CHEM 322: PHYSICAL CHEMISTRY II



Mary Crawford
Knox College

LibreTexts™

Knox College

Chem 322: Physical Chemistry II

Mary Crawford

This text is disseminated via the Open Education Resource (OER) LibreTexts Project (https://LibreTexts.org) and like the thousands of other texts available within this powerful platform, it is freely available for reading, printing, and "consuming."

The LibreTexts mission is to bring together students, faculty, and scholars in a collaborative effort to provide an accessible, and comprehensive platform that empowers our community to develop, curate, adapt, and adopt openly licensed resources and technologies; through these efforts we can reduce the financial burden born from traditional educational resource costs, ensuring education is more accessible for students and communities worldwide.

Most, but not all, pages in the library have licenses that may allow individuals to make changes, save, and print this book. Carefully consult the applicable license(s) before pursuing such effects. Instructors can adopt existing LibreTexts texts or Remix them to quickly build course-specific resources to meet the needs of their students. Unlike traditional textbooks, LibreTexts' web based origins allow powerful integration of advanced features and new technologies to support learning.



LibreTexts is the adaptable, user-friendly non-profit open education resource platform that educators trust for creating, customizing, and sharing accessible, interactive textbooks, adaptive homework, and ancillary materials. We collaborate with individuals and organizations to champion open education initiatives, support institutional publishing programs, drive curriculum development projects, and more.

The LibreTexts libraries are Powered by NICE CXone Expert and was supported by the Department of Education Open Textbook Pilot Project, the California Education Learning Lab, the UC Davis Office of the Provost, the UC Davis Library, the California State University Affordable Learning Solutions Program, and Merlot. This material is based upon work supported by the National Science Foundation under Grant No. 1246120, 1525057, and 1413739.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation nor the US Department of Education.

Have questions or comments? For information about adoptions or adaptions contact info@LibreTexts.org or visit our main website at https://LibreTexts.org.

This text was compiled on 01/12/2026

TABLE OF CONTENTS

Licensing

1: Chemical Kinetics

- 1.1: Reaction Rates
- 1.2: Reaction Order
- 1.3: Molecularity of a Reaction
- 1.4: More Complex Reactions
- 1.5: The Effect of Temperature on Reaction Rates
- 1.6: Potential Energy Surfaces
- 1.7: Theories of Reaction Rates
- 1.8: Isotope Effects in Chemical Reactions
- 1.9: Reactions in Solution
- 1.10: Fast Reactions in Solution
- 1.11: Oscillating Reactions
- 1.12: Chemical Kinetics (Exercises)

2: Chemical Kinetics II

- 2.1: The Rates of Chemical Reactions
- 2.2: Integrated Rate Laws
- 2.3: Reactions Approaching Equilibrium
- 2.4: The Arrhenius Equation
- 2.5: Reaction Mechanisms
- 2.6: Examples of Reaction Mechanisms
- 2.7: Photochemistry
- 2.8: Enzymes

3: Reaction Dynamics

- 3.1: Collision Theory
- 3.2: Diffusion-controlled Reactions
- 3.3: Transition-state Theory
- 3.4: The Dynamics of Molecular Collisions
- 3.5: Electron Transfer in Homogeneous Systems
- 3.6: Processes at Electrodes

4: Enzyme Kinetics

- 4.1: General Principles of Catalysis
- 4.2: The Equations of Enzyme Kinetics
- 4.3: Chymotrypsin- A Case Study
- 4.4: Multisubstrate Systems
- 4.5: Enzyme Inhibition
- 4.6: Allosteric Interactions
- 4.7: The Effect of pH on Enzyme Kinetics
- 4.8: The Effect of Temperature on Enzyme Kinetics
- 4.9: Exercises

5: Lasers, Laser Spectroscopy, and Photochemistry

- 5.1: Electronically Excited Molecules
- 5.2: Transitions Modeled as Kinetics
- 5.3: Two-Level Systems Cannot Form Population Inversions
- 5.4: Population Inversion via Three-Level Systems
- 5.5: Laser Fundamentals
- 5.6: The Helium-Neon Laser
- 5.7: High-Resolution Laser Spectroscopy
- 5.8: Photochemical Dynamics

6: Nuclear Magnetic Resonance Spectroscopy

- 6.1: Nuclei Have Intrinsic Spin Angular Momenta
- 6.2: Magnetic Moments Interact with Magnetic Fields
- 6.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz
- 6.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded
- 6.5: Chemical Shifts is Sensitive to Chemical Environment of the Nucleus
- 6.6: Spin-Spin Coupling Results in Multiplets in NMR Spectra
- 6.7: Spin-Spin Coupling Between Chemically Equivalent Protons Is Not Observed
- 6.8: The n+1 Rule Applies Only to First-Order Spectra
- 6.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method

7: Molecular Spectroscopy

- 7.1: The Electromagnetic Spectrum
- 7.2: Rotational Transitions Accompany Vibrational Transitions
- 7.3: The Vibration-Rotation Spectrum
- 7.4: The Pure Rotational Spectrum has Unequal Spacings
- 7.5: Vibrational Overtones
- 7.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
- 7.7: The Franck-Condon Principle
- 7.8: Rotational Spectra of Polyatomic Molecules
- 7.9: Normal Modes in Polyatomic Molecules
- 7.10: Irreducible Representation of Point Groups
- 7.11: Time-Dependent Perturbation Theory
- 7.12: The Selection Rule for the Rigid Rotator
- 7.13: The Harmonic Oscillator Selection Rule
- 7.14: Group Theory Determines Infrared Activity
- 7.15: Molecular Spectroscopy (Exercises)

8: The Schrödinger Equation and a Particle in a Box

- 8.1: The Schrödinger Equation
- 8.2: Linear Operators in Quantum Mechanics
- 8.3: The Schrödinger Equation is an Eigenvalue Problem
- 8.4: The Quantum Mechanical Free Particle
- 8.5: Wavefunctions Have a Probabilistic Interpretation
- 8.6: The Energy of a Particle in a Box is Quantized
- 8.7: Wavefunctions Must Be Normalized
- 8.8: The Average Momentum of a Particle in a Box is Zero
- 8.9: Particle in a Finite Box and Tunneling (optional)

- 8.10: The Uncertainty Principle Redux - Estimating Uncertainties from Wavefunctions
- 8.11: A Particle in a Two-Dimensional Box
- 8.12: A Particle in a Three-Dimensional Box
- 8.13: The Schrödinger Equation and a Particle in a Box (Exercises)

9: Postulates and Principles of Quantum Mechanics

- 9.1: The Wavefunction Specifies the State of a System
- 9.2: Quantum Operators Represent Classical Variables
- 9.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators
- 9.4: The Time-Dependent Schrödinger Equation
- 9.5: The Eigenfunctions of Operators are Orthogonal
- 9.6: Heisenburg Uncertainy Principle III - Commuting Operators
- 9.7: Postulates and Principles of Quantum Mechanics (Exercises)

10: The Harmonic Oscillator and the Rigid Rotor

- 10.1: A Harmonic Oscillator Obeys Hooke's Law
- 10.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule
- 10.3: The Harmonic Oscillator is an Approximation
- 10.4: The Harmonic Oscillator Energy Levels
- 10.5: The Harmonic Oscillator and Infrared Spectra
- 10.6: The Harmonic-Oscillator Wavefunctions Involve Hermite Polynomials
- 10.7: Hermite Polynomials are either Even or Odd Functions
- 10.8: The Energy Levels of a Rigid Rotor
- 10.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
- 10.10: The Harmonic Oscillator and the Rigid Rotor (Exercises)

11: The Hydrogen Atom

- 11.1: The Schrödinger Equation for the Hydrogen Atom Can Be Solved Exactly
- 11.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics
- 11.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision
- 11.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers
- 11.5: s Orbitals are Spherically Symmetric
- 11.6: Orbital Angular Momentum and the p-orbitals
- 11.7: The Helium Atom Cannot Be Solved Exactly
- 11.8: The Hydrogen Atom (Exercises)

12: Approximation Methods

- 12.1: Slater's Rules for Shielding
- 12.2: The Variational Method
- 12.3: Linear Variational Method and the Secular Determinant
- 12.4: Trial Functions Can Be Linear Combinations of Functions with Variational Parameters
- 12.5: Perturbation Theory Expresses the Solutions in Terms of Solved Problems
- 12.6: Approximation Methods (Exercises)

13: Multielectron Atoms

- 13.1: Atomic and Molecular Calculations are Expressed in Atomic Units
- 13.2: Perturbation Theory and the Variational Method for Helium
- 13.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method

- 13.4: An Electron Has An Intrinsic Spin Angular Momentum
- 13.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
- 13.6: Antisymmetric Wave Functions can be Represented by Slater Determinants
- 13.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data
- 13.8: Term Symbols Gives Detailed Descriptions of an Electron Configuration
- 13.9: Multi-electron Considerations - A Closer Look at Helium
- 13.10: The Allowed Values of J - the Total Angular Momentum Quantum Number
- 13.11: Hund's Rules Determine the Term Symbols of the Ground Electronic States
- 13.12: Using Atomic Term Symbols to Describe Atomic Spectra
- 13.13: Multielectron Atoms (Exercises)

14: Bonding in Polyatomic Molecules

- 14.1: Hybrid Orbitals Account for Molecular Shape
- 14.2: Different Hybrid Orbitals Used for Bonding in Water
- 14.3: Why is BeH_2 Linear and H_2O Bent?
- 14.4: Photoelectron Spectroscopy
- 14.5: The \(\pi\)-Electron Approximation of Conjugation
- 14.6: Butadiene is Stabilized by a Delocalization Energy

15: Computational Quantum Chemistry

- 15.1: Overview of Quantum Calculations
- 15.2: Gaussian Basis Sets
- 15.3: Extended Basis Sets
- 15.4: Orbital Polarization Terms
- 15.5: The Ground-State Energy of H_2
- 15.6: Quantum Calculations

16: MathChapters

- 16.1: Complex Numbers
- 16.2: Probability and Statistics
- 16.3: Vectors
- 16.4: Spherical Coordinates
- 16.5: Determinants
- 16.6: Matrices
- 16.7: Numerical Methods
- 16.8: Partial Differentiation
- 16.9: Series and Limits
- 16.10: The Binomial Distribution and Stirling's Appromixation

Index

Glossary

Detailed Licensing

Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

1: Chemical Kinetics

Chemical kinetics is the study of the speed with which a *chemical* reaction occurs and the factors that affect this speed. This information is especially useful for determining how a reaction occurs.

Topic hierarchy

1.1: Reaction Rates
1.2: Reaction Order
1.3: Molecularity of a Reaction
1.4: More Complex Reactions
1.5: The Effect of Temperature on Reaction Rates
1.6: Potential Energy Surfaces
1.7: Theories of Reaction Rates
1.8: Isotope Effects in Chemical Reactions
1.9: Reactions in Solution
1.10: Fast Reactions in Solution
1.11: Oscillating Reactions
1.12: Chemical Kinetics (Exercises)

1: Chemical Kinetics is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

1.1: Reaction Rates

In this Module, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations. Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

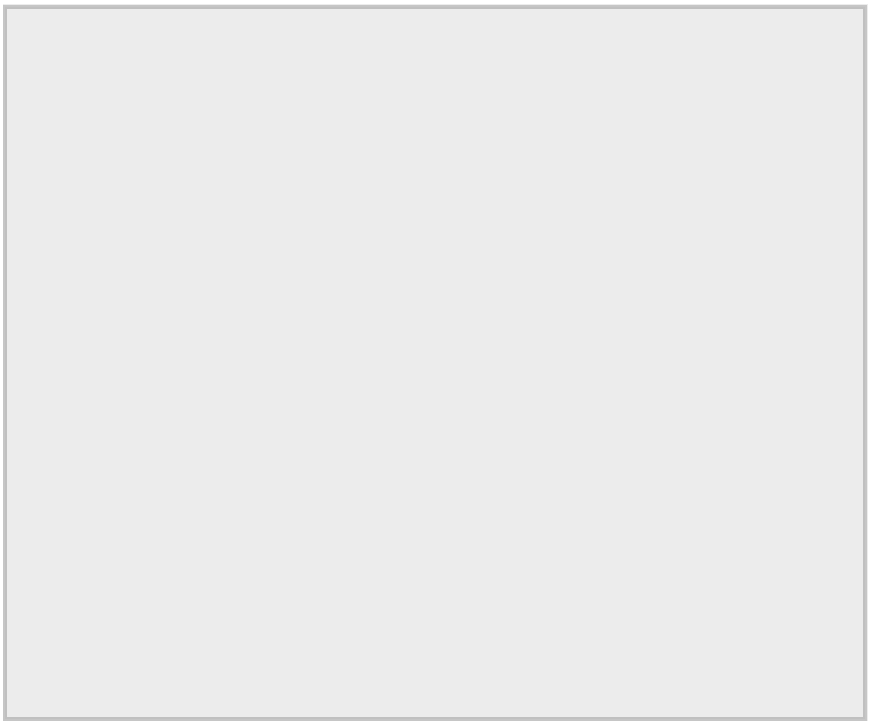


Figure **1.1.1** The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure **1.1.1**; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure **1.1.1**. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{1.1.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation 1.1.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*

Study 1: The Hydrolysis of Aspirin

We can use Equation 1.1.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure **1.1.2**.



Figure 1.1.2

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 1.1.1 and are shown in the graph in Figure 1.1.3. These data were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

Table 1.1.1: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\text{rate}_{(t=0\text{–}2.0\ \text{h})} = \frac{[\text{salicyclic acid}]_2 - [\text{salicyclic acid}]_0}{2.0\ \text{h} - 0\ \text{h}} \tag{1.1.2}$$

$$= \frac{0.040 \times 10^{-3}\ \text{M} - 0\ \text{M}}{2.0\ \text{h}} = 2.0 \times 10^{-5}\ \text{M/h} \tag{1.1.3}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\text{rate}_{(t=0\text{–}2.0\ \text{h})} = -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\,\text{h} - 0\,\text{h}} \tag{1.1.4}$$

$$= -\frac{(5.51 \times 10^{-3}\ \text{M}) - (5.55 \times 10^{-3}\ \text{M})}{2.0\ \text{h}} \tag{1.1.5}$$

$$= 2 \times 10^{-5}\ \text{M/h} \tag{1.1.6}$$

If the reaction rate is calculated during the last interval given in Table 1.1.1(the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\text{rate}_{(t=200-300\text{h})} = \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\,\text{h} - 200\,\text{h}} \tag{1.1.7}$$

$$= -\frac{(3.73 \times 10^{-3}\ \text{M}) - (2.91 \times 10^{-3}\ \text{M})}{100\ \text{h}} \tag{1.1.8}$$

$$= 8.2 \times 10^{-6}\ \text{M/h} \tag{1.1.9}$$

Study 2: The Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \tag{1.1.10}$$

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{1.1.11}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 1.1.11 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 1.1.10) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) \tag{1.1.12}$$

✔ Example 1.1.1

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

A. Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.
B. For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2, the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

? Exercise 1.1.1

The key step in the industrial production of sulfuric acid is the reaction of SO_2 with O_2 to produce SO_3.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)} \tag{1.1.13}$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer

$$\text{rate} = -\frac{\Delta[O_2]}{\Delta t} = -\frac{\Delta[SO_2]}{2\Delta t} = \frac{\Delta[SO_3]}{2\Delta t}$$

✔ Example 1.1.2

Using the reaction shown in Example **1.1.1**, calculate the reaction rate from the following data taken at 56°C:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)} \tag{1.1.14}$$

Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A. Using the equations in Example **1.1.1**, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.
B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example **1.1.1**, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5,

$$\text{rate} = -\frac{\Delta[N_2O_5]}{2\Delta t} = -\frac{[N_2O_5]_{600} - [N_2O_5]_{240}}{2(600\text{ s} - 240\text{ s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197\text{ M} - 0.0388\text{ M}}{2(360\text{ s})} = 2.65 \times 10^{-5}\text{ M/s}$$

Similarly, NO_2 can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[NO_2]}{4\Delta t} = \frac{[NO_2]_{600} - [NO_2]_{240}}{4(600\text{ s} - 240\text{ s})} = \frac{0.0699\text{ M} - 0.0314\text{ M}}{4(360\text{ s})} = 2.67 \times 10^{-5}\text{ M/s} \tag{1.1.15}$$

Allowing for experimental error, this is the same rate obtained using the data for N_2O_5. The data for O_2 can also be used:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{[O_2]_{600} - [O_2]_{240}}{600\text{ s} - 240\text{ s}} = \frac{0.0175\text{ M} - 0.00792\text{ M}}{360\text{ s}} = 2.66 \times 10^{-5}\text{ M/s} \tag{1.1.16}$$

Again, this is the same value obtained from the N_2O_5 and NO_2 data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

? Exercise 1.1.2

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)} \tag{1.1.17}$$

Time (s)	$[SO_2]$ (M)	$[O_2]$ (M)	$[SO_3]$ (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer 9.0×10^{-6} M/s

Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

$$rate = \lim_{\Delta t \to 0} \frac{-\Delta[R]}{\Delta t} = -\frac{d[R]}{dt} \tag{1.1.18}$$

The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

> *Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, t = 0. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to t = 0.*

1.1: Reaction Rates is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **9.1: Reaction Rates** is licensed CC BY-NC-SA 4.0.

1.2: Reaction Order

The kinetic theory of gases can be used to model the frequency of collisions between hard-sphere molecules, which is proportional to the reaction rate. Most systems undergoing a chemical reaction, however, are much more complex. The reaction rates may be dependent on specific interactions between reactant molecules, the phase(s) in which the reaction takes place, etc. The field of chemical kinetics is thus by-and-large based on empirical observations. From experimental observations, scientists have established that reaction rates almost always have a power-law dependence on the concentrations of one or more of the reactants. In the following sections, we will discuss different power laws that are commonly observed in chemical reactions.

0th Order Reaction Kinetics

Consider a closed container initially filled with chemical species A. At $t = 0$, a stimulus, such as a change in temperature, the addition of a catalyst, or irradiation, causes an irreversible chemical reaction to occur in which A transforms into product B:

$$a\mathrm{A} \longrightarrow b\mathrm{B} \tag{1.2.1}$$

The rate that the reaction proceeds, r, can be described as the change in the concentrations of the chemical species with respect to time:

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = \frac{1}{b}\frac{d[\mathrm{B}]}{dt} \tag{1.2.2}$$

where $[\mathrm{X}]$ denotes the molar concentration of chemical species X with units of $\frac{\mathrm{mol}}{\mathrm{L}^3}$.

Let us first examine a reaction $\mathrm{A} \longrightarrow \mathrm{B}$ in which the reaction rate, r, is constant with time:

$$r = -\frac{d[\mathrm{A}]}{dt} = k \tag{1.2.3}$$

where k is a constant, also known as the rate constant with units of $\frac{\mathrm{mol}}{\mathrm{m}^3\mathrm{s}}$. Such reactions are called zeroth order reactions because the reaction rate depends on the concentrations of species A and B to the 0th power. Integrating $[\mathrm{A}]$ with respect to T, we find that

$$[\mathrm{A}] = -kt + c_1 \tag{1.2.4}$$

At $t = 0$, $[\mathrm{A}](0) = [\mathrm{A}]_0$. Plugging these values into the equation, we find that $c_1 = [\mathrm{A}]_0$. The final form of the equation is:

$$[\mathrm{A}] = [\mathrm{A}]_0 - kt \tag{1.2.5}$$

A plot of the concentration of species A with time for a 0th order reaction is shown in Figure 1.2.1, where the slope of the line is $-k$ and the y-intercept is $[\mathrm{A}]_0$. Such reactions in which the reaction rates are independent of the concentrations of products and reactants are rare in nature. An example of a system displaying 0th order kinetics would be one in which a reaction is mediated by a catalyst present in small amounts.

1st Order Reaction Kinetics

Experimentally, it is observed than when a chemical reaction is of the form

$$\sum_i \nu_i \mathrm{A}_i = 0 \tag{1.2.6}$$

the reaction rate can be expressed as

$$r = k \prod_{\text{reactants}} [\mathrm{A}_i]^{\nu_i} \tag{1.2.7}$$

where it is assumed that the stoichiometric coefficients ν_i of the reactants are all positive. Thus, or a reaction $\mathrm{A} \longrightarrow \mathrm{B}$, the reaction rate depends on $[\mathrm{A}]$ raised to the first power:

$$r = \frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] \tag{1.2.8}$$

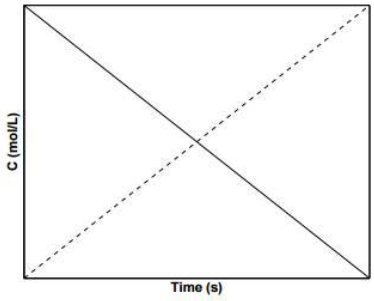


Figure 1.2.1: Plots of [A] (solid line) and [B] (dashed line) over time for a 0th order reaction.

For first order reactions, k has the units of $\frac{1}{\text{s}}$. Integrating and applying the condition that at $t = 0$ s, $[\text{A}] = [\text{A}]_0$, we arrive at the following equation:

$$[\text{A}] = [\text{A}]\, e^{-kt} \tag{1.2.9}$$

Figure 1.2.2 displays the concentration profiles for species A and B for a first order reaction. To determine the value of k from

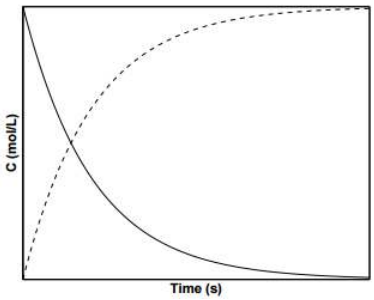


Figure 1.2.2: Plots of [A] (solid line) and [B] (dashed line) over time for a 1st order reaction.

experimental data, it is convenient to take the natural log of Equation 1.2.9:

$$\ln([\text{A}]) = \ln([\text{A}]_0) - kt \tag{1.2.10}$$

For a first order irreversible reaction, a plot of $\ln([\text{A}])$ vs. t is straight line with a slope of $-k$ and a y-intercept of $\ln([\text{A}]_0)$.

2nd Order Reaction Kinetics

Another type of reaction depends on the square of the concentration of species A - these are known as second order reactions. For a second order reaction in which $2\text{A} \longrightarrow \text{B}$, we can write the reaction rate to be

$$r = -\frac{1}{2}\frac{d[\text{A}]}{dt} = k[\text{A}]^2 \tag{1.2.11}$$

For second order reactions, k has the units of $\frac{\text{m}^3}{\text{mol} \cdot \text{s}}$. Integrating and applying the condition that at $t = 0$ s, $[\text{A}] = [\text{A}]_0$, we arrive at the following equation for the concentration of A over time:

$$[\text{A}] = \frac{1}{2kt + \frac{1}{[\text{A}]_0}} \tag{1.2.12}$$

Figure 1.2.3 shows concentration profiles of A and B for a second order reaction. To determine k from experimental data for

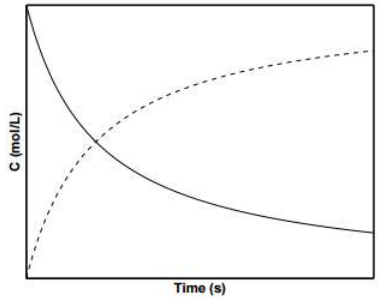


Figure 1.2.3: Plots of [A] (solid line) and [B] (dashed line) over time for a 2nd order reaction.

second-order reactions, it is convenient to invert Equation 1.2.12:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt \tag{1.2.13}$$

A plot of $1/[A]$ vs. t will give rise to a straight line with slope k and intercept $1/[A]_0$.

Second order reaction rates can also apply to reactions in which two species react with each other to form a product:

$$A + B \xrightarrow{k} C \tag{1.2.14}$$

In this scenario, the reaction rate will depend on the concentrations of both A and B to the first order:

$$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B] \tag{1.2.15}$$

To integrate the above equation, we need to write it in terms of one variable. Since the concentrations of A and B are related to each other via the chemical reaction equation, we can write:

$$[B] = [B]_0 - ([A]_0 - [A]) = [A] + [B]_0 - [A]_0 \tag{1.2.16}$$

$$\frac{d[A]}{dt} = -k[A]([A] + [B]_0 - [A]_0) \tag{1.2.17}$$

We can then use partial fractions to integrate:

$$kdt = \frac{d[A]}{[A]([A] + [B]_0 - [A]_0)} = \frac{1}{[B]_0 - [A]_0}\left(\frac{d[A]}{[A]} - \frac{d[A]}{[B]_0 - [A]_0 + [A]}\right) \tag{1.2.18}$$

$$kt = \frac{1}{[A]_0 - [B]_0}\ln\frac{[A][B]_0}{[B][A]_0} \tag{1.2.19}$$

Figure 1.2.4 displays the concentration profiles of species A, B, and C for a second order reaction in which the initial concentrations of A and B are not equal.

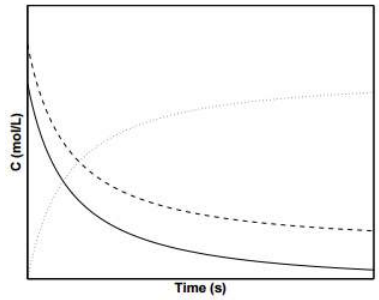


Figure 1.2.4: Plots of [A] (solid line), [B] (dashed line) and [C] (dotted line) over time for a 2nd order reaction in which the initial concentrations of the reactants, $[A]_0$ and $[B]_0$, are not equal.

Contributors and Attributions

- Mark Tuckerman (New York University)

1.2: Reaction Order is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **9.2: Reaction Order** is licensed CC BY-NC-SA 4.0.

1.3: Molecularity of a Reaction

In general, it is necessary to experimentally measure the concentrations of species over time in order to determine the apparent rate law governing the reaction. If the reactions are elementary reactions, (i.e. they cannot be expressed as a series of simpler reactions), then we can directly define the rate law based on the chemical equation. For example, an elementary reaction in which a single reactant transforms into a single product, is unimolecular reaction. These reactions follow 1st order rate kinetics. An example of this type of reaction would be the isomerization of butane:

$$nC_4H_{10} \longrightarrow iC_4H_{10} \tag{1.3.1}$$

From the chemical reaction equation, we can directly write the rate law as

$$\frac{d\left[nC_4H_{10}\right]}{dt} = -k\left[nC_4H_{10}\right] \tag{1.3.2}$$

without the need to carry out experiments.

Elementary bimolecular reactions that involve two molecules interacting to form one or more products follow second order rate kinetics. An example would be the following reaction between a nitrate molecule and carbon monoxide to form nitrogen dioxide and carbon dioxide:

$$NO_3 + CO \longrightarrow NO_2 + CO_2 \tag{1.3.3}$$

For the above elementary reaction, we can directly write the rate law as:

$$\frac{d\left[NO_3\right]}{dt} = -k\left[NO_3\right]\left[CO\right] \tag{1.3.4}$$

Trimolecular elementary reactions involving three reactant molecules to form one or more products are rare due to the low probability of three molecules simultaneously colliding with one another.

1.3: Molecularity of a Reaction is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **9.3: Molecularity of a Reaction** is licensed CC BY-NC-SA 4.0.

1.4: More Complex Reactions

A major goal in chemical kinetics is to determine the sequence of elementary reactions, or the reaction mechanism, that comprise complex reactions. For example, Sherwood Rowland and Mario Molina won the Nobel Prize in Chemistry in 1995 for proposing the elementary reactions involving chlorine radicals that contribute to the overall reaction of $O_3 \rightarrow O_2$ in the troposphere. In the following sections, we will derive rate laws for complex reaction mechanisms, including reversible, parallel and consecutive reactions.

Parallel Reactions

Consider the reaction in which chemical species $\mathbf{A}$ undergoes one of two irreversible first order reactions to form either species $\mathbf{B}$ or species $\mathbf{C}$:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \tag{1.4.1}$$

$$\mathrm{A} \xrightarrow{k_2} \mathrm{C} \tag{1.4.2}$$

The overall reaction rate for the consumption of $\mathbf{A}$ can be written as:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] - k_2[\mathrm{A}] = -(k_1 + k_2)[\mathrm{A}] \tag{1.4.3}$$

Integrating $[\mathrm{A}]$ with respect to t, we obtain the following equation:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{1.4.4}$$

Plugging this expression into the equation for $\frac{d[\mathrm{B}]}{dt}$, we obtain:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] = k_1[\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{1.4.5}$$

Integrating $[\mathrm{B}]$ with respect to t, we obtain:

$$[\mathrm{B}] = -\frac{k_1[\mathrm{A}]_0}{k_1 + k_2}\left(e^{-(k_1+k_2)t}\right) + c_1 \tag{1.4.6}$$

At $t = 0$, $[\mathrm{B}] = 0$. Therefore,

$$c_1 = \frac{k_1[\mathrm{A}]_0}{k_1 + k_2} \tag{1.4.7}$$

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right) \tag{1.4.8}$$

Likewise,

$$[\mathrm{C}] = \frac{k_2[\mathrm{A}]_0}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right) \tag{1.4.9}$$

The ratio of $[\mathrm{B}]$ to $[\mathrm{C}]$ is simply:

$$\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_1}{k_2} \tag{1.4.10}$$

An important parallel reaction in industry occurs in the production of ethylene oxide, a reagent in many chemical processes and also a major component in explosives. Ethylene oxide is formed through the partial oxidation of ethylene:

$$2\,C_2H_4 + O_2 \xrightarrow{k_1} 2\,C_2H_4O \tag{1.4.11}$$

However, ethylene can also undergo a combustion reaction:

$$C_2H_4 + 3\,O_2 \xrightarrow{k_2} 2\,CO_2 + 2\,H_2O \tag{1.4.12}$$

To select for the first reaction, the oxidation of ethylene takes place in the presence of a silver catalyst, which significantly increases k_1 compared to k_2. Figure 1.4.1 displays the concentration profiles for species A, B, and C in a parallel reaction in which $k_1 > k_2$.

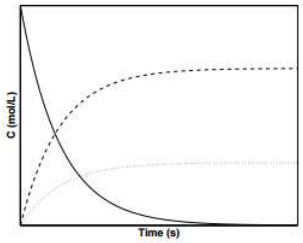


Figure 1.4.1: Plots of [A] (solid line), [B] (dashed line) and [C] (dotted line) over time for a parallel reaction.

Consecutive Reactions

Consider the following series of first-order irreversible reactions, where species A reacts to form an intermediate species, I, which then reacts to form the product, P:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{1.4.13}$$

We can write the reaction rates of species A, I and P as follows:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] \tag{1.4.14}$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{I}] \tag{1.4.15}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] \tag{1.4.16}$$

As before, integrating [A] with respect to t leads to:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t} \tag{1.4.17}$$

The concentration of species I can be written as

$$[\mathrm{I}] = \frac{k_1[\mathrm{A}]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{1.4.18}$$

Then, solving for [P], we find that:

$$[\mathrm{P}] = [\mathrm{A}]_0\left[1 + \frac{1}{k_1 - k_2}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right] \tag{1.4.19}$$

Figure 1.4.2 displays the concentration profiles for species A, I, and P in a consecutive reaction in which $k_1 = k_2$. As can be seen from the figure, the concentration of species I reaches a maximum at some time, t_{max}. Oftentimes, species I is the desired product. Returning to the oxidation of ethylene into ethylene oxide, it is important to note another reaction in which ethylene oxide can decompose into carbon dioxide and water through the following reaction

$$C_2H_4O + \frac{5}{2}O_2 \xrightarrow{k_3} 2\,CO_2 + 2\,H_2O \tag{1.4.20}$$

Thus, to maximize the concentration of ethylene oxide, the oxidation of ethylene is only allowed proceed to partial completion before the reaction is stopped.

Finally, in the limiting case when $k_2 \gg k_1$, we can write the concentration of P as

$$[\mathrm{P}] \approx [\mathrm{A}]_0\left\{1 + \frac{1}{-k_2}k_2 e^{-k_1 t}\right\} = [\mathrm{A}]_0\left(1 - e^{-k_1 t}\right) \tag{1.4.21}$$

Thus, when $k_2 \gg k_1$, the reaction can be approximated as $\mathrm{A} \rightarrow \mathrm{P}$ and the apparent rate law follows 1st order kinetics.

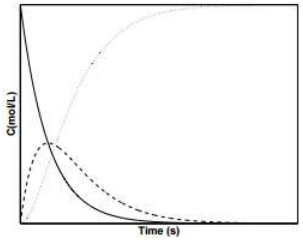


Figure 1.4.2: Plots of [A] (solid line), [I] (dashed line) and [P] (dotted line) over time for consecutive first order reactions.

Consecutive Reactions With an Equilibrium

Consider the reactions

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{1.4.22}$$

We can write the reaction rates as:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{I}] \tag{1.4.23}$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}] - k_2[\mathrm{I}] \tag{1.4.24}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] \tag{1.4.25}$$

The exact solutions of these is straightforward, in principle, but rather involved, so we will just state the exact solutions, which are

$$[\mathrm{A}](t) = \frac{[\mathrm{A}]_0}{2\lambda}\left[(\lambda - k_1 + K)\, e^{-(k_1+K-\lambda)t/2} + (\lambda + k_1 - K)\, e^{-(k_1+K+\lambda)t/2}\right] \tag{1.4.26}$$

$$[\mathrm{I}](t) = \frac{k_1[\mathrm{A}]_0}{\lambda}\left[e^{-(k_1+K-\lambda)t/2} - e^{-(k_1+K+\lambda)t/2}\right] \tag{1.4.27}$$

$$[\mathrm{P}](t) = 2k_1k_2[\mathrm{A}]_0\left[\frac{2}{(k_1+K)^2-\lambda^2} - \frac{1}{\lambda}\left(\frac{e^{-(k_1+K-\lambda)t/2}}{k_1+K-\lambda} - \frac{e^{-(k_1+K+\lambda)t/2}}{k_1+K+\lambda}\right)\right] \tag{1.4.28}$$

where

$$K = k_2 + k_{-1} \tag{1.4.29}$$

$$\lambda = \sqrt{(k_1-K)^2 - 4k_1k_{-1}} \tag{1.4.30}$$

Steady-State Approximations

Consider the following consecutive reaction in which the first step is reversible:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{1.4.31}$$

We can write the reaction rates as:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{I}] \tag{1.4.32}$$

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}] - k_2[\mathrm{I}] \tag{1.4.33}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] \tag{1.4.34}$$

These equations can be solved explicitly in terms of [A], [I], and [P], but the math becomes very complicated quickly. If, however, $k_2 + k_{-1} \gg k_1$ (in other words, the rate of consumption of I is much faster than the rate of production of I), we can make the approximation that the concentration of the intermediate species, I, is small and constant with time:

$$\frac{d[\mathrm{I}]}{dt} \approx 0 \tag{1.4.35}$$

Equation 21.22 can now be written as

$$\frac{d[\mathrm{I}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{I}]_{ss} - k_2[\mathrm{I}]_{ss} \approx 0 \tag{1.4.36}$$

where $[\mathrm{I}]_{ss}$ is a constant represents the steady state concentration of intermediate species, $[\mathrm{I}]$. Solving for $[\mathrm{I}]_{ss}$,

$$[\mathrm{I}]_{ss} = \frac{k_1}{k_{-1} + k_2}[\mathrm{A}] \tag{1.4.37}$$

We can then write the rate equation for species A as

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{I}]_{ss} = -k_1[\mathrm{A}] + k_{-1}\frac{k_1}{k_{-1} + k_2}[\mathrm{A}] = -\frac{k_1 k_2}{k_{-1} + k_2}[\mathrm{A}] \tag{1.4.38}$$

Integrating,

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-\frac{k_1 k_2}{k_{-1} + k_2}t} \tag{1.4.39}$$

Equation 21.28 is the same equation we would obtain for apparent 1st order kinetics of the following reaction:

$$\mathrm{A} \xrightarrow{k'} \mathrm{P} \tag{1.4.40}$$

where

$$k' = \frac{k_1 k_2}{k_{-1} + k_2} \tag{1.4.41}$$

Figure 1.4.3 displays the concentration profiles for species, A, I, and P with the condition that $k_2 + k_{-1} \gg k_1$. These types of reaction kinetics appear when the intermediate species, I, is highly reactive.

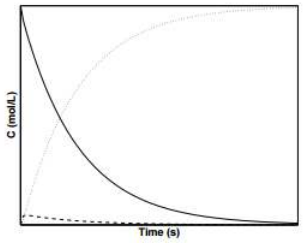


Figure 1.4.3: Plots of $[\mathrm{A}]$ (solid line), $[\mathrm{I}]$ (dashed line) and $[\mathrm{P}]$ (dotted line) over time for $k_2 + k_{-1} \gg k_1$.

Lindemann Mechanism

Consider the isomerization of methylisonitrile gas, CH_3NC, to acetonitrile gas, CH_3CN:

$$CH_3NC \xrightarrow{k} CH_3CN \tag{1.4.42}$$

If the isomerization is a unimolecular elementary reaction, we should expect to see 1st order rate kinetics. Experimentally, however, 1st order rate kinetics are only observed at high pressures. At low pressures, the reaction kinetics follow a 2nd order rate law:

$$\frac{d[CH_3NC]}{dt} = -k[CH_3NC]^2 \tag{1.4.43}$$

To explain this observation, J.A. Christiansen and F.A. Lindemann proposed that gas molecules first need to be energized via intermolecular collisions before undergoing an isomerization reaction. The reaction mechanism can be expressed as the following two elementary reactions

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M} \tag{1.4.44}$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{B} \tag{1.4.45}$$

where M can be a reactant molecule, a product molecule or another inert molecule present in the reactor. Assuming that the concentration of A^* is small, or $k_1 \ll k_2 + k_{-1}$, we can use a steady-state approximation to solve for the concentration profile of species B with time:

$$\frac{d[\mathrm{A}^*]}{dt} = k_1[\mathrm{A}][\mathrm{M}] - k_{-1}[\mathrm{A}^*]_{ss}[\mathrm{M}] - k_2[\mathrm{A}^*]_{ss} \approx 0 \tag{1.4.46}$$

Solving for $[\mathrm{A}^*]$,

$$[\mathrm{A}^*] = \frac{k_1[\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{1.4.47}$$

The reaction rates of species A and B can be written as

$$-\frac{d[\mathrm{A}]}{dt} = \frac{d[\mathrm{B}]}{dt} = k_2[\mathrm{A}^*] = \frac{k_1 k_2[\mathrm{M}][\mathrm{A}]}{k_2 + k_{-1}[\mathrm{M}]} = k_{\mathrm{obs}}[\mathrm{A}] \tag{1.4.48}$$

where

$$k_{\mathrm{obs}} = \frac{k_1 k_2[\mathrm{M}]}{k_2 + k_{-1}[\mathrm{M}]} \tag{1.4.49}$$

At high pressures, we can expect collisions to occur frequently, such that $k_{-1}[\mathrm{M}] \gg k_2$. Equation 21.33 then becomes

$$-\frac{d[\mathrm{A}]}{dt} = \frac{k_1 k_2}{k_{-1}}[\mathrm{A}] \tag{1.4.50}$$

which follows 1st order rate kinetics.

At low pressures, we can expect collisions to occurs infrequently, such that $k_{-1}[\mathrm{M}] \ll k_2$. In this scenario, equation 21.33 becomes

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}][\mathrm{M}] \tag{1.4.51}$$

which follows second order rate kinetics, consistent with experimental observations.

Equilibrium Approximations

Consider again the following consecutive reaction in which the first step is reversible:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P} \tag{1.4.52}$$

Now let us consider the situation in which $k_2 \ll k_1$ and k_{-1}. In other words, the conversion of I to P is slow and is the *rate-limiting step*. In this situation, we can assume that $[\mathrm{A}]$ and $[\mathrm{I}]$ are in equilibrium with each other. As we derived before for a reversible reaction in equilibrium,

$$K_{\mathrm{eq}} = \frac{k_1}{k_{-1}} \approx \frac{[\mathrm{I}]}{[\mathrm{A}]} \tag{1.4.53}$$

or, in terms of $[\mathrm{I}]$,

$$[\mathrm{I}] = K_{\mathrm{eq}}[\mathrm{A}] \tag{1.4.54}$$

These conditions also result from the exact solution when we set $k_2 \approx 0$. When this is done, we have the approximate expressions from the exact solution:

$$K \approx k_{-1} \tag{1.4.55}$$

$$\lambda \approx \sqrt{\left(k_1 - k_{-1}\right)^2 + 4k_1k_{-1}} = \sqrt{k_1^2 + 2k_1k_{-1} + k_{-1}^2} = k_1 + k_{-1} \tag{1.4.56}$$

$$\lambda - k_1 + K \approx k_1 + k_{-1} + k_1 - k_{-1} = 2k_1 \tag{1.4.57}$$

$$\lambda + k_1 - K \approx k_1 + k_{-1} + k_1 - k_{-1} = 2k_1 \tag{1.4.58}$$

$$k_1 + K - \lambda \approx k_1 + k_{-1} - k_1 - k_{-1} = 0 \tag{1.4.59}$$

$$k_1 + K + \lambda \approx k_1 + k_{-1} + k_1 + k_{-1} = 2\left(k_1 + k_{-1}\right) \tag{1.4.60}$$

and the approximate solutions become

$$[\mathrm{A}](t) = \frac{[\mathrm{A}]_0}{2\left(k_1 + k_{-1}\right)}\left[2k_{-1} + 2k_1 e^{-(k_1 + k_{-1})t}\right] \tag{1.4.61}$$

$$[\mathrm{I}](t) = \frac{k_1[\mathrm{A}]_0}{\left(k_1 + k_{-1}\right)}\left[1 - e^{-(k_1 + k_{-1})t}\right] \tag{1.4.62}$$

In the long-time limit, when equilibrium is reached and transient behavior has decayed away, we find

$$\frac{[\mathrm{I}]}{[\mathrm{A}]} \equiv K_{\mathrm{eq}} \rightarrow \frac{k_1}{k_{-1}} \tag{1.4.63}$$

Plugging the above equation into the expression for $d[\mathrm{P}]/dt$,

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{I}] = k_2K_{\mathrm{eq}}[\mathrm{A}] = \frac{k_1k_2}{k_{-1}}[\mathrm{A}] \tag{1.4.64}$$

The reaction can thus be approximated as a 1st order reaction

$$\mathrm{A} \xrightarrow{k'} \mathrm{P} \tag{1.4.65}$$

with

$$k' = \frac{k_1k_2}{k_{-1}} \tag{1.4.66}$$

Figure 1.4.4 displays the concentration profiles for species, A, I, and P with the condition that $k_2 \ll k_1 = k_{-1}$. When $k_1 = k_{-1}$, we expect $[\mathrm{A}] = [\mathrm{I}]$. As can be seen from the figure, after a short initial startup time, the concentrations of species A and I are approximately equal during the reaction.

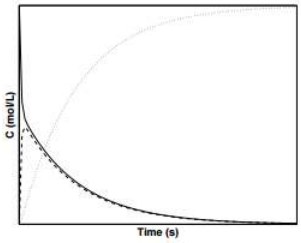


Figure 1.4.4: Plots of [A] (solid line), [I] (dashed line) and [P] (dotted line) over time for $k_2 \ll k_1 = k_{-1}$.

This page titled 1.4: More Complex Reactions is shared under a not declared license and was authored, remixed, and/or curated by Mark E. Tuckerman.

- **1.20: Complex reaction mechanisms** by Mark Tuckerman is licensed CC BY-NC-SA 4.0.

1.5: The Effect of Temperature on Reaction Rates

When molecules collide, the kinetic energy of the molecules can be used to stretch, bend, and ultimately break bonds, leading to chemical reactions. If molecules move too slowly with little kinetic energy, or collide with improper orientation, they do not react and simply bounce off each other. However, if the molecules are moving fast enough with a proper collision orientation, such that the kinetic energy upon collision is greater than the minimum energy barrier, then a reaction occurs. The minimum energy requirement that must be met for a chemical reaction to occur is called the activation energy, E_a.



Figure 1.5.1: In Greek mythology Sisyphus was punished by being forced roll an immense boulder up a hill, only to watch it roll back down, and to repeat this action forever. If this were a chemical reaction, then it would never be observed, since the reactants must overcome the energy barrier to get to the other side (products).

The reaction pathway is similar to what happens in Figure 1.5.1. To get to the other end of the road, an object must roll with enough speed to completely roll over the hill of a certain height. The faster the object moves, the more kinetic energy it has. If the object moves too slowly, it does not have enough kinetic energy necessary to overcome the barrier; as a result, it eventually rolls back down. In the same way, there is a minimum amount of energy needed in order for molecules to break existing bonds during a chemical reaction. If the kinetic energy of the molecules upon collision is greater than this minimum energy, then bond breaking and forming occur, forming a new product (provided that the molecules collide with the proper orientation).

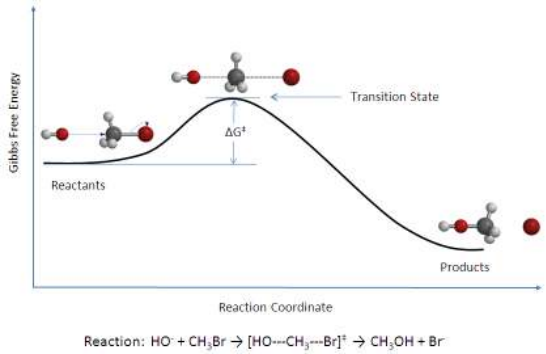


Figure 1.5.2: Reaction coordinate diagram for the bimolecular nucleophilic substitution (S_N2) reaction between bromomethane and the hydroxide anion. from Wikipedia.

The activation energy (E_a), labeled $\Delta G^{\ddagger}$ in Figure 1.5.2, is the energy difference between the reactants and the activated complex, also known as transition state. In a chemical reaction, the transition state is defined as the highest-energy state of the system. If the molecules in the reactants collide with enough kinetic energy and this energy is higher than the transition state energy, then the reaction occurs and products form. In other words, the higher the activation energy, the harder it is for a reaction to occur and vice versa.

Overcoming the energy barrier from thermal energy involves addressing the fraction of the molecules that possess enough kinetic energy to react at a given temperature. According to kinetic molecular theory, a population of molecules at a given temperature is distributed over a variety of kinetic energies that is described by the Maxwell-Boltzman distribution law.

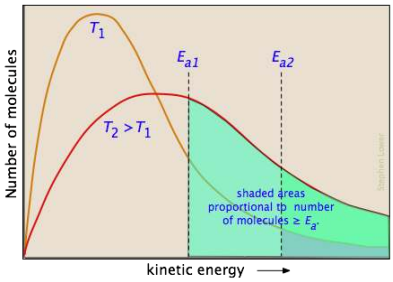
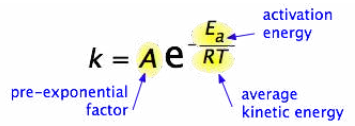


Figure **1.5.3 :** Kinetic energy distributions (similar to Maxwell-Boltzman distributions for velocity) for a gas at two temperatures and critical energies for overcoming an activation barrier.

The two distribution plots shown here are for a lower temperature T_1 and a higher temperature T_2. The area under each curve represents the total number of molecules whose energies fall within particular range. The shaded regions indicate the number of molecules which are sufficiently energetic to meet the requirements dictated by the two values of E_a that are shown. It is clear from these plots that the fraction of molecules whose kinetic energy exceeds the activation energy increases quite rapidly as the temperature is raised. This the reason that virtually all chemical reactions (and all elementary reactions) proceed more rapidly at higher temperatures.

Arrhenius Equation

By 1890 it was common knowledge that higher temperatures speed up reactions, often doubling the rate for a 10-degree rise, but the reasons for this were not clear. Finally, in 1899, the Swedish chemist Svante Arrhenius (1859-1927) combined the concepts of activation energy and the Boltzmann distribution law into one of the most important relationships in physical chemistry:



Take a moment to focus on the meaning of this equation, neglecting the *A* factor for the time being. First, note that this is another form of the exponential decay law discussed in the previous section of this series. What is "decaying" here is not the concentration of a reactant as a function of time, but the magnitude of the rate constant as a function of the exponent $-E_a/RT$. And what is the significance of this quantity? Recalling that *RT* is the *average kinetic energy*, it becomes apparent that the exponent is just the ratio of the activation energy E_a to the average kinetic energy. The larger this ratio, the smaller the rate (hence the negative sign). This means that high temperature and low activation energy favor larger rate constants, and thus speed up the reaction. Because these terms occur in an exponent, their effects on the rate are quite substantial.

Svante August Arrhenius

Svante August Arrhenius (19 February 1859 – 2 October 1927) was a Swedish scientist, originally a physicist, but often referred to as a chemist, and one of the founders of the science of physical chemistry. He received the Nobel Prize for Chemistry in 1903, becoming the first Swedish Nobel laureate, and in 1905 became director of the Nobel Institute where he remained until his death. The Arrhenius equation, Arrhenius definition of an acid, lunar crater Arrhenius, the mountain of Arrheniusfjellet and the Arrhenius Labs at Stockholm University are named after him. Today, Arrhenius is best known for his study published in 1896, on the greenhouse effect.



The two plots in Figure 1.5.4 show the effects of the activation energy (denoted here by $E^{\ddagger}$) on the rate constant. Even a modest activation energy of 50 kJ/mol reduces the rate by a factor of 10^8.

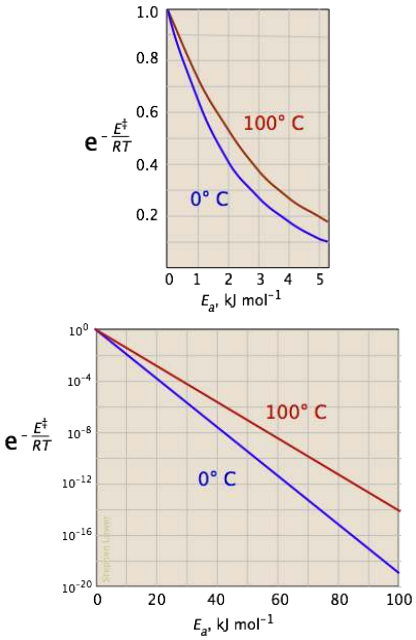


Figure 1.5.4: Arrhenius plots. The logarithmic scale in the right-hand plot leads to nice straight lines.

Looking at the role of temperature, a similar effect is observed. (If the *x*-axis were in "kilodegrees" the slopes would be more comparable in magnitude with those of the kilojoule plot at the above right.)

Determining the activation energy

The Arrhenius equation

$$k = Ae^{-E_a/RT} \tag{1.5.1}$$

can be written in a non-exponential form that is often more convenient to use and to interpret graphically (Figure 1.5.4). Taking the logarithms of both sides and separating the exponential and pre-exponential terms yields

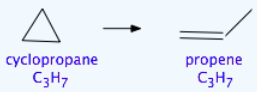
$$\ln k = \ln\left(Ae^{-E_a/RT}\right) = \ln A + \ln\left(e^{-E_a/RT}\right) \tag{1.5.2}$$

$$\ln k = \ln A + \frac{-E_a}{RT} = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \tag{1.5.3}$$

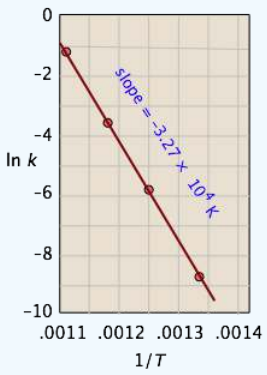
which is the equation of a straight line whose slope is $-E_a/R$. This affords a simple way of determining the activation energy from values of *k* observed at different temperatures, by plotting $\ln k$ as a function of $1/T$.

Example 1.5.1: Isomerization of Cyclopropane

For the isomerization of cyclopropane to propene,



the following data were obtained (calculated values shaded in pink):



T, °C	477	523	577	623
$1/T$, $K^{-1} \times 10^3$	1.33	1.25	1.18	1.11
k, s^{-1}	0.00018	0.0027	0.030	0.26
ln k	–8.62	–5.92	–3.51	–1.35

From the calculated slope, we have

$-(E_a/R) = -3.27 \times 10^4$ K

$E_a = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(-3.27 \times 10^4 \text{ K}) = 273 \text{ kJ mol}^{-1}$

This activation energy is high, which is not surprising because a carbon-carbon bond must be broken in order to open the cyclopropane ring. (C–C bond energies are typically around 350 kJ/mol.) This is why the reaction must be carried out at high temperature.

Calculating E_a without a plot

Because the ln k vs.-1/T plot yields a straight line, it is often convenient to estimate the activation energy from experiments at only two temperatures. The ln A term is eliminated by subtracting the expressions for the two ln-k terms via the following steps:

$$\ln k_1 = \ln A - \frac{E_a}{k_B T_1} \tag{1.5.4}$$

at T_1 and

$$\ln k_2 = \ln A - \frac{E_a}{k_B T_2} \tag{1.5.5}$$

at T_2. By rewriting the second equation:

$$\ln A = \ln k_2 + \frac{E_a}{k_B T_2} \tag{1.5.6}$$

and substitute for $\ln A$ into the first equation:

$$\ln k_1 = \ln k_2 + \frac{E_a}{k_B T_2} - \frac{E_a}{k_B T_1} \tag{1.5.7}$$

This simplifies to:

$$\ln k_1 - \ln k_2 = -\frac{E_a}{k_B T_1} + \frac{E_a}{k_B T_2} \tag{1.5.8}$$

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{k_B}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{1.5.9}$$

Example 1.5.2

A widely used rule-of-thumb for the temperature dependence of a reaction rate is that a **ten degree** rise in the temperature approximately doubles the rate. This is not generally true, especially when a strong covalent bond must be broken. For a reaction that does show this behavior, what would the activation energy be?

Solution

Center the ten degree interval at 300 K. Substituting into the above expression yields

$$E_a = \frac{(8.314)(\ln 2/1)}{\frac{1}{295} - \frac{1}{305}} = \frac{(8.314)(0.693)}{0.00339 K^{-1} - 0.00328\ K^{-1}} \tag{1.5.10}$$

= (5.76 J mol^{-1} K^{-1}) / (0.00011 K^{-1}) = 52400 J mol^{-1} = **52.4 kJ mol^{-1}**

Example 1.5.3

It takes about 3.0 minutes to cook a hard-boiled egg in Los Angeles, but at the higher altitude of Denver, where water boils at 92°C, the cooking time is 4.5 minutes. Use this information to estimate the activation energy for the coagulation of egg albumin protein.

Solution

The ratio of the rate constants at the elevations of Los Angeles and Denver is 4.5/3.0 = 1.5, and the respective temperatures are **373 K** and **365 K**. With the subscripts 2 and 1 referring to Los Angeles and Denver respectively:

$$E_a = \frac{(8.314)(\ln 1.5)}{\frac{1}{365\ \text{K}} - \frac{1}{373\ \text{K}}} = \frac{(8.314)(0.405)}{0.00274\ \text{K}^{-1} - 0.00268\ \text{K}^{-1}} \tag{1.5.11}$$

$$= \frac{(3.37\ \text{J mol}^{-1}\text{K}^{-1})}{5.87 \times 10^{-5}\ \text{K}^{-1}} = 5740\ \text{J mol}^{-1} = 5.73\ \text{kJ mol}^{-1} \tag{1.5.12}$$

Comment: This low value seems reasonable because thermal denaturation of proteins primarily involves the disruption of relatively weak hydrogen bonds; no covalent bonds are broken (although disulfide bonds can interfere with this interpretation).

The pre-exponential factor

Up to this point, the pre-exponential term, *A* in the Arrhenius equation, has been ignored because it is not directly involved in relating temperature and activation energy, which is the main practical use of the equation.

$$k = Ae^{-E_a/RT}$$

However, because *A* multiplies the exponential term, its value clearly contributes to the value of the rate constant and thus of the rate. Recall that the exponential part of the Arrhenius equation expresses the fraction of reactant molecules that possess enough kinetic energy to react, as governed by the Maxwell-Boltzmann law. This fraction can run from zero to nearly unity, depending on the magnitudes of E_a and of the temperature.

If this fraction were 0, the Arrhenius law would reduce to

$$k = A \tag{1.5.13}$$

In other words, A is the fraction of molecules that would react if either the activation energy were zero, or if the kinetic energy of all molecules exceeded E_a — admittedly, an uncommon scenario (although barrierless reactions have been characterized).

The Role of Collisions

What would limit the rate constant if there were no activation energy requirements? The most obvious factor would be the rate at which reactant molecules come into contact. This can be calculated from kinetic molecular theory and is known as the *frequency-* or *collision factor*, Z.

$$k = A e^{-\frac{E_a}{RT}}$$

$A = Z \times \rho$ (frequency factor, steric factor)

In some reactions, the relative orientation of the molecules at the point of collision is important, so a geometrical or *steric factor* (commonly denoted by ρ (Greek lower case *rho*) can be defined. In general, we can express A as the product of these two factors:

$$A = Z\rho \tag{1.5.14}$$

Values of ρ are generally very difficult to assess; they are sometime estimated by comparing the observed rate constant with the one in which A is assumed to be the same as Z. Usually, the more complex the reactant molecules, the lower the steric factors. The deviation from unity can have different causes: the molecules are not spherical, so different geometries are possible; not all the kinetic energy is delivered into the right spot; the presence of a solvent (when applied to solutions) and other factors (Figure **1.5.4**).

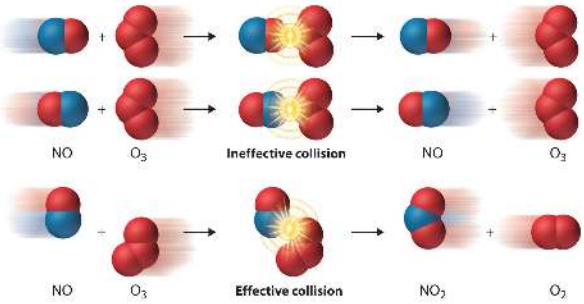


Figure **1.5.5**: The Effect of Molecular Orientation on the Reaction of NO and O_3. Most collisions of NO and O_3 molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of O_3 are likely to produce NO_2 and O_2, even if the molecules collide with $E > E_a$.

Contributors and Attributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- Wikipedia

1.5: The Effect of Temperature on Reaction Rates is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **9.5: The Effect of Temperature on Reaction Rates** is licensed CC BY-NC-SA 4.0.

1.6: Potential Energy Surfaces

A potential energy surface (PES) describes the potential energy of a system, especially a collection of atoms, in terms of certain parameters, normally the positions of the atoms. The surface might define the energy as a function of one or more coordinates; if there is only one coordinate, the surface is called a potential energy curve or energy profile. It is helpful to use the analogy of a landscape: for a system with two degrees of freedom (e.g. two bond lengths), the value of the energy (analogy: the height of the land) is a function of two bond lengths (analogy: the coordinates of the position on the ground). The Potential Energy Surface represents the concepts that each geometry (both external and internal) of the atoms of the molecules in a chemical reaction is associated with it a unique potential energy. This creates a smooth energy “landscape” and chemistry can be viewed from a topology perspective (of particles evolving over "valleys""and passes").

Potential Energy Curves (1-D Potential Energy Surfaces)

The PES is the energy of a molecule as a function of the positions of its nuclei $\boldsymbol{r}$. This energy of a system of two atoms depends on the distance between them. At large distances the energy is zero, meaning “no interaction”. At distances of several atomic diameters attractive forces dominate, whereas at very close approaches the force is repulsive, causing the energy to rise. The attractive and repulsive effects are balanced at the minimum point in the curve. Plots that illustrate this relationship are quite useful in defining certain properties of a chemical bond.

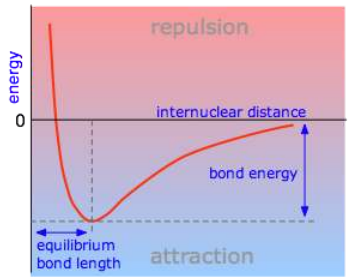


Figure **1.6.1**: A potential Energy Curve for a covalent bond.

The internuclear distance at which the potential energy minimum occurs defines the **bond length**. This is more correctly known as the *equilibrium* bond length, because thermal motion causes the two atoms to vibrate about this distance. In general, the stronger the bond, the smaller will be the bond length.

Attractive forces operate between all atoms, but unless the potential energy minimum is at least of the order of *RT*, the two atoms will not be able to withstand the disruptive influence of thermal energy long enough to result in an identifiable molecule. Thus we can say that a chemical bond exists between the two atoms in H_2. The weak attraction between argon atoms does not allow Ar_2 to exist as a molecule, but it does give rise to the *van Der Waals force* that holds argon atoms together in its liquid and solid forms.

Potential, Kinetic, and Total Energy for a System

Potential energy and kinetic energy Quantum theory tells us that an electron in an atom possesses kinetic energy $\boldsymbol{K}$ as well as potential energy $\boldsymbol{V}$, so the total energy $\boldsymbol{E}$ is always the sum of the two: $\boldsymbol{E = V + K}$. The relation between them is surprisingly simple: $\boldsymbol{K = -0.5V}$. This means that when a chemical bond forms (an exothermic process with $\boldsymbol{\Delta E < 0}$), the decrease in potential energy is accompanied by an increase in the kinetic energy (embodied in the momentum of the bonding electrons), but the magnitude of the latter change is only half as much, so the change in potential energy always dominates. The bond energy $\boldsymbol{-\Delta E}$ has half the magnitude of the fall in potential energy.

Mathematical definition and computation

The geometry of a set of atoms can be described by a vector, r, whose elements represent the atom positions. The vector $\boldsymbol{r}$ could be the set of the Cartesian coordinates of the atoms, or could also be a set of inter-atomic distances and angles. Given $\boldsymbol{r}$, the energy as a function of the positions, $\boldsymbol{V(r)}$, is the value of $\boldsymbol{V(r)}$ for all values of $\boldsymbol{r}$ of interest. Using the landscape analogy from the introduction, $\boldsymbol{V(r)}$ gives the height on the "energy landscape" so that the concept of a potential energy surface arises. An example is

the PES for water molecule (Figure **1.6.1**) that show the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958 nm and H-O-H bond angle of 104.5°

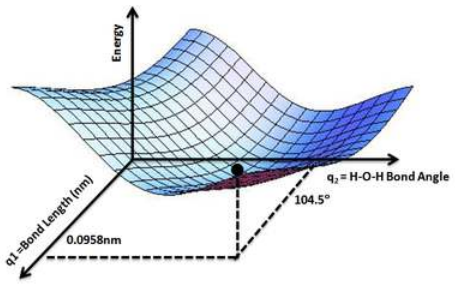


Figure **1.6.2**: PES for water molecule: Shows the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958nm and H-O-H bond angle of 104.5°. of Wikipedia (Credit: Aimnature).

The Dimensionality of a Potential Energy Surface

To define an atom's location in 3-dimensional space requires three coordinates (e.g., x, y,and z or r, θ and phi in Cartesian and Spherical coordinates) or *degrees of freedom*. However, a reaction and hence the corresponding PESs do not depend of the absolute position of the reaction, only the relative positions (internal degrees). Hence both translation and rotation of the entire system can be removed (each with 3 degree of freedom, assuming non-linear geometries). So the dimensionality of a PES is

$$3N-6 \tag{1.6.1}$$

where N is the number of atoms involves in the reaction, i.e., the number of atoms in each reactants). The PES is a hypersurface with many degrees of freedom and typically only a few are plotted at any one time for understanding. See Calculate Number of Vibrational Modes to get a more details picture of how this applies to calculating the number of vibrations in a molecule

To study a chemical reaction using the PES as a function of atomic positions, it is necessary to calculate the energy for **every atomic** arrangement of interest. Methods of calculating the energy of a particular atomic arrangement of atoms are well described in the computational chemistry article, and the emphasis here will be on finding approximations of $(V(r)$ to yield fine-grained energy-position information.

For very simple chemical systems or when simplifying approximations are made about inter-atomic interactions, it is sometimes possible to use an analytically derived expression for the energy as a function of the atomic positions. An example is

$$H + H_2 \rightarrow H_2 + H \tag{1.6.2}$$

system as a function of the **three** H-H distances. For more complicated systems, calculation of the energy of a particular arrangement of atoms is often too computationally expensive for large scale representations of the surface to be feasible.

Application of Potential Energy Surfaces

A PES is a conceptual tool for aiding the analysis of molecular geometry and chemical reaction dynamics. Once the necessary points are evaluated on a PES, the points can be classified according to the first and second derivatives of the energy with respect to position, which respectively are the gradient and the curvature. Stationary points (or points with a zero gradient) have physical meaning: energy minima correspond to physically stable chemical species and saddle points correspond to transition states, the highest energy point on the reaction coordinate (which is the lowest energy pathway connecting a chemical reactant to a chemical product). Three

- PES do not show kinetic energy, only potential energy.
- At T = 0 K (no KE), species will want to be at the lowest possible potential energy, (i.e., at a minimum on the PES).
- Between any two minima (valley bottoms) the lowest energy path will pass through a maximum at a **saddle point**, which we call that saddle point a transition-state structure.

The PES concept finds application in fields such as chemistry and physics, especially in the theoretical sub-branches of these subjects. It can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction.

Contributors and Attributions

- Wikipedia
- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

---

1.6: Potential Energy Surfaces is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

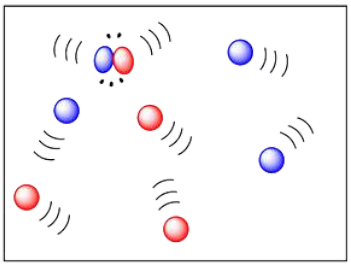
- **9.6: Potential Energy Surfaces** is licensed CC BY-NC-SA 4.0.

1.7: Theories of Reaction Rates

The macroscopic discussion of kinetics discussed in previous sections can be now expanded into a more microscopic picture in terms of molecular level properties (e..g, mass and velocities) involving two important theories: (1) collision theory and (2) transition-state theory.

Collision Theory

If two molecules need to collide in order for a reaction to take place, then factors that influence the ease of collisions will be important. The more energy there is available to the molecules, the faster they will move around, and the more likely they are to bump into each other. Higher temperatures ought to lead to more collisions and a greater frequency of reactions between molecules. In the drawing below, the cold, sluggish molecules on the left are not likely to collide, but the energetic molecules on the right are due to collide at any time.



The rate at which molecules collide which is the frequency of collisions is called the collision frequency, Z, which has units of collisions per unit of time. Given a container of molecules A and B, the collision frequency between A and B is defined by:

$$Z = N_A N_B \sigma_{AB} \sqrt{\frac{8k_B T}{\pi \mu_{AB}}} \tag{1.7.1}$$

where:

- N_A and N_B are the numbers of molecules A and B, and is directly related to the concentrations of A and B.
- The mean speed of molecules obtained from the Maxwell-Boltzmann distribution for thermalized gases

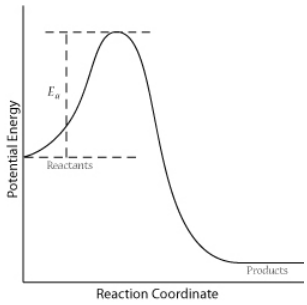
$$\sqrt{\frac{8k_B T}{\pi \mu_{AB}}} \tag{1.7.2}$$

- σ_{AB} is the averaged sum of the collision cross-sections of molecules A and B. The collision cross section represents the collision region presented by one molecule to another.
- μ is the reduced mass and is given by

$$\mu = \frac{m_A m_B}{m_A + m_B} \tag{1.7.3}$$

The concepts of collision frequency can be applied in the laboratory: (1) The temperature of the environment affects the average speed of molecules. Thus, reactions are heated to increase the reaction rate. (2) The initial concentration of reactants is directly proportional to the collision frequency; increasing the initial concentration will speed up the reaction.

For a successful collision to occur, the reactant molecules must collide with enough kinetic energy to break original bonds and form new bonds to become the product molecules. This energy is called the activation energy for the reaction; it is also often referred to as the energy barrier.



The fraction of collisions with enough energy to overcome the activation barrier is given by:

$$f = e^{\frac{-E_a}{RT}} \tag{1.7.4}$$

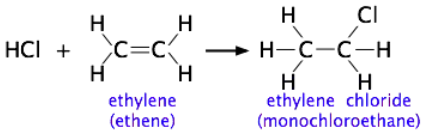
where:

- f is the fraction of collisions with enough energy to react
- E_a is the activation energy

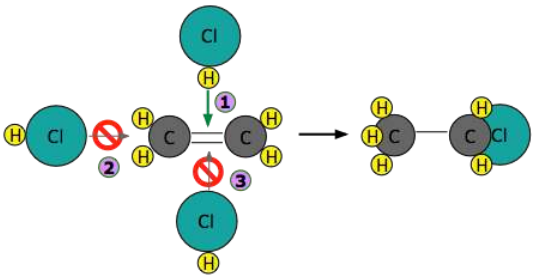
The fraction of successful collisions is directly proportional to the temperature and inversely proportional to the activation energy.

> The fraction of successful collisions is directly proportional to the temperature and inversely proportional to the activation energy.

The more complicated the structures of the reactants, the more likely that the value of the rate constant will depend on the trajectories at which the reactants approach each other. This kind of *electrophilic addition reaction* is well-known to all students of organic chemistry. Consider the addition of a hydrogen halide such as HCl to the double bond of an alkene, converting it to a chloroalkane.



Experiments have shown that the reaction only takes place when the HCl molecule approaches the alkene with its hydrogen-end, and in a direction that is approximately perpendicular to the double bond, as shown at (1) below.



The reason for this becomes apparent when we recall that HCl is highly polar owing to the high electronegativity of chlorine, so that the hydrogen end of the molecule is slightly positive. The steric factor, ρ is then introduced to represent is the probability of the reactant molecules colliding with the right orientation and positioning to achieve a product with the desirable geometry and stereospecificity. Values of ρ are generally very difficult to assess and range from 0 to 1, but are sometime estimated by comparing the observed rate constant with the one in which the preexponential constant A is assumed to be the same as Z.

The lesson you should take from this example is that once you start combining a variety of chemical principles, you gradually develop what might be called "chemical intuition" which you can apply to a wide variety of problems. This is far more important than memorizing specific examples.

All Three Factors Combined

The rate constant of the gas-phase reaction is proportional to the product of the *collision frequency* and the *fraction of successful reactions*. As stated above, sufficient kinetic energy is required for a successful reaction; however, they must also collide properly. Compare the following equation to the Arrhenius equation:

$$k = Z\rho e^{\frac{-E_a}{RT}} \tag{1.7.5}$$

where

- k is the rate constant for the reaction
- ρ is the steric factor.
- Zρ is the pre-exponential factor, A, of the Arrhenius equation. It is the frequency of total collisions that collide with the right orientation. In practice, it is the pre-exponential factor that is directly determined by experiment and then used to calculate the steric factor.
- E_a is activation energy
- T is absolute temperature
- R is gas constant.

Although the collision theory deals with gas-phase reactions, its concepts can also be applied to reactions that take place in solvents; however, the properties of the solvents (for example: solvent cage) will affect the rate of reactions. Ultimately, collision theory illustrates how reactions occur; it can be used to approximate the rate constants of reactions, and its concepts can be directly applied in the laboratory. Read this for a more detailed discussion of Collision Theory.

Transition-State Theory

Transition state theory (TST) provides a more accurate alternative to the previously used Arrhenius equation and the collision theory. The transition state theory attempts to provide a greater understanding of activation energy, E_a, and the thermodynamic properties involving the transition state. Collision theory of reaction rate, although intuitive, lacks an accurate method to predict the probability factor for the reaction. The theory assumes that reactants are hard spheres rather than molecules with specific structures. In 1935, Henry Eyring helped develop a new theory called the transition state theory to provide a more accurate alternative to the previously used Arrhenius equation and the collision theory. The Eyring equation involves the statistical frequency factory, v, which is fundamental to the theory.

According to TST, between the state where molecules are reactants and the state where molecules are products, there is a state known as the transition state. In the transition state, the reactants are combined in a species called the activated complex. The theory suggests that there are three major factors that determine whether a reaction will occur:

1. The concentration of the activated complex
2. The rate at which the activated complex breaks apart
3. The way in which the activated complex breaks apart: whether it breaks apart to reform the reactants or whether it breaks apart to form a new complex, the products.

Collision theory proposes that not all reactants that combine undergo a reaction. However, assuming the stipulations of the collision theory are met and a successful collision occurs between the molecules, transition state theory allows one of two outcomes: a return to the reactants, or a rearranging of bonds to form the products.

Consider a bimolecular reaction:

$$A + B \rightarrow C \tag{1.7.6}$$

$$K = \frac{[C]}{[A][B]} \tag{1.7.7}$$

where K is the equilibrium constant. In the transition state model, the activated complex AB is formed:

$$A + B \rightleftharpoons AB^{\ddagger} \rightarrow C \tag{1.7.8}$$

$$K^{\ddagger} = \frac{[AB]^{\ddagger}}{[A][B]} \tag{1.7.9}$$

There is an energy barrier, called activation energy, in the reaction pathway. A certain amount of energy is required for the reaction to occur. The transition state, $AB^{\ddagger}$, is formed at maximum energy. This high-energy complex represents an unstable intermediate. Once the energy barrier is overcome, the reaction is able to proceed and product formation occurs.

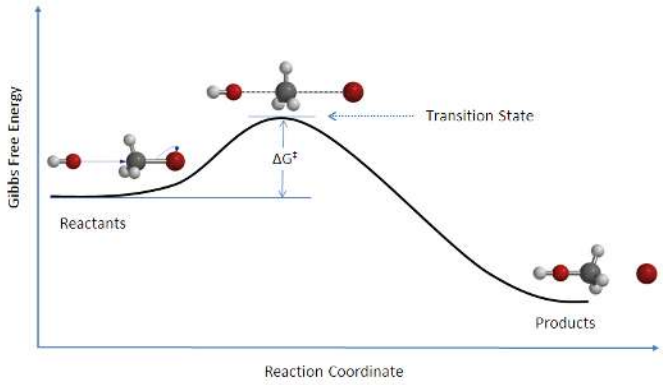


Figure **1.7.1**: Reaction coordinate diagram for the bimolecular nucleophilic substitution (S_N2) reaction between bromomethane and the hydroxide anion. form Wikipedia.

The rate of a reaction is equal to the number of activated complexes decomposing to form products. Hence, it is the concentration of the high-energy complex multiplied by the frequency of it surmounting the barrier.

$$rate = v[AB^{\ddagger}] \tag{1.7.10}$$
$$= v[A][B]K^{\ddagger} \tag{1.7.11}$$

The rate can be rewritten:

$$rate = k[A][B] \tag{1.7.12}$$

Combining Equations 1.7.12 and 1.7.11 gives:

$$k[A][B] = v[A][B]K^{\ddagger} \tag{1.7.13}$$
$$k = vK^{\ddagger} \tag{1.7.14}$$

where

- v is the frequency of vibration,
- k is the rate constant and
- $K^{\ddagger}$ is the thermodynamic equilibrium constant.

Statistical mechanics (not shown) provides that the frequency, v, is equivalent to the thermal energy, k_BT, divided by Planck's constant, h.

$$v = \frac{k_BT}{h} \tag{1.7.15}$$

where

- k_B is the Boltzmann's constant (1.381 x 10^{-23} J/K),
- T is the absolute temperature in Kelvin (K) and
- h is Planck's constant (6.626 x 10^{-34} Js).

Substituting Equation 1.7.15 into Equation 1.7.14 :

$$k = \frac{k_BT}{h}K^{\ddagger} \tag{1.7.16}$$

Equation ref is often tagged with another term (M^{1-m}) that makes the units equal with M is the molarity and m is the molecularly of the reaction.

$$k = \frac{k_B T}{h} K^{\ddagger} (M^{1-m}) \tag{1.7.17}$$

It is important to note here that the equilibrium constant $K^{\ddagger}$ can be calculated by absolute, fundamental properties such as bond length, atomic mass, and vibration frequency. This gives the transition rate theory the alternative name absolute rate theory, because the rate constant, k, can be calculated from fundamental properties.

Thermodynamics of Transition State Theory

To reveal the thermodynamics of the theory, $K^{\ddagger}$ must be expressed in terms of $\Delta G^{\ddagger}$. $\Delta G^{\ddagger}$ is simply,

$$\Delta G^{o\ddagger} = G^{o}(transitionstate) - G^{o}(reactants) \tag{1.7.18}$$

By definition, at equilibrium, $\Delta G^{\ddagger}$ can be expressed as:

$$\Delta G^{\ddagger} = -RT \ln K^{\ddagger} \tag{1.7.19}$$

Rearrangement gives:

$$[K]^{\ddagger} = e^{-\frac{\Delta G^{\ddagger}}{RT}} \tag{1.7.20}$$

From Equation 1.7.17

$$k = ve^{-\frac{\Delta G^{\ddagger}}{RT}} (M^{1-m}) \tag{1.7.21}$$

It is also possible to obtain terms for the change in enthalpy and entropy for the transition state. Because

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{1.7.22}$$

it follows that the derived equation becomes,

$$k = \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} M^{1-m} \tag{1.7.23}$$

Equation 1.7.23 is known as the Eyring Equation and was developed by Henry Eyring in 1935, is based on transition state theory and is used to describe the relationship between reaction rate and temperature. It is similar to the Arrhenius Equation, which also describes the temperature dependence of reaction rates.

The linear form of the Eyring Equation is given below:

$$\ln \frac{k}{T} = \frac{-\Delta H^{\dagger}}{R} \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} \tag{1.7.24}$$

The values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be determined from kinetic data obtained from a $\ln \frac{k}{T}$ vs. $\frac{1}{T}$ plot. The Equation is a straight line with negative slope, $\frac{-\Delta H^{\ddagger}}{R}$, and a y-intercept, $\frac{\Delta S^{\ddagger}}{R} + \ln \frac{k_B}{h}$.

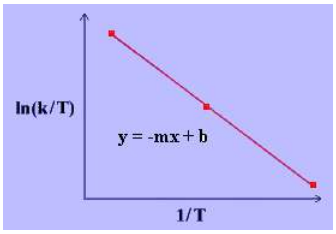


Figure 1.7.2: Linearized TST theory

Conclusion

In this article, the complete thermodynamic formulation of the transition state theory was derived. This equation is more reliable than either the Arrhenius equation and the equation for the Collision Theory. However, it has its limitations, especially when

considering the concepts of quantum mechanics. Quantum mechanics implies that tunneling can occur, such that particles can bypass the energy barrier created by the transition state. This can especially occur with low activation energies, because the probability of tunneling increases when the barrier height is lowered.

In addition, transition state theory assumes that an equilibrium exists between the reactants and the transition state phase. However, in solution non-equilibrium situations can arise, upsetting the theory. Several more complex theories have been presented to correct for these and other discrepancies. This theory still remains largely useful in calculating the thermodynamic properties of the transition state from the overall reaction rate. This presents immense usefulness in medicinal chemistry, in which the study of transition state analogs is widely implemented.

References

1. Chang, Raymond. Physical Chemistry for the Biosciences. University Science Books, California 2005
2. Truhlar, D. G.; Garrett, B. C.; Klippenstein, S. J., Current Status of Transition-State Theory. The Journal of physical chemistry 1996, 100, (31), 12771-12800
3. Laidler, K.; King, C., Development of transition-state theory. The Journal of physical chemistry 1983, 87, (15), 2657
4. Lienhard, Gustav, Enzyme Catalysis and Transition -State Theory: Transition State Analogs. Cold Spring Harb Symp Quant Biol 1972. 36:45-51

Contributors and Attributions

- Phong Dao, Bilal Latif, Lu Zhao (UC Davis)

1.7: Theories of Reaction Rates is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **9.7: Theories of Reaction Rates** is licensed CC BY-NC-SA 4.0.

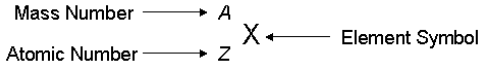
1.8: Isotope Effects in Chemical Reactions

The **kinetic isotope effect** (KIE) is a phenomenon associated with isotopically substituted molecules exhibiting different reaction rates. Isotope effects such as KIEs are invaluable tools in both physical and biological sciences and are used to aid in the understanding of reaction kinetics, mechanisms, and solvent effects.

Introduction

Research was first introduced on this topic over 50 years ago and has grown into an enormous field. The scientists behind much of the understanding and development of kinetic isotope effects were Jacob Bigeleisen and Maria Goeppert Mayer who published the first paper on isotope effects [J. Chem. Phys., 15, 261 (1947)]. Kinetic isotope effects specifically explore the change in rate of a reaction due to isotopic substitution.

An element is identified by its symbol, mass number, and atomic number. The atomic number is the number of protons in the nucleus while the mass number is the total number of protons and neutrons in the nucleus. Isotopes are two atoms of the same element that have the same number of protons but different numbers of neutrons. Isotopes are specified by the mass number.



As an example consider the two isotopes of chlorine, you can see that their mass numbers vary, with ^{35}Cl being the most abundant isotope, while their atomic numbers remain the same at 17.

$$^{35}Cl \text{ and } ^{37}Cl \tag{1.8.1}$$

The most common isotope used in light atom isotope effects is hydrogen (^{1}H) commonly replaced by its isotope deuterium (^{2}H). Note: Hydrogen also has a third isotope, tritium (^{2}H). Isotopes commonly used in heavy atom isotope effects include carbon (^{12}C, ^{13}C, nitrogen (^{14}N, ^{15}N), oxygen, sulfur, and bromine. Not all elements exhibit reasonably stable isotopes (i.e. Fluorine, ^{19}F), but those that due serve as powerful tools in isotope effects.

Potential Energy Surfaces

Understanding potential energy surfaces is important in order to be able to understand why and how isotope effects occur as they do. The harmonic oscillator approximation is used to explain the vibrations of a diatomic molecule. The energies resulting from the quantum mechanic solution for the harmonic oscillator help to define the internuclear potential energy of a diatomic molecule and are

$$E_n = \left(n + \frac{1}{2}\right) h\nu \tag{1.8.2}$$

where

- n is a positive integer (n=1,2,3...),
- h is Planck's constant and
- ν is the frequency of vibration.

The Morse potential is an analytic expression that is used as an approximation to the intermolecular potential energy curves:

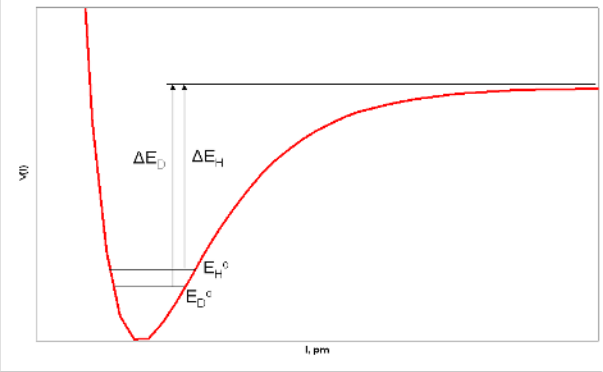
$$V(l) = D_e\left(1-e^{-\beta(l-l_o)}\right)^2 \tag{1.8.3}$$

where

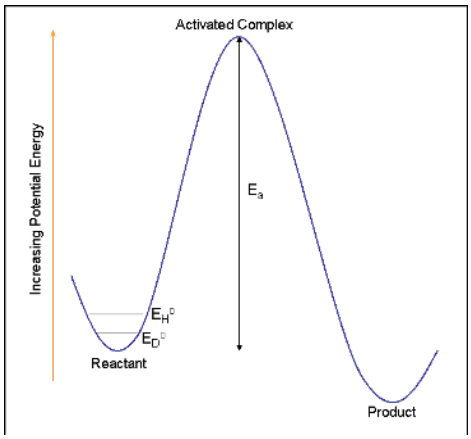
- $V(l)$ is the potential energy,
- D_e is the dissociation energy of the molecule,
- β is the measure of the curvature of the potential at its minimum,
- l is displacement, and
- l_o is the equilibrium bond length.

The D_e, β, and l_o variables can be looked up in a textbook or CRC handbook.

Below is an example of a Morse potential curve with the zero point vibrational energies of two isotopic molecules (for example R-H and R-D where R is a group/atom that is much heavier than H or D). The y-axis is potential energy and the x axis is internuclear distance. In this figure E_D^o and E_H^o correspond to the zero point energies of deuterium and hydrogen. The zero point energy is the lowest possible energy of a system and equates to the ground state energy. Zero point energy is dependent upon the reduced mass of the molecule as will be shown in the next section. The heavier the molecule or atom, the lower the frequency of vibration and the smaller the zero point energy. Lighter molecules or atoms have a greater frequency of vibration and a higher zero point energy. We see this is the figure below where deuterium is heavier than hydrogen and therefore has the lower zero point energy.



This results in different bond dissociation energies for R-D and R-H. The bond dissociation energy for R-D (E_D) is greater than the bond dissociation energy of R-H (E_H). This difference in energy due to isotopic replacement results in differing rates of reaction, the effect that is measured in kinetic isotope effects. The reaction rate for the conversion of R-D is slower than the reaction rate for the conversion of R-H.



It is important to note that isotope replacement does not change the electronic structure of the molecule or the potential energy surfaces of the reactions the molecule may undergo. Only the rate of the reaction is affected.

Activation Energies

The energy of the vibrational levels of a vibration (i.e., a bond) in a molecule is given by

$$E_n = \left(n + \frac{1}{2}\right) h\nu \tag{1.8.4}$$

where we assume that the molecule is in its ground state and we can compare zero-point vibrational energies,

$$E_o = \left(\frac{1}{2}\right) h\nu \tag{1.8.5}$$

Using the harmonic oscillator approximation the fundamental vibrational frequency is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{1.8.6}$$

where

- k is the force constant of the bond and
- μ is the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{1.8.7}$$

The Arrhenius equation is used to determine reaction rates and activation energies and since we are interested in the change in rate of reactions with different isotopes, this equation is very important,

$$k = Ae^{-\frac{E_a}{kT}} \tag{1.8.8}$$

where

- k is the reaction rate,
- E_a is the activation energy, and
- A is the Arrhenius constant.

The Arrhenius equation can be used to compare the rates of a reaction with R-H and R-D,

$$k_H = A_H e^{-\frac{E_a^H}{kT}} \tag{1.8.9}$$

$$k_D = A_D e^{-\frac{E_a^D}{kT}} \tag{1.8.10}$$

where k_H and k_D are the rates of reaction associated with R-H and the isotope substituted R-D. We will then assume the Arrhenius constants are equal ($A_H = A_D$). The ratio of the rates of reaction gives an approximation for the isotope effect resulting in:

$$\frac{k_H}{k_D} = e^{-\frac{E_a^H - E_a^D}{kT}} \tag{1.8.11}$$

By using the relationship that for both R-H and R-D

$$E_o = \left(\frac{1}{2}\right) h\nu \tag{1.8.12}$$

a substitution can be made resulting in

$$\frac{k_H}{k_D} = e^{\frac{h(\nu_H - \nu_D)}{2kT}} \tag{1.8.13}$$

The vibrational frequency (Equation 5) can then be substituted for R-H and R-D and the value of the expected isotope effect can be calculated.

$$\frac{k_H}{k_D} = e^{\frac{h\left(\frac{k_{RH}}{\mu_{RH}} - \frac{k_{RD}}{\mu_{RD}}\right)}{4\pi kT}} \tag{1.8.14}$$

The same general procedure can be followed for any isotope substitution.

In summary, the greater the mass the more energy is needed to break bonds. A heavier isotope forms a stronger bond. The resulting molecule has less of a tendency to dissociate. The increase in energy needed to break the bond results in a slower reaction rate and the observed isotope effect.

Kinetic Isotope Effects

Kinetic Isotope Effects (KIEs) are used to determine reaction mechanisms by determining rate limiting steps and transition states and are commonly measured using NMR to detect isotope location or GC/MS to detect mass changes. In a KIE experiment an atom is replaced by its isotope and the change in rate of the reaction is observed. A very common isotope substitution is when hydrogen

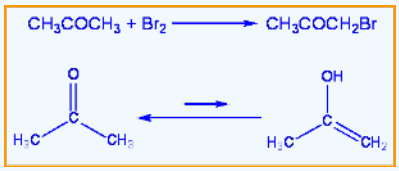
is replaced by deuterium. This is known as a deuterium effect and is expressed by the ratio k_H/k_D (as explained above). Normal KIEs for the deuterium effect are around 1 to 7 or 8. Large effects are seen because the percentage mass change between hydrogen and deuterium is great. Heavy atom isotope effects involve the substitution of carbon, oxygen, nitrogen, sulfur, and bromine, with effects that are much smaller and are usually between 1.02 and 1.10. The difference in KIE magnitude is directly related to the percentage change in mass. Large effects are seen when hydrogen is replaced with deuterium because the percentage mass change is very large (mass is being doubled) while smaller percent mass changes are present when an atom like sulfur is replaced with its isotope (increased by two mass units).

