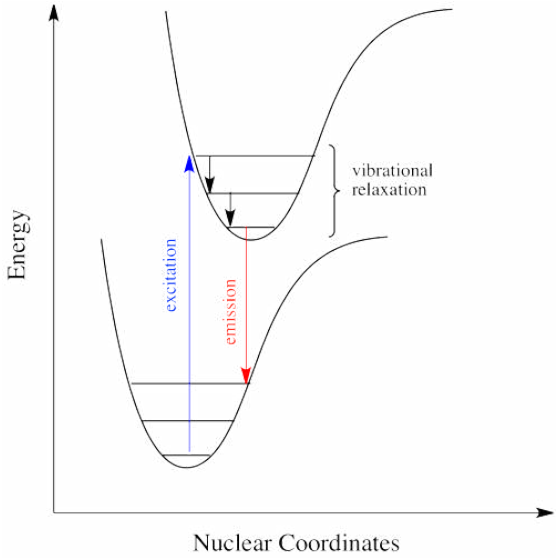


Figure 9.11.5: Excitation, followed by vibrational relaxation, and then emission.

Figure 9.11.6 shows the fluorescence transitions of a hypothetical diatomic molecule in which the equilibrium bond length of the ground state and the first singlet excited state are identical. In this molecule all absorptions involve transitions from the lowest vibrational level of the electronic ground state ($v'' = 0$) to various vibrational levels in the excited electronic state. Because vibrational relaxation occurs more rapidly than fluorescence, the fluorescence spectrum is composed of lines showing transitions from the lowest vibrational level of the excited state ($v' = 0$) to various vibrational levels in the electronic ground state.

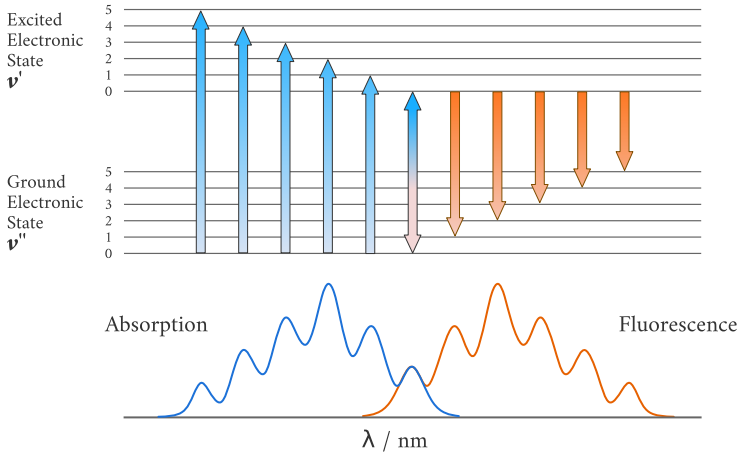


Figure 9.11.6: Absorption and fluorescence transitions in a hypothetical diatomic molecule in which the equilibrium bond length of the ground state is equal to the equilibrium bond length of the excited state. (CC BY-NC; Ümit Kaya, via LibreTexts)

Just how does a molecule undergo vibrational relaxation? Vibrational energy is the energy used to lengthen or shorten bonds, or to widen or squeeze bond angles. Given a big enough molecule, some of this vibrational energy could be transferred into bond lengths and angles further away from the electronic transition. Otherwise, if the molecule is small, it may transfer some of its energy in collisions with other molecules. In molecules, as one molecule drops to a lower vibrational state, the other will hop up to a higher vibrational state with the energy it gains. In Figure 9.11.7 below, the red molecule is in an electronic excited and vibrational state. In a collision, it transfers some of its vibrational energy to the blue molecule.

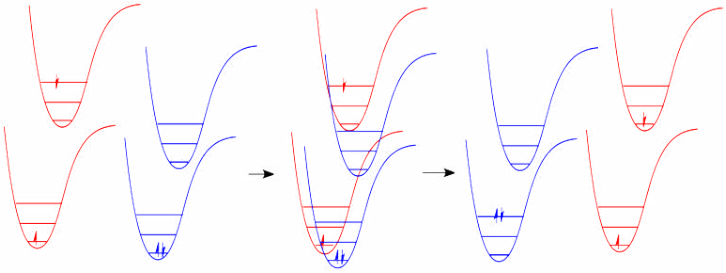


Figure **9.11.7**: The transfer of vibrational energy (heat) through a collision.

Note

There are many examples of energy being transferred this way in everyday life. In a game of pool, one billiard ball can transfer its energy to another, sending it toward the pocket. Barry Bonds can transfer a considerable amount of energy through his bat into a baseball, sending it out of the park, just as Serena Williams can send a whole lot of energy whizzing back at her sister.