Primary KIEs

Primary kinetic isotope effects are rate changes due to isotopic substitution at a site of bond breaking in the rate determining step of a reaction.

Example

Consider the bromination of acetone: kinetic studies have been performed that show the rate of this reaction is independent of the concentration of bromine. To determine the rate determining step and mechanism of this reaction the substitution of a deuterium for a hydrogen can be made.



When hydrogen was replaced with deuterium in this reaction a $\frac{k_H}{k_D}$ of 7 was found. Therefore the rate determining step is the tautomerization of acetone and involves the breaking of a C-H bond. Since the breaking of a C-H bond is involved, a substantial isotope effect is expected.

Heavy Atom Isotope Effects

A rule of thumb for heavy atom isotope effects is that the maximum isotopic rate ratio is proportional to the square root of the inverse ratio of isotopic masses.



- Expected:

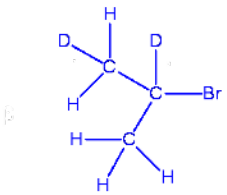
$$\frac{k_{32}}{k_{34}} = \sqrt{\frac{34}{32}} = 1.031 \tag{1.8.15}$$

- Experimental:

$$\frac{k_{32}}{k_{34}} = 1.072 \tag{1.8.16}$$

Secondary KIEs

Secondary kinetic isotope effects are rate changes due to isotopic substitutions at a site other than the bond breaking site in the rate determining step of the reaction. These come in three forms: α, β, and γ effects.



β secondary isotope effects occur when the isotope is substituted at a position next to the bond being broken.

$$(CH_3)_2CHBr + H_2O \xrightarrow{k_H} (CH_3)_2CHOH \quad (1.8.17)$$

$$(CD_3)_2CHBr + H_2O \xrightarrow{k_D} (CD_3)_2CHOH \quad (1.8.18)$$

This is thought to be due to hyperconjugation in the transition state. Hyperconjugation involves a transfer of electron density from a sigma bond to an empty p orbital (for more on hyperconjugation see outside links).

Solvent Effects in Reactions

Reactions may be affected by the type of solvent used (for example H_2O to D_2O or ROH to ROD). There are three main ways solvents effect reactions:

1. The solvent can act as a reactant resulting in a primary isotope effect.
2. Rapid hydrogen exchange can occur between substrate molecules labeled with deuterium and hydrogen atoms in the solvent. Deuterium may change positions in the molecule resulting in a new molecule that is then reacted in the rate determining step of the reaction.
3. The nature of solvent and solute interactions may also change with differing solvents. This could change the energy of the transition state and result in a secondary isotope effects.

References

1. Baldwin, J.E., Gallagher, S.S., Leber, P.A., Raghavan, A.S., Shukla, R.; J. Org. Chem. **2004**, 69, 7212-7219 (This is a great paper using kinetic isotope effects to determine a reaction mechanism. It will interest the organic chemistry oriented reader.)
2. Bigeleisen, J., Goeppert, M., J. Chem. Phys. **1947**, 15, 261.
3. Chang, R.; Physical Chemistry for the Chemical and Biological Sciences; University Science Books: Sausalito, CA, 2000, pp 480-483.
4. Isaacs, N.; Physical Organic Chemistry; John Wiley & Sons Inc.: New York, NY; **1995**, 2nd ed, pp 287-313.
5. March, J., Smith, M.B.; March's Advanced Organic Chemistry; John Wiley & Sons, Inc.: Hoboken, NJ, **2007**; 6th ed.
6. McMurry, J.; Organic Chemistry; Brooks & Cole: Belmont, CA; **2004**, 6th ed.
7. McQuarrie, D.; Quantum Chemistry; University Science Books: Sausalito, CA, **2008**, 2nd ed.
8. Rouhi, A.; C&EN. 1997, 38-42.

Problems

1. Describe the difference between primary and secondary kinetic isotope effects.
2. Estimate the k_{N-H}/k_{N-D} for a deuterium substitution on nitrogen given that v_H=9.3x1013 Hz and the activation energy is equal to 5.31 kJ/mol.
3. Using the 'rule of thumb' for heavy isotope effects, calculate the expected effect for a bromine isotope substitution, ^{79}Br and ^{81}Br.
4. Explain some of the main ways kinetic isotope effects are used.
5. As discussed, the rate-limiting step in the bromination of acetone is the breaking of a carbon-hydrogen bond. Estimate kC-H/KC-D for this reaction at 285 K. (Given: vtilde$_{C-H}$=3000 cm^{-1} and vtilde$_{C-D}$=2100 cm^{-1})

Solutions

1. Primary isotope effects involve isotopic substitution at the bond being broken in a reaction, while secondary isotope effects involve isotopic Substitution on bonds adjacent to the bond being broken.
2. 8.5
3. 1.0126
4. To determine reaction mechanisms, to determine rate limiting steps in reactions, to determine transition states in reactions.
5. 9.685

1.8: Isotope Effects in Chemical Reactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Kinetic Isotope Effects** is licensed CC BY-NC-SA 4.0.

1.9: Reactions in Solution

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Describe some of the major differences between the kinetics of reactions in the gas phase, compared with those in liquid solutions.
- What role do solvent cages play in solution kinetics?
- Explain the distinction between diffusion-control and activation-control of reaction rates in solutions.
- How can the polarity of a solvent affect the energetics of a reaction mechanism?

The kinetics fundamentals we covered in the earlier sections of this lesson group relate to processes that take place in the gas phase. But chemists and biochemists are generally much more concerned with solutions. This lesson will take you through some of the extensions of basic kinetics that you need in order to understand the major changes that occur when reactions take place in liquid solutions.

What's different about kinetics in liquid solutions?

Most of the added complications of kinetics and rate processes in liquid solutions arise from the *much higher density* of the liquid phase. In a typical gas at atmospheric pressure, the molecules occupy only about 0.2 per cent of the volume; the other 99.8 percent is empty space. In a liquid, molecules may take up more than half the volume, and the "empty" spaces are irregular and ever-changing as the solvent molecules undergo thermal motions of their own.

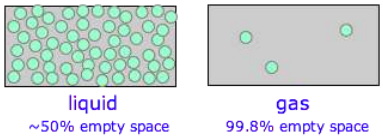


Figure **1.9.1**: Liquid vs. Gases.

In a typical liquid solution, the solvent molecules massively outnumber the reactant solute molecules, which tend to find themselves momentarily (~10^{-11} sec) confined to a "hole" within the liquid. This trapping becomes especially important when the solvent is strongly hydrogen-bonded as is the case with water or alcohol.

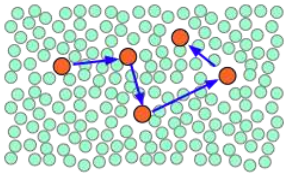
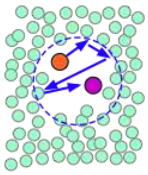
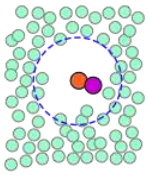
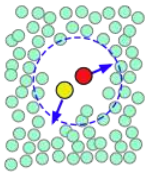
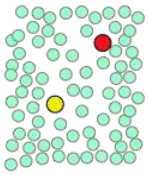


Figure **1.9.2**: Brownian motion of a particle in solution

When thermal motions occasionally release a solute molecule from this trap, it will jump to a new location. The jumps are very fast (10^{-12} - 10^{-13} sec) and short (usually a few solvent-molecule diameters), and follow an entirely random pattern, very much as in **Brownian motion**. Consider a simple bimolecular process A + B → products. The reactant molecules will generally be jumping from hole to hole in the solvent matrix, only occasionally finding themselves in the same *solvent cage* where thermal motions are likely to bring them into contact.

Table 1.9.1: Solvent cages and encounter pairs

			
A pair of reactants end up in the same solvent cage, where they bounce around randomly and exchange kinetic energy with the solvent molecules.	Eventually the two reactants form an *encounter pair*. If they fail to react the first time, they have many more opportunities during the lifetime of the cage.	The products form and begin to move away from each other.	Finally, after about 10^{-11} sec, the solvent cage breaks up and the products diffuse away.

The process can be represented as

$$A + B \rightarrow \{AB\} \rightarrow \text{products} \tag{1.9.1}$$

in which the $\{AB\}$ term represents the caged reactants including the *encounter pair* and the activated complex.

Contrast this scenario with a similar reaction taking place in the gas phase; the molecules involved in the reaction will often be the only ones present, so a significant proportion of the collisions will be A-B encounters. However, if the collision should fail to be energetically or geometrically viable, the reactant molecules fly apart and are unlikely to meet again anytime soon. In a liquid, however, the solute molecules are effectively in a constant state of collision — if not with other reactants, then with solvent molecules which can exchange kinetic energy with the reactants. So once an A-B encounter pair forms, the two reactants get multiple whacks at each other, greatly increasing the probability that they will obtain the kinetic energy needed to kick them over the activation hump before the encounter pair disintegrates.

Limiting Cases: Diffusion-Controlled and Activation-Controlled Reactions

The encounter pair model introduces some new rate parameters:

$$\mathrm{A + B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AB} \longrightarrow \text{products} \tag{1.9.2}$$

The first step is an equilibrium between the reactants outside and inside the solvent cage. The rate constants k_1 and k_2 reflect those relating to diffusion of molecules through the solvent; their values are strongly dependent on the viscosity (and thus the temperature) of the solvent. (Note that k_1 is a second-order rate constant, while k_2 is first-order.)

Diffusion is the transport of a substance through a concentration gradient; that is, from a region of higher concentration to one of lower concentration. Think of the way the color of tea spreads out when a tea bag is immersed in hot water. Diffusion occurs because random thermal motions are statistically more likely to move molecules out of a region of higher concentration than in the reverse direction, simply because in the latter case fewer molecules are available to make the reverse trip. Eventually the concentrations become uniform and equilibrium is attained.

As molecules diffuse through a liquid, they must nudge neighboring molecules out of the way. The work required to do this amounts to an activation energy, so diffusion can be thought of as a kinetic process with its own rate constant k_d and activation energy. These parameters depend on the sizes of the solute and solvent molecules and on how strongly the latter interact with each other. This suggests two important *limiting cases* for reactions in solution.

For water at room temperature, k_1 is typically 10^9-10^{10} $\mathrm{dm^{-3}\ mol^{-1}\ s^{-1}}$ and k_2 is around 10^{-9}-10^{-10} $\mathrm{dm^{-3}\ mol^{-1}\ s^{-1}}$. Given these values, $k_3 > 10^{12}$ $\mathrm{s^{-1}}$ implies diffusion control, while values $< 10^9$ $\mathrm{s^{-1}}$ are indicative of activation control.

- **Diffusion Controlled ($k_3 \gg k_2$)**: If the activation energy of the A+B reaction is very small or if escape of molecules from the {AB} cage is difficult, the kinetics will be dominated by k_1, and thus by the activation energy of diffusion. Such a process is said to be *diffusion controlled*. Reactions in aqueous solution in which $E_a > 20$ kJ/mol are likely to fall into this category.

- **Activation Controlled** *($k_3 \ll k_2$)*: Alternatively, if the activation energy of the A+B reaction dominates the kinetics, and the reaction is *activation-controlled*.

Several general kinds of reactions are consistently very "fast" and thus are commonly found to be diffusion-controlled in most solvents:

Gas-phase rate constants are normally expressed in units of mol s^{-1}, but rate constants of reactions in solution are conventionally given in mol/L units, or $dm^3\ mol^{-1}\ s^{-1}$. Conversion between them depends on a number of assumptions and is non-trivial.

- **Recombination of atoms and radicals**

  For example the formation of I_2 from I atoms in hexane at 298 K has $k_3 = 1.3\times10^{12}\ dm^3\ mol^{-1}\ s^{-1}$.

- **Acid-base reactions** which involve the transport of H^+ and OH^- ions tend to be very fast.

  The most famous of these is one of the fastest reactions known:

  $$H^+ + OH^- \rightarrow H_2O$$

  for which $k_3 = 1.4\times10^{11}\ dm^3\ mol^{-1}\ s^{-1}$ at 298 K.

Polar solvents such as water and alcohols interact with ions and polar molecules through attractive dipole-dipole and ion-dipole interactions, leading to lower-energy solvated forms which stabilize these species. In this way, a polar solvent can alter both the thermodynamics and kinetics (rate) of a reaction.

Solvent Thermodynamic Effect

If the products of the reaction are markedly more or less polar than the reactants, solvent polarity can change the overal thermodynamics (equilibrium constant) of the reaction. Nowhere is this more apparent than when an ionic solid such as salt dissolves in water. The Na^+ and Cl^- ions are bound together in the solid through strong coulombic forces; pulling the solid apart in a vacuum or in a nonpolar solvent is a highly endothermic process. In contrast, dissolution of NaCl in water is slightly exothermic and proceeds spontaneously.

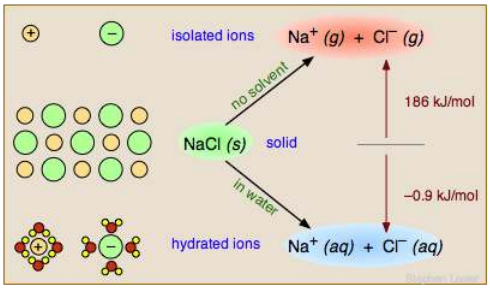
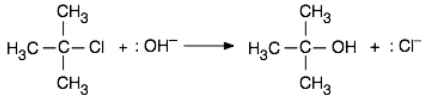


Figure **1.9.3**: The solvent thermodynamics effect for table salt in water.

The water facilitates this process in two important ways. First, its high dielectric constant of 80 reduces the force between the separated ions to 1/80 of its normal value. Secondly, the water molecules form a *solvation shell* around the ions (lower left), rendering them energetically (thermodynamically) more stable than they were in the NaCl solid.

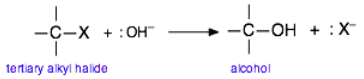
Solvent Kinetic Effect

In the same way, a reaction whose mechanism involves the formation of an intermediate or activated complex having a polar or ionic character will have its activation energy, and thus its rate, subject to change as the solvent polarity is altered. As an example we will consider an important class of reactions that you will hear much about if you take a course in organic chemistry. When an aqueous solution of a strong base such as KOH is added to a solution of *tertiary*-butyl chloride in ethanol, the chlorine is replaced by a hydroxyl group, leaving *t*-butyl alcohol as a product:

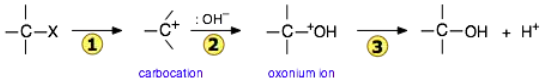


This reaction is one of a large and important class known as *S_N1 nucleophilic substitution processes* that are discussed in most organic chemistry courses. In these reactions, a species that possesses a pair of non-bonding electrons (also called a *nucleophile* or *Lewis base*) uses them to form a new bond with an *electrophile* — a compound in which a carbon atom has a partial positive charge owing to its bonds to electron-withdrawing groups. In the example here, other nucleophiles such as NH_3 or even H_2O would serve as well.

In order to reflect the generality of this process and to focus on the major changes that take place, we will represent this reaction as



Extensive studies of this class of reactions in the 1930's revealed that it proceeds in two activation energy-controlled steps, followed by a simple dissociation into the products:



In step ①, which is rate-determining, the chlorine leaves the alkyl chloride which becomes an intermediate known as a *carbocation* ("cat-ion"). These ions, in which the central carbon atom lacks a complete octet, are highly reactive, and in step ② the carbocation is attacked by the hydroxide ion which supplies the missing electron. The immediate product is another cation in which the positive charge is on the oxygen atom. This *oxonium ion* is unstable and rapidly dissociates (③)into the alcohol and a hydrogen ion.

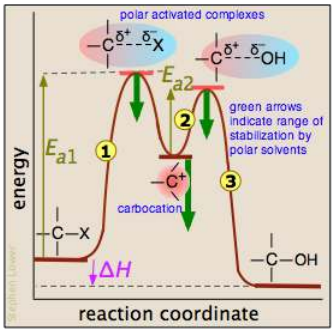


Figure **1.9.4**: reaction Coordinate

The reaction coordinate diagram helps us understand the effect of solvent polarity on this reaction. Polar solvent molecules interact most strongly with species in which the electric charge is concentrated in one spot. Thus the carbocation is stabilized to a greater degree than are the activated complexes in which the charge is spread out between the positive and negative ends. As the heavy green arrows indicate, a more polar solvent will stabilize the carbocation more than it will either of the activated complexes; the effect is to materially reduce the activation energy of the rate-determining step, and thus speed up the reaction. Because neither the alkyl chloride nor the alcohol is charged, the change in solvent polarity has no effect on the equilibrium constant of the reaction. This is dramatically illustrated by observing the rate of the reaction in solvents composed of ethanol and water in varying amounts:

Table **1.9.2**: Data

% water	10	20	30	40	50	60
$k_1 \times 10^6$	1.7	9.1	40.3	126	367	1294

1.9: Reactions in Solution is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.5: Kinetics of Reactions in Solution** by Stephen Lower is licensed CC BY 3.0. Original source: http://www.chem1.com/acad/webtext/virtualtextbook.html.

1.10: Fast Reactions in Solution

The traditional experimental methods described above all assume the possibility of following the reaction after its components have combined into a homogeneous mixture of known concentrations. But what can be done if the time required to complete the mixing process is comparable to or greater than the time needed for the reaction to run to completion?

Flow methods

Flow instruments are a rapid mixing devices used to study the chemical kinetics of fast reactions in solution. There are different flavors that can be implement depending on the nature of the reaction as discussed below.

Continuous Flow Approach

For reactions that take place in milliseconds, the standard approach since the 1950s has been to employ a flow technique of some kind. An early example was used to study fast gas-phase reactions in which one of the reactants is a free radical such as OH that can be produced by an intense microwave discharge acting on a suitable source gas mixture. This gas, along with the other reactant being investigated, is made to flow through a narrow tube at a known velocity.

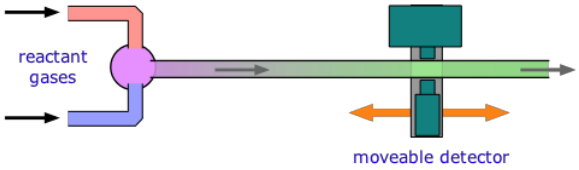


Figure **1.10.1**: A continuous flow fast kinetic system.

If the distance between the point at which the reaction is initiated and the product detector is known, then the time interval can be found from the flow rate. By varying this distance, the time required to obtain the maximum yield can then be determined. Although this method is very simple in principle, it can be complicated in practice.

Stopped Flow Approach

Owing to the rather large volumes required, continuous flow method is more practical for the study of gas-phase reactions than for solutions, for which the stopped-flow method described below is generally preferred. These are by far the most common means of studying fast solution-phase reactions over time intervals of down to a fraction of a millisecond. The use of reasonably simple devices is now practical even in student laboratory experiments. These techniques make it possible to follow not only changes in the concentrations of reactants and products, but also the buildup and decay of reaction intermediates.

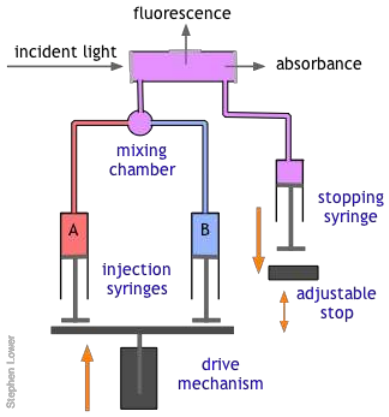


Figure **1.10.2**: A stop flow fast kinetic system.

The basic stopped-flow apparatus consists of two or more coupled syringes that rapidly inject the reactants into a small mixing chamber and then through an observation cell that can be coupled to instruments that measure absorption, fluorescence, light scattering, or other optical or electrical properties of the solution. As the solution flows through the cell, it empties into a stopping syringe that, when filled, strikes a backstop that abruptly stops the flow. The volume that the stopping syringe can accept is

adjusted so that the mixture in the cell has just become uniform and has reached a steady state; at this point, recording of the cell measurement begins and its change is followed.

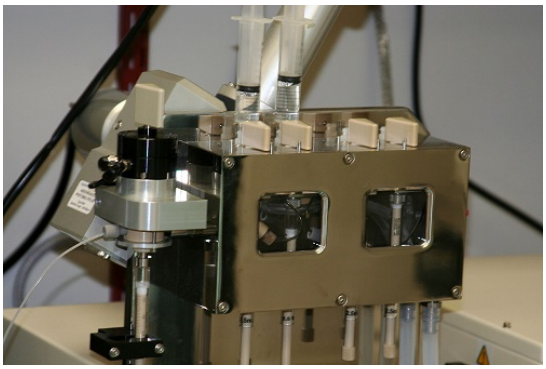


Figure **1.10.3**: Stop-flow equipment at a biochemistry research laboratory for measuring rapid reactions and properties such as enzyme kinetics. from Wladimir Labeikovsky.

Quenched Flow Approach

In a quenched-flow instrument, the reaction is stopped after a certain amount of time has passed after mixing. The stopping of the reaction is called quenching and it can be achieved by various means, for example by mixing with another solution, which stops the reaction (chemical quenching), quickly lowering the temperature (freeze quenching) or even by exposing the sample to light of a certain wavelength (optical quenching).

Of course, there are many reactions that cannot be followed by changes in light absorption or other physical properties that are conveniently monitored. In such cases, it is often practical to *quench* (stop) the reaction after a desired interval by adding an appropriate quenching agent. For example, an enzyme-catalyzed reaction can be stopped by adding an acid, base, or salt solution that denatures (destroys the activity of) the protein enzyme. Once the reaction has been stopped, the mixture is withdrawn and analyzed in an appropriate manner.

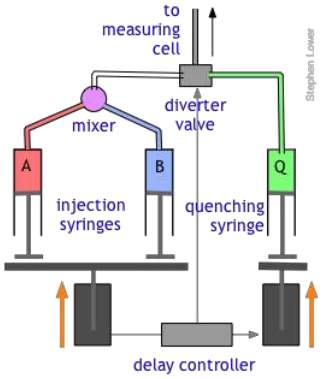


Figure **1.10.4**: A quench flow fast kinetic system.

The quenched-flow technique works something like the stopped-flow method described above, with a slightly altered plumbing arrangement. The reactants A and B are mixed and fed directly through the diverter valve to the measuring cell, which is not shown in this diagram. After a set interval that can vary from a few milliseconds to 200 sec or more, the controller activates the quenching syringe and diverter valve, flooding the cell with the quenching solution.

Relaxation Methods

To investigate reactions that are complete in less than a millisecond, one can start with a pre-mixed sample in which one of active reactants is generated *in situ*. Alternatively, a rapid change in pressure or temperature can alter the composition of a reaction that has already achieved equilibrium.

Flash Photolysis

Many reactions are known which do not take place without light of wavelength sufficiently short to supply the activation energy needed to break a bond, often leading to the creation of a highly reactive radical. A good example is the combination of gaseous Cl_2 with H_2, which proceeds explosively when the system is illuminated with visible light. In *flash photolysis*, a short pulse of light is used to initiate a reaction whose progress can be observed by optical or other means.

Photolysis refers to the use of light to decompose a molecule into simpler units, often ions or free radicals. In contrast to *thermolysis* (decomposition induced by high temperature), photolysis is able to inject energy into a molecule almost instantaneously and can be much "cleaner," meaning that there are fewer side reactions that often lead to complex mixtures of products. Photolysis can also be highly *specific*; the wavelength of the light that triggers the reaction can often be adjusted to activate one particular kind of molecule without affecting others that might be present.

Norrish and Porter

All this had been known for a very long time, but until the mid-1940's there was no practical way of studying the kinetics of the reactions involving the highly reactive species produced by photolysis. In 1945, Ronald Norrish of Cambridge University and his graduate student George Porter conceived the idea of using a short-duration flash lamp to generate gas-phase CH_2 radicals, and then following the progress of the reaction of these radicals with other species by means of absorption spectroscopy.

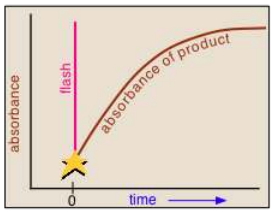


Figure **1.10.5**: Basic principle of a flash-photolysis relaxation experiment where an excitation pulse purturbed a system at equilibrium and the subsequent dynamics are resolved in time.

In a flash photolysis experiment, recording of the absorbance of the sample cell contents is timed to follow the flash by an interval that can be varied in order to capture the effects produced by the product or intermediate as it is formed or decays. Norrish and Porter shared the 1967 Nobel Prize in Chemistry for this work.

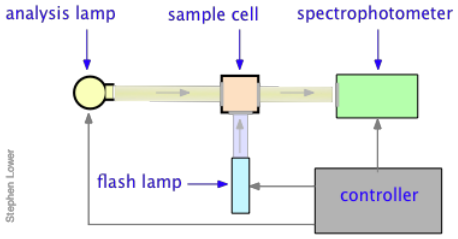


Figure **1.10.6**: A flash-photolysis relaxation experiment

Many reactions, especially those that take place in solution, occur too rapidly to follow by flow techniques, and can therefore only be observed when they are already at equilibrium. The classical examples of such reactions are two of the fastest ones ever observed, the dissociation of water

$$2H_2O \rightarrow H_3O^+ + OH^- \tag{1.10.1}$$

and the formation of the triiodide ion in aqueous solution

$$I^- + I_2 \rightarrow I_3^- \tag{1.10.2}$$

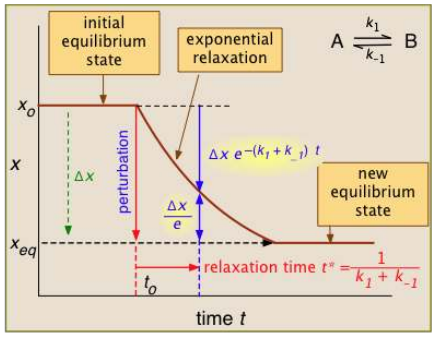
Reactions of these kinds could not be studied until the mid-1950s when techniques were developed to shift the equilibrium by imposing an abrupt physical change on the system.

Temperature Jumps

The rate constants of reversible reactions can be measured using a relaxation method. In this method, the concentrations of reactants and products are allowed to achieve equilibrium at a specific temperature. Once equilibrium has been achieved, the temperature is rapidly changed, and then the time needed to achieve the new equilibrium concentrations of reactants and products is measured. For example, if the reaction

$$\mathbf{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{B} \tag{1.10.3}$$

is endothermic, then according to the Le Chatelier principle, subjecting the system to a rapid jump in temperature will shift the equilibrium state to one in which the product B has a higher concentration. The composition of the system will than begin to shift toward the new equilibrium composition at a rate determined by the kinetics of the process.



For the general case illustrated here, the quantity "*x*" being plotted is a measurable quantity such as light absorption or electrical conductivity that varies linearly with the composition of the system. **In a first-order process**, *x* will vary with time according to

$$x_t = x_o e^{-kt} \tag{1.10.4}$$

After the abrupt perturbation at time t_o, the relaxation time t^* is defined as the half-time for the return to equilibrium — that is, as the time required for x_o to decrease by \($\Delta x/e = \Delta x/2.718$\). The derivation of t^* and the relations highlighted in yellow can be found in most standard kinetics textbooks. Temperature jumps are likely most commonly used.

The rate law for the reversible reaction in Equation 1.10.3 can be written as

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\,[\mathrm{A}] - k_{-1}\,[\mathrm{B}] \tag{1.10.5}$$

Consider a system comprising **A** and **B** that is allowed to achieve equilibrium concentrations at a temperature, T_1. After equilibrium is achieved, the temperature of the system is instantaneously lowered to T_2 and the system is allowed to achieve new equilibrium concentrations of **A** and **B**, $[\mathrm{A}]_{\mathrm{eq},2}$ and $[\mathrm{B}]_{\mathrm{eq},2}$. During the transition time from the first equilibrium state to the second equilibrium state, we can write the instantaneous concentration of **A** as

$$[\mathrm{A}] = [\mathrm{B}]_{\mathrm{eq},1} - [\mathrm{B}] \tag{1.10.6}$$

The rate of change of species **B** can then be written as

$$\frac{d\,[\mathrm{B}]}{dt} = k_1\left([\mathrm{B}]_{\mathrm{eq},1} - [\mathrm{B}]\right) - k_{-1}\,[\mathrm{B}] = k_1\,[\mathrm{B}]_{\mathrm{eq},1} - (k_1 + k_{-1})\,[\mathrm{B}] \tag{1.10.7}$$

At equilibrium, $d\,[\mathrm{B}]\,/dt = 0$ and $[\mathrm{B}] = [\mathrm{B}]_{\mathrm{eq},2}$, allowing us to write

$$k_1\,[\mathrm{B}]_{\mathrm{eq},1} = (k_1 + k_{-1})\,[\mathrm{B}]_{\mathrm{eq},2} \tag{1.10.8}$$

Using the above equation, we can rewrite the rate equation as

$$\frac{d\mathrm{B}}{\left([\mathrm{B}]_{\mathrm{eq},2} - [\mathrm{B}]\right)} = (k_1 + k_{-1})\,dt \tag{1.10.9}$$

Integrating yields

$$-\ln\left([\mathrm{B}]-[\mathrm{B}]_{\mathrm{eq},2}\right)=-\left(k_1+k_{-1}\right)t+C \tag{1.10.10}$$

We can rearrange the above equation in terms of $\mathbf{B}$

$$[\mathrm{B}]=Ce^{-(k_1+k_{-1})t}+[\mathrm{B}]_{\mathrm{eq},2} \tag{1.10.11}$$

At $t=0$, $[\mathrm{B}]=[\mathrm{B}]_{\mathrm{eq},1}$, so $C=[\mathrm{B}]_{\mathrm{eq},1}-[\mathrm{B}]_{\mathrm{eq},2}$. Plugging the the value of C, we arrive at

$$[\mathrm{B}]-[\mathrm{B}]_{\mathrm{eq},2}=\left([\mathrm{B}]_{\mathrm{eq},1}-[\mathrm{B}]_{\mathrm{eq},2}\right)e^{-(k_1+k_{-1})t} \tag{1.10.12}$$

which can also be expressed as

$$\Delta[\mathrm{B}]=\Delta[\mathrm{B}]_0\,e^{-(k_1+k_{-1})t}=\Delta[\mathrm{B}]_0\,e^{-t/\tau} \tag{1.10.13}$$

where $\Delta[\mathrm{B}]$ is the difference in the concentration of $\mathbf{B}$ from the final equilibrium concentration after the perturbation, and τ is the *relaxation time*. A plot of $\ln\left(\Delta[\mathrm{B}]/\Delta[\mathrm{B}]_0\right)$ versus t will be linear with a slope of $-(k_1+k_{-1})$, where k_1 and k_{-1} are the rate constants at temperature, T_2.

Contributors and Attributions

- Mark Tuckerman (New York University)
- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

This page titled 1.10: Fast Reactions in Solution is shared under a not declared license and was authored, remixed, and/or curated by Stephen Lower via source content that was edited to the style and standards of the LibreTexts platform.

- **9.10: Fast Reactions in Solution** by Stephen Lower is licensed CC BY-NC-SA 4.0. Original source: http://www.chem1.com/acad/webtext/virtualtextbook.html.

1.11: Oscillating Reactions

It should be clear by now that chemical kinetics is governed by the mathematics of systems of differential equations. Thus far, we have only looked at reaction systems that give rise to purely *linear* differential equations, however, in many instances the rate equations are nonlinear. When the differential equations are nonlinear, the behavior is considerably more complex. In particular, nonlinear equations can lead to oscillatory solutions and can also exhibit the phenomenon of *chaos*. Chaotic systems are systems that are highly sensitive to small changes in the parameters of the equations or in the initial conditions. Basically, this means that the behavior of a chaotic system can be unpredictable, since such small changes can occur in the form of small errors in determining the parameters (rounding to the nearest tenth or hundredth) or in specifying the initial conditions, and these small changes can cause the system to evolve in time in a very different way.

The Iodine Clock Reaction

The iodine clock reaction is a popular chemistry experiment in which one can visualize how different rate constants in consecutive reactions affect the concentration of species during the reaction. Iodine anions (I^-) are colorless. When I^- is reacted with hydrogen peroxide and protons, triiodide is formed, which has a dark blue color. Consider the following series of irreversible reactions:

$$H_2O_2 + 3\,I^- + 2\,H^+ \xrightarrow{k_1} I_3^- + 2\,H_2O \tag{1.11.1}$$

$$I_3^- + 2\,S_2O_3^{2-} \xrightarrow{k_2} 3\,I^- + S_4O_6^{2-} \tag{1.11.2}$$

The rate laws for this system are

$$\frac{d\left[I_3^-\right]}{dt} = k_1\left[I^-\right]^3 - k_2\left[I_3^-\right]\left[S_2O_3^{2-}\right]^2 \tag{1.11.3}$$

$$\frac{d\left[I^-\right]}{dt} = -k_1\left[I^-\right]^3 + 3k_2\left[I_3^-\right]\left[S_2O_3^{2-}\right]^2 \tag{1.11.4}$$

$$\frac{d\left[S_2O_3^{2-}\right]}{dt} = -k_2\left[I_3^-\right]\left[S_2O_3^{2-}\right]^2 \tag{1.11.5}$$

In order to make the equations look a little simpler, let us introduce the variables:

$$x = \left[I^-\right], \quad y = \left[I_3^-\right], \quad z = \left[S_2O_3^{2-}\right] \tag{1.11.6}$$

In terms of these, the rate equations are

$$\frac{dx}{dt} = -k_1x^3 + 3k_2yz^2 \tag{1.11.7}$$

$$\frac{dy}{dt} = k_1x^3 - k_2yz^2 \tag{1.11.8}$$

$$\frac{dz}{dt} = -k_2yz^2 \tag{1.11.9}$$

If we solve these numerically, we find the following time dependence of the three concentrations: This is a clear example of nonlinearity. Note how the concentration of I_3^- remains close to 0 for a period of time and then suddenly starts to increase. In a sense, think of the “straw that broke the camel’s back”. As we pile straws on the back of the camel, the camel remains upright until that last straw, which suddenly breaks the back of the camel, and the camel suddenly falls to the ground. This is also an illustration of nonlinearity.



***Video* 1.11.1:** *Famous iodine clock reaction: oxidation of potassium iodide by hydrogen peroxide (https://www.youtube.com/watch?v=_qhYDuJt8fI).*

Despite the complexity of the rate equations, we can still analyze the approximately and predict the behavior seen in Figure 1.11.1. In this reaction mechanism, $k_2 \gg k_1$. Given the rate law for I_3^-,

$$\frac{d[I_3^-]}{dt} = k_1[I^-]^3 - k_2[I_3^-][S_2O_3^{2-}]^2 \tag{1.11.10}$$

if we use the steady-state approximation, we can set the $\frac{d[I_3^-]}{dt}$ equal to 0, yielding

$$[I_3^-] = \frac{k_1}{k_2}\frac{[I^-]^3}{[S_2O_3^{2-}]^2} \tag{1.11.11}$$

Since $k_2 \gg k_1$, the concentration of $[I_3^-]$ is approximately 0 as long as there are $S_2O_3^{2-}$ ions present. As soon as all of the $S_2O_3^{2-}$ is consumed, the concentration of I_3^- can build up in the solution, changing the solution to a dark blue color. Figure 1.11.1 displays the concentration profiles for I^-, I_3^-, and $S_3O_3^{2-}$. As can be seen from the figure, the concentration of I_3^- (red line) remains at approximately $0\ \text{mol/L}$ until all of the $S_2O_3^{2-}$ (blue line) has been depleted.

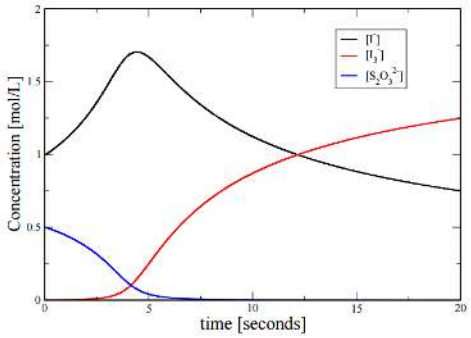


Figure 1.11.1: Concentrations as functions of time of the three species in the iodine clock reaction.

Oscillating Reactions

In all of the examples we have seen thus far, the concentration of intermediate species displays a single maximum during the course of the reaction. There is another class of reactions called *oscillating reactions* in which the concentration of intermediate species oscillates with time. Consider the following series of reactions

$$\mathrm{A} + \mathrm{Y} \xrightarrow{k_1} \mathrm{X} \tag{1.11.12}$$

$$\mathrm{X} + \mathrm{Y} \xrightarrow{k_2} \mathrm{P} \tag{1.11.13}$$

$$\mathrm{B} + \mathrm{X} \xrightarrow{k_3} 2\,\mathrm{X} + \mathrm{Z} \tag{1.11.14}$$

$$2\,\mathrm{X} \xrightarrow{k_4} \mathrm{Q} \tag{1.11.15}$$

$$\mathrm{Z} \xrightarrow{k_5} \mathrm{Y} \tag{1.11.16}$$

In the above reaction mechanism, **A** and **B** are reactants; **X**, **Y**, and **Z** are intermediates; and **P** and **Q** are products. The third reaction in which **B** and **X** react to form **X** and **Z** is known as an "autocatalytic reaction" in which at least one of the reactants is also a product. Such reactions are a key feature of oscillating reactions, as will be discussed below.



***Video* 1.11.2:** *The famous Belousov Zhabotinsky chemical reaction in a petri dish. The action is speeded up 8 x from real life. Pacemaker nucleation sites emit circular waves. Breaking the wavefront with a wire triggers pairs of spiral defects which emit more closely spaced waves which eventually fill the container.*

Let us assume that the concentrations of **A** and **B** are large, such that we can approximate them to be constant with time. The rate equation for species **X** can be written as

$$\frac{d[\mathrm{X}]}{dt} = k_1[\mathrm{A}][\mathrm{Y}] - k_2[\mathrm{X}][\mathrm{Y}] + k_3[\mathrm{B}][\mathrm{X}] - 2k_4[\mathrm{X}]^2 \tag{1.11.17}$$

Using the steady-state approximation, we can set $d\mathrm{X}/dt = 0$ and rewrite Equation 1.11.17 as

$$(-2k_4)[\mathrm{X}]^2 + (k_2[\mathrm{Y}] - k_3[\mathrm{B}])[\mathrm{X}] + k_1[\mathrm{A}][\mathrm{Y}] = 0 \tag{1.11.18}$$

We can then use the quadratic formula to solve for **X**:

$$[\mathrm{X}] = -\frac{(k_2[\mathrm{Y}] - k_3[\mathrm{B}]) \pm \sqrt{(k_2[\mathrm{Y}] - k_3[\mathrm{B}])^2 - 4(-2k_4)(k_1[\mathrm{A}][\mathrm{Y}])}}{2(-2k_4)} \tag{1.11.19}$$

Thus, there are two solutions for the concentration of **X** accessible to the reaction system. To examine solutions for [X], let us first assume that [Y] is large. Under these conditions, the first two reactions in the reaction mechanism largely determine the concentration of [X]. We can thus approximate Equation 1.11.17 as

$$0 \approx k_1[\mathrm{A}][\mathrm{Y}] - k_2[\mathrm{X}][\mathrm{Y}] \tag{1.11.20}$$

Solving for [X] yields

$$[\mathrm{X}] \approx \frac{k_1[\mathrm{A}]}{k_2} \tag{1.11.21}$$

As the reaction continues, species **Y** is depleted and the assumption that [Y] is large becomes invalid. Instead the 3rd and 4th steps of the reaction mechanism determine the concentration of **X**. In this limit, we can approximate Equation 1.11.17 as

$$0 \approx k_3[\mathrm{B}][\mathrm{X}] - 2k_4[\mathrm{X}]^2 \tag{1.11.22}$$

Solving for [X] yields

$$[\mathrm{X}] \approx \frac{k_3[\mathrm{B}]}{2k_4} \tag{1.11.23}$$

In the second mechanism, the autocatalytic reaction step leads to an increase in the concentration of **X** and **Z**, which in turn leads to an increase in the concentration of **Y**. The feedback loop between the production of species **X** and **Y** leads to oscillatory behavior in the system. This reaction mechanism is known as the Belousov-Zhabotinksii reaction first discovered in the 1950s.

- The autocatalytic reaction of **X** in which **X** reacts with **B** to form more **X** in reaction **3**
- The regeneration of species **Y** in reaction **5**
- The competition between reaction **2** and **3** for the consumption of **X** and the involvement of **Y** in reaction **2**

The actual Belousov-Zhabotinskii reaction is complex, involving many individual steps, and involves the oscillation between the concentration of $HBrO_2$ and Br^-. The reaction equations are

$$BrO_3^- + Br^- + 2\,H^+ \longrightarrow HBrO_2 + HOBr \tag{1.11.24}$$
$$HBrO_2 + Br^- + H^+ \longrightarrow 2\,HOBr \tag{1.11.25}$$
$$HOBr + Br^- + H^+ \longrightarrow Br_2 + H_2O \tag{1.11.26}$$
$$2\,HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+ \tag{1.11.27}$$
$$BrO_3^- + HBrO_2 + H^+ \longrightarrow 2\,BrO_2 + H_2O \tag{1.11.28}$$
$$BrO_2 + Ce^{3+} + H^+ \longrightarrow HBrO_2 + Ce^{4+} \tag{1.11.29}$$
$$BrO_2 + Ce^{4+} + H_2O \longrightarrow BrO_3^- + Ce^{3+} + 2\,H^+ \tag{1.11.30}$$

The essential steps in this mechanism can be reduced to the following set of reactions. Note that we leave this unbalanced and only include the species whose concentrations as functions of time we seek.

$$BrO_3^- + Br^- \xrightarrow{k_1} HBrO_2 + HOBr \tag{1.11.31}$$
$$HBrO_2 + Br^- \xrightarrow{k_2} 2\,HOBr \tag{1.11.32}$$
$$BrO_3^- + HBrO_2 \xrightarrow{k_3} 2\,HBrO_2 + 2\,Ce^{4+} \tag{1.11.33}$$
$$2\,HBrO_2 \xrightarrow{k_4} BrO_3^- + HOBr \tag{1.11.34}$$
$$Ce^{4+} \xrightarrow{k_5} fBr^- \tag{1.11.35}$$

Setting the variables as follows:

$$x = [HBrO_2], \quad y = [Br^-], \quad z = [Ce^{4+}] \tag{1.11.36}$$

We make the approximation that $[BrO_3^-]$ to be a constant a. In this case, the rate equations become

$$\frac{dx}{dt} = k_1 ay - k_2 xy + k_3 ax - k_4 x^2 \tag{1.11.37}$$
$$\frac{dy}{dt} = -k_1 ay - k_2 xy + fk_5 z \tag{1.11.38}$$
$$\frac{dz}{dt} = 2k_3 ax - k_5 z \tag{1.11.39}$$

Solving these equations numerically, we obtain the trajectory of two of the species show in the Figure **1.11.2**.

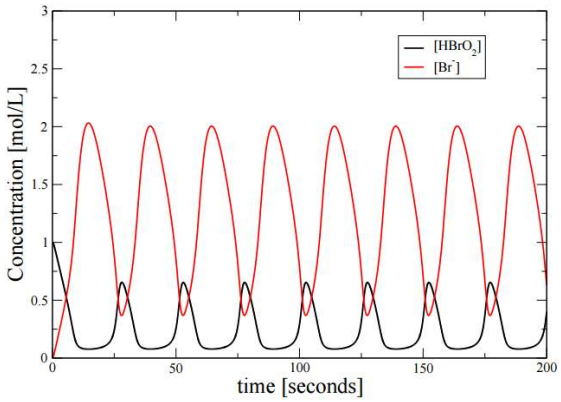


Figure **1.11.2**: Oscillating pattern of the concentrations in the Belousov-Zhabotinskii reaction.

On the other hand, we can drive this system to become chaotic by changing the parameters a little. When this is done, we find the follow plot of the concentration of x:

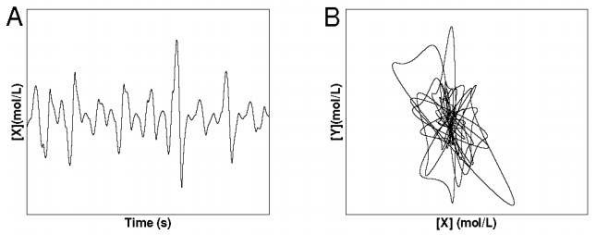


Figure **1.11.3**: Chaotic behavior in the Belousov-Zhabotinskii reaction.

Contributors and Attributions

- Mark Tuckerman (New York University)

1.11: Oscillating Reactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **9.11: Oscillating Reactions** is licensed CC BY-NC-SA 4.0.

1.12: Chemical Kinetics (Exercises)

9.1: Reaction Rates

Q9.1

Write the rate of reaction in terms of the rate of disappearance of reactant and the rate of formation of products:

a. $NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$
b. $2C_2H_{6(g)} + 7O_{2(g)} \rightarrow 4CO_{2(g)} + 6H_2O_{(aq)}$
c. $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$
d. $4OH_{(g)} + H_2S_{(g)} \rightarrow SO_{2(g)} + 2H_2O_{(aq)} + H_{2(g)}$

S9.1

1. $\text{rate of reaction} = \frac{-\Delta[NO]}{\Delta t} = \frac{-\Delta[O_3]}{\Delta t} = \frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$
2. $\text{rate of reaction} = \frac{-\Delta[C_2H_6]}{2\Delta t} = \frac{-\Delta[O_2]}{7\Delta t} = \frac{\Delta[CO_2]}{4\Delta t} = \frac{\Delta[H_2O]}{6\Delta t}$
3. $\text{rate of reaction} = \frac{-\Delta[H_2]}{\Delta t} = \frac{-\Delta[I_2]}{\Delta t} = \frac{\Delta[HI]}{2\Delta t}$
4. $\text{rate of reaction} = \frac{-\Delta[OH]}{4\Delta t} = \frac{-\Delta[H_2S]}{\Delta t} = \frac{\Delta[SO_2]}{\Delta t} = \frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t}$

9.2: Reaction Order

Q9.2

Determine the value of the rate constant for the elementary reaction:

$$I_{2(g)} + H_{2(g)} \rightarrow 2HI_{(aq)} \tag{1.12.1}$$

given that when $[Br_2]$ is 0.15 M and $[H_2]$ is 0.2M, the rate of reaction is 0.005 M s^{-1} at 298 K.

S9.2

rate of reaction = $k[Br_2][H_2]$

0.005 Ms^{-1} =k (0.15M)^2(0.2M)

k= 1.11 $M^{-1}s^{-1}$

Q9.3

Given the rate of the third order reaction:

$$A + B + C \rightarrow P \tag{1.12.2}$$

is 0.05 Ms^{-1}

If the [A] = 0.05 M, [B] = 0.01M, and [C] = 0.25M. What is the third order rate constant?

S9.3

rate of reaction = k[A][B][C]

0.05Ms^{-1} =k (0.05M)(0,01M)(0.25M)

k= 0.05Ms^{-1}/(0.05) (0.01)(0.25) M^3

k= 400$M^{-2}s^{-1}$

Q9.3

What are the units of the rate constant for a second-order reaction?

S9.3

The reaction rate:

$$Rate = \frac{d[A]}{dt} = -k[A]^2 \tag{1.12.3}$$

The rate constant of a second-order reaction, k, is $M^{-1}min^{-1}$ or $M^{-1}s^{-1}$

Q9.4

Calculate the fraction of the starting quantity of A that will be used up after 60 s. Given the reaction below which is found to be the first order in A and $t_{1/2} = 40\ s$

$$A \rightarrow B + C \tag{1.12.4}$$

S9.4

with \(t_{1/2} = 40 \; s\]

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{40} = 0.0173 s^{-1}$$

The remain of fraction A after 60 s:

$$[A] = [A]_o e^{-kt}$$

$$\frac{[A]}{[A]_o} = e^{-(0.0173 s^{-1})(60 s)} = 0.354$$

The fraction will be used up after 60s:

$$1 - 0.354 = 0.646$$

Q9.5

Given the first order reaction is completed 90% in 30 mins at 298 K. Calculate the rate constant.

S9.5

90%= 0.9

$$[A] = [A]_o e^{-kt}$$

$$\frac{[A]}{[A]_o} = e^{-kt}$$

$$\ln \frac{[A]}{[A]_o} = -kt$$

$$\ln 0.9 = -30k$$

$$k = -\frac{\ln 0.9}{30} = 0.00351 min^{-1}$$

Q9.6

Assume the half life of the first order decay of radioactive isotope takes about 1 year (365 days). How long will it take the radioactivity of that isotope to decay by 60%?

S9.6

$$t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{365} = 0.00189 day^{-1}$$

60% is lost

100%- 60%= 40% is remained

40%= 0.4

$$\frac{[A]}{[A]_o} = 0.4$$

$$\frac{[A]}{[A]_o} = e^{-kt}$$

$$\ln \frac{[A]}{[A]_o} = -kt$$

$$t = \frac{-1}{k} \ln \frac{[A]}{[A]_o} = \frac{-1}{0.00189} \ln 0.4 = 484.81 days$$

Q9.7a

The decomposition of dinitrogen peroxide (N_2O_5) is a first-order reaction with a rate constant of 0.045 min^{-1} at 300 K.

$$2N_2O_{5(g)} \rightarrow 4NO_2(g) + O_2 \tag{1.12.5}$$

If there were initially 0.040 mol of N_2O_5, calculate the moles of N_2O_5 remaining after 5 minutes.

S9.7a

The integrated rate equation of a first-order reaction is:

$$[A] = [A]_0 e^{-kt} \tag{1.12.6}$$

Substituting concentration for moles of reactant and plugging in the known values:

$$n_A = 0.040_0 e^{-0.045*5} \tag{1.12.7}$$

$$n_A = 0.032 \tag{1.12.8}$$

Q9.7b

You forgot to do your lab assignment the day before and realize you only have 5 hours to reduce your initial concentration of your reactant by 90%. You know the half life is 2 hours and before you get out of bed, you wonder if you can even finish the lab on time. Assuming you have a first order reactant, will 5 hours be enough time for your compound to reduce by 90%?

S9.7b

First, you need to figure the half life of your compound. We do this by solving for **k**:

$$t_{1/2} = \frac{0.693}{k} \tag{1.12.9}$$

$$k = \frac{0.693}{t\frac{1}{2}} \tag{1.12.10}$$

$$k = \frac{0.693}{2hrs} = 0.3465 \tag{1.12.11}$$

with this half life, we can find the time it will take by solving for **t:**

$$ln\frac{[A]}{[A]_o} = -kt \tag{1.12.12}$$

We do not have the initial and final concentration, but that is okay.

Assuming the initial concentration is 100 g, we can assume that the final concentration is 10 g because that would be reduced 90% as stated in the problem.

$$ln\frac{[10]}{[100]} = -kt \tag{1.12.13}$$

$$\frac{ln[0.1]}{-0.3465} = t = 6.65\ hours \tag{1.12.14}$$

So 5 hours will be definitely not enough time to reduce the compound

Q9.8a

Assume you are dealing with a first order reactant. You know your rate constant is 1.5x10^{-4}/min, but your employer wants to the half-life of the reactant?

S9.8a

$$t_{1/2} = \frac{0.693}{k} \tag{1.12.15}$$

$$t_{1/2} = \frac{0.693}{1.5x10^{-4}} \tag{1.12.16}$$

$$= 4.62 \times 10^{3}\ mins \tag{1.12.17}$$

Q9.8b

The half-life of a second order reaction

$$2A \rightarrow P \tag{1.12.18}$$

is given by:

$$t_{1/2} = \frac{1}{k[A]_o} \tag{1.12.19}$$

Calculate the half-life of a reaction with initial reactant concentration [A] = 0.90 M and a rate constant of 0.20 M^{-1} min^{-1}.

S9.8b

$$t_{1/2} = \frac{1}{0.20 \times 0.90} = 0.18 min^{-1} \tag{1.12.20}$$

Q9.9a

A reaction

$$A \rightarrow B \tag{1.12.21}$$

is observed. You do not know the stoichiometry of the reactants or products, but observe that when you increase the initial concentration of A from 0.4 M to 0.8 M, the half-life decreased from 10 minutes to 5 minutes. Determine the reaction order and the rate constant.

S9.9a

A reaction whose half-life changes when the reactant concentration is changed is a second-order reaction.

$$t_{1/2} = \frac{1}{k[A]_o} \tag{1.12.22}$$

$$k = \frac{1}{[A]_0 t_{1/2}} \tag{1.12.23}$$

$$k = \frac{1}{(0.4M)(5min)} = 0.5 M^{-1} min^{-1} \tag{1.12.24}$$

Q9.9b

You notice the initial concentration has no affect on the half-life. From this information alone, what can you determine about the the order of the reactant?

S9.9b

You can determine from this information that it would be a first order reactant. The concentration of first order reactants has not affect on the rate or half-life of the reactant. This can be seen in the formula. t_{\frac{1}{2}}=\frac{0.693}{k} This formula does not account for the initial concentration of the reactant.

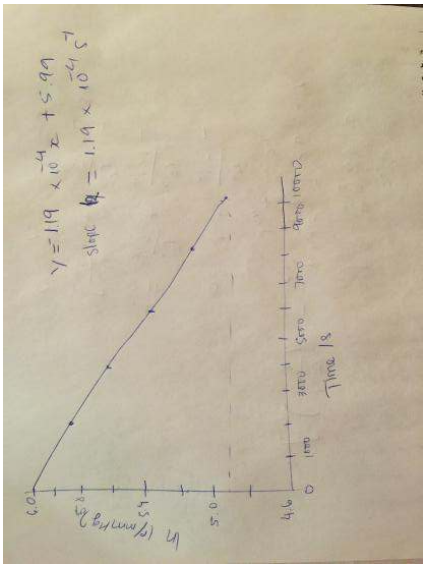
Q9.10a

Calculate the order of the reaction and the rate constant of Cytobutane decompose to ethylene based on equation

$$\[C_4H_{8\ g)} \rightarrow 2C_2H_{4(g)}\]$$

and temperature at 215^0C, constant volume, the pressure 200, 158, 124, 98, 77.5, 61 mmHg.

S9.10a



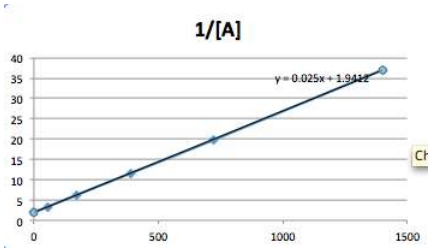
Q9.10b

Given the following data of concentration [A] over a period of time, decide if the data represents first order or second order. Solve for K. Show graphs.

Time	[A]
0	0.5
54	0.3
171	0.16
390	0.08
720	0.05
1400	0.027

S9.10b

The data best fits a Second order graph.



The equation for a second order reaction is:

$$1/[A]= kt+ 1/[A_0]$$

When solving for K, the equation is rearranged to:

$$\underline{1/[A]- 1/[A_0]} = k$$

t

Plug in the numbers given:

$\underline{1/[.3]- 1/[.5]}= k$

(0-54)

.025=k

One, can also obtain the slop of the graph and k=.025

Q9.11a

If a compound's ½ life is 15.6 days. What is the value of k? How long will it take to decompose to 10%. Use first order reaction.

S9.11a

Equation for half-life of a First-Order Reaction is:

$$t_{½} = \frac{\ln(2)}{k} \quad (1.12.25)$$

If we plug in the information given:

$$15.6 days = \frac{\ln(2)}{k} \quad (1.12.26)$$

$$k = 4.4 \times 10^{-2}\, day^{-1} \quad (1.12.27)$$

The second equation needed is the first order reaction, which is:

$$\ln([A]/[A_0])= -kt_{1/2}$$

so, ln ($[A]/[A_0]$)=.1

t=-1/k x ln($[A]/[A_0]$)

t= -1/(4.4 x 10^{-2} day^{-1}) x (.1)

t=52 days

12) In a second order reaction 2A--> products, the final concentration is .28M. What is the initial concentration if k=.32$M^{-1}s^{-1}$ and the times is 5 seconds.

Solution:

Second order reaction equation is:

$1/[A]= kt+ 1/[A_0]$

Filling the information given:

$1/[.28M]=.32M^{-1}s^{-1}(5)+ 1/[A_0]$

$1/[A_0]= 1.97$

$[A_0]= .50M$

Q9.11b

Calculate the half life of a compound if 90% of a given sample of the compound decomposed in 30min

S9.11b

$$[A]=[A]_0\ e^{\wedge}\text{-}kt$$

$$[A]_0 = 90\%$$

$$[A] = 10\%$$

t = 30min * 60s/1min = 1800s

[10%]/[90%]=e^ -k*1800

ln[10%/90%]/1800 = k = 3.95E-4

t1/2= ln(2)/k

t1/2 = .693/3.95E-4= 1754s

1754s*1min/60s = 29 min

Q9.12

Given rate constant for second order reaction

$$2NO_{2(g)} \rightarrow 2NO_{(g)} + O_{2(g)} \quad (1.12.28)$$

is 1.08 $M^{-1}s^{-1}$ at 600 ^{0} C. Find the time that would take for the concentration of NO_2 from 1.24 M to 0.56 M?

S9.12

$$1/[A] - 1/[A]_0 = kt$$

$$t = 1/k\ (\ 1/[A] - 1/[A]_0)$$

$$= (1/\ 1.08\ M^{-1}s^{-1}\ )\ (1/0.56 - 1/1.24) = 7.2\ s$$

Q9.13a

Is which order of reaction half-life is independent of initial concentration?

S9.13a

First order because the half-life equation for first order is

$t_{1/2=}$ ln(2)/k, it does not have $[A_0]$

Q9.13b

The decomposition of N2) is the first order. At 365^{0}C, t1/2 is 1.79 x 10^3 min. given intial pressure of 1.05 atm.. Calculate total pressure.

S9.13b

$$P = P_{N_2O} + P_{N_2} + P_{O_2} \quad (1.12.29)$$

$$= 0.525 + 0.525 + 0.2625 = 1.31\ atm \quad (1.12.30)$$

Q9.14a

The integrated rate law for the zero-order reaction A → B is $[A]_t = [A]_0 - kt$

a) skektch the following plots:

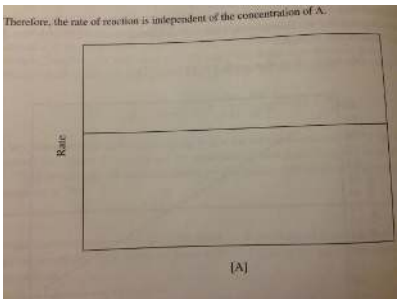
(i) rate vs. [A]

(ii) [A] vs. t

S9.14a

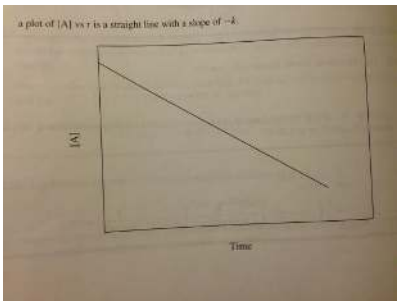
rate = k

rate is independent of [A]



(ii) [A] vs. t

$[A]_t = [A]_0 - kt$



b) Derive an expression for the half-life of the reaction.

At $t = t_{1/2}$, $[A] = [A]_0/2$ so, $[A]_0/2 = [A]_0 - kt_{1/2}$

$t_{1/2} = 1/2k\ [A\}_0$

c) Calculate the time in half-lives when the integrated rate law is no longer valid (that is, when [A] = 0)

$[A]_t = 0 = [A]_0 - kt$

$t_{1/2} = 1/2k\ [A\}_0 \Rightarrow k = 1/2t_{1/2}\ [A\}_0$

Therefore, to consume all of the reactants it takes

$t = [A\}_0/k = [A]_0/2$ so, $[A]_0 / (1/(2t_{1/2}))\ [A]_0 = 2t_{1/2}$

integrated rate law is no longer valid after 2 half-lives

Q9.14b

Jack, Jill, and you are in a physical chemistry class. The professor writes the following equations on the black board.

$$A \rightarrow B \tag{1.12.31}$$

$$[A] = [A_0]e^{-kt} \tag{1.12.32}$$

a. The professor assigns you to derive the first-order reaction in front of the class.
b. Jack was assigned to find the rate constant if the reaction half-life is 10 hours. Since you are a good friend of Jack, you decide to help him double check his answer by solving for the rate constant.

S9.14b

a)

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t -kdt \tag{1.12.33}$$

$$\ln[A]\ |_{[A]_0}^{[A]} = -kt \tag{1.12.34}$$

$$\ln[A] - \ln[A]_0 = -kt \tag{1.12.35}$$

$$\ln \frac{[A]}{[A]_0} = -kt \tag{1.12.36}$$

$$\frac{[A]}{[A]_0} = e^{-kt} \tag{1.12.37}$$

$$[A] = [A_0]e^{-kt} \tag{1.12.38}$$

b)

$$t_{1/2} = \frac{\ln 2}{k} \tag{1.12.39}$$

$$10hours = \frac{\ln 2}{k} \tag{1.12.40}$$

$$k = \frac{\ln 2}{10hours} \times \frac{1hour}{60min} \times \frac{1min}{60secs} \tag{1.12.41}$$

$$k = \tag{1.12.42}$$

Q9.15a

In the nuclear industry, workers use a rule of thumb that the readioactivity from any sample will be relatively harmless after 10 half-lives. Calculate the fraction of a radioactive sample that remains after this time period (hint: Radioactive decay obeys first-order kinetics)

S9.15a

$$[A] = [A]_o e^{-kt}$$

$$t_{1/2} = \ln 2 / k$$

$$[A] = (100)e^{-(1)(10)} = .00454$$

% remaining after 10 half-lives

Q9.15b

As a school field trip to apply what you learned in physical chemistry class, you and your class went to a nuclear power plant. The plant's manager, Mr. Setsaw gives the class a tour of the facilities. When the class reaches the simulation room, a meltdown simulation is offered to the class, but only if the class can answer his questions can the class experience it.

a. Radioactive decay occurs in what order?
b. The gas used in the simulation is harmless because the fraction of the original remaining is 0.004 and the time that passed 30 years. What is the rate constant?

S9.15b

a) Radioactive decay occurs in first order.

b)

$$\frac{[A]}{[A]_0} = e^{-kt} \tag{1.12.43}$$

$$0.004 = e^{-k\,30years} \tag{1.12.44}$$

$$\ln[0.004] = -k\,30years \tag{1.12.45}$$

$$k = \frac{-30}{\ln[0.004]} \tag{1.12.46}$$

$$k = \tag{1.12.47}$$

Q9.16a

Many reactions involving heterogeneous catalysis are zero order; that is, rate = k. An example is the decomposition of phosphine (PH_3) over tungsten (W):

$$4\,PH_3\,(g) \longrightarrow P_4\,(g) + 6\,H_2\,(g) \tag{1.12.48}$$

The rate for this reaction is independent of [PH_3] as long as phosphine's pressure is sufficiently high (>= 1 atm). Explain.

S9.16a

With sufficient PH_3, all of the catalytic sites on the tungsten surface are occupied. Further increases in the amount of phosphine cannot affect the reaction, and the rate is independent of [PH_3].

Q9.16b

Jill and you just went to an enzyme kinetic workshop. However, Jill is confused about why at high concentrations of substrates the reaction order is zero-order. Please explain to Jill in a way that anyone can understand.

S9.16b

At high concentrations of substrates, all the enzymes are working at their fastest rate. As soon as the enzyme is done converting one substrate to its product, another substrate comes into the active site. Therefore, the rate of the enzyme working is constant and this is the definition for zero-order reaction.

9.3: Molecularity of a Reaction

Q9.41a

A mixture of compounds M and N whose half-lives are 40 minutes and 17 minutes, respectively. They decompose by first-order kinetics. If their concentrations are equal initially, how long does concentration of N to be half that of M?

S9.41a

[I] is the initial concentration of M and N

$\ln \frac{[M]}{[I]} = -k_M t$ (1)

$\ln \frac{[N]}{[I]} = -k_N t$ (2)

(1)-(2)= $\ln \frac{[M]}{[N]} = -t\,(k_M - k_N)$

So, to have [N] equals half to [M], we have

$\ln 2 = -t\,(\frac{ln2}{40} - \frac{ln2}{17})$

-> t = 30.1 min

Q9.41b

Compounds A and B both decay by first-order kinetics. The half-life of A is 20 minutes and the half-life of B is 48 minutes. If a container initially contains equal concentrations of compounds A and B, after how long will the concentration of B be twice that of A?

S9.41b

1. Write, in mathematical terms, the information given in the problem and what the problem is asking for.

$$t_{1/2,A} = 20.0 min \tag{1.12.49}$$

$$t_{1/2,B} = 48.0 min \tag{1.12.50}$$

$$[A]_0 = [B]_0 \tag{1.12.51}$$

A and B decay by first-order, so

$$-\frac{d[A]}{dt} = k_A[A] \tag{1.12.52}$$

$$-\frac{d[B]}{dt} = k_B[B] \tag{1.12.53}$$

(Note: the rate constants for A and B are not equal, so indicate which is which with subscripts.)

Want find t at which the following is true:

$$[B] = 2[A] \tag{1.12.54}$$

2. Substitute the integrated rate equations for [A] and [B]

$$[B]_0 e^{-k_B t} = 2[A]_0 e^{-k_A t} \tag{1.12.55}$$

3. Write expressions for the rate constants in terms of half-lives, and substitute into the equation.

$$t_{1/2,A} = \frac{ln2}{k_A} \Rightarrow k_A = \frac{ln2}{t_{1/2,A}} \tag{1.12.56}$$

$$t_{1/2,B} = \frac{ln2}{k_B} \Rightarrow k_B = \frac{ln2}{t_{1/2,B}} \tag{1.12.57}$$

$$[B]_0 e^{-\frac{ln2}{t_{1/2,B}}t} = 2[A]_0 e^{-\frac{ln2}{t_{1/2,B}}t} \tag{1.12.58}$$

4. Solve for t

Since initial concentrations of A and B are equal:

$$e^{-\frac{ln2}{t_{1/2,B}}t} = 2e^{-\frac{ln2}{t_{1/2,B}}t} \tag{1.12.59}$$

Take natural log of both sides:

$$-\frac{t}{t_{1/2,B}} ln2 = \left(1 - \frac{t}{t_{1/2,A}}\right) ln2 \tag{1.12.60}$$

$$t = \frac{1}{\frac{1}{t_{1/2,A}} - \frac{1}{t_{1/2,B}}} \tag{1.12.61}$$

5. Plug in values for half-lives

\[t = \dfrac{1}{\dfrac{1}{20.0 min} - \dfrac{1}{48.0 min}} = 34.2\ min \]

Answer: 34.2 minutes

Q9.42a

In Q3 thermodynamics and in Q9 chemical kinetics, the term “reversible “ is used. How do you understand this term? (it has a same meaning in these two chapters)

S9.42a

Actually, this word is used to describe a “reversible” reaction in which both forward and backward reactions can happen in kinetics. In thermodynamics, “reversible” is used to describe a process that is in equilibrium along the pathway from the initial to final states.

Q9.42b

If a reaction has come to thermodynamic equilibrium, can we say anything in particular about the system's kinetics?

S9.42b

Equilibrium occurs when all reactants and products are being consumed at the same rate that they are created. Take the simple example:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \tag{1.12.62}$$

When the system is at equilibrium,

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0 \tag{1.12.63}$$

$$k_{-1}[A] = k_1[B] \tag{1.12.64}$$

$$\frac{k_{-1}}{k_1} = \frac{[B]}{[A]} \tag{1.12.65}$$

$$K_{eq} = \frac{k_{-1}}{k_1} \tag{1.12.66}$$

Q9.43a

The recombination of bromine atoms in an organic solvent, like carbon tetrafloride, is considered as a diffusion-controlled process

$$Br + Br \rightarrow Br_2 \tag{1.12.67}$$

we have the viscosity of CF_4 is 9.80 x 10^{-4} Nsm^{-2} at 30°C, what is the rate of recombination at 30°C?

S9.43a

$k_D = \frac{8\,RT}{3\eta}$

$= \frac{8(8.314\ JK{-}1mol{-}1)(303.2\ K)x1000L}{(3x9.8x0.0001\ Nsm{-}2)x(1m3)}$

$= 6.86 \times 10^{9}\ M^{-1}s^{-1}$

Q9.43b

Calculate the rate constant of the diffusion-controlled reaction

$$2I \rightarrow I_2 \tag{1.12.68}$$

in dichloromethane at 15°C, which has a viscosity of 0.449 mPa·s at 15°C.

S9.43b

1. Use equation 9.50 to calculate the rate constant.

$$k_D = \frac{8}{3}\frac{RT}{\eta} \tag{1.12.69}$$

$$k_D = \frac{8}{3}\frac{8.314\frac{J}{mol\ K} \times 288\ K \times \frac{N\ m}{J}}{0.449\ mPa\ s \times \frac{Pa}{1000\ mPa} \times \frac{N/m^2}{Pa}} \times \frac{1000\ L}{m^3} \tag{1.12.70}$$

Answer:

$$k_D = 1.42 \times 10^{10} M^{-1} s^{-1} \tag{1.12.71}$$

Q9.52

Japanese survivors have been exposed to the risk of radiation after the atomic bomb. One man was measured to have iodine-131 levels at 9.7 mC. Calculate the number of atoms of I-131 to which this radioactivity corresponds.

S9.52

First, convert the rate mCi s^{-1}

1 mCi=1.10X10^{-3} Ci

1 Ci=3.7 X 10^{10} s^{-1}

The rate (r can be derived as such

$$r = (9.7\ Ci)\left(\frac{1\ Ci}{1000\ mCi}\right)\left(\frac{3.7 \times 10^{10}\ s^{-1}}{1\ Ci}\right) = 3.59 \times 10^{8} s^{-1} \tag{1.12.72}$$

The accepted value for the half life of I-131 is 8.02 days. Using this information, the number of I-131 atoms can be calculated using the nuclear decay equation. Use the

Nuclear Decay Equation:

$$\lambda N = \frac{\ln 2}{t_{1/2}} N \tag{1.12.73}$$

or

$$N = \frac{\ln 2}{t_{1/2}} r \tag{1.12.74}$$

The half-life for the radioactive beta decay of iodine is 8.02 days

$$^{131}_{53}\mathrm{I} \rightarrow {}^{131}_{54}\mathrm{Xe} + \beta + \bar{\nu}_e \tag{1.12.75}$$

therefore, the rate is

$$r = 3.59 \times 10^{8} s^{-1} \tag{1.12.76}$$

Plug into the equation and convert days to seconds.

(8.02 days/ln2)(24 hours/1 day)(3600 seconds/1 hour)(3.59X 10^{-8}) = 2.49 X 10^{14} I-131 atoms.

N= (

Q9.54

Calculate the rate law for the following acid-catalyzed reaction:

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_3COCH_2Br + H^+ + Br^- \tag{1.12.77}$$

Expt. #	$[CH_3COCH_3]_o$/ M	$[Br_2]_o$ /M	$[H^+]_o$ /M	Rate of Disappearance Br_2/ M*s^{-1}
1	0.3	0.05	0.05	5.7×10^{-5}
2	0.3	0.1	0.05	5.7×10^{-5}
3	0.3	0.05	0.05	1.2×10^{-4}
4	0.4	0.05	0.2	3.1×10^{-4}
5	0.4	0.05	0.05	7.6×10^{-5}

S9.54

Find the rate law.
rate = k[CH3COCH3]^x [Br2]^y [H+]^z

[exp 1] / [exp 5]:
5.7e-5 / 7.6e-5 = (0.30/0.40)^x (0.050/0.050)^y (0.050/0.050)^z
3/4 = (3/4)^x
x = 1

[exp 1] / [exp 2]:
5.7e-5 / 5.7e-5 = (0.30/0.30) (0.050/0.10)^y (0.050/0.050)^z
1 = (1/2)^y
y = 0

[exp 1] / [exp 3]:
5.7e-5 / 1.2e-4 = (0.30/0.30) (0.050/0.10)^z
19/40 = (1/2)^z
z ≈ 1

Use [exp 1] to find rate constant.
5.7e-5 M/s = k(0.30 M)(0.050 M)
k = 3.8e-3 M^(-1)-s^(-1)

"calculate the rate of disappearance of bromine if the initial concentration are .600mol/L, 0.200 mol/L, and .10 mol/L for propanone, bromine and H+."
rate = (3.8e-3 M^(-1)-s^(-1))(0.600 M)(0.10 M)
rate = 2.28e-4 M/s

Q9.55

Determine the rate law for the following reaction:

$$N_2O_2 + H_2 \rightarrow H_2O + N_2O \tag{1.12.78}$$

In addition, determine which of the following actions would alter the value of k?

a. Increase in pressure of N_2O_2
b. Increase in volume size of container
c. Increase in temperature
d. Addition of catalyst to the container.
e. None of the above ;a rate constant is always constant.

Q9.56

Consider the mechanism for the association of iodine atoms to create molecular iodine.

$$2I_{(g)} \rightleftharpoons I^*_{2(g)} \tag{1.12.79}$$

$$I^*_2(g) + M(g) \rightarrow I_{2(g)} + M_{(g)} \tag{1.12.80}$$

With the respect of the first step is at equilibrium, determine the expected rate law (d/dt)[I2(g)] in terms of k1, k-1, k2, [I], and [M].

Q9.57

Consider the following reaction:

$$C_3H_{8(g)} + 5O_{2(g)} -> 3CO_{2(g)} + 4H_2O_{(g)} \tag{1.12.81}$$

If propane (C3H8) is burning at a rate of 0.15 M/s^-1, calculate the rate of formation of CO2.

9.4: More Complex Reactions

S9.57

First, express the reaction with the differential rate equation for the reactants and products involved.

$$-(d/dt)[C3H8] = (1/3)(d/dt)[CO2]$$

Then, use the given burning rate of propane and plug it into the differential equation.

$$(d/dt)[CO2] = 3(0.15M/s^-1)$$

$$(d/dt)[CO2] = 0.45\ M/s^-1$$

9.5: The Effect of Temperature on Reaction Rates

Q9.26

If kept in a refrigerator, fresh fish will last for 3 days. If kept in a freezer, it will last for 6 months. Assuming that the temperature in the refrigerator is 5°C, and the temperature in the freezer is -10°C, calculate the activation energy for the bacterial spoiling of fish. Assume that the spoiling time is the 1/e lifetime instead of the half-life.

Q9.27

Find the activation energy of a reaction whose rate constant is multiplied by 6.50 when T is increased from 300.0 K to 310.0 K. For a reaction with E_a = 19 kJ/mol, by what factor is k multiplied when T increases from 300.0 K to 310.0 K?

Q9.28

The kinetics of the browning of juice from Golden Delicious apples was studied; at 20°C $k=7.87\times10^{-3}$/week, and at 37°C k=0.139/week. What is the activation energy for the browning of Golden Delicious apple juice?

9.6: Potential Energy Surfaces

9.7: Theories of Reaction Rates

9.8: Isotope Effects in Chemical Reactions

9.9: Reactions in Solution

9.10: Fast Reactions in Solution

9.11: Oscillating Reactions

1.12: Chemical Kinetics (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

2: Chemical Kinetics II

A physical chemistry Textmap organized around the textbook by Atkins and De Paula

Physical Chemistry

Template:HideTOC

2.1: The Rates of Chemical Reactions
2.2: Integrated Rate Laws
2.3: Reactions Approaching Equilibrium
2.4: The Arrhenius Equation
2.5: Reaction Mechanisms
2.6: Examples of Reaction Mechanisms
2.7: Photochemistry
2.8: Enzymes

2: Chemical Kinetics II is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.1: The Rates of Chemical Reactions

2.1: The Rates of Chemical Reactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.2: Integrated Rate Laws

2.2: Integrated Rate Laws is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.3: Reactions Approaching Equilibrium

2.3: Reactions Approaching Equilibrium is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.4: The Arrhenius Equation

2.4: The Arrhenius Equation is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.5: Reaction Mechanisms

2.5: Reaction Mechanisms is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.6: Examples of Reaction Mechanisms

2.6: Examples of Reaction Mechanisms is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.7: Photochemistry

2.7: Photochemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

2.8: Enzymes

2.8: Enzymes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

3: Reaction Dynamics

A physical chemistry Textmap organized around the textbook by Atkins and De Paula

Physical Chemistry

Template:HideTOC

3.1: Collision Theory
3.2: Diffusion-controlled Reactions
3.3: Transition-state Theory
3.4: The Dynamics of Molecular Collisions
3.5: Electron Transfer in Homogeneous Systems
3.6: Processes at Electrodes

3: Reaction Dynamics is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

3.1: Collision Theory

3.1: Collision Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

3.2: Diffusion-controlled Reactions

Diffusion can be described as the random movement of particles through space, usually due to a concentration gradient. Diffusion is a spontaneous process and is a result of the random thermal motions between two particles. The diffusion coefficient (D) can be solved for with Fick's laws of diffusion, which are broken up into two laws.

Fick's First Law of Diffusion

Fick's first law of diffusion is given by the following equation:

$$J = -D\frac{dc}{dx} \tag{3.2.1}$$

where

- J is the flux and is defined by the number or particles that are moving past a given region divided by the area of that region multiplied by the time interval.
- The units of J are mol m^{-2} s^{-1}.
- The letter D represents the diffusion coefficient with units m^2 s and
- c is the concentration of the gradient with units molecules m^{-3}.

Equation 3.2.1 indicates that if the flux and the change in the concentration over time are known, then the diffusion coefficient can be calculated. The negative sign indicates that the concentration gradient is negative. The first law can only be applied to systems in which the conditions remain the same— in other words, if the flux coming into the system equals the flux going out. Fick's second law is more applicable to physical science and other systems that are changing. This second law is applied to systems in which the condition are not steady, or the solution in not equal throughout.

Fick's Second Law of Diffusion

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \tag{3.2.2}$$

Where $\frac{dc}{dt}$ represents the rate of change of concentration in a certain area and $\frac{d^2c}{dx^2}$ represents the changes that the change in concentration can take; this would not be a smooth curve. This term accounts for a varying concentration in the system. If the concentration does not vary, then

$$\frac{d^2c}{dx^2} = 0 \tag{3.2.3}$$

Diffusion can be thought of as a series of random steps that the particle takes as it moves from where it started. These steps can either lead the particle away from where it started, or lead back to where it started. This means that the overall path that a particle takes can look like line overlapping itself multiple times. A third way to calculate the diffusion concentration is through the **Einstein-Smoluchowski equation**:

$$D = \frac{\lambda^2}{2\tau} \tag{3.2.4}$$

where λ is the length that each step takes, and τ is the time that each step takes. In this particular model, each step is the same distance.

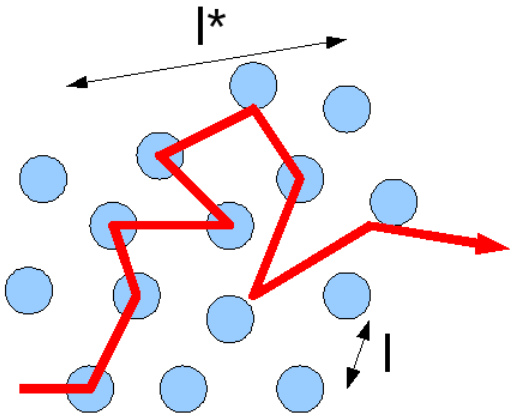


Figure **3.2.1**: Scheme showing the mean free path l and the transport length l*. from Wikipedia

The diffusion coefficient is useful because it can tell you something about the system. For example, different substances have different diffusion coefficients, so knowing this can give you an idea of the substance. Ions at room temperature usually have a diffusion coefficient of 0.6×10^{-9} to 2×10^{-9} m^2/s, and biological molecules fall in the range 10^{-11} to 10^{-10} m^2/s. The diffusion coefficient changes as the properties of the system change. For example, at higher temperatures, the diffusion coefficient is greater because the molecules have more thermal motion. The diffusion coefficient is also related to the viscosity of the solution. The greater the diffusion coefficient, the lower the viscosity. Because the rate of diffusion depends on the temperature of the system, the Arrhenius equation can be applied. Applying this equation gives:

$$D = [D]_o e^{-Ea/RT} \tag{3.2.5}$$

The dependence of the diffusion coefficient on the viscosity can be modeled by the Stokes-Einstein relation:

$$D = \frac{kT}{6\pi\eta a} \tag{3.2.6}$$

where a is the radius of the molecule and η is the coefficient of viscosity and is defined by:

$$\eta = \eta_o e^{Ea/RT} \tag{3.2.7}$$

This equation demonstrates the dependence of viscosity on temperature.

Contributors and Attributions

- Laura Dickson (UC Davis)

3.2: Diffusion-controlled Reactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **9: Diffusion** is licensed CC BY-NC-SA 4.0.

3.3: Transition-state Theory

3.3: Transition-state Theory is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

3.4: The Dynamics of Molecular Collisions

3.4: The Dynamics of Molecular Collisions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

3.5: Electron Transfer in Homogeneous Systems

3.5: Electron Transfer in Homogeneous Systems is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

3.6: Processes at Electrodes

3.6: Processes at Electrodes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

4: Enzyme Kinetics

Enzyme kinetics is the study of the chemical reactions that are catalyzed by enzymes. In enzyme kinetics, the reaction rate is measured and the effects of varying the conditions of the reaction are investigated.

4.1: General Principles of Catalysis
4.2: The Equations of Enzyme Kinetics
4.3: Chymotrypsin- A Case Study
4.4: Multisubstrate Systems
4.5: Enzyme Inhibition
4.6: Allosteric Interactions
4.7: The Effect of pH on Enzyme Kinetics
4.8: The Effect of Temperature on Enzyme Kinetics
4.9: Exercises

Thumbnail: Enzyme changes shape by induced fit upon substrate binding to form enzyme-substrate complex. Hexokinase has a large induced fit motion that closes over the substrates adenosine triphosphate and xylose. Binding sites in blue, substrates in black and Mg^{2+} cofactor in yellow. (PDB: 2E2N, 2E2Q). (CC BY 4.0l Thomas Shafee).

4: Enzyme Kinetics is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

4.1: General Principles of Catalysis

As can be seen from the Arrhenius equation, the magnitude of the activation energy, E_a, determines the value of the rate constant, k, at a given temperature and thus the overall reaction rate. Catalysts provide a means of reducing E_a and increasing the reaction rate. Catalysts are defined as substances that participate in a chemical reaction but are not changed or consumed. Instead they provide a new mechanism for a reaction to occur which has a lower activation energy than that of the reaction without the catalyst. *Homogeneous catalysis* refers to reactions in which the catalyst is in solution with at least one of the reactants whereas *heterogeneous catalysis* refers to reactions in which the catalyst is present in a different phase, usually as a solid, than the reactants. Figure 4.1.1 shows a comparison of energy profiles of a reaction in the absence and presence of a catalyst.

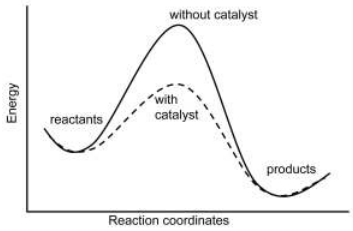


Figure 4.1.1: Comparison of energy profiles with and without catalyst present.

Consider a non-catalyzed elementary reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{P} \tag{4.1.1}$$

which proceeds at rate k at a certain temperature. The reaction rate can be expressed as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] \tag{4.1.2}$$

In the presence of a catalyst C, we can write the reaction as

$$\mathrm{A} + \mathrm{C} \xrightarrow{k_{cat}} \mathrm{P} + \mathrm{C} \tag{4.1.3}$$

and the reaction rate as

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] - k_{cat}[\mathrm{A}][\mathrm{C}] \tag{4.1.4}$$

where the first term represents the uncatalyzed reaction and the second term represents the catalyzed reaction. Because the reaction rate of the catalyzed reaction is often magnitudes larger than that of the uncatalyzed reaction (i.e. $k_{cat} \gg k$), the first term can often be ignored.

Acid Catalysis

A common example of homogeneous catalysts are acids and bases. For example, given an overall reaction is $\mathrm{S} \rightarrow \mathrm{P}$. If k is the rate, then

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{S}] \tag{4.1.5}$$

The purpose of an enzyme is to enhance the rate of production of the product P. The equations of the acid-catalyzed reaction are

$$\mathrm{S} + \mathrm{A}H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{S}H^+ + \mathrm{A}^- \tag{4.1.6}$$

$$\mathrm{S}H^+ + H_2O \xrightarrow{k_2} \mathrm{P} + H_3O^+ \tag{4.1.7}$$

$$H_3O^+ + \mathrm{A}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{A}H + H_2O \tag{4.1.8}$$

The full set of kinetic equations is

$$\frac{d[\mathrm{S}]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] \tag{4.1.9}$$

$$\frac{d[\mathrm{A}H]}{dt} = -k_1[\mathrm{S}][\mathrm{A}H] + k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_{-3}[\mathrm{A}H] + k_3[H_3O^+][\mathrm{A}^-] \tag{4.1.10}$$

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_2[\mathrm{S}H^+] \tag{4.1.11}$$

$$\frac{d[\mathrm{A}^-]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{S}H^+][\mathrm{A}^-] - k_2[\mathrm{A}^-][H_3O^+] + k_{-3}[\mathrm{A}H] \tag{4.1.12}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{S}H^+] \tag{4.1.13}$$

$$\frac{d[H_3O^+]}{dt} = -k_2[\mathrm{S}H^+] - k_3[H_3O^+][\mathrm{A}^-] + k_{-3}[\mathrm{A}H] \tag{4.1.14}$$

We cannot easily solve these, as they are nonlinear. However, let us consider two cases $k_2 \gg k_{-1}[\mathrm{A}^-]$ and $k_2 \ll k_{-1}[\mathrm{A}^-]$. In both cases, $\mathrm{S}H^+$ is consumed quickly, and we can apply a steady-state approximation:

$$\frac{d[\mathrm{S}H^+]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] - k_{-1}[\mathrm{A}^-][\mathrm{S}H^+] - k_2[\mathrm{S}H^+] = 0 \tag{4.1.15}$$

Rearranging in terms of $\mathrm{S}H^+$ yields

$$[\mathrm{S}H^+] = \frac{k_1[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2} \tag{4.1.16}$$

and the rate of production of P can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{S}H^+] = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-] + k_2} \tag{4.1.17}$$

In the case where $k_2 \gg k_{-1}[\mathrm{A}^-]$, Equation 4.1.17 can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_1[\mathrm{S}][\mathrm{A}H] \tag{4.1.18}$$

which is known as a general acid-catalyzed reaction. On the other hand, if $k_2 \ll k_{-1}[\mathrm{A}^-]$, we can use an equilibrium approximation to write the rate of production of P as

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1k_2[\mathrm{S}][\mathrm{A}H]}{k_{-1}[\mathrm{A}^-]} = \frac{k_1k_2}{k_{-1}K}[\mathrm{S}][H^+] \tag{4.1.19}$$

where K is the acid dissociation constant:

$$K = \frac{[\mathrm{A}^-][H^+]}{[\mathrm{A}H]} \tag{4.1.20}$$

In this case, the reaction is hydrogen ion-catalyzed.

Enzyme Catalysis

To live, grow, and reproduce, microorganisms undergo a variety of chemical changes. They alter nutrients so they can enter the cell and they change them once they enter in order to synthesize cell parts and obtain energy.

Metabolism refers to all of the organized chemical reactions in a cell. Reactions in which chemical compounds are broken down are called **catabolic reactions** while reactions in which chemical compounds are synthesized are termed **anabolic reactions**. All of these reactions are under the control of enzymes.

Enzymes are substances present in the cell in small amounts that function to **speed up or catalyze chemical reactions**. On the surface of the enzyme is usually a small crevice that functions as an **active site** or catalytic site to which one or two specific substrates are able to bind. (Anything that an enzyme normally combines with is called a **substrate**.) The binding of the substrate to the enzyme causes the flexible enzyme to change its shape slightly through a process called **induced fit** to form a tempore intermediate called an **enzyme-substrate complex** (Figure 1).

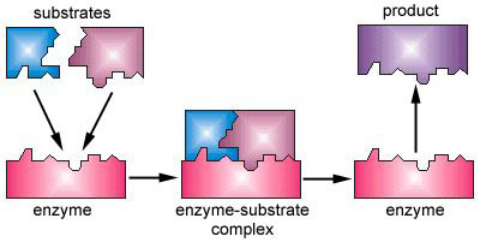


Figure 4.1.2 : Enzymes are substances present in the cell in small amounts which speed up or catalyze chemical reactions. Enzymes speed up the rate of chemical reactions because they lower the energy of activation, the energy that must be supplied in order for molecules to react with one another. Enzymes lower the energy of activation by forming an enzyme-substrate complex.

Enzymes speed up the rate of chemical reactions because they lower the energy of activation, the energy that must be supplied in order for molecules to react with one another (Figure 4.1.3). Like homogeneous catalysts discussed above, enzymes lower the energy of activation by forming an enzyme-substrate complex allowing products of the enzyme reaction to be formed and released (Figure 4.1.2).

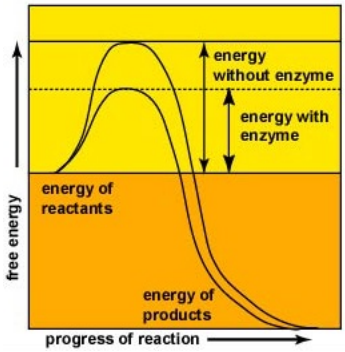
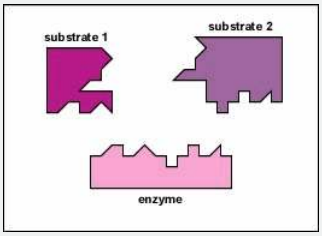


Figure 4.1.3 : An enzyme speeds up a chemical reaction by lowering its energy of activation, the energy that must be supplied in order for molecules to react with one another.

Enzyme-Substrate Reactions

Enzymes are substances present in the cell in small amounts which speed up or catalyze chemical reactions. Enzymes speed up the rate of chemical reactions because they lower the energy of activation, the energy that must be supplied in order for molecules to react with one another. Enzymes lower the energy of activation by forming an enzyme-substrate complex.



Many enzymes require a nonprotein **cofactor** to assist them in their reaction. In this case, the protein portion of the enzyme, called an **apoenzyme**, combines with the cofactor to form the whole enzyme or **haloenzyme** (Figure 4.1.4). Some cofactors are ions such as Ca^{++}, Mg^{++}, and K^{+}; other cofactors are organic molecules called **coenzymes** which serve as carriers for chemical groups or electrons. NAD^{+}, $NADP^{+}$, FAD, and coenzyme A (CoA) are examples of coenzymes.

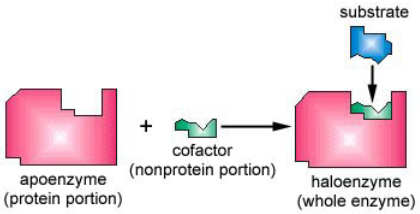


Figure 4.1.4 : An apoenzyme and cofactor combine to form a haloenzyme. If the cofactor is an organic molecule, it is called a coenzyme.

Enzymes are generally globular proteins. (Some RNA molecules called ribozymes can also be enzymes. These are usually found in the nuclear region of cells and catalyze the splitting of RNA molecules.). Enzymes are catalysts that breakdown or synthesize more complex chemical compounds. They allow chemical reactions to occur fast enough to support life. Enzymes speed up the rate of chemical reactions because they lower the energy of activation, the energy that must be supplied in order for molecules to react with one another. Anything that an enzyme normally combines with is called a substrate. Enzymes are very efficient with a typically enzyme generally able to catalyze between 1 and 10,000 molecules of substrate per second. The means that enzymes are only have to be present in small amounts in the cell since. They are not altered during their reaction and are highly specific for their substrate, with generally one specific enzyme dedicated for each specific chemical reaction.

Factors that affect the rate of enzyme reactions

Enzyme activity is affected by a number of factors including:

a. **The concentration of enzyme**: Assuming a sufficient concentration of substrate is available, increasing enzyme concentration will increase the enzyme reaction rate.
b. **The concentration of substrate**: At a constant enzyme concentration and at lower concentrations of substrates, the substrate concentration is the limiting factor. As the substrate concentration increases, the enzyme reaction rate increases. However, at very high substrate concentrations, the enzymes become saturated with substrate and a higher concentration of substrate does not increase the reaction rate.
c. **Inhibitors:** inhibitors will inhibit the activity of enzyme and decrease the rate of reaction. Enzyme inhibitors will bind to enzyme active sites and could modify the chemistry of an active site which can stop a substrate from entering.
d. **The temperature**: Each enzyme has an optimum temperature at which it works best. A higher temperature generally results in an increase in enzyme activity (Arrhenius kinetics). As the temperature increases, molecular motion increases resulting in more molecular collisions. If, however, the temperature rises above a certain point, the heat will denature the enzyme, causing it to lose its three-dimensional functional shape by denaturing its hydrogen bonds. Cold temperature, on the other hand, slows down enzyme activity by decreasing molecular motion.
e. **The pH**: Each enzyme has an optimal pH that helps maintain its three-dimensional shape. Changes in pH may denature enzymes by altering the enzyme's charge. This alters the ionic bonds of the enzyme that contribute to its functional shape.
f. **The salt concentration**: Each enzyme has an optimal salt concentration. Changes in the salt concentration may also denature enzymes.

Applications of Enzymes

Enzymes are essential to maintain homeostasis because any malfunction of an enzyme could lead to diseases. Therefore, pharmaceutical companies study enzyme to manipulate and synthesis new medicine. Besides their medicinal applications, enzymes in industry are important because enzymes help breaking down cellulose, wastes, etc. Enzymes are essential in the process of making new products in many industries such as pharmaceutical, food, paper, wine, etc.

References

1. "Chapter 4 Enzyme."Copyrighted IHW, Oct. 2005. Web. 5 Mar. 2011. biologymad.com/resources/Ch%2...0-20enzyme.pdf
2. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, CA: University Science Books, 2005. Pages 363-384.

Contributors and Attributions

- Mark Tuckerman (New York University)
- Dr. Gary Kaiser (COMMUNITY COLLEGE OF BALTIMORE COUNTY, CATONSVILLE CAMPUS)

4.1: General Principles of Catalysis is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **10.1: General Principles of Catalysis** is licensed CC BY-NC-SA 4.0.

4.2: The Equations of Enzyme Kinetics

In biological systems, enzymes act as catalysts and play a critical role in accelerating reactions, anywhere from 10^3 to 10^{17} times faster than the reaction would normally proceed. Enzymes are high-molecular weight proteins that act on a substrate, or reactant molecule, to form one or more products.

Michaelis-Menten Enzyme Kinetics

Enzymes are highly specific catalysts for biochemical reactions, with each enzyme showing a selectivity for a single reactant, or **substrate**. For example, the enzyme acetylcholinesterase catalyzes the decomposition of the neurotransmitter acetylcholine to choline and acetic acid. Many enzyme–substrate reactions follow a simple mechanism that consists of the initial formation of an enzyme–substrate complex, ES, which subsequently decomposes to form product, releasing the enzyme to react again.

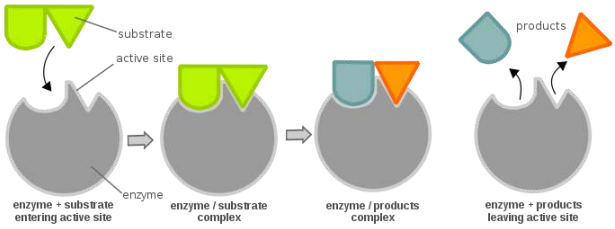


Figure 4.2.1: An enzyme catalyzes the reaction of two substrates and to form one product. from Wikipedia.

This is described within the following multi-step mechanism

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P \tag{4.2.1}$$

where k_1, k_{-1}, k_2, and k_{-2} are rate constants. The reaction's rate law for generating the product $[P]$ is

$$rate = \frac{d[P]}{dt} = k_2[ES] - k_{-2}[E][P] \tag{4.2.2}$$

However, if we make measurement early in the reaction, the concentration of products is negligible, i.e.,

$$[P] \approx 0 \tag{4.2.3}$$

and we can ignore the back reaction (second term in right side of Equation 4.2.2). Then under these conditions, the reaction's rate is

$$rate = \frac{d[P]}{dt} = k_2[ES] \tag{4.2.4}$$

To be analytically useful we need to write Equation 4.2.4 in terms of the reactants (e.g., the concentrations of enzyme and substrate). To do this we use the **steady-state approximation**, in which we assume that the concentration of ES remains essentially constant. Following an initial period, during which the enzyme–substrate complex first forms, the rate at which ES forms

$$\frac{d[ES]}{dt} = k_1[E][S] = k_1([E]_0 - [ES])[S] \tag{4.2.5}$$

is equal to the rate at which it disappears

$$-\frac{d[ES]}{dt} = k_{-1}[ES] + k_2[ES] \tag{4.2.6}$$

where $[E]_0$ is the enzyme's original concentration. Combining Equations 4.2.5 and 4.2.6 gives

$$k_1([E]_0 - [ES])[S] = k_{-1}[ES] + k_2[ES] \tag{4.2.7}$$

which we solve for the concentration of the enzyme–substrate complex

$$[ES] = \frac{[E]_0[S]}{\frac{k_{-1} + k_2}{k_1} + [S]} = \frac{[E]_0[S]}{K_m + [S]} \tag{4.2.8}$$

where K_m is the **Michaelis constant**. Substituting Equation 4.2.8 into Equation 4.2.4 leaves us with our final rate equation.

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_m + [S]} \tag{4.2.9}$$

A plot of Equation 4.2.9, as shown in Figure 4.2.1, is instructive for defining conditions where we can use the rate of an enzymatic reaction for the quantitative analysis of an enzyme or substrate.

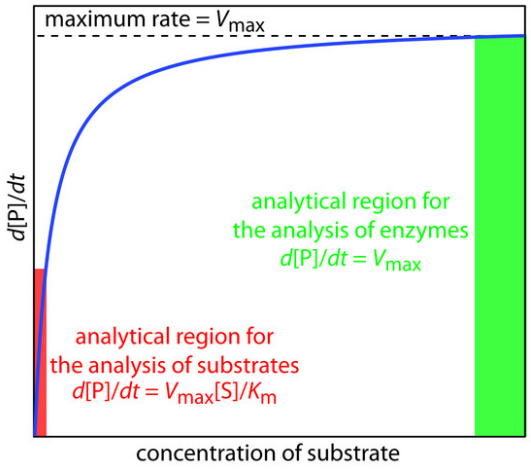


Figure 4.2.1 : Plot of Equation 4.2.9 showing limits for the analysis of substrates and enzymes in an enzyme-catalyzed chemical kinetic method of analysis. The curve in the region highlighted in red obeys equation 4.2.11 and the curve in the area highlighted in green follows Equation 4.2.10.

For high substrate concentrations, where $[S] \gg K_m$, Equation 4.2.9 simplifies to

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_m + [S]} \approx \frac{k_2[E]_0[S]}{[S]} = k_2[E]_0 = V_{max} \tag{4.2.10}$$

where V_{max} is the maximum rate for the catalyzed reaction. Under these conditions the reaction is zero-order in substrate and we can use V_{max} to calculate the enzyme's concentration, typically using a variable-time method. At lower substrate concentrations, where $[S] \ll K_m$, Equation 4.2.9 becomes

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_m + [S]} \approx \frac{k_2[E]_0[S]}{K_m} = \frac{V_{max}[S]}{K_m} \tag{4.2.11}$$

The reaction is now first-order in substrate, and we can use the rate of the reaction to determine the substrate's concentration by a fixed-time method.

The Michaelis constant K_m is the substrate concentration at which the reaction rate is at half-maximum, and is an inverse measure of the substrate's affinity for the enzyme—as a small K_m indicates high affinity, meaning that the rate will approach V_{max} more quickly. The value of K_m is dependent on both the enzyme and the substrate, as well as conditions such as temperature and pH.

> *The Michaelis constant K_m is the substrate concentration at which the reaction rate is at half-maximum.*

From the last two terms in Equation 4.2.11, we can express V_{max} in terms of a **turnover number** (k_{cat}):

$$V_{max} = k_{cat}[E]_o \tag{4.2.12}$$

where $[E]_0$ is the enzyme concentration and k_{cat} is the turnover number, defined as the maximum number of substrate molecules converted to product per enzyme molecule per second. Hence, the turnover number is defined as the maximum number of chemical conversions of substrate molecules per second that a single catalytic site will execute for a given enzyme concentration $[E]_o$.

Example 4.2.1: Turnover number of acetylcholinesterase

Acetylcholinesterase (AChE) may be one of the fastest enzymes. It hydrolyzes acetylcholine to choline and an acetate group. One of the earliest values of the turnover number was 3×10^7 (molecules of acetylcholine) per minute per molecule of enzyme. A more recent value at 25°C, pH = 7.0, acetylcholine concentration of $2.5 \times 10^{-3}\ M$, was found to be $7.4 \times 10^5\ min^{-1}$ (*J Biol Chem. 236 (8): 2292–5.*).

There may be some 30 active centers per molecule. AChE is a serine hydrolase that reacts with acetylcholine at close to **the diffusion-controlled rate**. A diffusion-controlled reaction occurs so quickly that the reaction rate is the rate of transport of the reactants through the solution; as quickly as the reactants encounter each other, they react.

The Significance of K_M and V_{max}

The Michaelis-Menten model is used in a variety of biochemical situations other than enzyme-substrate interaction, including antigen-antibody binding, DNA-DNA hybridization, and protein-protein interaction. It can be used to characterize a generic biochemical reaction, in the same way that the **Langmuir equation** can be used to model generic adsorption of biomolecular species. When an empirical equation of this form is applied to microbial growth. The experimentally determined parameters values vary wildly between enzymes (Table 4.2.1):

Table 4.2.1: Enzyme Kinetic parameters

Enzyme	K_m (M)	k_{cat} (1/s)	k_{cat}/K_m (1/M.s)
Chymotrypsin	1.5×10^{-2}	0.14	9.3
Pepsin	3.0×10^{-4}	0.50	1.7×10^3
Tyrosyl-tRNA synthetase	9.0×10^{-4}	7.6	8.4×10^3
Ribonuclease	7.9×10^{-3}	7.9×10^2	1.0×10^5
Carbonic anhydrase	2.6×10^{-2}	4.0×10^5	1.5×10^7
Fumarase	5.0×10^{-6}	8.0×10^2	1.6×10^8

While K_m is equal to the substrate concentration at which the enzyme converts substrates into products at half its maximal rate and hence is related to the affinity of the substrate for the enzyme. The catalytic rate k_{cat} is the rate of product formation when the enzyme is saturated with substrate and therefore reflects the enzyme's maximum rate. The rate of product formation is dependent on both how well the enzyme binds substrate and how fast the enzyme converts substrate into product once substrate is bound. For a kinetically perfect enzyme, every encounter between enzyme and substrate leads to product and hence the reaction velocity is only limited by the rate the enzyme encounters substrate in solution. From Equation 4.2.8, the catalytic efficiency of a protein can be evaluated.

$$\frac{k_{cat}}{K_m} = \frac{k_2}{K_m} = \frac{k_1 k_2}{k_{-1} + k_2} \tag{4.2.13}$$

This k_{cat}/K_m ratio is called the specificity constant measure of how efficiently an enzyme converts a substrate into product. It has a theoretical upper limit of 10^8 – 10^{10} /M.s; enzymes working close to this, such as fumarase, are termed superefficient (Table 4.2.1).

Determining V_m and K_m from experimental data can be difficult and the most common way is to determine initial rates, v_0, from experimental values of $[P]$ or $[S]$ as a function of time. Hyperbolic graphs of v_0 vs. $[S]$ can be fit or transformed as we explored with the different mathematical transformations of the hyperbolic binding equation to determine K_d. These included:

- nonlinear hyperbolic fit (e.g., Figure 4.2.1)
- double reciprocal plot (e.g., Lineweaver–Burk plot discussed below
- Eadie-Hofstee plot

Lineweaver–Burk plot

Another commonly-used plot in examining enzyme kinetics is the **Lineweaver-Burk plot**, in with the inverse of the reaction rate, $1/r$, is plotted against the inverse of the substrate concentration $1/[\mathrm{S}]$. Rearranging Equation 4.2.10,

$$\frac{1}{r} = \frac{K_M + [\mathrm{S}]}{k_2 [\mathrm{E}]_0 [\mathrm{S}]} = \frac{K_M}{k_2 [\mathrm{E}]_0} \frac{1}{[\mathrm{S}]} + \frac{1}{k_2 [\mathrm{E}]_0} \tag{4.2.14}$$

Tthe Lineweaver–Burk plot (or double reciprocal plot) is a graphical representation of the Lineweaver–Burk equation of enzyme kinetics, described by Hans Lineweaver and Dean Burk in 1934 (Figure 4.2.2). The Lineweaver-Burk plot results in a straight line with the slope equal to $K_M/k_2 [\mathrm{E}]_0$ and y-intercept equal to $1/k_2 [\mathrm{E}]_0$ which is $1/V_{max}$ via Equation 4.2.10.

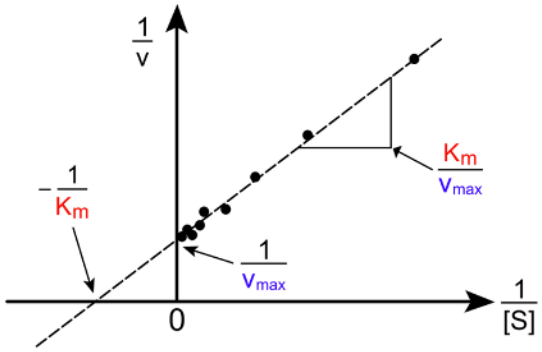


Figure 4.2.2 : Lineweaver–Burk plot of Michaelis–Menten kineitcs.

The plot provides a useful graphical method for analysis of the Michaelis–Menten equation:

$$V = \frac{V_{\max}[S]}{K_m + [S]} \tag{4.2.15}$$

Taking the reciprocal gives

$$\frac{1}{V} = \frac{K_m + [S]}{V_{max}[S]} = \frac{K_m}{V_{max}} \frac{1}{[S]} + \frac{1}{V_{max}} \tag{4.2.16}$$

where

- V is the reaction velocity (the reaction rate),
- K_m is the Michaelis–Menten constant,
- V_{max} is the maximum reaction velocity, and
- $[S]$ is the substrate concentration.

The Lineweaver–Burk plot was widely used to determine important terms in enzyme kinetics, such as K_m and V_{max}, before the wide availability of powerful computers and non-linear regression software. The y-intercept of such a graph is equivalent to the inverse of V_{max}; the x-intercept of the graph represents $-1/K_m$. It also gives a quick, visual impression of the different forms of enzyme inhibition.

Example 4.2.2

The reaction between nicotineamide mononucleotide and ATP to form nicotineamide–adenine dinucleotide and pyrophosphate is catalyzed by the enzyme nicotinamide mononucleotide adenylyltransferase. The following table provides typical data obtained at a pH of 4.95. The substrate, S, is nicotinamide mononucleotide and the initial rate, *v*, is the μmol of nicotinamide–adenine dinucleotide formed in a 3-min reaction period.

[S] (mM)	v (µmol)	[S] (mM)	v (µmol)
0.138	0.148	0.560	0.324
0.220	0.171	0.766	0.390
0.291	0.234	1.460	0.493

Determine values for V_{max} and K_m.

Solution

Figure 13.12 shows the Lineweaver–Burk plot for this data and the resulting regression equation. Using the *y*-intercept, we calculate V_{max} as

$$V_{max} = 1 / y\text{−intercept} = 1 / 1.708 \text{ mol} = 0.585 \text{ mol}$$

and using the slope we find that K_m is

$$K_m = \text{slope} \times V_{max} = 0.7528 \text{ molimM} \times 0.585 \text{ mol} = 0.440 \text{ mM}$$

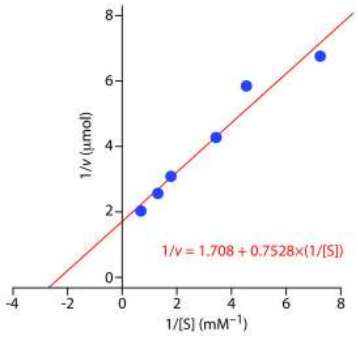
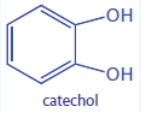


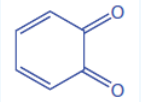
Figure 13.12: Linweaver–Burk plot and regression equation for the data in Example 13.6.

? -diphenyl oxidase

The following data are for the oxidation of catechol (the substrate) to *o*-quinone by the enzyme *o*-diphenyl oxidase. The reaction is followed by monitoring the change in absorbance at 540 nm. The data in this exercise are adapted from jkimball.



catechol



o-quinone

[catechol] (mM)	0.3	0.6	1.2	4.8
rate (ΔAU/min)	0.020	0.035	0.048	0.081

Determine values for V_{max} and K_m.

Click here to review your answer to this exercise.

The double reciprocal plot distorts the error structure of the data, and it is therefore unreliable for the determination of enzyme kinetic parameters. Although it is still used for representation of kinetic data, non-linear regression or alternative linear forms of the

Michaelis–Menten equation such as the **Hanes-Woolf plot** or **Eadie–Hofstee plot** are generally used for the calculation of parameters.

Problems with the Method

The Lineweaver–Burk plot is classically used in older texts, but is prone to error, as the *y*-axis takes the reciprocal of the rate of reaction – in turn increasing any small errors in measurement. Also, most points on the plot are found far to the right of the *y*-axis (due to limiting solubility not allowing for large values of $[S]$ and hence no small values for $1/[S]$), calling for a large extrapolation back to obtain *x*- and *y*-intercepts.

When used for determining the type of enzyme inhibition, the Lineweaver–Burk plot can distinguish competitive, non-competitive and uncompetitive inhibitors. Competitive inhibitors have the same y-intercept as uninhibited enzyme (since V_{max} is unaffected by competitive inhibitors the inverse of V_{max} also doesn't change) but there are different slopes and x-intercepts between the two data sets. Non-competitive inhibition produces plots with the same x-intercept as uninhibited enzyme (K_m is unaffected) but different slopes and y-intercepts. Uncompetitive inhibition causes different intercepts on both the y- and x-axes but the same slope.

Eadie–Hofstee Plot

The Eadie–Hofstee plot is a graphical representation of enzyme kinetics in which reaction rate is plotted as a function of the ratio between rate and substrate concentration and can be derived from the Michaelis–Menten equation (4.2.9) by inverting and multiplying with V_{max}:

$$\frac{V_{max}}{v} = \frac{V_{max}(K_m + [S])}{V_{max}[S]} = \frac{K_m + [S]}{[S]} \tag{4.2.17}$$

Rearrange:

$$V_{max} = \frac{vK_m}{[S]} + \frac{v[S]}{[S]} = \frac{vK_m}{[S]} + v \tag{4.2.18}$$

Isolate v:

$$v = -K_m \frac{v}{[S]} + V_{max} \tag{4.2.19}$$

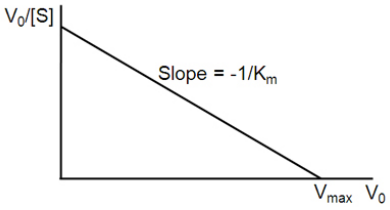


Figure **4.2.3** : The Eadie-Hofstee plot is a more accurate linear plotting method with v is plotted against v/[S].

A plot of v against $v/[S]$ will hence yield V_{max} as the y-intercept, V_{max}/K_m as the x-intercept, and K_m as the negative slope (Figure **4.2.3**). Like other techniques that linearize the Michaelis–Menten equation, the Eadie-Hofstee plot was used historically for rapid identification of important kinetic terms like K_m and V_{max}, but has been superseded by nonlinear regression methods that are significantly more accurate and no longer computationally inaccessible. It is also more robust against error-prone data than the Lineweaver–Burk plot, particularly because it gives equal weight to data points in any range of substrate concentration or reaction rate (the Lineweaver–Burk plot unevenly weights such points). Both Eadie-Hofstee and Lineweaver–Burk plots remain useful as a means to present data graphically.

Problems with the Method

One drawback from the Eadie–Hofstee approach is that neither ordinate nor abscissa represent independent variables: both are dependent on reaction rate. Thus any experimental error will be present in both axes. Also, experimental error or uncertainty will propagate unevenly and become larger over the abscissa thereby giving more weight to smaller values of v/[S]. Therefore, the typical measure of goodness of fit for linear regression, the correlation coefficient R, is not applicable.

Contributors and Attributions

David Harvey (DePauw University)

- World Public Library
- Wikipedia
- Dr. S.K. Khare (IIT Delhi) via NPTEL

4.2: The Equations of Enzyme Kinetics is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **10.2: The Equations of Enzyme Kinetics** is licensed CC BY-NC-SA 4.0.

4.3: Chymotrypsin- A Case Study

Chymotrypsin is a digestive enzyme belonging to a super family of enzymes called serine proteases. It uses an active serine residue to perform hydrolysis on the C-terminus of the aromatic amino acids of other proteins. Chymotrypsin is a protease enzyme that cleaves on the C-terminal phenylalanine (F), tryptophan (W), and tyrosine (Y) on peptide chains. It shows specificity for aromatic amino acids because of its hydrophobic pocket.

Introduction

Chymotrypsin is one of the most studied enzymes due to its two phase kinetics: pre-steady-state and steady state. The study of these two kinetic states gives evidence of the "Ping-Pong" mechanism, the formation of covalent complexes leading to covalent hydrolysis reactions, and the rate of the catalyzed reactions. Synthesis of chymotrypsin occurs primarily in the pancreas. Instead of the active form, however, it is produced as an inactive zymogen called chymotrypsinogen to prevent its protease activity from digesting the pancreas. Upon secretion into the lumen of the small intestine, it is converted to its active form by another enzyme called trypsin. This dependence of a different enzyme for the activation of a protease is a common way for the body to prevent the digestion of organs and other harmful enzymatic side-effects.

Chymotrypsin operates through a general mechanism known as the ping-pong mechanism (Figure **4.3.1**) whereby the enzyme reacts with a substrate to form an enzyme intermediate. This intermediate has different properties than the initial enzyme, so to regenerate the initial enzymatic activity, it must react with a secondary substrate. This process is illustrated below:

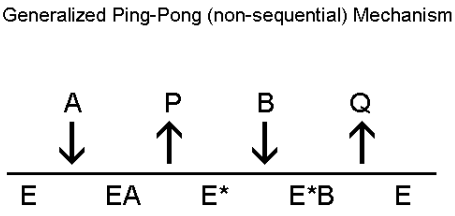
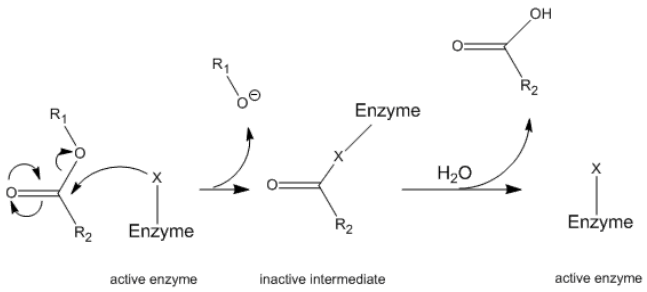


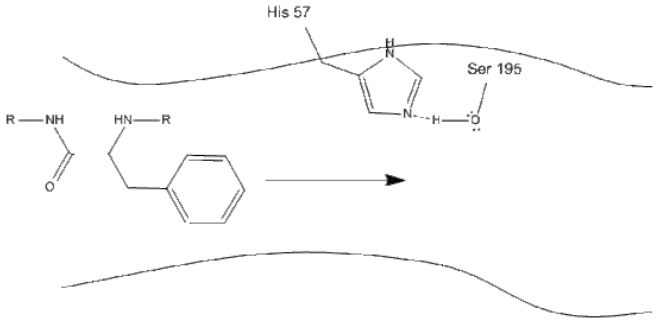
Figure **4.3.1**: Generic Ping-Pong Mechanism

More specifically, chymotrypsin operates through a particular type of ping-pong mechanism called covalent hydrolysis. This means that the enzyme first forms a covalent bond with the target substrate, displacing the more stable moiety into solution. This enzyme-substrate complex is called the enzyme intermediate. The intermediate then reacts with water, which displaces the remaining part of the initial substrate and reforms the initial enzyme.

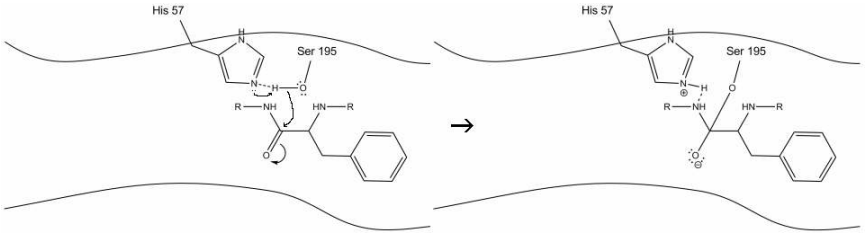


Chymotrypsin, like most enzymes, is specific in the types of substrates with which it reacts. As a protease, it cleaves polypeptides, and its inherent specificity allows it to act only on the carboxy-terminal of aromatic residues. It is a somewhat complicated mechanism, and is best explained in a series of steps.

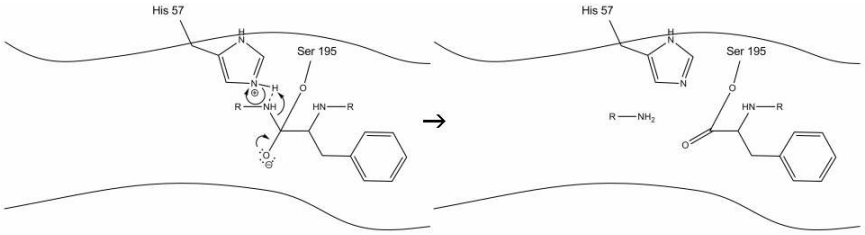
Step 1: The target enters the active site of chymotrypsin, and it is held there by hydrophobic interactions between exposed non-polar groups of enzyme residues and the non-polar aromatic side-chain of the substrate. It is important to note the hydrogen bond between the Schiff nitrogen on histidine-57 and the oxygen side-chain of serine-195.



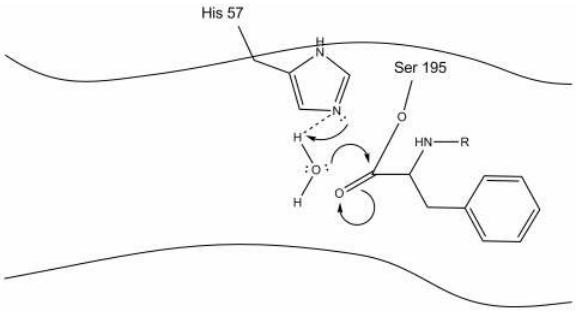
Step 2: Aided by the histidine-serine hydrogen bonding, the hydroxyl group on serine-195 performs a nucleophilic attack on the carbonyl carbon of an aromatic amino acid while simultaneously transferring the hydroxyl hydrogen to the histidine Schiff nitrogen. This attack pushes the pi carbonyl electrons onto the carbonyl oxygen, forming a short-lived intermediate consisting of a c-terminal carbon with four single bonds: an oxygen anion, the beta-carbon of the aromatic amino acid, the n-terminus of the subsequent amino acid of the substrate protein, and the serine-195 side-chain oxygen.



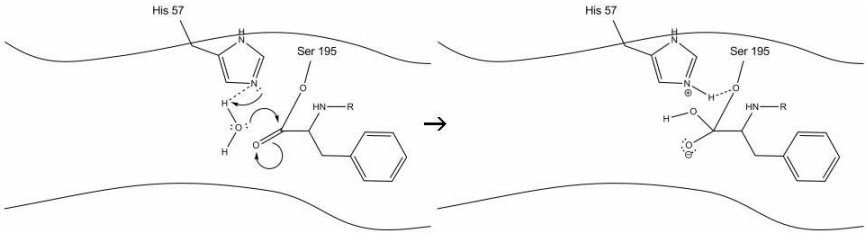
Step 3: This intermediate is short-lived, as the oxyanion electrons reform the pi bond with the c-terminus of the aromatic amino acid. The bond between the carboxy-terminus of the aromatic amino acid and the n-terminus of the subsequent residue is cleaved, and its electrons are used to extract the hydrogen of the protonated Schiff nitrogen on histidine-57. The bonds between the carbonyl carbon and the serine-195 oxygen remain in an ester configuration. This is called the acyl-enzyme intermediate. The c-terminal side of the polypeptide is now free to dissociate from the active site of the enzyme.



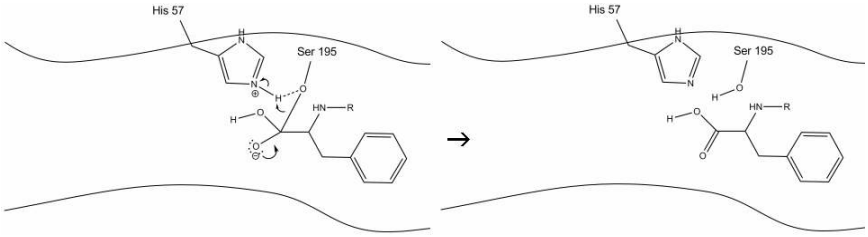
Step 4: Water molecules are now able to enter and bind to active site through hydrogen bonding between the hydrogen atoms of water and the histidine-57 Schiff nitrogen.



Step 5: The water oxygen now makes a nucleophilic attack on the carbonyl carbon of the acyl-enzyme intermediate, pushing the carbonyl's pi electrons onto the carbonyl carbon as histidine-57 extracts one proton from water. This forms another quaternary carbon covalently bonded with serine, a hydroxyl, an oxyanion, and the aromatic amino acid. The proton on the recently protonated histidine-57 is now able to make a hydrogen bond with the serine oxygen.



Step 6: The oxyanion electrons reform the carbonyl pi bond, cleaving the bond between the carbonyl carbon and the serine hydroxyl. The electrons in this bond are used by the serine oxygen to deprotonate the histidine Schiff nitrogen and reform the original enzyme. The substrate no longer has affinity for the active site, and it soon dissociates from the complex.



Kinetics

Experiments were conducted in 1953 by B.S. Hartley and B.A. Kilby to investigate the kinetics of chymotrypsin-catalyzed hydrolysis. Instead of using a poly-peptide chain as a substrate, they used a nitro-phenyl ester, p-nitrophenyl acetate, that resembles an aromatic amino acid. Hydrolysis of this compound by chymotrypsin at the carbonyl group yields acetate and nitrophenolate, the latter of which absorbs near 400 nm light and its concentration can thus be measured by spectrophotometry (Figure **4.3.2**).

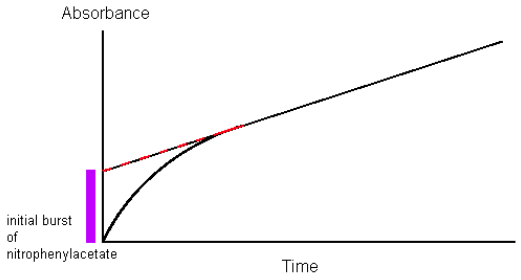


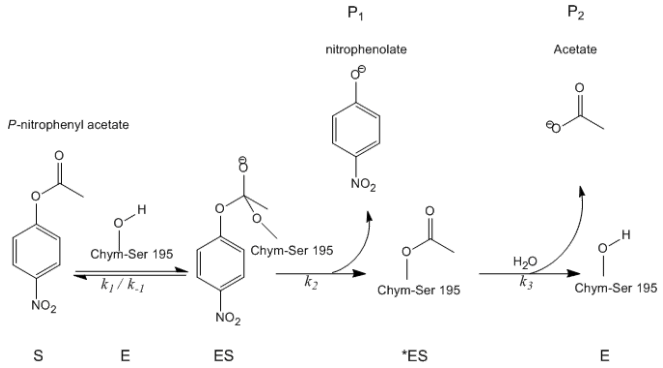
Figure **4.3.2***: Catalytic activity of he hydrolysis of p-nitropenolate under*

Spectrophotometric analysis of chymotrypsin acting on nitrophenylacetate showed that nitrophenolate was produced at a rate independent of substrate concentration, proving that the only factor contributing to the rate of product formation is the concentration of enzyme; this is typical for enzyme-substrate kinetics. However, when the slope of the 0-order absorbance plot was traced back to the starting point (time = 0), it was found that the initial concentration of nitrophenolate was not 0. In fact, it showed a 1:1 stoichiometric ratio with the amount of chymotrypsin used in the assay. This can only be explained by the fact that hydrolysis by chymotrypsin is biphasic in nature, meaning that it proceeds in two distinct steps.

1. The first step, which describes the **initial burst** of nitrophenolate seen in Hartley and Kilby's absorbance plot, is the fastest. The attack of the nitrophenyl acetate substrate by chymotrypsin immediately cleaves the nitrophenolate moiety and leaves the acetate group attached to chymotrypsin, rendering the enzyme inactive.

2. The second step has been deduced to involve the hydrolysis of the acetate group from the inactivated chymotrypsin to regenerate the original enzyme.

To analytically determine the rate of catalysis, all substrates, products, and intermediates must be defined. Refer to the figure below:



Using these abbreviations, kinetic analysis becomes less cumbersome.

1. The initial amount of enzyme can be represented as the sum of the free enzyme, the bound enzyme, and the inactive intermediate.

$$[E]_o = [ES] + [^*ES] + [E]$$

2. Assuming the initial step is the faster than the subsequent steps, the rate of nitrophenolate production can be described as:

$$\frac{d[P_1]}{dt} = k_2[ES]$$

3. Likewise, the rate of acetate formation can be represented by the equation:

$$\frac{d[P_2]}{dt} = k_3[^*ES]$$

4. Therefore, the net change in concentration of the inactive intermediate can be deduced:

$$\frac{d[^*ES]}{dt} = k_2[ES] - k_3[^*ES]$$

5. The last inference that can be made from analysis of the measured kinetics data (Figure **4.3.2**) is that the first step of the reaction equilibrates rapidly, and thus the change in bound substrate can be described in the following equation. This is a principal tenet in analyzing **the kinetics of chymotrypsin and is a ubiquitous mechanism in biological enzyme** catalysis.

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] = 0$$

6. Where:

$$\frac{k_{-1}}{k_1} = K_s = \frac{[E][S]}{[ES]}$$

7. Combining all of these quantities, we can deduce the catalytic rate constant as:

$$k_{cat} = \frac{k_2 k_3}{k_2 + k_3}$$

8. In ester hydrolysis, $k_3 >> k_2$, so the resultant catalytic rate constant simplifies to:

$$k_{cat} = k_2$$

which is in agreement with the observed zeroth-order kinetics of Figure **4.3.2**.

Table 4.3.1: Kinetic Constants of the Chymotrypsin-Catalyzed Hydrolysis of p-Nitrophenyl Trimethylacetate at pH 8.2. 0.01 M tris-HCL buffer, ionic strength 0.06, 25.6 ± 0.1 °C, 1.8% (v/v) acetonitrile-water. From M.L. Bender, F.J. Kezdy and F.C. Wedler, J. Chem. Educ. 44, 84 (1967

k_2	$0.37 \pm 0.11\ s^{-1}$
k_3	$(1.3 \pm 0.02) \times 10^{-4}\ s^{-1}$
K_s	$(1.6 \pm 0.5) \times 10^{-3}$
k_{cat}	1.3 × 10-4 s^{-1}
K_M	5.6×10^{-7}

? Exercise 4.3.1

Speculate on how the catalytic rate constant can be determined from the spectrophotogram.

Answer

The catalytic rate constant can be deduced from the graph by simply determining the slope of the line where the reaction demonstrates 0-order kinetics (the linear part)

? Exercise 4.3.2

How can product be consistently produced if the rate of change of the ES complex is 0?

Answer

This is pre-equilibrium kinetics in action. The ES complex is formed from E and S at a faster rate than any other step in the reaction. As soon as ES is converted to *ES, another mole of ES is produced from an infinite supply of E + S. This means that the amount of ES and E + S is constantly at equilibrium, and thus the change of either with respect to time is 0.

? Exercise 4.3.3

How would the rate of product formation change if:

a. the substrate concentration was doubled.
b. the enzyme concentration was doubled.
c. The reaction was carried out in mono-deuterated water instead of H2O (comment qualitatively).

Answer

a. No change.
b. Two fold increase.
c. Since water is involved in the final, slowest step of the mechanism, deuterating the water would decrease the rate of the overall reaction from 5 to 30-fold.

? Exercise 4.3.4

Explain the role of hydrogen bonding in protein hydrolysis catalyzed by chymotrypsin.

Answer

Initially, hydrogen bonding between the enzymes histidine and serine side chains weakens the bond of serine's O-H. This allows for a facilitated nucleophilic attack of the hydroxyl Oxygen on the substrates carbonyl group. Conversely, in the final step of the reaction, the bound serine oxygen forms a hydrogen bond with a protonated histidine, which allows for easier cleavage from the substrate.

? Exercise 4.3.5

What would the spectrophotogram look like if the reaction proceeded via a steady-state mechanism instead of pre-equilibrium.

Answer

The graph would show similar 0-order kinetics, but the line would intercept the Y-axis at an absorbance of 0 instead of the 1:1 mole ratio of nitrophenolate to enzyme.

References

1. Chang, Raymond. Physical Chemistry for the Biosciences. Sansalito, CA: University Science, 2005.
2. Segel, Irwin H., Enzyme Kinetics: Behavior and Analysis of Rapid Equilibrium and Steady-State Enzyme Systems (Wiley Classics Library)
3. Garret, Reginald. Grishman, Charles. Biochemistry. University of Virginia, 2007
4. Whitaker, John., Princles of Enzymology for the Food Sciences. University of California, Davis. 1994
5. “Chymotrypsin Mechanism” viewable at: www.sumanasinc.com/webcontent...motrypsin.html
6. Sumanas Inc, viewed on February 25th, 2009.
7. M.L. Bender, F.J. Kezdy and F.C. Wedler, J. Chem. Educ. 44, 84 (1967)

4.3: Chymotrypsin- A Case Study is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **7.2: Chymotrypsin** by Elissa Nysetvold is licensed CC BY-NC-SA 4.0.

4.4: Multisubstrate Systems

The Michaelis –Menten model of enzyme kinetics was derived for single substrate reactions. Enzymatic reactions requiring multiple substrates and yielding multiple products are more common and yielding multiple products are more common than single-substrate reaction. In these types of reactions, the all the substrates involved are bound to the enzyme before catalysis of the reaction takes place to release the products. Sequential reactions can be either ordered or random. In contrast to the Michealis-Menton kinetics where a binary Enzyme-Substrate complex is generated in the mechanism ($[ES]$, in bisubstrate enzyme reactions, a ternary complex of the enzyme and two substrates is generated:

$$A + B \overset{E}{\longrightleftharpoons} P + Q \tag{4.4.1}$$

Bisubstrate reactions account for ~ 60% of the known enzymatic reactions. Multi-substrate reactions follow complex rate equations that describe how the substrates bind and in what sequence. The analysis of these reactions is much simpler if the concentration of substrate A is kept constant and substrate B varied. Under these conditions, the enzyme behaves just like a single-substrate enzyme and a plot of v by $[S]$ gives apparent K_M and V_{max} constants for substrate B. If a set of these measurements is performed at different fixed concentrations of A, these data can be used to work out what the mechanism of the reaction is. For an enzyme that takes two substrates A and B and turns them into two products P and Q, there are two types of mechanism: ternary complex and ping–pong.

How do you resolve the enzymes kinetics of these more complicated systems? The answer is fairly straightforward. You keep one of the substrates (B, for example) fixed, and vary the other substrate (A) and obtain a **series** of hyperbolic plots of v_o vs A at different fixed B concentrations. This would give a series of linear $1/v$ vs. $1/A$ double-reciprocal plots (Lineweaver-Burk plots) as well. The pattern of Lineweaver-Burk plots depends on how the reactants and products interact with the enzyme.

Sequential Mechanism

In this mechanism, both substrates must bind to the enzyme before any products are made and released.The substrates might bind to the enzyme in a random fashion (A first then B or vice-versa) or in an ordered fashion (A first followed by B). An abbreviated notation scheme developed by W.W. Cleland is shown in Figure **4.4.1** for the sequential random and sequential ordered mechanisms (Figure **4.4.1**). For both mechanisms, Lineweaver-Burk plots at varying A and different fixed values of B give a series of intersecting lines. Derivative curves can be solved to obtain appropriate kinetic constants. In ordered sequential reactions, all the substrates are first bound to the enzyme in a **defined order or sequence**. The products, too, are released after catalysis in a defined order or sequence.

An example is the lactate dehydrogenase enzyme, which is a protein that catalyzes glucose metabolism. In this ordered mechanism, the coenzyme, NADH, always binds first, with pyruvate binding afterward. During the reaction, the pyruvate is reduced to lactate while NADH is oxidized to NAD^+ by the enzyme. Lactate is then released first, followed by the release of NAD^+.

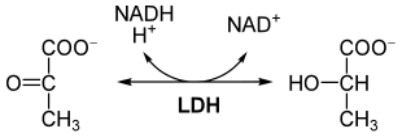


Figure **4.4.2 :** *Reaction of the lactate dehydrogenase: pyruvate (left) is oxidized to lactate (right) by expense of NADH*

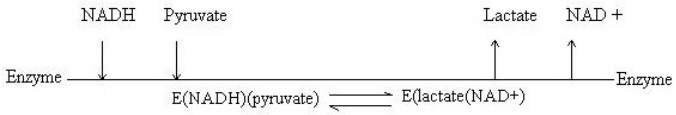


Figure **4.4.3 :** Ordered Sequential Mechanism for the lactate dehydrogenase enzyme

This is a characteristic of a ternary complex, which consists of three molecules that are bound together. Before catalysis, the substrates and coenzyme are bound to the enzyme. After catalysis, the complex consists of the enzyme and products, NAD^+ and lactate.

In random sequential reactions, the substrates and products are bound and then released in no preferred order, or "random" order (Figure **4.4.1**). An example is the creatine kinase enzyme, which catalyzes creatine and ATP (the two substrates) to form phosphocreatine and ADP (teh Products) in Figure **4.4.4**. In this case, **either** substrates may bind first and either products may be

released first. A ternary complex is still observed for random sequential reactions. Before catalysis, the complex is generated that includes the enzyme, ATP, and creatine. After catalysis, the complex consists of the enzyme, ADP, and phosphocreatine.

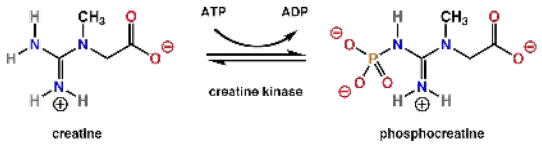


Figure 4.4.4: The metabolism of creatine follows a random sequential mechanism.

Ping-Pong Mechanism

In this mechanism, one substrate bind first to the enzyme followed by product P release. Typically, product P is a fragment of the original substrate A.The rest of the substrate is covalently attached to the enzyme E, which is designated as E'. Now the second reactant, B, binds and reacts with the enzyme to form a covalent adduct with the A as it is covalentattached to the enzyme to form product Q. This is now released and the enzyme is restored to its initial form, E. This represents a ping-pong mechanism. An abbreviated notation scheme is shown below for the ping-pong mechanisms. For this mechanism, Lineweaver-Burk plots at varying A and different fixed values of B give a series of parallel lines. An example of this type of reaction might be low molecular weight protein tyrosine phosphatase against the small substrate p-initrophenylphosphate (A) which binds to the enzyme covalently with the expulsion of the product P, the p-nitrophenol leaving group. Water (B) then comes in and covalently attacks the enzyme, forming an adduct with the covalently bound phosphate releasing it as inorganic phosphate. In this particular example, however, you cannot vary the water concentration and it would be impossible to generate the parallel **Lineweaver-Burk** plots characteristic of ping-pong kinetics.

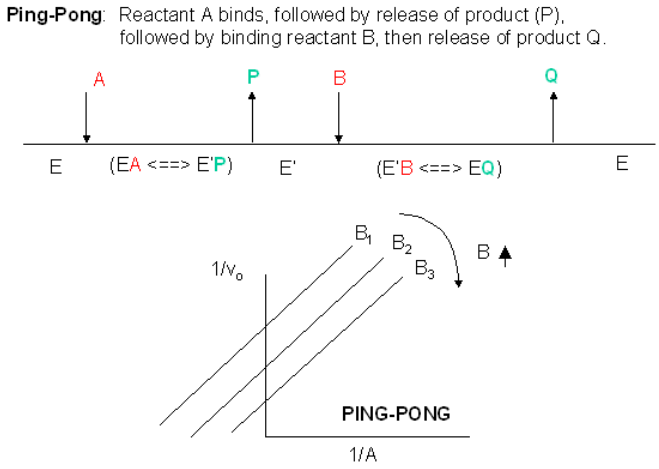


Figure 4.4.5): The Ping-Pong mechanism and associated **Lineweaver-Burk**.

Contributors and Attributions

- Prof. Henry Jakubowski (College of St. Benedict/St. John's University)

4.4: Multisubstrate Systems is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **10.4: Multisubstrate Systems** is licensed CC BY-NC-SA 4.0.

4.5: Enzyme Inhibition

Enzymes can be regulated in ways that either promote or reduce their activity. There are many different kinds of molecules that inhibit or promote enzyme function, and various mechanisms exist for doing so. In some cases of enzyme inhibition, for example, an inhibitor molecule is similar enough to a substrate that it can bind to the active site and simply block the substrate from binding. When this happens, the enzyme is inhibited through competitive inhibition, because an inhibitor molecule competes with the substrate for active site binding. On the other hand, in noncompetitive inhibition, an inhibitor molecule binds to the enzyme in a location other than an allosteric site and still manages to block substrate binding to the active site.

Elucidating Mechanisms for the Inhibition of Enzyme Catalysis

When an **inhibitor** interacts with an enzyme it decreases the enzyme's catalytic efficiency. An irreversible inhibitor covalently binds to the enzyme's active site, producing a permanent loss in catalytic efficiency even if we decrease the inhibitor's concentration. A reversible inhibitor forms a noncovalent complex with the enzyme, resulting in a temporary decrease in catalytic efficiency. If we remove the inhibitor, the enzyme's catalytic efficiency returns to its normal level.

There are several pathways for the reversible binding of an inhibitor to an enzyme, as shown in Figure **4.5.1**. In **competitive inhibition** the substrate and the inhibitor compete for the same active site on the enzyme. Because the substrate cannot bind to an enzyme–inhibitor complex, EI, the enzyme's catalytic efficiency for the substrate decreases. With **noncompetitive inhibition** the substrate and the inhibitor bind to different active sites on the enzyme, forming an enzyme–substrate–inhibitor, or ESI complex. The formation of an ESI complex decreases catalytic efficiency because only the enzyme–substrate complex reacts to form the product. Finally, in **uncompetitive inhibition** the inhibitor binds to the enzyme–substrate complex, forming an inactive ESI complex.

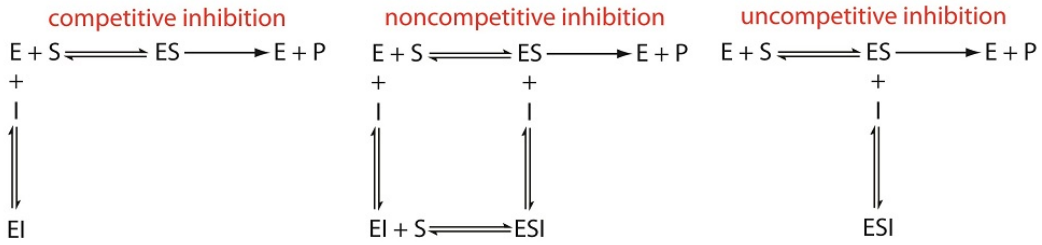


Figure **4.5.1** : Mechanisms for the reversible inhibition of enzyme catalysis. E: enzyme, S: substrate, P: product, I: inhibitor, ES: enzyme–substrate complex, EI: enzyme–inhibitor complex, ESI: enzyme–substrate–inhibitor complex.

We can identify the type of reversible inhibition by observing how a change in the inhibitor's concentration affects the relationship between the rate of reaction and the substrate's concentration. As shown in Figure 13.14, when we display kinetic data using as a Lineweaver-Burk plot it is easy to determine which mechanism is in effect. For example, an increase in slope, a decrease in the *x*-intercept, and no change in the *y*-intercept indicates competitive inhibition. Because the inhibitor's binding is reversible, we can still obtain the same maximum velocity—thus the constant value for the *y*-intercept—by adding enough substrate to completely displace the inhibitor. Because it takes more substrate, the value of K_m increases, which explains the increase in the slope and the decrease in the *x*-intercept's value.

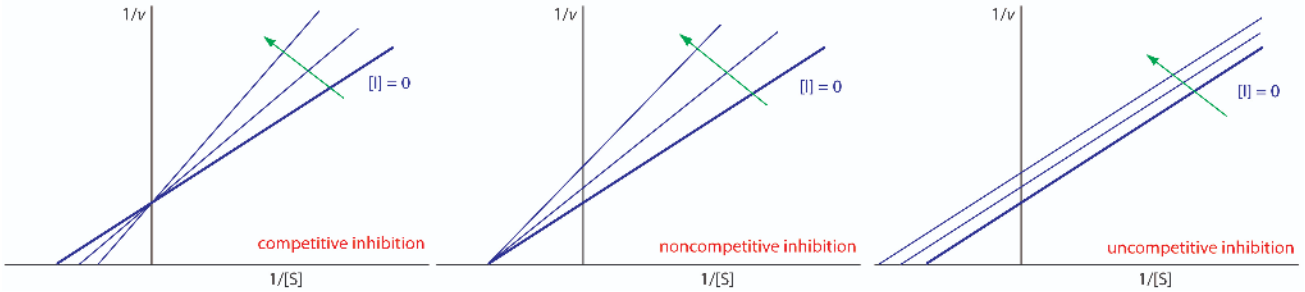


Figure **4.5.2**: Linweaver–Burk plots for competitive inhibition, noncompetitive inhibition, and uncompetitive inhibition. The thick blue line in each plot shows the kinetic behavior in the absence of inhibitor, and the thin blue lines in each plot show the change in behavior for increasing concentrations of the inhibitor. In each plot, the inhibitor's concentration increases in the direction of the green arrow.

Example 4.5.1

Practice Exercise 13.3 provides kinetic data for the oxidation of catechol (the substrate) to *o*-quinone by the enzyme *o*-diphenyl oxidase in the absence of an inhibitor. The following additional data are available when the reaction is run in the presence of *p*-hydroxybenzoic acid, PBHA. Is PBHA an inhibitor for this reaction and, if so, what type of inhibitor is it?

[catechol] (mM)	0.3	0.6	1.2	4.8
rate (ΔAU/min)	0.011	0.019	0.022	0.060

Solution

Figure **4.5.3** shows the resulting Lineweaver–Burk plot for the data in Practice Exercise 13.3 and Example 13.7. Although the *y*-intercepts are not identical in value—the result of uncertainty in measuring the rates—the plot suggests that PBHA is a competitive inhibitor for the enzyme's reaction with catechol.

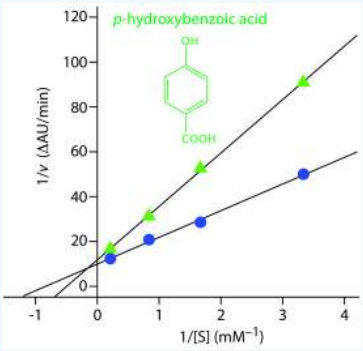


Figure **4.5.3**: Lineweaver–Burk plots for the data in Practice Exercise 13.3 and Example 13.7.

Exercise 4.5.1

Practice Exercise 13.3 provides kinetic data for the oxidation of catechol (the substrate) to *o*-quinone by the enzyme *o*-diphenyl oxidase in the absence of an inhibitor. The following additional data are available when the reaction is run in the presence of phenylthiourea. Is phenylthiourea an inhibitor for this reaction and, if so, what type of inhibitor is it? The data in this exercise are adapted from jkimball.

[catechol] (mM)	0.3	0.6	1.2	4.8
rate (ΔAU/min)	0.010	0.016	0.024	0.040

Click here to review your answer to this exercise.

Contributors and Attributions

- David Harvey (DePauw University)

4.5: Enzyme Inhibition is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **10.5: Enzyme Inhibition** is licensed CC BY-NC-SA 4.0.

4.6: Allosteric Interactions

Learning Objectives

- When a substrate binds to one enzymatic subunit, the rest of the subunits are stimulated and become active. Ligands can either have non-cooperativity, positive cooperativity or negative cooperativity.

A significant portion of enzymes function such that their properties can be studied using the Michaelis-Menten equation. However, a particular class of enzymes exhibit kinetic properties that cannot be studied using the Michaelis-Menten equation. The rate equation of these unique enzymes is characterized by an "S-shaped" sigmoidal curve, which is different from the majority of enzymes whose rate equation exhibits hyberbolic curves. Allosteric regulation is the regulation of an enzyme or other protein by binding an effector molecule at the protein's allosteric site (that is, a site other than the protein's active site). Effectors that enhance the protein's activity are referred to as allosteric activators, whereas those that decrease the protein's activity are called allosteric inhibitors. The term allostery refers to the fact that the regulatory site of an allosteric protein is **physically distinct** from its active site. Allosteric regulations are a natural example of control loops, such as feedback from downstream products or feedforward from upstream substrates. Long-range allostery is especially important in cell signaling.

Allosteric Modulation (Cooperativity)

Cooperativity is a phenomenon displayed by enzymes or receptors that have multiple binding sites where the affinity of the binding sites for a ligand is increased, positive cooperativity, or decreased, negative cooperativity, upon the binding of a ligand to a binding site. We also see cooperativity in large chain molecules made of many identical (or nearly identical) subunits (such as DNA, proteins, and phospholipids), when such molecules undergo phase transitions such as melting, unfolding or unwinding. This is referred to as subunit cooperativity (discussed below).

An example of positive cooperativity is the binding of oxygen to hemoglobin. One oxygen molecule can bind to the ferrous iron of a heme molecule in each of the four chains of a hemoglobin molecule. Deoxy-hemoglobin has a relatively low affinity for oxygen, but when one molecule binds to a single heme, the oxygen affinity increases, allowing the second molecule to bind more easily, and the third and fourth even more easily. The oxygen affinity of 3-oxy-hemoglobin is ~300 times greater than that of deoxy-hemoglobin. This behavior leads the affinity curve of hemoglobin to be sigmoidal, rather than hyperbolic as with the monomeric myoglobin. By the same process, the ability for hemoglobin to lose oxygen increases as fewer oxygen molecules are bound.

Negative allosteric modulation (also known as allosteric inhibition) occurs when the binding of one ligand **decreases** the affinity for substrate at other active sites. For example, when 2,3-BPG binds to an allosteric site on hemoglobin, the affinity for oxygen of all subunits decreases. This is when a regulator is absent from the binding site.

Another instance in which negative allosteric modulation can be seen is between ATP and the enzyme Phosphofructokinase within the negative feedback loop that regulates glycolysis. Phosphofructokinase (generally referred to as PFK) is an enzyme that catalyses the third step of glycolysis: the phosphorylation of Fructose-6-phosphate into Fructose 1,6-bisphosphate. PFK can be allosterically inhibited by high levels of ATP within the cell. When ATP levels are high, ATP will bind to an allosteric site on phosphofructokinase, causing a change in the enzyme's three-dimensional shape. This change causes its affinity for substrate (fructose-6-phosphate and ATP) at the active site to decrease, and the enzyme is deemed inactive. This causes glycolysis to cease when ATP levels are high, thus conserving the body's glucose and maintaining balanced levels of cellular ATP. In this way, ATP serves as a negative allosteric modulator for PFK, despite the fact that it is also a substrate of the enzyme.

Sigmoidal kinetic profiles are the result of enzymes that demonstrate positive cooperative binding. cooperativity refers to the observation that binding of the substrate or ligand at one binding site affects the affinity of other sites for their substrates. For enzymatic reactions with multiple substrate binding sites, this increased affinity for the substrate causes a rapid and coordinated increase in the velocity of the reaction at higher $[S]$ until V_{max} is achieved. Plotting the V_0 vs. $[S]$ for a cooperative enzyme, we observe the characteristic sigmoidal shape with low enzyme activity at low substrate concentration and a rapid and immediate increase in enzyme activity to V_{max} as $[S]$ increases. The phenomenon of cooperativity was initially observed in the oxygen-hemoglobin interaction that functions in carrying oxygen in blood. Positive cooperativity implies allosteric binding – binding of the ligand at one site increases the enzyme's affinity for another ligand at a site different from the other site. Enzymes that demonstrate

cooperativity are defined as allosteric. There are several types of allosteric interactions: homotropic (positive) and heterotropic (negative).

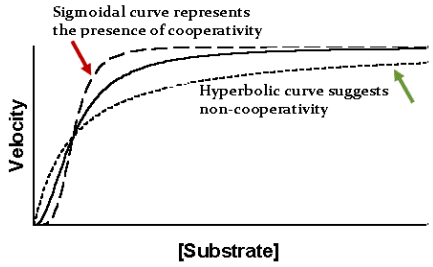


Figure 4.6.1: Rate of Reaction (velocity) vs. Substrate Concentration.

Positive and negative allosteric interactions (as illustrated through the phenomenon of cooperativity) refer to the enzyme's binding affinity for other ligands at other sites, as a result of ligand binding at the initial binding site. When the ligands interacting are all the same compounds, the effect of the allosteric interaction is considered homotropic. When the ligands interacting are different, the effect of the allosteric interaction is considered heterotropic. It is also very important to remember that allosteric interactions tend to be driven by ATP hydrolysis.

The Hill Equation

The degree of cooperativity is determined by Hill equation (Equation 4.6.1) for non-Michaelis-Menten kinetics. The Hill equation accounts for allosteric binding at sites other than the active site. n is the "**Hill coefficient**."

$$\theta = \frac{[L]^n}{K_d + [L]^n} = \frac{[L]^n}{K_a^n + [L]^n} \tag{4.6.1}$$

where

- θ is the fraction of ligand binding sites filled
- $[L]$ is the ligand concentration
- K_d is the apparent dissociation constant derived from the law of mass action (equilibrium constant for dissociation)
- K_a is the ligand concentration producing half occupation (ligand concentration occupying half of the binding sides), that is also the microscopic dissociation constant
- n is the Hill coefficient that describes the cooperativity

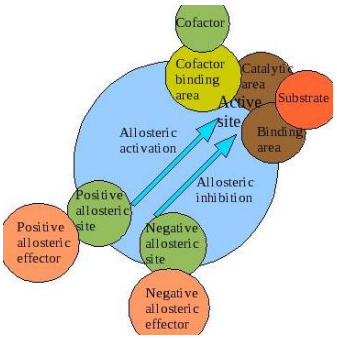
Taking the logarithm of both sides of the equation leads to an alternative formulation of the Hill Equation.

$$\log\left(\frac{\theta}{1-\theta}\right) = n\log[L] - \log K_d \tag{4.6.2}$$

- when $n < 1$, there is negative cooperativity
- when $n = 1$, there is no cooperativity
- when $n > 1$, there is positive cooperativity

Allosteric Models

Currently, there are 2 models for illustrating cooperativity: the concerted model and the sequential model. Most allosteric effects can be explained by the concerted MWC model put forth by Monod, Wyman, and Changeux, or by the sequential model described by Koshland, Nemethy, and Filmer. Both postulate that enzyme subunits exist in one of two conformations, tensed (T) or relaxed (R), and that relaxed subunits bind substrate more readily than those in the tense state. The two models differ most in their assumptions about subunit interaction and the preexistence of both states.



The Concerted model

The concerted model of allostery, also referred to as the symmetry model or MWC model, postulates that enzyme subunits are connected in such a way that a conformational change in one subunit is necessarily conferred to all other subunits. Thus, all subunits must exist in the same conformation. The model further holds that, in the absence of any ligand (substrate or otherwise), the equilibrium favours one of the conformational states, T or R. The equilibrium can be shifted to the R or T state through the binding of one ligand (the allosteric effector or ligand) to a site that is different from the active site (the allosteric site).

The Sequential model

The sequential model of allosteric regulation holds that subunits are not connected in such a way that a conformational change in one induces a similar change in the others. Thus, all enzyme subunits do not necessitate the same conformation. Moreover, the sequential model dictates that molecules of substrate bind via an induced fit protocol. In general, when a subunit randomly collides with a molecule of substrate, the active site, in essence, forms a glove around its substrate. While such an induced fit converts a subunit from the tensed state to relaxed state, it does not propagate the conformational change to adjacent subunits. Instead, substrate-binding at one subunit only slightly alters the structure of other subunits so that their binding sites are more receptive to substrate. To summarize:

- subunits need not exist in the same conformation
- molecules of substrate bind via induced-fit protocol
- conformational changes are not propagated to all subunits

Note: Allosteric database

Allostery is a direct and efficient means for regulation of biological macromolecule function, produced by the binding of a ligand at an allosteric site topographically distinct from the orthosteric site. Due to the often high receptor selectivity and lower target-based toxicity, allosteric regulation is also expected to play an increasing role in drug discovery and bioengineering. The AlloSteric Database (ASD, provides a central resource for the display, search and analysis of the structure, function and related annotation for allosteric molecules. Currently, ASD contains allosteric proteins from more than 100 species and modulators in three categories (activators, inhibitors, and regulators). Each protein is annotated with detailed description of allostery, biological process and related diseases, and each modulator with binding affinity, physicochemical properties and therapeutic area. Integrating the information of allosteric proteins in ASD should allow the prediction of allostery for unknown proteins, to be followed with experimental validation. In addition, modulators curated in ASD can be used to investigate potential allosteric targets for a query compound, and can help chemists to implement structure modifications for novel allosteric drug design.

Summary

Allosteric enzymes are an exception to the Michaelis-Menten model. Because they have more than two subunits and active sites, they do not obey the Michaelis-Menten kinetics, but instead have sigmoidal kinetics. Since allosteric enzymes are cooperative, a sigmoidal plot of V_0 versus $[S]$ results: There are distinct properties of Allosteric Enzymes that makes it different compared to other enzymes.

1. One is that allosteric enzymes do not follow the Michaelis-Menten Kinetics. This is because allosteric enzymes have multiple active sites. These multiple active sites exhibit the property of cooperativity, where the binding of one active site affects the

affinity of other active sites on the enzyme. As mentioned earlier, it is these other affected active sites that result in a sigmoidal curve for allosteric enzymes.

2. Allosteric Enzymes are influenced by substrate concentration. For example, at high concentrations of substrate, more enzymes are found in the R state. The T state is favorite when there is an insufficient amount of substrate to bind to the enzyme. In other words, the T and R state equilibrium depends on the concentration of the substrate.
3. Allosteric Enzymes are regulated by other molecules. This is seen when the molecules 2,3-BPG, pH, and CO2 modulates the binding affinity of hemoglobin to oxygen. 2,3-BPG reduces binding affinity of O2 to hemoglobin by stabilizing the T- state. Lowering the pH from physiological pH=7.4 to 7.2 (pH in the muscles and tissues) favors the release of O_2. Hemoglobin is more likely to release oxygen in CO_2 rich areas in the body.

There are two primary models for illustrating cooperativity. **The concerted model** (also called the **Monod-Wyman-Changeux** model) illustrates cooperativity by assuming that proteins have two or more subunits, and that each part of the protein molecule is able to exist in either the relaxed (R) state or the tense (T) state - the tense state of a protein molecule is favored when it doesn't have any substrates bound. All aspects, including binding and dissociation constants are the same for each ligand at the respective binding sites. **The sequential model** aims to demonstrate cooperativity by assuming that the enzyme/protein molecule affinity is relative and changes as substrates bind. Unlike the concerted model, the sequential model accounts for different species of the protein molecule.

4.6: Allosteric Interactions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **10.6: Allosteric Interactions** by World Public Library is licensed CC BY-NC-SA 4.0.

4.7: The Effect of pH on Enzyme Kinetics

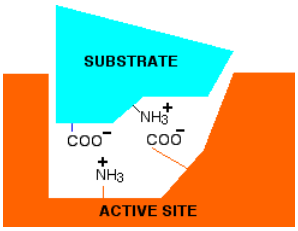
In the same way that every enzyme has an optimum temperature, so each enzyme also has an optimum pH at which it works best. For example, trypsin and pepsin are both enzymes in the digestive system which break protein chains in the food into smaller bits - either into smaller peptide chains or into individual amino acids. Pepsin works in the highly acidic conditions of the stomach. It has an optimum pH of about 1.5. On the other hand, trypsin works in the small intestine, parts of which have a pH of around 7.5. Trypsin's optimum pH is about 8.

Table **4.7.1**: pH for Optimum Activity

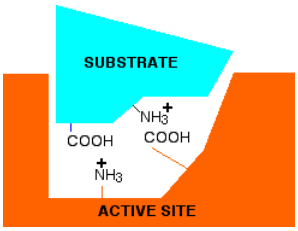
Enzyme	Optimal pH	Enzyme	Optimal pH
Lipase (pancreas)	8.0	Invertase	4.5
Lipase (stomach)	4.0 - 5.0	Maltase	6.1 - 6.8
Lipase (castor oil)	4.7	Amylase (pancreas)	6.7 - 7.0
Pepsin	1.5 - 1.6	Amylase (malt)	4.6 - 5.2
Trypsin	7.8 - 8.7	Catalase	7.0
Urease	7.0		

If you think about the structure of an enzyme molecule, and the sorts of bonds that it may form with its substrate, it isn't surprising that pH should matter. Suppose an enzyme has an optimum pH around 7. Imagine that at a pH of around 7, a substrate attaches itself to the enzyme via two ionic bonds. In the diagram below, the groups allowing ionic bonding are caused by the transfer of a hydrogen ion from a -COOH group in the side chain of one amino acid residue to an $-NH_2$ group in the side chain of another.

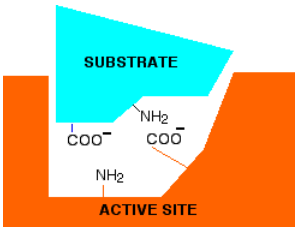
In this simplified example, that is equally true in both the substrate and the enzyme.



Now think about what happens at a lower pH - in other words under acidic conditions. It won't affect the $-NH_3^+$ group, but the $-COO^-$ will pick up a hydrogen ion. What you will have will be this:



You no longer have the ability to form ionic bonds between the substrate and the enzyme. If those bonds were necessary to attach the substrate and activate it in some way, then at this lower pH, the enzyme won't work. What if you have a pH higher than 7 - in other words under alkaline conditions. This time, the $-COO^-$ group won't be affected, but the $-NH_3^+$ group will lose a hydrogen ion. That leaves . . .



Again, there is no possibility of forming ionic bonds, and so the enzyme probably won't work this time either. At extreme pH's, something more drastic can happen. Remember that the tertiary structure of the protein is in part held together by ionic bonds just like those we've looked at between the enzyme and its substrate. At very high or very low pH's, these bonds within the enzyme can be disrupted, and it can lose its shape. If it loses its shape, the active site will probably be lost completely. This is essentially the same as denaturing the protein by heating it too much.

Kinetics

The rates of enzyme-catalysed reactions vary with pH and often pass through a maximum as the pH is varied. If the enzyme obeys Michaelis-Menten kinetics the kinetic parameters k_0 and k_A often behave similarly. The pH at which the rate or a suitable parameter is a maximum is called the *pH optimum* and the plot of rate or parameter against pH is called a *pH profile*. Neither the pH optimum nor the pH profile of an enzyme has any absolute significance and both may vary according to which parameter is plotted and according to the conditions of the measurements.

If the pH is changed and then brought back to its original value, the behavior is said to be *reversible* if the original properties of the enzyme are restored; otherwise it is *irreversible*. Reversible pH behavior may occur over a narrow range of pH, but effects of large changes in pH are in most cases irreversible. The diminution in rate as the pH is taken to the acid side of the optimum can be regarded as inhibition by hydrogen ions. The diminution in rate on the alkaline side can be regarded as inhibition by hydroxide ions. The equations describing pH effects are therefore analogous to inhibition equations. For single-substrate reactions the pH behavior of the parameters k_0 and k_A can sometimes be represented by an equation of the form

$$k = \frac{k_{opt}}{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}} \tag{4.7.1}$$

in which k represents k_0 or k_A, and k_{opt} is the value of the same parameter that would be observed if the enzyme existed entirely in the optimal state of protonation; it may be called the *pH-independent* value of the parameter. The constants K_1 and K_2 can sometimes be identified as acid dissociation constants for the enzyme. substrates or other species in the reaction mixture. The identification is, however, never straight forward and has to be justified by independent evidence. The behavior is frequently much more complicated than represented by Equation 4.7.1.

It is not accidental that this section has referred exclusively to pH dependences of k_0 and k_A. The pH dependence of the initial rate or, worse, the extent of reaction after a given time is rarely meaningful; the pH dependence of the Michaelis constant is often too complex to be readily interpretable.

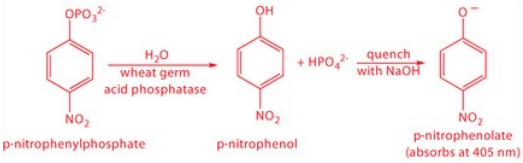
> *The pH dependence of the Michaelis constant is often too complex to be readily interpretable.*

Quenching Enzyme Activity

In principle, we can use any of the range of possible analytical techniques to follow a reaction's kinetics provided that the reaction does not proceed to any appreciable extent during the time it takes to make a measurement. As you might expect, this requirement places a serious limitation on kinetic methods of analysis. If the reaction's kinetics are slow relative to the analysis time, then we can make our measurements without the analyte undergoing a significant change in concentration. When the reaction's rate is too fast—which often is the case—then we introduce a significant error if our analysis time is too long.

One solution to this problem is to stop, or **quench** the reaction by adjusting experimental conditions. For example, many reactions show a strong pH dependency, and may be quenched by adding a strong acid or a strong base. Figure 13.7 shows a typical example

for the enzymatic analysis of *p*-nitrophenylphosphate using the enzyme wheat germ acid phosphatase to hydrolyze the analyte to *p*-nitrophenol.



The reaction has a maximum rate at a pH of 5. Increasing the pH by adding NaOH quenches the reaction and converts the colorless *p*-nitrophenol to the yellow-colored *p*-nitrophenolate, which absorbs at 405 nm.

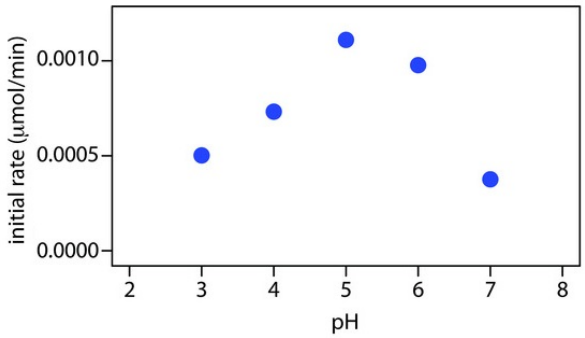


Figure 13.7: Initial rate for the enzymatic hydrolysis of p-nitrophenylphosphate using wheat germ acid phosphatase. Increasing the pH quenches the reaction and coverts colorless p-nitrophenol to the yellow-colored p-nitrophenolate, which absorbs at 405 nm. The data are adapted from socrates.hunter.cuny.edu.

4.7: The Effect of pH on Enzyme Kinetics is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **10.7: The Effect of pH on Enzyme Kinetics** by David Harvey, Jim Clark is licensed CC BY-NC-SA 4.0. Original source: https://www.chemguide.co.uk/organicprops/aminoacids/enzymes2.html.
- **13.2: Chemical Kinetics** by David Harvey is licensed CC BY-NC-SA 4.0.

4.8: The Effect of Temperature on Enzyme Kinetics

Enzymes are generally globular proteins, acting alone or in larger complexes. Like all proteins, enzymes are linear chains of amino acids that fold to produce a three-dimensional structure. The sequence of the amino acids specifies the structure which in turn determines the catalytic activity of the enzyme. Although structure determines function, a novel enzyme's activity **cannot** yet be predicted from its structure alone. Enzyme structures unfold (denature) when heated or exposed to chemical denaturants and this disruption to the structure typically causes a loss of activity.

Protein folding is key to whether a globular protein or a membrane protein can do its job correctly. It must be folded into the right shape to function. But hydrogen bonds, which play a big part in folding, are rather weak, and it does not take much heat, acidity, or other stress to break some and form others, denaturing the protein. This is one reason why tight homeostasis is physiologically necessary in many life forms.

Denaturation

Denaturation is a process in which proteins or nucleic acids lose the quaternary structure, tertiary structure and secondary structure which is present in their native state, by application of some external stress or compound such as a strong acid or base, a concentrated inorganic salt, an organic solvent (e.g., alcohol or chloroform), radiation or heat. If proteins in a living cell are denatured, this results in disruption of cell activity and possibly cell death. Denatured proteins can exhibit a wide range of characteristics, from conformational change and loss of solubility to aggregation due to the exposure of hydrophobic groups.

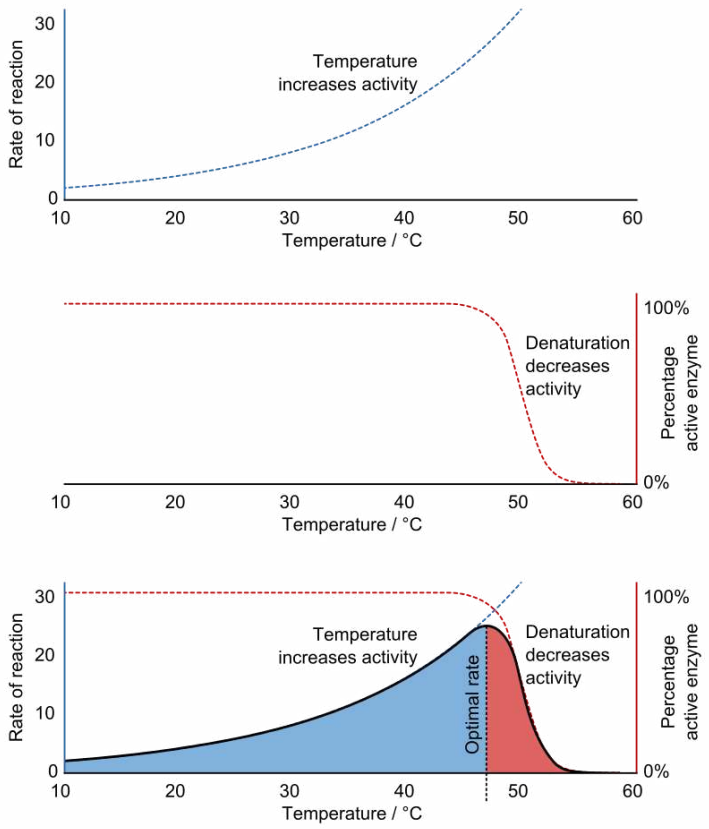


Figure **4.8.1**: Enzyme activity initially increases with temperature until the enzyme's structure unfolds (denaturation), leading to an optimal rate of reaction at an intermediate temperature. (CC-BY-SA-4.0; Thomas Shafee)

Enzyme denaturation is normally linked to temperatures above a species' normal level; as a result, enzymes from bacteria living in volcanic environments such as hot springs are prized by industrial users for their ability to function at high temperatures, allowing enzyme-catalyzed reactions to be operated at a very high rate.

Contributors and Attributions

- Wikipedia

4.8: The Effect of Temperature on Enzyme Kinetics is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

- **10.8: The Effect of Temperature on Enzyme Kinetics** is licensed CC BY-SA 4.0.

4.9: Exercises

10.1: General Principles of Catalysis

Q10.1a

One day in class about enzyme kinetics, Jack comes over to you and asks, "I know enzymes are biological catalysts, but I do not understand how it works. Can you explain how enzymes make reactions go faster? And is it only faster in one direction?"

S10.1a

Because the activation energy is the energy hill between reactants and products, enzymes decreasing the size of the hill also decreases the amount of energy needed for reactions to go in either direction. A smaller energy hill allows reactants and products to overcome the barrier quicker, resulting a faster reaction rate.

Q10.1b

If your student colleagues argues that a catalysts affects only the rate of only one direction of a reaction. Explain why he is correct or not.

S10.1b

False. Catalysts affect rate by providing an alternative mechanism which has a lower transition state energy. It's impossible to lower transition state energy for only one direction of a reaction. (It'd be like making a hill shorter from the north, but keeping it the same height from the south.)

Q10.1c

How does the enzyme catalysis affect both forward and reverse reaction?

S10.1c

The enzyme catalyst lowers the Gibb energy of transition state, which reduces the activation energy of both reactions. Therefore, it makes reactions occur faster.

Q10.2a

Given enzyme-catalyzed reaction k_1 = 4x10^6 M^{-1} s^{-1} , k_{-1} =6x10^4 s^{-1} and k_2= 2.0x10^3 s^{-1}. Determine if the enzyme –substrate binding follow the equilibrium or not ?

S10.2a

The dissociation constant $k_s = k_{-1} / k_1$ =6x10^4 s^{-1}/ 4x10^6 M^{-1} s^{-1} = 0.15 M

The Michaelis constant $k_M = k_{-1} + k_2 / k_1$= 6x10^4 s^{-1}+ 2.0x10^3 s^{-1}/ 4x10^6 M^{-1} s^{-1} =0.155M

The two constant are not equal. Therefore, the binding does not follow the equilibrium scheme.

Q10.2b

Is it appropriate to use the rapid equilibrium scheme to model the kinetics of a catalyzed reaction with the following rate constants?

$$k_1 = 7 \times 10^7\ M^{-1}\ s^{-1} \tag{4.9.1}$$

$$k_{-1} = 8 \times 10^5\ s^{-1} \tag{4.9.2}$$

$$k_2 = 5 \times 10^4\ s^{-1} \tag{4.9.3}$$

S10.2b

Assuming rapid equilibrium is appropriate when $k_{-1} \gg k_2$, so that K_M = K_S. In this case, the values of k_{-1} and k_2 are not dramatically different, so we can calculate K_S and K_M and compare.

1. Calculate K_M:

$$K_M = \frac{k_{-1} + k_2}{k_1} \tag{4.9.4}$$

$$K_M = \frac{8 \times 10^5\ s^{-1} + 5 \times 10^4\ s^{-1}}{7 \times 10^7\ M^{-1}\ s^{-1}} \tag{4.9.5}$$

$$K_M = 0.01\ M \tag{4.9.6}$$

2. Calculate K_S:

$$K_S = \frac{k_{-1}}{k_1} \tag{4.9.7}$$

$$K_M = \frac{8 \times 10^5\ s^{-1}}{7 \times 10^7\ M^{-1}\ s^{-1}} \tag{4.9.8}$$

$$K_M = 0.01\ M \tag{4.9.9}$$

Since $K_M = K_S$, it is appropriate to assume rapid equilibrium.

Q10.2c

Given k_1= 7 x 10^6 M-1s-1, k_{-1}=6 x 10^4 s^{-1}, k_3= 2 x 10^3 s^{-1}, determine if the enzyme substance binding follow the equilibrium or steady state scheme?

$$K_s = \frac{k_{-1}}{k_1} \tag{4.9.10}$$

$$= \frac{6 \times 10^4\ s^{-1}}{7 \times 10^6 M^{-1} s^{-1}} \tag{4.9.11}$$

$$= 8.8 \times 10^{-3} M \tag{4.9.12}$$

$$K_M = k_{-1} + k_2 \tag{4.9.13}$$

$$= \frac{6 \times 10^4 s^{-1} + 2 \times 10^3 s^{-1}}{7 \times 10^6 M^{-1} s^{-1}} \tag{4.9.14}$$

$$= 8.9 \times 10^{-3} M \tag{4.9.15}$$

Q10.3a

The substrate N-acetylglycine ethyl ester can be catalyzed by the enzyme carbonic anhydrase. This enzyme has a turnover rate of 30,000 s^{-1}. Determine how long it will take carbonic anhydrase to cleave the substrate.

S10.3a

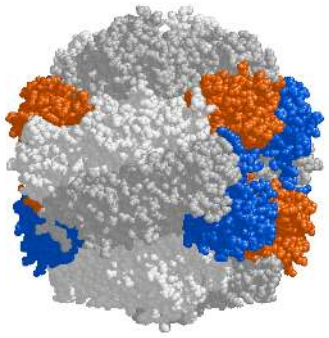
We already know the turnover number (k_{cat}). The amount of time necessary to cleave the substrate is the reciprocal of the turnover rate.

$$t = \frac{1}{k} = \frac{1}{30,000\ s^{-1}} = 3.33 \times 10^{-5} \tag{4.9.16}$$

$$(5\ minutes)(7.1 \times 10^{-6}) = 3.5 \times 10^{-5} \tag{4.9.17}$$

Q10.3b

RuBisCO is an enzyme in the Calvin cycle that fixes atmospheric carbon and has a turnover rate of 3.3 s^{-1}. How long does it take RuBisCO to fix one molecule of carbon dioxide?



Spacefilling structure of RuBisCO created using Rasmol and the 8RUC file from the Protein Data Bank.

S10.3b

The turnover number is the number of molecules of substrate per unit time (when the enzyme is fully saturated). So simply take the reciprocal to find the time per molecule of substrate.

$$\frac{1}{3.3\ s^{-1}} = 0.30\ s \tag{4.9.18}$$

Note: RuBisCO is a notoriously slow enzyme.

Q10.3c

The catalyze of acetylcholine has a rate 50000 s^{-1} . Calculate the time for the enzyme to cleave one Ach molecule.

S10.3c

$$t= 1/k_2 =1/ 50000 = 2.0 \text{ x} 10^{-5}s$$

Q10.3d

Carbonic anhydrase, an enzyme that catalyzes the dehydration of carbonic acid to form carbonic acid, has the turnover rate of k_{cat} 4.0x 10^5 s^{-1}. Calculate how long does it take does it take for the enzyme to cleave one molecule carbonic acid?

S10.3d

The time required for the enzyme to cleave one molecule carbonic acid:

$$t=1/k_{cat} = 1/ 4\text{x}10^5 s^{-1} =2.5\text{x}10^{-6}s = 2.5\mu s$$

Q10.3e

p-nitrophenyl acetate(PNPA) is catalyzed by chymotrypsin to yield p-nitrophenolate ion and acetate ion. The turnover rate of that enzyme is 40,000 s^{-1}. How long will it take for the enzyme to produce 1 mole of Nitrophenyl acetate?

S10.3e

It takes 1 second to convert all 40,000 molecule substrate into the product, so: $t = \frac{40,000}{9.5x10^5}$ = 3.8 sec.

10.2: The Equations of Enzyme Kinetics

Q10.4

What is plotted on the x and y axes on a Lineweaver-Burk plot? Show how to derive the equation for the plot from the equation

$$v_0 = \frac{V_{max}[S]}{K_M + [S]} \tag{4.9.19}$$

and explain how V_{max} and K_M can be found from the graph's intercepts. *Hint: A Lineweaver-Burk plot is also sometimes called a double reciprocal plot.*

S10.4

The x-axis is $1/v_0$, and the x-axis is $1/V_{max}$.