Exercise 9.11.1

How does the energy of an electronic absorption compare to other processes? To find out, you might consider the excitation of an entire mole of molecules, rather than a single molecule absorbing a single photon. Calculate the energy in kJ/mol for the following transitions.

a. absorbance at 180 nm (ultraviolet)
b. absorbance at 476 nm (blue)
c. absorbance at 645 nm (red)

Answer

One method to carry out this calculation: $\frac{1}{x\,\text{nm}} \times \frac{1\,\text{nm}}{1x10^{-9}\,\text{m}} \times 6.626x10^{-34}\,\text{Js} \times \frac{3.000x10^{8}\,\text{m}}{\text{s}} \times \frac{6.022x10^{23}\,\text{photons}}{1.000\,\text{mole}} \times \frac{1\,\text{kJ}}{1000\,\text{J}}$

a. 665.0 kJ/mol
b. 251.5 kJ/mol
c. 185.6 kJ/mol

Exercise 9.11.2

How does the energy of an excitation between vibrational states compare to that of an electronic excitation? Typically, infrared absorptions are reported in cm^{-1}, which is simply what it looks like: the reciprocal of the wavelength in cm. Because wavelength and frequency are inversely related, wavenumbers are considered a frequency unit. Calculate the energy in kJ/mol for the following transitions.

a. absorbance at 3105 cm^{-1}
b. absorbance at 1695 cm^{-1}
c. absorbance at 963 cm^{-1}

Answer

One method to carry out this calculation: $x\,\text{cm}^{-1} \times \frac{100\,\text{cm}}{1\,\text{m}} \times 6.626x10^{-34}\,\text{Js} \times \frac{3.000x10^{8}\,\text{m}}{\text{s}} \times \frac{6.022x10^{23}\,\text{photons}}{1.000\,\text{mole}} \times \frac{1\,\text{kJ}}{1000\,\text{J}}$

a. 37.14 kJ/mol
b. 20.27 kJ/mol
c. 11.52 kJ/mol

By comparing these answers with those from Exercise **9.11.1**, we can see that the energy difference between vibrational states is an order of magnitude less than the energy difference between electronic states.

9.11.3.2: Internal Conversion

If electrons can get to a lower energy state, and give off a little energy at a time, relaxing to lower and lower vibrational levels, do they need to give off a photon at all? Maybe they can relax all the way down to the ground state via vibrational relaxation. That is certainly the case. Given many vibrational energy levels, and an excited state that is low enough in energy so that some of its lower vibrational levels overlap with some of the higher vibrational levels of the ground state, an electron can relax from an excited electronic state back to the ground state without releasing a photon (Figure \(\PageIndex{8}).

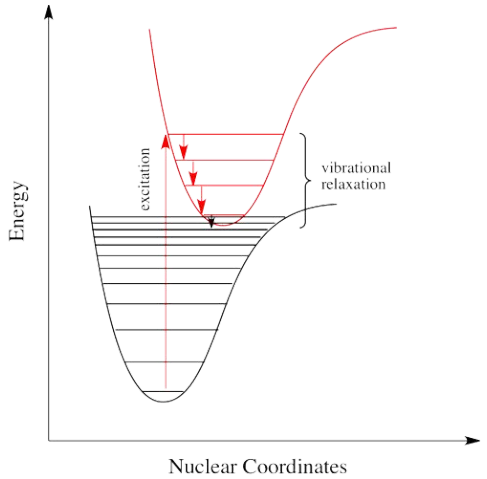


Figure **9.11.8**: Relaxation of an excited state particle to the ground state through the nonradiative process of internal conversion.

This event is called a "radiationless transition", because it occurs without release of a photon. The electron simply slides over from a low vibrational state of the excited electronic state to a high vibrational state of the electronic ground state. If the electron simply keeps dropping a vibrational level at a time back to the ground state, the process is called **"internal conversion"**.

Internal conversion has an important consequence. Because the absorption of UV and visible light can result in energy transfer into vibrational states, much of the energy that is absorbed from these sources is converted into heat. That can be a good thing if you happen to be a marine iguana trying to warm up in the sun after a plunge in the icy Pacific. It can also be a tricky thing if you are a process chemist trying to scale up a photochemical reaction for commercial production of a pharmaceutical, because you have to make sure the system has adequate cooling available.

9.11.3.3: Intersystem Crossing

Intersystem crossing is a process that leads to the electron getting caught between the excited state and the ground state. Just as, little by little, vibrational relaxation can lead the electron back onto the ground state energy surface, it can also lead the electron into states that are intermediate in energy in which the spin multiplicity has changed.

For example, suppose an organic molecule undergoes electronic excitation. Generally, organic molecules have no unpaired electrons. Their ground states are singlet states. According to one of the selection rules for electronic excitation, the excited state must also have no unpaired electrons. In other words, the spin on the electron that gets excited is the same after excitation as it was before excitation.

However, that's not the lowest possible energy state for that electron. When we think about atomic orbital filling, there is a rule that governs the spin on the electrons in degenerate orbitals: in the lowest energy state, **spin is maximized** (Hund's rule). In other words, when we draw a picture of the valence electron configuration of nitrogen, we show nitrogen's three p electrons each in its own orbital, with their spins parallel.



Figure **9.11.9**: The diagram on the left shows the energetically stable quartet spin state. The diagram on the right shows the less stable doublet spin state.

In Figure **9.11.9**, the diagram on the left, with three unpaired electrons, all with parallel spins, shows a nitrogen in the quartet spin state. This is the most stable state. Having one of those spins point the other way would result in a different, higher energy spin

state. The diagram on the right shows a different a different spin state, in which one pair of electrons in the p level is spin-paired, one up and one down, even though they are in different p orbitals. That would leave one electron without an opposite partner, so the nitrogen would be in a doublet spin state. The spin state on the left is **lower** in energy than the state on the right. That's just one of the rules of quantum mechanics (**Hund's rule**): maximize spin when degenerate orbitals are singly occupied.

A similar argument can be made for a molecule with the triplet state lower in energy than the singlet state, as shown in Figure **9.11.10**. Why didn't the electron get excited to the triplet state in the first place? That is a forbidden (unlikely) electronic transition. But sliding down vibrationally onto the triplet state from the singlet excited state is not, because it doesn't involve absorption or emission of a photon.