1. Take the reciprocal of both sides of the equation.

$$\frac{1}{v_0} = \frac{K_M + [S]}{V_{max}[S]} \tag{4.9.20}$$

$$\frac{1}{v_0} = \frac{K_M}{V_{max}}\frac{1}{[S]} + \frac{1}{V_{max}} \tag{4.9.21}$$

2. Set $1/[S] = 0$ to find the y-intercept, and show that it relates to V_{max}.

$$Yint = \frac{1}{V_{max}} \tag{4.9.22}$$

$$V_{max} = \frac{1}{Yint} \tag{4.9.23}$$

3. Set $1/v_0 = 0$ to find the x-intercept, and show that it relates to K_M.

$$0 = \frac{K_M}{V_{max}}Xint + \frac{1}{V_{max}} \tag{4.9.24}$$

$$\frac{K_M}{V_{max}}Xint = -\frac{1}{V_{max}} \tag{4.9.25}$$

$$Xint = -\frac{1}{K_M} \tag{4.9.26}$$

$$K_M = -\frac{1}{Xint} \tag{4.9.27}$$

Q10.4a

Derive the Michaelis-Menten equation by assuming rapid equilibrium.

$$E + S \overset{K_1}{\rightleftharpoons} ES \overset{K_2}{\rightarrow} E + P \tag{4.9.28}$$

$$v_0 = \frac{V_{max}[S]}{K_M + [S]} \tag{4.9.29}$$

S10.4a

$\frac{[E][S]}{dt} = K_{-1}[ES]$ $\frac{[ES]}{dt} = K_1[E][S]$ $\frac{[E][S]}{dt} = \frac{[ES]}{dt}$ $K_{-1}[ES] = K_1[E][S]$ $K_M\frac{k_{-1}}{K_1} = \frac{[E][S]}{[ES]}$

given that $[E]_0 = [E] + [ES]$

$K_M = \frac{[E]_0 - [ES][S]}{[ES]}$ $K_M = \frac{[E]_0[S] - [ES][S]}{[ES]}$ $K_M \times [ES] = [E]_0[S] - [ES][S]$ $K_M \times [ES] + [ES][S] = [E]_0[S]$ $(K_M + [S])[ES] = [E_0][S]$

$[ES] = \frac{[E_0][S]}{K_M + [S]}$

since $\frac{d[P]}{dt} = k_2[ES]$

$v_0 = \frac{K_2[E_0][S]}{K_M + [S]}$

since $v_{max} = k_2[E]_0$

$v_0 = \frac{V_{max}[S]}{K_M + [S]}$

Q10.4b

We know that the Michaelis Menten derivation for the following reaction:

$$\mathrm{E + S \rightleftharpoons ES \longrightarrow E + P} \tag{4.9.30}$$

However, what if the reaction took place in a different scenario whereby:

$$\mathbf{E + S \rightleftharpoons ES_1 \longrightarrow ES_2 \longrightarrow E + P} \tag{4.9.31}$$

What would be the corresponding Michaelis-Menten Ebe quation now?

S10.4b

This is the an outline for determining an expression for the rate of substrate conversion in the given case:

1. Set up the reaction with rate constants, assuming $k_{-2} \approx k_{-3} \approx 0$:

$$\mathbf{E + S} \underset{\mathbf{k_{-1}}}{\overset{\mathbf{k_1}}{\rightleftharpoons}} \mathbf{ES_1} \xrightarrow{\mathbf{k_2}} \mathbf{ES_2} \xrightarrow{\mathbf{k_3}} \mathbf{E + P} \tag{4.9.32}$$

2. Set up the differential equations describing the reaction, i.e. the rate of change for each component with time. The rate of substrate change, for example, will be

$$\frac{d[\mathrm{S}]}{dt} = -k_1[\mathrm{E}][\mathrm{S}] + k_{-1}[\mathrm{ES_1}] \tag{4.9.33}$$

3. Choose initial conditions and set up two equations for conservation of mass. For example, the initial concentration of enzyme must equal the sum of the concentrations of E, ES_1 and ES_2.
4. Make the *steady-state assumpt*: assume that the concentrations of the intermediate complexes do not change on the time-scale of product formation, i.e.

$$\frac{d[\mathrm{ES_1}]}{dt} \approx \frac{d[\mathrm{ES_2}]}{dt} \approx 0 \tag{4.9.34}$$

5. Solve for $-r_S$, the negative rate of substrate conversion, obtaining the Michaelis-Menten expression describing the kinetics of the given situtation.

Q10.4c

Prove that K_s equals the concentration S when the initial rate is half its maximum value.

S10.4c

We have: $v_o = \dfrac{V_{max}\,[S]}{K_M + [S]}$

Divided both said by 1 $\dfrac{1}{v_o} = \dfrac{K_M + [S]}{V_{max}\,[S]}$

$$\frac{1}{v_o} = \frac{K_M}{V_{max}\,[S]} + \frac{[S]}{V_{max}\,[S]}$$

$$\frac{1}{v_o} = \frac{K_M}{V_{max}\,[S]} + \frac{1}{V_{max}}$$

When the initial rate is half its maximum value: $v_o = \dfrac{V_{max}}{2}$

$$\frac{2}{V_{max}} = \frac{K_M}{V_{max}\,[S]} + \frac{1}{V_{max}}$$

$$\frac{2}{V_{max}} - \frac{1}{V_{max}} = \frac{K_M}{V_{max}\,[S]}$$

$$\frac{1}{V_{max}} = \frac{K_M}{V_{max}\,[S]}$$

$$\frac{V_{max}}{V_{max}} = \frac{K_M}{[S]}$$

$$[S] = K_M$$

Q10.5a

An enzyme that has a K_m value of $4.6 \times 10^{-5}\ M$ is studied at an initial substrate concentration of 0.041 M. After a minute, it is found that 7.3 uM of product has been produced. Calculate the value of Vmax and the amount of product formed after 4.5 minutes.

Q10.5b

An solution initially contains a catalytic amount of an enzyme with K_M = 1.5 mM, 0.25 M of substrate, and no product. After 45 seconds, the solution contains 25 µM of product. Find V_{max} and the concentration of product after 2.0 minutes.

Hint: [S] >> K_M

S10.5b

1. Find the initial velocity.

$$v_0 = \frac{25\ \mu M}{0.75\ min} \tag{4.9.35}$$

$$v_0 = 33.3\ \mu M/min \tag{4.9.36}$$

2. Use v_0, [S], and K_M to solve for V_{max}.

$$v_0 = \frac{V_{max}[S]}{K_M + [S]} \tag{4.9.37}$$

$$V_{max} = v_0 \left(\frac{K_M}{[S]} + 1 \right) \tag{4.9.38}$$

$$V_{max} = 33.3\ \mu M/min \left(\frac{1.5\ mM}{0.25\ M} \times \frac{M}{1000\ mM} + 1 \right) \tag{4.9.39}$$

$$V_{max} = 33.3\ \mu M/min \tag{4.9.40}$$

Notice that $v_0 = V_{max}$. Since [S] >>K_M, the reaction will continue with a velocity of V_{max} for the remainder of the two minutes.

3. Predict [P] after 2.0 minutes at the rate V_{max}.

$$[P] = V_{max} \times t \tag{4.9.41}$$

$$[P] = 33.3\ \mu M/min \times 2.0\ min \tag{4.9.42}$$

$$[P] = 66.6\ \mu M \tag{4.9.43}$$

Q10.5c

A particular enzyme at a research facility is being studied by a group of graduate students. This enzyme has a K_m value of 5.0 X 10^{-6} M. The students study this enzyme with an initial substrate concentration of 0.055 M. At one minute, 7 µM of product was made. What is the amount of product produced after 5 minutes. What is the V_{max} ?

S10.5c

$V_o = V_{max}[substrate]/K_m + [substrate]$ 7.0 X 10^{-6} M = V_{max} (0.055 M) / (5.0 X 10^{-6} M + .055 M) V_{max} = 7.1 X 10^{-6} M/min At 5 minutes the amount of product formed is:

Q10.5d

Calculate the value v_o if an enzyme has $K_M = 5.4 * 10^{-4}$, value $V_{max} = 48 \mu M min^{-1}$ and $[S] = 0.001 M$

S10.5d

We have: $v_o = \frac{V_{max}\,[S]}{K_M + [S]}$

$$v_o = \frac{48 * 0.001}{5.4 * 10^{-4} + 0.001} = 31 \mu M min^{-1}$$

Q10.6a

Given the values, [S]/10^-4 M 3.0 4.6 10.5 16.5

vo/10^-6 M * min^-1. 2.64 3.5 6.2 7.8

construct a Lineweaver-Burk plot, and assuming Michaelis-Menten kinetics, calculate the values of Vmax, Km, and k2 using the constructed plot.

Q10.6b

The data below represents the data recorded after the hydrolysis of a substrate by an enzyme.

[S]/10-4 M	2.1	4.2	9.3	14.2
vo / 10-6 M · min-1	1.2	3.1	6.3	9.1

Calculate V_{max}, K_m and K_2 using a Lineweaver-Burk plot. Assume Michaelis. Given $[E\}_0$ is 5.0 X 10^{-6} M

S10.6b

(1/[S])/10-3 M-1	(1/vo)/ 10-5 M-1 · min
4.8	8.3
2.4	3.2
1.1	1.6
0.7	1.1

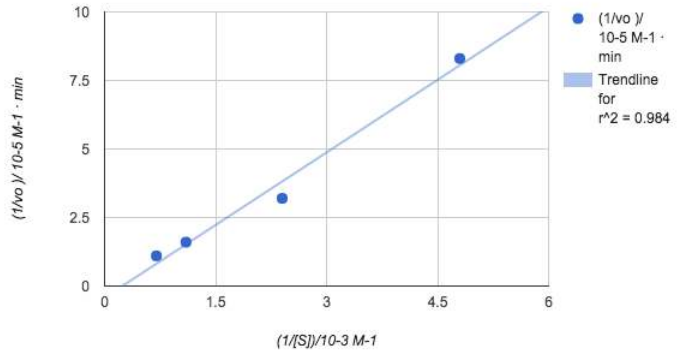


Figure: Lineweaver-Burk Plot

The linear equation for the graph above is: y=176x+4.23X10^4 To solve for V_{max} use: Intercept= $1/V_{max}$ V_{max} = 1/(.4.23X10^4) = 2.36 X 10^{-5} To solve for K_m use Slope= K_m/V_{max} (176)(2.36 X 10^{-5}) = 4.2 X 10^{-5} To solve for K_2 use K_2 = V_{max}/ $[E\}_0$ = (2.36 X 10^{-5})(5.0 X 10^{-6} M)= 4.72 min^{-1}

Q10.6c

Using the table below, calculate the K_M, V_{max}, and slope.

$\frac{1}{V_0}(10^{-3}\frac{sec}{M^{-1}})$ (4.9.44)	$\frac{1}{[S]}(10^2 M^{-1})$ (4.9.45)
2.9	0.3
3.2	1.2
4.4	1.8
5.1	3.3

S10.6c

slope=$\frac{5.1 \times 10^{-3} - 2.9 \times 10^{-3}}{3.3 \times 10^{2} - 0.3 \times 10^{2}} = 6.73 \times 10^{-6}$ $6.73 \times 10^{-6} \times 0.3 \times 10^{2} + \frac{1}{V_{max}} = 2.9 \times 10^{-3}$ $\frac{1}{V_{max}} = 0.00270$ $V_{max} = 370.62 Ms^{-1}$ $6.73 \times 10^{-6} \times \frac{-1}{K_M} + 0.00270 = 0$ $\frac{-1}{K_M} = -0.00943$ $K_M = 106.044$

Q10.6d

Given the value $[S]$= 0.00032 and $K_M = 3.5 * 10^{-5}$. Find the ratio between v_o and V_{max}

S10.6d

$$v_o = \frac{V_{max}\,[S]}{K_M + [S]}$$

Divided both side by 1: $\frac{1}{v_o} = \frac{K_M}{V_{max}\,[S]} + \frac{1}{V_{max}}$

Divided both side by 1 again: $v_o = \frac{V_{max}\,[S]}{K_{max}} + V_{max}$

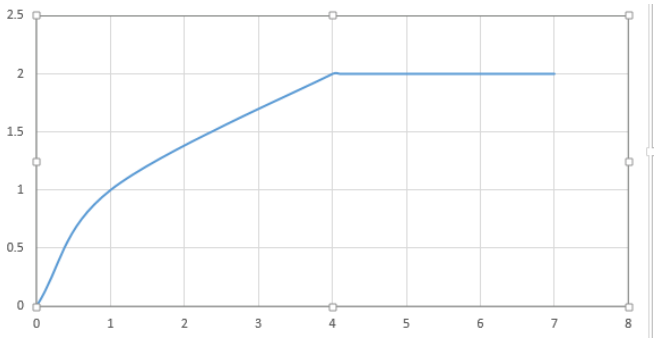
$$v_o = V_{max}\left(\frac{[S]}{K_{max}} + 1\right)$$

$$\frac{v_o}{V_{max}} = \frac{[S]}{K_M} + 1$$

$$\frac{v_o}{V_{max}} = \frac{0.00032}{3.5 * 10^{-5}} + 1 = \frac{71}{7} = 10.14$$

Q10.7a

From this graph determine the K_M and V_{max}?



S10.7b

From his graph we can see that the value K_M is 2. Then we look to see where K_M is half. At that point, we see that $K_M/2$ is 1 and the x-value for that coordinate is 1. This means V_{max} is 1.

Q10.7b

Neutral sphingomyelinase 2 converts sphingomyelin into ceramide and phosphocholine. Assume its V_{max} is 35 µM min^{-1}. When you provide 3 x 10^{-5} M of sphingomyelin, you observe an initial velocity of 6.0 µM min^{-1}. Calculate the K_M for this reaction, rounding to 3 significant figures.

S10.7b

$$\frac{1}{V_o} = \frac{K_M}{V_{max}[S]} + \frac{1}{V_{max}} \tag{4.9.46}$$

$$\frac{1}{6.0} = \frac{K_M}{(35)(30)} + \frac{1}{35} \tag{4.9.47}$$

$$\frac{1}{6} - \frac{1}{35} = \frac{K_M}{1050} \tag{4.9.48}$$

K_M = 145 µM

Q10.8a

We are given a second order equation: r=k[A][B]. The concentration of A is 0.05g and the concentration of B is 2.5g. We decide this difference is great enough to treat this as a pseudo first reaction? What concentration is held constant and why? Write the new equation.

S10.8a

We hold B constant because the concentration is so much larger, so it should be close to constant for the reaction. The new equation would be r=k'[a]

Q10.9a

Name and briefly describe two types of reactions that do not follow Michaelis-Menten kinetics.

S10.9a

Irreversible inhibition - the inhibitor binds covalently and irreversibly to the enzyme Allosteric interactions - the binding of effectors at allosteric sites (away from the active site) influence substrate binding.

Q10.9b

For the reaction mechanism below, how does the concentration of C affect the concentration of B?

$$A \leftrightharpoons B \rightarrow C \tag{4.9.49}$$

S10.9b

Because the second state is *irreversible* (i.e., since arrow), it does not matter if you have a large or little concentration of C, it would not affect B and hence the kinetics of the reaction. However, the concentration of A would clearly affect the concentration of B.

10.3: Chymotrypsin: A Case Study

Q1

1. Speculate on how the catalytic rate constant can be determined from the spectrophotogram.
2. How can product be consistently produced if the rate of change of the ES complex is 0?
3. How would the rate of product formation change if:
    a. the substrate concentration were doubled?
    b. the enzyme concentration were doubled?
    c. The reaction was carried out in mono-deuterated water instead of H_2O (comment qualitatively)?
4. Explain the role of hydrogen bonding in protein hydrolysis catalyzed by chymotrypsin.
5. What would the spectrophotogram look like if the reaction proceeded via a steady-state mechanism instead of pre-equilibrium.

S2

1. The catalytic rate constant can be deduced from the graph by simply determining the slope of the line where the reaction demonstrates 0-order kinetics (the linear part).
2. This is pre-equilibrium kinetics in action. The ES complex is formed from E and S at a faster rate than any other step in the reaction. As soon as ES is converted to *ES, another mole of ES is produced from an infinite supply of E + S. This means that the amount of ES and E + S is constantly at equilibrium, and thus the change of either with respect to time is 0.
    a. No change.
    b. Two-fold increase.
    c. Because water is involved in the final, slowest step of the mechanism, deuterating the water would decrease the rate of the overall reaction from 5- to 30-fold.
3. Initially, hydrogen bonding between the enzymes histidine and serine side chains weakens the bond of serine's O-H. This allows a facilitated nucleophilic attack of the hydroxyl oxygen on the substrates carbonyl group. Conversely, in the final step of the reaction, the bound serine oxygen forms a hydrogen bond with a protonated histidine, which allows for easier cleavage from the substrate.
4. The graph would show similar 0-order kinetics, but the line would intercept the Y-axis at an absorbance of 0 instead of the 1:1 mole ratio of nitrophenolate to enzyme.

10.4: Multisubstrate Systems

10.5: Enzyme Inhibition

10.6: Allosteric Interactions

10.7: The Effect of pH on Enzyme Kinetics

10.4: Multisubstrate Systems

10.5: Enzyme Inhibition

10.6: Allosteric Interactions

10.7: The Effect of pH on Enzyme Kinetics

4.9: Exercises is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

5: Lasers, Laser Spectroscopy, and Photochemistry

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Chem 110A ● Chem 110B ● Chem 110C ● **Agenda ● Homework ● Worksheet Activities**

Photochemistry is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400 – 750 nm) or infrared radiation (750 – 2500 nm). Photochemical reactions are valuable in organic and inorganic chemistry because they proceed differently than thermal reactions. Many thermal reactions have a photochemical counterpart. Photochemical paths offer an advantage over thermal methods of forming thermodynamically disfavored products, thereby overcoming large activation barriers in a short period of time, and allowing reactions otherwise inaccessible by thermal processes. Everyday examples include photosynthesis, the degradation of plastics or the formation of vitamin D with sunlight.

5.1: Electronically Excited Molecules

5.2: Transitions Modeled as Kinetics

5.3: Two-Level Systems Cannot Form Population Inversions

5.4: Population Inversion via Three-Level Systems

5.5: Laser Fundamentals

5.6: The Helium-Neon Laser

5.7: High-Resolution Laser Spectroscopy

5.8: Photochemical Dynamics

5: Lasers, Laser Spectroscopy, and Photochemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

5.1: Electronically Excited Molecules

To understand how lasers work we must first describe how a molecule in an excited state can relax back to the ground state because the light emitted by a laser is influenced by these relaxation processes. The two radiative decay pathways for an excited molecule are fluorescence and phosphorescence. Fluorescence differs from phosphorescence in that the energy transition that is responsible for fluorescence does not involve a change in electron spin multiplicity. Thus fluorescence lifetimes are short (10^{-9} - 10^{-6} s). In phosphorescence, there is a change in electron spin multiplicity, resulting in a longer lifetime of the excited state (second to minutes). A description of electron spin and the differences between singlet and triplet states will clarify the difference between fluorescence and phosphorescence.

Spin Multiplicity - Singlet and Triplet Excited States

The Pauli Exclusion principle states that two electrons in an atom cannot have the same four quantum numbers (n, l, m_l, m_s). Therefore, because two electrons can occupy each orbital, these two electrons must have opposite spin states. These opposite spin states are called spin pairing. Because of this spin pairing, most molecules are diamagnetic, and are not attracted or repelled by an external magnetic or electric field. Molecules that contain unpaired electrons (free radicals) do have magnetic moments that are attracted to an external magnetic or electric field.

A molecule is said to be in a singlet state when all the electron spins are paired in the molecular electronic state, and the electronic energy levels do not split when the molecule is exposed to a magnetic field. A doublet state occurs when there is an unpaired electron that gives two possible orientations when exposed to a magnetic field and imparts different energies to the system. A singlet or a triplet state can form when one electron is excited to a higher energy level. In an excited singlet state, the promoted electron retains the spin orientation it had in the ground state (i.e., paired). In a triplet excited state, the promoted electron undergoes a change in spin, and so has the same spin orientation (parallel) to the unpaired electron that remains in the ground state orbital. The difference between the spins of ground singlet, excited singlet, and excited triplet is shown in Figure 5.1.1. The terms singlet, doublet and triplet are derived using the equation for multiplicity, 2S+1, where S is the total spin angular momentum (sum of all the electron spins). Individual spins are denoted as spin up (s = +1/2) or spin down (s = -1/2). If we were to calculate the multiplicity for the singlet ground state or the singlet excited state, the equation would be

$$2(+1/2 + -1/2) + 1 = 2(0) + 1 = 1$$

In a similar fashion, the spin multiplicity for the triplet excited state can be calculated as

$$2(+1/2 + +1/2) + 1 = 2(1) + 1 = 3$$

which gives a triplet state as expected.

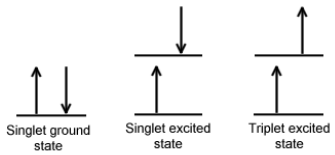


Figure 5.1.1: Spin in the ground and excited states (Tyler Matthews - Paint Shop Pro, Public Domain, https://commons.wikimedia.org/w/inde...curid=64926546)

The difference between a molecule in the ground and the triplet excited state is that the molecule is diamagnetic in the ground state and paramagnetic in the triplet excited state. This difference in spin state makes the transition from singlet to triplet (or triplet to singlet) less likely than the singlet-to-singlet transitions. For this reason, the lifetime of the triplet state is longer than the lifetime of the singlet state by a factor of roughly 10^4 seconds. The transition from ground to excited triplet state has a low probability of occurring, thus these absorption bands are less intense than singlet-singlet state absorption bands. However, an excited triplet state can be populated from an excited singlet state of certain molecules. Jablonski diagrams can be used to explain transitions such as this that occur in photoluminescence molecules.

Jablonski Diagrams

Aleksander Jablonski was a Polish academic who devoted his life to the study of molecular absorbance and emission of light. He developed a graphic representation that shows the possible consequences of applying photons from the visible spectrum of light to a particular molecule. These schematics are referred to as Jablonski diagrams.

A Jablonski diagram is an energy diagram, arranged with energy on a vertical axis. The energy levels can be quantitatively denoted, but most of these diagrams use energy levels schematically. The rest of the diagram is arranged into columns. Every column usually represents a specific spin multiplicity for a particular species. However, some diagrams divide energy levels within the same spin multiplicity into different columns. Within each column, horizontal lines represent eigenstates for that particular molecule. Bold horizontal lines are representations of the limits of electronic energy states. Within each electronic energy state are multiple vibrational energy states that may be coupled with the electronic state. Usually only a portion of these vibrational eigenstates are represented due to the massive number of possible vibrations in a molecule. Each of these vibrational energy states can be subdivided even further into rotational energy levels; however, typical Jablonski diagrams omit such intense levels of detail.

Through the use of straight and wavy lines, these figures show transitions between eigenstates that occur from the exposure of a molecule to a particular wavelength of light. Straight lines show the conversion between a photon of light and the energy of an electron. Wavy lines show nonradiative transitions of electrons. Within a Jablonski diagram several different pathways show how an electron may accept and then dissipate the energy from a photon. Thus, most diagrams start with arrows originating from the ground electronic state and finish with arrows returning to the ground electronic state.

The Jablonski diagram that drawn below is a partial energy diagram that represents the energy of a photoluminescent molecule in its different energy states. The lowest and darkest horizontal line represents the ground-state electronic energy of the molecule which is the singlet state labeled as S_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.

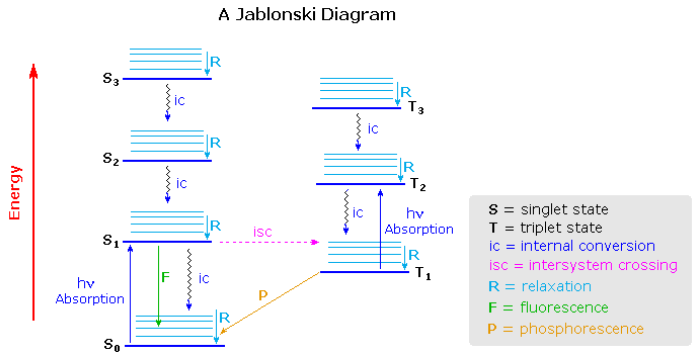


Figure 5.1.2: Partial Jablonski Diagram for Absorption, Fluorescence, and Phosphorescence. (Bill Reusch, Michigan State University).

Deactivation Processes

A molecule that is excited can return to the ground state by several combinations of mechanical steps that will be described below and shown in Figure 5.1.2.The deactivation process of fluorescence and phosphorescence involve an emission of a photon radiation as shown by the straight arrow in Figure 5.1.2. The wiggly arrows in Figure 5.1.2 are deactivation processes without the use of radiation. The favored deactivation process is the route that is most rapid and spends the least time in the excited state. If the rate constant for relaxation is more favorable in the radiationless path, the fluorescence will be less intense or absent.

Relaxation and Fluorescence

Often, when an excited state species relaxes, giving off a photon, the wavelength of the photon is different from the one that initially led to excitation. When this happens, the photon is invariably red-shifted; its wavelength is longer than the initial one. This situation is called "fluorescence" (Figure 5.1.3).

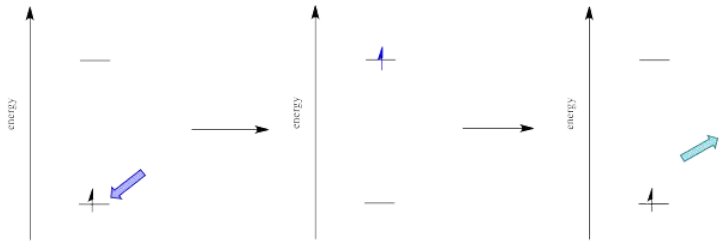


Figure 5.1.3: The absorption of purple light by a ground state particle, leading to the creation of an excited state particle. This excited state particle then emits blue light as it returns to the ground state.

How can that be? Isn't energy quantized? How is the molecule suddenly losing some of the energy that the original photon brought with it? This energy discrepancy is related to the Franck-Condon principle from the previous page. When an electron is promoted to an electronic excited state, it often ends up in an excited vibrational state as well (Figure 5.1.4). Vibrational energy, however, is not exchanged exclusively by means of photons. It can be gained or lost through molecular collisions and heat transfer.

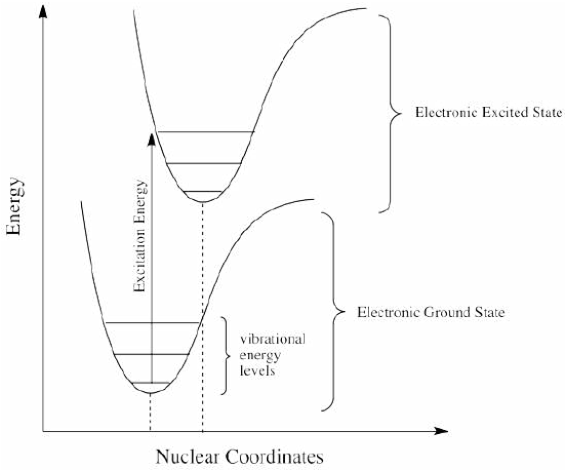


Figure 5.1.4: Transition from the ground state to an excited vibrational state within the excited electronic state.

Thus, an excited state molecule with an electron in a high-energy vibrational level within an excited electronic state might simply re-emit a photon of exactly the same wavelength as the one that was absorbed. But the excited electron is much more likely to relax into the lowest vibrational state within the excited electronic state, losing some of that initial excitation energy as heat. When the electron relaxes to this lower vibrational state, the energy gap between this excited state and the ground state is a little smaller. The photon that is emitted upon fluorescence will have lower energy and longer wavelength than a photon emitted from the original, higher vibrational level, excited state. See Figure 5.1.5.

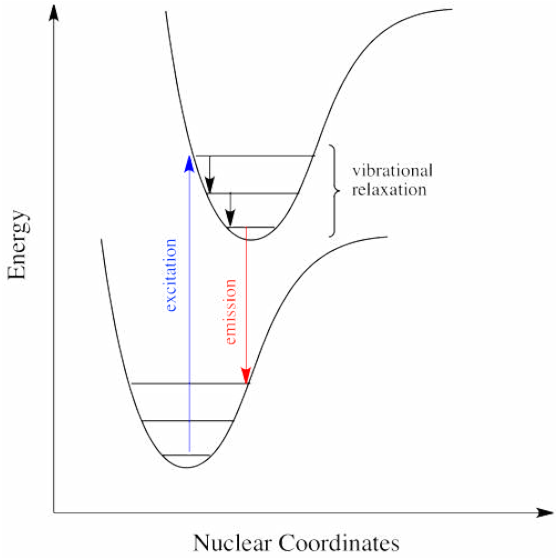


Figure 5.1.5: Excitation, followed by vibrational relaxation, and then emission.

Figure 5.1.6 shows the fluorescence transitions of a hypothetical diatomic molecule in which the equilibrium bond length of the ground state and the first singlet excited state are identical. In this molecule all absorptions involve transitions from the lowest vibrational level of the electronic ground state ($v'' = 0$) to various vibrational levels in the excited electronic state. Because vibrational relaxation occurs more rapidly than fluorescence, the fluorescence spectrum is composed of lines showing transitions from the lowest vibrational level of the excited state ($v' = 0$) to various vibrational levels in the electronic ground state.

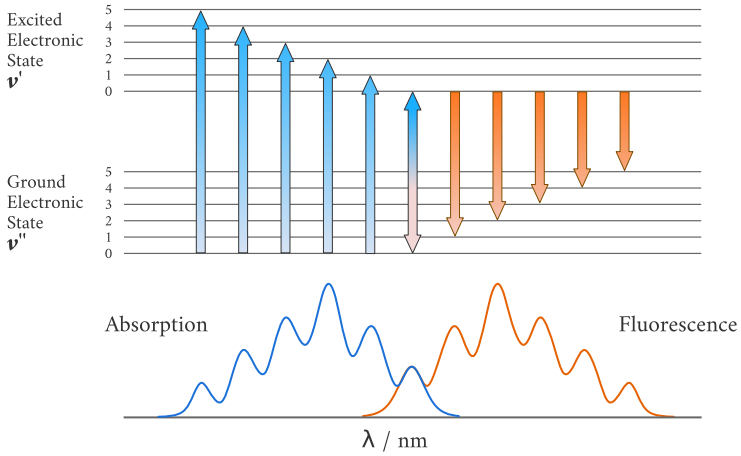


Figure 5.1.6: Absorption and fluorescence transitions in a hypothetical diatomic molecule in which the equilibrium bond length of the ground state is equal to the equilibrium bond length of the excited state. (CC BY-NC; Ümit Kaya, via LibreTexts)

Just how does a molecule undergo vibrational relaxation? Vibrational energy is the energy used to lengthen or shorten bonds, or to widen or squeeze bond angles. Given a big enough molecule, some of this vibrational energy could be transferred into bond lengths and angles further away from the electronic transition. Otherwise, if the molecule is small, it may transfer some of its energy in collisions with other molecules. In molecules, as one molecule drops to a lower vibrational state, the other will hop up to a higher vibrational state with the energy it gains. In Figure 5.1.7 below, the red molecule is in an electronic excited and vibrational state. In a collision, it transfers some of its vibrational energy to the blue molecule.

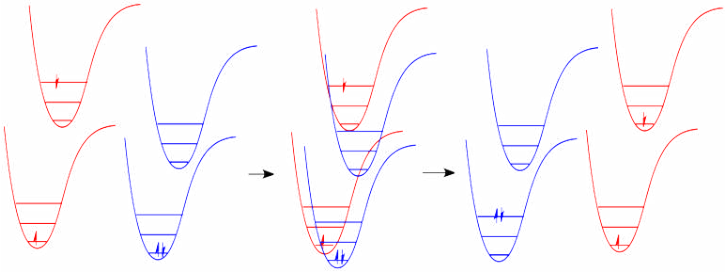


Figure 5.1.7: The transfer of vibrational energy (heat) through a collision.

Note

There are many examples of energy being transferred this way in everyday life. In a game of pool, one billiard ball can transfer its energy to another, sending it toward the pocket. Barry Bonds can transfer a considerable amount of energy through his bat into a baseball, sending it out of the park, just as Serena Williams can send a whole lot of energy whizzing back at her sister.

Exercise 5.1.1

How does the energy of an electronic absorption compare to other processes? To find out, you might consider the excitation of an entire mole of molecules, rather than a single molecule absorbing a single photon. Calculate the energy in kJ/mol for the following transitions.

a. absorbance at 180 nm (ultraviolet)
b. absorbance at 476 nm (blue)
c. absorbance at 645 nm (red)

Answer

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 5.1.2

How does the energy of an excitation between vibrational states compare to that of an electronic excitation? Typically, infrared absorptions are reported in cm^{-1}, which is simply what it looks like: the reciprocal of the wavelength in cm. Because wavelength and frequency are inversely related, wavenumbers are considered a frequency unit. Calculate the energy in kJ/mol for the following transitions.

a. absorbance at 3105 cm^{-1}
b. absorbance at 1695 cm^{-1}
c. absorbance at 963 cm^{-1}

Answer

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 5.1.1, we can see that the energy difference between vibrational states is an order of magnitude less than the energy difference between electronic states.

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}).

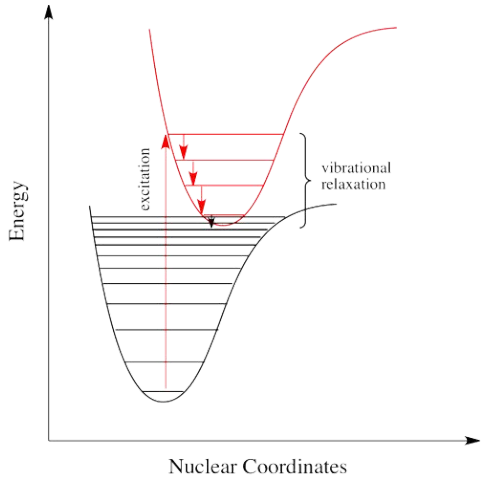


Figure **5.1.8**: Relaxation of an excited state particle to the ground state through the nonradiative process of internal conversion.

This event is called a "radiationless transition", because it occurs without release of a photon. The electron simply slides over from a low vibrational state of the excited electronic state to a high vibrational state of the electronic ground state. If the electron simply keeps dropping a vibrational level at a time back to the ground state, the process is called **"internal conversion"**.

Internal conversion has an important consequence. Because the absorption of UV and visible light can result in energy transfer into vibrational states, much of the energy that is absorbed from these sources is converted into heat. That can be a good thing if you happen to be a marine iguana trying to warm up in the sun after a plunge in the icy Pacific. It can also be a tricky thing if you are a process chemist trying to scale up a photochemical reaction for commercial production of a pharmaceutical, because you have to make sure the system has adequate cooling available.

Intersystem Crossing

Intersystem crossing is a process that leads to the electron getting caught between the excited state and the ground state. Just as, little by little, vibrational relaxation can lead the electron back onto the ground state energy surface, it can also lead the electron into states that are intermediate in energy in which the spin multiplicity has changed.

For example, suppose an organic molecule undergoes electronic excitation. Generally, organic molecules have no unpaired electrons. Their ground states are singlet states. According to one of the selection rules for electronic excitation, the excited state must also have no unpaired electrons. In other words, the spin on the electron that gets excited is the same after excitation as it was before excitation.

However, that's not the lowest possible energy state for that electron. When we think about atomic orbital filling, there is a rule that governs the spin on the electrons in degenerate orbitals: in the lowest energy state, **spin is maximized** (Hund's rule). In other words, when we draw a picture of the valence electron configuration of nitrogen, we show nitrogen's three p electrons each in its own orbital, with their spins parallel.



Figure **5.1.9**: The diagram on the left shows the energetically stable quartet spin state. The diagram on the right shows the less stable doublet spin state.

In Figure **5.1.9**, the diagram on the left, with three unpaired electrons, all with parallel spins, shows a nitrogen in the quartet spin state. This is the most stable state. Having one of those spins point the other way would result in a different, higher energy spin

state. The diagram on the right shows a different a different spin state, in which one pair of electrons in the p level is spin-paired, one up and one down, even though they are in different p orbitals. That would leave one electron without an opposite partner, so the nitrogen would be in a doublet spin state. The spin state on the left is **lower** in energy than the state on the right. That's just one of the rules of quantum mechanics (**Hund's rule**): maximize spin when degenerate orbitals are singly occupied.

A similar argument can be made for a molecule with the triplet state lower in energy than the singlet state, as shown in Figure 5.1.10. Why didn't the electron get excited to the triplet state in the first place? That is a forbidden (unlikely) electronic transition. But sliding down vibrationally onto the triplet state from the singlet excited state is not, because it doesn't involve absorption or emission of a photon.

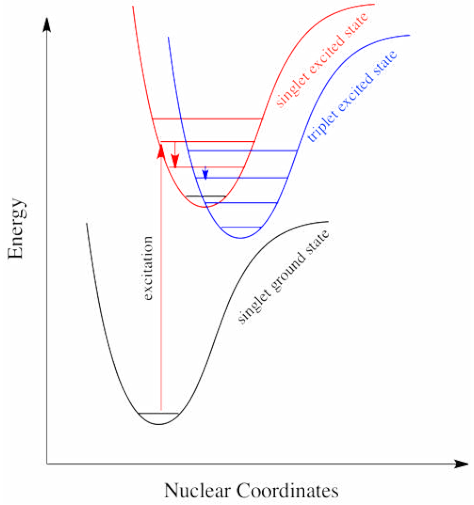


Figure 5.1.10: Intersystem crossing from a singlet excited state to a triplet excited state.

Intersystem crossing can have important consequences in reaction chemistry because it allows access to triplet states that are not normally available in many molecules. Because triplet states feature unpaired electrons, their reactivity is often typified by radical processes. That means an added suite of reactions can be accessed via this process.

Phosphorescence: A Radiationless Transition Followed by Emission

Intersystem crossing is one way a system can end up in a triplet excited state. Even though this state is lower in energy than a singlet excited state, it cannot be accessed directly via electronic excitation because that would violate the spin selection rule (\Delta S=0\). Once intersystem crossing has occurred, the process of reattaining the ground state slows down dramatically. The quick way back to ground state is to emit a photon. But because that would involve a change in spin state, it is not allowed. Realistically speaking, that means it takes a long time. By "a long time", we might mean a few seconds, several minutes, or possibly even hours. Eventually, the electron can drop back down, accompanied by the emission of a photon. This situation is called "phosphorescence" (Figure \(\PageIndex{11}).

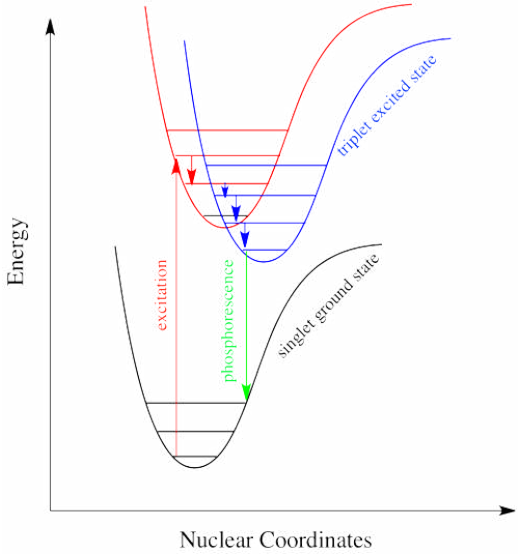


Figure **5.1.11**: The process of phosphorescence - excitation, followed by vibrational relaxation, intersystem crossing, and phosphorescence.

Many plants and animals use phosphorescence as a means of signaling. Molecules that display phosphorescence are also often incorporated into toys and shirts so that they will glow in the dark.

External Conversion

Deactivation of the excited electronic state may also involve the interaction and energy transfer between the excited state and the solvent or solute in a process called **external conversion.** Low temperature and high viscosity lead to enhanced fluorescence because they reduce the number of collision between molecules, thus slowing down this type of deactivation process.

Absorption and Emission Rates

The table below compares the absorption and emission rates of fluorescence and phosphorescence. The rate of photon absorption is very rapid. Fluorescence emission occurs at a slower rate. Since the triplet to singlet (or reverse) is a forbidden transition, meaning it is less likely to occur than the singlet-to-singlet transition, the rate of triplet to singlet is typically slower. Therefore, phosphorescence emission requires more time than fluorescence.

Table 15.1.1 : Rates of Absorption and Emission comparison.

Process	Radiative Process?	Transition	Timescale (sec)
Light Absorption (Excitation)	yes	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	no	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	no	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	no	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	yes	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	yes	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay to Ground State (Internal Conversion)	no	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

References

1. D. A. Skoog, et al. "Principles of Instrumental Analysis" 6th Edition, Thomson Brooks/Cole. 2007

2. D. C. Harris and M.D. Bertolucci "Symmetry and Spectroscopy, An Introduction to Vibrational and Electronic Spectroscopy" Dover Publications, Inc., New York. 1989.

Contributors and Attributions

- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)
- Diana Wong (UCD)
- Tom Neils (Grand Rapids Community College)

5.1: Electronically Excited Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **15.1: Electronically Excited Molecules can Relax by a Number of Processes** is licensed CC BY-NC-SA 4.0.

5.2: Transitions Modeled as Kinetics

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{5.2.1}$$

You can see from Equation 5.2.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 5.2.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

5.2: Transitions Modeled as Kinetics is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

5.3: Two-Level Systems Cannot Form Population Inversions

Energy State Populations

For reasons that we cannot explain, it appears that all things in nature prefer to go to the lowest energy state available to them. This seems to be how nature behaves. Apples fall all the way to the ground, once they are let go by the tree branches they grew on. Of course unless they fall into a hole, in which case they go even lower than the ground level - to the bottom of the hole. To raise the energy of the fallen apple someone, or something, has to intervene. A child must pick it up off the ground, for example. Otherwise, the apple will remain at its lowest point. Similarly, atoms tend to prefer to always stay in their ground state, unless some intervening force causes them to reach an excited state. In the language used in the study of lasers, any process that feeds energy into a collection of atoms or molecules and causes them to vacate their ground state is referred to as an energy pump, or simply as a pump.

In most lamps electricity is used, by one mechanism or other, to pump atoms out of their ground-state into some excited state. We have already seen that incandescent bulbs produce light from Radiative transitions after excitation via collisions of the electrons in an electric current with the filament atoms. As we've also seen, other light sources, like the fluorescent lamps or neon tubes, use gas or vapor for their medium of excitation instead of a solid filament. In most lamps, the pumping mechanism is electricity. This is also the case for most lasers, but in some lasers optical pumping is the mechanism that is used to cause excitation. In optical pumping a light source generates photons with enough energy that they are able to get absorbed by the atoms in the lasing medium and cause them to go into an excited state.

Evidently, all excitations occur "instantaneously", but de-excitations can lag by a measurable time interval that depends on the properties of the excited state. That is to say, an atom in an excited state does not instantaneously de-excite. The time that it spends, on average, in that excited level is called the lifetime of that state. Lifetimes can vary in duration depending on the atom and on the energy level. Excited state lifetimes are typically a few nanoseconds (10-9 s, or a billionth of a second), but they could be as short as a picosecond (10-12 s, or a thousand times shorter still) or as long as a few milliseconds (10-3 s). The ground state, of course, has an infinitely long lifetime since an atom in its ground state can no longer decrease its energy. So, the most stable of states is the ground state. Long-lived states are referred to as meta-stable states.

In the case of Radiative emission, atoms happen to take two very distinctly different approaches: spontaneous emission, or stimulated emission. Spontaneous emission refers to the case when the excited atom de-excites, rather randomly whenever it "feels like it", and emits a photon. This photon has an energy equal to the difference between the two energy levels of the transition, but its direction of travel and its other properties, such as polarization are random. Stimulated emission was first theorized by Albert Einstein in 1917. For stimulated emission to occur a second, non-participating yet stimulating, photon must be present. The energy of this second photon must exactly match the allowed energy of the transition. Then the emitted photon will not only have the same energy as the stimulating one, but it will also travel in the same direction, and will be essentially identical to it.

So, independent of what type of medium is used in a laser, in the absence of a pump the atoms or molecules are almost all in their ground state. Let us imagine that we could count the number of atoms in our laser medium that are in each energy state and denote the ones which are in their ground state by Ngs , those in the first excite state by N1, those in the second excited state by N2 , and so on. Then in the absence of a pump we are mostly certain that N1= N2 = ... = 0, and Ngs = total number of all the atoms in the medium. Once the pump is turned on it will deplete the number of atoms that were originally in the ground state and increases the number of atoms in the excited states that it is pumping to. Because excited atoms de-excite quickly and return to their ground states by spontaneous emission, in almost all lasers even when the pump is feeding energy into the medium the number of atoms in their ground state remains many times more than atoms in any other energy state. That is to say, almost always we could safely state that:

$$N_{\text{ground state}} \text{ much bigger than } N_{\text{any other state}} .$$

To make a laser we need to not only excite the atoms in the laser medium, but somehow encourage them to undergo a decay through stimulated emission. In stimulated emission a passer-by photon which has an energy exactly equal to the transition energy stimulates the atom to emit a photon, identical to the passer-by photon, instantly. The problem with this is that the same passer-by photon could instead get absorbed by a de-excited atom. So, aside from pumping the atoms to excited states, we need to use clever procedures to insure that there are more excited atoms that could use the passer-by photon for stimulated emission than there are

de-excited atoms which could absorb it; i.e. we need to generate a population inversion. Although Einstein predicted stimulation emission in 1917, it was not found experimentally for over 10 years and took over another 30 years just to predict the possibility of a laser. This is basically because it was not considered possible to produce a population inversion because of the above inequality.

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 monochromaticlight, i.e. photons of the same frequency (or wavelength).Thirdly, it would be desirable if our laser's output were collimated, producing a sharply defined "pencil-like" beam of light (this is not crucial, but clearly a desirable condition). Lastly, it would also be desirable for our laser to be efficient, i.e. the higher the ratio of output energy - to - input energy, the better.

Let us begin by examining the requirements for our first condition for lasing, coherence. This condition is satisfied only when the lasing transition occurs through stimulated emission. As we have already seen, stimulated emission produces identical photons that are of equal energy and phase and travel in the same direction. But for stimulated emission to take place a "passer-by" photon whose energy is just equal to the de-excitation energy must approach the excited atom before it de-excites via spontaneous emission. Typically, a photon emitted by the spontaneous emission serves as the seed to trigger a collection of stimulated emissions. Still, if the lifetime of the excited state is too short, then there will not be enough excited atoms around to undergo stimulated emission. So, the first criteria that we need to satisfy is that the upper lasing state must have a relatively long lifetime, otherwise known as a meta-stablestate, with typical lifetimes in the milliseconds range. In addition to the requirement of a long lifetime, we need to ensure that the likelihood of absorption of the "passer-by" photons is minimized. This likelihood is directly related to the ratio of the atoms in their ground state versus those in the excited state. The smaller this ratio, the more likely that the "passer-by" photon will cause a stimulated emission rather than get absorbed. So, to satisfy this requirement, we need to produce a population inversion: create more atoms in the excited state than those in the ground state.

Achieving population inversion in a two-level atom is not very practical. Such a task would require a very strong pumping transition that would send any decaying atom back into its excited state. This would be similar to reversing the flow of water in a water fall. It can be done, but is very energy costly and inefficient. In a sense, the pumping transition would have to work against the lasing transition.

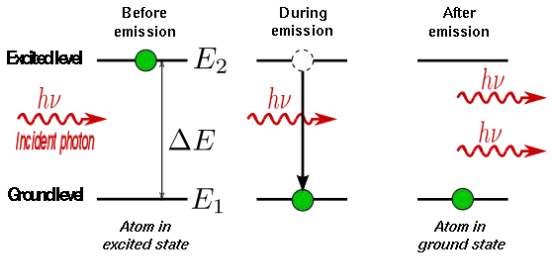
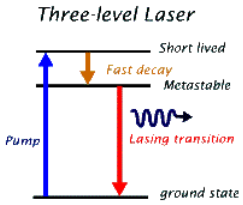


Figure 1: Stimulated emission in a two-level transition. (CC BY-SA 4.0; V1adis1av)

It is clear, from the above diagram, that in the two-level atom the pump is, in a way, the laser itself! Such a two-level laser would work only in jolts. That is to say, once the population inversion is achieved the laser would lase. But immediately it would end up with more atoms in the lower level. Such two-level lasers involve a more complicated process. We will see, in later material, examples of these in the context of excimer lasers, which are pulsed lasers. For a continuous laser action we need to consider other possibilities, such as a three-level atom.

Lasing in Three-Level Systems

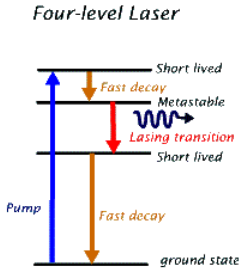
In fact, the first laser that was demonstrated to operate was a three-level laser, Maiman's ruby laser.



In the above diagram of a three level laser the pump causes an excitation from the ground state to the second excited state. This state is a rather short-lived state, so that the atom quickly decays into the first excited level. [Decays back to the ground state also occur, but these atoms can be pumped back to the second excited state again.] The first excited state is a long-lived (i.e. metastable) state which allows the atom to "wait" for the "passer-by" photon while building up a large population of atoms in this state. The lasing transition, in this laser, is due to the decay of the atom from this first excited metastable state to the ground state. If the number of atoms in the ground state exceeds the number of atoms that are pumped into the excited state, then there is a high likelihood that the "lasing photon" will be absorbed and we will not get sustained laser light. The fact that the lower lasing transition is the ground state makes it rather difficult to achieve efficient population inversion. In a ruby laser this task is accomplished by providing the ruby crystal with a very strong pulsating light source, called a flash lamp. The flash lamp produces a very strong pulse of light that is designed to excite the atoms from their ground state into any short-lived upper level.t In this way the ground state is depopulated and population inversion is achieved until a pulse of laser light is emitted. In the ruby laser the flash lamp light lasts for about 1/1000 of a second (1 ms) and can be repeated about every second. The duration of the laser pulse is shorter than this, typically 0.1 ms. In some pulsed lasers the pulse duration can be tailored using special methods to be much shorter than this, down to about 10 fs (where 1 fs = 10-15 s or one thousandth of a millionth of a millionth of a second). So, the output of a three-level laser is not continuous, but consists of pulses of laser light.

Lasing in Four-Level Systems

To achieve a continuous beam of laser light a four-level laser is required.



Here, the lower laser level is not the ground state. As a result, even a pump that may not be very efficient could produce population inversion, so long as the upper level of the laser transition is longer lived than the lower level. Of course, all attempts are made to design a pump that maximizes the number of excited atoms. A typical four-level laser is the helium-neon (He-Ne) gas laser. In these lasers electric pumping excites helium atoms to an excited state whose energy is roughly the same as the upper short-lived state in the neon atom. The sole purpose of the helium atoms is to exchange energy with neon atoms via collisional excitation. As it turns out, this is a very efficient way of getting neon atoms to lase.

Laser components

All lasers have three primary components:

- Medium
- Pump
- Resonant Cavity

The laser medium can be gaseous, liquid, or a solid. These could include atoms, molecules, or collections of atoms that would be involved in a laser transition. Typically, a laser is distinguished by its medium, even though two lasers using different media may

have more in common than two which have similar media.

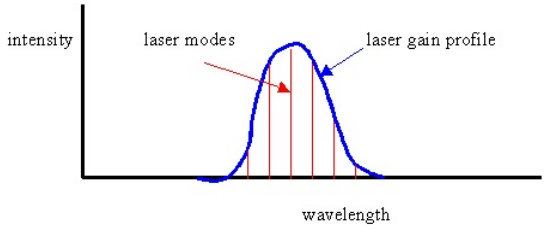
There are three different laser pumps: electromagnetic, optical, and chemical. Most lasers are pumped electro-magnetically, meaning via collisions with either electrons or ions. Dye lasers and many solid state lasers are pumped optically; however, solid state lasers are typically pumped with a broad band (range of wavelengths) flash-lamp type light source, or with a narrow band semiconductor laser. Chemically pumped lasers, using chemical reactions as an energy source, are not very efficient. So far, these lasers have been made to work not so much for their usefulness as for their curious operation.

Up to now in our discussion of laser theory we have not really seen how the beam is generated. We know that photons emitted by stimulated emission travel coherently in the same direction, but what is it that defines the beam direction and what allows the intensity of the laser light to get large? The answer to these two questions is coupled together in the resonant cavity. Laser resonant cavities usually have two flat or concave mirrors, one on either end, that reflect lasing photons back and forth so that stimulated emission continues to build up more and more laser light. The "back" mirror is made as close to 100% reflective as possible, while the "front" mirror typically is made only 95 - 99% reflective so that the rest of the light is transmitted by this mirror and leaks out to make up the actual laser beam outside the laser device.

The resonant cavity thus accounts for the directionality of the beam since only those photons that bounce back and forth between the mirrors lead to amplification of the stimulated emission. Once the beam escapes through the front mirror it continues as a well-directed laser beam. However, as the beam exits the laser it undergoes diffraction and does have some degree of spreading. Typically this beam divergence is as small as 0.05o but even this small amount will be apparent if the beam travels long distances.

Even more, the resonant cavity also accounts for the amplification of the light since the path through the laser medium is elongated by repeated passes back and forth. Typically this amplification grows exponentially, similar to the way compound interest works in a bank. The more money in your bank account, with compound interest, the faster you earn more interest dollars. Similarly, the more photons there are to produce stimulated emission, the larger the rate at which new coherent photons are produced. The term used for laser light is gain, or the number of additional photons produced per unit path length.

The last question to address in this section is: why is the resonant cavity called by that name? What does resonance have to do with having mirrors on either end of a region containing the laser medium? Recall that when we discussed resonance on a string, we spoke about the wave traveling one way along the string (say to the right) interfering with the wave reflected at the end traveling back to the left. At a resonant frequency, there are points at which the two waves exactly add or cancel all the time, leading to a standing wave. At other frequencies the waves will randomly add or cancel and the wave will not have a large amplitude. The case of a light wave traveling back and forth in the resonant cavity is exactly analogous in that only at certain resonant frequencies will the light wave be amplified. The required condition is easy to see. The mirror separation distance, L, must be equal to a multiple of half a wavelength of light, just as we saw in the case of a string. In symbols, we have that L = nl/2, where l is the wavelength of the light and n is some integer. In the case of light, because of the small wavelength n is a very large number, implying that there are a huge number of resonant frequencies. On the other hand, only those resonant frequencies that are amplified by the laser medium will have large amplitudes and so usually there are only a few so-called laser modes or laser resonant frequencies present in the light from a laser, as shown in the figure.



Questions on Laser Components

- What are the three primary components of a laser?
- What different types of laser medium are used?
- What is a pump? Describe the different types of pumps.
- What is a resonant cavity?
- Describe how the resonant cavity produces a collimated laser beam.

- What is the beam divergence of a laser caused by? What is a typical value for it?
- What does the term gain mean? Is it related to pain?
- Describe why a typical laser has only a few modes, while the resonant cavity produces a huge number of them.

Contributors

- Jay Newman and Seyffie Maleki (Union College)

5.3: Two-Level Systems Cannot Form Population Inversions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Laser Theory** is licensed CC BY-NC-SA 4.0.

5.4: Population Inversion via Three-Level Systems

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{5.4.1}$$

You can see from Equation 5.4.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 5.4.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

5.4: Population Inversion via Three-Level Systems is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

5.5: Laser Fundamentals

LASER is an acronym for Light Amplification by Stimulated Emission of Radiation. Laser is a type of light source which has the unique characteristics of directionality, brightness, and monochromaticity. The goal of this module is to explain how a laser operates (stimulated or spontaneous emission), describe important components, and give some examples of types of lasers and their applications.

Introduction

The word LASER is an acronym for Light Amplification by Stimulated Emission of Radiation. In 1916, Albert Einstein discovered the physical principle responsible for this amplification, and the foundation principle is called stimulated emission. It was widely accepted at that time that laser would represent a big leap in science and technology, even before Theodore H. Maiman built the first one in 1960. The 1951 Nobel Prize in physics was shared by Charles H. Townes, Nokolay Basov, and Aleksandr Prokhorov, in citation, “For Fundamental work in the field of quantum electronics, which has led to the construction of oscillator and amplifiers based on the maser-laser principle”.

The early lasers developed in the 1950s by Charles H. Townes and Arthur Shawlow were gas and solid-state lasers for use in spectroscopy. The principles of lasers were adapted from masers. MASER is an acronym that stands for Microwave Amplification by Stimulated Emission of Radiation. It uses the idea of stimulated emission and population inversion to produce a coherent amplified radiation of light in the microwave region. Stimulated emission is when an electron in an excited state falls back to ground state after absorbing energy from an incident photon. Amplified radiation or light is produced with the same direction and energy as the incident light. Population inversion is when you have a greater population of electrons in the excited state than in ground state. Population inversion is achieved through various pumping mechanisms. The laser uses these same ideas except that the electromagnetic wave created is in the visible light region. When emission begins the light oscillates within the resonant cavity and gains magnitude. Once enough light has been acquired, the laser beam is produced. This allows lasers to be used as a powerful light source. Three unique characteristics of a laser are its properties of monochromaticity, directionality, and brightness.

The monochromaticity of lasers is due to the fact that lasers are highly selective in the wavelength of light produced, which in itself is due to the resonant frequency inside the active material. Resonant frequency means that the light is oscillating in a single mode creating a monochromatic beam of light. The property of directionality depends on the angle of which the light propagates out of the source. Since lasers have large spatial and temporal coherence directionality is maximized. Temporal coherence is when there are small fluctuations in the phase. Spatial coherence has small changes in the amplitude of the emitted light. Like monochromaticity, directionality is dependent on the resonant cavity of the active material. The property of brightness is a result of the directionality and the coherence of the light. Due to these properties, lasers today are used in simple laser pointers, cutting devices, the development of military technologies, spectroscopy, and medical treatments. Their direct application to spectroscopy has allowed scientists to measure lifetimes of excited state molecules, structural analysis, probing far regions of the atmosphere, photochemistry and their use as ionization sources.

History

One of the most important characteristics of light is that it has wave-like properties and that it is an electromagnetic wave. Experiments on the blackbody radiation demonstrated a comprehensive idea of emission and absorption of electromagnetic waves. In 1900, Max Plank developed the theory that electromagnetic waves can only exist in distinct quantities of energy, which are directly proportional to a given frequency (ν). In 1905, Albert Einstein proposed the dual nature of light, having both wave-like and particle-like properties. He used the photoelectric effect to show that light acts as a particle, with energy inversely proportional to the wavelength of light. This is important, because the number of particles is directly related to how intense a light beam will be. In 1915, Einstein introduced the idea of stimulated emission- a key concept to lasers.

In 1957, Townes and Shawlow proposed the concept of lasers in the infrared and optical region by adapting the concept of masers to produce monochromatic and coherent radiation. In 1953, Townes was the first to build a maser with an ammonia gas source. Masers use stimulated emission to generate microwaves. Townes and other scientists wanted to develop the optical maser to generate light. Optical masers would soon adopt the name LASER: Light Amplification by Stimulated Emission of Radiation. An optical maser would need more energy than what can be provided by microwave frequencies and a resonant cavity of the order of

1μm or less. Townes and Shawlow proposed the use of a Fabry-Pérot interferometer equipped with parallel mirrors, where Interference of radiation which is traveling back and forth between parallel mirrors in the cavity allowed for selection of certain wavelengths. Townes built an optical maser with potassium gas. That failed because the mirrors degraded over time. In 1957, Gordon Gould improved upon Townes' and Shawlow's laser concept. It was Gould who renamed the optical maser to laser. In April 1959, Gould filed a patent for the laser and later in March 1960, Townes and Shawlow had also made a request for a patent. Since Gould's notebook was officially dated the idea was his first, but he did not receive the patent until 1977.

Components

A laser consists of three main components: a lasing medium, a resonant or optical cavity, and an output coupler. The lasing medium consists of a group of atoms, molecules , or ions in solid, liquid or gaseous form, which acts as an amplifier for light waves. For amplification, the medium has to achieve population inversion, which means in a state in which the number of atoms in the upper energy level is greater than the number of atoms in the lower energy level. The output coupler serves as energy source which provides for obtaining such a state of population inversion between a pair of energy levels of the atomic system. When the active medium is placed inside an optical resonator, the system acts as an oscillator.

Figure 1. Diagram of a typical laser, showing the three major parts.

Lasing Medium

The lasing medium is the component used to achieve lasing, such as chromium in the aluminum oxide crystal-found in a ruby laser. Helium and neon gas are two materials most commonly used in gas lasers. These are only a few examples of lasing mediums or materials that have been used in the past and present states of the laser. For further information about different types of lasing mediums please refer to the section where *Types of Lasers* is discussed.

Optical Cavity and Output Coupler

Rays of light moving along an optical path tend to diverge over time, because the energy of radiation has very high frequency. Therefore an optical cavity is needed to refocus the light. **Figure 1**, represents the basics of an optical cavity where the light inside moves back and forth between two mirrors. These redirect and focus the light each time it hits the surface of the mirrors. There are two types of cavities: stable cavities and unstable cavities. A stable cavity is when the ray of light does not diverge far from the optical axis. An unstable cavity is when the ray of light bounces off and away from a mirrors surface. The importance of the cavities is that it allows for the laser to have properties of directionality, monochromaticity and brightness.

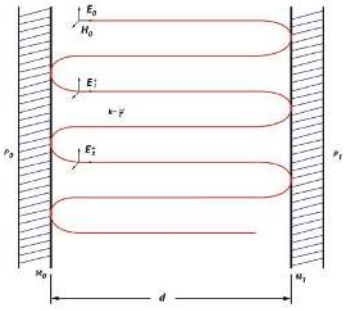


Figure 2. an optical cavity where the light inside moves back and forth between two mirrors

Light oscillating between the first mirror (M_o) and the second mirror (M_1) separated by distance, d, will have a round-trip phase shift (RTPS) of $2\theta=2kd=q2\pi-\phi$. In **Figure 1**, a round-trip can be described as the beam traveling from M_o to M_1back to M_o. Resonance occurs in the cavity because the light propagating between the two mirrors is uniform. The ABCD law describes that an optical cavity has a field distribution, because it reproduces itself as it is making these round-trips between the two parallel mirrors. The ABCD law was first applied to a Gaussian beam with a beam parameter, q, which is described as

$$q_2 = \frac{(Aq_1 + B)}{(Cq_1 + D)}$$

This law states that the beam, which is oscillating through an optical system, will experience some changing as it moves in the cavity. Fields that are created in an optical cavity have analogous shape and phase as they make each trip back and forth. However,

the one thing that changes is the size of the field because the electromagnetic wave is unrestricted, unlike a wave in a short-circuited coaxial cable used to build a resonator or a microwave cavity mode. Since there is a field distribution of $E_o$at the surface of M_o, it can be said that there is a field distribution at the surface of M_1. Since there will be a change in size of the field this means that the electromagnetic wave will have change in amplitude by $\rho_0 * \rho_1$ and a phase factor of $e^{-}jk2d$, creating additional fields. This is an example of a phasorial addition of all fields between M_o and M_1, creating a total field E_T (**Figure 2**). Phasorial addition is described by RTPS, where each additional E_n will have a delay of angle ϕ which is related to kd.

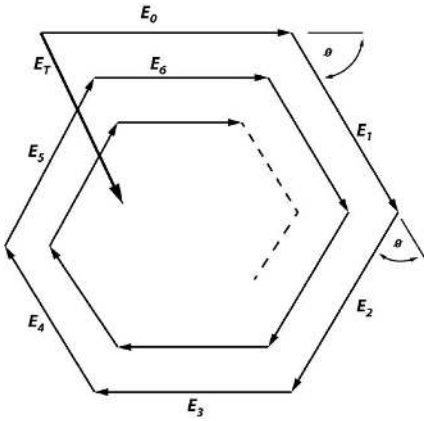


Figure 3. Totle field E_T

E_T will always be greater than $E_o$only if ρ_0 and $\rho_1$are not greater than 1 and ϕ=0. In this case, when ϕ=0 resonance is enhanced because all factors such as E_T travelling between M_o and M_1, the intensity of the electromagnetic waves, number of photons traveling between $M_o$and M_1, and the amount of energy that is stored are maximized. The resonant wavelength can also be determined by using the relationship between RTPS, and because

$$k = \frac{\omega n}{c} = \frac{2\pi}{\lambda}$$

Using $2\theta = 2kd = q2\pi$

$$\frac{2\pi 2d}{\lambda} = q2\pi$$

$$d = \frac{q\lambda}{2}$$

Where the wavelength of interest is given by $\lambda = \lambda_0/n$, where n is the index of refraction and λ_0 is the free-space wavelength .

Since we are dealing with light as a wave, the light in the resonant cavity can be described in terms of frequency, ν. Where

$$k2d = \omega\frac{2nd}{c} = 2\pi\nu\frac{2nd}{c} = q(2\pi)$$

$$\nu = q\frac{c}{2nd}$$

A Fabry-Pérot interferometer is a prime example of an optical cavity used in a laser. The Fabry-Pérot is equipped with two parallel mirrors, one that is completely reflective and the other that is partially reflective. As light is accumulating in the cavity after taking several round trips between the two mirrors, some light is transmitted through the partially reflective mirror and a laser beam is produced. The beam can be in pulsed mode or continuous-wave (CW) mode. To increase the performance of the resonant cavity, the length of the cavity (d) must be considered as a way to avoid a decrease in the laser beam intensity due to any diffraction losses. The size of the aperture of the cavity is also important because it determines the strength or the intensity of the laser beam. In fact, determining the best length of a resonant cavity will enhance the coupling conditions of the output coupler by producing a frequency that is stable, which ultimately generates a laser beam that is coherent and has high power.

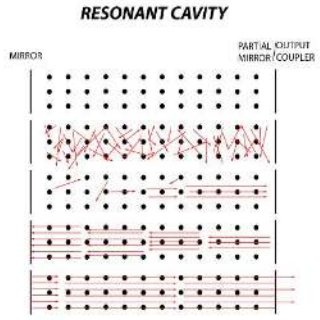


Figure 4. The first stage shows that all molecules present are in the ground state since there is no excitation energy present in the cavity. In the second stage, molecules become excited causing spontaneous emission of photons. In the third stage, photons collide with excited molecules causing an amplification of the light. This results in stimulated emission where the photon that is released has the same energy and direction of the photon that created it. Last is the fourth stage, where stimulated emission causes amplification of the light, and those photons that are traveling parallel to the cavities axis will hit one of the parallel mirrors and will be reflected back along the same axis. As the light is building up from the back and forth movement from one mirror to another, some of the light will pass through the partial mirror or the output coupler as a beam of rays. The remaining light in the cavity will continue producing more photons as long as there is a population inversion.

There are essentially six stages in the lasing process. First is the ground state where there is no excitation of the lasing medium. Second is pumping, which is applied to the medium where spontaneous emission occurs. Then the third stage is when emitted photons collide with an excited molecule where stimulated emission occurs. In the fourth stage the photons are produced in multiples, however those moving parallel in the cavity will hit a mirror and then hit the second mirror. During the fifth stage this process continues until there is an accumulation of light that is coherent and of a specific frequency. Finally, the sixth stage is when the light or laser beam exits the partially reflective mirror which is also known as the output coupler. An output coupler is the last important component of a laser because it must be efficient to produce an output of light with maximum intensity. If the output coupler is too transparent than there is much more loss of electromagnetic waves and this will decrease lasing significantly because population inversion will no longer be maintained. If the output coupler or partially reflective mirror is too reflective, then all the accumulated light that is built up in the resonant cavity will be trapped in the cavity. The beam will not pass through the output coupler, producing little to no light making the laser ineffective.

Emission

Lasers create a high energy beam of light by stimulated emission or spontaneous emission. Within in a molecule there are discrete energy levels. A simple molecular description has a low energy ground state (E_1) and a high energy excited state (E_2). When an electromagnetic wave, referred to as the incident light, irradiates a molecule there are two processes that can occur: absorption and stimulated emission.

Absorption occurs when the energy of the incident light matches the energy difference between the ground and excited state, causing the population in the ground state to be promoted to the excited state. The rate of absorption is given by the equation:

$$\frac{dN_1}{dt} = -W_{12}N_1$$

Where N_1 is the population in E_1, and W_{12} is the probability of this transition. The probability of the transition can also be related to the photon flux (intensity of incident light):

$$W_{12} = \sigma_{12}F$$

Where F is the photon flux and σ_{12} is the cross section of the transition with units of area. When absorption occurs photons are removed from the incident light and the intensity of the light is decreased.

Stimulated emission is the reverse of absorption. Stimulated emission has two main requirements: there must be population in the excited state and the energy of the incident light must match the difference between the excited and ground state. When these two requirements are met, population from the excited state will move to the ground energy level. During this process a photon is emitted with the same energy and direction as the incident light. Unlike absorption, stimulated emission adds to the intensity of the incident light. The rate for stimulated emission is similar to the rate of absorption, except that it uses the population of the higher energy level:

$$W_{21} = \sigma_{21} F$$

Like absorption the probability of the transition is related to the photon flux of the incident light through the equation:

$$\frac{dN_2}{dt} = -W_{21} N_2$$

When absorption and stimulated emission occur simultaneously in a system the photon flux of the incident light can increase or decrease. The change in the photon flux is a combination of the rate equations for absorption and stimulated emission. This is given by the equation:

$$dF = \sigma F(N_2 - N_1) d\tau$$

Spontaneous emission has the same characteristics as stimulated emission except that no incident light is required to cause the transition from the excited to ground state. Population in the excited state is unstable and will decay to the ground state through several processes. Most decays involve non-radiative vibrational relaxation, but some molecules will decay while emitting a photon matching the energy of the energy difference between the two states. The rate of spontaneous emission is given by:

$$\frac{dN_2}{dt} = -AN_2$$

Where A is the spontaneous emission probability which depends on the transition involved. The coefficient A is an Einstein coefficient obtained from the spontaneous emission lifetime. Since spontaneous emission is not competing with absorption, the photon flux is based solely on the rate of spontaneous emission.

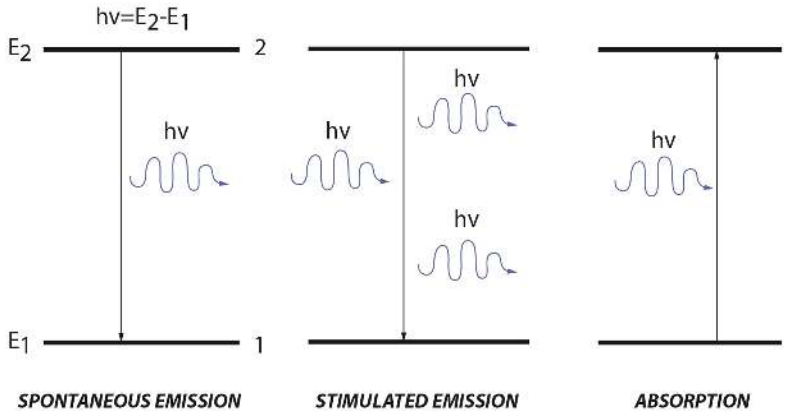


Figure 5. Diagram of spontaneous emission, stimulated emission and absorption in a two energy level system

The population ratio of a molecule or atom is found using the Boltzmann distribution and the energy of the ground state (E_1) and the excited state (E_2):

$$\frac{N_2}{N_1} = e^{\frac{-(E_2 - E_1)}{kT}}$$

Under normal conditions, the majority, if not all, of the population is in the lower energy level (E_1). This is because the energy of the excited is greater than the ground state. Normal thermal energy available (kT) is not enough to overcome the difference, and the ratio of population favors the ground state. For example, if the difference in energy between two states absorbes light at 500nm, the ratio of N_1 to N_2 is 5.1×10^{41}:1. The photon flux of the incident light is directly proportional to the difference in populations. Since the ground state has more populations, the photon flux decreases: there is more absorption occurring than stimulated emission. In order to increase the photon flux there must be more population in the excited state than in the ground state, generally known as a population inversion.

In a two level energy system it is impossible to create the population inversion needed for a laser. Instead three or four level energy systems are generally used (**Figure 5**).

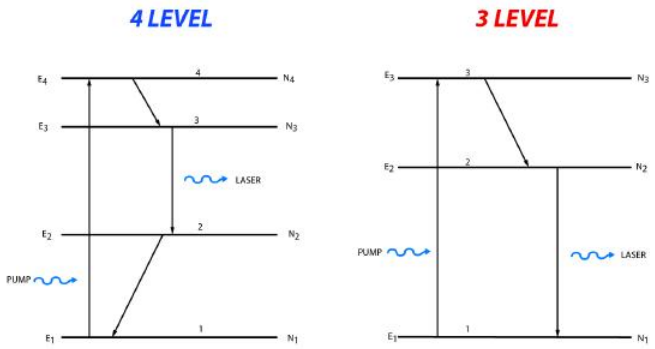


Figure 6. Three and four level energy system

Three level processes involve pumping of population from the lowest energy level to the highest, third energy state. The population can then decay down to the second energy level or back down to the first energy level. The population that makes it to the second energy level is available for stimulated emission. Light matching the energy difference between the second and first energy level will cause a stimulated emission. Four level systems follow roughly the same process except that population is moved from the lowest state to the highest fourth level. Then it decays to the third level and lasing happens when the incident light matches the energy between the third and second level. After lasing there is decay to the first level.

Pumping Process

Pumping is the movement of population from the ground state to a higher excited state. The general rate at which this is done is given by:

$$(\frac{dN_g}{dt})_p = W_p N_g$$

Where N_g is the population in the ground level and W_p is the pump rate. Pumping can be done optically, electronically, chemically (see chemical laser), using gases at high flow rates, and nuclear fission. Only optical and electrical pumping will be discussed in detail.

Optical Pumping

Optical pumping uses light to create the necessary population inversion for a laser. Usually high pressure xenon or krypton lamps are used to excite solid or liquid laser systems. The active material in the laser absorbs the light from the pump lamp, promoting the population from the ground state to the higher energy state. The material used in the laser can be continuously exposed to the pumping light which creates a continuous wave laser (CW). A pulsed laser can be created by using flashes of pumping light.

In optical pumping there are three types of efficiency: transfer, lamp radiative, and pump quantum efficiency. Transfer efficiency is the ratio of the energy created by the lamp and the power of the light emitted by the laser. The lamp radiative efficiency is the measure of how much electrical power is converted into light in the optical lamp. Pump quantum efficiency accounts for the ratio of population that decays to the correct energy level and population that decays either back to the ground state or another incorrect energy level. For example, the overall pumping rate of the first ruby laser was around 1.1%.

The average pump rate for optical pumping depends on the total efficiency of the pump (η_p), volume of the laser material (V), ground state population (N_g), power input (P), and frequency of the lasing transition (ν_0):

$$\langle W_p \rangle = \eta_p (P/(V N_g \hbar \upsilon_0))$$

Electrical Pumping

Electrical pumping is a much more complicated process than optical pumping. Usually used for gas and semiconducting lasers, electrical pumping uses electrical current to excite and promote the ground state population. In a simple gas laser that contains only one species (A), current passes through the gas medium and creates electrons that collide with the gas molecules to produce excited state molecules (A^*):

$$A + e \longrightarrow A^* + e$$

During electron impact either an ion or an excited state can be created. The ability to make the excited state depends mostly on the material used in the laser and not the electrical pumping source making it difficult to describe the efficiency of the pumping. Total efficiencies have been calculated and tabulated for most active materials used in electrical pumping. Where eficiencies range from a < 0.1% N_2 gas laser to 70% for some CO_2 gas lasers.

Like the pumping rate of optical pumps, the rate of electrical pumping is found using the overall efficiency of the pump, power applied, and population of the ground state. However instead of using the frequency of the ground to upper state transition, electrical pumping uses the energy of the upper state ($\hbar\omega_p$) and the volume of the electron discharge (V):

$$\langle W_p \rangle = \eta_p (P/(V N_g \hbar \omega_p))$$

Pulsed operation

Q-Switching

The technique of Q switching allows the generation of laser pulses of short duration from a few nanoseconds to a few tens of nanoseconds and high peak power from a few megawatts to a few tens of megawatts.

Suggest we put a shutter into the laser cavity. If the shutter is closed, laser action cannot occur and the population inversion can be very high. If the shutter is opened suddenly, the stored energy will be released in a short and intense light pulse. This technique is known as Q-switching. Q here denotes the ratio of the energy stored to the energy dissipated in the cavity. This technique is used in many types of solid-stat lasers and CO_2 lasers to get a high-power pulsed output.

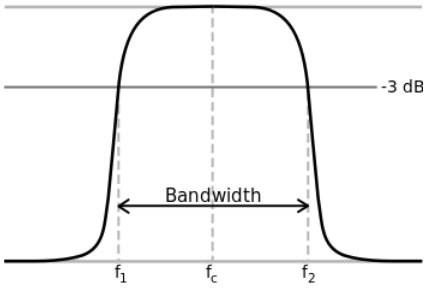


Figure 7. The bandwidth, Δf , or f1 to f2, of a damped oscillator is shown on a graph of energy versus frequency. The Q factor of the damped oscillator, or filter, is $f_c/\Delta f$. The higher the Q, the narrower and 'sharper' the peak is.

To produce high inversion required for Q-switching, four requirements must be satisfied.

1. The lifetime of the upper level must be longer than cavity buildup time.
2. The pumping flux duration must be longer than the cavity build up time.
3. The initial cavity losses must be high enough during the pumping duration to prevent oscillation occurring.
4. The cavity losses must be reduced instantaneously.

Mode-Locking

The technique of mode locking allows the generation of laser pulses of ultrashort duration from less than a picosecond to femtoseconds and very high peak, a few gigawatts.

Mode-locking is achieved by inducing the different longitudinal modes of a laser to a locked mode. When combining the electromagnetic waves modes with different frequencies and random phases, they produce a random and average output. When the modes are added in phase, they combine to produce a total amplitude and intensity output with a repeated pulse.

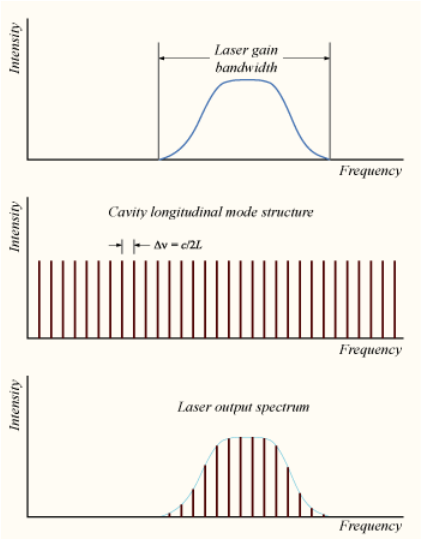


FIgure 8:Laser mode structure

Types of Lasers

There are many different types of lasers with a wide range applications, and below is a brief description of some of the main types.

Solid State Lasers

A solid-state laser is one that uses a solid active medium generally in a rod shape. Inside the active material is a dopant that acts as the light emitting source. Optical pumping is used to create population inversion of the active material. Solid-state lasers generally use stimulated emission as the mechanism for creating the high energy beam.

Ruby Laser

The ruby laser was the first operating laser and was built in 1960. It has a three-level (**Figure 6**) energy system that uses aluminum oxide with some of the aluminum atom replaced with chromium as its active material. The chromium in the aluminum oxide crystal is the active part of the laser. Electrons in the ground state of chromium absorb the incident light and become promoted to higher energy states. The short lived excited state relaxes down to a metastable state with a longer lifetime. Laser emission happens when there is relaxation from the metastable state back to the ground state.

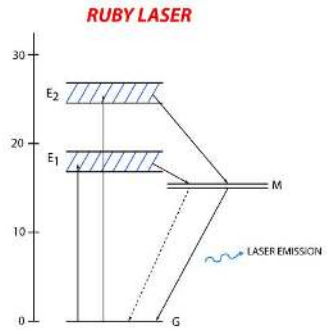


Figure 9. Schematic of Ruby laser

A xenon flash lamp emitting light at wavelengths of 6600Å and 4000Å (matching the energy needed to excite the chromium atoms). In order to create resonance of the incident light in the active material silver platting was put at both ends of the ruby rod. One end was completely covered while the other end was partially covered so lasing light could exit the system.

Nd: YAG Laser

Nd: YAG laser are the most popular type of solid state laser. The laser medium is a crystal of $Y_3Al_5O_{12}$ which are commonly called YAG, an acronym for yttrium aluminum garnet. A simplified energy-level scheme for Nd:YAG is shown in Fig. 9. The λ=1.06 μm

laser transition is the strongest of the $4F_{3/2} \rightarrow 4I_{11/2}$ transitions.

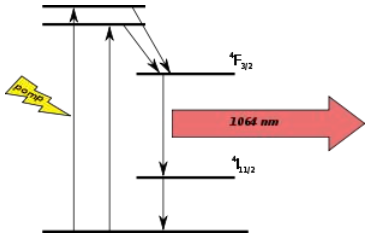


Figure 10. Simplified energy level diagram of the $^4F_{3/2}$---$4I_{11/2}$ laser transition in Nd:YAG showing the four- level nature of the system

The major application of the Nd laser is in various form of material processing: drilling, spot welding, and laser marking. Because they can be focused to a very small spot, the laser are also used in resistor trimming and in circuit mask , memory repair and also in cutting out specialized circuits. Medical applications include many types of surgeries. Many medical applications take advantage of low-loss optical fiber delivery systems that can be inserted into the body to wherever is needed. Nd lasers are also used in military applications such as range finding and target designation. High power pilsed versions are also used for X-ray spectral regions. In addition, Nd lasers are used in scientific lab as good sources for pumping dye laser and other types of lasers.

Semiconductor Laser

The semiconductor laser is another type of solid state laser that uses a semiconducting material like germanium or silicon. When the temperature of the semiconducting material is increased, electrons move from the valence band to the conducting band creating holes in the valence band (**Figure 7**). In between the conducting band and valence band is a region where there are no energy levels, called the band gap. Applying a voltage to the semiconductor causes electrons to move to the conduction band creating a population inversion. Irradiating a semiconductor with incident light matching the energy of the forbidden area causes a large transition from the conduction band to the valence band, increasing and amplifying the incident light.

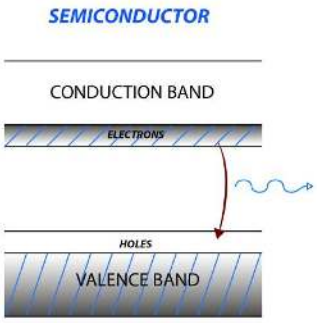


Figure 11. Schematic of semicondecor laser

Gas Lasers

A gas laser contains active material composed of a mixture of gases with similar energy states inside a small gas chamber. Electrical pumping is used to create the population inversion where one gas is excited through collisions with electrons and in turn excites the other gas through collisions.

Helium-Neon Laser

The helium-neon laser was the first gas laser. It consists of a long narrow tube that contains He and Ne gas. Mirrors are placed at both ends of the gas tube to form the resonant cavity with one of the mirrors partially reflecting the incident light. Stimulated emission of the gas mixture is carried out by first exciting the He gas to a higher energy state through electron collision with electrons from the electronic pumping source (electrical pumping). Then the excited He atoms collide with the Ne atoms transferring their energy and exciting them to a higher energy level. The Ne atoms in the higher energy level will then relax to a lower metastable energy state. Lasing occurs when there is relaxation from the metastable state to a lower energy state causing spontaneous emission. The Ne gas then returns to the ground state when it collides with the outer walls of the gas tube (**Figure 8**).

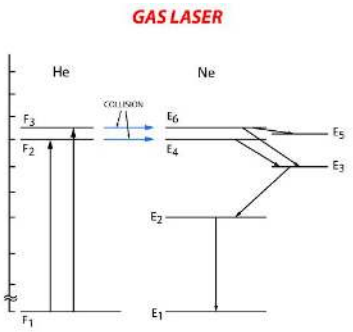


Figure 12. Schematic of gas laser

Carbon Dioxide Laser

The carbon dioxide laser is a gas laser that uses the energy difference between rotational-vibrational energy levels. Within the vibrational levels of CO_2 there are rotational sub-energy levels. A mixture of N_2 and CO_2 gas are placed inside a chamber. The N_2 atoms are excited through an electrical pumping mechanism. The excited atoms then collide with the CO_2 atoms transfer energy. This transfer of energy causes the CO_2 to go into a higher vibrational level. The excited CO_2 molecules then go through spontaneous emission when they are relaxed to lower rotational-vibrational levels increasing the signal of the incident light (**Figure 9**). Carbon dioxide lasers are extremely efficient, around 70%, and powerful compared to other gas lasers making them useful for welding and cutting.

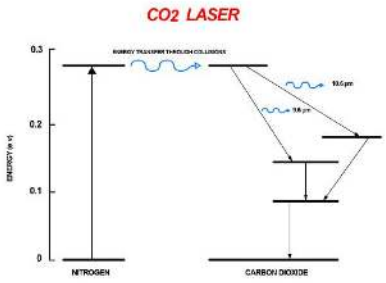


Figure 13. Schematic of carbondioxide laser

Liquid Lasers

Liquid lasers consist of a liquid active material usually composed of an organic dye compound. The most common type of liquid laser uses rhodamine 6G (**Figure 10**) dye mixed with alcohol and is excited by different types of lasers, such as an argon-ion laser or a nitrogen laser. Organic dyes are large compounds that have absorption bands in the UV or visible region with a strong intense fluorescence spectrum. The free π electrons of the dye are excited using an optical pumping source and the transition from the S_1 to the S_0 state creates the lasing light (see Jablonski diagrams). Liquids are generally used because they can easily be tuned to emit a certain wavelength by changing the resonant frequency within the cavity. Wavelengths from the visible to the infrared can be covered. There are many benefits of liquid lasers, some include that they can be cooled in a relative amount of time, they cannot be damaged unlike a solid-laser, and their production is cost-effective. The efficiency of liquid lasers is low because the lifetime of the excited state is relatively short; there are many non-radiative decay processes, and the material degrades over time. Liquid lasers tend to be used only as a pulse laser when tunability is required. Liquid lasers can be used for high-resolution spectroscopy since they are easily tuned over a wide range of wavelengths. They can also be used because they have concentrations which are manageable when dissolved in solids or other liquids.

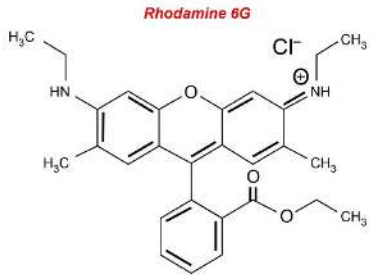


Figure 14. Rhodamine 6G molecule

Chemical Lasers

Chemical lasers are different from other lasers because the population inversion is the direct product of a chemical reaction when energy is released as a result of an exothermic reaction. Usually reactions involve gases where the energy created is used to make vibrationally excited molecules. Light used for lasing is then created from vibrational-rotational relaxation like in the CO_2 gas laser. An example of a chemical laser is the HF gas laser. Inside the gas chamber fluorine and hydrogen react to form an excited HF molecule:

$F + H_2 \rightarrow HF + H$

The excess energy from the reaction allows HF to stay in its excited state. As it relaxes, light is emitted through spontaneous emission. Deuterium can also be used in place of hydrogen. Deterium fluoride is useds for applications that require high-power. For example, MIRACL was built for military research and was known to produce 2.2 megawatts of power. The uniqueness of a chemical laser is that the power required for lasing is produced in the reaction itself.

Laser Applications

The applications of lasers are numerous and cover scientific and technological fields. In general, these applications are a direct consequence of the special characteristics of lasers. Below are a few examples of the laser applications, for a complete list please go to en.Wikipedia.org/wiki/List_of...ons_for_lasers

Lidar

Lidar is short for light detection and ranging which is an optical remote sensing technology can be used for monitoring the environment. A typical lidar system involves a transmitter of laser radiation and a receiver for the detection and analysis of backscattered light. A beam expander is usually used at transmitter to reduce divergence of the laser beam before it propagates into the atmosphere. The receiver includes a wavelength filter, a photo detector, and computers and electronics for data acquisition and analysis.

Lidar system dates back to the 1930, because of the laser, it has become one of the primary tools in atmospheric and environmental research. Other than that, Lidar has been put into various uses. In agriculture, lidar can be used to create topographic map to help farmer to decide appropriate amount of fertilizing to achieve a better crop yield. In Archaeology, lidar can be used to create a geographic information system to help archaeologists to find sites. In transportation, lidar has been used in autonomous cruise control system to prevent road accident and policemen are also using lidar speed gun to enforce the speed limit regulation.