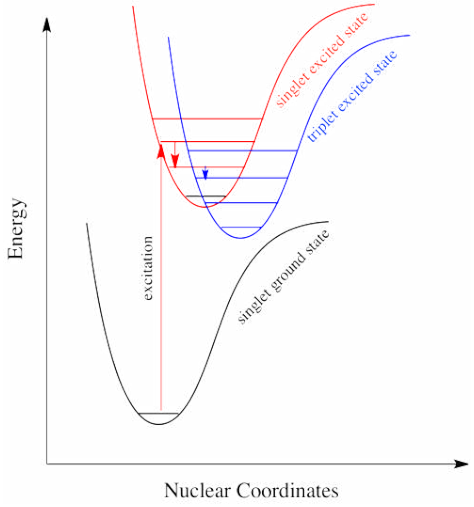


Figure **9.11.10**: Intersystem crossing from a singlet excited state to a triplet excited state.

Intersystem crossing can have important consequences in reaction chemistry because it allows access to triplet states that are not normally available in many molecules. Because triplet states feature unpaired electrons, their reactivity is often typified by radical processes. That means an added suite of reactions can be accessed via this process.

9.11.3.4: Phosphorescence: A Radiationless Transition Followed by Emission

Intersystem crossing is one way a system can end up in a triplet excited state. Even though this state is lower in energy than a singlet excited state, it cannot be accessed directly via electronic excitation because that would violate the spin selection rule (\Delta S=0\). Once intersystem crossing has occurred, the process of reattaining the ground state slows down dramatically. The quick way back to ground state is to emit a photon. But because that would involve a change in spin state, it is not allowed. Realistically speaking, that means it takes a long time. By "a long time", we might mean a few seconds, several minutes, or possibly even hours. Eventually, the electron can drop back down, accompanied by the emission of a photon. This situation is called "phosphorescence" (Figure \(\PageIndex{11}).

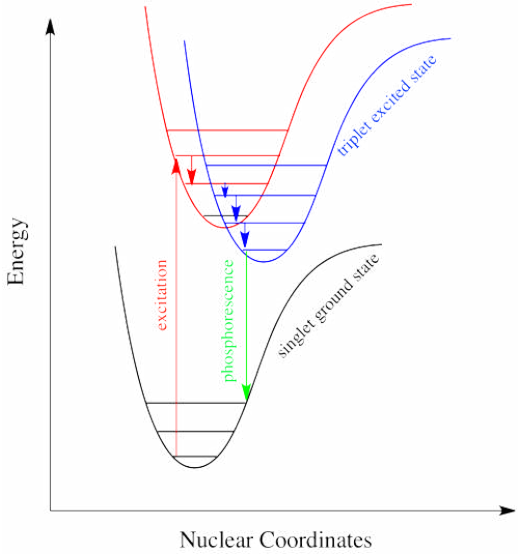


Figure **9.11.11**: The process of phosphorescence - excitation, followed by vibrational relaxation, intersystem crossing, and phosphorescence.

Many plants and animals use phosphorescence as a means of signaling. Molecules that display phosphorescence are also often incorporated into toys and shirts so that they will glow in the dark.

9.11.3.5: External Conversion

Deactivation of the excited electronic state may also involve the interaction and energy transfer between the excited state and the solvent or solute in a process called **external conversion.** Low temperature and high viscosity lead to enhanced fluorescence because they reduce the number of collision between molecules, thus slowing down this type of deactivation process.

9.11.4: Absorption and Emission Rates

The table below compares the absorption and emission rates of fluorescence and phosphorescence. The rate of photon absorption is very rapid. Fluorescence emission occurs at a slower rate. Since the triplet to singlet (or reverse) is a forbidden transition, meaning it is less likely to occur than the singlet-to-singlet transition, the rate of triplet to singlet is typically slower. Therefore, phosphorescence emission requires more time than fluorescence.

Table 15.1.1 : Rates of Absorption and Emission comparison.

Process	Radiative Process?	Transition	Timescale (sec)
Light Absorption (Excitation)	yes	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	no	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	no	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	no	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	yes	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	yes	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay to Ground State (Internal Conversion)	no	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

9.11.5: References

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Index

A

Angular momentum
- 3.16: Angular Momentum

angular momentum quantum number
- 4.6: The Wavefunctions

Anharmonicity
- 3.8: The Harmonic Oscillator Approximates Molecular Vibrations
- 8.9: Vibrational Overtones

anharmonicity constant
- 8.9: Vibrational Overtones

antibonding molecular orbital
- 6.5: The H_2^+ Prototypical Species
- 6.8: Bonding and Antibonding Orbitals

aromaticity
- 6.22: Benzene and Aromaticity

Asymmetric Tops
- 7.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule
- 8.6: Rotational Spectra of Polyatomic Molecules

atomic orbitals
- 4.6: The Wavefunctions

atomic term symbols
- 5.11: Term Symbols Gives a Detailed Description of an Electron Configuration
- 9.1: Using Atomic Term Symbols to Interpret Atomic Spectra

Atomic units
- 5.2: Atomic and Molecular Calculations are Expressed in Atomic Units

azimuthal quantum number
- 4.6: The Wavefunctions

B

Balmer series
- 4.1: The Hydrogen Atomic Spectrum

basis functions
- 5.4: Single-electron Wavefunctions and Basis Functions
- 6.2: The Orbital Approximation and Orbital Configurations

benzene ring
- 6.22: Benzene and Aromaticity

blackbody radiation
- 1.2: Blackbody Radiation Cannot Be Explained Classically
- 1.3: Quantum Hypothesis Used for Blackbody Radiation Law

Bohr magneton
- 5.5: An Electron has an Intrinsic Spin Angular Momentum

Boltzman Distribution
- 7.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution

Boltzmann Factor
- 7.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System

bond order
- 6.11: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

bonding molecular orbital
- 6.5: The H_2^+ Prototypical Species
- 6.8: Bonding and Antibonding Orbitals

bosons
- 5.6: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

bracketing theorem
- 6.3: Linear Variational Method and the Secular Determinant

C

central potential
- 4.4: The Schrödinger Equation

centrifugal distortion
- 8.12: Unequal Spacings in Vibration-Rotation Spectra

characteristic rotational temperature
- 7.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule

Classical Harmonic Oscillator
- 3.6: A Harmonic Oscillator Obeys Hooke's Law

commutator
- 2.6: Linear Operators in Quantum Mechanics
- 2.12: Commuting Operators Allow Infinite Precision

Commuting Operators
- 2.12: Commuting Operators Allow Infinite Precision

correspondence principle
- 2.7: Quantum Operators Represent Classical Variables
- 2.8: The Schrödinger Equation is an Eigenvalue Problem

Coulomb integral
- 6.7: Chemical Bond Stability
- 6.20: The pi-Electron Approximation of Conjugation

cyclic permutations (angular momenta)
- 3.17: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

D

Davisson–Germer Eexperiment
- 1.6: de Broglie Waves can be Experimentally Observed

de Broglie thermal wavelength
- 7.3: Translational Partition Functions of Monotonic Gases

de Broglie wavelength
- 1.5: Matter Has Wavelike Properties

degeneracy
- 3.4: A Particle in a Three-Dimensional Box
- 7.6: Most Molecules are Rotationally Excited at Ordinary Temperatures

delocalization energy
- 6.21: Butadiene is Stabilized by a Delocalization Energy

Diatomic Vibration
- 8.7: The Harmonic Oscillator and Infrared Spectra

E

effective nuclear charge
- 5.3: The Variational Method Approximation

eigenfunction
- 2.8: The Schrödinger Equation is an Eigenvalue Problem
- 2.9: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

eigenvalue
- 2.9: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

eigenvalue equation
- 2.6: Linear Operators in Quantum Mechanics

eigenvalue problem
- 2.8: The Schrödinger Equation is an Eigenvalue Problem
- 2.9: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

Einstein Solid Model
- 7.15: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature

Einstein temperature
- 7.15: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature

electron diffraction
- 1.6: de Broglie Waves can be Experimentally Observed

equipartition theorem
- 7.17: The Equipartition Principle

exchange integral
- 6.7: Chemical Bond Stability

Exchange Operator
- 5.6: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

exchange term
- 5.10: Hartree-Fock Calculations Give Good Agreement with Experimental Data

expectation value
- 3.3: The Average Momentum of a Particle in a Box is Zero

F

fermions
- 5.6: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

fine structure
- 9.1: Using Atomic Term Symbols to Interpret Atomic Spectra

free electron model
- 3.2: The Free Electron Model

frozen orbital approximation
- 5.10: Hartree-Fock Calculations Give Good Agreement with Experimental Data

G

groups
- 10.2: Symmetry Operations Define Groups

H

Hückel theory
- 6.20: The pi-Electron Approximation of Conjugation

Hückel's rule
- 6.22: Benzene and Aromaticity

Hamiltonian operator
- 2.7: Quantum Operators Represent Classical Variables

Harmonic oscillator
- 3.8: The Harmonic Oscillator Approximates Molecular Vibrations
- 3.9: The Harmonic Oscillator Energy Levels
- 8.7: The Harmonic Oscillator and Infrared Spectra

Hartree equations
5.10: Hartree-Fock Calculations Give Good Agreement with Experimental Data
Heisenberg uncertainty principle
2.11: The Heisenberg Uncertainty Principle
Hermite polynomials
3.10: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials
3.11: Hermite Polynomials are either Even or Odd Functions
Hermitian operators
2.6: Linear Operators in Quantum Mechanics
2.10: Eigenfunctions of Operators are Orthogonal
6.3: Linear Variational Method and the Secular Determinant
Hooke's Law
3.6: A Harmonic Oscillator Obeys Hooke's Law
Hund's Rules
5.13: Hund's Rules Determine the Term Symbols of the Ground Electronic States
hydrogen atom Schrödinger equation
4.6: The Wavefunctions

I
identity operation
10.3: Symmetry Operations as Matrices
infrared spectroscopy
8.7: The Harmonic Oscillator and Infrared Spectra
8.10: Vibrational Spectroscopy Techniques
intrinsic spin
5.5: An Electron has an Intrinsic Spin Angular Momentum
inversion operation
10.3: Symmetry Operations as Matrices
IR spectra
8.7: The Harmonic Oscillator and Infrared Spectra
irreducible representations
10.6: Characters of Irreducible Representations
10.11: Irreducible Representation of Point Groups

L
laplacian
2.7: Quantum Operators Represent Classical Variables
Laplacian operator
2.1: The Schrödinger Equation
LCAO
6.7: Chemical Bond Stability
lenard
1.4: Photoelectric Effect Explained with Quantum Hypothesis
Linear Combination of Atomic Orbitals (LCAO)
6.3: Linear Variational Method and the Secular Determinant
6.5: The H_2^+ Prototypical Species
Linear Variational Method
5.4: Single-electron Wavefunctions and Basis Functions
Lyman series
4.2: The Rydberg Formula and the Hydrogen Atomic Spectrum