Laser in Material Processing

The beam of a laser is usually a few millimeters in diagram. For most material processing applications, lenses are used to increase the intensity of the beam. The beam from a laser is either plane or spherical. After passing through a lens, the beam should get focused to a point. But in actual practice, diffraction effects have to be taken into consideration, the incoming will focus into a region of radius. If λ is the wavelength of the laser light, a is the radius of the beam, and f is the focal length of the lens, then the radius of the region is

$$b = \frac{\lambda f}{a}$$

If P represents the power of the laser beam, the intensity I, obtained at the focused region would be given by,

$$I = \frac{P}{\pi b^2} = \frac{Pa^2}{\pi\pi\lambda^2 f^2}$$

The high-power (P>100w) laser are widely used in material processing such as welding, drilling, cutting, surface treatment, and alloying. The main advantage of the laser beam can be summarized as follow: (1) The heating produced by the laser is less than that in conventional process. Material distortion is considerably reduced. (2) Possibility of working in inaccessible region. Any region which can be seen can be processed by a laser. (3) The process can be better controlled and easily automatized. However, against all these advantages, the disadvantages are: (1) high cost of the laser system. (2) Reliability and reproducibility problems of the laser system. (3) Safety problems.

Laser in Medicine

In field of medicine, the major use of lasers is for surgery such as laser eye surgery commonly known as LASIK. Besides that, there are also a few diagnosetic applications such as clinical use of flow microfluormeters, Doppler velocimetry to measure the blood velocity, laser fluorescence bronchoscope to detect tumors in their early phase.

For surgery, the laser beams are used instead of a conventional scalpel. The infrared beam from the CO^2 laser is strongly absorbed by water molecules in the tissue. It produces a rapid evaporation of these molecules, consequently cutting the tissue. The main advantage of laser beam surgery can be summarized as follows: (1) High precision. The incision can be made with a high precision particularly when the beam is directed by means of a microscope. (2) Possibility of operating in inaccessible region. Laser surgery can be operated in any region of the body which can be observed by means of an optical system. (4) Limited damage to blood vessel and adjacent tissue. However, the disadvantages are: (1) considerable cost. (2) Smaller velocity of the laser scalpel. (3) Reliability and safety problems associated with the laser procedure.

References

1. Arias, P., Jaeckey, J., Redondo, J., & Ringwald, A. (2010). Optimizing light-shining-through-a-wall experiments for axion and other weakly interacting slim particle searches. *The American Physical Society*, *82*(11), DOI: 10.1103/PhysRevD.82.11501
2. Bertolotti, M. (1999). *The History of the Laser.* Philadelphia, PA: Institute of Physics Publishing.
3. Ferrai, G., et al. (2010). Coherent Addition of Laser Beams in Resonant Passive Optical Cavities. *OpticsInfoBase*, *35(18)*, DOI: 10.1364/OL.35.003105
4. Hecht, J. (1992). *Laser pioneers*. San Diego, CA: Academic Press Limited.
5. Horn, D. T. (1988). *Laser experimenter's handbook*. Blue Ridge Summit, PA: Tab Books Inc.
6. Kenichi, I. (1988). *Fundamentals of Laser Optics.* Yokohama, Japan: Plenum Press.
7. Khanin, Y. (1995). *Principles of Laser Dynamics.* (P. Press, Ed.) New York, NY: Elsevier.
8. Verdeyen, J. (1989). *Laser Electronics.* Englewood Cliffs, NJ: Prentice-Hall, Inc.
9. Milonni,P.,Eberly, J., (2010) *Laser Physics*.Hoboken NJ:John Wiley&Sons, Inc.
10. Silfvast,W.,(1996) *Laser Fundamentals*. New York,NY: the Press Syndicate of the university of Cambridge.
11. Thyagarajan, K. (1981) *Lasers: Theory and Application.* New York, NY: Plenum Press.
12. Hooker,S., Webb,C., (2010) Laser Physics. Oxford, NY:Oxford University Press.
13. Svelto, O. (1982). *Principles of Lasers.* (2nd, Ed.) New York, NY: Plenum Press.
14. Coherent, I. (Ed.). (1980). *Lasers Operation, Equipment, Application and Design.* Palo Alto, CA: McGraw-Hill.

Outside Links

- http://en.Wikipedia.org/wiki/Laser
- en.Wikipedia.org/wiki/List_of_laser_types
- en.Wikipedia.org/wiki/Q_factor
- en.Wikipedia.org/wiki/Mode-locking

Problems

1. Determine the free-space wavelength (λ_0) in Å, and frequency of the resonant cavity for a beam parameter q_1 that is 632,110 and q_2 that is 632,111 in a helium-neon gas laser at 1 atm. The index of refraction n is 1.00, the length of the resonant cavity is 20 cm and the wavelength region of interest is 6328Å.

2. What wavelength of light will be released by the spontaneous emission of Ne gas, where the the energy difference between the excited and ground state is 9.9 x 10^{-19} J.
3. What is the population ratio of the above question at 300K.

Answers

1. For q_1 $\lambda_0 = 6328.0125\angstrom$ Å, q_2 $\lambda_0 = 6328.0025\angstrom$ Å, and v=474 THz for both q values
2. 200 nm
3. N_2/N_1=1.9 x 10^{-105}

Contributors and Attributions

- Greg Allen (UCD), Arpana Vaniya (UCD), Zheng Zhang (UC Davis)

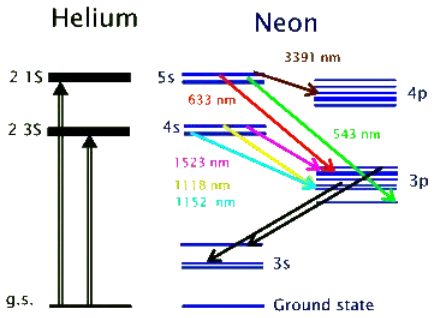
5.5: Laser Fundamentals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Overview of Lasers** is licensed CC BY-NC-SA 4.0.

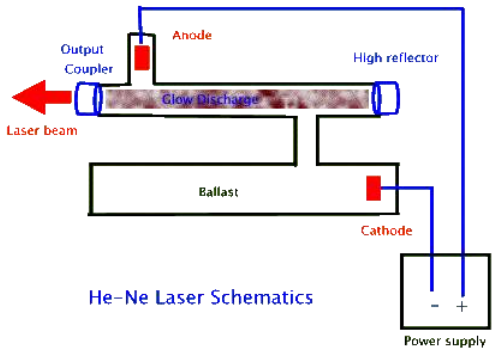
5.6: The Helium-Neon Laser

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 use helium atoms to excite neon atoms. It is the atomic transitions in the neon that produces the laser light. The most commonly used neon transition in these lasers produces red light at 632.8 nm. But these lasers can also produce green and yellow light in the visible as well as UV and IR (Javan's first He-Ne operated in the IR at 1152.3 nm). By using highly reflective mirrors designed for one of these many possible lasing transitions, a given He-Ne's output is made to operate at a single wavelength.

He-Ne lasers typically produce a few to tens of mW (milli-Watt, or 10^{-3} W) of power. They are not sources of high power laser light. Probably one of the most important features of these lasers is that they are highly stable, both in terms of their wavelength (mode stability) and intensity of their output light (low jitter in power level). For these reasons, He-Ne lasers are often used to stabilize other lasers. They are also used in applications, such as holography, where mode stability is important. Until the mid 1990's, He-Ne lasers were the dominant type of lasers produced for low power applications - from range finding to scanning to optical transmission, to laser pointers, etc. Recently, however, other types of lasers, most notably the semiconductor lasers, seem to have won the competition because of reduced costs.

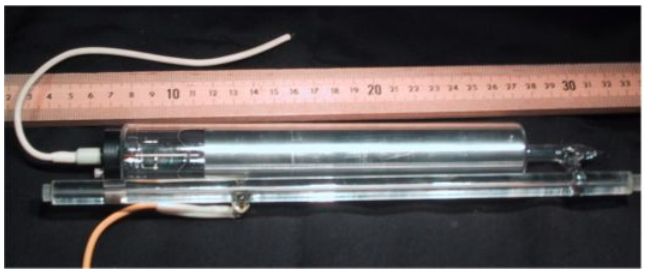


The above energy level diagram shows the two excited states of helium atom, the 2 3S and 2 1S, that get populated as a result of the electromagnetic pumping in the discharge. Both of these states are metastable and do not allow de-excitations via radiative transitions. Instead, the helium atoms give off their energy to neon atoms through collisional excitation. In this way the 4s and 5s levels in neon get populated. These are the two upper lasing levels, each for a separate set of lasing transitions. Radiative decay from the 5s to the 4s levels are forbidden. So, the 4p and 3p levels serve as the lower lasing levels and rapidly decay into the metastable 3s level. In this way population inversion is easily achieved in the He-Ne. The 632.8 nm laser transition, for example, involves the 5s and 3p levels, as shown above.



In most He-Ne lasers the gas, a mixture of 5 parts helium to 1 part neon, is contained in a sealed glass tube with a narrow (2 to 3 mm diameter) bore that is connected to a larger size tube called a ballast, as shown above. Typically the laser's optical cavity

mirrors, the high reflector and the output coupler, form the two sealing caps for the narrow bore tube. High voltage electrodes create a narrow electric discharge along the length of this tube, which then leads to the narrow beam of laser light. The function of the ballast is to maintain the desired gas mixture. Since some of the atoms may get imbedded in the glass and/or the electrodes as they accelerate within the discharge, in the absence of a ballast the tube would not last very long. To further prolong tube lifetime some of these lasers also use "getters", often metals such as titanium, that absorb impurities in the gas.



Above photograph shows a commercial He-Ne tube. The thicker cylinder closest to the meter-stick (shown for scale) is the ballast. The thinner tube houses the resonant cavity where the lasing occurs. Notice the two mirrors that seal the two ends of the bore. For mode stability reasons, these mirrors are concave; they serve as the output coupler and the high reflector.

A typical commercially available He-Ne produces about a few mW of 632.8 nm light with a beam width of a few millimeters at an overall efficiency of near 0.1%. This means that for every 1 Watt of input power from the power supply, 1 mW of laser light is produced. Still, because of their long operating lifetime of 20,000 hours or more and their relatively low manufacturing cost, He-Ne lasers are among the most popular gas lasers.

5.6: The Helium-Neon Laser is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Gas Lasers** is licensed CC BY-NC-SA 4.0.

5.7: High-Resolution Laser Spectroscopy

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{5.7.1}$$

You can see from Equation 5.7.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 5.7.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

5.7: High-Resolution Laser Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

5.8: Photochemical Dynamics

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{5.8.1}$$

You can see from Equation 5.8.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 5.8.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

5.8: Photochemical Dynamics is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

CHAPTER OVERVIEW

6: Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) is a physical phenomenon in which nuclei in a magnetic field absorb and re-emit electromagnetic radiation. This energy is at a specific resonance frequency which depends on the strength of the magnetic field and the magnetic properties of the isotope of the atoms. Many scientific techniques exploit NMR phenomena to study molecular physics, crystals, and non-crystalline materials through nuclear magnetic resonance spectroscopy. NMR is also routinely used in advanced medical imaging techniques, such as in magnetic resonance imaging (MRI).

6.1: Nuclei Have Intrinsic Spin Angular Momenta
6.2: Magnetic Moments Interact with Magnetic Fields
6.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz
6.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded
6.5: Chemical Shifts is Sensitive to Chemical Environment of the Nucleus
6.6: Spin-Spin Coupling Results in Multiplets in NMR Spectra
6.7: Spin-Spin Coupling Between Chemically Equivalent Protons Is Not Observed
6.8: The n+1 Rule Applies Only to First-Order Spectra
6.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method

6: Nuclear Magnetic Resonance Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

6.1: Nuclei Have Intrinsic Spin Angular Momenta

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{6.1.1}$$

You can see from Equation 6.1.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 6.1.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

6.1: Nuclei Have Intrinsic Spin Angular Momenta is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

6.2: Magnetic Moments Interact with Magnetic Fields

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{6.2.1}$$

You can see from Equation 6.2.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 6.2.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

6.2: Magnetic Moments Interact with Magnetic Fields is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

6.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{6.3.1}$$

You can see from Equation 6.3.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 6.3.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

6.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

6.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{6.4.1}$$

You can see from Equation 6.4.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 6.4.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

6.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

6.5: Chemical Shifts is Sensitive to Chemical Environment of the Nucleus

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{6.5.1}$$

You can see from Equation 6.5.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 6.5.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

6.5: Chemical Shifts is Sensitive to Chemical Environment of the Nucleus is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

6.6: Spin-Spin Coupling Results in Multiplets in NMR Spectra

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{6.6.1}$$

You can see from Equation 6.6.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 6.6.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

6.6: Spin-Spin Coupling Results in Multiplets in NMR Spectra is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

6.7: Spin-Spin Coupling Between Chemically Equivalent Protons Is Not Observed

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{6.7.1}$$

You can see from Equation 6.7.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 6.7.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

6.7: Spin-Spin Coupling Between Chemically Equivalent Protons Is Not Observed is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

6.8: The n+1 Rule Applies Only to First-Order Spectra

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{6.8.1}$$

You can see from Equation 6.8.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 6.8.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

6.8: The n+1 Rule Applies Only to First-Order Spectra is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

6.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{6.9.1}$$

You can see from Equation 6.9.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 6.9.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

6.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Uncertainty Principle** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

CHAPTER OVERVIEW

7: Molecular Spectroscopy

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Chem 110A ● Chem 110B ● Chem 110C ● **Agenda ● Homework ● Worksheet Activities**

Molecular spectroscopy is the study of absorption of light by molecules. In the gas phase at low pressures, molecules exhibit absorption in narrow lines which are very characteristic of the molecule as well as the temperature and pressure of its environment.

7.1: The Electromagnetic Spectrum
7.2: Rotational Transitions Accompany Vibrational Transitions
7.3: The Vibration-Rotation Spectrum
7.4: The Pure Rotational Spectrum has Unequal Spacings
7.5: Vibrational Overtones
7.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
7.7: The Franck-Condon Principle
7.8: Rotational Spectra of Polyatomic Molecules
7.9: Normal Modes in Polyatomic Molecules
7.10: Irreducible Representation of Point Groups
7.11: Time-Dependent Perturbation Theory
7.12: The Selection Rule for the Rigid Rotator
7.13: The Harmonic Oscillator Selection Rule
7.14: Group Theory Determines Infrared Activity
7.15: Molecular Spectroscopy (Exercises)

7: Molecular Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.1: The Electromagnetic Spectrum

Electromagnetic radiation—light—is a form of energy whose behavior is described by the properties of both waves and particles. Some properties of electromagnetic radiation, such as its refraction when it passes from one medium to another are explained best by describing light as a wave. Other properties, such as absorption and emission, are better described by treating light as a particle. The exact nature of electromagnetic radiation remains unclear, as it has since the development of quantum mechanics in the first quarter of the 20th century.[1] Nevertheless, the dual models of wave and particle behavior provide a useful description for electromagnetic radiation.

Electromagnetic radiation consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity. In a vacuum electromagnetic radiation travels at the speed of light, c, which is $2.997\ 92 \times 10^8$ 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, 3.00×10^8 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 **7.1.1** shows an example of plane-polarized electromagnetic radiation, consisting of a single oscillating electric field and a single oscillating magnetic field.

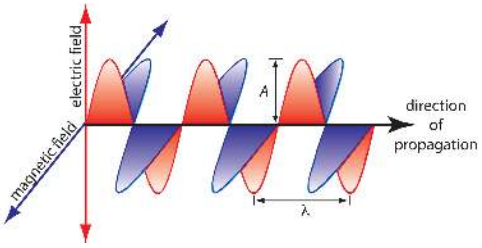


Figure **7.1.1**: Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, A, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation.[2] For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_t = A_e \sin(2\pi\nu t + \phi) \tag{7.1.1}$$

where A_t is the magnitude of the electric field at time t, A_e is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and ϕ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at $t = 0$. The identical equation for the magnetic field is

$$A_t = A_m \sin(2\pi\nu t + \phi) \tag{7.1.2}$$

where A_m is the magnetic field's maximum amplitude.

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 **7.1.1**). For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (1 nm = 10^{-9} m), and for infrared radiation it is given in microns (1 μm = 10^{-6} m). The relationship between wavelength and frequency is

$$\lambda = \frac{c}{\nu} \tag{7.1.3}$$

Another unit useful unit is the **wavenumber**, $\tilde{\nu}$, which is the reciprocal of wavelength

$$\tilde{\nu} = \frac{1}{\lambda} \tag{7.1.4}$$

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

Example 7.1.1

In 1817, Josef Fraunhofer studied the spectrum of solar radiation, observing a continuous spectrum with numerous dark lines. Fraunhofer labeled the most prominent of the dark lines with letters. In 1859, Gustav Kirchhoff showed that the D line in the sun's spectrum was due to the absorption of solar radiation by sodium atoms. The wavelength of the sodium D line is 589 nm. What are the frequency and the wavenumber for this line?

Solution

The frequency and wavenumber of the sodium D line are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{589 \times 10^{-9} \text{ m}} = 5.09 \times 10^{14} \text{ s}^{-1} \tag{7.1.5}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{589 \times 10^{-9} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 1.70 \times 10^4 \text{ cm}^{-1} \tag{7.1.6}$$

Exercise 7.1.1

Another historically important series of spectral lines is the Balmer series of emission lines form hydrogen. One of the lines has a wavelength of 656.3 nm. What are the frequency and the wavenumber for this line?

Click here to review your answer to this exercise.

Regions of the Spectrum

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 7.1.2). The boundaries between the regions of the electromagnetic spectrum are not rigid, and overlap between spectral regions is possible.

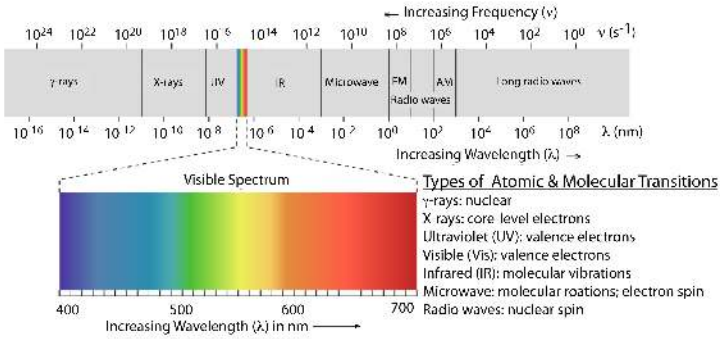


Figure 7.1.2: The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.wikipedia.org).

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 7.1.1 provides a list of several representative examples.

Table* 7.1.1: Examples of Spectroscopic Techniques Involving an Exchange of Energy Between a Photon and the Sample*

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Techniquea
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis	*UV/Vis spectroscopy* *atomic absorption spectroscopy*
	IR	*infrared spectroscopy* raman spectroscopy
	Microwave	microwave spectroscopy
	Radio wave	electron spin resonance spectroscopy nuclear magnetic resonance spectroscopy
emission (thermal excitation)	UV/Vis	*atomic emission spectroscopy*
photoluminescence	X-ray	X-ray fluorescence
	UV/Vis	*fluorescence spectroscopy* *phosphorescence spectroscopy* atomic fluorescence spectroscopy
chemiluminescence	UV/Vis	chemiluminescence spectroscopy

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. The given equation:

$$\Delta E = E_u - E_l = h$$

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 infared range correlates to the rotation of small molecules.
- Frequency falls between 10^{13} - 10^{14} which is in the infared 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.

Absorption and Emission

In absorption spectroscopy a photon is absorbed by an atom or molecule, which undergoes a transition from a lower-energy state to a higher-energy, or excited state (Figure **7.1.3**). The type of transition depends on the photon's energy. The electromagnetic spectrum in Figure **7.1.2**, for example, shows that absorbing a photon of visible light promotes one of the atom's or molecule's valence electrons to a higher-energy level. When an molecule absorbs infrared radiation, on the other hand, one of its chemical bonds experiences a change in vibrational energy.

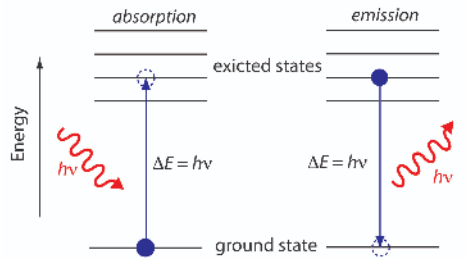


Figure **7.1.3**: Simplified energy diagram showing the absorption and emission of a photon by an atom or a molecule. When a photon of energy hv strikes the atom or molecule, absorption may occur if the difference in energy, ΔE, between the ground state and the excited state is equal to the photon's energy. An atom or molecule in an excited state may emit a photon and return to the ground state. The photon's energy, hv, equals the difference in energy, ΔE, between the two states.

When it absorbs electromagnetic radiation the number of photons passing through a sample decreases. The measurement of this decrease in photons, which we call **absorbance**, is a useful analytical signal. Note that the each of the energy levels in Figure **7.1.3** has a well-defined value because they are quantized. Absorption occurs only when the photon's energy, *h*ν, matches the difference in energy, Δ*E*, between two energy levels. A plot of absorbance as a function of the photon's energy is called an **absorbance spectrum**. Figure **7.1.4**, for example, shows the absorbance spectrum of cranberry juice.

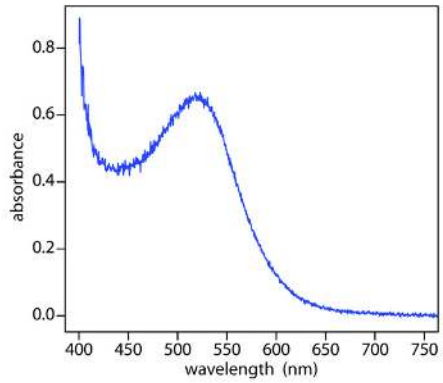


Figure **7.1.3**). As a result, the juice appears red.

When an atom or molecule in an excited state returns to a lower energy state, the excess energy often is released as a photon, a process we call **emission** (Figure **7.1.4**). There are several ways in which an atom or molecule may end up in an excited state, including thermal energy, absorption of a photon, or by a chemical reaction. Emission following the absorption of a photon is also called **photoluminescence**, and that following a chemical reaction is called **chemiluminescence**. A typical emission spectrum is shown in Figure **7.1.5**.

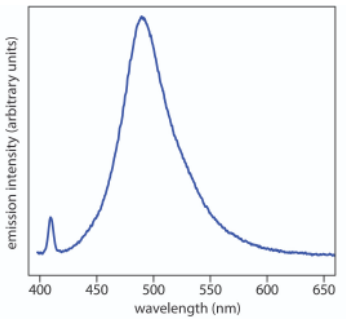


Figure **7.1.5**: Photoluminescence spectrum of the dye coumarin 343, which is incorporated in a reverse micelle suspended in cyclohexanol. The dye's absorbance spectrum (not shown) has a broad peak around 400 nm. The sharp peak at 409 nm is from the laser source used to excite coumarin 343. The broad band centered at approximately 500 nm is the dye's emission band. Because the dye absorbs blue light, a solution of coumarin 343 appears yellow in the absence of photoluminescence. Its photoluminescent emission is blue-green. Source: data from Bridget Gourley, Department of Chemistry & Biochemistry, DePauw University).

Contributors

- Jim Clark (Chemguide.co.uk)
- - Gamini Gunawardena from the OChemPal site (Utah Valley University)
- David Harvey (DePauw University)

7.1: The Electromagnetic Spectrum is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.2: Rotational Transitions Accompany Vibrational Transitions

Each of the modes of vibration of diatomic molecules in the gas phase also contains closely-spaced (1-10 cm^{-1} difference) energy states attributable to rotational transitions that accompany the vibrational transitions. A molecule's rotation can be affected by its vibrational transition because there is a change in bond length, so these rotational transitions are expected to occur. Since vibrational energy states are on the order of 1000 cm^{-1}, the rotational energy states can be superimposed upon the vibrational energy states.

Selection Rules

Rotational and Vibration transitions (also known as rigid rotor and harmonic oscillator) of molecules help us identify how molecules interact with each other, their bond length as mentioned in previous section. In order to know each transitions, we have to consider other terms like wavenumber, force constant, quantum number, etc. There are rotational energy levels associated with all vibrational levels. From this, vibrational transitions can couple with rotational transitions to give **rovibrational spectra**. Rovibrational spectra can be analyzed to determine average bond length.

We treat the molecule's **vibrations** as those of a harmonic oscillator (ignoring anharmonicity). The energy of a vibration is quantized in discrete levels and given by

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$

Where v is the vibrational quantum number and can have integer values 0, 1, 2..., and ν is the frequency of the vibration given by:

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

where k is the force constant and μ is the reduced mass of a diatomic molecule with atom masses m_1 and m_2, given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{7.2.1}$$

We treat the molecule's **rotations** as those of a rigid rotor (ignoring centrifugal distortion from non-rigid rotor aspects). The energy of a rotation is also quantized in discrete levels given by

$$E_r = \frac{h^2}{8\pi^2 I}J(J+1)$$

In which I is the moment of inertia, given by

$$I = \mu r^2$$

where μ is the reduced mass (Equation 7.2.1) and r is the equilibrium bond length.

Experimentally, frequencies or wavenumbers are measured rather than energies, and dividing by h or hc gives more commonly seen term symbols, $F(J)$ using the rotational quantum number J and the rotational constant B in either frequency

$$F(J) = \frac{E_r}{h} = \frac{h}{8\pi^2 I}J(J+1) = BJ(J+1)$$

or wavenumbers

$$\tilde{F}(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 cI}J(J+1) = \tilde{B}J(J+1)$$

> It is important to note in which units one is working since the rotational constant is always represented as B, whether in frequency or wavenumbers.

- **Vibrational Transition Selection Rules**: At room temperature, typically only the lowest energy vibrational state v= 0 is populated, so typically $v_0 = 0$ and $\Delta v = +1$. The full selection rule is technically that $\Delta v = \pm 1$, however here we assume energy

can only go upwards because of the lack of population in the upper vibrational states.

- **Rotational Transition Selection Rules**: At room temperature, states with J≠0 can be populated since they represent the fine structure of vibrational states and have smaller energy differences than successive vibrational levels. Additionally, ΔJ = ±1 since a photon contains one quantum **of angular momentum** and we abide by the principle of **conservation of energy**. This is also the selection rule for rotational transitions.

These two selection rules mean that the transition ΔJ = 0 (i.e. J" = 0 and J' = 0, but $\nu_0 \neq 0$ is forbidden and the pure vibrational transition is not observed in most cases. The rotational selection rule gives rise to an R-branch (when ΔJ = +1) and a P-branch (when ΔJ = -1). Each line of the branch is labeled R(J) or P(J), where J represents the value of the lower state Figure 13.2.1).

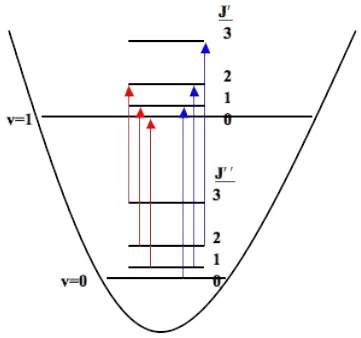


Figure 13.2.1 : Rotation-Vibration Transitions. Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels.

R-branch

When ΔJ = +1, i.e. the rotational quantum number in the ground state is one more than the rotational quantum number in the excited state – R branch (in French, *riche* or rich). To find the energy of a line of the R-branch:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{7.2.2}$$
$$= h\nu_0 + hB\left[(J+1)(J+2) - J(J+1)\right] \tag{7.2.3}$$
$$= h\nu_0 + 2hB(J+1) \tag{7.2.4}$$

P-branch

When ΔJ = -1, i.e. the rotational quantum number in the ground state is one less than the rotational quantum number in the excited state – P branch (in French, *pauvre* or poor). To find the energy of a line of the P-branch:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{7.2.5}$$
$$= h\nu_0 + hB\left[J(J-1) - J(J+1)\right] \tag{7.2.6}$$
$$= h\nu_0 - 2hBJ \tag{7.2.7}$$

Q-branch

When ΔJ = 0, i.e. the rotational quantum number in the ground state is the same as the rotational quantum number in the excited state – Q branch (simple, the letter between P and R). To find the energy of a line of the Q-branch:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \tag{7.2.8}$$
$$= h\nu_0 \tag{7.2.9}$$

The Q-branch can be observed in polyatomic molecules and diatomic molecules with electronic angular momentum in the ground electronic state, e.g. nitric oxide, NO. Most diatomics, such as O_2, have a small moment of inertia and thus very small angular momentum and yield no Q-branch.

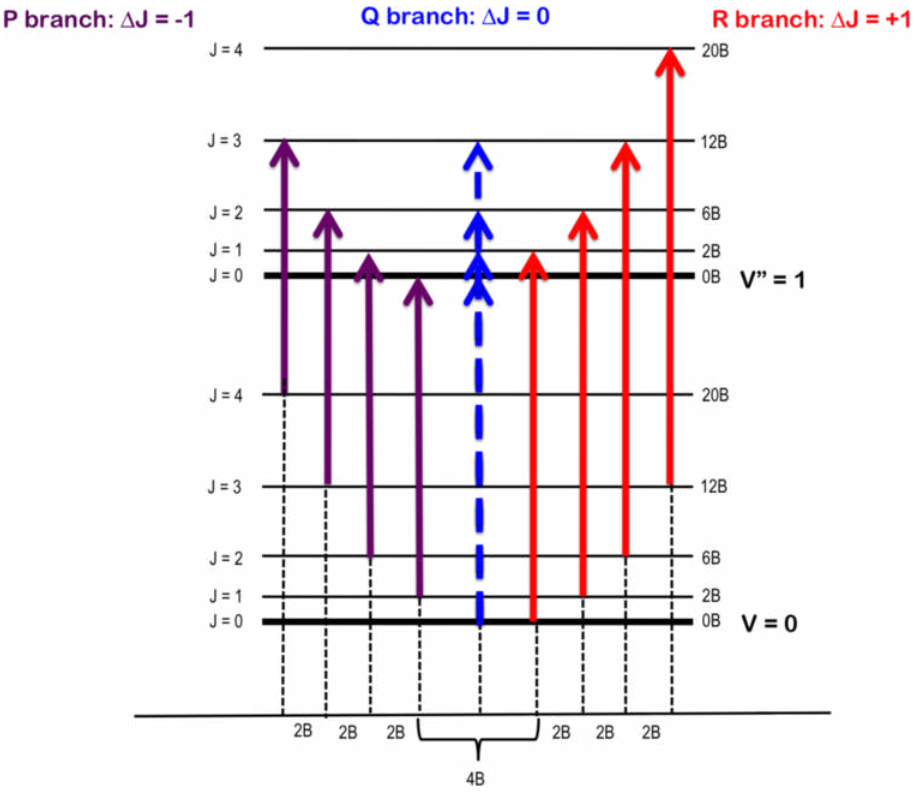


Figure 13.2.3 : Cartoon depiction of rotational energy levels, J, imposed on vibrational energy levels, v. The transitions between levels that would result in the P- and R-branches are depicted in purple and red, respectively, in addition to the theoretical Q-branch line in blue.

As seen in Figure 13.2.2 , the lines of the P-branch (represented by purple arrows) and R-branch (represented by red arrows) are separated by specific multiples of B (i.e, $2B$), thus the bond length can be deduced without the need for pure rotational spectroscopy.

The total nuclear energy of the combined rotation-vibration terms, $S(v, J)$, can be written as the sum of the vibrational energy and the rotational energy

$$S(v, J) = G(v) + F(J)$$

where $G(v)$ represents the energy of the harmonic oscillator, ignoring anharmonic components and $S(J)$ represents the energy of a rigid rotor, ignoring centrifugal distortion.

From this, we can derive

$$S(v, J) = \nu_0 \left(v + \frac{1}{2}\right) + BJ(J+1)$$

The spectrum we expect, based on the conditions described above, consists of lines equidistant in energy from one another, separated by a value of $2B$. The *relative* intensity of the lines is a function of the rotational populations of the ground states, i.e. the intensity is proportional to the number of molecules that have made the transition. The *overall* intensity of the lines depends on the vibrational transition dipole moment.

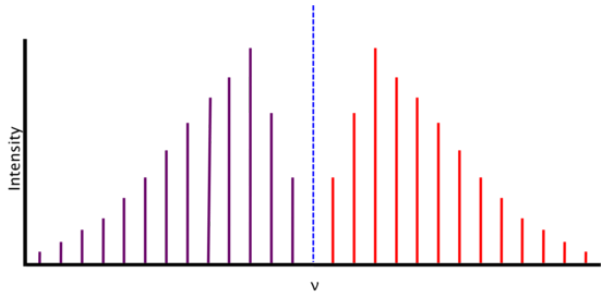


Figure 13.2.3 : A cartoon depiction of an ideal rovibrational spectrum.

In Figure 13.2.2 , between $P(1)$ and $R(0)$ lies the zero gap, where the the first lines of both the P- and R-branch are separated by $4B$, assuming that the rotational constant B is equal for both energy levels. The zero gap is also where we would expect the Q-branch, depicted as the dotted line, if it is allowed.

Advanced Concept: Occupations (Peak Intensities)

The relative intensity of the P- and R-branch lines depends on the thermal distribution of electrons; more specifically, they depend on the population of the lower J state. If we represent the population of the Jth upper level as N_J and the population of the lower state as N_0, we can find the population of the upper state relative to the lower state using the Boltzmann distribution:

$$\frac{N_J}{N_0} = (2J+1)e^{\left(-\frac{E_r}{kT}\right)}$$

(2J+1) gives the degeneracy of the Jth upper level arising from the allowed values of M_J (+J to –J). As J increases, the degeneracy factor increases and the exponential factor decreases until at high J, the exponential factor wins out and N_J/N_0 approaches zero at a certain level, J_{max}. Thus, when

$$\frac{d}{dJ}\left(\frac{N_J}{N_0}\right) = 0$$

by differentiation, we obtain

$$J_{max} = \left(\frac{kT}{2hB}\right)^{\frac{1}{2}} - \frac{1}{2}$$

This is the reason that rovibrational spectral lines increase in energy to a maximum as J increases, then decrease to zero as J continues to increase, as seen in Figure 13.2.2 .

From this relationship, we can also deduce that in heavier molecules, B will decrease because the moment of inertia will increase, and the decrease in the exponential factor is less pronounced. This results in the population distribution shifting to higher values of J. Similarly, as temperature increases, the population distribution will shift towards higher values of J.

7.2: Rotational Transitions Accompany Vibrational Transitions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **13.2: Rotations Accompany Vibrational Transitions** by Joya Cooley is licensed CC BY 4.0.

7.3: The Vibration-Rotation Spectrum

Vibration-rotation interaction describes the inversely proportional relationship of the rotational constant and the vibrational state. The rotational constants decrease as the vibrational states increase, and their interaction influences the frequencies at where the lines of R and P branches occurred. This effect can be observed well on a rotational-vibrational spectrum, and the vibration-rotation relationship also has its own mathematical form.

Introduction

When a rotational transition occurs with a vibrational transition, the vibrational-rotational spectrum of R branch and P branch is observed. 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.

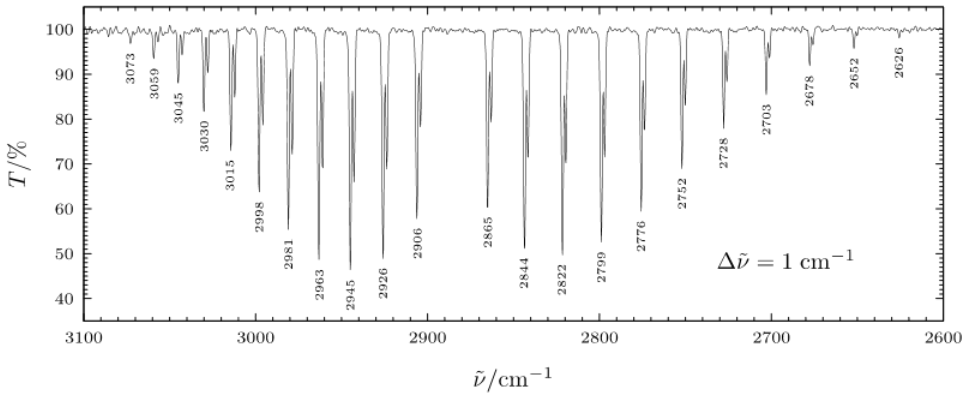


Figure used with permission from Wikipedia.

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.

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.

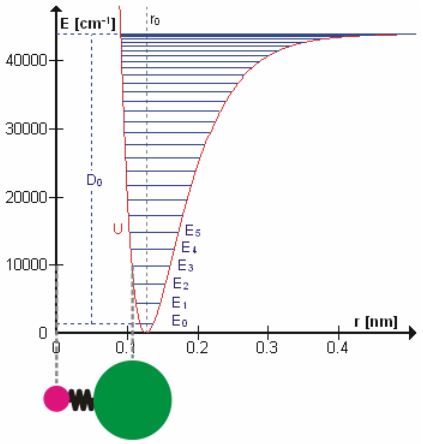


Figure used with permission from Wikipedia.

So far, there are two relationship established above

$$\tilde{B} \propto R_e^2 \tag{7.3.1}$$

(inversely proportional)

and

$$R_e^2 \propto v \tag{7.3.2}$$

(i.e., directly proportional). Therefore,

$$\tilde{B} \propto v \tag{7.3.3}$$

(i.e., 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.

Frequencies of R and P Branches

The energies of the rigid rotator-harmonic oscillator is

$$\tilde{E}_{v,J} = G(v) + F(J) = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}J(J+1) \tag{7.3.4}$$

or in term of $\tilde{B}_v$

$$\tilde{E}_{v,J} = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}_v J(J+1) \tag{7.3.5}$$

Frequencies of vibrational transition from $v = 0 \rightarrow 1$ can be calculated from the equation above as the following:

For R branch, allowed $J = 0, 1, 2, ...$

$$\tilde{\nu}_R(\Delta J = +1) = \tilde{E}_{1,J+1} - \tilde{E}_{0,J} \tag{7.3.6}$$

$$= \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1) \tag{7.3.7}$$

$$= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{7.3.8}$$

For P branch, allowed $J = 1, 2, 3, ...$

$$\tilde{\nu}_P(\Delta J = -1) = \tilde{E}_{1,J-1} - \tilde{E}_{0,J} \tag{7.3.9}$$

$$= \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{7.3.10}$$

According to the vibration-rotation interaction, $\tilde{B}_1 < \tilde{B}_0$ because $R_e^2(v=1) > R_e^2(v=0)$.

Decrease in Spacing of Lines in the R Branch with Increasing J

A closer look at

$$\tilde{\nu}_R = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{7.3.11}$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value for increasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}+$(smaller and smaller value) as J increase. Because the rotational frequencies keep getting smaller, the spacing between lines in R branch decreases as J increases.

Increasing in Spacing of Lines in the P Branch with Decreasing J

Using the same analysis as above,

$$\tilde{\nu}_P = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{7.3.12}$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value even for decreasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}-$(smaller and smaller value) as J decreases. Because the rotational frequencies keep getting larger, the spacing between lines in P branch increase as J decreases.

References

1. McQuarrie, Donald A. Quantum Chemistry. New York: University Science Books, 2007.

Problems

1. Why does the bond length increase as the vibrational state increases? Answer
2. Explain the decrease in line spacing for the R region as J increase. Answer
3. Explain the increase in line spacing for the P region as J decrease. Answer
4. Despite being parts of the same spectrum, why do P region and R region have different line spacing characteristics as discussed above. (Hint: Are their spacing characteristics really different?)
5. Given the relationship

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}(v = \frac{1}{2}) \tag{7.3.13}$$

What type of graph is expected for the graph of $\tilde{B}_v$ vs. v''?

Answers

1. Above
2. Above
3. Above
4. The spacing characteristics of R and P are exactly the same because the spacing always decreases as J increase regardless of the region. Spacing in P increases only because we look at it backwardly as J decreases.
5. The equation should give a linear relationship, so the graph is a straight line with a negative slope.

Contributors

- Dayton Dang

7.3: The Vibration-Rotation Spectrum is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.4: The Pure Rotational Spectrum has Unequal Spacings

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.

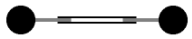


Figure 7.4.1: This animation can serve as an illustration of one of the aspects of the conservation of angular momentum. The animation is a schematic representation of two weights that are connected to each other. The two weights are circling around their common center of mass, the center of mass is stationary. The connection between the weight consists of pistons. When the connecting pistons contract, the rotation rate goes up. When the inward force exerted by the pistons relaxes the weight slide outwards, and the rotation rate goes down. (Public domain; Cleonis).

Centrifugal force,

$$F_c = \mu r_c \omega^2 = L^2/\mu {r_c}^3 \tag{7.4.1}$$

Equating the restoring force to the centrifugal force, one gets

$$k(r_c - r_e) = \frac{L^2}{\mu {r_c}^3} \tag{7.4.2}$$

$$r_c - r_e = \frac{L^2}{k\mu {r_c}^3} \cong \frac{L^2}{k\mu {r_e}^3} \tag{7.4.3}$$

Total energy, on adding kinetic energy, as expressed in Equation 7.4.3 to the potential energy,

$$\frac{1}{2}k(r_c - r_e)^2 \tag{7.4.4}$$

is given by

$$E_r = \frac{L^2}{2\mu {r_c}^2} + \frac{1}{2}k\,(r_c - r_e)^2 \tag{7.4.5}$$

Using $(r_c - r_e) = \Delta r$ and eliminating r_c from equation 7.4.5, one gets

$$E_r = \frac{L^2}{2\mu\ {r_e}^2(1 + \Delta r/r_e)^2} + \frac{1}{2}k\Delta r^2 \tag{7.4.6}$$

$$= \frac{L^2(1 - 2\Delta r/r_e)}{2\mu\ {r_e}^2} + \frac{1}{2}k\Delta r^2 \tag{7.4.7}$$

using

$$(1 + \Delta r/r_e)^{-2} \approx (1 - 2\Delta r/r_e) \tag{7.4.8}$$

$$E_r = \frac{L^2}{2\mu {r_e}^2} - \frac{L^4}{k\mu^2 {r_e}^6} + \frac{1}{2}k\frac{L^4}{k^{2\mu 2}{r_e}^6} \tag{7.4.9}$$

$$= \frac{L^2}{2\mu {r_e}^2} - \frac{1}{2}\frac{L^4}{k\mu^2 {r_e}^6} \tag{7.4.10}$$

$$= \frac{\hbar^2\, J(J+1)}{2\mu {r_e}^2} - \frac{\hbar^4\, J^2(J+1)^2}{2k\mu^2 {r_e}^6} \tag{7.4.11}$$

Use of Equation 7.4.3 and of the relation regarding angular momentum of a rotor

$$L = \hbar\sqrt{J(J+1)} \tag{7.4.12}$$

has been made to obtain relation in Equation 7.4.11, which may be expressed in cm^{-1} as

$$F(J) = \underbrace{\tilde{B}J(J+1)}_{\text{rigid rotator term}} \underbrace{-\tilde{D}J^2(J+1)^2 cm^{-1}}_{\text{centrifugal stretching}} \tag{7.4.13}$$

where

$$\tilde{B} = \frac{\hbar}{4\pi\,\mu\, {r_e}^2 c}\ (\text{in cm}^{-1}) \tag{7.4.14}$$

and

$$\tilde{D} = \frac{\hbar^3}{4\pi k\,\mu^2\, {r_e}^6\, c}\ (\text{in cm}^{-1}) \tag{7.4.15}$$

First term in the Equation 7.4.13 is same as for the rigid rotator; second term is the consequence of the centrifugal stretching. Recall Equation 7.4.3 wherein k is the spring constant that, as we will see in the following section, plays the same role as in the vibrational motion. In other words, centrifugal stretching constant $\tilde{D}$ is not only measures the influence of centrifugal force, but also hints upon the interaction between the rotational and vibrational motions.

Since $\tilde{D}$ is positive, it is clear from Equation 7.4.13 that the energy levels for the non-rigid rotator are slightly lower on energy scale than those of rigid rotator for the corresponding J values; the magnitude of decrease in energy of the non-rigid rotator states increases with J as shown in the Figure 7.4.2.

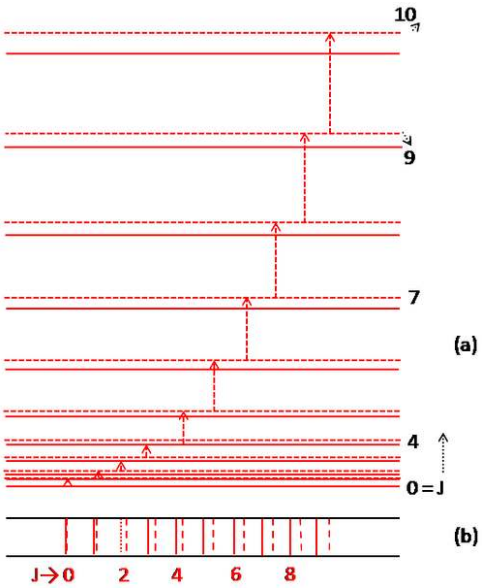


Figure 7.4.2: Energy levels and the transitions of rigid rotator (broken red lines) & of non-rigid rotator (solid red lines). (b) resulting spectra from both the models

Consequently, on applying the selection rule $\Delta J = \pm 1$, rotational spectrum of a non-rigid rotator consists of a series of lines (red lines) wherein separation, unlike the case of spectral series (broken red lines) of a rigid rotator, between the consecutive rotational

lines decreases with increase in J , as shown in the Figure **7.4.2**. It may be noted that value of D is very small compared to B with the result that the influence of D is significant only for very large J values.

For example, for HCl the values are $B \sim 10.4 \ \ cm^{-1}$ and $D \sim 0.0004\, cm^{-1}$. Usually, D is ignored in the calculations. Figure **7.4.2** exaggerates the decrease in energy to visualize its effect. Nevertheless, non-rigid rotator is the model that describes the rotational motion more accurately and hence explains the spectral experimental observations not only in the microwave region but also the rotation-vibration spectra and the rotational structure of the electronic bands discussed in the later sections.

Contributors

- http://202.141.40.218/wiki/index.php...r_Spectroscopy

7.4: The Pure Rotational Spectrum has Unequal Spacings is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.5: Vibrational Overtones

Although the harmonic oscillator proves useful for modeling lower energy levels, like $v = 0, 1$, it fails at higher numbers of v. It not only fails to properly model atomic bonds and dissociations, but also is unable to match spectra showing additional lines that are not accounted for in the harmonic oscillator model.

Anharmonicity

Until this point, we have been using the harmonic oscillator to describe the internuclear potential energy of the vibrational motion. Fundamental vibrational frequencies of a molecule corresponds to a transition of $\Delta v = \pm 1$. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator approximation (Figure **7.5.1**). For example, the parabolic potential of the Harmonic Oscillator approximation means that the vibrations can hold any amount of energy and bonds can stretch to any length, while in real molecules if the atoms are too far apart the bond will dissociate.

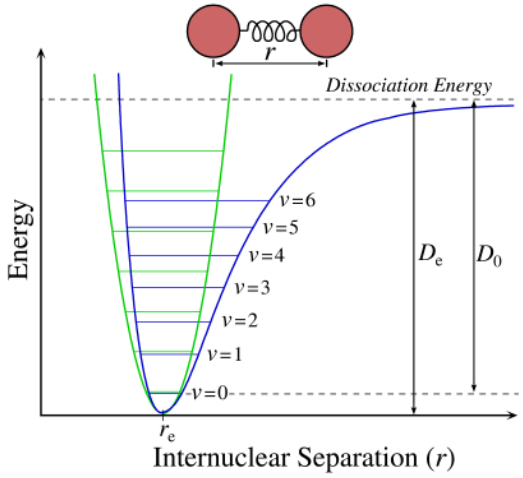


Figure **7.5.1** : Pictured above is the Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left is compression of the bond, towards the right is extension. (CC BY-SA 3.0; Created by Mark Somoza March 26 2006).

As you can see in Figure **7.5.1** , the harmonic oscillator potential well (in green) only roughly fits over the more accurate anharmonic oscillator well (in blue). The blue curve accounts for dissociation at large R values, which the green curve does not even remotely cover. However, this is just one important difference between the harmonic and anharmonic (real) oscillators.

The real potential energy can be expanded in the Taylor series.

$$V(R) = V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}(R-R_e)^4 + \ldots \tag{7.5.1}$$

This expansion was discussed in detail previously. The first term in the expansion is ignored since the derivative of the potential at R_e is zero (i.e., at the bottom of the well). The Harmonic Oscillator approximation only uses the next term, the quadratic term, in the series

$$V_{HO}(R) \approx V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2$$

or in terms of a spring constant, ignoring the absolute energy term($V(R_e)$) and defining r to equal the displacement from equilibrium ($r = R - R_e$), then we get the "standard" harmonic oscillator potential:

$$V_{HO}(R) = \frac{1}{2}kr^2$$

Alternatively, the expansion in Equation 7.5.1 can be shortened to the cubic term

$$V(x) = \frac{1}{2}kr^2 + \frac{1}{6}\gamma r^3 \tag{7.5.2}$$

where

- $V(x_0) = 0$, and $r = R - R_0$.
- k is the harmonic force constant, and
- γ is the first (i.e., cubic) *anharmonic* term

It is important to note that this approximation is only good for R near R_0.

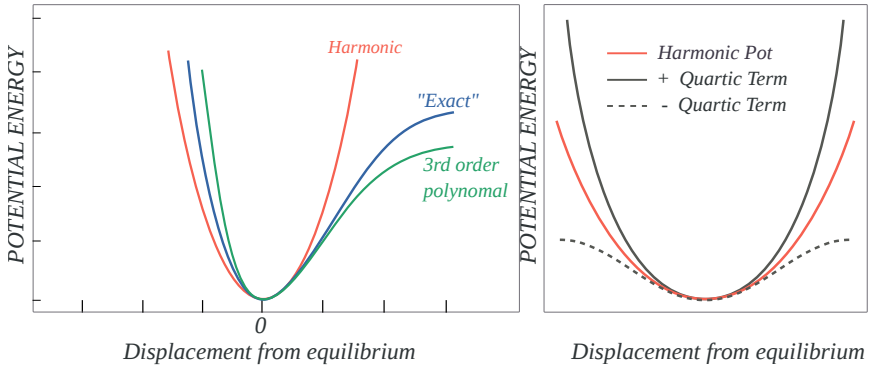


Figure 7.5.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

The harmonic oscillator approximation gives by the following energies:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right)$$

When the cubic term in the expansion (Equation 7.5.2) is included, and the Schrödinger equation is solved using perturbation theory this gives:

$$E_v = \tilde{\nu}\left(v + \frac{1}{2}\right) - \tilde{\chi_e}\tilde{\nu}\left(v + \frac{1}{2}\right)^2$$

where $\tilde{\chi_e}$ is the **anharmonicity constant**. It is much smaller than 1, which makes sense because the terms in the Taylor series approach zero. This is why, although E_v technically includes all of the Taylor series, we only concern ourselves with the first and second terms. The rest are so small and barely add to the total and thus can be ignored. To get a more accurate approximation, more terms can be included, but otherwise, can be ignored. Almost all diatomics have experimentally determined $\frac{d^2V}{dx^2}$ for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 have had terms up to $n < 10$ determined of Equation 7.5.1.

Overtones

The Harmonic Oscillator approximation predicts that there will be only one line in the spectrum of a diatomic molecule, while experimental data shows there is in fact one dominant line--**the fundamental**--and other weaker lines. How can we account for these extra lines?

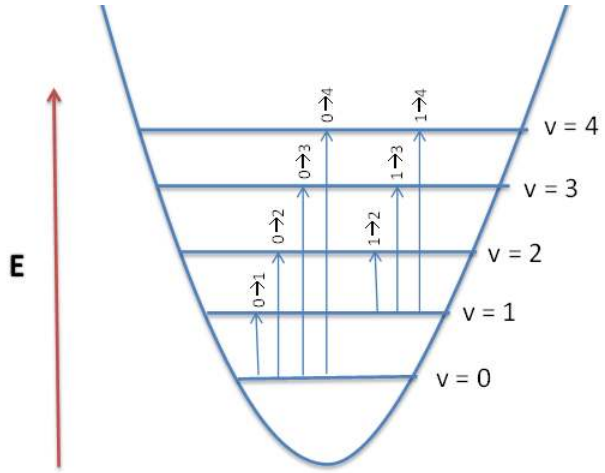


Figure **7.5.3** : A diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potential energy for the harmonic (quadratic) oscillator. The transition $0 \rightarrow 1$ is the fundamental, transitions $0 \rightarrow n$ (n>1) are called overtones, and transitions $1 \rightarrow n$ (n > 1) are called hot transitions (hot bands).

Any resonant frequency above the fundamental frequency is referred to as an *overtone*. In the IR spectrum, overtone bands are multiples of the fundamental absorption frequency. As you can recall, the energy levels in the Harmonic Oscillator approximation are evenly spaced apart. Energy is proportional to the frequency absorbed, which in turn is proportional to the wavenumber, the first overtone that appears in the spectrum will be twice the wavenumber of the fundamental. That is, first overtone $v = 0 \rightarrow 2$ is (approximately) twice the energy of the fundamental, $v = 0 \rightarrow 1$.

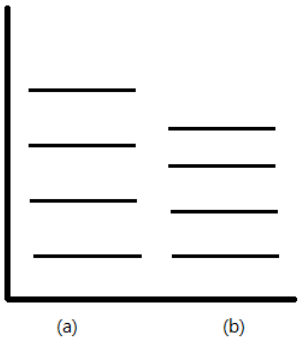


Figure **7.5.4** : An exaggerated view of the energy levels. (a) would be the harmonic oscillator, with the evenly spaced out energy levels. (b) would be the anharmonic, with the energy levels compressing until they converge.

The levels are not equally spaced, like in the harmonic oscillator, but decrease as v increases, until it ultimately converges, as implied by Figure **7.5.4**. Also as a result of anharmonicity, the $\Delta v = \pm 1$ selection rule is no longer valid and v can be any number. This leads to the observation of higher order transitions, or **overtones**, which result from the transition of the ground state to higher energy levels.

Anharmonic Oscillator Selection Rules

For the anharmonic oscillator, the selection rule is $\Delta V = \text{any number}$. That is, there are no selection rules (for state to state transitions)

Overtones occur when a vibrational mode is excited from $v = 0$ to $v = 2$ (the first overtone) or $v = 0$ to $v = 3$ (the second overtone). The fundamental transitions, $v = \pm 1$, are the most commonly occurring, and the probability of overtones rapidly decreases as $\Delta v > \pm 1$ gets bigger. Based on the harmonic oscillator approximation, the energy of the overtone transition will be approximately v times the fundamental associated with that particular transition. The anharmonic oscillator calculations show that the overtones are usually less than a multiple of the fundamental frequency. Overtones are generally not detected in larger molecules.

This is demonstrated with the vibrations of the diatomic **HCl** in the gas phase:

Table **7.5.1** : HCl vibrational spectrum.

Transition	$\tilde{\nu}_{obs}$ [cm^{-1}]	$\tilde{\nu}_{obs}$ Harmonic [cm^{-1}]	$\tilde{\nu}_{obs}$ Anharmonic [cm^{-1}]
$0 \rightarrow 1$ (fundamental)	2885.9	2885.9	2,885.3
$0 \rightarrow 2$ (first overtone)	5668.0	5771.8	5,665.0
$0 \rightarrow 3$ (second overtone)	8347.0	8657.7	8,339.0
$0 \rightarrow 4$ (third overtone)	10 923.1	11 543.6	10,907.4
$0 \rightarrow 5$ (fourth overtone)	13 396.5	14 429.5	13,370

We can see from Table **7.5.1** that the anharmonic frequencies correspond much better with the observed frequencies, especially as the vibrational levels increase. Because the energy levels and overtones are closer together in the anharmonic model, they are also more easily reached. This means that there is a higher chance of that level possibly being occupied, meaning it can show up as additional, albeit weaker intensity lines (the weaker intensity indicates a smaller probability of the transition occuring).

? Exercise 13.5.1

HCl has a fundamental band at 2885.9 cm^{-1} and an overtone at 5668.1 cm^{-1} Calculate $\tilde{\nu}$ and $\tilde{\chi_e}$.

? Exercise 13.5.2

Write out the Taylor series, and comment on the trend in the increasing terms. Using a test number x, please add terms 3, 4, and 5, then compare this to term 2. How do they compare? We have seen that the anharmonic terms increase the accuracy of our oscillator approximation. Why don't we care so much about terms past the second?

References

1. Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry; Part B: Application in Coordination, Organometallic, and Bioinorganic Chemistry, 5th Edition (Nakamoto, Kazuo)
2. Lyle McAfee Journal of Chemical Education 2000 77 (9), 1122
3. Stuart, Barbara. *Infrared Spectroscopy: Fundamentals and Applications*. Wiley, 2004. Print.

7.5: Vibrational Overtones is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **13.5: Vibrational Overtones** by Alexandra Holmes, Hannah Toru Shay is licensed CC BY 4.0.

7.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information

Molecules can also undergo changes in electronic transitions during microwave and infrared absorptions. The energy level differences are usually high enough that it falls into the visible to UV range; in fact, most emissions in this range can be attributed to electronic transitions.

Electron Transitions are not Purely Electronic

We have thus far studied *rovibrational transitions*--that is, transitions involving both the vibrational and rotational states. Similarly, electronic transitions tend to accompany both rotational and vibrational transitions. These are often portrayed as an electronic potential energy cure with the vibrational level drawn on each curve. Additionally, each vibrational level has a set of rotational levels associated with it.

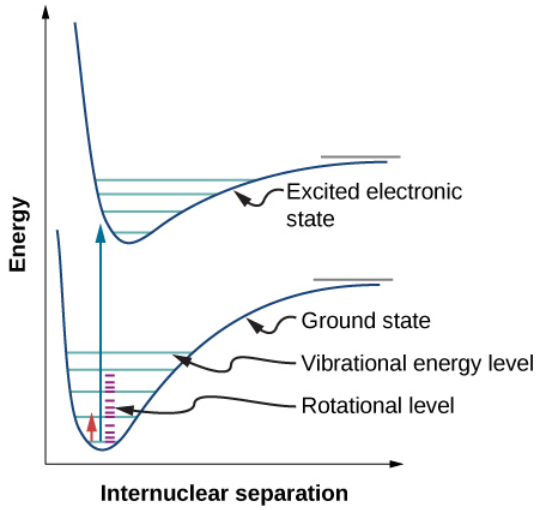


Figure **7.6.1** : Three types of energy levels in a diatomic molecule: electronic, vibrational, and rotational. If the vibrational quantum number (n) changes by one unit, then the rotational quantum number (l) changes by one unit. (CC BY 3.0; OpenStax).

Recall that in the Born-Oppenheimer approximation, nuclear kinetic energies can be ignored (e.g., fixed) to solve for electronic wavefunctions and energies, which are much faster than rotation or vibration. As such, it is important to note that unlike rovibrational transitions, electronic transitions aren't dependent on rotational or transitional terms and are assumed to be separate. Therefore, when using an anharmonic oscillator-nonrigid rotator approximation (and excluding translation energy), the total energy of a diatomic is:

$$\tilde{E}_{total} = \tilde{\nu}_{el} + G(v) + F(J) \tag{7.6.1}$$

where $\tilde{\nu}_{el}$ is the electronic transition energy change in wavenumbers, $G(n)$ is the vibrational energy with energy level v (assuming anharmonic oscillator), and $F(J)$ is the rotational energy, assuming a nonrigid rotor. Equation 7.6.1 can be expanded accordingly:

$$\tilde{E}_{total} = \underbrace{\tilde{\nu}_{el}}_{\text{electronic}} + \underbrace{\tilde{\nu}_e\left(v+\frac{1}{2}\right) - \tilde{\chi}_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^2}_{\text{vibrational}} + \underbrace{\tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2}_{\text{rotational}} \tag{7.6.2}$$

Notice that both the vibration constant ($\tilde{\nu}_e$) and anharmonic constant ($\tilde{\chi}_e$) are electronic state dependent (and hence the rotational constants would be too, but are ignored here). Since rotational energies tend to be so small compared to electronic, their effects are minimal and are typically ignored when we do calculations and are referred to as *vibronic* transitions.

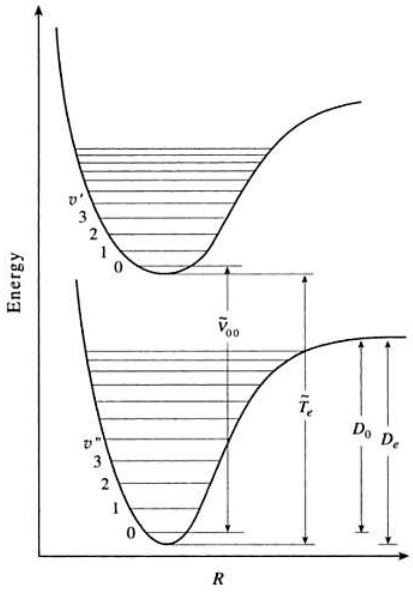


Figure **7.6.2** : As you can see, electronic transitions involve two energy potential wells! The vibrational levels are included, but rotational levels are excluded.

The eigenstate-to-eigenstate transitions (e.g., $\mathbf{1 \rightarrow 2}$) possible are numerous and have absorption lines at

$$\tilde{\nu}_{obs} = \tilde{E}_2 - \tilde{E}_1 \tag{7.6.3}$$

and for simplification, we refer to constants associated with these states as $|'\rangle$ and $|''\rangle$, respectively. So Equation 7.6.3 is

$$\tilde{\nu}_{obs} = E''\tilde{(v'')} - E'\tilde{(v')}$$

Also important to note that typically vibronic transitions are usually the result of the vibrational $v' = 0$ vibratonal state. Within this assumption and excluding the rotational contributions (due to their low energies), Equation 7.6.2 can be used with Equation 7.6.3 to get

$$\tilde{\nu}_{obs} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right) + \tilde{\nu}'_e v'' - \tilde{\chi}'_e\tilde{\nu}'_e v''(v''+1) \tag{7.6.4}$$

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 7.6.4 is then

$$\tilde{\nu}_{00} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right)$$

This is the lowest energy possible to observe in an electronic transition although it may be of low intensity as discussed in the following section.

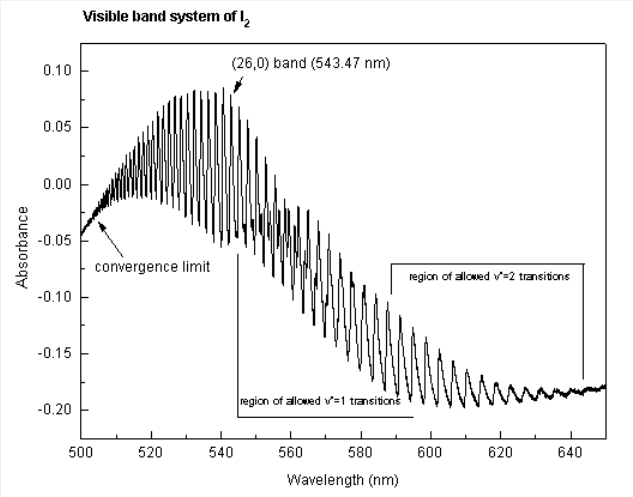
Iodine

The absorption spectrum of iodine yields information about the excited state well rather than the ground state well (notice that equation 7.6.4 depends primarily on excited state parameters). In this experiment you will characterize the excited state well by extracting values for the following excited state parameters.

Recall that as v' increases, the vibrational energy spacing decreases. At the upper edge of the well, the vibrational energy spacing decreases to 0, which means that the energies form a continuum rather than being quantized. It is at this limit that **bond dissociation occurs**. The energy required to dissociate the bond is actually D'_o rather than D'_e because the molecule cannot have less than **the zero point energy**.

The vibrational-electronic spectrum of I_2 in the region from 500-650 nm displays a large number of well-defined bands which, for the most part, correspond to v'<-- 0 transitions connecting the v" = 0 vibrational level of the ground electronic state (denoted as $X^1\Sigma^+$) to many different vibrational levels v' of the excited $B^3\Pi$ electronic state. Under the conditions of this

experiment (i.e., low resolution), the rotational lines within each band are not resolved. However, the peaks may be identified as R-branch band heads (1). For a molecule as heavy as I_2, the position of each band head is within a few tenths of one cm^{-1} of the band origin (2), and for the purposes of this experiment, the distinction between the two may be ignored. The general features of the absorption spectrum are shown below:



Each small bump, or peak, such as the (26,0) band labelled on the spectrum, corresponds to a transition between two vibrational levels and is called a *band*. Each band is comprised of several hundred *lines*, each of which involves different upper and lower rotational quantum numbers; as mentioned, these lines are not resolved in the present experiment. The region of maximum absorption in each band is caused by many of these lines falling together; it is called the *band head*. The set of all of these bands is referred to as the *visible band system* of I_2.

If the sample is hot, then excited vibrational levels of the ground state may be populated, and these also will absorb light. The *hot bands* arising from absorption from v"=1 and v"=2 are shown very approximately on the absorption spectrum above.

At a point called the *convergence limit*, the spacing between bands decreases to zero. Beyond this convergence limit, the spectrum is continuous because the excited state of the I_2 molecule is not bound. One of the purposes of this experiment is to identify this convergence limit accurately.

7.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information** is licensed CC BY-SA 4.0.

7.7: The Franck-Condon Principle

Learning Objectives

- To explain the vibrational fine structure in electronic spectroscopy for bound excited states in terms of the Franck-Condon approximation
- To calculate the vibrational progressions (Franck-Condon factors) in a single displaced harmonic oscillator vibronic system.

The **Franck-Condon Principle** describes the intensities of vibronic transitions, or the absorption or emission of a photon. It states that when a molecule is undergoing an electronic transition, such as ionization, the nuclear configuration of the molecule experiences no significant change. This is due in fact that nuclei are much more massive than electrons and the electronic transition takes place faster than the nuclei can respond. When the nucleus realigns itself with the new electronic configuration, the theory states that it must undergo a vibration.

If we picture the vertical transition from ground to excited electronic state as occurring from a vibrational wavefunction that gives a probability distribution of finding the nuclei in a give region of space we can determine the probability of a given vibrational level from the overlap integral $S_{v',v}$ which gives the overlap of the vibrational wavefunction in the ground and excited state. The v' quantum numbers refer to the ground state and the v quantum numbers refer to the excited state. The transition probability can be separated into electronic and nuclear parts using the Condon approximation.

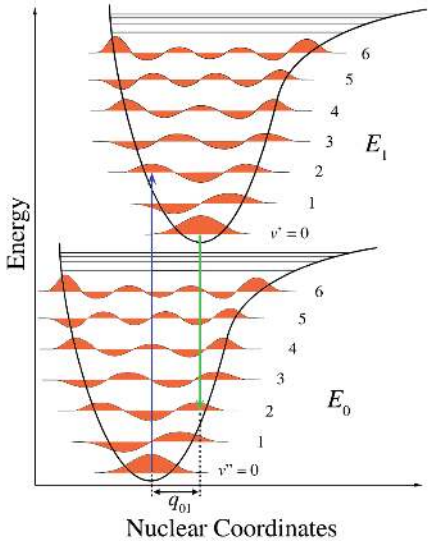


Figure 7.7.1 : Franck–Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v' = 2$. (CC-SA-BY-3.0; Samoza).

In Figure 7.7.1 , the nuclear axis shows a consequence of the internuclear separation and the vibronic transition is indicated by the blue and green vertical arrows. This figure demonstrates three things:

1. An absorption leads to a higher energy state,
2. fluorescence leads to a lower energy state, and
3. the shift in nuclear coordinates between the ground and excited state is indicative of a new equilibrium position for nuclear interaction potential. The fact that the fluorescence arrow is shorter than the absorption indicates that it has less energy, or that its wavelength is longer.

The Classical Condon approximation

Condon approximation is the assumption that the electronic transition occurs on a time scale short compared to nuclear motion so that the transition probability can be calculated at a fixed nuclear position.

This change in vibration is maintained during a state termed the **rapid electronic excitation**. The resulting Coulombic forces produce an equilibrium as shown in the figure for the nuclei termed a turning point. The turning point can be mapped by drawing a vertical line from the minimum of the lower curve to the intersection of the higher electronic state. This procedure is termed a **vertical transition** and was discussed before in the context of photoelectron spectroscopy (another electronic spectroscoy).

The Franck-Condon Principle explains the relative intensities of vibronic transitions by relating the probability of a vibrational transition to the overlap of the vibrational wavefunctions. It states that the probability of a vibrational transition occurring is weighted by the Franck-Condon overlap integral:

$$\begin{aligned} _{i\rightarrow f} &= \left|\langle \psi^*_{final} \left|\mu\right| \psi_{initial}\rangle\right|^2 \\ &= \left|\int \psi^*_{final} \mu \psi_{initial} d\tau\right|^2 \end{aligned}$$

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 **7.7.1**).

The Quantum Franck-Condon Principle

The Franck-Condon Principle has both a Classical and Quantum application. Classically, the Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

The Franck-Condon principle is based on the Born-Oppenheimer approximation, which allows separation of the electronic q and nuclear Q wavefunctions given the total wavefunction.

$$|\psi_{total}(Q,q) = |\psi_{nuc}(Q)\rangle \psi_{el}(Q;q)\rangle$$

Since the transition operator, $\hat{\mu}(q)$, is dependent only on the electronic component, the nuclear components can be separated from the transition moment integral that dictates the probability of the transition occurring:

$$\langle \psi^*_{total,f} \left|\hat{\mu}\right| \psi_{total,i}\rangle = \langle \psi^*_{nuc,f} \left|\langle \psi^*_{el,f} \left|\mu\right| \psi_{el,i}\rangle\right| \psi_{nuc,i}\rangle \quad (7.7.1)$$

$$= \underbrace{\langle \psi^*_{nuc,f} | \psi_{nuc,i}\rangle}_{\text{nuclear overlap}} \langle \psi^*_{el,f} \left|\mu\right| \psi_{el,i}\rangle \quad (7.7.2)$$

If the nuclear overlap integral is zero for this transition, then the transition will not be observed, irrespective of the magnitude of the electronic factor.

S_{00} Transition Evaluated within Harmonic Oscillator Model

The nuclear overlap for the zero-zero transition S_{00} can be calculated quite simply using the definition of the Gaussian form of the harmonic oscillator wavefunctions.

The zero-point wavefunction in the ground electronic state is

$$|\psi(R)\rangle = \left|\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2}\right\rangle$$

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

$$S_{00} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} e^{-\alpha(R-Q_e)^2/2} dR \tag{7.7.3}$$

The exponent in Equation 7.7.3 can be expanded as

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(2R^2 - RR_e - 2RQ_e + R_e^2 + Q_e^2)/2} dR \tag{7.7.4}$$

and we use

$$(R_e + Q_e)^2 = R_e^2 + Q_e^2 + 2R_eQ_e$$

and

$$(R_e - Q_e)^2 = R_e^2 + Q_e^2 - 2R_eQ_e$$

to substitute and complete the square inside the integral. We can express

$$R_e^2 + Q_e^2 = \frac{1}{2}[(R_e + Q_e)^2 + (R_e - Q_e)^2].$$

Thus, the integral in Equation 7.7.4 is

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \int_{-\infty}^{\infty} e^{-\alpha\{R - 1/2(R_e + Q_e)\}^2} dR$$

The integral is a **Gaussian integral**. You can show that if we let $z = \sqrt{\alpha}\{R - 1/2(R_e + Q_e)\}$ then $dz = \sqrt{\alpha} dR$ and the integral becomes

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \frac{1}{\sqrt{\alpha}} \int_{-\infty}^{\infty} e^{z^2} dz \tag{7.7.5}$$

this integral has been solved already, from a table of integrals, Equation 7.7.5 becomes

$$S_{00} = e^{-\alpha(R_e - Q_e)^2/4}$$

We would follow the same procedure to calculate that overlap of the zeroth level vibration in the ground to the first excited vibrational level of the excited state: S_{01}.

S_{01} Transition Evaluated within Harmonic Oscillator Model

To calculate the overlap of zeroth ground state level ($v = 0$) with the first excited state level ($v' = 1$) we use the Hermite polynomial $H_1(x) = 2x$ for describing the excited state wavefunction (see here for a review on harmonic oscillator wavefunctions). Here $x = \sqrt{\alpha}(R - Q_e)$.

$$S_{01} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle \tag{7.7.6}$$

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 7.7.6) is then

$$S_{01} = \frac{1}{\sqrt{2}} \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} \sqrt{\alpha} 2(R - Q_e) e^{-\alpha(R-Q_e)^2/2}$$

and

$$S_{01} = \sqrt{\frac{2\alpha^2}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \int_{-\infty}^{\infty} (R - Q_e) e^{-\alpha\{R - 1/2(R_e + Q_e)^2\}}$$

The same substitutions can be made as above so that the integral can be written as (not shown and to be demonstrated in a homework exercises) and the final result is

$$S_{01} = \sqrt{\frac{\alpha^2}{2}} (R_e - Q_e) e^{-\alpha(R_e - Q_e)^2/4}$$

We could continue and calculate that overlap of the zeroth level in the ground state with all the higher light vibrational levels: S_{02}, S_{03}, etc. Each term corresponds to a transition with a different energy since the vibrational levels have different energies. The absorption band then has the appearance of a progression (a Franck-Condon progression) of transitions between different levels each with its own probability.

Franck-Condon Progressions

To understand the significance of the above formula for the FC factor, let us examine a ground and excited state potential energy surface at $T = 0$ Kelvin. Shown below are two states separated by 8,000 cm^{-1} in energy. This is energy separation between the bottoms of their potential wells, but also between the respective zero-point energy levels. Let us assume that the wavenumber of the vibrational mode is 1,000 cm^{-1} and that the bond length is increased due to the fact that an electron is removed from a bonding orbital and placed in an anti-bonding orbital upon electronic excitation.

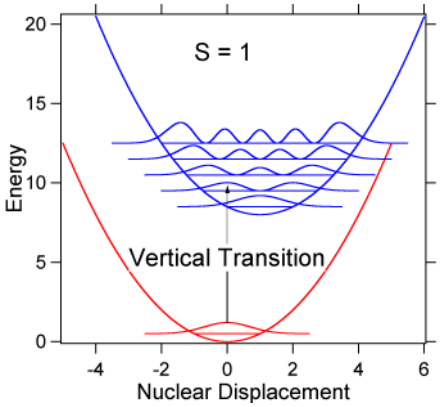


Figure **7.7.2** : Wavefunctions transitions for a harmonic oscillator model system with moderate displacement (S=1).

According to the above model for the Franck-Condon factor we would generate a "stick" spectrum (Figure **7.7.3**) where each vibrational transition is infinitely narrow and transition can only occur when $E = h\nu$ exactly. For example, the potential energy surfaces were given for S = 1 and the transition probability at each level is given by the sticks (black) in the figure below.

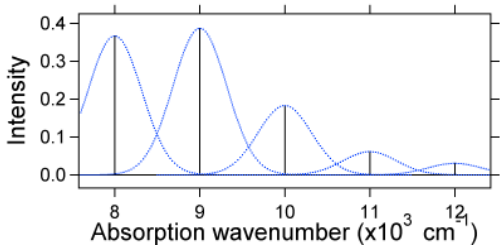


Figure **7.7.3** : Stick spectrum, dressed with Gaussians, for the moderate displacement (S=1) harmonic oscillator system from Figure **7.7.2** .

The dotted Gaussians that surround each stick give a more realistic picture of what the absorption spectrum should look like. In this first place each energy level (stick) will be given some width by the fact that the state has a finite lifetime. Such broadening is called homogeneous broadening since it affects all of the molecules in the ensemble in a similar fashion. There is also broadening due to small differences in the environment of each molecule. This type of broadening is called inhomogeneous broadening. Regardless of origin the model above was created using a Gaussian broadening

The nuclear displacement between the ground and excited state determines the shape of the absorption spectrum. Let us examine both a smaller and a large excited state displacement. If $S = ½$ and the potential energy surfaces in this case are:

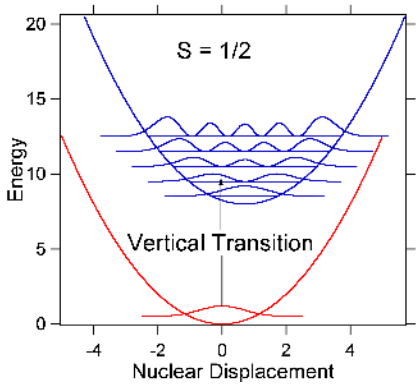


Figure **7.7.4** : Wavefunctions transitions for a harmonic oscillator model system with small displacement (S=1/2).

For this case the "stick" spectrum has the appearance in Figure **7.7.5**

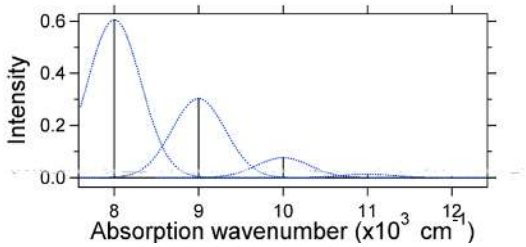


Figure **7.7.5** : Stick spectrum, dressed with Gaussians, for the small displacement (S=1/2) harmonic oscillator system from Figure **7.7.4**.

Note that the zero-zero or $S_{0,0}$ vibrational transition is much large in the case where the displacement is small.

> As a general rule of thumb the S constant gives the ratio of the intensity of the $v = 2$ transition to the $v = 1$ transition. In this case since $S = 0.5$, the $v = 2$ transition is 0.5 the intensity of $v = 1$ transition.

As an example of a larger displacement the disposition of the potential energy surfaces for S = 2 is shown below.

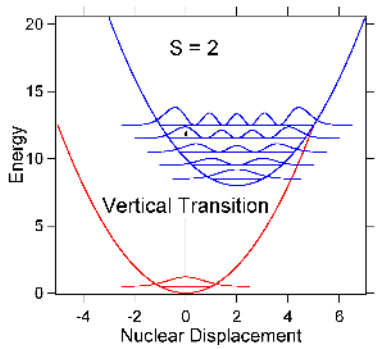


Figure **7.7.6** : Wavefunctions transitions for a harmonic oscillator model system with strong displacement (S=2).

The larger displacement results in decreased overlap of the ground state level with the v = 0 level of the excited state. The maximum intensity will be achieved in higher vibrational levels as shown in the stick spectrum.

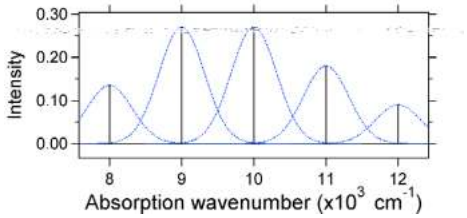


Figure **7.7.7** : Stick spectrum, dressed with Gaussians, for the large displacement (S=2) harmonic oscillator system from Figure **7.7.6**.

The absorption spectra plotted below all have the same integrated intensity, however their shapes are altered because of the differing extent of displacement of the excited state potential energy surface.

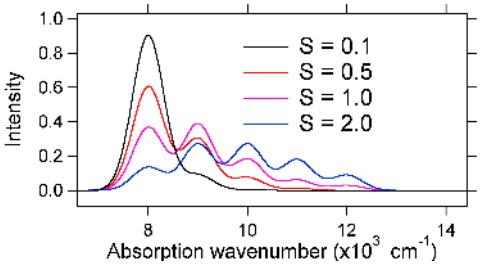


Figure **7.7.8** : Stick spectra, dressed with Gaussians, for the small to large displacements in harmonic oscillator system described above.

So the nature of the relative vibronic band intensities can tell us whether there is a displacement of the equilibrium nuclear coordinate that accompanied a transition. When will there be an increase in bond length (i.e., $Q_e > R_e$)? This occurs when an electron is promoted from a bonding molecular orbital to a non-bonding or anti-bonding molecular orbitals (i.e., when the bond order is less in the excited state than the ground state).

- Non-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ non-bonding molecular orbital

In short, when the bond order is lower in the excited state than in the ground state, then $Q_e > R_e$; an increase in bond length will occur when this happens.

References

1. J.M. Luis, D.M. Bishop, B. Kirtman. *A different approach for calculating Franck–Condon factors including anharmonicity.* J. Chem. Phys., 120 (2004), pp. 813–822.
2. Atkins, Peter and Julio de Paula. Physical Chemistry for the Life Sciences. 2006. New York, NY: W.H. Freeman and Company. p. 563-564
3. Franck-Condon Principle. 1996, 68, 2243. IUPAC Compendium of Chemical Terminology 2nd Edition (1997). www.iupac.org/goldbook/F02510.pdf
4. E.Rabinowitch and Govindjee. Light Absorption and Fate of Excitation of Energy. 1969. Franck-Condon Principle. http://www.life.uiuc.edu/govindjee/b...em494/Abs.html

7.7: The Franck-Condon Principle is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **13.7: The Franck-Condon Principle** by Matthew Ziering, Stefan Franzen is licensed CC BY-NC-SA 4.0.

7.8: Rotational Spectra of Polyatomic Molecules

Quick Review of Diatomic Rotation

As discussed previously, the Schrödinger equation for the angular motion of a rigid (i.e., having fixed bond length R) diatomic molecule is

$$\frac{\hbar^2}{2\mu}\left[\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{R^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\psi\rangle = E|\psi\rangle$$

or

$$\frac{L^2}{2\mu R^2}|\psi\rangle = E|\psi\rangle$$

The Hamiltonian in this problem contains only the kinetic energy of rotation; no potential energy is present because the molecule is undergoing unhindered "free rotation". The angles θ and φ describe the orientation of the diatomic molecule's axis relative to a laboratory-fixed coordinate system, and μ is the reduced mass of the diatomic molecule

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The eigenvalues corresponding to each eigenfunction are straightforward to find because H_{rot} is proportional to the L^2 operator whose eigenvalues have already been determined. The resultant rotational energies are given as:

$$E_J = \frac{\hbar^2 J(J+1)}{2\mu R^2} = BJ(J+1) \tag{7.8.1}$$

and are independent of M. B is the rotational constant. Thus each energy level is labeled by J and is $2J+1$-fold degenerate (because M ranges from $-J$ to J). The rotational energy in Equation 7.8.1 can be expressed in terms of the moment of inertia I

$$I = \sum_i m_i R_i^2 \tag{7.8.2}$$

where m_i is the mass of the ith atom and R is its distance from the center of mass of the molecule. This moment of inertia replaces μR^2 in the denominator of Equation 7.8.1:

$$E_J = \frac{\hbar^2 J(J+1)}{2I} = BJ(J+1) \tag{7.8.3}$$

Rotation of Polyatomic Molecules

In contrast to diatomic molecules (Equation 7.8.2), the rotational motions of polyatomic molecules in three dimensions are characterized by multiple moments of inertia. typically reflected in an 3×3 inertia tensor. It is common in rigid body mechanics to express in these moments of inertia in *lab-based Cartesian coordinates* via a notation that explicitly identifies the x, y, and z axes such as I_{xx} and I_{xy}, for the components of the inertia tensor.

$$I = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{xx} & I_{xy} & I_{zz} \end{bmatrix} \tag{7.8.4}$$

The components of this tensor can be assembled into a matrix given by

$$I_{xx} = \sum_{k=1}^{N} m_k(y_k^2 + z_k^2)$$

$$I_{yy} = \sum_{k=1}^{N} m_k(x_k^2 + z_k^2)$$

$$I_{zz} = \sum_{k=1}^{N} m_k (x_k^2 + y_k^2)$$

$$I_{yx} = I_{xy} = -\sum_{k=1}^{N} m_k x_k y_k$$

$$I_{zx} = I_{xz} = -\sum_{k=1}^{N} m_k x_k z_k$$

$$I_{zy} = I_{yz} = -\sum_{k=1}^{N} m_k y_k z_k.$$

The rotational motions of polyatomic molecules are characterized by moments of inertia that are defined in a *molecule based coordinates* with axes that are labeled a, b, and c. Measured in the body frame the inertia matrix (Equation 7.8.4) is a constant real symmetric matrix, which can be decomposed into a diagonal matrix, given by

$$I = \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix}$$

These labels are assigned so that I_c is the **largest** principal moment of inertia with an order of the three moments set as

$$I_a < I_b < I_c$$

The rotational kinetic energy operator for a rigid non-linear polyatomic molecule is then expressed as

$$H_{rot} = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} \tag{7.8.5}$$

The components of the quantum mechanical angular momentum operators along the three principal axes are:

$$J_a = -i\hbar \cos\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \sin\chi \frac{\partial}{\partial\theta} \tag{7.8.6}$$

$$J_b = i\hbar \sin\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \cos\chi \frac{\partial}{\partial\theta} \tag{7.8.7}$$

$$J_c = -\frac{ih\partial}{\partial\chi} \tag{7.8.8}$$

The angles θ, φ, and χ are the **Euler angles** needed to specify the orientation of the rigid molecule relative to a laboratory-fixed coordinate system. The corresponding square of the total angular momentum operator J^2 can be obtained as

$$J^2 = J_a^2 + J_b^2 + J_c^2 \tag{7.8.9}$$

$$= -\frac{\partial^2}{\partial\theta^2} - \cot\theta \frac{\partial}{\partial\theta} - \left(\frac{1}{\sin\theta} \right) \left(\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial\chi^2} - 2\cos\theta \frac{\partial^2}{\partial\varphi\partial\chi} \right) \tag{7.8.10}$$

and the component along the lab-fixed Z axis is

$$J_Z = -ih \frac{\partial}{\partial\varphi}.$$

Spherical Tops

When the three principal moment of inertia values are identical, the molecule is termed a spherical top. In this case, the total rotational energy Equation 7.8.5 can be expressed in terms of the total angular momentum operator J^2

$$H_{rot} = \frac{J^2}{2I}$$

As a result, the eigenfunctions of H_{rot} are those of J^2 (and J_a as well as J_Z both of which commute with J_2 and with one another; J_Z is the component of J along the lab-fixed Z-axis and commutes with J_a because

$$J_Z = -ih\frac{\partial}{\partial\varphi}$$

and

$$J_a = -ih\frac{\partial}{\partial\chi}$$

act on different angles. The energies associated with such eigenfunctions are

$$E(J,K,M) = \frac{\hbar^2 J(J+1)}{2I^2}$$

for all K (i.e., J a quantum numbers) ranging from -J to J in unit steps and for all M (i.e., J Z quantum numbers) ranging from -J to J. Each energy level is therefore $(2J+1)^2$ degenarate because there are $2J+1$ possible K values and $2J+1$ possible M values for each J. The eigenfunctions of J^2, J_Z and J_a, $|J,M,K>$ are given in terms of the set of rotation matrices $D_{J,M,K}$:

$$|J,M,K\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D^*_{J,M,K}(\theta,\varphi,\chi)$$

which obey

$$J^2\left|J,M,K\right\rangle = \hbar^2 J(J+1)\left|J,M,K\right\rangle$$

$$J_a\left|J,M,K\right\rangle = \hbar K\left|J,M,K\right\rangle$$

$$J_Z\left|J,M,K\right\rangle = \hbar M\left|J,M,K\right\rangle$$

Symmetric Tops

Symmetrical tops are molecules with two rotational axes that have the same inertia and one unique rotational axis with a different inertia. Symmetrical tops can be divided into two categories based on the relationship between the inertia of the unique axis and the inertia of the two axes with equivalent inertia. If the unique rotational axis has a greater inertia than the degenerate axes the molecule is called an **oblate symmetrical top** (Figure 13.8.1). If the unique rotational axis has a lower inertia than the degenerate axes the molecule is called a **prolate symmetrical top**. For simplification think of these two categories as either frisbees for oblate tops or footballs for prolate tops.

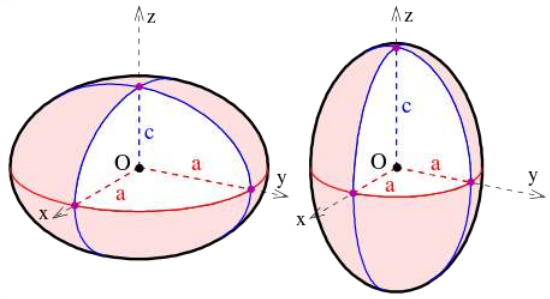


Figure 13.8.1 : The assignment of semi-axes on a spheroid. It is oblate if $c < a$ (left) and prolate if $c > a$ (right). (CC BY-SA 4.0; Ag2gaeh)

Again, the rotational kinetic energy, which is the full rotational Hamiltonian, can be written in terms of the total rotational angular momentum operator J^2 and the component of angular momentum along the axis with the unique principal moment of inertia.