M
matrix representation
10.3: Symmetry Operations as Matrices
microscopic reversibility
9.2: The Dynamics of Transitions can be Modeled by Rate Equations
microwave spectroscopy
8.4: Microwave Rotational Spectroscopy
millikan
1.4: Photoelectric Effect Explained with Quantum Hypothesis
molar absorptivity
9.8: The Beer-Lambert Law
molar heat capacities
7.16: Molar Heat Capacities
molecular term symbols
6.18: Molecular Term Symbols Describe Electronic States of Molecules
6.19: Molecular Term Symbols Designate Symmetry
moment of inertia tensor
8.6: Rotational Spectra of Polyatomic Molecules
Morse potential
3.8: The Harmonic Oscillator Approximates Molecular Vibrations
8.7: The Harmonic Oscillator and Infrared Spectra
multiplicity
5.11: Term Symbols Gives a Detailed Description of an Electron Configuration

N
neglect of differential overlap (NDO)
6.20: The pi-Electron Approximation of Conjugation
nodes
3.3: The Average Momentum of a Particle in a Box is Zero
normal modes
10.10: Normal Modes in Polyatomic Molecules

O
oblate top
8.6: Rotational Spectra of Polyatomic Molecules
Operators
2.6: Linear Operators in Quantum Mechanics
2.7: Quantum Operators Represent Classical Variables
2.8: The Schrödinger Equation is an Eigenvalue Problem
orbital angular momentum
3.17: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision
orbital approximation
5.1: The Helium Atom Cannot Be Solved Exactly
5.3: The Variational Method Approximation
6.2: The Orbital Approximation and Orbital Configurations
orbital configurations
6.2: The Orbital Approximation and Orbital Configurations
orthogonality
2.10: Eigenfunctions of Operators are Orthogonal
3.1: The Energy of a Particle in a Box is Quantized
Orthonormality
3.1: The Energy of a Particle in a Box is Quantized
overlap
6.6: The Overlap Integral
overlap integral
6.6: The Overlap Integral
overtones
8.9: Vibrational Overtones

P
Particle in a 3D Box
3.4: A Particle in a Three-Dimensional Box
Particle in a box
3.1: The Energy of a Particle in a Box is Quantized
Partition Function (Rotational)
7.7: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number
Paschen series
4.2: The Rydberg Formula and the Hydrogen Atomic Spectrum
Pauli’s exclusion principle
5.6: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
penetration
5.3: The Variational Method Approximation
permutation operator
5.6: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
Pfund series
4.2: The Rydberg Formula and the Hydrogen Atomic Spectrum
photoelectric effect
1.4: Photoelectric Effect Explained with Quantum Hypothesis
photons
1.4: Photoelectric Effect Explained with Quantum Hypothesis
physical
8.1: The Electromagnetic Spectrum
Planck's constant
1.3: Quantum Hypothesis Used for Blackbody Radiation Law
plane of symmetry
10.1: Symmetry Elements and Operations Define the Point Groups
population inversion
9.3: A Two-Level System Cannot Achieve a Population Inversion
9.4: Population Inversion can be Achieved in a Three-Level System
principal quantum number
4.6: The Wavefunctions
Probabilistic Interpretation
2.4: Wavefunctions Have a Probabilistic Interpretation
probability density
2.4: Wavefunctions Have a Probabilistic Interpretation
probability distribution
2.11: The Heisenberg Uncertainty Principle
prolate top
8.6: Rotational Spectra of Polyatomic Molecules

Q
quanta
1.3: Quantum Hypothesis Used for Blackbody Radiation Law
quantum number
3.1: The Energy of a Particle in a Box is Quantized

R
radial probability density
4.6: The Wavefunctions
raman spectroscopy
10.13: Raman- Application

Redox in Acid Solution
3.7: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule
reduced mass
3.6: A Harmonic Oscillator Obeys Hooke's Law
reducing agent
8.7: The Harmonic Oscillator and Infrared Spectra
reflection operation
10.3: Symmetry Operations as Matrices
resonance integral
6.20: The pi-Electron Approximation of Conjugation
Rigid rotor
8.5: The Selection Rule for the Rigid Rotor
rotation operation
10.3: Symmetry Operations as Matrices
Rotational of Polyatomic Molecules
8.6: Rotational Spectra of Polyatomic Molecules
rovibrational spectroscopy
8.11: Rotations Accompany Vibrational Transitions
Rydberg constant
4.2: The Rydberg Formula and the Hydrogen Atomic Spectrum

S

Scanning Tunneling Microscopy (STM)
3.5: Tunneling
Schmidt orthogonalization theorem
2.10: Eigenfunctions of Operators are Orthogonal
Schrödinger equation
2.1: The Schrödinger Equation
Secular Determinant
6.3: Linear Variational Method and the Secular Determinant
secular equations
6.3: Linear Variational Method and the Secular Determinant
6.8: Bonding and Antibonding Orbitals
Selection rules
8.5: The Selection Rule for the Rigid Rotor
8.7: The Harmonic Oscillator and Infrared Spectra
shielding
5.3: The Variational Method Approximation
Slater determinant wavefunction
5.7: Antisymmetric Wavefunctions can be Represented by Slater Determinants
5.8: Electron Configurations, The Pauli Exclusion Principle, The Aufbau Principle, and Slater Determinants
Slater Orbitals
5.4: Single-electron Wavefunctions and Basis Functions
spherical harmonics
3.15: Spherical Harmonics
Spherical Tops
8.6: Rotational Spectra of Polyatomic Molecules
Spin Multiplicity
9.11: Electronically Excited Molecules can Relax by a Number of Processes
STO
6.4: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters
Stokes shift
9.11: Electronically Excited Molecules can Relax by a Number of Processes
Symmetric Tops
7.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule
8.6: Rotational Spectra of Polyatomic Molecules
symmetry number
7.7: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number
7.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule
symmetry operations
10.3: Symmetry Operations as Matrices

T

total angular momentum
5.12: The Allowed Values of J - the Total Angular Momentum Quantum Number
Total Angular Momentum Quantum Number (J)
5.12: The Allowed Values of J - the Total Angular Momentum Quantum Number
total orbital angular momenta
5.11: Term Symbols Gives a Detailed Description of an Electron Configuration
translational partition function
7.3: Translational Partition Functions of Monotonic Gases
trial wavefunction
6.3: Linear Variational Method and the Secular Determinant
tunneling
3.5: Tunneling
turning points
3.6: A Harmonic Oscillator Obeys Hooke's Law

U

Ultraviolet Catastrophe
1.2: Blackbody Radiation Cannot Be Explained Classically

V

Variational Method
5.3: The Variational Method Approximation
6.3: Linear Variational Method and the Secular Determinant
vertical transition
9.10: The Franck-Condon Principle
vibrational spectroscopy
8.10: Vibrational Spectroscopy Techniques
vibrational temperature
7.9: Most Molecules are in the Ground Vibrational State

W

wavefunction
2.1: The Schrödinger Equation
Wavefunction Normalization
2.5: Wavefunctions Must Be Normalized
Wien’s Displacement Law
1.2: Blackbody Radiation Cannot Be Explained Classically

Y

Young double slit
1.6: de Broglie Waves can be Experimentally Observed

Z

Zeeman effect
5.5: An Electron has an Intrinsic Spin Angular Momentum
zero point energy
3.1: The Energy of a Particle in a Box is Quantized

Glossary

Sample Word 1 | Sample Definition 1

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By Page

- CHM 311: Physical Chemistry I (Lebanon Valley College) - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: The Path to Quantum Mechanics - *Undeclared*
    - 1.1: Prelude to the Foundations of Quantum Mechanics - *CC BY-NC-SA 3.0*
    - 1.2: Blackbody Radiation Cannot Be Explained Classically - *CC BY 4.0*
    - 1.3: Quantum Hypothesis Used for Blackbody Radiation Law - *CC BY-NC-SA 4.0*
    - 1.4: Photoelectric Effect Explained with Quantum Hypothesis - *CC BY-NC-SA 4.0*
    - 1.5: Matter Has Wavelike Properties - *CC BY-NC-SA 4.0*
    - 1.6: de Broglie Waves can be Experimentally Observed - *CC BY-NC-SA 4.0*
  - 2: Foundations of Quantum Mechanics - *Undeclared*
    - 2.1: The Schrödinger Equation - *CC BY-NC-SA 4.0*
    - 2.2: The Postulates of Quantum Mechanics - *CC BY-NC-SA 4.0*
    - 2.3: The Wavefunction Specifies the State of a System - *CC BY-NC-SA 4.0*
    - 2.4: Wavefunctions Have a Probabilistic Interpretation - *CC BY-NC-SA 4.0*
    - 2.5: Wavefunctions Must Be Normalized - *CC BY-NC-SA 4.0*
    - 2.6: Linear Operators in Quantum Mechanics - *CC BY-NC-SA 4.0*
    - 2.7: Quantum Operators Represent Classical Variables - *CC BY-NC-SA 4.0*
    - 2.8: The Schrödinger Equation is an Eigenvalue Problem - *CC BY-NC-SA 4.0*
    - 2.9: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators - *CC BY-NC-SA 4.0*
    - 2.10: Eigenfunctions of Operators are Orthogonal - *CC BY-NC-SA 4.0*
    - 2.11: The Heisenberg Uncertainty Principle - *CC BY 4.0*
    - 2.12: Commuting Operators Allow Infinite Precision - *CC BY-NC-SA 4.0*
  - 3: Model Systems in Quantum Mechanics - *Undeclared*
    - 3.1: The Energy of a Particle in a Box is Quantized - *CC BY-NC-SA 4.0*
    - 3.2: The Free Electron Model - *CC BY-NC-SA 4.0*
    - 3.3: The Average Momentum of a Particle in a Box is Zero - *CC BY-NC-SA 4.0*
    - 3.4: A Particle in a Three-Dimensional Box - *CC BY-NC-SA 4.0*
    - 3.5: Tunneling - *CC BY 4.0*
    - 3.6: A Harmonic Oscillator Obeys Hooke's Law - *CC BY-NC-SA 4.0*
    - 3.7: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule - *CC BY-NC-SA 4.0*
    - 3.8: The Harmonic Oscillator Approximates Molecular Vibrations - *CC BY 4.0*
    - 3.9: The Harmonic Oscillator Energy Levels - *CC BY-NC-SA 4.0*