For prolate tops, Equation 7.8.5 becomes

$$H_{rot} = \frac{J^2}{2I} + J_a^2\left(\frac{1}{2I_a} - \frac{1}{2I}\right)$$

For oblate tops, Equation 7.8.5 becomes

$$H_{rot} = \frac{J^2}{2I} + J_c^2\left(\frac{1}{2I_c} - \frac{1}{2I}\right)$$

As a result, the eigenfunctions of H_{rot} are those of J^2 and J_a or J_c (and of J_Z), and the corresponding energy levels.

The energies for prolate tops are

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I^2} + h^2 K^2 \left(\frac{1}{2I_a} - \frac{1}{2I}\right)$$

and the energies for oblate tops are

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I2} + h^2 K^2 \left(\frac{1}{2I_c} - \frac{1}{2I}\right)$$

again for K and M (i.e., J_a or J_c and J_Z quantum numbers, respectively) ranging from $-J$ to J in unit steps. Since the energy now depends on K, these levels are only $2J+1$ degenerate due to the $2J+1$ different M values that arise for each J value. The eigenfunctions $|J,M,K>$ are the same rotation matrix functions as arise for the spherical-top case.

Asymmetric Tops

The rotational eigenfunctions and energy levels of a molecule for which all three principal moments of inertia are distinct (a **asymmetric top**) can not easily be expressed in terms of the angular momentum eigenstates and the J, M, and K quantum numbers. However, given the three principal moments of inertia I_a, I_b, and I_c, a matrix representation of each of the three contributions to the general rotational Hamiltonian in Equation 7.8.5 can be formed within a basis set of the $\{|J,M,K\rangle\}$ rotation matrix functions. This matrix will **not** be diagonal because the $|J,M,K\rangle$ functions are not eigenfunctions of the asymmetric top H_{rot}. However, the matrix can be formed in this basis and subsequently brought to diagonal form by finding its eigenvectors {C n, J,M,K } and its eigenvalues $\{E_n\}$. The vector coefficients express the asymmetric top eigenstates as

$$\psi_n(\theta,\varphi,\chi) = \sum_{J,M,K} C_{n,J,M,K} |J,M,K\rangle$$

Because the total angular momentum J^2 still commutes with H_{rot}, each such eigenstate will contain only one J-value, and hence Ψ_n can also be labeled by a J quantum number:

$$\psi_{n,J}(\theta,\varphi,\chi) = \sum_{M,K} C_{n,J,M,K} |J,M,K\rangle$$

To form the only non-zero matrix elements of H_{rot} within the $|J,M,K\rangle$ basis, one can use the following properties of the rotation-matrix functions:

$$\langle j,\rangle = \langle j,\rangle = 1/2 < j,\rangle = h2[J(J+1) - K2],$$

$$\langle j,\rangle = h^2 K^2$$

$$\langle j\rangle = -\langle j\rangle = h^2[J(J+1) - K(K\pm1)]1/2[J(J+1) - (K\pm1)(K\pm2)]1/2\langle j\rangle = 0$$

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.

7.8: Rotational Spectra of Polyatomic Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **13.8: Rotational Spectra of Polyatomic Molecules** by Jack Simons is licensed CC BY-NC-SA 4.0.

7.9: Normal Modes in Polyatomic Molecules

Normal modes are used to describe the different vibrational motions in molecules. Each mode can be characterized by a different type of motion and each mode has a certain symmetry associated with it. Group theory is a useful tool in order to determine what symmetries the normal modes contain and predict if these modes are IR and/or Raman active. Consequently, IR and Raman spectroscopy is often used for vibrational spectra.

Degrees of Freedom

In general, a normal mode is an independent motion of atoms in a molecule that occurs without causing movement to any of the other modes. Normal modes, as implied by their name, are orthogonal to each other. In order to discuss the quantum-mechanical equations that govern molecular vibrations it is convenient to convert Cartesian coordinates into so called normal coordinates. Vibrations in polyatomic molecules are represented by these normal coordinates.

A molecule can have three types of degrees of freedom and a total of 3N degrees of freedom, where N equals the number of atoms in the molecule. These degrees of freedom can be broken down into three categories.

- **Translational**: These are the simplest of the degrees of freedom. These entail the movement of the entire molecule's center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.
- **Rotational**: These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational**: These are any other types of movement not assigned to rotational or translational movement and thus there are 3N – 6 degrees of vibrational freedom for a nonlinear molecule and 3N – 5 for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Table 13.9.1 : Overview of degrees of freedom

	Total Degrees of Freedom	Translational degrees of freedom	Rotational degrees of freedom	Vibrational degrees of freedom
Nonlinear Molecules	3N	3	3	3N **-6**
Linear Molecules	3N	3	2	3N - 5

Each of these degrees of freedom is able to store energy. However, In the case of rotational and vibrational degrees of freedom, energy can only be stored in discrete amounts. This is due to the quantized break down of energy levels in a molecule described by quantum mechanics. In the case of rotations the energy stored is dependent on the rotational inertia of the gas along with the corresponding quantum number describing the energy level.

✔ Example 13.9.1 : Ethane vs. Carbon Dioxide

Ethane, C_2H_6 has eight atoms ($N = 8$) and is a nonlinear molecule so of the $3N = 24$ degrees of freedom, three are translational and three are rotational. The remaining 18 degrees of freedom are internal (vibrational). This is consistent with:

$$3N - 6 = 3(8) - 6 = 18$$

Carbon Dioxide, CO_2 has three atoms ($N = 3$ and is a linear molecule so of the $3N = 9$ degrees of freedom, three are translational and two are rotational. The remaining 4 degrees of freedom are vibrational. This is consistent with:

$$3N - 5 = 3(3) - 5 = 4$$

The normal modes of vibration are: asymmetric, symmetric, wagging, twisting, scissoring, and rocking for polyatomic molecules.

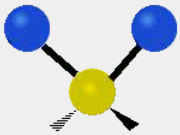
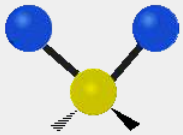
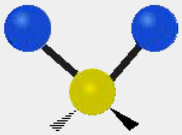
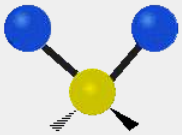
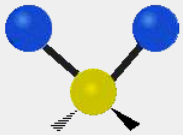
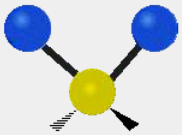
Symmetricical Stretching	Asymmetrical Stretching	Wagging
		
Twisting	**Scissoring**	**Rocking**
		

Figure 13.9.1 : *Six types of Vibrational Modes. Taken from publisher en.Wikipedia.org/wiki/Infrared_spectroscopy with permission from copyright holder.*

Normal Modes

If there is no external field present, the energy of a molecule does not depend on its orientation in space (its translational degrees of freedom) nor its center of mass (its rotational degrees of freedom). The potential energy of the molecule is therefore made up of its vibrational degrees of freedom only of $3N-6$ (or $3N-5$ for linear molecules). The difference in potential energy is given by:

$$\Delta V = V(q_1, q_2, q_3, ..., q_n) - V(0, 0, 0, ..., 0) \tag{7.9.1}$$

$$= \frac{1}{2}\sum_{i=1}^{N_{vib}}\sum_{j=1}^{N_{vib}}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right) q_i q_j \tag{7.9.2}$$

$$= \frac{1}{2}\sum_{i=1}^{N_{vib}}\sum_{j=1}^{N_{vib}} f_{ij} q_i q_j \tag{7.9.3}$$

where q represents the equilibrium displacement and N_{vib} the number of vibrational degrees of freedom.

For simplicity, the *anharmonic* terms are neglected in this equation (i.e., higher order terms are ignore). A theorem of classical mechanics states that the cross terms can be eliminated from the above equation (the details of the theorem are very complex and will not be discussed in detail). By using matrix algebra a new set of coordinates $\{Q_j\}$ can be found such that

$$\Delta V = \frac{1}{2}\sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{7.9.4}$$

Note that there are no cross terms in this new expression. These new coordinates are called **normal coordinates** or **normal modes**. With these new normal coordinates in hand, the Hamiltonian operator for vibrations can be written as follows:

$$\hat{H}_{vib} = -\sum_{j=1}^{N_{vib}} \frac{\hbar^2}{2\mu_i}\frac{d^2}{dQ_j^2} + \frac{1}{2}\sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{7.9.5}$$

The total wavefunction is a product of the individual wavefunctions and the energy is the sum of independent energies. This leads to:

$$\hat{H}_{vib} = \sum_{j=1}^{N_{vib}} \hat{H}_{vib,j} = \sum_{j=1}^{N_{vib}} \left(\frac{-\hbar^2}{2\mu_j}\frac{d^2}{dQ_i^2} + \frac{1}{2}\sum_{j=1}^{N_{vib}} F_j Q_j^2\right) \tag{7.9.6}$$

and the wavefunction is then

$$\psi_{vib} = Q_1, Q_2, Q_3 \ldots, Q_{vib}$$
$$= \psi_{vib,1}(Q_1)\psi_{vib,2}(Q_2)\psi_{vib,3}(Q_3), \ldots, \psi_{vib,N_{vib}}(Q_{N_{vib}})$$

and the total vibrational energy of the molecule is

$$E_{vib} = \sum_{j=1}^{N_{vib}} h\nu_j \left(v_j + \frac{1}{2}\right) \tag{7.9.7}$$

where $v_j = 0, 1, 2, 3 \ldots$.

The consequence of the result stated in the above equations is that each vibrational mode can be treated as a harmonic oscillator approximation. There are N_{vib} harmonic oscillators corresponding to the total number of vibrational modes present in the molecule.

Pictorial description of normal coordinates using CO

The normal coordinate q is used to follow the path of a normal mode of vibration. As shown in Figure 13.9.2 the displacement of the C atom, denoted by $\Delta r_o(\mathrm{C})$, and the displacement of the O atom, denoted by $\Delta r_o(\mathrm{O})$, occur at the same frequency. The displacement of atoms is measured from the equilibrium distance in ground vibrational state, r_o.

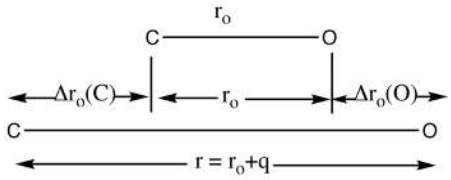


Figure 13.9.2 : The Normal coordinate for CO is equation to $\Delta r(C) + \Delta r(O)$

7.9: Normal Modes in Polyatomic Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **13.9: Normal Modes in Polyatomic Molecules** by Kristin Kowolik is licensed CC BY-NC-SA 4.0.

7.10: Irreducible Representation of Point Groups

There exists an important fact about normal coordinates. Each of these coordinates belongs to an irreducible representation of the point the molecule under investigation. Vibrational wavefunctions associated with vibrational energy levels share this property as well. The normal coordinates and the vibration wavefunction can be categorized further according to the point group they belong to. From the character table predictions can be made for which symmetries can exist. The irreducible representation offers insight into the IR and/or Raman activity of the molecule in question.

Symmetry of normal modes

It is important to realize that every normal mode has a certain type of symmetry associated with it. Identifying the point group of the molecule is therefore an important step. With this in mind it is not surprising that every normal mode forms a basis set for an irreducible representation of the point group the molecule belongs to. For a molecule such as water, having a structure of $\mathbf{XY_2}$, 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:

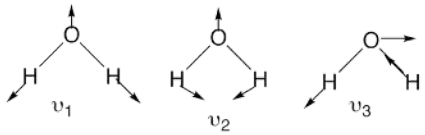


Figure 13.10.1 : Three normal modes of water

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:

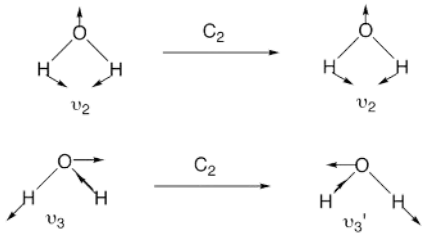


Figure 13.10.2 : Symmetry operations on the symmetric and asymmetric stretches of water

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).

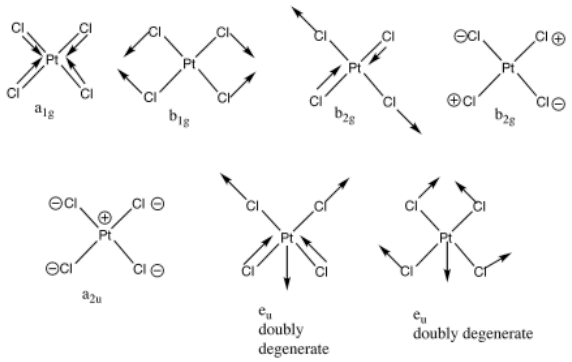


Figure 13.10.3 : A_{1g}, b_{1g} and e_u are stretching vibrations whereas b_{2g}, a_{2u}, b_{2u} and e_u are bending vibrations.

7.10: Irreducible Representation of Point Groups is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **13.10: Irreducible Representation of Point Groups** by Kristin Kowolik is licensed CC BY-NC-SA 4.0.

7.11: Time-Dependent Perturbation Theory

In time-independent perturbation theory the perturbation Hamiltonian is static (i.e., possesses no time dependence). Time-independent perturbation theory was presented by Erwin Schrödinger in a 1926 paper,shortly after he produced his theories in wave mechanics. Time-dependent perturbation theory, developed by Paul Dirac, studies the effect of a time-dependent perturbation $V(t)$ applied to a time-independent Hamiltonian H_0. Since the perturbed Hamiltonian is time-dependent, so are its energy levels and eigenstates. Thus, the goals of time-dependent perturbation theory are slightly different from time-independent perturbation theory, where one may be interested in the following quantities:

- The time-dependent expectation value of some observable A, for a given initial state.
- The time-dependent amplitudes of those quantum states that are energy eigenkets (eigenvectors) in the unperturbed system.

The first quantity is important because it gives rise to the classical result of a measurement performed on a macroscopic number of copies of the perturbed system. The second quantity looks at the time-dependent probability of occupation for each eigenstate. This is particularly useful in laser physics, where one is interested in the populations of different atomic states in a gas when a time-dependent electric field is applied. We will briefly examine the method behind Dirac's formulation of time-dependent perturbation theory. Choose an energy basis $|n\rangle$ for the unperturbed system. (We drop the (0) superscripts for the eigenstates, because it is not useful to speak of energy levels and eigenstates for the perturbed system.)

If the unperturbed system is in eigenstate $|j\rangle$ at time $t = 0$, its state at subsequent times varies only by a phase (this is the Schrödinger picture, where state vectors evolve in time and operators are constant)

$$|j(t)\rangle = e^{-iE_j t/\hbar}\big|j\big\rangle$$

Now, introduce a time-dependent perturbing Hamiltonian $H_1(t)$. The Hamiltonian of the perturbed system is

$$H = H_0 + H_1(t)$$

Let $|\psi(t)\rangle$ denote the quantum state of the perturbed system at time t and obeys the time-dependent Schrödinger equation,

$$H\left|\psi(t)\right\rangle = i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle$$

The quantum state at each instant can be expressed as a linear combination of the complete eigenbasis of $|n\rangle$:

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}\Big|n\big\rangle$$

where the $c_n(t)$ coefficients are to be determined complex functions of t which we will refer to as **amplitudes**

We have explicitly extracted the exponential phase factors $\exp(-iE_n t/\hbar)$ on the right hand side. This is only a matter of convention, and may be done without loss of generality. The reason we go to this trouble is that when the system starts in the state $|j\rangle$ and no perturbation is present, the amplitudes have the convenient property that, for all t, $c_j(t) = 1$ and $c_n(t) = 0$ if $n \neq j$.

The square of the absolute amplitude $c_n(t)$ is the probability that the system is in state n at time t, since

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}\Big|n\big\rangle$$

Plugging into the Schrödinger equation and using the fact that $\partial/\partial t$ acts by a chain rule, one obtains

$$\sum_n \left(i\hbar\frac{\partial c_n}{\partial t} - c_n(t)V(t)\right)e^{-iE_n t/\hbar}|n\rangle = 0\ .$$

By resolving the identity in front of V, this can be reduced to a set of partial differential equations for the amplitudes,

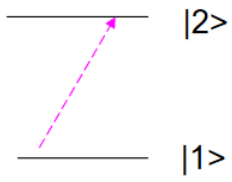
$$\frac{\partial c_n}{\partial t} = \frac{-i}{\hbar}\sum_k \langle n\,|H_1(t)|\,k\rangle\, c_k(t)\, e^{-i(E_k - E_n)t/\hbar}\ .$$

The matrix elements of H_1 play a similar role as in time-independent perturbation theory, being proportional to the rate at which amplitudes are shifted between states. Note, however, that the direction of the shift is modified by the exponential phase factor. Over times much longer than the energy difference $E_k - E_n$, the phase winds around 0 several times. If the time-dependence of H_1 is sufficiently slow, this may cause the state amplitudes to oscillate (e.g., such oscillations are useful for managing radiative transitions in a laser).

Two-Level System

Consider the two level system (i.e. $n = 1, 2$)

$$|\psi\rangle = \sum_{n=1,2} c_n(t) \Big| n \rangle_o$$



Solution of time-dependent perturbation for two level system:

$$i\hbar \frac{\partial c_1(t)}{\partial t} = c_1(t) H_{11}(t) + c_2 e^{-i\omega_o t} H_{12}(t)$$

$$i\hbar \frac{\partial c_2(t)}{\partial t} = c_2(t) H_{22}(t) + c_1 e^{+i\omega_o t} H_{21}(t)$$

where the matrix elements of the permutation (in terms of the eigenstates of $H(0)$) are

$$\langle m | H_1(t) | n \rangle = H_{mn}(t)$$

Assume initial state is $n = 1$, and $H_{11} = H_{22} = 0$

$$|\psi(t = 0)\rangle = |1\rangle$$

Probability of particle at $n = 2$ at time t after the perturbation is turned on (i.e., incident light):

$$c_2(t) = \frac{-i}{\hbar} \int_o^t e^{i\omega_o t} dt' H_{21}(t') \tag{7.11.1}$$

where

$$H_1(t) = \cos(\omega t) V(r)$$

$V(r)$ is an amplitude of polarization vector, which we can ignore for now.

If we assume incident frequency of incident light ω is comparable to the natural frequency of oscillation from ω_o

$$\omega \approx \omega_o$$

then Equation 7.11.1 can be simplified to

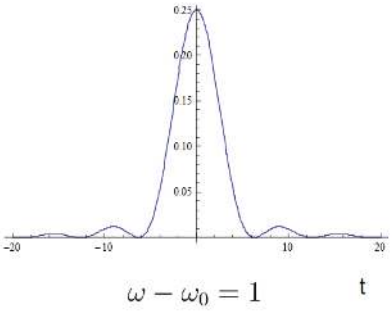
$$c_2(t) = -\frac{2i}{\hbar} \frac{\sin(\omega - \omega_o)t/2}{(\omega - \omega_o)t} e^{i(\omega_0 - \omega)t/2} H_{21}$$

Transition Probability

Assume initial state is $n = 1$, and probability of transition from $n = 1$ state to $n = 2$ state is:

$$P_{12}(t) = |c_2(t)|^2 = \frac{4}{\hbar^2} \left| \frac{\sin(\omega - \omega_o)t/2}{(\omega - \omega_o)t} \right|^2 |H_{21}|^2$$

What does this mean? Strangely, it means that the probability of making a transition is actually oscillating sinusoidally (squared)! If you want to cause a transition, should turn off perturbation after time $\pi/|\omega - \omega_o|$or some odd multiple, when the system is in upper state with maximum probability.



$P_{12}(t)$ is peaked at $\omega - \omega_o = 0$. The height of $|H_{12}t/2\hbar|^2$ and width of $4\pi/t$ gets higher and narrower as time goes on. Recall this is perturbative treatment, however, and $P_{12}(t)$ cannot get bigger than 1, so perturbation theory breaks down eventually.

7.11: Time-Dependent Perturbation Theory is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

- **13.11: Time-Dependent Perturbation Theory** by Wikipedia is licensed CC BY-SA 4.0.

7.12: The Selection Rule for the Rigid Rotator

A **selection rule** describes how the probability of transitioning from one level to another cannot be **zero**. It has two sub-pieces: a **gross selection rule** and a **specific selection rule**. A gross selection rule illustrates characteristic requirements for atoms or molecules to display a spectrum of a given kind, such as an IR spectroscopy or a microwave spectroscopy. Once the atom or molecules follow the gross selection rule, the specific selection rule must be applied to the atom or molecules to determine whether a certain transition in quantum number may happen or not.

Selection rules specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation. Incident electromagnetic radiation presents an oscillating electric field $E_0 \cos(\omega t)$ that interacts with a transition dipole. The dipole operator is $\mu = e \cdot r$ where r is a vector pointing in a direction of space.

A dipole moment of a given state is

$$\mu_z = \int \Psi_1{}^* \mu_z \Psi_1 \, d\tau$$

A transition dipole moment is a transient dipolar polarization created by an interaction of electromagnetic radiation with a molecule

$$(\mu_z)_{12} = \int \Psi_1{}^* \mu_z \Psi_2 \, d\tau$$

In an experiment we present an electric field along the z axis (in the laboratory frame) and we may consider specifically the interaction between the transition dipole along the x, y, or z axis of the molecule with this radiation. If μ_z is zero then a transition is forbidden. The selection rule is a statement of when μ_z is non-zero.

> *The selection rule is a statement of when μ_z is non-zero.*

Rotational transitions

We can use the definition of the transition moment and the spherical harmonics to derive selection rules for a rigid rotator. Once again we assume that radiation is along the z axis.

$$(\mu_z)_{J,M,J',M'} = \int_0^{2\pi} \int_0^{\pi} Y_{J'}^{M'}(\theta,\phi) \mu_z Y_J^M(\theta,\phi) \sin\theta \, d\phi, d\theta$$

Notice that m must be non-zero in order for the transition moment to be non-zero. This proves that a molecule must have a permanent dipole moment in order to have a rotational spectrum. The spherical harmonics can be written as

$$Y_J^M(\theta,\phi) = N_{JM} P_J^{|M|}(\cos\theta) e^{iM\phi}$$

where N_{JM} is a normalization constant. Using the standard substitution of $x = \cos q$ we can express the rotational transition moment as

$$(\mu_z)_{J,M,J',M'} = \mu N_{JM} N_{J'M'} \int_0^{2\pi} e^{I(M-M')\phi} \, d\phi \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

The integral over f is zero unless M = M' so $\Delta M = 0$ is part of the rigid rotator selection rule. Integration over ϕ for $M = M'$ gives 2π so we have

$$(\mu_z)_{J,M,J',M'} = 2\pi\mu N_{JM} N_{J'M'} \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

We can evaluate this integral using the identity

$$(2J+1)x \, P_J^{|M|}(x) = (J - |M| + 1) P_{J+1}^{|M|}(x) + (J - |M|) P_{J-1}^{|M|}(x)$$

Substituting into the integral one obtains an integral which will vanish unless $J' = J+1$ or $J' = J-1$.

$$\int_{-1}^{1} P_{J'}^{|M'|}(x) \left(\frac{(J - |M| + 1)}{(2J+1)} P_{J+1}^{|M|}(x) + \frac{(J - |M|)}{(2J+1)} P_{J-1}^{|M|}(x) \right) dx$$

This leads to the selection rule $\Delta J = \pm 1$ for absorptive rotational transitions. Keep in mind the physical interpretation of the quantum numbers J and M as the total angular momentum and z-component of angular momentum, respectively. As stated above in the section on electronic transitions, these selection rules also apply to the orbital angular momentum ($\Delta l = \pm 1$, $\Delta m = 0$).

7.12: The Selection Rule for the Rigid Rotator is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **13.12: The Selection Rule for the Rigid Rotor** is licensed CC BY-SA 4.0.

7.13: The Harmonic Oscillator Selection Rule

Selection rules are a very important concept in spectroscopy and physical chemistry, as they directly complement the concept that systems on the atomic level are quantized. Quantization tells us how electrons, neutrons, and protons are set up, and selection rules tell us how, energetically speaking, they may move about. For example, the principal quantum number, n, determines the energy state of particles in the Particle in a Box model. With respect to real systems, the quantum number n describes electronic transitions, such as the excitation of an electron. There are other transitions, such as the rotational transition, which applies to the rigid rotator model and occurs where there are spherical harmonics. Vibrational transitions occur where there is a system that can be visualized as two masses connected by a spring, such as a diatomic molecule.

Selection rules can be very useful in spectroscopy for obtaining information about an unknown substance; any given substance has properties and behaviors that operate within the selection rules and determine the wavelengths of electromagnetic radiation (light) that cause transitions. By tracking these properties, chemists can use techniques like IR spectroscopy to determine the chemical structure of a molecule. For example, a selection rule might govern how a quantum number changes during a transition. That quantum number appears in equations that determine the energy transition based on the mass and other structural properties of a molecule. Thus, if one knows the selection rules and the energy transition, he or she can determine other properties about the molecule, such as its mass or its bond strength.

Example: Evaluating vibrational transitions using a transition moment integral.

Vibrational systems are described by the harmonic oscillator wavefunctions, which look like

$$\Psi_v(x) = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

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.

7.13: The Harmonic Oscillator Selection Rule is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **13.13: The Harmonic Oscillator Selection Rule** by Alex Krueger is licensed CC BY-NC-SA 4.0.

7.14: Group Theory Determines Infrared Activity

Determining if a Normal Modes is IR or Raman Active

A transition from $v \rightarrow v'$ is IR active if the **transition moment integral** contains the totally symmetric irreducible representation of the point group the molecule belongs to. The transition moment integral is derived from the one-dimensional harmonic oscillator. Using the definition of electric dipole moment μ, the integral is:

$$M(v \rightarrow v') = \langle \textbf{final wavefunction} \left|\vec{\mu}\right| \textbf{initial wavefunction} \rangle$$

or in terms of vibrational wavefunctions for a specific normal mode $|\phi(v)\rangle$

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) \left|\vec{\mu}\right| \phi(v = 0) \rangle \tag{7.14.1}$$

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 7.14.1 becomes

$$M(v \rightarrow v') = \vec{\mu} \langle \phi(v' \neq 0) | \phi(v = 0) \rangle \tag{7.14.2}$$

Since $|\phi(v = 0)\rangle$ and $|\phi(v =\neq 0)\rangle$ are mutually orthogonal to each other, the integral in Equation 7.14.1 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):

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) \left|\alpha\right| \phi(v = 0) \rangle \tag{7.14.3}$$

Following a similar argument as above, α must be nonzero for the transition to be allowed and exhibits Raman scattering.

Character Table

For a molecule to be IR active the dipole moment has to change during the vibration. For a molecule to be Raman active the polarizability of the molecule has to change during the vibration. The reducible representation $\mathbf{\Gamma_{vib}}$ can also be found by determining the reducible representation of the 3N degrees of freedom of H_2O, $\mathbf{\Gamma}_{tot}$. By applying Group Theory it is straightforward to find $\mathbf{\Gamma_{x,y,z}}$ as well as UMA (number of unmoved atoms). Again, using water as an example with C_{2v} symmetry where 3N = 9, $\mathbf{\Gamma_{tot}}$ can be determined:

C_{2v}	E	C_2	σ (xz)	σ (yz)	
$\mathbf{T_{x,y,z}}$	3	-1	1	1	
UMA	3	1	1	3	
$\mathbf{\Gamma_{tot}}$	**9**	**-1**	**1**	**3**	$\mathbf{=3a_1 + a_2 + 2b_1 + 3b_2}$
Note that $\mathbf{\Gamma}_{tot}$ contains nine degrees of freedom consistent with 3N = 9.					

$\mathbf{\Gamma}_{tot}$ contains $\mathbf{\Gamma}_{translational}$, $\mathbf{\Gamma}_{rotational}$ as well as $\mathbf{\Gamma}_{vibrational}$. $\mathbf{\Gamma}_{trans}$ can be obtained by finding the irreducible representations corresponding to x,y and z in the right side of the character table, $\mathbf{\Gamma}_{rot}$ by finding the ones corresponding to R_x, R_y and R_z. $\mathbf{\Gamma}_{vib}$ can be obtained by $\mathbf{\Gamma}_{tot}$ - $\mathbf{\Gamma}_{trans}$ - $\mathbf{\Gamma}_{rot}$.

$$\mathbf{\Gamma}_{vib}(H_2O) = (3a_1 + a_2 + 2b_1 + 3b_2) - (a_1 + b_1 + b_2) - (a_2 + b_1 + b_2) = 2a_1 + b_2$$

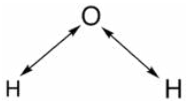
In order to determine which modes are IR active, a simple check of the irreducible representation that corresponds to x,y and z and a cross check with the reducible representation Γ_{vib} is necessary. If they contain the same irreducible representation, the mode is IR active.

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.

References

1. Merlin, J.C., Cornard, J.P., *J. Chem. Educ*., **2006**, 83 (9), p 1383. **DOI:** 10.1021/ed083p1393
2. McGuinn, C.J., *J. Chem. Educ*., **1982**, 59 (10), p 813. **DOI:** 10.1021/ed059p813
3. Harris, D.C., Bertolucci, M.D., *Symmetry and Spectroscopy: An introduction to Vibrational and Electronic Spectroscopy*. Dover Publocations, Inc., New York, **1989**.
4. McQuarrie, D. A., Simon, J.D., *Physical Chemistry: A Molecular Approach*, University Science Books, Sausalito, California, **1997**; 518-521.
5. Housecroft, C.E., Sharpe, A.G., **Inorganic Chemistry.** Pearson Education Limited, England, **2008**, 107.
6. Atkins, P., dePaula, J., *Physical Chemistry*, W.H. Freeman and Company, New York, **2002**, 520-523.
7. Bishop, D.M., *Group Theory and Chemistry*, Dover Publications, Inc, New York, **1973**, 166.

7.14: Group Theory Determines Infrared Activity is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **13.14: Group Theory Determines Infrared Activity** by Kristin Kowolik is licensed CC BY-NC-SA 4.0.

7.15: Molecular Spectroscopy (Exercises)

These are homework exercises to accompany Chapter 13 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q13.1

1. Calculate the energy difference for radiation wavenumber of, $\nu = 1.00 cm^{-1}$ including the type of molecular process that absorbs of this radiation corresponding to.
2. Given the wavelength of 3.4 x 10^{-4}, which molecular process does it fall into?
3. What are other advantages of knowing the spectroscopy of molecules?
4. Do you think the spectroscopy and molecular processes of the molecules have relationship to temperature? Explain.
5. What is other form that you can express in above equation?

Q13.20

The vibrational term of a diatomic molecule is

$$G(v) = (v + \frac{1}{2})\nu_e - (v + \frac{1}{2})^2 \chi_e \nu_e \tag{7.15.1}$$

Show that the spacing between adjacent levels is given by

$$\Delta G = G(v+1) - G(v) = \nu_e - 2\chi_e \nu_e (v+1)$$

Show that the maximum vibrational quantum number, v_{max} is given by

$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{7.15.2}$$

Use this result to show that the dissociation energy of the diatomic molecule can be written as

$$D_e = \frac{\nu_e - \nu_e \chi_e^2}{4\chi_e} \approx \frac{\nu_e}{4\chi_e} \tag{7.15.3}$$

Explain how the constants ν_e and χ_e can be evaluated from a plot of ΔG versus $v + 1$, called a Birge-Sponer plot. After finding these constants, determine the dissociation energy of the molecule. Use the following experimental data of H_2 to determine the dissociation energy of the molecule.

v	G(v) / cm^{-1}
0	4161.12
1	8087.11
2	11782.35
3	15250.36
4	18497.92
5	21505.65
6	24287.83
7	26830.97
8	29123.93
9	31150.19
10	32886.65
11	34301.83
12	35351.01
13	35972.97

Explain why your plot is not linear for high values of v. How does this dissocation energy differ with the experimental value of $38269.48 cm^{-1}$.

S13.20

$$\Delta G = G(v+1) - G(v) = \left(v+\frac{3}{2}\right)\nu_e - \left(v+\frac{3}{2}\right)^2 \chi_e\nu_e - \left(v+\frac{1}{2}\right)\nu_e + \left(v+\frac{1}{2}\right)^2 \chi_e\nu_e = \nu_e - \chi_e\nu_e(2v+2) = \nu_e - 2\chi_e\nu_e(v+1)$$

In the limit that $\Delta G \to 0, v \to v_{max}$, solving for v_{max} gives

$$0 = \nu_e - 2\chi_e\nu_e(v_{max}+1) \tag{7.15.4}$$

$$2\chi_e(v_{max}+1) = 1 \tag{7.15.5}$$

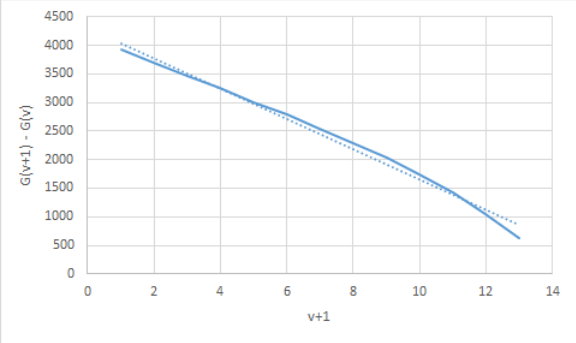
$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{7.15.6}$$

The molecule dissociates in the limit $\Delta G \to 0$, so the dissociation energy is given by

$$D_e = G(v_{max}) = (\frac{1}{2\chi_e} - \frac{1}{2})\nu_e - (\frac{1}{2\chi_e} - \frac{1}{2})^2\chi_e\nu_e = \frac{\nu_e}{2\chi_e}(1-\chi_e) - \frac{\nu_e}{4\chi_e}(1-\chi_e)^2 \tag{7.15.7}$$
$$= \frac{\nu_e}{4\chi_e}(2 - 2\chi_e - 1 + 2\chi_e - \chi_e^2) = \frac{\nu_e}{4\chi_e}(1-\chi_e^2) \approx \frac{\nu_e}{4\chi_e}$$

The final step can be made if we assume χ_e to be very small.

Looking at the equation for ΔG, we conclude that a plot of ΔG versus $v+1$ will have an intercept of ν_e and a slope of $-2\chi_e\nu_e$. The experimental data points for H_2 can be plotted as such:



If we use a best linear fit, we determine that the intercept is $\nu_e = 4164.4cm^{-1}$ and the slope is $-2\chi_e\nu_e = -232.01cm^{-1}$. Thus, $\chi_e = 0.0279$. Then, the dissociation energy is

$$D_e = \frac{\nu_e}{4\chi_e} = 37400cm^{-1} \tag{7.15.8}$$

The plot is not linear for large values of v because the potential curve is not well described by the anharmonic potential energy function.

Q13.21

An analysis of the vibrational spectrum of the ground-state homonuclear diatomic molecule Na_2 gives $\tilde{\nu}_e = 159.125\ cm^{-1}$ and $\tilde{\nu}_e\tilde{x}_e = 0.7255\ cm^{-1}$. Suggest an experimental method that can be used to determine there spectroscopic parameters. Use $\nu_{max} = \frac{1}{2\tilde{x}_e} - 1$ to determine the number of bound vibrational levels for ground state of Na_2.

S13.21

First solve for $\tilde{x}$:

$$\tilde{x} = \frac{0.7255\ cm^{-1}}{159.125\ cm^{-1}} = 4.5593 \times 10^{-3}\ cm^{-1} \tag{7.15.9}$$

Then plug it in to the equation:

$$\nu_{max} = \frac{1}{2 \times 4.5593 \times 10^{-3}\ cm^{-1}} - 1 = 109.67\ cm^{-1} \tag{7.15.10}$$

There are 109 bound vibrational levels for the ground state of Ne_2.

Q13.22

A Morse potential is a decent representation of internuclear potential and is modeled by

$$U(q) = D_e(1 - e^{-/betaq})^2 \tag{7.15.11}$$

where $q = R - R_e$. Prove the force constant for the Morse Potential is evaluated

$$k = 2D_e\beta^2 \tag{7.15.12}$$

If $D_e = 6.23 \times 10^{-19} J \cdot Molecule^{-1}$ and $\beta = 1.37 \times 10^{10} m^{-1}$ for a given compound, calculate the force constant for that compound.

S13.22

Using a Maclaurin series expansion of the Morse potential, the formula can be rewritten

$$U(q) = D_e(1 - e^{-\beta q})^2 = D_e(1 - (1 - \beta q + \frac{\beta^2 q^2}{2}O(q)^3))^2 = D_e(\beta^2 q^2 + O(q)^3) \tag{7.15.13}$$

We know that

$$U(q) = \frac{kq^2}{2} \tag{7.15.14}$$

assuming that $O(q)^3$ approaches zero, we get

$$\frac{kq^2}{2} = D_e(\beta^2 q^2 + O(q)^3) \implies k = 2D_e\beta^2 \tag{7.15.15}$$

Plugging in our given values, we get

$$l = 2(6.23 \times 10^{-19} J \cdot Molecule^{-1})(1.37 \times 10^{10})^2 = 234 N \cdot m^{-1} \tag{7.15.16}$$

Q13.23

Given that $D_e = 7.33 \times 10^{-19} J \cdot molecule^{-1}, \tilde{v}_e = 1580.0 cm^{-1}, and R_e = 121 pm$, find k and β for $^{16}O_2$.

S13.23

Assuming a a harmonic oscillator model, we can use the equation:

$$\tilde{v}_e = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{7.15.17}$$

We can find k from the parameters given in the problem. Solving for k gives

$$k = (2\pi c \tilde{v}_e)^2 \mu \tag{7.15.18}$$

$$= [2\pi(3 \times 10^{10} cm \cdot s^{-1})(1580.0 cm^{-1})]^2 (7.9975 amu)(1.661 x 10^{-27} kg \cdot amu^{-1}) \tag{7.15.19}$$

$$= 1176.3 N \cdot m^{-1} \tag{7.15.20}$$

Using the equation:

$$\beta = \left(\frac{k}{2D_e}\right)^{1/2} \tag{7.15.21}$$

We can solve for β using the information above

$$\beta = \left[\frac{1176.3 N \cdot m^{-1}}{2(7.33 \times 10^{-19} J)}\right]^{1/2} \tag{7.15.22}$$

$$= 2.84 \times 10^{10} m^{-1} \tag{7.15.23}$$

Q13.24

The fundamental line in the IR spectrum of $^{12}C^{16}O\ cm^{-1}$, and the first overtone occurs at 4260.0 cm^{-1}. Find $\tilde{v}_e$ and $\tilde{x}_e\tilde{v}_e$ for $^{12}C^{16}O$.

S13.24

The equations for the fundamental frequency and the overtone are

$$\tilde{v} = \tilde{v}_e - 2\tilde{x}_e\tilde{v}_e \tag{7.15.24}$$

and

$$\tilde{v} = 2\tilde{v}_e - 6\tilde{x}_e\tilde{v}_e, \tag{7.15.25}$$

respectively.

We can set the fundamental frequency equal to $2143.0\ cm^{-1}$ and the first overtone equal to $4260.0\ cm^{-1}$ which is given from the problem statement. Then, we want to solve for $\tilde{x}_e\tilde{v}_e$.

Multiply the fundamental frequency by 3 and subtract the overtone.

$$\tilde{v}_e = [3(2143.0) - 4260.0] cm^{-1} = 2169.0 cm^{-1} \tag{7.15.26}$$

Then multiply the fundamental frequency by 2 and subtract from the overtone.

$$\tilde{x}_e\tilde{v}_e = 13.0cm^{-1} \tag{7.15.27}$$

Q13.24

Which of the following molecules exhibit a microwave rotational absorption spectrum: BF_2,SO_2,C_2F_2,NO_3^-

S13.24

SO_2

notes: microwave rotational absorption correlates to the rotation of polyatomic molecules. Would BF_2 and NO_3^- also fall in this range?

Q13-25 Slightly Incorrect

Calculate the fundamental and the first two overtones of

$$H^{35}Cl \tag{7.15.28}$$

given

$$\tilde{v}_e = 2990.946cm^{-1} \tag{7.15.29}$$

$$\tilde{x}_e\tilde{v}_e = 52.819cm^{-1} \tag{7.15.30}$$

S13-25

Use equation,

$$\tilde{v_{obs}} = \tilde{v}_e\nu - \tilde{x}_e\tilde{v}_e\nu(\nu+1) \tag{7.15.31}$$

with v =1,2...

The fundamental frequency is given by v=1 and the first two overtones are given by v=2 and v=3.

Fundamental:

$$\tilde{v_{obs}} = \tilde{v}_e - 2\tilde{x}_e\tilde{v}_e = 2990.946cm^{-1} - 2(52.819cm^{-1}) = 2885.308cm^{-1} \tag{7.15.32}$$

First overtone:

$$\tilde{v_{obs}} = 2\tilde{v}_e - 6\tilde{x}_e\tilde{v}_e = 2990.946cm^{-1} - 6(52.819cm^{-1}) = 5664.978cm^{-1} \tag{7.15.33}$$

Second overtone:

$$\tilde{v_{obs}} = 3\tilde{v}_e - 12\tilde{x}_e\tilde{v}_e = 3(2990.946cm^{-1}) - 12(52.819cm^{-1}) = 8339.01cm^{-1} \tag{7.15.34}$$

Q13.26

Plot the

$$\frac{\nu_{obs}}{\nu} \tag{7.15.35}$$

versus

$$(\nu+1) \tag{7.15.36}$$

for the anharmonic oscillator approximation and use it to determine the values of

$$\nu_e \tag{7.15.37}$$

and

$$x_e\nu_e \tag{7.15.38}$$

for

$$H^35Cl \tag{7.15.39}$$

. Use the information in Table13.4.

S13.26

$$\nu_{obs} = \nu_{obs}\nu - x_e\nu_e\nu(\nu+1) \tag{7.15.40}$$

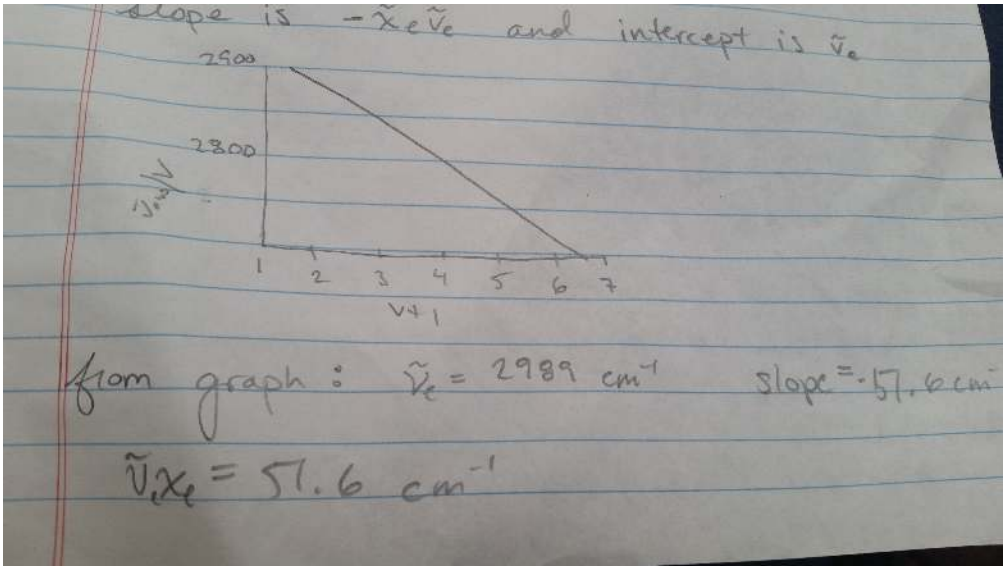
$$\frac{\nu_{obs}}{\nu} = \nu_e - x_e\nu_e(\nu+1) \tag{7.15.41}$$

The slope is

$$-x_e\nu_e \tag{7.15.42}$$

and the intercept is

$$\nu_e \tag{7.15.43}$$



The problem is nice and straight forward. It would be great for an explanation of why the slope is negative for an insight of the graph

Q13.31

Phosphorus nitride (PN) is a heteronuclear diatomic molecule that is a similar to N_2 with a triple bond, although is substantially weaker because P is a larger atomic radius than N. Using the following data, calculate $\tilde{\nu_e}'$ and $\tilde{\chi_e}'\ \tilde{\nu_e}'$ for PN.

IR Transition	$\tilde{\nu_{abs}}\ [cm^{-1}]$
$0 \rightarrow 0$	39,699.10
$0 \rightarrow 1$	40,786.80
$0 \rightarrow 2$	41,858.90

S13.31

We will use the following equation:

$$\tilde{\nu_{abs}} = \tilde{\nu_{0,0}}' + \tilde{\nu_e}'\tilde{\nu}' - \tilde{\chi_e}'\tilde{\nu_e}'\tilde{\nu}'(\nu'+1) \tag{7.15.44}$$

Plugging in the appropriate values of ν', we get:

According to your table $\tilde{\nu_{0,0}}'$ should be 39,699.10 not 29,699.10.

- $\nu' = 0$:

$$\tilde{\nu_{0,0}}' = 29,699.10\ cm^{-1} \quad (1)$$

- $\nu' = 1$:

$$\tilde{\nu_{0,0}}' + \tilde{\nu_e}' - 2\tilde{\chi_e}'\tilde{\nu_e}' = 40,786.80\ cm^{-1} \quad (2)$$

- $\nu' = 2$:

$$\tilde{\nu_{0,0}}' + 2\tilde{\nu_e}' - 6\tilde{\chi_e}'\tilde{\nu_e}' = 41,858.90\ cm^{-1} \quad (3)$$

Solving as a system of equations, we subtract:

(2) - (1) = (4), (3) - (1) = (5), and finally (5) - 2x(4) = (6)

Equation (6) can be solved for $\tilde{\chi_e}'\tilde{\nu_e}'$, and then plugged back in to equation (4) or equation (5) to solve for $\tilde{\nu_e}'$. The answer is:

$$\tilde{\chi_e}'\tilde{\nu_e}' = 1103.3\ cm^{-1} \quad (7.15.45)$$

and

$$\tilde{\nu_e}' = 7.80\ cm^{-1} \quad (7.15.46)$$

from my calculations $\tilde{\nu_e}' = 1103.3$ and $\tilde{\chi_e}'\tilde{\nu_e}' = 7.80$ it looks like you had them switched

Q13.32

The frequencies of the first few vibronic transitions to an excited state of NaCl* are as follows:

Vibronic Transitions	$0 \rightarrow 0$	$0 \rightarrow 1$	$0 \rightarrow 2$
$\tilde{\nu}_{obs}/cm^{-1}$	12376	89706	15219

*not accurate values for NaCl

Use these data to calculate the values of $\tilde{\nu}_e$ and $\tilde{\nu}_e\tilde{x}_e$ for the excited state of NaCl

S13.32

$A = \tilde{\nu}_e', B = \tilde{\nu}_e'\tilde{x}_e'$

$12376 = \tilde{\nu}_0, 0$

$89706 = \tilde{\nu}_0, 0 + \tilde{\nu}_e' - 2\tilde{\nu}_e'\tilde{x}_e' - 12376 = \tilde{\nu}_0, 0 = 77330 = +\tilde{\nu}_e' - 2\tilde{\nu}_e'\tilde{x}_e'$ (1)

$15219 = \tilde{\nu}_0, 0 + 2\tilde{\nu}_e' - 6\tilde{\nu}_e'\tilde{x}_e' - 12376 = \tilde{\nu}_0, 0 = 2843 = 2\tilde{\nu}_e' - 6\tilde{\nu}_e'\tilde{x}_e'$ (2)

77330 + 2B = A (1a)

2843 = 2A - 6B (2a)

77330+2B = A

2843 - 154660 = -2B

B = 75908.5 cm^{-1} = $\tilde{\nu}_e'$

A = 229147 cm^{-1} = $\tilde{\nu}_e'\tilde{x}_e'$

Q13.33

Determine the number of translational, rotational, and vibrational degrees of freedom in

a. Xe
b. HCl
c. CS_2
d. hemoglobin containing 9272 molecules

The total number of degrees of freedom is 3N, where N is the number of atoms in the molecule. All molecules have three translational degrees of freedom. A nonlinear molecule has three rotational degrees of freedom and a linear molecule has two rotational degrees of freedom. A linear molecule has $3N-5$ vibrational degrees of freedom and a nonlinear molecule has 3N — 6 vibrational degrees of freedom.

S13.33

The number of translational degrees of freedom is 3, the number of rotational degrees of freedom is 2 for linear molecules and 3 for non-linear molecules. Therefore, the remaining degrees of freedom, which is equal to 3N-5 for linear molecules or 3N-6 for non-linear molecules, is equal to the number of vibrational degrees of freedom.

	Translation	Rotation	Vibration	Total
Xe	3	0	0	3
HCl	3	2	1	6
CS_2	3	2	4	9
hemoglobin	3	3	27810	27816

Q13.36

Classify each of the following molecules as either a prolate or an oblate symmetric top: XeF_4, $ClCH_3$, NH_3, and C_6H_6.

S13.36

- XeF_4 :oblate
- $ClCH_3$:prolate
- NH_3:prolate
- C_6H_6:oblate

Q13.37

Solve for the components of the moment of inertia of a trigonal planar molecule if all the masses are m, the bond lengths are unit length, and all bond angles are $120°$.

S13.37

$$I_{xx} = \sum m_j y_j^2 = m(1)^2 + 2m(sin^2 30°) = \frac{3}{2}m \tag{7.15.47}$$

$$I_{yy} = \sum m_j x_j^2 = m(0)^2 + 2m(cos^2 30°) = \frac{3}{2}m \tag{7.15.48}$$

$$I_{zz} = \sum m_j x_j^2 + \sum m_j y_j^2 = 3m \tag{7.15.49}$$

Q13.38

This problem illustrates how the principal moments of inertia can be obtained as an eigenvalue problem. Consider a molecule where all the masses are unit masses and the long and short bond lengths are 2 and 1, respectively.

Show that

$$I_{xx} = 2\cos^2\theta + 8\sin^2\theta \tag{7.15.50}$$

$$I_{yy} = 8\cos^2\theta + 2\sin^2\theta \tag{7.15.51}$$

$$I_{xy} = -6\cos\theta\sin\theta \tag{7.15.52}$$

Solve the secular determinant equation for λ

$$\begin{vmatrix} I_{xx} - \lambda & I_{xy} \\ I_{xy} & I_{yy} - \lambda \end{vmatrix} = 0 \tag{7.15.53}$$

and compare the result with the values of I_{xx} and I_{yy} that you would obtain if you align the "molecule" and coordinate system such that $\theta = 180°$. What does this comparison tell you? What are the values of I_{xx} and I_{yy} if $\theta = 90$?

S13.38

We use trigonometric functions to find the x and y components

$$I_{xx} = \sum m_i y_i^2 = 2(1)(2\sin\theta)^2 + 2(1)\left[\sin\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\sin^2\theta + 2\cos^2\theta \tag{7.15.54}$$

$$I_{yy} = \sum m_i x_i^2 = 2(1)(2\cos\theta)^2 + 2(1)\left[\cos\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\cos^2\theta + 2\sin^2\theta \tag{7.15.55}$$

$$\begin{aligned} I_{xy} = -\sum m_i x_i y_i &= -(2\cos\theta)(2\sin\theta) - 2\left[\cos(\pi) + \theta\right]\left[\sin(\pi) + \theta\right] \\ &- \left[\sin\left(\frac{\pi}{2}\right) - \theta\right]\left[\cos\left(\frac{\pi}{2}\right) - \theta\right] - \left[\cos\left(\frac{\pi}{2}\right) + \theta\right]\left[\sin\left(\frac{\pi}{2}\right) + \theta\right] \\ &= -6\cos\theta\sin\theta \end{aligned} \tag{7.15.56}$$

The secular determinantal equation becomes

$$\begin{vmatrix} 8\sin^2\theta + 2\cos^2\theta - \lambda & -6\cos\theta\sin\theta \\ -6\cos\theta\sin\theta & 8\cos^2\theta + 2\sin^2\theta - \lambda \end{vmatrix} = 0 \tag{7.15.57}$$

Expanding the determinant gives

$$0 = \lambda^2 - \lambda(10)(\sin\theta^2 + \cos\theta^2) + 16(\sin\theta^2 + \cos\theta^2)^2 \tag{7.15.58}$$

$$0 = \lambda^2 - 10\lambda + 16 \tag{7.15.59}$$

$$\lambda = 5 \pm 3 \tag{7.15.60}$$

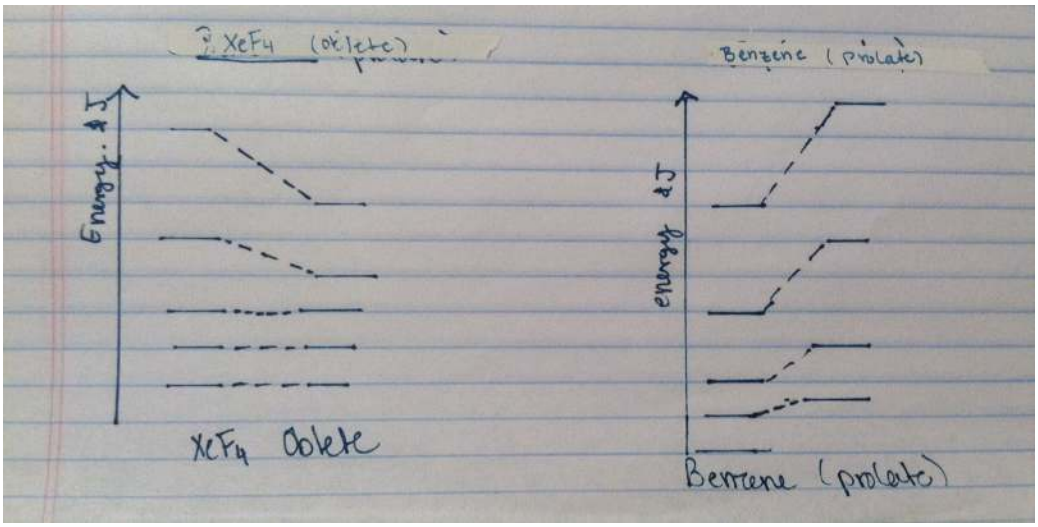
If $\theta = 180°$ then $I_{xx} = 2, I_{yy} = 8, and I_{xy} = 0$. If $\theta = 90°$ then $I_{xx} = 8, I_{yy} = 2, and I_{xy} = 0$. This tells us that the coordinate system does not affect the values of the principal momentum of inertia.

Q13.39

Sketch the energy level diagram of NH_3 (a prolate symmetric top molecule) and XeF_4 (an oblate symmetric top). How do they differ?

S13.39

The energies increase as the J levels increases for the prolate symmetry and the energies decrease as J increases for the oblate symmetry



7.15: Molecular Spectroscopy (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

8: The Schrödinger Equation and a Particle in a Box

The particle in a box model (also known as the infinite potential well or the infinite square well) describes a particle free to move in a small space surrounded by impenetrable barriers. The model is mainly used as a hypothetical example to illustrate the differences between classical and quantum systems. In classical systems, for example a ball trapped inside a large box, the particle can move at any speed within the box and it is no more likely to be found at one position than another. However, when the well becomes very narrow (on the scale of a few nanometers), quantum effects become important. The particle may only occupy certain positive energy levels. The particle in a box model provides one of the very few problems in quantum mechanics which can be solved analytically, without approximations. This means that the observable properties of the particle (such as its energy and position) are related to the mass of the particle and the width of the well by simple mathematical expressions. Due to its simplicity, the model allows insight into quantum effects without the need for complicated mathematics. It is one of the first quantum mechanics problems taught in undergraduate physics courses, and it is commonly used as an approximation for more complicated quantum systems.

8.1: The Schrödinger Equation
8.2: Linear Operators in Quantum Mechanics
8.3: The Schrödinger Equation is an Eigenvalue Problem
8.4: The Quantum Mechanical Free Particle
8.5: Wavefunctions Have a Probabilistic Interpretation
8.6: The Energy of a Particle in a Box is Quantized
8.7: Wavefunctions Must Be Normalized
8.8: The Average Momentum of a Particle in a Box is Zero
8.9: Particle in a Finite Box and Tunneling (optional)
8.10: The Uncertainty Principle Redux - Estimating Uncertainties from Wavefunctions
8.11: A Particle in a Two-Dimensional Box
8.12: A Particle in a Three-Dimensional Box
8.13: The Schrödinger Equation and a Particle in a Box (Exercises)

Thumbnail: The quantum wavefunction of a particle in a 2D infinite potential well of dimensions L_x and L_y. The wavenumbers are $n_x = 2$ and $n_y = 2$. (Public Domain; Inductiveload).

8: The Schrödinger Equation and a Particle in a Box is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.1: The Schrödinger Equation

3.01: The Schrödinger Equation

8.1: The Schrödinger Equation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.2: Linear Operators in Quantum Mechanics

3.02: Linear Operators in Quantum Mechanics

8.2: Linear Operators in Quantum Mechanics is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.3: The Schrödinger Equation is an Eigenvalue Problem

3.03: The Schrödinger Equation is an Eigenvalue Problem

8.3: The Schrödinger Equation is an Eigenvalue Problem is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.4: The Quantum Mechanical Free Particle

3.04: The Quantum Mechanical Free Particle

8.4: The Quantum Mechanical Free Particle is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.5: Wavefunctions Have a Probabilistic Interpretation

3.05: Wavefunctions Have a Probabilistic Interpretation

8.5: Wavefunctions Have a Probabilistic Interpretation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

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

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

8.6: The Energy of a Particle in a Box is Quantized is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.7: Wavefunctions Must Be Normalized

3.07: Wavefunctions Must Be Normalized

8.7: Wavefunctions Must Be Normalized is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

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

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

8.8: The Average Momentum of a Particle in a Box is Zero is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.9: Particle in a Finite Box and Tunneling (optional)

3.09: Particle in a Finite Box (and Tunneling)

8.9: Particle in a Finite Box and Tunneling (optional) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.10: The Uncertainty Principle Redux - Estimating Uncertainties from Wavefunctions

3.09: The Uncertainty Principle Redux

8.10: The Uncertainty Principle Redux - Estimating Uncertainties from Wavefunctions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.11: A Particle in a Two-Dimensional Box

3.10: A Particle in a Two-Dimensional Box

This page titled 8.11: A Particle in a Two-Dimensional Box is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Mark E. Tuckerman.

8.12: A Particle in a Three-Dimensional Box

3.11: A Particle in a Three-Dimensional Box

8.12: A Particle in a Three-Dimensional Box is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.13: The Schrödinger Equation and a Particle in a Box (Exercises)

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

8.13: The Schrödinger Equation and a Particle in a Box (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

9: Postulates and Principles of Quantum Mechanics

It can help us to formulate the core postulates underlying our use of quantum mechanics. If chapter 1 is the *Declaration of Independence* (from classical mechanics), then this chapter is the *Constitution* of Quantum mechanics where all our discussions rely on.

9.1: The Wavefunction Specifies the State of a System
9.2: Quantum Operators Represent Classical Variables
9.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators
9.4: The Time-Dependent Schrödinger Equation
9.5: The Eigenfunctions of Operators are Orthogonal
9.6: Heisenburg Uncertainy Principle III - Commuting Operators
9.7: Postulates and Principles of Quantum Mechanics (Exercises)

9: Postulates and Principles of Quantum Mechanics is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

9.1: The Wavefunction Specifies the State of a System

Learning Objectives

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

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

Postulate I

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

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

$$P(x)=\psi^*(x)\psi(x) \tag{9.1.1}$$

$$=|\psi(x)|^2 \tag{9.1.2}$$

Hence, for valid (e.g., well-behaved) wavefunctions, the normalized probability in Equation 9.1.2 holds true, such that the integral over all space is equal to 1.

$$\int_{-\infty}^{\infty}\psi^*(x)\psi(x)\,dx=1 \tag{9.1.3}$$

Equation 9.1.3 means that the chance to find a particle is 100% somewhere within all space (e.g. somewhere between $-\infty$ and $+\infty$). A wavefunction is said to be **square-integrable** if Equation 9.1.3 can be satisfied (so that the Born Interpretation to be applicable).

Definition: Square-Integrable Functions

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

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

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

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

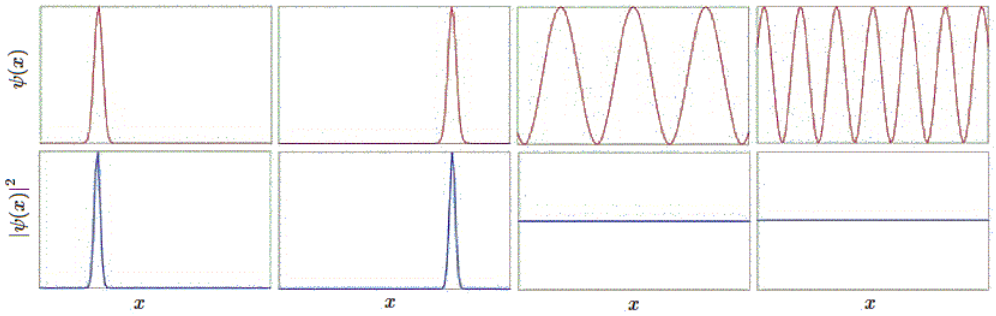


Figure 4.1.1 : Examples of good wavefunctions, $\psi(x)$, (red, top) and corresponding probability densities, $P(x)$, (blue, bottom).

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

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

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

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

for all k, so the corresponding probability densities, $P(x)$, are the same except for the normalization constant (Equation 9.1.2). We saw before that it does not make a whole lot of sense to think of a sinusoidal wave as being localized in some place. Indeed, the positions for these two wavefunctions are ill-defined, so they are not well-localized, and the uncertainty in the position is large in each case. This is Heisenberg Uncertainty Principle in action.

Ill-behaved (invalid) Wavefunctions

The Born interpretation in Equation 9.1.2 means that many wavefunctions which would be acceptable mathematical solutions of the Schrödinger equation are **not acceptable** because of their implications for the physical properties of the system. To satisfy this interpretation, wavefunctions must be:

- single valued,
- continuous, and
- finite.

These aspects mean that the valid wavefunction must be one-to-one, it cannot have an undefined slope, and cannot go to $-\infty$ or $+\infty$. For example, the wavefunction must not be infinite over any finite region. If it is, then the integral in Equation 9.1.3 is equal to infinity. This implies that the particle described by such a wavefunction has a zero probability of being anywhere where the wavefunction is not infinite, but is certain to be found at all points where the wavefunction is infinite.

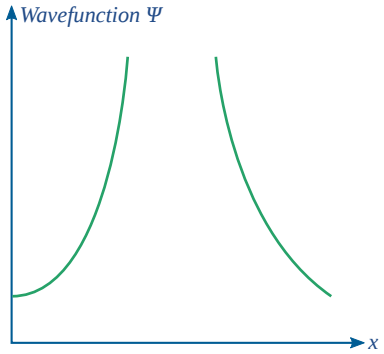


Figure 4.1.2 : This function is an invalid wavefunction since the amplitude is going to infinity over a region (the middle in this case). (CC BY-NC; Ümit Kaya via LibreTexts)

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

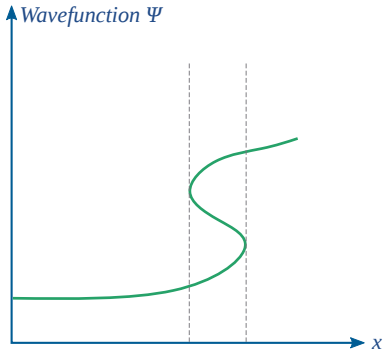


Figure 4.1.3 : This function is an invalid wavefunction since it is not a proper function (i. e., not one-to-one). (CC BY-NC; Ümit Kaya via LibreTexts)

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

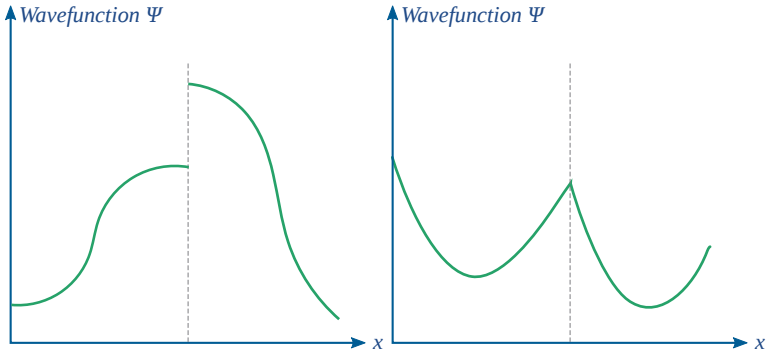


Figure 4.1.4 : These functions are invalid wavefunctions. (left) The first derivative of a function gives its gradient at a given point, and it thus exists as long as the function is continuous - only if there is a break in the function is there a point at which its first derivative does not exist. (right)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

Exercise 4.1.1

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

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

Contributors and Attributions

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

9.1: The Wavefunction Specifies the State of a System is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **4.1: The Wavefunction Specifies the State of a System** is licensed CC BY-NC-SA 4.0.

9.2: Quantum Operators Represent Classical Variables

Learning Objectives

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

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

Postulate II: The Correspondence Principle

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

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

$$\vec{r} = (x,y,z) \tag{9.2.1}$$

$$= x\vec{i} + y\vec{j} + z\vec{k} \tag{9.2.2}$$

The operator for a component of linear momentum is

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \tag{9.2.3}$$

and the operator for kinetic energy in one dimension is

$$\hat{T}_x = \left(-\frac{\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} \tag{9.2.4}$$

and in three dimensions

$$\hat{p} = -i\hbar\nabla \tag{9.2.5}$$

and

$$\hat{T} = \left(-\frac{\hbar^2}{2m}\right)\nabla^2 \tag{9.2.6}$$

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

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{9.2.7}$$

The Hamiltonian Operator

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

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

rather than Newton's second law,

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

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

Table 4.2.1 : Some common Operators in Quantum Mechanics

Name	Observable Symbol	Operator Symbol	Operation
Position (in 1D)	x	$\hat{X}$	Multiply by x
Position (in 3D)	$\vec{r}$	$\hat{R}$	Multiply by $\vec{r}$
Momentum (in 1D)	p_x	$\hat{P}_x$	$-i\hbar\frac{d}{dx}$
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	$\hat{L_z}$	$-i\hbar\left[x\frac{d}{dy}-y\frac{d}{dx}\right]$

9.2: Quantum Operators Represent Classical Variables is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **4.2: Quantum Operators Represent Classical Variables** is licensed CC BY-NC-SA 4.0.

9.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

Learning Objectives

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

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

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x,y,z) \tag{9.3.1}$$

Using this notation, we write the Schrödinger Equation as

$$\hat{H}\,|\psi(x,y,z)\rangle = E|\,\psi(x,y,z)\rangle \tag{9.3.2}$$

Equation 9.3.2 says that the Hamiltonian operator operates on the wavefunction to produce the energy, which is a number, (a quantity of Joules), times the wavefunction. Such an equation, where the operator, operating on a function, produces a constant times the function, is called an **eigenvalue equation**. The function is called an **eigenfunction**, and the resulting numerical value is called the **eigenvalue**. Eigen here is the German word meaning self or own.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is the eigenvalue, and the system is said to be in an eigenstate. Equation 9.3.2 states this principle mathematically for the case of energy as the observable.

Postulate III: Obtaining Observables Requires Solving Eigenvalue Problems

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

$$\hat{A}\,|\Psi\rangle = a|\,\Psi\rangle \tag{9.3.3}$$

Consider a general real-space operator $A(x)$. When this operator acts on a general wavefunction $\psi(x)$ the result is usually a wavefunction with a completely different shape. However, there are certain special wavefunctions which are such that when A acts on them the result is just a multiple of the original wavefunction. These special wavefunctions are called *eigenstates*, and the multiples are called *eigenvalues*. Thus, if

$$A\,|\psi_a(x)\rangle = a|\,\psi_a(x)\rangle \tag{9.3.4}$$

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

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

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

where use has been made of Equation 9.3.4 and the normalization condition. Moreover,

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

So the variance of A is

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

The fact that the variance is *zero* implies that every measurement of A is bound to yield the same result: namely, a. Thus, the eigenstate ψ_a is a state which is associated with a *unique* value of the dynamical variable corresponding to A. This unique value is simply the associated eigenvalue determined by Equation 9.3.4.

Expectation Values

We have seen that $|\psi(x,t)|^2$ is the probability density of a measurement of a particle's displacement yielding the value x at time t. Suppose that we made a large number of independent measurements of the displacement on an equally large number of identical quantum systems. In general, measurements made on different systems will yield different results. However, from the definition of probability, the mean of all these results is simply

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi|^2 dx \tag{9.3.5}$$

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

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)|\psi|^2 dx. \tag{9.3.6}$$

Postulate IV

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

$$\langle a\rangle = \langle \psi\,|a|\,\psi\rangle \tag{9.3.7}$$

$$= \int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx \tag{9.3.8}$$

If an unnormalized wavefunction where used, then Equation 9.3.8 changes to

$$\langle a\rangle = \frac{\langle \psi\,|a|\,\psi\rangle}{\langle\psi|\psi\rangle} \tag{9.3.9}$$

$$= \frac{\int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx}{\int_{-\infty}^{\infty} \psi^*\psi dx} \tag{9.3.10}$$

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

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x - \langle x\rangle)^2 |\psi|^2 dx \tag{9.3.11}$$

$$\equiv \langle x^2\rangle - \langle x\rangle^2, \tag{9.3.12}$$

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

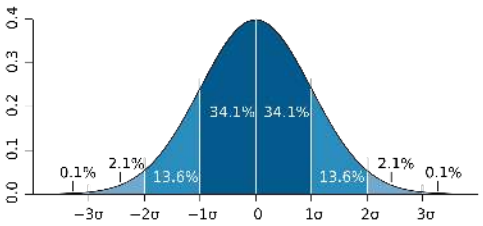


Figure 4.3.1 : A plot of a normal distribution (or bell-shaped curve) where each band has a width of 1 standard deviation. image usd with permission from Wikipedia.

Example 4.3.1

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

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

Solution

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

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

We can confirm that the wavefunction is normalized.

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

Hence, the Equation 9.3.8 is the relevant equation to use.

Solution a

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

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

Solution b

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

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

Solution c

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

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

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

Solution d

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

Expanding the Wavefunction

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

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

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

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

$$A\phi_i = a_i \phi_i$$

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

$$\int_{-\infty}^{\infty} \phi_i^* \phi_j dx = \delta_{ij}. \tag{9.3.13}$$

Here, δ_{ij} is called the **Kronecker delta-function**, and takes the value unity when its two indices are equal, and zero otherwise. It follows from Equations 9.3.10 and 9.3.13 that

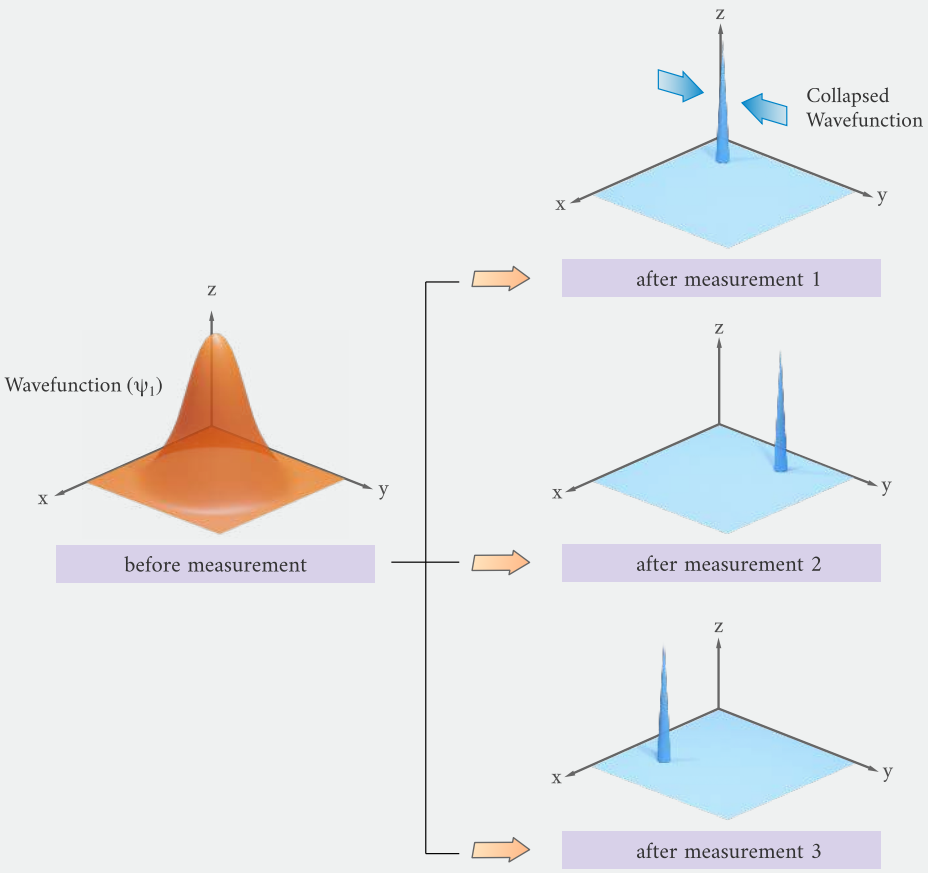
$$c_i = \int_{-\infty}^{\infty} \phi_i^* \psi dx. \tag{9.3.14}$$

Thus, the expansion coefficients in Equation 9.3.14 are easily determined, given the wavefunction ψ and the eigenstates ϕ_i. Moreover, if ψ is a properly normalized wavefunction then Equations 9.3.10 and 9.3.13 yield

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

Collapsing the Wavefunction

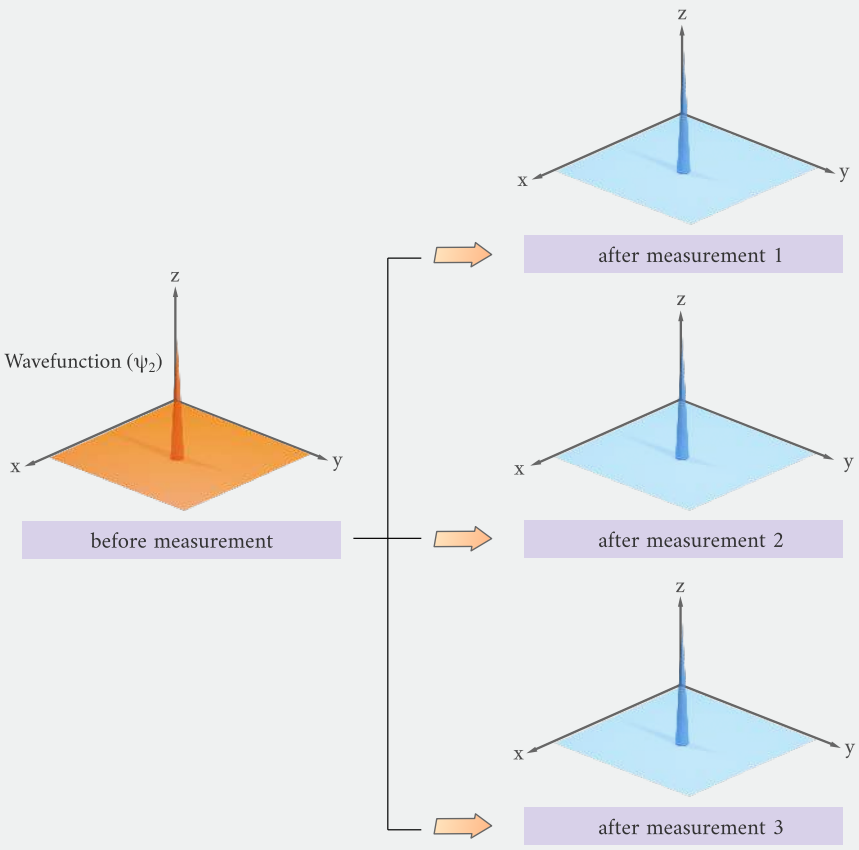
Wavefunction collapse is said to occur when a wavefunction—initially in a superposition of several eigenstates—appears to reduce to a single eigenstate (by "observation"). A particle (or a system in general) can be found in a given state $\psi(x,t)$. Suppose now a measurement is performed on the wavefuction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



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

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

https://chem.libretexts.org/@go/page/287022



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

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

Contributors and Attributions

- Richard Fitzpatrick (Professor of Physics, The University of Texas at Austin)
- Wikiversity

9.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators** is licensed CC BY-NC-SA 4.0.

9.4: The Time-Dependent Schrödinger Equation

Learning Objectives

- Recognize the differences between the time-dependent and the time-independent Schrödinger equations
- To distinguish between stationary and non-stationary wavefunctions

There are two "flavors" of Schrödinger equations: the time-dependent and the time-independent versions. While the time-dependent Schrödinger equation predicts that wavefunctions can form standing waves (called stationary states), that if classified and understood, then it becomes easier to solve the time-dependent Schrödinger equation for any state. Stationary states can also be described by the time-independent Schrödinger equation (used only when the Hamiltonian is not explicitly time dependent). However, it should be noted that the solutions to the time-independent Schrödinger equation still have time dependencies.

Time-Dependent Wavefunctions

Recall that the time-independent Schrödinger equation

$$\hat{H}\psi(x) = E\psi(x) \tag{9.4.1}$$

yields the allowed energies and corresponding wavefunctions. However, it does not tell us how the system evolves in time. It would seem that something is missing, since, after all, classical mechanics tells us how the positions and velocities of a classical system evolve in time. The time dependence is given by solving Newton's second law

$$m\frac{d^2x}{dt^2} = F(x) \tag{9.4.2}$$

But where is t in quantum mechanics? First of all, what is it that must evolve in time? The answer is that the wavefunction (and associated probability density) must evolve. Suppose, therefore, that we prepare a system at $t = 0$ according to a particular probability density $p(x, 0)$ related to an amplitude $\Psi(x, 0)$ by

$$p(x, 0) = |\Psi(x, 0)|^2 \tag{9.4.3}$$

How will this initial amplitude $\Psi(x, 0)$ look at time t later? Note, by the way, that $\Psi(x, 0)$ does *not* necessarily need to be one of the eigenstates $\psi_n(x)$. To address this, we refer to the time-dependent Schrödinger equation that tells us how $\Psi(x, t)$ will evolve starting from the initial condition $\Psi(x, 0)$:

$$\hat{H}\Psi(x, t) = i\hbar\frac{\partial}{\partial t}\Psi(x, t) \tag{9.4.4}$$

It is important to know how it works physically and when it is sufficient to work with the time-independent version of the Schrödinger equation (Equation 9.4.1).

Postulate V

The time dependence of wavefunctions is governed by the Time-Dependent Schrödinger Equation (Equation 9.4.4).

Stationary States

Suppose that we are lucky enough to choose

$$\Psi(x, 0) = \psi_n(x)$$

with corresponding probability density

$$p(x, 0) = |\psi_n(x)|^2 \tag{9.4.5}$$

We will show that

$$\Psi(x, t) = \psi_n(x)e^{-iE_nt/\hbar} \tag{9.4.6}$$

From the time-dependent Schrödinger equation

$$\frac{d\Psi}{dt} = \psi_n(x)\left(\frac{-iE_n}{\hbar}\right)e^{-iE_nt/\hbar}$$
$$i\hbar\frac{d\Psi}{dt} = E_n\psi_n(x)e^{-iE_nt/\hbar}$$

Similarly

$$\begin{aligned}\hat{H}\Psi(x,t) &= e^{-iE_nt/\hbar}\hat{H}\psi_n(x)\\ &= e^{-iE_nt/\hbar}E_n\psi_n(x)\end{aligned}$$

Hence $\psi_n(x)exp(-iE_nt/\hbar)$ satisfies the Time-Dependent Schrödinger Equation (Equation 9.4.4).

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

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

the probability does not change in time and for this reason, $\psi_n(x)$ is called a *stationary state*. In such a state, the energy remains **fixed** at the well-defined value E_n.

Nonstationary States

Suppose, however, that we had chosen $\Psi(x,0)$ to be some arbitrary linear combination of the two lowest energy states:

$$\Psi(x,0) = a\psi_1(x) + b\psi_2(x) \tag{9.4.7}$$

for example

$$\Psi(x,0) = \frac{1}{\sqrt{2}}[\psi_1(x) + \psi_2(x)] \tag{9.4.8}$$

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

$$p(x,t) = |\Psi(x,t)|^2 \neq p(x,0) \tag{9.4.9}$$

For such a mixture to be possible, there must be sufficient energy in the system that there is some probability of measuring the particle to be in its excited state.

Finally, suppose we start with a state

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

and we let this state evolve in time. At any point in time, the state $\Psi(x,t)$ will be some mixture of $\psi_1(x)$ and $\psi_2(x)$, and this mixture changes with time. Now, at some specific instance in time t, we measure the energy and obtain a value E_1. What is the state of the system *just after* the measurement is made? Once we make the measurement, then we know with 100% certainty that the energy is E_1. From the above discussion, there is only one possibility for the state of the system, and that has to be the wavefunction $\psi_1(x)$, since in this state we know with 100% certainty that the energy is E_1. Hence, just after the measurement, the state *must be* $\psi_1(x)$, which means that because of the measurement, any further dependence on $\psi_2(x)$ drops out, and for all time thereafter, there is *no* dependence on $\psi_2(x)$. Consequently, any subsequent measurement of the energy would yield the value E_1 with 100% certainty. This discontinuous change in the quantum state of the system as a result of the measurement is known as the **collapse of the wavefunction**. The idea that the evolution of a system can change as a result of a measurement is one of the topics that is currently debated among quantum theorists.

The Quantum Observer Effect

> The fact that measuring a quantum system changes its time evolution means that the experimenter is now coupled to the quantum system. This **observer effect** means that the act of observing will influence the phenomenon being observed. In classical mechanics, this coupling does not exist. A classical system will evolve according to Newton's laws of motion independent of whether or not we observe it. This is not true for quantum systems. The very act of observing the system changes how it evolves in time.
>
> Put another way, by simply observing a system, we change it!

9.4: The Time-Dependent Schrödinger Equation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **4.4: The Time-Dependent Schrödinger Equation** by Mark E. Tuckerman is licensed CC BY-NC-SA 4.0.

9.5: The Eigenfunctions of Operators are Orthogonal

Learning Objectives

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

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

Hermitian Operators

Since the eigenvalues of a quantum mechanical operator correspond to measurable quantities, the eigenvalues must be real, and consequently a quantum mechanical operator must be Hermitian. To prove this, we start with the premises that ψ and φ are functions, $\int d\tau$ represents integration over all coordinates, and the operator $\hat{A}$ is **Hermitian** by definition if

$$\int \psi^* \hat{A} \psi \, d\tau = \int (\hat{A}^* \psi^*) \psi \, d\tau \tag{9.5.1}$$

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

$$\hat{A}\psi = a\psi \tag{9.5.2}$$

$$\hat{A}^* \psi^* = a^* \psi^* = a\psi^* \tag{9.5.3}$$

Note that $a^* = a$ because the eigenvalue is real. Multiply Equation 9.5.2 and 9.5.3 from the left by ψ^* and ψ, respectively, and integrate over the full range of all the coordinates. Note that ψ is normalized. The results are

$$\int \psi^* \hat{A} \psi \, d\tau = a \int \psi^* \psi \, d\tau = a \tag{9.5.4}$$

$$\int \psi \hat{A}^* \psi^* \, d\tau = a \int \psi \psi^* \, d\tau = a \tag{9.5.5}$$

Since both integrals equal a, they must be equivalent.

$$\int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau \tag{9.5.6}$$

The operator acting on the function,

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

produces a new function. Since functions commute, Equation 9.5.6 can be rewritten as

$$\int \psi^* \hat{A} \psi d\tau = \int (\hat{A}^* \psi^*) \psi d\tau \tag{9.5.7}$$

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

Orthogonality Theorem

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

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

Proof

ψ and φ are two eigenfunctions of the operator Â with real eigenvalues a_1 and a_2, respectively. Since the eigenvalues are real, $a_1^* = a_1$ and $a_2^* = a_2$.

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

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

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

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

$$\int \psi \hat{A}^*\psi^* \, d\tau = a_2 \int \psi\psi^* \, d\tau \tag{9.5.8}$$

Subtract the two equations in Equation 9.5.8 to obtain

$$\int \psi^* \hat{A}\psi \, d\tau - \int \psi \hat{A}^*\psi^* \, d\tau = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{9.5.9}$$

The left-hand side of Equation 9.5.9 is zero because $\hat{A}$ is Hermitian yielding

$$0 = (a_1 - a_2) \int \psi^*\psi \, d\tau \tag{9.5.10}$$

If a_1 and a_2 in Equation 9.5.10 are not equal, then the integral **must** be zero. This result proves that **nondegenerate eigenfunctions** of the same operator are orthogonal.

□

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

$$\int_{-\infty}^{\infty} \psi_1^*\psi_2 \, dx = 0. \tag{9.5.11}$$

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

$$A\psi_a = a\psi_a \tag{9.5.12}$$

$$A\psi_a' = a'\psi_a' \tag{9.5.13}$$

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

$$\int_{-\infty}^{\infty} (A\psi_a)^*\psi_{a'} dx = a \int_{-\infty}^{\infty} \psi_a^*\psi_{a'} dx, \tag{9.5.14}$$

$$\int_{-\infty}^{\infty} \psi_a^*(A\psi_{a'}) dx = a' \int_{-\infty}^{\infty} \psi_a^*\psi_{a'} dx. \tag{9.5.15}$$

However, from Equation 9.5.9, the left-hand sides of the above two equations are equal. Hence, we can write

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

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

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

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

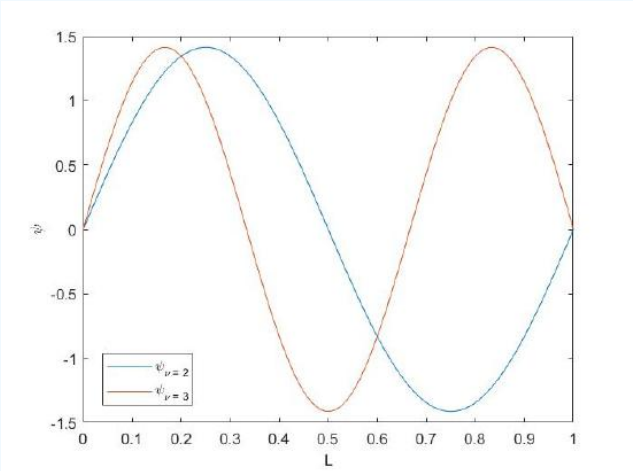
> The eigenvalues of operators associated with experimental measurements are all *real*.

Example4.5.1

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

Solution

The two PIB wavefunctions are qualitatively similar when plotted



These wavefunctions are orthogonal when

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

and when the PIB wavefunctions are substituted this integral becomes

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

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

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

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

Orthogonality of Degenerate Eigenstates

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

$$S = \int_{-\infty}^{\infty} \psi_a^* \psi_a' dx, \tag{9.5.16}$$

It is easily demonstrated (but not here) that

$$\psi_a'' = \frac{|S|}{\sqrt{1-|S|^2}} \left(\psi_a - S^{-1}\psi_a'\right) \tag{9.5.17}$$

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

Theorem: Gram-Schmidt Orthogonalization

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

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

Proof

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

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

then ψ_a and ψ_a'' will be orthogonal.

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

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

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.

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

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

Contributors and Attributions

- Richard Fitzpatrick (Professor of Physics, The University of Texas at Austin)

9.5: The Eigenfunctions of Operators are Orthogonal is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **4.5: Eigenfunctions of Operators are Orthogonal** is licensed CC BY-NC-SA 4.0.