- 3.10: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials - *CC BY-NC-SA 4.0*
- 3.11: Hermite Polynomials are either Even or Odd Functions - *CC BY-SA 4.0*
- 3.12: Spherical Polar Coordinates - *CC BY-NC-SA 4.0*
- 3.13: Potential Energy and the Hamiltonian - *CC BY-NC-SA 4.0*
- 3.14: Solution to the Schrödinger Equation - *CC BY-NC-SA 4.0*
- 3.15: Spherical Harmonics - *CC BY-NC-SA 4.0*
- 3.16: Angular Momentum - *CC BY-NC-SA 4.0*
- 3.17: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision - *CC BY-NC-SA 4.0*
- 3.18: Application to the Rotation of Real Molecules - *CC BY-NC-SA 4.0*

o 4: The Hydrogen Atom - *Undeclared*

- 4.1: The Hydrogen Atomic Spectrum - *CC BY-NC-SA 4.0*
- 4.2: The Rydberg Formula and the Hydrogen Atomic Spectrum - *CC BY-NC-SA 4.0*
- 4.3: Bohr's Hydrogen Atom - *CC BY-NC-SA 4.0*
- 4.4: The Schrödinger Equation - *CC BY-NC-SA 4.0*
- 4.5: Other One-Electron Systems - *CC BY-NC-SA 4.0*
- 4.6: The Wavefunctions - *CC BY-NC-SA 4.0*
- 4.7: s-orbitals are Spherically Symmetric - *CC BY-NC-SA 4.0*
- 4.8: Orbital Angular Momentum and the p-Orbitals - *CC BY-NC-SA 4.0*

o 5: Many Electron Atoms - *Undeclared*

- 5.1: The Helium Atom Cannot Be Solved Exactly - *CC BY-NC-SA 4.0*
- 5.2: Atomic and Molecular Calculations are Expressed in Atomic Units - *CC BY-SA 4.0*
- 5.3: The Variational Method Approximation - *CC BY-NC-SA 4.0*
- 5.4: Single-electron Wavefunctions and Basis Functions - *CC BY-NC-SA 4.0*
- 5.5: An Electron has an Intrinsic Spin Angular Momentum - *CC BY-NC-SA 4.0*
- 5.6: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons - *CC BY-NC-SA 4.0*
- 5.7: Antisymmetric Wavefunctions can be Represented by Slater Determinants - *CC BY-NC-SA 4.0*
- 5.8: Electron Configurations, The Pauli Exclusion Principle, The Aufbau Principle, and Slater Determinants - *CC BY-NC-SA 4.0*
- 5.9: The Self-Consistent Field Approximation (Hartree-Fock Method) - *CC BY-NC-SA 4.0*
- 5.10: Hartree-Fock Calculations Give Good Agreement with Experimental Data - *CC BY-NC-SA 4.0*
- 5.11: Term Symbols Gives a Detailed Description of an Electron Configuration - *CC BY 4.0*
- 5.12: The Allowed Values of J - the Total Angular Momentum Quantum Number - *CC BY-NC-SA 4.0*
- 5.13: Hund's Rules Determine the Term Symbols of the Ground Electronic States - *CC BY-NC-SA 4.0*

o 6: Molecular Structure and Bonding - *Undeclared*

- 6.1: The Born-Oppenheimer Approximation - *CC BY-NC-SA 4.0*
- 6.2: The Orbital Approximation and Orbital Configurations - *CC BY-NC-SA 4.0*
- 6.3: Linear Variational Method and the Secular Determinant - *CC BY-NC-SA 4.0*
- 6.4: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters - *CC BY-NC-SA 4.0*
- 6.5: The H_2^+ Prototypical Species - *CC BY-NC-SA 4.0*
- 6.6: The Overlap Integral - *CC BY-NC-SA 4.0*
- 6.7: Chemical Bond Stability - *CC BY-NC-SA 4.0*
- 6.8: Bonding and Antibonding Orbitals - *CC BY-NC-SA 4.0*
- 6.9: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital - *CC BY-NC-SA 4.0*
- 6.10: Molecular Orbitals Can Be Ordered According to Their Energies - *CC BY-NC-SA 4.0*
- 6.11: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule - *CC BY-NC-SA 4.0*
- 6.12: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle - *CC BY-NC-SA 4.0*
- 6.13: Diatomic Molecules of the First and Second Periods - *CC BY-SA 4.0*
- 6.14: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic - *CC BY-NC-SA 4.0*
- 6.15: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules - *CC BY-NC-SA 4.0*
- 6.16: Orbital ionization energies - *CC BY-SA 4.0*
- 6.17: Polar bonds - *CC BY-SA 4.0*

- 6.18: Molecular Term Symbols Describe Electronic States of Molecules - *CC BY 4.0*
- 6.19: Molecular Term Symbols Designate Symmetry - *CC BY-NC-SA 4.0*
- 6.20: The pi-Electron Approximation of Conjugation - *CC BY-NC-SA 4.0*
- 6.21: Butadiene is Stabilized by a Delocalization Energy - *CC BY-SA 4.0*
- 6.22: Benzene and Aromaticity - *CC BY-NC-SA 4.0*