9.6: Heisenburg Uncertainy Principle III - Commuting Operators

Learning Objectives

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

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

Commuting Operators

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

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

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

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

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

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

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

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

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

$$\hat{B}\hat{A}\psi = \hat{A}\hat{B}\psi = \hat{A}b\psi = b\hat{A}\psi \tag{9.6.1}$$

Equation 9.6.1 says that $\hat{A}\psi$ is an eigenfunction of $\hat{B}$ with eigenvalue b, which means that when $\hat{A}$ operates on ψ, it cannot change ψ. At most, $\hat{A}$ operating on ψ can produce a constant times ψ.

$$\hat{A}\psi = a\psi \tag{9.6.2}$$

$$\hat{B}(\hat{A}\psi) = \hat{B}(a\psi) = a\hat{B}\psi = ab\psi = b(a\psi) \tag{9.6.3}$$

Equation 9.6.3 shows that Equation 9.6.2 is consistent with Equation 9.6.1. Consequently ψ also is an eigenfunction of $\hat{A}$ with eigenvalue a.

Example 4.6.1

Do the following pairs of operators commute?

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

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

$$\sigma_A \sigma_B \geq \left| \int \psi^* [\hat{A}\hat{B} - \hat{B}\hat{A}] \psi \, d\tau \right| \tag{9.6.4}$$

where the integral inside the square brackets is called the **commutator**, and $\left| \right|$ signifies the modulus or absolute value. If $\hat{A}$ and $\hat{B}$ commute, then the right-hand-side of Equation 9.6.4 is zero, so either or both σ_A and σ_B could be zero, and there is no restriction on the uncertainties in the measurements of the eigenvalues a and b. If $\hat{A}$ and $\hat{B}$ do not commute, then the right-hand-side of Equation 9.6.4 will not be zero, and neither σ_A nor σ_B can be zero unless the other is infinite. Consequently, both a and b cannot be eigenvalues of the same wavefunctions and cannot be measured simultaneously to arbitrary precision.

? Exercise4.6.1

Show that the commutator for position and momentum in one dimension equals $-i\hbar$ and that the right-hand-side of Equation 9.6.4 therefore equals $\hbar/2$ giving $\sigma_x \sigma_{px} \geq \frac{\hbar}{2}$.

Applications

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

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

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

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

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

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

9.6.2A ✓ Example

Determine whether the following two operators commute:

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

and

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

9.6.2B ✓ Example

Determine whether the following two operators commute:

$$\hat{I} = 5$$

and

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

9.6.2C? Exercise

Show that the components of the angular momentum do not commute.

$$\hat{L}_x = -i\hbar\left[-\sin\left(\phi\frac{\delta}{\delta\theta}\right) - \cot(\Theta)\cos\left(\phi\frac{\delta}{\delta\phi}\right)\right]$$

$$\hat{L}_y = -i\hbar\left[\cos\left(\phi\frac{\delta}{\delta\theta}\right) - \cot(\Theta)\cos\left(\phi\frac{\delta}{\delta\phi}\right)\right]$$

$$\hat{L}_z = -i\hbar\frac{\delta}{\delta\theta}$$

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

9.6: Heisenburg Uncertainy Principle III - Commuting Operators is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **4.6: Commuting Operators Allow Infinite Precision** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

9.7: Postulates and Principles of Quantum Mechanics (Exercises)

Solutions to select questions can be found online.

4.3

The function $\psi^*\psi$ has to be real, nonnegative, finite, and of definite value everywhere. Why?

4.5

Why are the following functions not acceptable wave functions for a 1D particle in a box with length a ? N is a normalization constant.

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

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

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

4.12

Show that the sets of functions: $\sqrt{\dfrac{2}{L}}\sin\left(\dfrac{n\pi x}{L}\right)$ where n = 1,2,3... is orthonormal.

4.13

Show that $a\cdot b\cdot c = \sum_{ik} a_i b_i c_k e_k$

$$\sum_i a_i e_i \cdot \sum_j b_j e_j \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$\sum_i \sum_j a_i b_j (e_i \cdot e_j) \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$e_i \cdot e_j = \delta_{ij} = 1$$

when $i = j$

$$\sum_i a_i b_i \cdot \sum_k c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

$$\sum_{ik} a_i b_i c_k e_k = \sum_{ik} a_i b_i c_k e_k$$

4.14

Determine if the following operators commute

$$\hat{B} = \frac{d}{dx}$$

and

$$\hat{C} = x^5$$

4.15

Do the following combinations of angular momentum operators commute? Show work to the justify the answer (do not just write "yes" or no").

a. $\mathbf{L}_x$ and $\mathbf{L}_y$

b. $\mathbf{L}_y$ and $\mathbf{L}_z$

c. $\mathbf{L}_z$ and $\mathbf{L}_x$

with

$$\mathbf{L}_x = -\mathrm{i}\,\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\mathbf{L}_y = -\mathrm{i}\,\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\mathbf{L}_z = -\mathrm{i}\,\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Estimate the answer to Part C based on the pattern gathered from parts A and B; no work necessary for Part C.

4.17

For two operators to commute, what property must hold? Use the operators $\hat{L}^2$ and $\hat{L}_z$ as an example to show that this property holds.

4.21

Show that the angular momentum and kinetic energy operators commute and therefore can be measured simultaneously to arbitrary precision.

4.22

Show that the position and angular momentum operator commutes. Can the position and angular momentum be measured simultaneously to a arbitrary precision?

4.25

If both $|\Psi_n\rangle$ and $|\Psi_m\rangle$ satisfy the **time-independent** Schrödinger Equation (these are called *stationary states*)

$$|\Psi_n(x,t)\rangle = \Psi_n(x)e^{-iE_n t/\hbar}$$

and

$$|\Psi_m(x,t)\rangle = \Psi_m(x)e^{-iE_m t/\hbar}$$

show that any linear superposition of the two wavefunctions

$$|\Psi(x,t)\rangle = c_n|\Psi_n(x,t)\rangle + c_m|\Psi_m(x,t)\rangle$$

also satisfies the **time-dependent** Schrödinger Equation.

4.26

Starting with

$$\langle x \rangle = \int \psi^*(x,t) x \psi(x,t) dx$$

and the time-independent Schrödinger equation, demonstrate that

$$\frac{d\langle x \rangle}{dt} = \int \psi^* \frac{i}{\hbar} (\hat{H}x - x\hat{H}) \psi dx$$

Given that

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

show that

$$\hat{H}x - x\hat{H} = -2\frac{\hbar^2}{2m}\frac{d}{dx}$$
$$= -\frac{\hbar^2}{m}\frac{i}{\hbar}\hat{P}_x = -\frac{ih}{m}\hat{P}_x$$

4.28

Derive the condition on operators that arises from forcing eigenvalues to be real with complex conjugates.

4.31

Prove that the position operator is Hermitian.

4.31

Prove that the momentum operator is a Hermitian

4.32

Which of the following operators are Hermitian:

a. x,
b. d/dx
c. hd^2/dx^2
d. id^2/dx^2

4.32

Determine whether the following operators are Hermitian and whether they commute:

$$\hat{A} = i\frac{d}{dx}$$

and

$$\hat{B} = i\frac{d^2}{dx^2}$$

Given that -∞<x<∞ and the operators functions are well behaved.

4.34

Consider two wavefunctions

$$\psi_1(x) = A\sin(k_1 x) + B\cos(k_1 x) \quad (9.7.1)$$

and

$$\psi_2(x) = C\sin(k_2 x) + D\cos(k_2 x)$$

Given the boundary conditions are:

$$\psi(0) = 0$$

and

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

$$A + B = C, k_1(A - B) = k_2 C$$

and given a expression of

$$R = \frac{B^2}{A^2} \quad (9.7.2)$$

Derive the simplest expression of R based on the terms from the boundary conditions provided above.

4.34

A particle is moving in a field. Half-way through the field, there is a line that represents potential energy. To the left of the line, the potential energy is

$$x < 0$$

and to the right of the line the potential energy is

$$x > 0$$

. If the particle's energy is less than the potential energy line will the particle reflect when the its energy is greater than the Potential energy barrier height?

9.7: Postulates and Principles of Quantum Mechanics (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

10: The Harmonic Oscillator and the Rigid Rotor

- **The harmonic oscillator is common:** It appears in many everyday examples: Pendulums, springs, electronics (such as the RLC circuit), standing waves on a string, etc. It's trivial to set up demonstrations of these phenomena, and we see them constantly.
- **The harmonic oscillator is intuitive:** We can picture the forces on systems such as pendulum or a plucked string. This makes it simple to study in the classroom. In contrast, there are many "everyday" examples that are not intuitive.
- **The harmonic oscillator is mathematically simple:** Math is part of physics. In studying simple harmonic motion, students can immediately use the formulas that describe its motion. These formulas are understandable: for example, the equation for frequency shows the intuitive result that increasing spring stiffness increases frequency.

10.1: A Harmonic Oscillator Obeys Hooke's Law

10.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

10.3: The Harmonic Oscillator is an Approximation

10.4: The Harmonic Oscillator Energy Levels

10.5: The Harmonic Oscillator and Infrared Spectra

10.6: The Harmonic-Oscillator Wavefunctions Involve Hermite Polynomials

10.7: Hermite Polynomials are either Even or Odd Functions

10.8: The Energy Levels of a Rigid Rotor

10.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

10.10: The Harmonic Oscillator and the Rigid Rotor (Exercises)

10: The Harmonic Oscillator and the Rigid Rotor is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

10.1: A Harmonic Oscillator Obeys Hooke's Law

The motion of two atoms in a diatomic molecule can be separated into translational, vibrational, and rotational motions. Both rotation and vibrational motions are internal motions that do not change the center of mass for the molecule (Figure 5.1.1), which is described by translational motion. Quantum translational motions can be modeled with the particle in a box model discussed previously and rotation and vibration can be modeled via the **rigid rotor** and **harmonic oscillator** models, respectively.



Figure 5.1.1 : Two atoms connected by a vibrating bond. There is a rotation around the common center of mass, and oscillation in bond distance. (CC SA-BY, 3.0; www.cleonis.nl).

Before delving into the quantum mechanical harmonic oscillator, we will introduce the classical harmonic oscillator (i.e., involving classical mechanics) to build an intuition that we will extend to the quantum world. A classical description of the vibration of a diatomic molecule is needed because the quantum mechanical description begins with replacing the classical energy with the Hamiltonian operator in the Schrödinger equation. It also is interesting to compare and contrast the classical description with the quantum mechanical picture.

The Classical Harmonic Oscillator

Simple harmonic oscillators about a potential energy minimum can be thought of as a ball rolling frictionlessly in a curved dish or a pendulum swinging frictionlessly back and forth (Figure 5.1.2). The restoring forces are precisely the same in either horizontal direction.

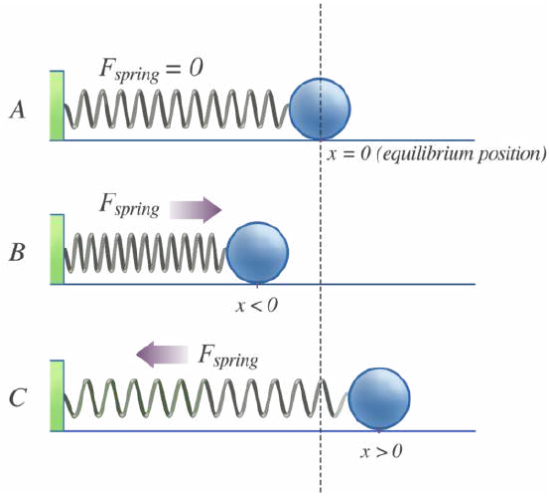


Figure 5.1.2 : A mass connected to a spring that follows Hooke's law is a system that, when displaced from its equilibrium position ($x_o = 0$), experiences a restoring force, F that is proportional to the displacement, x from the equilibrium length (x_o). (CC BY-NC; Ümit Kaya via LibreTexts)

If we consider the bond to behave like a mass on a spring (Figure 5.1.2), then this restoring force (F) is proportional to the displacement (x) from the equilibrium length (x_o) - this is *Hooke's Law*:

$$F = -kx \tag{10.1.1}$$

where k is the force constant. Hooke's Law says that the force is proportional to, but in opposite direction to, the displacement (x). The force constant reflects the **stiffness** of the spring. The idea incorporated into the application of Hooke's Law to a diatomic molecule is that when the atoms move away from their equilibrium positions, a restoring force is produced that increases proportionally with the displacement from equilibrium. The potential energy for such a system increases *quadratically* with the displacement.

$$V(x) = \frac{1}{2}kx^2 \tag{10.1.2}$$

Hooke's Law or the harmonic (i.e. quadratic) potential given by Equation 10.1.2 is an excellent *approximation* for the vibrational oscillations of molecules. The magnitude of the force constant k depends upon the nature of the chemical bond in molecular systems just as it depends on the nature of the spring in mechanical systems. The larger the force constant, the stiffer the spring or the stiffer the bond. Since it is the electron distribution between the two positively charged nuclei that holds them together, a double bond with more electrons has a larger force constant than a single bond, and the nuclei are held together more tightly.

Caution

A stiff bond with a large force constant is not necessarily a strong bond with a large dissociation energy. A harmonic oscillator has no dissociation energy since it CANNOT be broken - there is always a restoring force to keep the molecule together. This is one of many deficiencies in using the harmonic oscillator model to describe molecular vibrations.

Two atoms or one?

You may have questioned the applicability of the harmonic oscillator model involving one moving mass bound to a fix wall via a spring like in Figure 5.1.2 for the vibration of a diatomic molecule with two moving masses like in Figure 5.1.1 . It turned out the two are mathematically the same with internal vibration motion described by a single reduced particle with a reduced mass μ.

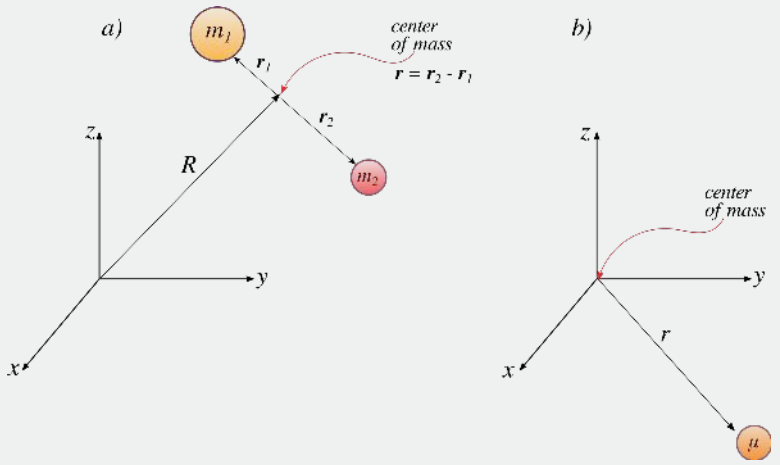


Figure 5.1.3 : Diagrams of the coordinate systems and relevant vectors for the motion of (a) a two-particle diatomic molecule with atoms of mass m_1 and m_2 and (b) the equivalent one-particle pseudo-particle of reduced mass μ. (CC BY-NC; Ümit Kaya via LibreTexts)

For a diatomic molecule, Figure 5.1.3 , the vector $\vec{r}$ corresponds to the internuclear axis. The magnitude or length of r is the bond length, and the orientation of r in space gives the orientation of the internuclear axis in space. Changes in the orientation correspond to rotation of the molecule, and changes in the length correspond to vibration. The change in the bond length from the equilibrium bond length is the **vibrational coordinate** for a diatomic molecule.

Example 5.1.1

a. Show that minus the first derivative of the harmonic potential energy function in Equation 10.1.2 with respect to x is the Hooke's Law force in Equation 10.1.1.
b. Show that the second derivative is the force constant, k.
c. At what value of x is the potential energy a minimum; at what value of x is the force zero?
d. Sketch graphs to compare the potential energy and the force for a system with a large force constant to one with a small force constant.

Solution a

Hooke's Law for a spring entails that the force applied on a spring F is equal to the force constant, $-k$ times the distance compressed or stretched, x (Equation 10.1.1). The derivative of $V(x) = 0.5kx^2$ is

$$V'(x) = (2)\left(\frac{1}{2}\right)kx = kx.$$

The negative of this is $-V'(x) = -kx$ which is exactly equal to Hooke's Law.

Solution b

The second derivative

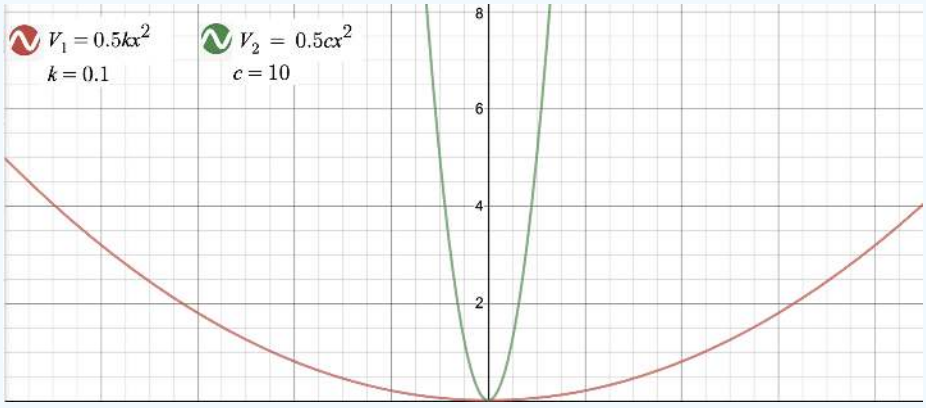
$$V''(x) = \frac{d}{dx}kx = k$$

Thus, the second derivative of this equation for potential energy is equal to the force constant, k.

Solution c

To find the minimum potential energy, it is easiest to set the first derivative equal to zero and solve for x. When $V'(x) = kx = 0$ then x must be equal to zero. Thus, the minimum potential energy is when x=0. Plugging this into Hooke's Law, $F(0) = -k(0) = 0$ so this is also the value for x when the force is zero.

Solution d



The force constant has a drastic effect on both the potential energy and the force. A system with a large force constant requires minimal change in x to have a drastic change in potential energy or force, whereas a system with a small force constant is the exact opposite phenomenon.

Solving the Harmonic Oscillator Model

The classical equation of motion for a one-dimensional simple harmonic oscillator with a particle of mass m attached to a spring having spring constant k is

$$m\frac{d^2x(t)}{dt^2} = -kx(t) \tag{10.1.3}$$

which can be rewritten in the standardform:

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0 \tag{10.1.4}$$

Equation 10.1.3 is a linear second-order differential equation that can be solved by the standard method of factoring and integrating. The resulting solution to Equation 10.1.3 is

$$x(t) = x_o \sin(\omega t + \phi) \tag{10.1.5}$$

with

$$\omega = \sqrt{\frac{k}{m}} \tag{10.1.6}$$

and the momentum has time dependence

$$\begin{aligned} p &= mv \\ &= mx_o\omega\cos(\omega t + \phi) \end{aligned}$$

Figure 5.1.4 show the displacement of the bond from its equilibrium length as a function of time. Such motion is called **harmonic**.

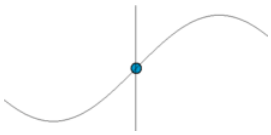


Figure 5.1.4 : Solution to the Harmonic Oscillator. Displacement (y-axis) is plotted as a function of time.

Example 5.1.2

Substitute the following functions into Equation 10.1.4 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 10.1.4.

$$\begin{aligned} \frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) &= 0 \\ \frac{d^2}{dt^2}\left(x_oe^{i\omega t}\right) + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_o\frac{d^2}{dt^2}\left(e^{i\omega t}\right) + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_oi^2\omega^2\left(e^{i\omega t}\right) + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_oi^2\omega^2e^{i\omega t} + \frac{k}{m}x_oe^{i\omega t} &= 0 \\ x_oi^2\omega^2 + \frac{k}{m}x_o &= 0 \\ -x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \;\text{ with }\; \omega &= \sqrt{\frac{k}{m}} \end{aligned}$$

Solution b

This requires simply placing the given function $x(t) = x_0e^{-i\omega t}$ into Equation 10.1.4.

$$\frac{d^2x(t)}{dt^2} + \frac{k}{m}x(t) = 0$$

$$\frac{d^2}{dt^2}\left(x_o e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o\frac{d^2}{dt^2}\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2\left(e^{-i\omega t}\right) + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 e^{-i\omega t} + \frac{k}{m}x_o e^{-i\omega t} = 0$$

$$x_o i^2\omega^2 + \frac{k}{m}x_o = 0$$

$$-x_o\frac{k}{m} + \frac{k}{m}x_o = 0 \text{ with } \omega = \sqrt{\frac{k}{m}}$$

? Exercise 5.1.1

Show that sine and cosine functions also are solutions to Equation 10.1.4.

? 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?

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

$$p = m\frac{dx}{dt} \tag{10.1.7}$$

so combining Equations 10.1.7 and 10.1.2, the total energy can be written as

$$E = T + V \tag{10.1.8}$$

$$= \frac{p^2}{2m} + \frac{k}{2}x^2 \tag{10.1.9}$$

The total energy of the harmonic oscillator is equal to the maximum potential energy stored in the spring when $x = \pm A$, called the *turning points (*Figure 5.1.5). The total energy (Equation 10.1.9) is continuously being shifted between potential energy stored in the spring and kinetic energy of the mass.

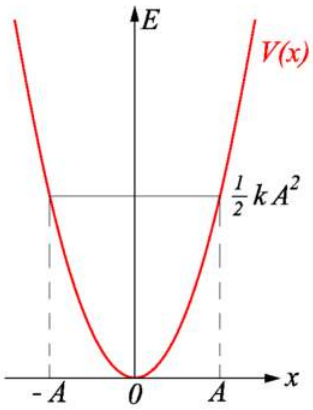


Figure 5.1.5 : The potential $V(x)$ for a harmonic oscillator. Vertical axis energy; horizontal axis displacement x. The potential energy $V(x) = ½kx^2$ is shown in red. (Paul Wormer Wikipedia).

The motion of a classical oscillator is confined to the region where its kinetic energy is nonnegative, which is what the energy relation Equation 10.1.9 says. Physically, it means that a classical oscillator can never be found beyond its turning points, and its energy depends only on how far the turning points are from its equilibrium position. The energy of a classical oscillator changes in a continuous way. The lowest energy that a classical oscillator may have is zero, which corresponds to a situation where an object is at rest at its equilibrium position. The zero-energy state of a classical oscillator simply means no oscillations and no motion at all (a classical particle sitting at the bottom of the potential well in Figure 5.1.5). When an object oscillates, no matter how big or small its energy may be, it spends the longest time near the turning points, because this is where it slows down and reverses its direction of motion. Therefore, the probability of finding a classical oscillator between the turning points is highest near the turning points and lowest at the equilibrium position. (Note that this is not a statement of preference of the object to go to lower energy. It is a statement about how quickly the object moves through various regions.)

Example5.1.3

a. What happens to the frequency of the oscillation as the vibration is excited with more and more energy?
b. What happens to the maximum amplitude of the vibration as it is excited with more and more energy?

Solution

a. Frequency

The energy of the harmonic oscillator can be written as

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$

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?

10.1: A Harmonic Oscillator Obeys Hooke's Law is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.1: A Harmonic Oscillator Obeys Hooke's Law** by Michael Fowler is licensed CC BY-NC-SA 4.0.

10.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

For studying the energetics of molecular vibration we take the simplest example, a diatomic heteronuclear molecule **AB**. Let the respective masses of atoms **A** and **B** be m_A and m_B. For diatomic molecules, we define the reduced mass μ_{AB} by:

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} \tag{10.2.1}$$

Reduced mass is the representation of a two-body system as a single-body one. When the motion (displacement, vibrational, rotational) of two bodies are only under mutual interactions, the inertial mass of the moving body with respect to the body at rest can be simplified to a reduced mass.

Reduced Mass

Viewing the multi-body system as a single particle allows the separation of the motion: vibration and rotation, of the particle from the displacement of the center of mass. This approach greatly simplifies many calculations and problems.

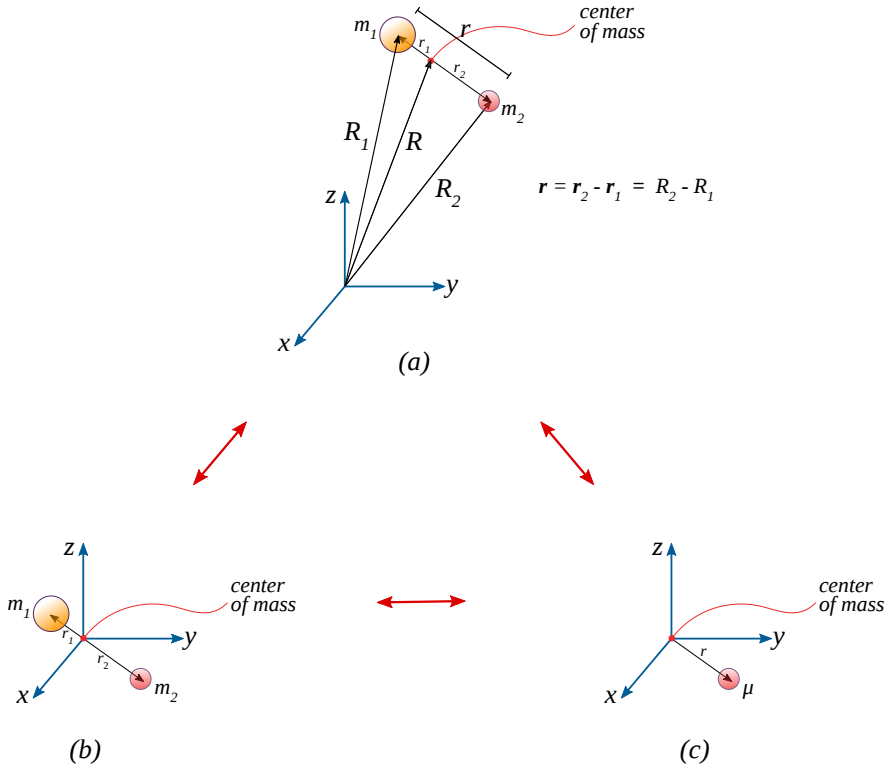


Figure 5.2.1 : a) the individual vectors to the particles m_1 and m_2 in the coordinate space and the resultant vector. b) center of mass. c) reduced mass. (CC BY-NC; Ümit Kaya via LibreTexts)

This concept is readily used in the general motion of diatomics, i.e. simple harmonic oscillator (vibrational displacement between two bodies, following Hooke's Law), the rigid rotor approximation (the moment of inertia about the center of mass of a two-body system), spectroscopy, and many other applications.

Example 5.2.1 : Reduced Mass

Determine the reduced mass of the two body system of a proton and electron with $m_{proton} = 1.6727 \times 10^{-27}\ kg$ and $m_{electron} = 9.110 \times 10^{-31}\ kg$).

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

$$V(x) \approx \frac{1}{2}kx^2 \tag{10.2.2}$$

One problem with this classical formulation is that it is not general. We cannot use it, for example, to describe vibrations of diatomic molecules, where quantum effects are important. This require the formulation for Schrödinger Equation using Equation 10.2.2.

$$\hat{H}\left|\psi\right\rangle = \left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]\left|\psi\right\rangle = E|\psi\rangle$$

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):

$$E_v = \hbar\left(\sqrt{\frac{k}{\mu}}\right)\left(v + \frac{1}{2}\right) \tag{10.2.3}$$

$$= h\nu\left(v + \frac{1}{2}\right) \tag{10.2.4}$$

with the natural vibrational frequency of the system given as

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{10.2.5}$$

and the mass, μ, is the reduced mass of the system (Equation 10.2.1).

Warning

Be careful to distinguish ν, the symbol for the natural frequency (as a Greek nu) from v the quantum harmonic oscillator quantum number (Latin v).

Caution: Do Not Use Atomic Weights to Calculate Reduced Masses

The vibrational frequencies given by Equation 10.2.5 depend on the force constants (k) and the atomic masses of the vibrating nuclei via the reduced mass (μ). It should be clear that the substitution of one isotope of an atom in a molecule for another isotope will affect the atomic masses and therefore the reduced mass (via Equation 10.2.1) and therefore the vibrational frequencies (via Equation 10.2.5).

It is important to remember that the Periodic Table gives only atomic weights of elements, which are scaled averages of atoms normally encountered in the laboratory (Table 5.2.1). To properly discuss vibrational frequencies of molecules, we need to know (or denote) the specific isotopes in the molecule. Check Table A4 for that information.

Table 5.2.1: Atomic Mass and Isotope Composition. Consult Table A4 for more extensive table.

isotope	atomic mass (in amu)	isotopic abundance (%)
^{1}H	1.007825	99.985
^{2}H	2.0140	0.015
^{35}Cl	35.968852	75.77
^{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 10.2.5 is used to predict the respective vibrational frequencies of these two molecules.

For $^{1}H^{35}Cl$:

$$\begin{aligned}\nu &= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \\ &= \frac{1}{2\pi}\sqrt{\frac{478\,N/m}{1.629 \times 10^{-27}\,kg}} \\ &= 8.6394 \times 10^{13} s^{-1}\end{aligned}$$

For $^{1}H^{37}Cl$:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{478\,N/m}{1.629 \times 10^{-27}\,kg}}$$

$$= 8.621 \times 10^{13} s^{-1}$$

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.

10.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule** by Eugene Lee is licensed CC BY-NC-SA 4.0.

10.3: The Harmonic Oscillator is an Approximation

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

$$V(x) = V(x_0) + \left.\frac{dV(x)}{dx}\right|_{x_0}^{x} (x - x_0) + \frac{1}{2!}\left.\frac{d^2V(x)}{dx^2}\right|_{x_0}^{x} (x - x_0)^2 + \ldots + \frac{1}{n!}\left.\frac{d^nV(x)}{dx^n}\right|_{x_0}^{x} (x - x_0)^n \tag{10.3.1}$$

It is important to note that this approximation is only good for x near x_0, and that x_0 stands for the equilibrium bond distance. $V(x)$ is often (but not always) shortened to the cubic term and can be rewritten as

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 \tag{10.3.2}$$

where $V(x_0) = 0$, k is the harmonic force constant (harmonic term), and γ is the first anharmonic term (i.e., cubic). As Figure 5.3.2 demonstrates, the harmonic oscillator (red curve) is a good approximation for the exact potential energy of a vibration (blue curve).

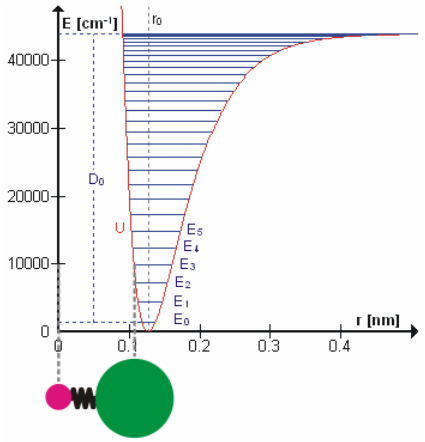


Figure 5.3.1 : The vibration of the **HCl** molecule is really an anharmonic oscillator, but can be approximated as a harmonic oscillator at low energies. In this animation, **HCl** is vibrating at the E_3 energy level. D_0 is dissociation energy here, r_0 bond length, V potential energy. Energy is expressed in wavenumbers. The hydrogen chloride molecule is attached to the coordinate system to show bond length changes on the curve. (CC BY-SA 3.0; Darekk2 via Wikipedia).

Adding anharmonic perturbations to the harmonic oscillator (Equation 10.3.2) better describes molecular vibrations. Anharmonic oscillation is defined as the deviation of a system from harmonic oscillation, or an oscillator not oscillating in simple harmonic motion. Anharmonic oscillation is described as the restoring force is no longer proportional to the displacement. Adding the cubic term (Figure 5.3.2 ; green curve) improves the harmonic oscillation approximation especially under greater displacement from equilibrium.

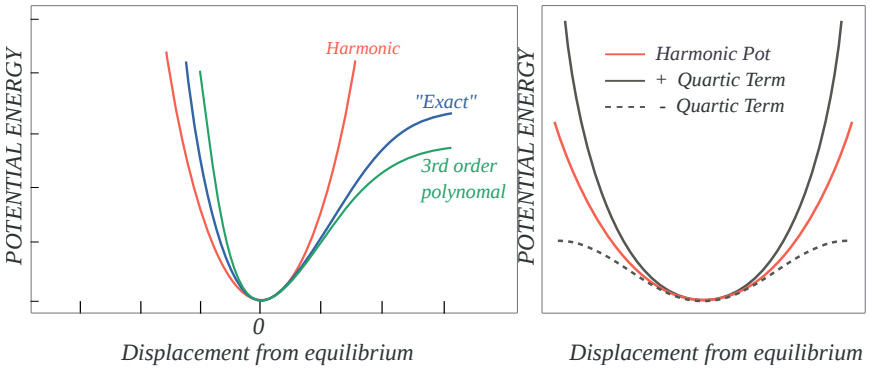


Figure 5.3.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

Naturally, adding higher order anharmonic terms, like quartic terms (Figure **10.3.2;**) 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 10.3.1.

Figure 5.3.1 shows the the general potential with (numerically) calculated energy levels (E_0, E_1 etc.). D_o is the dissociation energy, which is different from the well depth D_e. These vibrational energy levels of this plot can be calculated using the harmonic oscillator model (i.e., Equation 5.3.1 with the Schrödinger equation) and have the general form

$$E_v = \left(v + \frac{1}{2}\right) v_e - \left(v + \frac{1}{2}\right)^2 v_e x_e + \left(v + \frac{1}{2}\right)^3 v_e y_e + \text{higher terms}$$

where v is the vibrational quantum number and x_e and y_e are the first and second anharmonicity constants, respectively.

The $v = 0$ level is the vibrational ground state. Because this potential is less confining than a parabola used in the harmonic oscillator, the energy levels become **less widely** spaced at high excitation (Figure 5.3.1 ; top of potential).

Limitations of the Harmonic Oscillator Model for Molecular Vibrations

The harmonic oscillation is a great approximation of a molecular vibration, but has key limitations:

- Due to equal spacing of energy, all transitions occur at the **same** frequency (i.e. single line spectrum). However experimentally many lines are often observed (called overtones).
- The harmonic oscillator does not predict bond dissociation; you cannot break it no matter how much energy is introduced.

Morse Potentials are better Approximations of Vibrational Motion

A more powerful approach than just "patching up" the harmonic oscillator solution with anharmonic corrections is to adopt a different potential ($V(x)$). One such approach is the Morse potential, named after physicist Philip M. Morse, and a better approximation for the vibrational structure of the molecule than the harmonic oscillator because it explicitly includes the effects of *bond breaking* and accounts for the anharmonicity of real bonds (Figure 5.3.4).

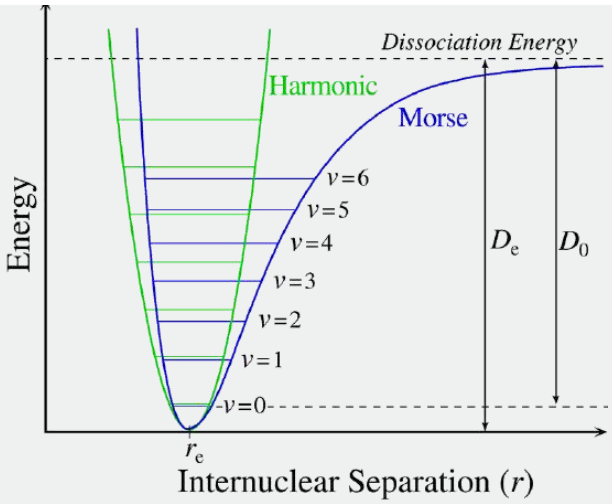


Figure 5.3.4 : The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by ħω, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e is larger than the true energy required for dissociation D_0 due to the zero point energy of the lowest ($v = 0$) vibrational level. from Wikipedia.

The Morse Potential is a good approximation to $V(x)$ and is best when looking for a general formula for all x from 0 to ∞, not just applicable for the local region around the x_o:

$$V(x) = D(1 - e^{-\beta(x-x_0)})^2 \tag{10.3.3}$$

with $V(x = x_0) = 0$ and $V(x = \infty) = D$.

The Morse Potential (Figure 5.3.4) approaches zero at infinite r_e and equals $-D_e$ at its minimum (i.e. $r = r_e$). It clearly shows that the Morse potential is the combination of a short-range repulsion term (small r values) and a long-range attractive term (large r values).

Solving the Schrödinger Equation with the Morse Potential (Equation 10.3.3) is not trivial, but can be done analytically.

$$\hat{H}\,|\psi\rangle = E_n|\,\psi\rangle$$

with

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} \\ &= \frac{-\hbar^2 d^2}{2m\,dx^2} + D(1 - e^{-\beta(x-x_0)})^2\end{aligned}$$

The solutions and energies for the Morse potential will not be used in this course and will not be discussed in more detail.

10.3: The Harmonic Oscillator is an Approximation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.3: The Harmonic Oscillator Approximates Molecular Vibrations** by Peter Kelly is licensed CC BY 4.0.

10.4: The Harmonic Oscillator Energy Levels

For a classical oscillator, we know exactly the position, velocity, and momentum as a function of time. The frequency of the oscillator (or normal mode) is determined by the reduced mass μ and the effective force constant k of the oscillating system and does not change unless one of these quantities is changed. There are no restrictions on the energy of the oscillator, and changes in the energy of the oscillator produce changes in the amplitude of the vibrations experienced by the oscillator.

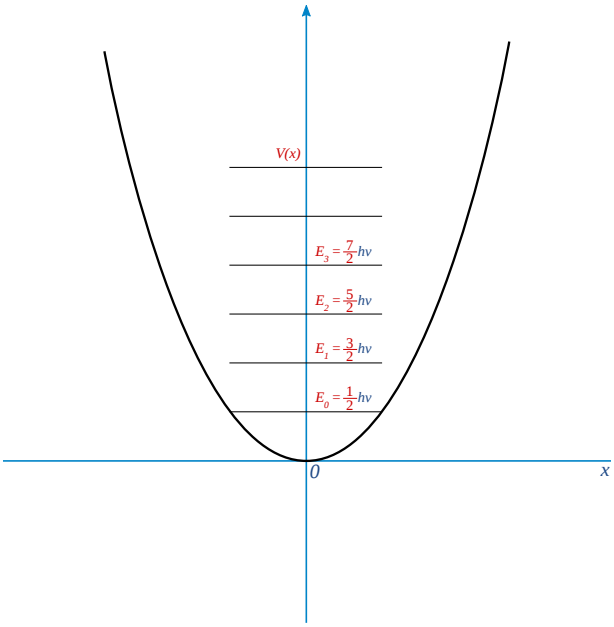


Figure 5.4.1 : Potential energy function and first few energy levels for harmonic oscillator. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

For the quantum mechanical oscillator, the oscillation frequency of a given normal mode is still controlled by the mass and the force constant (or, equivalently, by the associated potential energy function). However, the energy of the oscillator is limited to certain values. The allowed quantized energy levels are equally spaced and are related to the oscillator frequencies as given by Equation 10.4.1 and Figure 5.4.1 .

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega = \left(v + \frac{1}{2}\right)h\nu \tag{10.4.1}$$

with

$$v = 0, 1, 2, 3, \cdots \infty$$

In a quantum mechanical oscillator, we cannot specify the position of the oscillator (the exact displacement from the equilibrium position) or its velocity as a function of time; we can only talk about the probability of the oscillator being displaced from equilibrium by a certain amount. This probability is given by

$$P_{Q \to Q+dQ} = \int_{Q}^{Q+dQ} \psi_v^*(Q)\psi_v(Q)dQ \tag{10.4.2}$$

We can, however, calculate the average displacement and the mean square displacement of the atoms relative to their equilibrium positions. This average is just $\langle Q \rangle$, the expectation value for Q, and the mean square displacement is $\langle Q^2 \rangle$, the expectation value for Q^2. Similarly we can calculate the average momentum $\langle P_Q \rangle$, and the mean square momentum $\left\langle P_Q^2 \right\rangle$, but we cannot specify the momentum as a function of time.

Physically what do we expect to find for the average displacement and the average momentum? Since the potential energy function is *symmetric* around $Q = 0$, we expect values of $Q > 0$ to be equally as likely as $Q < 0$. The average value of Q therefore should be zero.

These results for the average displacement and average momentum do not mean that the harmonic oscillator is sitting still. As for the particle-in-a-box case, we can imagine the quantum mechanical harmonic oscillator as moving back and forth and therefore having an average momentum of zero. Since the lowest allowed harmonic oscillator energy, E_0, is $\frac{\hbar\omega}{2}$ and not 0, the atoms in a molecule must be moving even in the lowest vibrational energy state. This phenomenon is called the zero-point energy or the zero-point motion, and it stands in direct contrast to the classical picture of a vibrating molecule. Classically, the lowest energy available to an oscillator is zero, which means the momentum also is zero, and the oscillator is not moving.

? Exercise 5.4.1

Compare the quantum mechanical harmonic oscillator to the classical harmonic oscillator at $v = 1$ and $v = 50$.

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

$$\int_{-\infty}^{\infty} \psi_v^*(x)\psi_v(x)dx = 1 \tag{10.4.3}$$

and are orthogonal to each other.

$$\int_{-\infty}^{\infty} \psi_{v'}^*(x)\psi_v(x)dx = 0 \text{ for } v' \neq v \tag{10.4.4}$$

The fact that a family of wavefunctions forms an orthonormal set is often helpful in simplifying complicated integrals. We will use these properties when we determine the harmonic oscillator selection rules for vibrational transitions in a molecule and calculate the absorption coefficients for the absorption of infrared radiation.

Finally, we can calculate the probability that a harmonic oscillator is in the classically forbidden region. What does this tantalizing statement mean? Classically, the maximum extension of an oscillator is obtained by equating the total energy of the oscillator to the potential energy, because at the maximum extension all the energy is in the form of potential energy. If all the energy weren't in the form of potential energy at this point, the oscillator would have kinetic energy and momentum and could continue to extend further away from its rest position. Interestingly, as we show below, the wavefunctions of the quantum mechanical oscillator extend beyond the classical limit, i.e. beyond where the particle can be according to classical mechanics.

The lowest allowed energy for the quantum mechanical oscillator is called the **zero-point energy,** $E_0 = \frac{\hbar\omega}{2}$. Using the classical picture described in the preceding paragraph, this total energy must equal the potential energy of the oscillator at its maximum extension. We define this classical limit of the amplitude of the oscillator displacement as Q_0. When we equate the zero-point energy for a particular normal mode to the potential energy of the oscillator in that normal mode, we obtain

$$\frac{\hbar\omega}{2} = \frac{kQ_0^2}{2} \tag{10.4.5}$$

> *The zero-point energy is the **lowest** possible energy that a quantum mechanical physical system may have. Hence, it is the energy of its ground state.*

Recall that k is the effective force constant of the oscillator in a particular normal mode and that the frequency of the normal mode is given by Equation 10.4.1 which is

$$\omega = \sqrt{\frac{k}{\mu}} \tag{10.4.6}$$

10.4: The Harmonic Oscillator Energy Levels is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.4: The Harmonic Oscillator Energy Levels** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

10.5: The Harmonic Oscillator and Infrared Spectra

Learning Objectives

- Understand how the quantum harmonic oscillator model can be used to interpret the infrared spectra of diatomic molecules
- Understand the origin of the transition moment integral and selection rules and how they are related

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them. Chemical compounds have different chemical properties due to the presence of different functional groups. IR spectroscopy is one of the most common and widely used spectroscopic techniques. Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds.

IR Spectroscopy

Transitions between vibrational energy levels can be induced about by absorption or emission of radiation. To understand this, knowledge of both the initial and final eigenstates is needed. The energy of the vth eigenstate of a harmonic oscillator can be written as

$$E_v = \left(v + \frac{1}{2}\right) \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{10.5.1}$$

where h is Planck's constant and v is the vibrational quantum number and ranges from 0, 1, 2, 3,..., ∞. Equation 10.5.1 is often rewritten as

$$E_v = \left(v + \frac{1}{2}\right) h\nu_m \tag{10.5.2}$$

where ν_m is the vibrational frequency of the vibration. Equation 10.5.2 is often written as

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega$$

where ω is the angular frequency (i.e., $2\pi\nu$).

Transitions in vibrational energy levels can be brought about by absorption of radiation, provided the energy of the radiation ($h\nu_{photon}$) **exactly** matches the difference in energy ($\Delta E_{vv'}$) between the vibrational quantum state v to quantum state v'. This can be expressed as

$$\begin{aligned} h\nu_{photon} &= \Delta E_{vv'} \\ &= E_{v'} - E_v \\ &= \left(v' + \frac{1}{2}\right) h\nu_m - \left(v + \frac{1}{2}\right) h\nu_m \\ &= (v' - v)\, h\nu_m \end{aligned} \tag{10.5.3}$$

Let's consider only transitions between adjacent eigenstates (discussed in more details below) so

$$v' - v = \pm 1$$

which is positive if an IR photon is absorbed and negative if it is emitted. For the absorption of a IR photon, Equation 10.5.3 simplifies to

$$h\nu_{photon} = h\nu_m$$
$$= \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{10.5.4}$$

The frequency of radiation ν_{photon} that will bring about this change is **identical** to the classical vibrational frequency of the bond ν.

The Wavenumber as a Unit of Energy

The cm^{-1} is the wavenumber scale and it can also be defined as 1/wavelength in cm. A wavenumber is often used due to its direct relationship with both frequency and energy. The frequency of the absorbed radiation causes the molecular vibrational frequency for the absorption process:

$$\bar{\nu}(cm^{-1}) = \frac{1}{\lambda(\mu m)} \times 10^4 \left(\frac{\mu m}{cm}\right) \tag{10.5.5}$$
$$= \frac{\nu\,(Hz)}{c\,(cm/s)} \tag{10.5.6}$$

Equation 10.5.3 can be modified so that the radiation can be expressed in wavenumbers

$$\tilde{\nu}_m = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{10.5.7}$$

where c is the velocity of light (cm/s) and $\tilde{\nu}$ is the wavenumber of an absorption maximum (cm^{-1}).

Example 5.5.1: Hydrogen Halides

The force constants for typical diatomic molecules are in the range between 400 to 2000 $N \cdot m^{-1}$.

Molecule	HF	HCl	HBr	HI	CO	NO
Force constant, k ($N.m^{-1}$)	970	480	410	320	1860	1530

For the diatomic molecules listed above, calculate the following:

a. angular frequency ($rad \cdot s^{-1}$)
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 vth eigenstate of a harmonic oscillator is

$$E_v = (v + 1/2)\hbar\omega$$

So the ground state ($v = 0$) energy is

$$E_0 = \frac{1}{2}\hbar\omega$$

with

$$\begin{aligned}\omega &= 2\pi\nu \\ &= 5.54 \times 10^{14}\, rad/s\end{aligned}$$

We can then extra the ground state vibrational energy (aka zero-point energy) from

$$\begin{aligned}E_o &= \frac{1}{2}\hbar\omega \\ &= \frac{1}{2}\hbar(5.54 \times 10^{14} rad/s) \\ &= 2.916 \times 10^{-20}\ J\end{aligned}$$

The classical limit of the stretch is denoted as Q_0, this can be equated as potential energy in relation to the total E_0 found above as, at E_0, all of the energy would be potential energy in the form of the stretch. In comparison to the classic spring potential

$$V = \frac{1}{2}kQ_0^2$$

As described above, we can relate the two as

$$\frac{1}{2}\hbar\omega = \frac{1}{2}kQ_0^2$$

or,

$$2.916 \times 10^{-20} J = \frac{1}{2}481Q_0^2$$

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

$$\begin{aligned} \textbf{Percent bond length} &= \frac{Q_0}{x_{eq}} \times 100\% \\ &= \frac{0.0110\, nm}{0.127\, nm} \times 100\% \\ &= 8.66\% \end{aligned}$$

Selection Rules for IR Transitions

Photons can be absorbed or emitted, and the harmonic oscillator can transition from one vibrational energy state to another. Which transitions between vibrational states are allowed? When discussing the Bohr hydrogen atom in Chapter 1, we identified multiple transitions between different states as being responsible for the line spectra emission of the hydrogen atom. No limitations were identified so that any transition between any starting state and ending state was possible and this resulted in a complex pattern in the spectra. As we will identify later on, when considering mulit-electron atoms, there are **selection rules** that limits which transitions will be observed (i.e., are allowed).

A similar situation exist for the harmonic oscillator and IR transitions and a set of selection rules must be satisfied to ensure a particular transition is allowed. Selection rules result from evaluating a **transition moment integral** that expresses the probability of a transition from the v to the v' eigenstates:

$$\mu_T = \langle \psi_{v'} \left| \hat{\mu}(x) \right| \psi_v \rangle \tag{10.5.8}$$

$$= \int_{-\infty}^{\infty} \psi_{v'}^*(x)\hat{\mu}(x)\psi_v(x)dx \tag{10.5.9}$$

When the transition moment integral is zero for two specific eigenstates (i.e., $\psi_v(x)$ and $\psi_v'(x)$), then the probability of observing that transition is zero. In this case, this transition is called a **forbidden transition** (i.e., it will not be obversed). Transitions with low probabilities are call "weakly allowed transitions" since they will have small amplitudes in spectra and transitions with high probabilities are "strongly allowed transitions" and will exhibit high amplitudes in spectra.

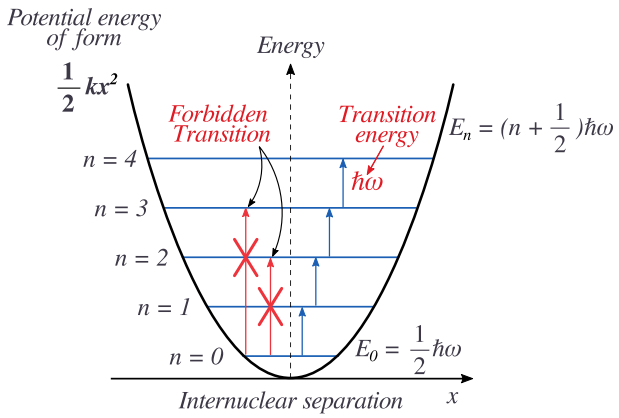


Figure 5.5.1: Possible transitions for a harmonic oscillator. Allowed transitions are labeled with blue arrows and forbidden transitions are labeled with red arrows. (CC BY-NC; Ümit Kaya via LibreTexts)

To evaluate Equation 10.5.9, we need to express the dipole moment operator, $\hat{\mu}$, in terms of the magnitude of the vibration x. The dipole moment operator is defined as

$$\hat{\mu} = \sum_{electrons} e\vec{r} + \sum_{nuclei} q\vec{R} \tag{10.5.10}$$

where the two sums are over all the electrons and nuclei and involve the particle charge ($-e$ or q) multiplying the position vector ($\vec{r}$ or $\vec{R}$, respectively). We can obtain this dipole moment operator in terms of the magnitude of the displacement coordinate, x, in a simple way by using a **Taylor series expansion** for the dipole moment around the equlibrium position ($x = 0$).

$$\hat{\mu}(x) = \mu_{x=0} + \left.\frac{d\mu(x)}{dx}\right|_{x=0} x + \left.\frac{d^2\mu(x)}{dx^2}\right|_{x=0} x^2 + \cdots \tag{10.5.11}$$

Retaining only the first two terms and substituting into Equation 10.5.9 produces

$$\mu_T = \mu_{x=0} \int_{-\infty}^{\infty} \psi_{v'}(x)\psi_v(x)dx + \left.\frac{d\mu(x)}{dx}\right|_{x=0} \int_{-\infty}^{\infty} x\psi_{v'}^*(x)\psi_v(x)dx \tag{10.5.12}$$

where $\mu_{x=0}$ is the **dipole moment** of the molecule when the nuclei are at their equilibrium positions, and

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0}$$

is the *linear* change in the dipole moment due to the displacement of the nuclei in the normal mode. The derivative is the linear change because it multiplies x and not a higher power of x in Equation 10.5.11. Both μ and

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0}$$

are moved outside of the integral because they are constants that no longer depend on x because they are evaluated at $x = 0$.

The integral in the first term in Equation 10.5.12 is 0 because any two harmonic oscillator wavefunctions are *orthogonal*. The integral in the second term of Equation 10.5.12 is zero except when $v' = v \pm 1$ as demonstrated in Exercise 5.5.1 . Also note that the second term is zero if

$$\left.\frac{d\mu(x)}{dx}\right|_{x=0} = 0 \tag{10.5.13}$$

Hence we can identify two "rules" that need to be satisfied for an IR photon to be absorb (or emitted) by a vibrating molecule.

Rules for IR Absorption

For IR absorption to occur two conditions must be met:

1. There must be a **change** in the dipole moment of the molecule as a result of a molecular vibration (or rotation). The change (or oscillation) in the dipole moment allows interaction with the alternating electrical component of the IR radiation. Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment.
2. If the frequency of the radiation ν_{photon} matches the natural frequency of the vibration (ν_m), the IR photon can be absorbed and the amplitude of the vibration increases.

? Exercise 5.5.1

Use one of the Hermite polynomial recursion relations to verify that the second integral in Equation 10.5.12 is 0 unless $v' = v \pm 1$.

If we are to observe absorption of infrared radiation due to a vibrational transition in a molecule, the transition moment cannot be zero. This condition requires that the dipole moment derivative Equation 10.5.13 **cannot** be zero and that the vibrational quantum number change by one unit. The normal coordinate motion must cause the dipole moment of the molecule to change in order for a molecule to absorb infrared radiation. If the normal coordinate oscillation does not cause the dipole moment to change then $\mu_T = 0$ and no infrared absorption is observed. So we can

$$\underbrace{\Delta v = \pm 1}_{\text{For allowed transitions}} \tag{10.5.14}$$

Consider oxygen and nitrogen molecules. Because they are symmetrical, their dipole moments are zero, $\mu = 0$. Since the vibrational motion (only bond stretching for a diatomic molecule) preserves this symmetry, the change in the dipole moment due to the vibrational motion also is zero, $\frac{d\mu(x)}{dx} = 0$. Consequently, oxygen and nitrogen do not absorb infrared radiation as a result of vibrational motion.

? Exercise 5.5.2

Explain why the molar absorptivity or molar extinction coefficients (ϵ) in Beer's Law for the IR absorption of some vibrations are greater than others.

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 10.5.4. The transition energy is the change in energy of the oscillator as it moves from one vibrational state to another, and it equals the photon energy.

$$\begin{aligned} \Delta E &= E_{final} - E_{initial} \\ &= h\upsilon_{photon} \\ &= \hbar\omega_{oscillator} \end{aligned}$$

For perfect harmonic oscillators, the only possible allowed transitions are $\Delta = \pm 1$ with all other transitions forbidden (Figure 5.5.1). This conclusion predicts that the vibrational absorption spectrum of a diatomic molecule consists of a single line since the energy levels are equally spaced in the harmonic oscillator model (Figure 5.5.1). If the vibration were anharmonic, then the levels would not be equally spaced and then transitions from $v = 0$ 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 $\mathbf{HCl}$ given that the fundamental is at 2,886 cm^{-1}.

10.5: The Harmonic Oscillator and Infrared Spectra is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.5: The Harmonic Oscillator and Infrared Spectra** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

10.6: The Harmonic-Oscillator Wavefunctions Involve Hermite Polynomials

Learning Objectives

- The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule

For a diatomic molecule, there is only one vibrational mode, so there will be only a single set of vibrational wavefunctions with associated energies for this system. For polytatomic molecules, there will be a set of wavefunctions with associated energy associated with each vibrational mode.

The Hamiltonian operator, the general quantum mechanical operator for energy, includes both a kinetic energy term, $\hat{T}$, and a potential energy term, $\hat{V}$.

$$\hat{H} = \hat{T} + \hat{V} \tag{10.6.1}$$

For the free particle and the particle in a box, the potential energy term used in the Hamiltonian was zero. As shown in Equation 10.6.1, the classical expression for the energy of a harmonic oscillator includes both a kinetic energy term and the harmonic potential energy term. Transforming this equation into the corresponding Hamiltonian operator gives,

$$\hat{H}(q) = \frac{1}{2\mu}\hat{P}_q^2 + \frac{k}{2}\hat{q}^2 \tag{10.6.2}$$

where $\hat{q}$ is the operator for the length of the normal coordinate, and $\hat{P}_q$ is the momentum operator associated with the normal coordinate. μ is an effective (reduced) mass, and k is an effective force constant, and these quantities will be different for each of the normal modes (vibrations).

Substituting the definitions for the operators yields

$$\hat{H}(q) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2} + \frac{k}{2}q^2 \tag{10.6.3}$$

since the operator for position or displacement is just the position or displacement. The time-independent Schrödinger Equation then becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_v(q)}{dq^2} + \frac{k}{2}q^2\psi_v(q) = E_v\psi_v(q) \tag{10.6.4}$$

or upon rearranging

$$\frac{d^2\psi_v(q)}{dq^2} + \frac{2\mu}{\hbar^2}\left(E_v - \frac{k}{2}q^2\right)\psi_v(q) = 0 \tag{10.6.5}$$

This differential equation is not straightforward to solve. Rather than fully develop the details of the solution, we will outline the method used because it represents a common strategy for solving differential equations. The steps taken to solve Equation 10.6.5 are to simplify the equation by collecting constants in the parameter β

$$\beta^2 = \frac{\hbar}{\sqrt{\mu k}} \tag{10.6.6}$$

and then changing the variable from q to x where

$$x = \frac{q}{\beta} \tag{10.6.7}$$

so that

$$\frac{d^2}{dq^2} = \frac{1}{\beta^2}\frac{d^2}{dx^2} \tag{10.6.8}$$

After substituting Equations 10.6.6 and 10.6.8 into Equation 10.6.5, the differential equation for the harmonic oscillator becomes

$$\frac{d^2\psi_v(x)}{dx^2} + \left(\frac{2\mu\beta^2 E_v}{\hbar^2} - x^2\right)\psi_v(x) = 0 \tag{10.6.9}$$

? Exercise 5.6.1

Make the substitutions given in Equations 10.6.6 and 10.6.8 into Equation 10.6.5 to get Equation 10.6.9.

Solving for the Quantum Wavefunctions

A common strategy for solving differential equations, which is employed here, is to find a solution that is valid for large values of the variable and then develop the complete solution as a product of this asymptotic solution and a power series. Since the potential energy approaches infinity as x and the coordinate q approach infinity, the wavefunctions must approach zero (this is, the wavefunctions must **converge to zero**):

$$\lim_{x\to\infty} \psi_v(x) = 0 \tag{10.6.10}$$

The function that has this property and satisfies the differential equation for large values of x is the exponential function, i.e.,

$$\lim_{x\to\infty} \phi_v(x)\exp\left(\frac{-x^2}{2}\right) = 0 \tag{10.6.11}$$

where the wavefunctions are

$$\psi_v(x) \propto \phi_v(x)\exp\left(\frac{-x^2}{2}\right)$$

The general expression for a power series of $\phi_v(x)$ is

$$\begin{aligned}\phi_v(x) &= \sum_{n=0}^{\infty} c_n(v)x^n \\ &= c_n(v)x + c_n(v)x^2 + c_n(v)x^3 + \cdots\end{aligned}$$

which can be truncated after the first term, after the second term, after the third term, etc. to produce a set of polynomials. There is one polynomial for each value of v where v can be equal to any integer value including zero.

$$\sum_{n=0}^{v} c_n x^n \tag{10.6.12}$$

Each of the truncations of the power series in Equation 10.6.12 can be multiplied by the exponential function in Equation 10.6.11 to create a family of valid solutions to the differential equation in Equation 10.6.9.

$$\psi_v(x) = \sum_{n=0}^{v} c_n x^n \exp\left(\frac{-x^2}{2}\right) \tag{10.6.13}$$

? Exercise 5.6.2

Write the first four polynomials, $v = 0$ to $v = 1$, $v = 12$, $v = 13$, $v = 14$ for Equation 10.6.12 and use suitable software to prepare plots of these polynomials. Identify the curves in the plots.

? Exercise 5.6.3

Confirm that the wavefunction given by Equation 10.6.13 is a solution to the harmonic oscillator Schrödinger Equation in Equation 10.6.9 for $v = 0$ and $v = 1$.

Hermite Polynomials

While polynomials in general approach ∞ (or $-\infty$) as x approaches ∞, the decreasing exponential term overpowers the polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of x or $-x$. The exact forms of

polynomials that solve Equation 10.6.9 are the **Hermite polynomials**, which are standard mathematical functions known from the work of Charles Hermite. The first eight Hermite polynomials, $H_v(x)$, are given below.

- $H_0 = 1$
- $H_1 = 2x$
- $H_2 = -2 + 4x^2$
- $H_3 = -12x + 8x^3$
- $H_4 = 12 - 48x^2 + 16x^4$
- $H_5 = 120x - 160x^3 + 32x^5$
- $H_6 = -120 + 720x^2 - 480x^4 + 64x^6$
- $H_7 = -1680x + 3360x^3 - 1344x^5 + 128x^7$

The first six Hermite polynomials are plotted in Figure 5.6.1 . Hermite polynomials will be discussed in more detail in the following Section.

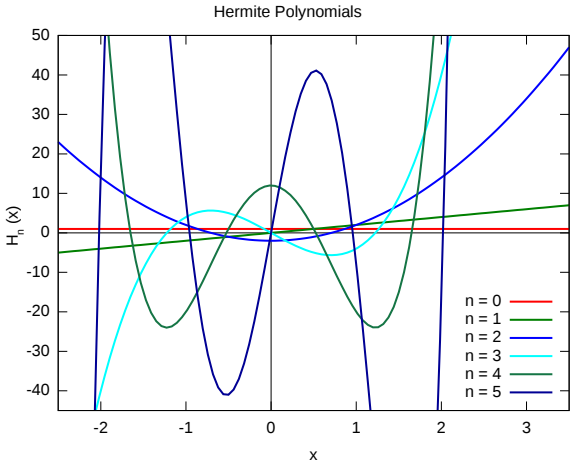


Figure 5.6.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

? Exercise 5.6.4

Determine the units of β and the units of x in the Hermite polynomials.

Because of the association of the wavefunction with a probability density, it is necessary for the wavefunction to include a normalization constant, N_v.

$$N_v = \frac{1}{(2^v v! \sqrt{\pi})^{1/2}} \tag{10.6.14}$$

The final form of the harmonic oscillator wavefunctions is thus

$$\psi_v(x) = N_v H_v(x) e^{-x^2/2} \tag{10.6.15}$$

Alternative and More Common Formulation of Harmonic Oscillator Wavefunctions

The harmonic oscillator wavefunctions are often written in terms of Q, the unscaled displacement coordinate (Equation 10.6.7) and a different constant α:

$$\alpha = 1/\sqrt{\beta} = \sqrt{\frac{k\mu}{\hbar^2}}$$

so Equation 10.6.15 becomes

$$\psi_v(x) = N_v'' H_v(\sqrt{\alpha} Q) e^{-\alpha Q^2/2}$$

with a slightly different normalization constant

$$N_v'' = \sqrt{\frac{1}{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

Exercise 5.6.5

Compute the normalization factor for $\psi_v(x)$ where $v = 0$ and $v = 4$. What is the purpose of N_v?

The energy eigenvalues for a quantum mechanical oscillator also are obtained by solving the Schrödinger equation. The energies are restricted to discrete values

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \tag{10.6.16}$$

with $v = 0, 1, 2, 3, \cdots$.

The energies depend both on the quantum number, v, and the oscillator frequency

$$\omega = \sqrt{\frac{k}{\mu}}$$

which in turn depends on the spring constant k and the reduced mass of the vibration μ.

Exercise 5.6.6

Determine the energy for the first ten harmonic oscillator energy levels in terms of $\hbar\omega$. Sketch an energy level diagram of these energies.

1. What insights do you gain from Equation 10.6.16, your calculations, and your diagram?
2. Is it possible to have a molecule that is not vibrating?
3. In terms of $\hbar\omega$, what is the energy of the photon required to cause a transition from one vibrational state to the next higher one?
4. If a transition from energy level $v = 9$ to $v = 10$ were observed in a spectrum, where would that spectral line appear relative to the one for the transition from level $v = 0$ to $v = 1$?
5. If a vibrational transition is observed at 3000 cm-1 in an infrared spectrum, what is the value of $\hbar\omega$ for the normal mode?
6. Identify all the possible meanings of $\Delta E = h\nu$ and the definition of the frequency, ν, in each case.

The normalized wavefunctions for the first four states of the harmonic oscillator are shown in Figure 5.6.2 , and the corresponding probability densities are shown in Figure 5.6.3 . You should remember the mathematical and graphical forms of the first few harmonic oscillator wavefunctions, and the correlation of v with E_v. The number of nodes in the wavefunction will help you to remember these characteristics. Also note that the functions fall off exponentially and that the symmetry alternates. For v equal to an even number, ψ_v is gerade; for v equal to an odd number, ψ_v is ungerade.

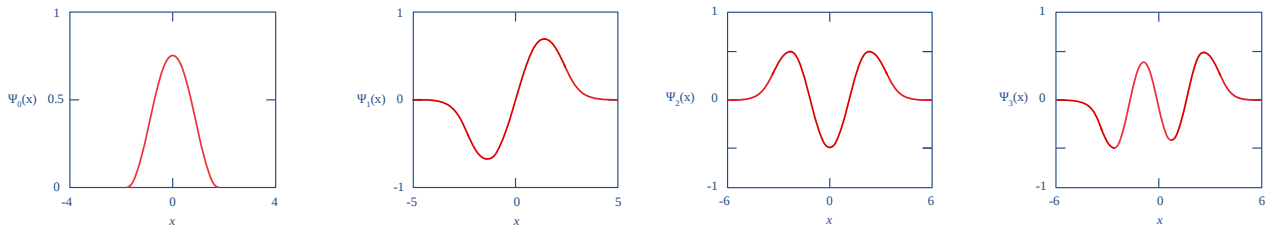


Figure 5.6.2 : The harmonic oscillator wavefunctions describing the four lowest energy states.

Exercise 5.6.7

Write a few sentences describing and comparing the plots in Figure 5.6.2 . How many nodes are there as a function of v? Do the wavefunctions converge at extreme displacement? Where is the most likely displacements for the oscillator to be found?

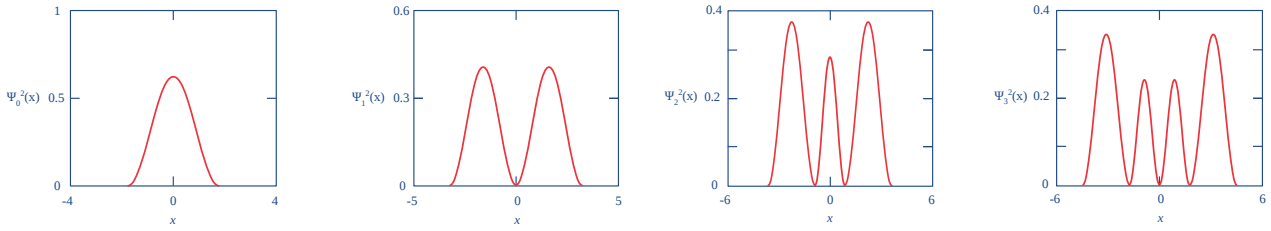


Figure 5.6.3 : The probability densities for the four lowest energy states of the harmonic oscillator.

Exercise 5.6.8

Explain how Figure 5.6.3 is related to Figure 5.6.2 . Explain the physical significance of the plots in Figure 5.6.3 in terms of the magnitude of the normal coordinate Q. Couch your discussion in terms of the HCl molecule. How would you describe the location of the atoms in each of the states? How does the oscillator position correspond to the energy of a particular level?

Exercise 5.6.9

Plot the probability density for energy level 10 of the harmonic oscillator. How many nodes are present? Plot the probability density for energy level 20. Compare the plot for level 20 with that of level 10 and level 1. Compare these quantum mechanical probability distributions to those expected for a classical oscillator. What conclusion can you draw about the probability of the location of the oscillator and the length of a chemical bond in a vibrating molecule? Extend your analysis to include a very high level, like level 50.

In completing Exercise 5.6.9 , you should have noticed that as the quantum number increases and becomes very large, the probability distribution approaches that of a classical oscillator. This observation is very general. It was first noticed by Bohr, and is called the Bohr Correspondence Principle. This principle states that classical behavior is approached in the limit of large values for a quantum number. A classical oscillator is most likely to be found in the region of space where its velocity is the smallest. This situation is similar to walking through one room and running through another. In which room do you spend more time? Where is it more likely that you will be found?

Examination of the quantum mechanical wavefunction for the lowest-energy state reveals that the wavefunction $\psi_0(x)$ extends beyond the classical limit (i.e., outside of the harmonic oscillator well, albeit slightly). Higher energy states have higher total energies, so the classical limits to the amplitude of the displacement will be larger for these states.

Tunneling in the Quantum Harmonic Oscillator

The observation that the wavefunctions are not zero at the classical limit means that the quantum mechanical oscillator has a finite probability of having a displacement that is larger than what is classically possible. The oscillator can be in a region of space where the potential energy is greater than the total energy. Classically, when the potential energy equals the total energy, the kinetic energy and the velocity are zero, and the oscillator cannot pass this point. A quantum mechanical oscillator, however, has a finite probability of passing this point. For a molecular vibration, this property means that the amplitude of the vibration is larger than what it would be in a classical picture. In some situations, a larger amplitude vibration could enhance the chemical reactivity of a molecule.

Exercise 5.6.10

Plot the probability density for $v = 0$ and $v = 1$ states. Mark the classical limits on each of the plots, since the limits are different because the total energy is different for $v = 0$ and $v = 1$. Shade in the regions of the probability densities that extend beyond the classical limit.

We should be able to calculate the probability that the quantum mechanical harmonic oscillator is in the classically forbidden region for the lowest energy state of the harmonic oscillator, the state with $v = 0$. The classically forbidden region is shown by the shading of the regions beyond Q_0 in the graph you constructed for Exercise 5.6.3 . The area of this shaded region gives the probability that the bond oscillation will extend into the forbidden region (Figure 5.6.3). To calculate this probability, we use

$$P[\text{forbidden}] = 1 - P[\text{allowed}] \tag{10.6.17}$$

because the integral from 0 to Q_0 for the allowed region can be found in integral tables and the integral from Q_0 to ∞ cannot. The form of the integral, $P[\text{allowed}]$, to evaluate is

$$P[\text{allowed}] = 2\int_0^{Q_0} \psi_0^*(Q)\psi_0(Q)dQ \tag{10.6.18}$$

The factor 2 appears in Equation 10.6.18 from the chancing the limits of integration from $-Q_0$ to $+Q_0$ into 0 to $+Q_0$; we can do this since the integrand is an even function, i. e., $f(-x) = f(x)$. To evaluate the integral in Equation 10.6.18, use the wavefunction and do the integration in terms of x. Recall that for $v = 0$, $Q = Q_0$ corresponds to $x = 1$. Including the normalization constant, Equation 10.6.18 produces

$$P[\text{allowed}] = \frac{2}{\sqrt{\pi}}\int_0^1 \exp(-x^2)dx \tag{10.6.19}$$

The integral in Equation 10.6.19 is called an error function (ERF) and can only be evaluated numerically. Values can be found in books of mathematical tables. When the limit of integration is 1, ERF(l) = 0.843 and P[forbidden] = 0.157. This result means that the quantum mechanical oscillator can be found in the forbidden region 16% of the time. This effect is substantial and leads to the phenomenon called *quantum mechanical tunneling*.

? Exercise 5.6.11

Numerically verify that $P[\text{allowed}]$ in Equation 10.6.19 equals 0.843. To obtain a value for the integral do not use symbolic integration or symbolic equals.

10.6: The Harmonic-Oscillator Wavefunctions Involve Hermite Polynomials is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.6: The Harmonic Oscillator Wavefunctions involve Hermite Polynomials** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

10.7: Hermite Polynomials are either Even or Odd Functions

Learning Objectives

- Understand key properties of the Hermite polynomials including orthogonality and symmetry.
- Be proficient at using symmetries of integrands to quickly solve integrals.

Hermite polynomials were defined by Laplace (1810) though in scarcely recognizable form, and studied in detail by Chebyshev (1859). Chebyshev's work was overlooked and they were named later after Charles Hermite who wrote on the polynomials in 1864 describing them as new. They were consequently not new although in later 1865 papers Hermite was the first to define the multidimensional polynomials. The first six Hermite polynomial are plotted in Figure 5.7.1 .

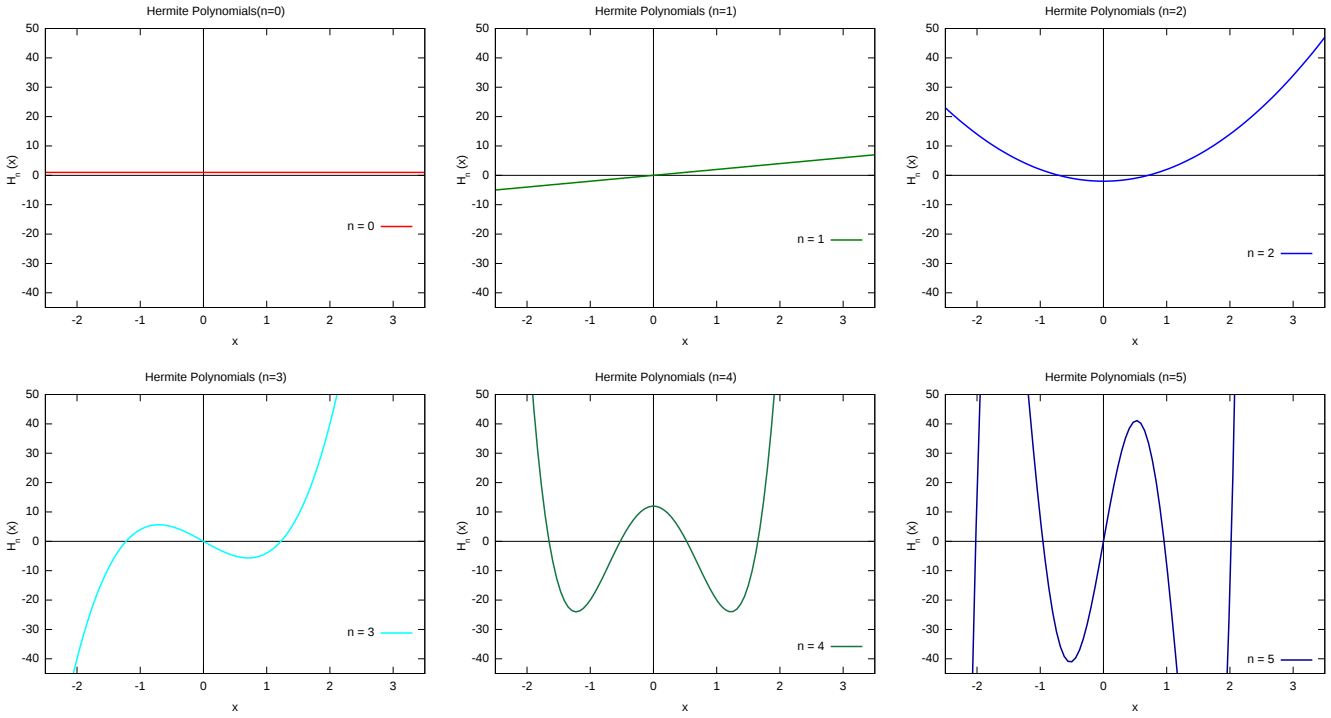


Figure 5.7.1 : The first six Hermite polynomials $H_n(x)$. (CC BY-SA 3.0 Unported; Alessio Damato, Vulpecula and others via Wikipedia)

Generating Formula

Any Hermite polynomial $H_n(x)$ can be generated from a previous one $H_{n-1}(x)$ via the following using the recurrence relation

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x). \tag{10.7.1}$$

Hermite Polynomials are Symmetric

Let $f(x)$ be a real-valued function of a real variable.

- Then f is **even** if the following equation holds for all x and -x in the domain of f

$$f(x) = f(-x)$$

- Then f is **odd** if the following equation holds for all x and -x in the domain of f

$$-f(x) = f(-x)$$

Even and odd are terms used to describe particularly well-behaved functions. An *even* function is symmetric about the y-axis (Figure 5.7.2 ; left). That is, if we reflect the graph of the function in the y-axis, then it does not change. Formally, we say that f is

even if, for all x and $-x$ in the domain of f, we have

$$f(-x) = f(x)$$

Two examples of even functions are $f(x) = x^2$ and $f(x) = \cos x$.

An *odd* function has rotational symmetry of order two about the origin (Figure 5.7.2 ; middle). That is, if we rotate the graph of the function 180° about the origin, then it does not change. Formally, we say that ff is odd if, for all x and $-x$ in the domain of f, we have

$$f(-x) = -f(x)$$

Examples of odd functions are $f(x) = x^3$ and $f(x) = \sin x$.

Naturally, not all functions can be classified as even or odd. For example $f = x^3 + 1$ shown in the right side of Figure 5.7.2 , is neither.

> You can also think of these properties as symmetry conditions at the origin. More symmetries in 3D space are discussed in Group Theory.

Without proof, we can identify several key features involving multiplication properties of even and odd functions:

- The product of two **even** functions is an **even** function.
- The product of two **odd** functions is an **even** function.
- The product of an **even** function and an **odd** function is an odd function.

This can be shown graphically as a product table like that in Table 5.7.1 .

Table 5.7.1 : Product table of 1D Functions

Product table	Odd Function (anti-symmetric)	Even Function (symmetric)	No symmetry (neither)
Odd Function (anti-symmetric)	Even Function (symmetric)	Odd Function (anti-symmetric)	who knows
Even Function (symmetric)	Odd Function (anti-symmetric)	Even Function (symmetric)	who knows
No symmetry (neither)	who knows	who knows	who knows

Notice that the Hermite polynomials in Figure 5.7.1 oscillate from even to odd. We can take advantage of that aspect in our calculation of Harmonic Oscillator wavefunctions. Hermite Polynomial is an even or odd function depends on its degree n. Based on

$$H_n(-x) = (-1)^n H_n(x) \tag{10.7.2}$$

- $H_n(x)$ is an even function, when n is even.
- $H_n(x)$ is an odd function, when n is odd.

Integration over Symmetric Functions

You often consider integrals of the form

$$I = \int_{-a}^{a} f(x)\,\mathrm{d}x$$

If f is odd or even, then sometimes you can make solving this integral easier. For example, we can rewrite that integral in the following way:

$$I = \int_{-a}^{a} f(x)\,\mathrm{d}x = \int_{-a}^{0} f(x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{10.7.3}$$

$$= \int_{0}^{a} f(-x)\,\mathrm{d}x + \int_{0}^{a} f(x)\,\mathrm{d}x \tag{10.7.4}$$

For an even function, we have $f(-x) = f(x)$ and Equation 10.7.4 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 10.7.4 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 10.7.5 and 10.7.6).

Solution

For the Hermite polynomials $H_n(x)$, the relevant inner product (using Dirac Notation)

$$\langle f, g\rangle = \int_{-\infty}^{\infty} f(x)g(x)\exp(-x^2)\,dx$$

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.

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:

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 0 \tag{10.7.5}$$

if $m \neq n$ and

$$\int_{-\infty}^{\infty} H_m(x)H_n(x)e^{-x^2/2}dx = 2^n n!\sqrt{\pi} \tag{10.7.6}$$

if $m = n$.

This will not be proved, but can the demonstrated using any of the Hermite polynomials listed in the previous section. The orthogonality property becomes important when solving the Harmonic oscillator problems. Note that the integral of Equation 10.7.6 is important for normalizing the quantum harmonic oscillator wavefunctions discussed in last Section.

Example 5.7.2 : Hermite Polynomials are Orthogonal

Demonstrate that $H_2(x)$ and $H_3(x)$ are orthogonal.

Solution

We need to confirm

$$\int_{-\infty}^{\infty} H_2(x)H_3(x)dx = 0$$

or when substituted

$$\int_{-\infty}^{\infty} (4x^2-2)(8x^3-12x)dx = 0$$

because it says I need to show it's orthogonal on $[-\infty,\infty]$ or we can just evaluate it on a finite interval $[-L,L]$, where L is a constant.

$$\begin{aligned}\int_{-L}^{L}(4x^2-2)(8x^3-12x)dx &= 8\left(\frac{2x^6}{3}-2x^4+\frac{3x^2}{2}\right)\Bigg|_{-L}^{L}\\ &= 8\left(\frac{2L^6}{3}-2L^4+\frac{3L^2}{2}\right)-8\left(\frac{2(-L)^6}{3}-2(-L)^4+\frac{3(-L)^2}{2}\right)\\ &= 0.\end{aligned}$$

Concluding

Hermite polynomials are a component in the harmonic oscillator wavefunction that dictates the symmetry of the wavefunctions. If your integration interval is symmetric around 0, then the integral over *any* integrable odd function is zero, no exception. Therefore as soon as you've found that your integrand is odd and your integration interval is symmetric, you're done. Also, for general functions, if you can easily split them into even and odd parts, you only have to consider the integral over the even part for symmetric integration intervals.

Another important property is that the product of two even or of two odd functions is even, and the product of an even and an odd function is odd. For example, if ff is even, $x \mapsto f(x)\sin(x)$ is odd, and therefore the integral over it is zero (provided it is well defined).

10.7: Hermite Polynomials are either Even or Odd Functions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.7: Hermite Polynomials are either Even or Odd Functions** by Delmar Larsen is licensed CC BY-SA 4.0.

10.8: The Energy Levels of a Rigid Rotor

Learning Objectives

- Compare the classical and quantum rigid rotor in three dimensions
- Demonstrate how to use the Separation of Variable technique to solve the 3D rigid rotor Schrödinger Equation
- Identify and interpret the two quantum numbers for a 3D quantum rigid rotor including the range of allowed values
- Describe the wavefunctions of the 3D quantum rigid rotor in terms of nodes, average displacements and most probable displacements
- Describe the energies of the 3D quantum rigid rotor in terms of values and degeneracies

Rigid rotor means when the distance between particles do not change as they rotate. A rigid rotor only approximates a rotating diatomic molecular if vibration is ignored.

The Classical Rigid Rotor in 3D

The **rigid rotor** is a mechanical model that is used to explain rotating systems. The linear rigid rotor model consists of two point masses located at fixed distances from their center of mass. The fixed distance between the two masses and the values of the masses are the only characteristics of the rigid model. However, for many actual diatomics this model is too restrictive since distances are usually not completely fixed and corrections on the rigid model can be made to compensate for small variations in the distance. Even in such a case the rigid rotor model is a useful model system to master.

For a rigid rotor, the total energy is the sum of kinetic (T) and potential (V) energies

$$E_{tot} = T + V \tag{10.8.1}$$

The potential energy, V, is set to 0 because the distance between particles does not change within the rigid rotor approximation. However, In reality, $V \neq 0$ because even though the average distance between particles does not change, the particles still vibrate. The rigid rotor approximation greatly simplifys our discussion.

Since $V = 0$ then $E_{tot} = T$ and we can also say that:

$$T = \frac{1}{2}\sum m_i v_i^2 \tag{10.8.2}$$

However, we have to determine v_i in terms of rotation since we are dealing with rotation motion. Since,

$$\omega = \frac{v}{r} \tag{10.8.3}$$

where ω is the **angular velocity**, we can say that:

$$v_i = \omega X r_i \tag{10.8.4}$$

Thus we can rewrite Equation 10.8.2 as:

$$T = \frac{1}{2}\sum m_i v_i \left(\omega X r_i\right) \tag{10.8.5}$$

Since ω is a scalar constant, we can rewrite Equation 10.8.5 as:

$$T = \frac{\omega}{2}\sum m_i \left(v_i X r_i\right) = \frac{\omega}{2}\sum l_i = \omega\frac{L}{2} \tag{10.8.6}$$

where l_i is the **angular momentum** of the ith particle, and L is the angular momentum of the *entire system*. Also, we know from physics that,

$$L = I\omega \tag{10.8.7}$$

where I is the moment of inertia of the rigid body relative to the axis of rotation. We can rewrite Equation 10.8.2 as

$$T = \omega \frac{I\omega}{2} = \frac{1}{2} I\omega^2 \tag{10.8.8}$$

Equation 10.8.8 shows that the energy of the rigid rotor scales with increasing angular frequency (i.e., the faster is rotates) and with increasing moment of inertia (i.e, the inertial resistance to rotation). Also, as expected, the classical rotational energy is not quantized (i.e., all possible rotational frequencies are possible).

The Quantum Rigid Rotor in 3D

It is convenient to discuss rotation with in the spherical coordinate system rather than the Cartesian system (Figure 5.8.1).

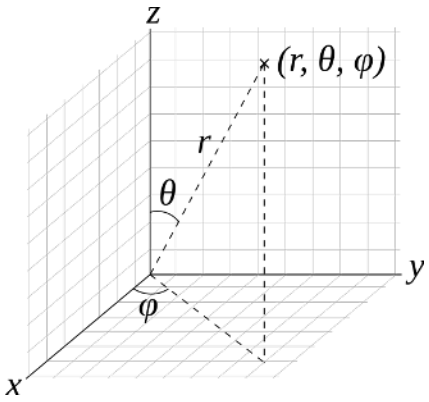


Figure 5.8.1 : The spherical coordinate system in terms of the Cartesian system. (Public Domain; Andeggs via Wikipedia).

To solve the Schrödinger equation for the rigid rotor, we will separate the variables and form single-variable equations that can be solved independently. Only two variables θ and φ are required in the rigid rotor model because the bond length, r, is taken to be the constant r_0. We first write the rigid rotor wavefunctions as the product of a theta-function depending only on θ and a phi-function depending only on φ

$$|\psi(\theta,\varphi)\rangle = |\Theta(\theta)\Phi(\varphi)\rangle \tag{10.8.9}$$

We then substitute the product wavefunction and the Hamiltonian written in spherical coordinates into the Schrödinger Equation 10.8.10

$$\hat{H}\,|\Theta(\theta)\Phi(\varphi)\rangle = E|\,\Theta(\theta)\Phi(\varphi)\rangle \tag{10.8.10}$$

to obtain

$$-\frac{\hbar^2}{2\mu r_0^2}\left[\frac{\partial}{\partial r_0} r_0^2 \frac{\partial}{\partial r_0} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{10.8.11}$$
$$|\Theta(\theta)\Phi(\varphi)\rangle = E|\,\Theta(\theta)\Phi(\varphi)\rangle$$

Since $r = r_0$ is constant for the **rigid rotor** and does not appear as a variable in the functions, the partial derivatives with respect to r are zero; i.e. the functions do not change with respect to r. We also can substitute the symbol I for the moment of inertia, μr_0^2 in the denominator of the left hand side of Equation 10.8.11, to give

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\Theta(\theta)\Phi(\varphi)\rangle = E|\,\Theta(\theta)\Phi(\varphi)\rangle \tag{10.8.12}$$

To begin the process of the Separating of Variables technique, multiply each side of Equation 10.8.12 by $\frac{2I}{\hbar^2}$ and $\frac{-\sin^2\theta}{\Theta(\theta)\Phi(\varphi)}$ to give

$$\frac{1}{\Theta(\theta)\psi(\varphi)}\left[\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\varphi^2}\right]\Theta(\theta)\Phi(\varphi) = \frac{-2IE\sin^2\theta}{\hbar^2} \tag{10.8.13}$$

Simplify the appearance of the right-hand side of Equation 10.8.13 by defining a parameter λ:

$$\lambda = \frac{2IE}{\hbar^2}. \tag{10.8.14}$$

Note that this λ has no connection to a wavelength; it is merely being used as an algebraic symbol for the combination of constants shown in Equation 10.8.14.

Inserting λ, evaluating partial derivatives, and rearranging Equation 10.8.13 produces

$$\frac{1}{\Theta(\theta)}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta\right)\Theta(\theta)\right]=-\frac{1}{\Phi(\varphi)}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) \tag{10.8.15}$$

? Exercise 5.8.1

Carry out the steps leading from Equation 10.8.13 to Equation 10.8.15. Keep in mind that, if y is not a function of x,

$$\frac{dy}{dx}=y\frac{d}{dx}$$

Equation 10.8.15 says that the function on the left, depending only on the variable θ, always equals the function on the right, depending only on the variable φ, for all values of θ and φ. The only way two different functions of independent variables can be equal for all values of the variables is if both functions are equal to a constant (review separation of variables). We call this constant m_J^2 because soon we will need the square root of it. The two differential equations to solve are the θ-equation

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)\Theta(\theta)+\left(\lambda\sin^2\theta-m_J^2\right)\Theta(\theta)=0 \tag{10.8.16}$$

and the φ-equation

$$\frac{d^2}{d\varphi^2}\Phi(\varphi)+m_J^2\Phi(\varphi)=0 \tag{10.8.17}$$

The partial derivatives have been replaced by total derivatives because only a single variable is involved in each equation.