7: Statistical Mechanics - *Undeclared*

- 7.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System - *CC BY 4.0*
- 7.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution - *CC BY 4.0*
- 7.3: Translational Partition Functions of Monotonic Gases - *CC BY-NC-SA 4.0*
- 7.4: Most Atoms are in the Ground Electronic State - *CC BY-NC-SA 4.0*
- 7.5: Pressure can be Expressed in Terms of the Canonical Partition Function - *CC BY-NC-SA 4.0*
- 7.6: Most Molecules are Rotationally Excited at Ordinary Temperatures - *CC BY-NC-SA 4.0*
- 7.7: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number - *CC BY-NC-SA 4.0*
- 7.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule - *CC BY-NC-SA 4.0*
- 7.9: Most Molecules are in the Ground Vibrational State - *CC BY-NC-SA 4.0*
- 7.10: Vibrational Partition Functions of Polyatomic Molecules Include the Partition Function for Each Normal Coordinate - *CC BY-NC-SA 4.0*
- 7.11: The Partition Function of Distinguishable, Independent Molecules is the Product of the Molecular Partition Functions - *CC BY 4.0*
- 7.12: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom - *CC BY 4.0*
- 7.13: The Average Ensemble Energy is Equal to the Observed Energy of a System - *CC BY 4.0*
- 7.14: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms - *CC BY-NC-SA 4.0*
- 7.15: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature - *CC BY-NC-SA 4.0*
- 7.16: Molar Heat Capacities - *CC BY-NC-SA 4.0*
- 7.17: The Equipartition Principle - *CC BY-NC-SA 4.0*
- 7.18: The Famous Equation of Statistical Thermodynamics is S=k ln W - *CC BY-NC-SA 4.0*
- 7.19: Entropy Can Be Expressed in Terms of a Partition Function - *CC BY-NC-SA 4.0*
- 7.20: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition - *CC BY-NC-SA 4.0*
- 7.21: Practical Absolute Entropies of Gases Can Be Calculated from Partition Functions - *CC BY-NC-SA 4.0*
- 7.22: Standard Entropies Depend Upon Molecular Mass and Structure - *CC BY-NC-SA 4.0*
- 7.23: Spectroscopic Entropies sometimes disgree with Calorimetric Entropies - *CC BY-NC-SA 4.0*

8: Molecular Spectroscopy - *Undeclared*

- 8.1: The Electromagnetic Spectrum - *CC BY 4.0*
- 8.2: Introduction to Spectroscopy - *CC BY-NC-SA 4.0*
- 8.3: Rotation of Linear Molecules - *CC BY 4.0*
- 8.4: Microwave Rotational Spectroscopy - *CC BY 4.0*
- 8.5: The Selection Rule for the Rigid Rotor - *CC BY-SA 4.0*
- 8.6: Rotational Spectra of Polyatomic Molecules - *CC BY-NC-SA 4.0*
- 8.7: The Harmonic Oscillator and Infrared Spectra - *CC BY-NC-SA 4.0*
- 8.8: The Harmonic Oscillator Selection Rule - *CC BY-NC-SA 4.0*
- 8.9: Vibrational Overtones - *CC BY 4.0*
- 8.10: Vibrational Spectroscopy Techniques - *CC BY-NC-SA 4.0*
- 8.11: Rotations Accompany Vibrational Transitions - *CC BY 4.0*
- 8.12: Unequal Spacings in Vibration-Rotation Spectra - *CC BY-NC-SA 4.0*
- 8.13: Unequal Spacings in Pure Rotational Spectra - *CC BY-NC-SA 4.0*

9: Electronic Spectroscopy - *Undeclared*

- 9.1: Using Atomic Term Symbols to Interpret Atomic Spectra - *CC BY-NC-SA 4.0*
- 9.2: The Dynamics of Transitions can be Modeled by Rate Equations - *CC BY-NC-SA 4.0*
- 9.3: A Two-Level System Cannot Achieve a Population Inversion - *CC BY-NC-SA 4.0*
- 9.4: Population Inversion can be Achieved in a Three-Level System - *CC BY-NC-SA 4.0*
- 9.5: What is Inside a Laser? - *CC BY-NC-SA 4.0*
- 9.6: The Helium-Neon Laser - *CC BY 4.0*
- 9.7: Modern Applications of Laser Spectroscopy - *CC BY-NC-SA 4.0*

- 9.8: The Beer-Lambert Law - *CC BY-NC 4.0*
- 9.9: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information - *CC BY-SA 4.0*
- 9.10: The Franck-Condon Principle - *CC BY-NC-SA 4.0*
- 9.11: Electronically Excited Molecules can Relax by a Number of Processes - *CC BY-NC-SA 4.0*

10: Group Theory and Symmetry - *Undeclared*

- 10.1: Symmetry Elements and Operations Define the Point Groups - *CC BY 4.0*
- 10.2: Symmetry Operations Define Groups - *CC BY 4.0*
- 10.3: Symmetry Operations as Matrices - *CC BY 4.0*
- 10.4: Molecules can be Represented by Reducible Representations - *CC BY 4.0*
- 10.5: Character Tables Summarize the Properties of a Point Group - *CC BY-NC-SA 4.0*
- 10.6: Characters of Irreducible Representations - *CC BY-NC-SA 4.0*
- 10.7: Molecular Orbitals can be Constructed on the Basis of Symmetry - *CC BY 4.0*
- 10.8: H_2O - *CC BY-SA 4.0*
- 10.9: The Exploitation of Symmetry Can Help Simplify Numerical Calculations - *CC BY 4.0*
- 10.10: Normal Modes in Polyatomic Molecules - *CC BY-NC-SA 4.0*
- 10.11: Irreducible Representation of Point Groups - *CC BY-NC-SA 4.0*
- 10.12: Group Theory Determines Infrared Activity - *CC BY-NC-SA 4.0*
- 10.13: Raman- Application - *CC BY 4.0*
- 10.14: Raman- Theory - *CC BY 4.0*

Back Matter - *Undeclared*

- Index - *Undeclared*
- Glossary - *Undeclared*
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