> *Often m_J is referred to as just m for convenience.*

? Exercise 5.8.2

Show how Equations 10.8.16 and 10.8.17 are obtained from Equation 10.8.15.

Solving the φ Equation

The φ-equation is similar to the Schrödinger Equation for the free particle. Since we already solved this previously, we immediately write the solutions:

$$\Phi_m(\varphi)=Ne^{\pm im_J\varphi} \tag{10.8.18}$$

where we introduce the number m to track how many wavelengths of the wavefunction occur around one rotation (similar to the wavelength description of the Bohr atom).

? Exercise 5.8.3

Substitute Equation 10.8.18 into Equation 10.8.17 to show that it is a solution to that differential equation.

The normalization condition, Equation 10.8.19 is used to find a value for N that satisfies Equation 10.8.18.

$$\int_0^{2\pi}\Phi^*(\varphi)\Phi(\varphi)d\varphi=1 \tag{10.8.19}$$

The range of the integral is only from 0 to 2π because the angle φ specifies the position of the internuclear axis relative to the x-axis of the coordinate system and angles greater than 2π do not specify additional new positions.

? Exercise 5.8.4

Use the normalization condition in Equation 10.8.19 to demonstrate that $N = 1/\sqrt{2\pi}$.

Values for m are found by using a **cyclic boundary condition**. The cyclic boundary condition means that since φ and $\varphi + 2\varphi$ refer to the same point in three-dimensional space, $\Phi(\varphi)$ must equal $\Phi(\varphi + 2\pi)$, i.e.

$$e^{im_J\varphi} = e^{im_J(\varphi+2\pi)} \tag{10.8.20}$$

$$= e^{im_J\varphi}e^{im_J 2\pi} \tag{10.8.21}$$

For the equality in Equation 10.8.21 to hold, $e^{im_J 2\pi}$ must equal 1, which is true only when

$$m_J = \cdots, -3, -2, -1, 0, 1, 2, 3, \cdots \tag{10.8.22}$$

In other words m_J can equal **any positive or negative integer or zero.**

? Exercise 5.8.5 : Cyclic Boundary Conditions

Use Euler's Formula to show that $e^{im_J 2\pi}$ equals 1 for m_J equal to zero or any positive or negative integer.

Thus, the Φ function is

$$\Phi_{m_J}(\varphi) = \sqrt{\frac{1}{2\pi}}e^{\pm im_J\varphi}$$

with

$$m_J = 0, \pm 1, \pm 2, \cdots$$

Solving the $\Theta(\theta)$ Equation

Finding the $\Theta(\theta)$ functions that are solutions to the θ-equation (Equation 10.8.16) is a more complicated process. Solutions are found to be a set of power series called *Associated Legendre Functions* (Table M2), which are power series of trigonometric functions, i.e., products and powers of sine and cosine functions. The $\Theta(\theta)$ functions, along with their normalization constants, are shown in the third column of Table 5.8.1 .

Table 5.8.1 : Spherical Harmonic Wavefunctions

m_J	J	$\Theta_J^{m_J}(\theta)$	$\Phi(\varphi)$	$Y_J^{m_J}(\theta,\varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}}(3\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$
1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$
-1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$
2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$
-2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$

The solution to the θ-equation requires that λ in Equation 10.8.15 be given by

$$\lambda = J(J+1) \tag{10.8.23}$$

where

$$J \geq |m_J| \tag{10.8.24}$$

J can be 0 or any positive integer greater than or equal to m_J. Each pair of values for the quantum numbers, J and m_J, identifies a rotational state with a wavefunction (Equation 10.8.9) and energy (below). Equation 10.8.24 means that J controls the allowed values of m_J.

> *Each pair of values for the quantum numbers, J and m_J, identifies a rotational state and hence a specific wavefunction with associated energy.*

The combination of Equations 10.8.14 and 10.8.23 reveals that the energy of this system is quantized.

$$E = \frac{\hbar^2 \lambda}{2I} = J(J+1)\frac{\hbar^2}{2I} \tag{10.8.25}$$

Using Equation 10.8.25, you can construct a rotational energy level diagram (Figure 5.8.2). For simplicity, use energy units of $\frac{\hbar^2}{2I}$.

- $J = 0$: The lowest energy state has $J = 0$ and $m_J = 0$. This state has an energy $E_0 = 0$. There is only **one state** with this energy, i.e. one set of quantum numbers, one wavefunction, and one set of properties for the molecule.
- $J = 1$: The next energy level is $J = 1$ with energy $\frac{2\hbar^2}{2I}$. There are **three states** with this energy because m_J can equal +1, 0, or -1. These different states correspond to different orientations of the rotating molecule in space. States with the same energy are said to be degenerate. The degeneracy of an energy level is the number of states with that energy. The degeneracy of the $J = 1$ energy level is 3 because there are three states with the energy $\frac{2\hbar^2}{2I}$.
- $J = 2$: The next energy level is for $J = 2$. The energy is $\frac{6\hbar^2}{2I}$, and there are **five states** with this energy corresponding to $m_J = +2, +1, 0, -1, -2$. The energy level degeneracy is five. Note that the spacing between energy levels increases as J increases. Also note that the degeneracy increases. The degeneracy is always $2J + 1$ because m_J ranges from $+J$ to $-J$ in integer steps, including 0.

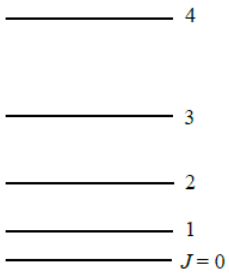


Figure 5.8.2 : Energy spacing for a rigid rotor (in 3D). Notice the energy depends only on J and not depend on m_J. That is, the energy of the rotor is not affected by its orientation.

> *Each allowed energy of rigid rotor is $(2J + 1)$-fold degenerate. Hence, there exist $(2J + 1)$ different wavefunctions with that energy.*

? Exercise 5.8.6

Compute the energy levels for a rotating molecule for $J = 0$ to $J = 5$ using units of $\frac{\hbar^2}{2I}$.

? Exercise 5.8.7

For $J = 0$ to $J = 5$, identify the degeneracy of each energy level and the values of the m_J quantum number that go with each value of the J quantum number. Construct a rotational energy level diagram including $J = 0$ through $J = 5$. Label each level

with the appropriate values for the quantum numbers J and m_J. Describe how the spacing between levels varies with increasing J.

Interpretation of Quantum Numbers for a Rigid Rotor

The m_J quantum number reflects the component of the angular momentum along the z direction (and hence is sometimes called the azimuthal quantum number). For a fixed value of J, the different values of m_J reflect the different **directions** the angular momentum vector could be pointing – for large, positive m_J the angular momentum is mostly along +z; if m_J is zero the angular momentum is orthogonal to z. Physically, the energy of the rotation does not depend on the direction, which is reflected in the fact that the energy depends only on J (Equation 10.8.25), which measures the length of the vector, not its direction given by m_J.

Example 5.8.7 : Molecular Oxygen

Calculate $J = 0$ to $J = 1$ rotational transition of the O_2 molecule with a bond length of 121 pm.

Solution

$$E = \frac{\hbar^2}{I} = \frac{\hbar^2}{\mu r^2}$$

$$\mu_{O2} = \frac{m_O m_O}{m_O + m_O} = \frac{(15.9994)(15.9994)}{15.9994 + 15.9994} = 7.9997$$

convert from atomic units to kilogram using the conversion: 1 au = 1.66 x 10^{-27} kg. Plug and chug.

$$E = 5.71 \times 10^{-27}\ Joules$$

Spherical Harmonics

A wavefunction that is a solution to the rigid rotor Schrödinger Equation (Equation 10.8.9) can be written as a single function $Y(\theta, \varphi)$, which is called a spherical harmonic function.

$$Y_J^{m_J}(\theta, \varphi) = \Theta_J^{|m_J|}(\theta)\Phi_{m_J}(\varphi) \tag{10.8.26}$$

The spherical harmonic wavefunction is labeled with m_J and J because its functional form depends on both of these quantum numbers. These functions are tabulated above for $J = 0$ through $J = 2$ and for $J = 3$ in the Spherical Harmonics Table (M4) Polar plots of some of the θ-functions are shown in Figure 5.8.3 .

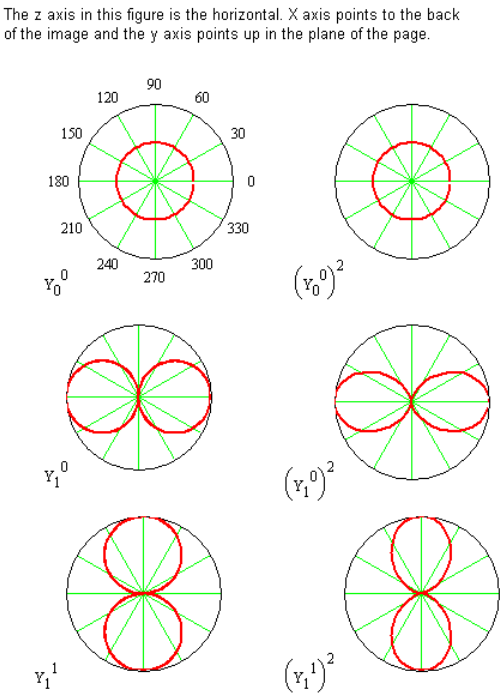


Figure 5.8.3 : Polar plots in which the distance from the center gives the value of the function Y for the indicated angle θ.

The two-dimensional space for a rigid rotor is defined as the surface of a sphere of radius r_0, as shown in Figure 5.8.2 .

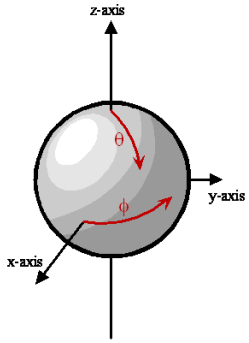


Figure 5.8.4 : Space for a rigid rotor is restricted to the surface of a sphere of radius r_0. The only degrees of freedom are motions along θ or φ on the surface of the sphere.

The probability of finding the internuclear axis at specific coordinates θ_0 and φ_0 within an infinitesimal area ds on this curved surface is given by

$$Pr\left[\theta_0, \varphi_0\right] = Y_J^{m_{J*}}(\theta_0, \varphi_0) Y_J^{m_J}(\theta_0, \varphi_0) ds \tag{10.8.27}$$

where the area element ds is centered at θ_0 and φ_0.

Within the Copenhagen interpretation of wavefunctions, the absolute square (or modulus squared) of the rigid rotor wavefunction $Y_J^{m_{J*}}(\theta, \varphi) Y_J^{m_J}(\theta, \varphi)$ gives the probability density for finding the internuclear axis oriented at θ to the z-axis and φ to the x-axis. In spherical coordinates the area element used for integrating θ and φ is

$$ds = \sin\theta \, d\theta \, d\varphi \tag{10.8.28}$$

? Exercise 5.8.8

Use calculus to evaluate the probability of finding the internuclear axis of a molecule described by the $J = 1$, $m_J = 0$ wavefunction somewhere in the region defined by a range in θ of 0° to 45°, and a range in of 0° to 90°. Note that a double

integral will be needed. Sketch this region as a shaded area on Figure 5.8.3 .

Consider the significance of the probability density function by examining the $J = 1$, $m_J = 0$ wavefunction. The Spherical Harmonic for this case is

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta \tag{10.8.29}$$

The polar plot of $(Y_1^0)^2$ is shown in Figure 5.8.3 . For $J = 1$ and $m_J = 0$, the probability of finding the internuclear axis is independent of the angle φ from the x-axis, and greatest for finding the internuclear axis along the z-axis, but there also is a probability for finding it at other values of θ as well. So, although the internuclear axis is not always aligned with the z-axis, the probability is highest for this alignment. Also, since the probability is independent of the angle φ, the internuclear axis can be found in any plane containing the z-axis with equal probability.

The $J = 1$, $m_J = 0$ function is 0 when θ = 90°. Therefore, the entire xy-plane is a **node**. This fact means the probability of finding the internuclear axis in this particular horizontal plane is 0 in contradiction to our classical picture of a rotating molecule. In the classical picture, a molecule rotating in a plane perpendicular to the xy-plane must have the internuclear axis lie in the xy-plane twice every revolution, but the quantum mechanical description says that the probability of being in the xy-plane is zero. This conclusion means that molecules are not rotating in the classical sense, but they still have some, but not all, of the properties associated with classical rotation. The properties they retain are associated with angular momentum.

? Exercise 5.8.9

For each state with $J = 0$ and $J = 1$, use the function form of the Y spherical harmonics and Figure 5.8.1 to determine the most probable orientation of the internuclear axis in a diatomic molecule, i.e., the most probable values for θ and θ.

? Exercise 5.8.10

Write a paragraph describing the information about a rotating molecule that is provided in the polar plot of $Pr[\theta, \theta]$ for the $J = 1$, $m_J = \pm 1$ state in Figure 5.8.1 . Compare this information to the classical picture of a rotating object.

Summary

There are two quantum numbers that describe the quantum behavior of a rigid rotor in three-deminesions: J is the total angular momentum quantum number and m_J is the z-component of the angular momentum. The spherical harmonics called $Y_J^{m_J}$ are functions whose probability $|Y_J^{m_J}|^2$ has the well known shapes of the s, p and d orbitals etc learned in general chemistry.

References

1. Anderson, J.M. Introduction to Quantum Chemistry, 1969, W.A. Benjamin, Inc, pg.91-100.
2. Atkins, Peter and de Paula, Julio. Physical Chemistry for the Life Sciences. New York: W.H. Freeman and Company. p. 515.

Contributors and Attributions

- Ian Huh
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Mark Tuckerman (New York University)
- MIT OpenCourseWare (Robert Guy Griffin and Troy Van Voorhis)

10.8: The Energy Levels of a Rigid Rotor is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.8: The Energy Levels of a Rigid Rotor** is licensed CC BY-NC-SA 4.0.

10.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

Learning Objectives

- Demonstrate how to use the 3D regid rotor to describe a rotating diatomic molecules
- Demonstate how microwave spectroscopy can get used to characterize rotating diatomic molecules
- Interprete a simple microwave spectrum for a diatomic molecule

To develop a description of the rotational states, we will consider the molecule to be a rigid object, i.e. the bond lengths are fixed and the molecule cannot vibrate. This model for rotation is called the rigid-rotor model. It is a good approximation (even though a molecule vibrates as it rotates, and the bonds are elastic rather than rigid) because the amplitude of the vibration is small compared to the bond length.

The rotation of a rigid object in space is very simple to visualize. Pick up any object and rotate it. There are orthogonal rotations about each of the three Cartesian coordinate axes just as there are orthogonal translations in each of the directions in three-dimensional space (Figures 5.9.1 and 5.9.2). These rotations are said to be *orthogonal* because one can not describe a rotation about one axis in terms of rotations about the other axes just as one can not describe a translation along the x-axis in terms of translations along the y- and z-axes. For a linear molecule, the motion around the interatomic axis (x-axis) is not considered a rotation.

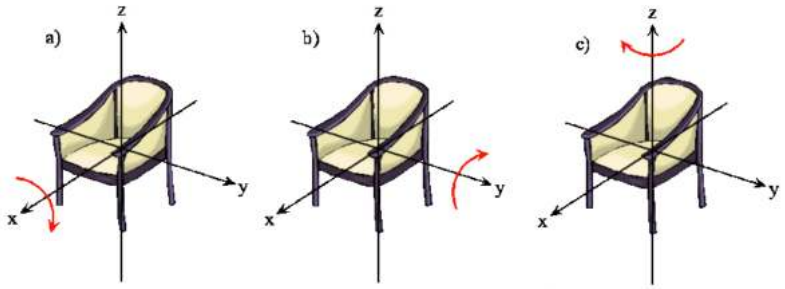


Figure 5.9.1 : Cartesian rotations of a chair. Rotations about the (a) x axis, (b) y axis, and (c) z axis.

In this section we examine the rotational states for a diatomic molecule by comparing the classical interpretation of the angular momentum vector with the probabilistic interpretation of the angular momentum wavefunctions. We want to answer the following types of questions. How do we describe the orientation of a rotating diatomic molecule in space? Is the molecule actually rotating? What properties of the molecule can be physically observed? In what ways does the quantum mechanical description of a rotating molecule differ from the classical image of a rotating molecule?

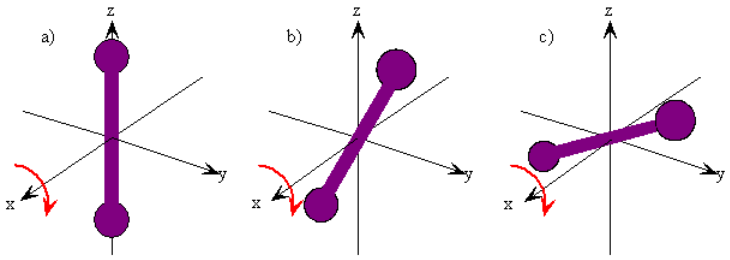


Figure 5.9.2 : Rotation of a diatomic molecule about the x axis.

Introduction to Microwave Spectroscopy

The permanent electric dipole moments of polar molecules can couple to the electric field of electromagnetic radiation. This coupling induces transitions between the rotational states of the molecules. The energies that are associated with these transitions are detected in the far infrared and microwave regions of the spectrum. For example, the microwave spectrum for carbon monoxide spans a frequency range of 100 to 1200 GHz, which corresponds to 3 - 40 cm^{-1}.

The selection rules for the rotational transitions are derived from the transition moment integral by using the spherical harmonic functions and the appropriate dipole moment operator, $\hat{\mu}$.

$$\mu_T = \int Y_{J_f}^{m_f *} \hat{\mu} Y_{J_i}^{m_i} \sin\theta \, d\theta \, d\varphi \tag{10.9.1}$$

or in braket notation

$$\mu_T = \langle Y_{J_f}^{m_f} \left| \hat{\mu} \right| Y_{J_i}^{m_i} \rangle \tag{10.9.2}$$

Evaluating the transition moment integral involves a bit of mathematical effort. This evaluation reveals that the transition moment depends on the square of the dipole moment of the molecule, μ^2 and the rotational quantum number, J, of the initial state in the transition,

$$\mu_T = \mu^2 \frac{J+1}{2J+1} \tag{10.9.3}$$

and that the selection rules for rotational transitions are

$$\Delta J = \pm 1 \tag{10.9.4}$$

and

$$\Delta m_J = 0, \pm 1 \tag{10.9.5}$$

A photon is absorbed for $\Delta J = +1$ and emitted for $\Delta J = -1$.

? Exercise 5.9.1

Explain why your microwave oven heats water, but not air. Hint: draw and compare Lewis structures for components of air and for water.

The energies of the Jth rotational levels are given by

$$E_J = J(J+1)\frac{\hbar^2}{2I} \tag{10.9.6}$$

with each Jth energy level having a degeneracy of $2J+1$ due to the different possible m_J values.

Microwave Transition Energies

The transition energies for absorption of radiation are given by

$$E_{photon} = \Delta E \tag{10.9.7}$$
$$= E_f - E_i \tag{10.9.8}$$
$$= h\nu \tag{10.9.9}$$
$$= hc\bar{\nu} \tag{10.9.10}$$

Substituting the relationship for energy (Equation 10.9.6) into Equation 10.9.8 results in

$$E_{photon} = E_f - E_i \tag{10.9.11}$$
$$= J_f(J_f+1)\frac{\hbar^2}{2I} - J_i(J_i+1)\frac{\hbar^2}{2I} \tag{10.9.12}$$

with J_i and J_f representing the rotational quantum numbers of the initial (lower) and final (upper) levels involved in the absorption transition.

Since microwave spectroscopists use frequency units and infrared spectroscopists use wavenumber units when describing rotational spectra and energy levels, both ν and $\bar{\nu}$ are important to calculate. When we add in the constraints imposed by the selection rules to identify possible transitions, J_f in Equation 10.9.12 can be replaced by $J_i + 1$, since the selection rule requires $J_f - J_i = 1$ for the

absorption of a photon (Equation 10.9.4). The equation for absorption transitions (Equation 10.9.12) then can be written in terms of the only the quantum number J_i of the initial state.

$$E_{photon} = h\nu \tag{10.9.13}$$

$$= hc\bar{\nu} \tag{10.9.14}$$

$$= 2(J_i + 1)\frac{\hbar^2}{2I} \tag{10.9.15}$$

Equation 10.9.15 can be rewritten as

$$E_{photon} = 2B(J_i + 1)$$

where B is the **rotational constant** for the molecule and is defined in terms of the *energy* of the absorbed photon

$$B = \frac{\hbar^2}{2I} \tag{10.9.16}$$

Often spectroscopists want to express the rotational constant in terms of *frequency* of the absorbed photon and do so by dividing Equation 10.9.16 by h

$$B(\text{in freq}) = \frac{B}{h} \tag{10.9.17}$$

$$= \frac{h}{8\pi^2\mu r_0^2} \tag{10.9.18}$$

More often, spectroscopists want to express the rotational constant in terms of *wavenumbers* ($\bar{\nu}$) of the absorbed photon by dividing Equation 10.9.16 by hc,

$$\tilde{B} = \frac{B}{hc} = \frac{h}{8\pi^2 c\mu r_0^2} \tag{10.9.19}$$

The rotational constant depends on the distance (R) and the masses of the atoms (via the reduced mass) of the nuclei in the diatomic molecule.

? Exercise 5.9.2

Construct a rotational energy level diagram for $J = 0$, 1, and 2 and add arrows to show all the allowed transitions between states that cause electromagnetic radiation to be absorbed or emitted.

? Exercise 5.9.3

Complete the steps going from Equation 10.9.12 to Equation 10.9.16 and identify the units of B at the end.

? Exercise 5.9.4

Infrared spectroscopists use units of wavenumbers. Rewrite the steps going from Equation 10.9.12 to Equation 10.9.16 to obtain expressions for $h\nu$ and B in units of wavenumbers. Note that to convert B in Hz to B in cm^{-1}, you simply divide the former by c.

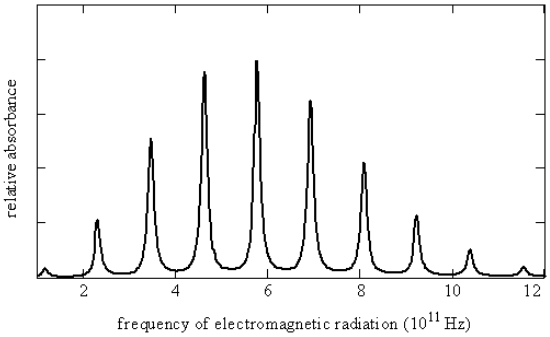


Figure 5.9.3: The rotation spectrum of $^{12}C^{16}O$ at 40 K. The peaks are tabulated in Table 5.9.1.

Figure 5.9.3 shows the rotational spectrum as a series of nearly equally spaced lines. The line positions ν_J, line spacings, and the maximum absorption coefficients (γ_{max}, the absorption coefficients associated with the specified line position) for each line in this spectrum are given here in Table 5.9.1.

Table 5.9.1 : Rotational Transitions in $^{12}C^{16}O$ at 40 K

J	ν_J (MHz)	Spacing from previous line (MHz)	γ_{max}
$0 \rightarrow 1$	115,271.21	0	0.0082
$1 \rightarrow 2$	230,538.01	115,266.80	0.0533
$2 \rightarrow 3$	345,795.99	115,257.99	0.1278
$3 \rightarrow 4$	461,040.76	115,244.77	0.1878
$4 \rightarrow 5$	576,267.91	115,227.15	0.1983
$6 \rightarrow 6$	691,473.03	115,205.12	0.1618
$6 \rightarrow 7$	806,651.78	115,178.68	0.1064
$7 \rightarrow 8$	921,799.55	115,147.84	0.0576
$8 \rightarrow 9$	1,036,912.14	115,112.59	0.0262
$9 \rightarrow 10$	1,151,985.08	115,072.94	0.0103

Let's try to reproduce Figure 5.9.3 from the data in Table 5.9.1 by using the quantum theory that we have developed so far. Equation 10.9.19 predicts a pattern of exactly equally spaced lines. The lowest energy transition is between $J_i = 0$ and $J_f = 1$ so the first line in the spectrum appears at a frequency of $2B$. The next transition is from $J_i = 1$ to $J_f = 2$ so the second line appears at $4B$. The spacing of these two lines is $2B$. In fact the spacing of all the lines is $2B$, which is consistent with the experimental data in Table 5.9.1 showing that the lines are very nearly equally spaced. The difference between the first spacing and the last spacing is less than 0.2%.

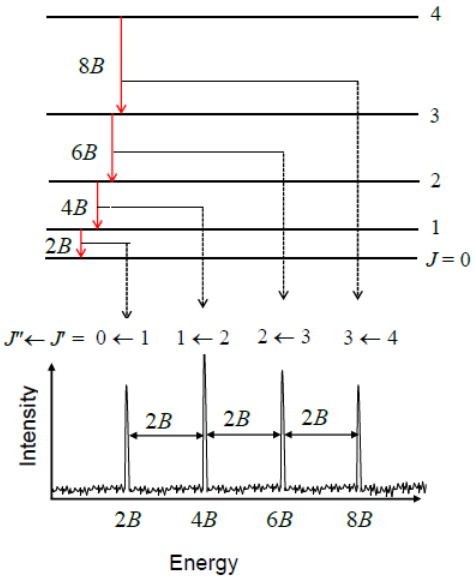


Figure 5.9.4 : Energy levels and line positions calculated in the rigid rotor approximation. (CC BY-SA 3.0; Nrrw via Wikipedia)

Exercise 5.9.5

Use Equation 10.9.19 to prove that the spacing of any two lines in a rotational spectrum is $2B$, i.e. derive:

$$\nu_{J_i+1} - \nu_{J_i} = 2B$$

Example 5.9.1 : Rotation of Sodium Hydride

The molecule $\mathbf{NaH}$ undergoes a rotational transition from $J = 0$ to $J = 1$ when it absorbs a photon of frequency $2.94 \times 10^{11}\ Hz$. What is the equilibrium bond length of the molecule?

Solution

We use $J = 0$ in the formula for the transition frequency

$$\nu = 2B = \frac{\hbar}{2\pi I} = \frac{\hbar}{2\pi\mu R_e^2}$$

Solving for R_e gives

$$R_e = \sqrt{\frac{\hbar}{2\pi\mu\nu}}$$

The reduced mass is given by

$$\begin{aligned}\mu &= \frac{m_{Na}m_H}{m_{Na}+m_H} \\ &= \frac{(22.989)(1.0078)}{22.989+1.0078} \\ &= 0.9655\end{aligned}$$

which is in atomic mass units or relative units. To convert to kilograms, we need the conversion factor $1\ au = 1.66 \times 10^{-27}\ kg$. Multiplying this by 0.9655 gives a reduced mass of $1.603 \times 10^{-27}\ kg$. Substituting in for R_e gives

$$\begin{aligned}R_e &= \sqrt{\frac{(1.055 \times 10^{-34}\ J \cdot s)}{2\pi(1.603 \times 10^{-27}\ kg)(2.94 \times 10^{11}\ Hz)}} \\ &= 1.899 \times 10^{-10}\ m \\ &= 1.89\ \mathring{A}\end{aligned}$$

Example 5.9.6

Use the frequency of the $J = 0$ to $J = 1$ transition observed for carbon monoxide to determine a bond length for $^{12}C^{16}O$.

Solution

- J=0: $v_0 = 115271.21\ \text{MHz}$
- J=1: $v_1 = 230538.01\ \text{MHz}$

$$\begin{aligned}\Delta v &= 230538.01\ \text{MHz} - 115271.21\ \text{MHz} \\ &= 115266.8\ \text{MHz} \\ &= 1.153 \times 10^{11}\ \text{Hz} \\ &= \frac{\hbar}{2\pi\mu R_e^2}\end{aligned}$$

The reduced mass is

$$\begin{aligned}\mu &= \frac{m_C m_O}{m_C + m_O} \\ &= \frac{12.01 \times 16.00}{12.01 + 16.00} \\ &= 6.86\ \text{amu}\end{aligned}$$

Convert to kg

$$6.86 amu \left(\frac{1.661 \times 10^{-27}\ \text{kg}}{12\ \text{amu}}\right) = 1.139 \times 10^{-26}\ \text{kg}$$

$$\begin{aligned}R_e &= \sqrt{\frac{\hbar}{2\pi\mu\Delta v}} \\ &= \sqrt{\frac{1.055 \times 10^{-34}\ J \cdot s}{2\pi \cdot 1.139 \times 10^{-26}\ \text{kg} \cdot 1.153 \times 10^{11}\ \text{Hz}}} \\ &= 1.131 \times 10^{-10}\text{m} \\ &= 1.131\ \mathring{A}\end{aligned}$$

Advanced: Non-Rigid Rotors

Centrifugal stretching of the bond as J increases causes the decrease in the spacing between the lines in an observed spectrum (Table 5.9.1). This decrease shows that the molecule is not really a rigid rotor. As the rotational angular momentum increases with increasing J, the bond stretches. This stretching increases the moment of inertia and decreases the rotational constant (Figure 5.9.5).



Figure 5.9.5 : Two atoms connected by a vibrating bond. There is a rotation around the common center of mass, and oscillation in bond distance. (CC SA-BY 3.0; www.cleonis.nl).

The effect of centrifugal stretching is smallest at low J values, so a good estimate for B can be obtained from the $J = 0$ to $J = 1$ transition. From B, a value for the bond length of the molecule can be obtained since the moment of inertia that appears in the definition of B (Equation 10.9.16) is the reduced mass times the bond length squared. When the centrifugal stretching is taken into account quantitatively, the development of which is beyond the scope of the discussion here, a very accurate and precise

value for B can be obtained from the observed transition frequencies because of their high precision. Rotational transition frequencies are routinely reported to 8 and 9 significant figures.

As we have just seen, quantum theory successfully predicts the line spacing in a rotational spectrum. An additional feature of the spectrum is the line intensities. The lines in a rotational spectrum do not all have the same intensity, as can be seen in Figure 5.9.3 and Table 5.9.1. This is related to the populations of the initial and final states. This aspect of spectroscopy will be discussed in more detail in the following chapters

---

10.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **5.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

10.10: The Harmonic Oscillator and the Rigid Rotor (Exercises)

Solutions to select questions can be found online.

5.7

Calculate the reduced mass of HCl molecule given that the mass of H atom is 1.0078 amu and the mass of Cl atom is 34.9688 amu. Note that 1 amu = 1.660565*10^{-27} kg.

5.8

Calculate the reduced mass for the Br_2, Cl_2, and I_2 diatomics.

5.14

$^{79}Br^{79}Br$ has a force constant of $240\ N \cdot m^{-1}$. Given this information:

a. Calculate the fundamental vibrational frequency and
b. Calculate the $^{79}Br^{79}Br$ zero point energy.

5.19

Prove that the second derivative of an even function is even and odd function is odd.

5.27

The Harmonic oscillator Hamiltonian obeys the reflective property:

$$\hat{H}(x) = \hat{H}(-x)$$

What does this say about the nature of the harmonic oscillator wave function?

5.28

If $\langle x \rangle$ is an odd function, what does that say about p_x?

Hint: use

$$\frac{d\langle p_x \rangle}{dt} = \left\langle \frac{-dV}{dx} \right\rangle$$

also known as **Ehrenfest's Theorem**, where V is the potential of a one dimensional harmonic oscillator.

Hence, $\langle p_x \rangle$ does not depend on time.

5.32

Convert ∇^2 from Cartesian coordinates to cylindrical coordinates.

5.37

Find the magnitude of angular momentum and the z component of angular momentum for electrons in a hydrogen-like species with

a. quantum numbers $n = 1, l = 0, m = 0$; and
b. $n = 2, l = 0, m = 0$.

Compare your answers and explain your results.

5.38

Apply the angular momentum operator in the x direction to the following functions ($Y(\theta, \phi)$).

a. $\frac{5\pi}{4} + 7\exp(\pi^2)$
b. $3\pi\sin(\theta)$
c. $\frac{3}{2}\cos(\theta)\exp(i\phi)$

5.41

Use the fact that $\hat{x}$ and $\hat{p}$ are Hermitian in the number operator

$$\hat{a}_- = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{p})$$

$$\hat{a}_+ = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{p})$$

and

$$\hat{H} = \frac{\hbar w}{2}(\hat{a}_-\hat{a}_+ + \hat{a}_+\hat{a}_-)$$

Show that

$$\int \psi_v^* \hat{v} \psi dx \geq 0$$

5.43

Determine the unnormalized wave function $\psi_\circ(x)$ given that $\hat{a}_- = 2^{-1/2}(\hat{x} + i\hat{p})$ and that $\hat{a_-}\psi_\circ = 0$ Then find the unnormalized wave function for $\psi_1(x)$ using $\hat{a}_+$.

5.46

Find the reduced mass of an electron in a Tritium atom. Set the mass of the Tritium to be $5.008267 \times 10^{-27}\ kg$. Then find the value of the Rydberg constant for the Tritium atom.

5.46

The mass of a deuterium atom is $3.343586 \times 10^{-27}\ kg$. First calculate the reduce mass of the deuterium atom. Then using the reduced mass calculated find the Rydberg constant for a deuterium atom.

5.47

What is the ratio of the frequency of spectral lines of C-14 that has been ionized 5 times and C-12 that has been ionized 5 times?

5.47

Calculate the Rydberg constant for a deuterium atom and atomic hydrogen given the reduced mass of a deuterium atom is $9.106909 \times 10^{-31} kg$ and the reduced mass of hydrogen is $9.104431 \times 10^{-31} kg$. Compare both of these answers with the experimental result ($109677.6 cm^{-1}$). Then determine the ratio of the frequencies of the lines in the spectra of atomic hydrogen and atomic deuterium.

5.46

Find the reduced mass of HCl where the mass of hydrogen in 1 amu and the mass of chloride is 35 amu.

10.10: The Harmonic Oscillator and the Rigid Rotor (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

11: The Hydrogen Atom

The solution of the Schrödinger equation (wave equation) for the hydrogen atom uses the fact that the Coulomb potential produced by the nucleus is isotropic (it is radially symmetric in space and only depends on the distance to the nucleus). Although the resulting energy eigenfunctions (the orbitals) are not necessarily isotropic themselves, their dependence on the angular coordinates follows completely generally from this isotropy of the underlying potential: the eigenstates of the Hamiltonian (that is, the energy eigenstates) can be chosen as simultaneous eigenstates of the angular momentum operator. This corresponds to the fact that angular momentum is conserved in the orbital motion of the electron around the nucleus. Therefore, the energy eigenstates may be classified by two angular momentum quantum numbers, ℓ and m (both are integers). The angular momentum quantum number $\ell = 0, 1, 2, \ldots$ determines the magnitude of the angular momentum. The magnetic quantum number $m = -\ell, \ldots, +\ell$ determines the projection of the angular momentum on the (arbitrarily chosen) z-axis.

11.1: The Schrödinger Equation for the Hydrogen Atom Can Be Solved Exactly

11.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics

11.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

11.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers

11.5: s Orbitals are Spherically Symmetric

11.6: Orbital Angular Momentum and the p-orbitals

11.7: The Helium Atom Cannot Be Solved Exactly

11.8: The Hydrogen Atom (Exercises)

Thumbnail: Depiction of a hydrogen atom with size of central proton shown, and the atomic diameter shown as about twice the Bohr model radius (image not to scale). (Public Domain; Bensaccount).

11: The Hydrogen Atom is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

11.1: The Schrödinger Equation for the Hydrogen Atom Can Be Solved Exactly

6.01: The Schrödinger Equation for the Hydrogen Atom Can Be Solved Exactly

11.1: The Schrödinger Equation for the Hydrogen Atom Can Be Solved Exactly is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

11.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics

The solutions to the hydrogen atom Schrödinger equation are functions that are products of a spherical harmonic function and a radial function:

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_l^{m_l}(\theta,\phi) \tag{11.2.1}$$

The wavefunctions for the hydrogen atom depend upon the three variables r, θ, and ϕ and the three quantum numbers n, l, and m_l. The variables give the position of the electron relative to the nucleus in spherical coordinates. The absolute square of the wavefunction, $|\psi(r,\theta,\phi)|^2$, evaluated at r, θ, and ϕ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r, θ, and ϕ.

? Exercise 6.2.1

What is the value of the integral (in braket notation)

$$\langle\psi(r,\theta,\phi)|\psi(r,\theta,\phi)\rangle \ ?$$

or expanded in integral notation (in Cartesian coordinates)

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} |\psi(x,y,z)|^2\,dx\,dy\,dz$$

or expanded in integral notation (in spherical coordinates)

$$\int_{0}^{+\infty}\int_{0}^{\pi}\int_{0}^{+2\pi} |\psi(r,\theta,\phi)|^2 r^2 \sin\theta\,d\theta\,d\phi\,dr$$

The quantum numbers have names:

- n is called the principal quantum number,
- l is called the angular momentum quantum number, and
- m_l is called the magnetic quantum number because (as we will see, the energy in a magnetic field depends upon m_l).

Often l is called the azimuthal quantum number because it is a consequence of the θ-equation, which involves the azimuthal angle Θ, referring to the angle to the zenith. These quantum numbers have specific values that are dictated by the physical constraints or boundary conditions imposed upon the Schrödinger equation: n must be an integer greater than 0, l can have the values 0 to n-1, and m_l can have $2l+1$ values ranging from $-l$ to $+l$ in unit or integer steps. The total number of orbitals with a particular value of n is n^2 - i.e., this is the **degeneracy** of the system.

Wavefunction Nomenclature

The values of the quantum number l usually are coded by a letter: s means 0, p means 1, d means 2, f means 3; the next codes continue alphabetically (e.g., g means $l = 4$). The quantum numbers specify the quantization of physical quantities. The discrete energies of different states of the hydrogen atom are given by n, the magnitude of the angular momentum is given by l, and one component of the angular momentum (usually chosen by chemists to be the z-component) is given by m_l.

The Φ function is found to have the quantum number m, where

$$\Phi_m(\phi) = A_m e^{im\phi}$$

and A_m is the normalization constant and $m = 0, \pm1, \pm2 ... \pm\infty$. The Θ function was solved and is known as *Legendre polynomials*, which have quantum numbers m and ℓ. When Θ and Φ are multiplied together, the product is known as **spherical harmonics** with labeling $Y_J^m(\theta,\phi)$.

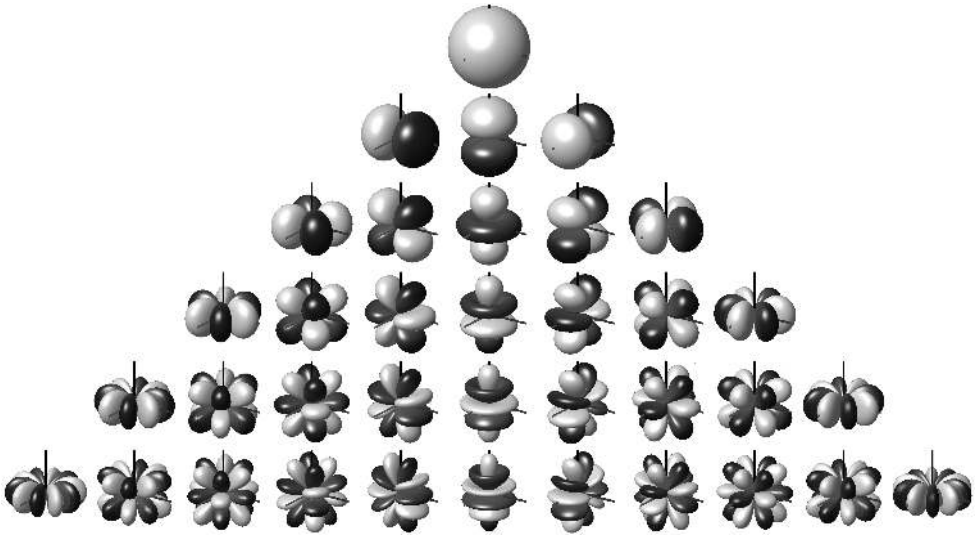


Figure 6.2.1: Spherical Harmonics as commonly displayed, sorted by increasing energies and aligned for symmetry.

Figure 6.2.1 shows the spherical harmonics Y_J^M, which are solutions of the angular Schrödinger equation. These are explicitly written in Table 6.2.1 . Notice that these functions are complex in nature.

Table 6.2.1 : spherical harmonics Y_J^M

m_J	J	$\Theta_J^{m_J}(\theta)$	$\Phi(\varphi)$	$Y_J^{m_J}(\theta,\varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$
1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$
-1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$
2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$
-2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{-2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$

? Exercise 6.2.2

Consider several values for n, and show that the number of orbitals for each n is n^2.

? Exercise 6.2.3

Construct a table summarizing the allowed values for the quantum numbers n, l, and m_l. for energy levels 1 through 7 of hydrogen.

? Exercise 6.2.4

The notation 3d specifies the quantum numbers for an electron in the hydrogen atom.

a. What are the values for n and l?

b. What are the values for the energy and angular momentum?
c. What are the possible values for the magnetic quantum number?
d. What are the possible orientations for the angular momentum vector?

Atomic Orbitals

The hydrogen atom wavefunctions, $\psi(r,\theta,\phi)$, are called **atomic orbitals**. An atomic orbital is a function that describes one electron in an atom. The wavefunction with $n = 1$, $l = 0$, and $m_l = 0$ is called the 1s orbital, and an electron that is described by this function is said to be "in" the 1s orbital, i.e. have a 1s orbital state. The constraints on n, ℓ, and m_ℓ that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

The first few solutions of the Schrödinger equation for the H atom are:

Table 6.2.1 : The solutions to the Schrödinger equation for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

	n	l	m_l	ψ_{n,l,m_l}
ψ_{100}	1	0	$m_l = 0$	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
ψ_{200}	2	0	$m_l = 0$	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(2-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
ψ_{210}	2	1	$m_l = 0$	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\cos\theta$
$\psi_{21\pm1}$	2	1	$m_l = \pm1$	$\frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\sin\theta e^{\pm i\phi}$
ψ_{300}	3	0	$m_l = 0$	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(27-18\frac{Zr}{a_0}+2\frac{Z^2r^2}{a_0^2}\right.$
ψ_{310}	3	1	$m_l = 0$	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}\cos$
$\psi_{31\pm1}$	3	1	$m_l = \pm1$	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{3a_0}}\sin$
ψ_{320}	3	2	$m_l = 0$	$\frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}}\left(3\cos^2\theta-1\right.$
$\psi_{32\pm1}$	3	2	$m_l = \pm1$	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}}\sin\theta\cos\theta e^{\pm i\phi}$
$\psi_{32\pm2}$	3	2	$m_l = \pm2$	$\frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a_0}}\sin^2\theta e^{\pm 2i\phi}$

We can take superposition states of the solutions to obtain real wavefunctions that do not have any imaginary components:

Table 6.2.2 : The real solutions to the Schrödinger equation for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

	n	l	m_l	$\psi_{n,l}$
ψ_{1s}	1	0	0	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
ψ_{2s}	2	0	0	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(2-\frac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}}$
ψ_{2p_z}	2	1	0	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\cos\theta$
ψ_{2p_x}	2	1	±1	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\sin\theta\cos\phi$
ψ_{2p_y}	2	1	±1	$\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a_0}}\sin\theta\sin\phi$
ψ_{3s}	3	0	0	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(27-18\frac{Zr}{a_0}+2\frac{Z^2r^2}{a_0^2}\right.$
ψ_{3p_z}	3	1	0	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right)e^{-\frac{Zr}{3a_0}}\cos$
ψ_{3p_x}	3	1	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right)e^{-\frac{Zr}{3a_0}}\sin$
ψ_{3p_y}	3	1	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r\left(6-\frac{Zr}{a_0}\right)e^{-\frac{Zr}{3a_0}}\sin$
$\psi_{3d_{z^2}}$	3	2	0	$\frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2e^{-\frac{Zr}{3a_0}}\left(3\cos^2\theta-1\right.$
$\psi_{3d_{xz}}$	3	2	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2e^{-\frac{Zr}{3a_0}}\sin\theta\cos\theta\cos$
$\psi_{3d_{yz}}$	3	2	±1	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2e^{-\frac{Zr}{3a_0}}\sin\theta\cos\theta\sin$
$\psi_{3d_{x^2-y^2}}$	3	2	±2	$\frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2e^{-\frac{Zr}{3a_0}}\sin^2\theta\cos 2\phi$
$\psi_{3d_{xy}}$	3	2	±2	$\frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{7}{2}} r^2e^{-\frac{Zr}{3a_0}}\sin^2\theta\sin 2\phi$

These are the wavefunctions that are most often depicted. Visualizing the variation of an electronic wavefunction with r, θ, and ϕ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron-deficient part of one molecule is attracted to an electron-rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately do not reveal the shape of an orbital very well. The shape can be revealed better in a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$. Do not confuse such plots with polar plots, which look similar. Probability densities also can be represented by contour maps, as shown in Figure 6.2.2 .

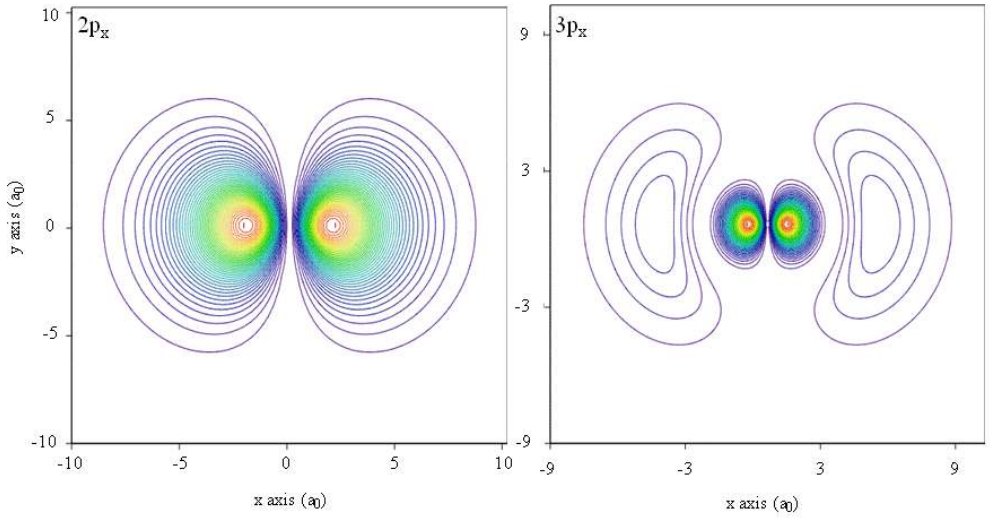


Figure 6.2.2: Contour plots in the x-y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low $R(r)^2$. The angular function used to create the figure was a linear combination of two Spherical Harmonic functions.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, $R(r)$, for the 1s, 2s, and 2p orbitals plotted in Figure 6.2.3 .

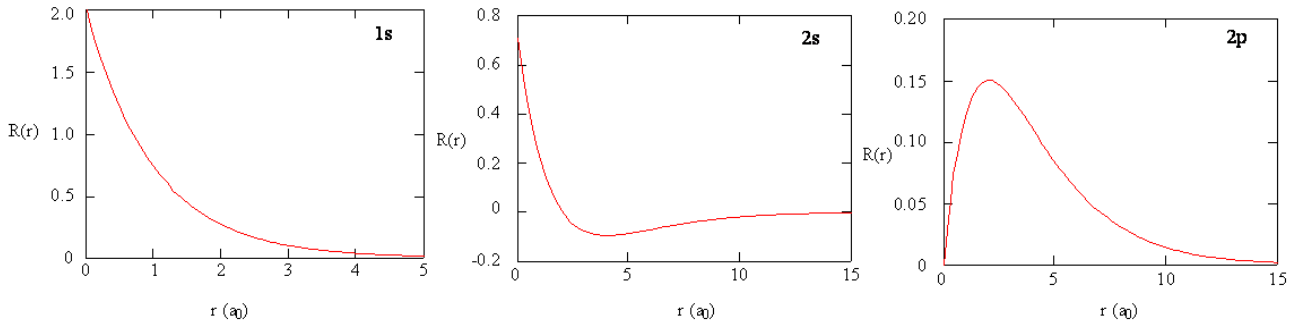


Figure 6.2.3: Radial function, $R(r)$, for the 1s, 2s, and 2p orbitals.

The 1s function in Figure 6.2.3 starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

Next notice how the radial function for the 2s orbital, Figure 6.2.3 , goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$, but p, d, f and all other functions go to zero at the origin. It is useful to remember that there are $n - 1 - l$ radial nodes in a wavefunction, which means that a 1s orbital has no radial nodes, a 2s has one radial node, and so on.

? Exercise 6.2.5

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

? Exercise 6.2.6

What mathematical feature of each of the radial functions controls the number of radial nodes?

? Exercise 6.2.7 : Radial Node

At what value of r does the 2s radial node occur?

Exercise 6.2.8

Make a table that provides the energy, number of radial nodes, and the number of angular nodes and total number of nodes for each function with $n = 1$, $n = 2$, and $n = 3$. Identify the relationship between the energy and the number of nodes. Identify the relationship between the number of radial nodes and the number of angular nodes.

The quantity $R(r)^*R(r)$ gives the radial probability density; i.e., the probability density for the electron to be at a point located the distance r from the proton. Radial probability densities for three atomic orbitals are plotted in Figure 6.2.4 .

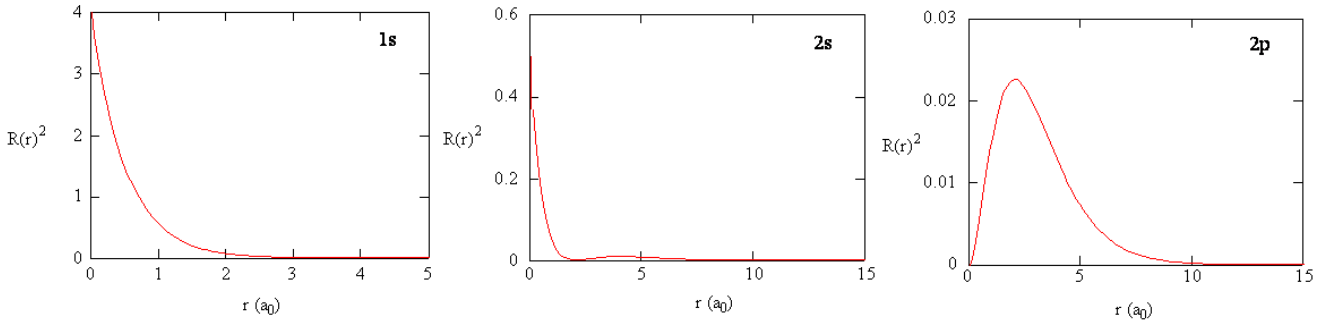


Figure 6.2.4: Radial probability densities for the 1s, 2s, and 2p orbitals.

Probabilities and Distribution Functions

When the **radial probability density** for every value of r is multiplied by the area of the spherical surface represented by that particular value of r, we get the radial distribution function. The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the proton. Since the area of a spherical surface is $4\pi r^2$, the **radial distribution function** is given by

$$\underbrace{4\pi r^2 R(r)^* R(r)}_{\text{radial probability density}}$$

Radial distribution functions are shown in Figure 6.2.5 . At small values of r, the radial distribution function is low because the small surface area for small radii modulates the high value of the radial probability density function near the nucleus. As we increase r, the surface area associated with a given value of r increases, and the r^2 term causes the radial distribution function to increase even though the radial probability density is beginning to decrease. At large values of r, the exponential decay of the radial function outweighs the increase caused by the r^2 term and the radial distribution function decreases.

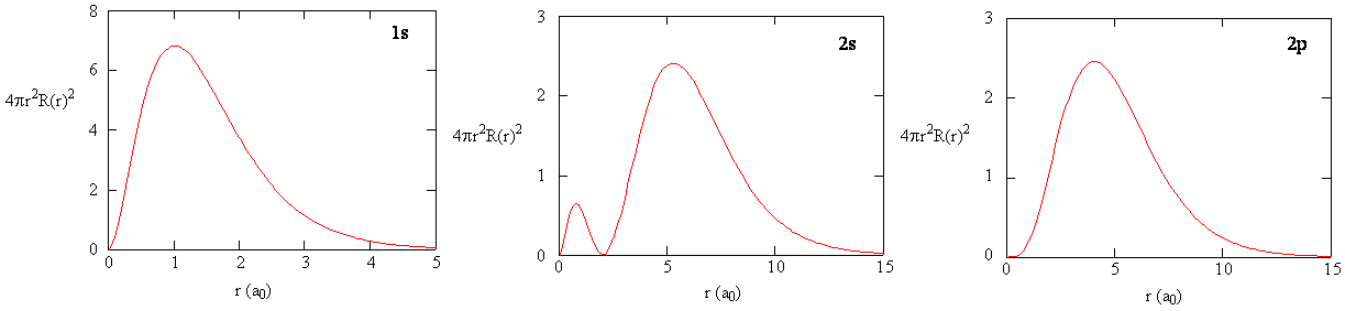


Figure 6.2.5: The radial distribution function for the 1s, 2s, and 2p orbitals.

Exercise 6.2.9

Write a quality comparison of the radial function and radial distribution function for the 2s orbital. See Figure 6.2.6 .

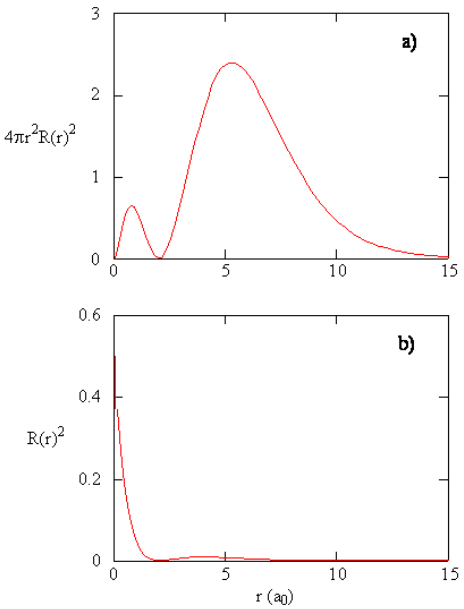


Figure 6.2.6: Comparison of a) the radial distribution function and b) the radial probability density for the 2s orbital.

11.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics** is licensed CC BY-NC-SA 4.0.
- **6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

11.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

Learning Objectives

- Understand how to measure the orbital angular momentum of an electron around a nucleus.
- Understand how the Heisenburgh Uncertainty Principle extends to orbital angular momenta.
- Manipulate the angular momenta cyclic permutations that allow two of the three projects to be simultaneous measured

Consider a particle described by the Cartesian coordinates $(x, y, z) \equiv \vec{r}$ and their conjugate momenta $(p_x, p_y, p_z) \equiv \vec{p}$. The classical definition of the *orbital angular momentum* of such a particle about the origin is (i.e., via the vector cross product):

$$\vec{L} = \vec{r} \times \vec{p}$$

which can be separated into projections into each of the primary axes :

Multiple \label

Extending this discussion to the quantum mechanics, we can assume that the operators $(\hat{L}_x, \hat{L}_y, \hat{L}_z) \equiv \vec{L}$ - that represent the components of orbital angular momentum in quantum mechanics - can be defined in an analogous manner to the corresponding components of classical angular momentum. In other words, we are going to assume that the above equations specify the angular momentum operators in terms of the position and linear momentum operators.

In Cartesian coordinates, the three operators for the orbital angular momentum components can be written as

$$\hat{L}_x = -\mathrm{i}\,\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \tag{11.3.1}$$

$$\hat{L}_y = -\mathrm{i}\,\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \tag{11.3.2}$$

$$\hat{L}_z = -\mathrm{i}\,\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \tag{11.3.3}$$

These can be transforming to operators in standard spherical polar coordinates,

Multiple \label

we obtain

Multiple \label

We can introduce a new operator $\hat{L}^2$:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{11.3.4}$$

$$= -\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \varphi^2} \right) \tag{11.3.5}$$

The eigenvalue problem for $\hat{L}^2$ takes the form

$$\hat{L}^2 \left| \psi \right\rangle = \lambda\, \hbar^2 \left| \psi \right\rangle \tag{11.3.6}$$

where $\psi(r, \theta, \varphi)$ is the wavefunction, and λ is a number. Let us write

$$\psi(r, \theta, \varphi) = R(r)\, Y(\theta, \varphi) \tag{11.3.7}$$

By definition,

$$\boxed{L^2 Y_l^{m_l} = l\,(l+1)\,\hbar^2\, Y_l^{m_l}} \tag{11.3.8}$$

where l is an integer. This is an important conclusion that argues the angular momentum is quantized with the square of the magnitude of the angular momentum only capable of assume one of the discrete set of values (Equation 11.3.8). From this, the **amplitude** of angular momentum can be expressed

$$\boxed{|\vec{L}| = \sqrt{L^2} = \sqrt{l(l+1)}\hbar} \tag{11.3.9}$$

Warning

We often refer to a particle in a state with angular momentum quantum number l as having angular momentum l, rather than saying that it has angular momentum of $\sqrt{l(l+1)}\hbar$ magnitude, primarily since it is awkward to say quickly.

The properties of spherical harmonics that the z-component of the angular momentum (L_z) is also quantized and can only assume a one of a discrete set of values

$$L_z Y_l^{m_l} = m\hbar Y_l^{m_l} \tag{11.3.10}$$

where m_l is an integer lying in the range $-l \leq m_l \leq l$.

- l is sometimes called "azimuthal quantum number" or "orbital quantum number"
- m_l is sometimes called "magnetic quantum number"

Simultaneous Measurements

Note that observables associated with $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ can, in principle, be measured. However, to determine if they can be measured *simultaneously* with infinite precision, the corresponding operators must **commute**. Remember that the fundamental commutation relations satisfied by the position and linear momentum operators are:

Multiple \label

where i and j stand for either x, y, or z. Consider the commutator of the operators $\hat{L}_x$ and $\hat{L}_z$:

Multiple \label

The **cyclic permutations** of the above result yield the fundamental commutation relations satisfied by the components of an orbital angular momentum:

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\hbar\hat{L}_z \tag{11.3.11}$$

$$[\hat{L}_y, \hat{L}_z] = \mathrm{i}\hbar\hat{L}_x \tag{11.3.12}$$

$$[\hat{L}_z, \hat{L}_x] = \mathrm{i}\hbar\hat{L}_y \tag{11.3.13}$$

The three commutation relations (Equations 11.3.11 - 11.3.13) are the foundation for the whole theory of angular momentum in quantum mechanics. Whenever we encounter three operators having these commutation relations, we know that the dynamical variables that they represent have identical properties to those of the components of an angular momentum (which we are about to derive). In fact, we shall assume that any three operators that satisfy the commutation relations (Equations 11.3.11 - 11.3.13) represent the components of some sort of angular momentum.

> *Any three operators that satisfy the cyclic commutation relations represent the components of some sort of angular momentum.*

Example 6.3.1 : Commutators

Show that the $\hat{L}^2$ and $\hat{L}_x$ operators commute.

Solution

We want to confirm that $[\hat{L}^2, \hat{L}_x] = 0$ that from Equation 11.3.4 this can be expanded

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x]$$

from the properties of commutators, this can be expanded

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2, \hat{L}_x] + [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x]$$

However,

$$[\hat{L}_x^2, \hat{L}_x] = \hat{L}_x^2\hat{L}_x - \hat{L}_x\hat{L}_x^2 = \hat{L}_x\hat{L}_x\hat{L}_x - \hat{L}_x\hat{L}_x\hat{L}_x = 0$$

So

$$\begin{aligned}[\hat{L}^2, \hat{L}_x] &= [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\ &= \hat{L}_y^2\hat{L}_x - \hat{L}_x\hat{L}_y^2 + \hat{L}_z^2\hat{L}_x - \hat{L}_x\hat{L}_z^2 \\ &= \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z\end{aligned}$$

Lets look at some related forms which can be used to simplify the above expression. The first two terms can and final two terms can be rewritten as different commutators

$$\begin{aligned}[\hat{L}_y, \hat{L}_x] &= \hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] \\ &= (\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y)\hat{L}_y + \hat{L}_y(\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y) \\ &= \cancel{\hat{L}_y\hat{L}_x\hat{L}_y} - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_y\hat{L}_y\hat{L}_x - \cancel{\hat{L}_y\hat{L}_x\hat{L}_y}\end{aligned}$$

The first & fourth terms cancel, giving

$$[\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] = \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y$$

Similarly,

$$[Lz, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] = \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z$$

So,

$$\begin{aligned}[\hat{L}^2, \hat{L}_x] &= [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] \\ &= -i\hbar\hat{L}_z\hat{L}_y - i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_y\hat{L}_z + ih\hat{L}_z\hat{L}_y \\ &= 0\end{aligned}$$

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).

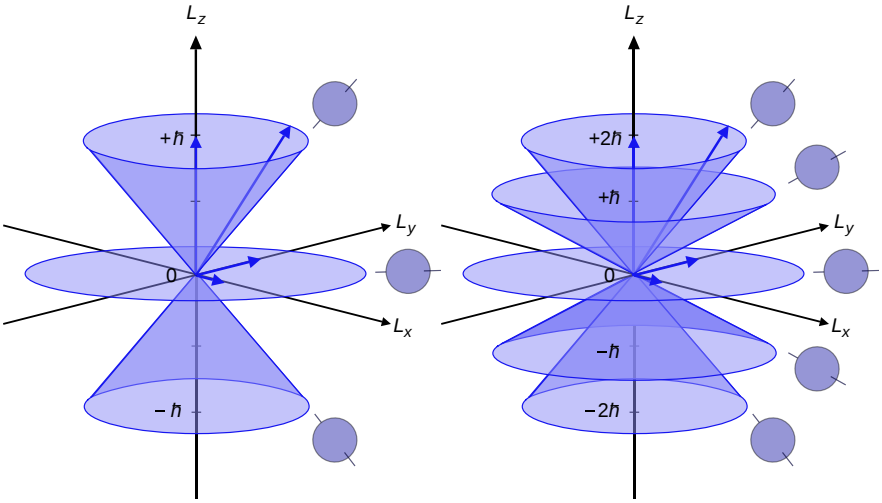


Figure 6.3.1 : Illustration of the vector model of orbital angular momentum. (left) A set of states with quantum numbers $l = 1$, and $m_l = -1, 0, +1,$. (right) A set of states with quantum numbers $l = 2$, and $m_l = -2, -1, 0, +1, +2$. (Public Domain; Maschen via Wikipedia)

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.

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

- Richard Fitzpatrick (Professor of Physics, The University of Texas at Austin)

11.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision** is licensed CC BY-NC-SA 4.0.

11.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers

Learning Objectives

- Recognize how the hydrogen atomic orbitals vary as a function of the three primary quantum numbers

The solutions to the hydrogen atom Schrödinger equation discussed previously are functions that are products of a **spherical harmonic function** and a **radial function**.

$$\psi_{n,l,m_l}(r,\theta,\varphi) = \underbrace{R_{n,l}(r)}_{radial}\underbrace{Y_l^{m_l}(\theta,\varphi)}_{angular} \tag{11.4.1}$$

The wavefunctions for the hydrogen atom depend upon the three variables r, θ, and φ and the three quantum numbers n, l, and m_l. The variables give the position of the electron relative to the proton in spherical coordinates. The absolute square of the wavefunction, $|\psi(r,\theta,\varphi)|^2$, evaluated at r, θ, and φ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r, θ, and φ.

Exercise 6.4.1

Evaluate the following integrals

a. $\langle\psi(r,\theta,\varphi)|\psi(r,\theta,\varphi)\rangle$
b. $\langle\psi(r,\theta,\varphi)|\psi(r',\theta',\varphi')\rangle$

The quantum numbers n, l, and m_l have names:

- n is called the **principal quantum number**,
- l is called the **angular momentum quantum number**, and
- m_l is called the **magnetic quantum number** because the energy in a magnetic field depends upon m_l.

Often l is called the azimuthal quantum number because it is a consequence of the θ-equation, which involves the azimuthal angle Θ, referring to the angle to the zenith.

The three quantum numbers have specific values that are dictated by the physical constraints or boundary conditions imposed upon the Schrödinger equation: n must be an integer greater than 0, l can have the values 0 to n-1, and m_l can have $2l+1$ values ranging from $-l$ to $+l$ in unit or integer steps. The values of the quantum number l usually are coded by a letter: s means 0, p means 1, d means 2, f means 3; the next codes continue alphabetically (e.g., g means $l = 4$). The quantum numbers specify the quantization of physical quantities. The discrete energies of different states of the hydrogen atom are given by n, the magnitude of the angular momentum is given by l, and one component of the angular momentum (usually chosen by chemists to be the z-component) is given by m_l. The total number of orbitals with a particular value of n is n^2.

Exercise 6.4.4

Consider several values for n, and show that the number of orbitals for each n is n^2.

Exercise 6.4.5

Construct a table summarizing the allowed values for the quantum numbers n, l, and m_l for energy levels 1 through 7 of hydrogen.

Exercise 6.4.6

The notation 3d specifies the quantum numbers for an electron in the hydrogen atom. What are the values for n and l ? What are the values for the energy and angular momentum? What are the possible values for the magnetic quantum number? What are the possible orientations for the angular momentum vector?

Radial Part of the Wavefunction

The asymptotic behavior (i.e., far away from the nucleus) to the radial part of the wavefunction is

$$R_{\text{asymptotic}}(r) \sim \exp\left(-\frac{r}{n}a_0\right) \tag{11.4.2}$$

where n will turn out to be a quantum number and a_0 is the Bohr radius (~52.9 pm). Note that this function decreases exponentially with distance, in a manner similar to the decaying exponential portion of the harmonic oscillator wavefunctions, but with a different distance dependence, r vs. r^2.

? Exercise 6.4.2

What happens to the magnitude of $R_{\text{asymptotic}}(r)$ as the distance r from the proton approaches infinity? Sketch a graph of the function, $R_{\text{asymptotic}}(r)$. Why might this behavior be expected for an electron in a hydrogen atom?

The polynomials produced by the truncation of the power series are related to the associated Laguerre polynomials, $L_{n,l}(r)$, where the set of c_i are constant coefficients.

$$L_{n,l}(r) = \sum_{r=0}^{n-l-1} c_i r^i \tag{11.4.3}$$

These polynomials are identified by two indices or quantum numbers, n and l. Physically acceptable solutions require that n must be greater than or equal to $l+1$. The smallest value for l is zero, so the smallest value for n is 1. The angular momentum quantum number affects the solution to the radial equation because it appears in the radial differential equation, (Equation 11.4.1).

The $R(r)$ functions that solve the radial differential Equation 11.4.1, are products of the associated Laguerre polynomials and the exponential factor, multiplied by a normalization factor ($N_{n,l}$) and $\left(\frac{r}{a_0}\right)^l$.

$$R(r) = N_{n,l}\left(\frac{r}{a_0}\right)^l L_{n,l}(r) e^{-\frac{r}{na_0}} \tag{11.4.4}$$

The decreasing exponential term overpowers the increasing polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of r. The first six radial functions are provided in Table 6.4.1 . Note that the functions in the table exhibit a dependence on Z, the atomic number of the nucleus. As discussed later in this chapter, other one electron systems have electronic states analogous to those for the hydrogen atom, and inclusion of the charge on the nucleus allows the same wavefunctions to be used for all one-electron systems. For hydrogen, $Z = 1$.

Table 6.4.3 : Radial functions for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

	n	l	$R_{n,l}(\rho)$
R_{10}	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$
R_{20}	2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}$
R_{21}	2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/2}$
R_{30}	3	0	$\frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18\rho+2\rho^2)e^{-\rho/3}$
R_{31}	3	1	$\frac{1}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6\rho+\rho^2)e^{-\rho/3}$
R_{32}	3	2	$\frac{1}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\rho^2 e^{-\rho/3}$

The constraint that n be greater than or equal to $l+1$ also turns out to quantize the energy, producing the same quantized expression for hydrogen atom energy levels that was obtained from the Bohr model of the hydrogen atom.

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2}$$

Bohr Theory vs. Schrödinger Theory

It is interesting to compare the results obtained by solving the Schrödinger equation with Bohr's model of the hydrogen atom. There are several ways in which the Schrödinger and Bohr models differ.

1. First, and perhaps most strikingly, the Schrödinger model does not produce well-defined orbits for the electron. The wavefunctions only give us the probability for the electron to be at various directions and distances from the proton.
2. Second, the quantization of angular momentum is different from that proposed by Bohr. Bohr proposed that the angular momentum is quantized in integer units of $\hbar$, while the Schrödinger model leads to an angular momentum of $\sqrt{(l(l+1)}\hbar$.
3. Third, the quantum numbers appear naturally during solution of the Schrödinger equation while Bohr had to postulate the existence of quantized energy states. Although more complex, the Schrödinger model leads to a better correspondence between theory and experiment over a range of applications that was not possible for the Bohr model.

Exercise 6.4.3

Explain how the Schrödinger equation leads to the conclusion that the angular momentum of the hydrogen atom can be zero, and explain how the existence of such states with zero angular momentum contradicts Bohr's idea that the electron is orbiting around the proton in the hydrogen atom.

Contributors and Attributions

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

11.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

11.5: s Orbitals are Spherically Symmetric

The hydrogen atom wavefunctions, $\psi(r,\theta,\varphi)$, are called atomic orbitals. An atomic orbital is a function that describes one electron in an atom. The wavefunction with $n = 1$, l = 0 is called the 1s orbital, and an electron that is described by this function is said to be "in" the ls orbital, i.e. have a 1s orbital state. The constraints on n, l, and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

Visualizing the variation of an electronic wavefunction with r, θ, and φ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron deficient part of one molecule is attracted to an electron rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

We can obtain an energy and one or more wavefunctions for every value of n, the principal quantum number, by solving Schrödinger's equation for the hydrogen atom. A knowledge of the wavefunctions, or probability amplitudes ψ_n, allows us to calculate the probability distributions for the electron in any given quantum level. When n = 1, the wavefunction and the derived probability function are independent of direction and depend only on the distance r between the electron and the nucleus. In Figure 6.5.1 , we plot both ψ_1 and P_1 versus r, showing the variation in these functions as the electron is moved further and further from the nucleus in any one direction. (These and all succeeding graphs are plotted in terms of the atomic unit of length, $a_0 = 0.529 \times 10^{-8}\,cm.$)

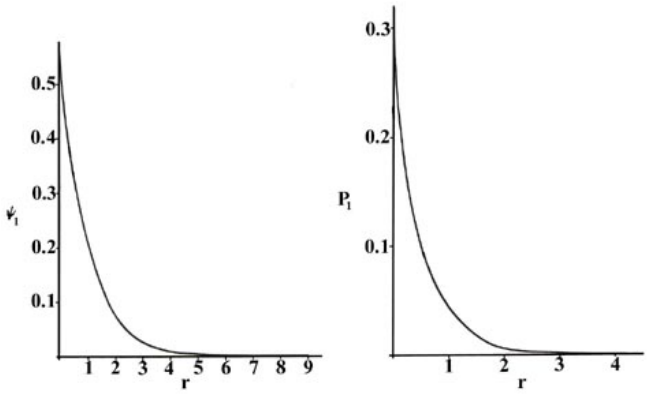


Figure 6.5.1 : The wavefunction and probability distribution as functions of r for the $n = 1$ level of the H atom. The functions and the radius r are in atomic units in this and succeeding figures.

Two interpretations can again be given to the P_1 curve. An experiment designed to detect the position of the electron with an uncertainty much less than the diameter of the atom itself (using light of short wavelength) will, if repeated a large number of times, result in Figure 6.5.1 for P_1. That is, the electron will be detected close to the nucleus most frequently and the probability of observing it at some distance from the nucleus will decrease rapidly with increasing r. The atom will be ionized in making each of these observations because the energy of the photons with a wavelength much less than 10^{-8} cm will be greater than K, the amount of energy required to ionize the hydrogen atom. If light with a wavelength comparable to the diameter of the atom is employed in the experiment, then the electron will not be excited but our knowledge of its position will be correspondingly less precise. In these experiments, in which the electron's energy is not changed, the electron will appear to be "smeared out" and we may interpret P_1 as giving the fraction of the total electronic charge to be found in every small volume element of space. (Recall that the addition of the value of P_n for every small volume element over all space adds up to unity, i.e., one electron and one electronic charge.)

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately does not reveal the shape of an orbital very well. The shape can be revealed better in

a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$.

We could also represent the distribution of negative charge in the hydrogen atom in the manner used previously for the electron confined to move on a plane (Figure 6.5.2), by displaying the charge density in a plane by means of a contour map. Imagine a plane through the atom including the nucleus. The density is calculated at every point in this plane. All points having the same value for the electron density in this plane are joined by a contour line (Figure 6.5.2). Since the electron density depends only on r, the distance from the nucleus, and not on the direction in space, the contours will be circular. A contour map is useful as it indicates the "shape" of the density distribution.

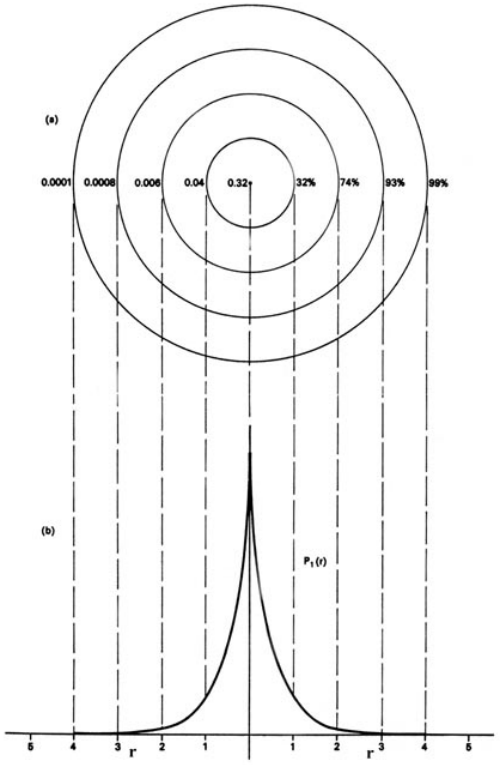


Figure 6.5.2 : (a) A contour map of the electron density distribution in a plane containing the nucleus for the $n = 1$ level of the H atom. The distance between adjacent contours is 1 au. The numbers on the left-hand side on each contour give the electron density in au. The numbers on the right-hand side give the fraction of the total electronic charge which lies within a sphere of that radius. Thus 99% of the single electronic charge of the H atom lies within a sphere of radius 4 au (or diameter = 4.2×10^{-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 **11.5.3**; starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

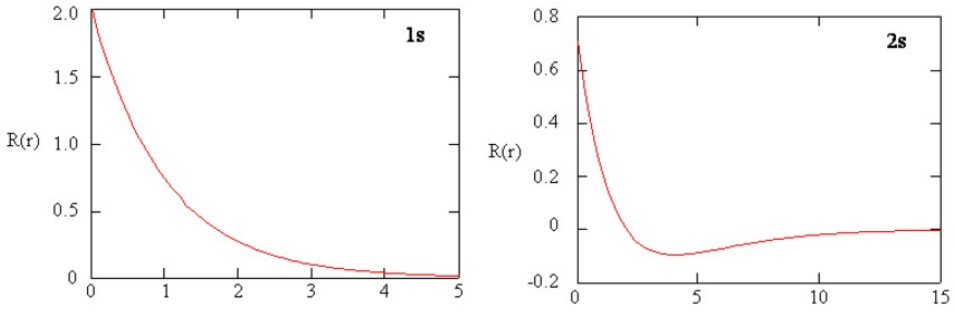


Figure 6.5.3 : Radial function, $R(r)$, for the 1s and 2s orbitals. For an interactive graph click here.

Next notice how the radial function for the 2s orbital, Figure **11.5.3**;, goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$.

? Exercise 6.5.1

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

? Exercise 6.5.2

What mathematical feature of each of the radial functions controls the number of radial nodes?

? Exercise 6.5.3 : Radial Nodes

At what value of r does the 2s radial node occur?

? Exercise 6.5.4

Make a table that provides the energy, number of radial nodes, and the number of angular nodes and total number of nodes for each function with $n = 1$, $n = 2$, and $n = 3$. Identify the relationship between the energy and the number of nodes. Identify the relationship between the number of radial nodes and the number of angular nodes.

Radial probability densities for the 1s and 2s atomic orbitals are plotted in Figure 6.5.4 .

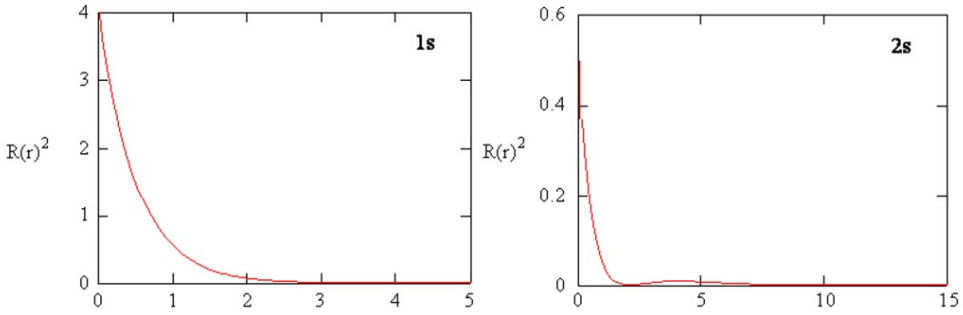


Figure 6.5.4 : Radial densities ($R(r)^*R(r)$) for the 1s and 2s orbitals.

Radial Distribution Functions

Rather than considering the amount of electronic charge in one particular small element of space, we may determine the total amount of charge lying within a thin spherical shell of space. Since the distribution is independent of direction, consider adding up all the charge density which lies within a volume of space bounded by an inner sphere of radius r and an outer concentric sphere with a radius only infinitesimally greater, say $r + \Delta r$. 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

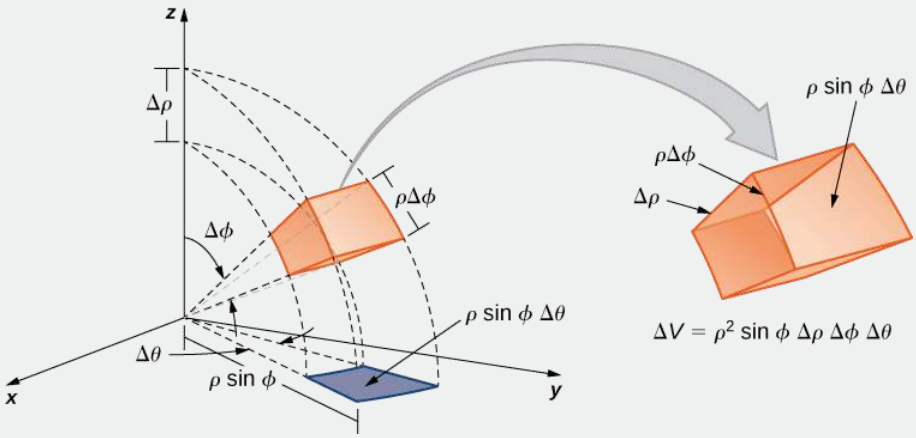
The reader may wonder why the volume of the shell is not taken as:

$$\frac{4}{3}\pi\left[(r+\Delta r)^3 - r^3\right]$$

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.

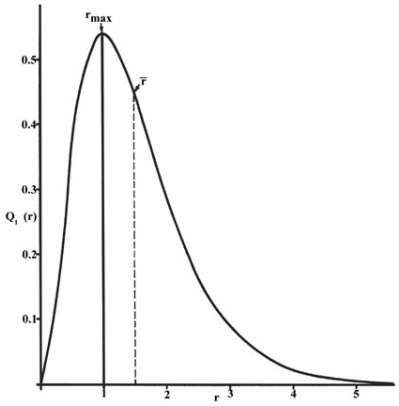


Figure 6.5.5 : The radial distribution function for an H atom. The value of this function at some value of r when multiplied by δr gives the number of electronic charges within the thin shell of space lying between spheres of radius r and $r + \delta r$.

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.

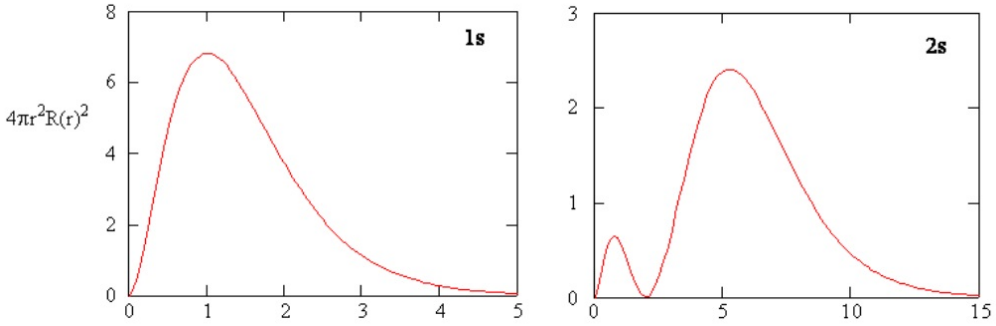


Figure 6.5.6 : The radial distribution function ($4\pi r^2 R(r)^* R(r)$) for the 1s and 2s orbitals. Compare to the radial functions in Figure 6.5.3 or the radial densities in Figure 6.5.4 . For an interactive graph click here.

Example 6.5.1 :

Calculate the probability of finding a 1s hydrogen electron being found within distance $2a_o$ from the nucleus.

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")

11.5: s Orbitals are Spherically Symmetric is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **6.5: s-orbitals are Spherically Symmetric** is licensed CC BY-NC-SA 4.0.

11.6: Orbital Angular Momentum and the p-orbitals

Learning Objectives

- To relate the classical orbital angular momentum for an particle to the quantum equivalent
- Characterize the mangnitude and orientation of orbital angular momentum for an electron in terms of quantum numbers

Classical Orbital Angular Momentum

The physical quantity known as angular momentum plays a dominant role in the understanding of the electronic structure of atoms. To gain a physical picture and feeling for the angular momentum it is necessary to consider a model system from the classical point of view. The simplest classical model of the hydrogen atom is one in which the electron moves in a circular orbit with a constant speed or angular velocity (Figure 6.6.1). Just as the linear momentum $m\vec{v}$ plays a dominant role in the analysis of linear motion, so angular momentum (L) plays the central role in the analysis of a system with circular motion as found in the model of the hydrogen atom.

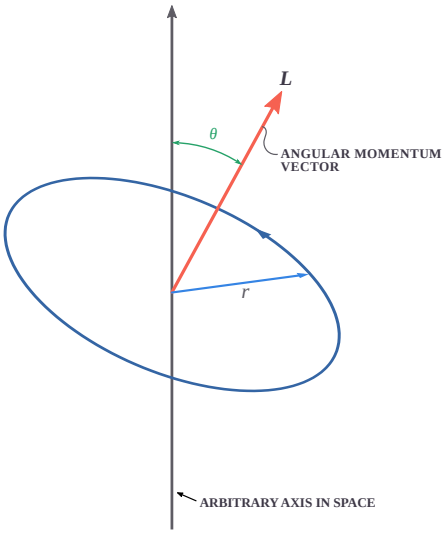


Figure 6.6.1 : The angular momentum vector for a classical model of the atom. (CC BY-NC; Ümit Kaya via LibreTexts)

In Figure 6.6.1 , m is the mass of the electron, $\vec{v}$ is the linear velocity (the velocity the electron would possess if it continued moving at a tangent to the orbit) and r is the radius of the orbit. The linear velocity $\vec{v}$ is a vector since it possesses at any instant both a magnitude and a direction in space. Obviously, as the electron rotates in the orbit the direction of $\vec{v}$ is constantly changing, and thus the linear momentum $m\vec{v}$ is ***not*** constant for the circular motion. This is so even though the speed of the electron (i.e, the magnitude of $\vec{v}$ which is denoted by $|\vec{v}|$) remains unchanged. According to Newton's second law, a force must be acting on the electron if its momentum changes with time. This is the force which prevents the electron from flying on tangent to its orbit. In an atom the attractive force which contains the electron is the electrostatic force of attraction between the nucleus and the electron, directed along the radius *r* at right angles to the direction of the electron's motion.

The angular momentum, like the linear momentum, is a vector and is defined as follows:

$$|\vec{L}| = mvr$$

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.

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:

$$|L| = \sqrt{l(l+1)}\hbar \tag{11.6.1}$$

with $l = 0, 1, 2, 3, ...n-1$.

Furthermore, the value of *n* limits the maximum value of the angular momentum as the value of *l* cannot be greater than *n* - 1. For the state *n* = 1 discussed above, l may have the value of zero only. When *n* = 2, *l* may equal 0 or 1, and for *n* = 3, *l* = 0 or 1 or 2, etc. When *l* = 0, it is evident from Equation 11.6.1 that the angular momentum of the electron is zero. The atomic orbitals which describe these states of zero angular momentum are called *s* orbitals. The *s* orbitals are distinguished from one another by stating the value of *n*, the principal quantum number. They are referred to as the 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 .

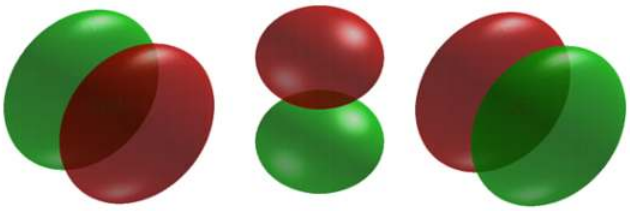


Figure 6.6.2 : The appearance of the three 2p orbitals in three-dimensional space. (CC BY-SA 3.0; I, Sarxos).

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.*

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.

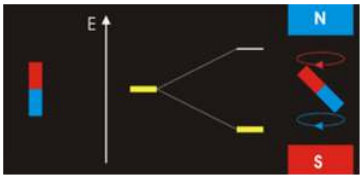


Figure 6.6.3 : The orbiting electron with a non-zero l value acts like a magnetic field with is no energetic difference for any particular orientation (only one energy state, on the left). However, in external magnetic field there is a high-energy state and a low-energy state depending on the relative 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.

$$|\psi_{2,1,0}\rangle = r\cos\theta R(r) \tag{11.6.2}$$

$$|\psi_{2,1,+1}\rangle = -\frac{r}{2}\sin\theta e^{i\phi} R(r) \tag{11.6.3}$$

$$|\psi_{2,1,-1}\rangle = +\frac{r}{2}\sin\theta e^{-i\phi} R(r) \tag{11.6.4}$$

The notation is $|\psi_{n,l,m_l}\rangle$ with $R(r)$ is the radial component of this wavefuction, θ is the angle with respect to the z-axis and ϕ is the angle with respect to the xz-plane.

$$R(r) = \sqrt{\frac{Z^5}{32\pi a_0^5}} e^{-Zr/2a_0}$$

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:

$$e^{i\phi} = \cos\phi + i\sin\phi \tag{11.6.5}$$

$$\sin\phi = \frac{e^{i\phi} - e^{-i\phi}}{2i} \tag{11.6.6}$$

$$\cos\phi = \frac{e^{i\phi} + e^{-i\phi}}{2} \tag{11.6.7}$$

We're also going to use $x = \sin\theta\cos\phi$ and $y = \sin\theta\sin\phi$.

$$\begin{aligned}
\psi_{2p_x} &= \frac{1}{\sqrt{2}}\left(\psi_{2,1,+1} - \psi_{2,1,-1}\right) \\
&= \frac{1}{2}\left(e^{i\phi} + e^{-i\phi}\right) r\sin\theta f(r) \\
&= r\sin\theta\cos\phi f(r) = x f(r) \\
\psi_{2p_y} &= \frac{i}{\sqrt{2}}\left(\psi_{2,1,+1} + \psi_{2,1,-1}\right) \\
&= \frac{1}{2i}\left(e^{i\phi} - e^{-i\phi}\right) r\sin\theta f(r) \\
&= r\sin\theta\sin\phi f(r) = y f(r)
\end{aligned}$$

So, while $m_l = 0$ corresponds to $|p_z\rangle$, $m_l = +1$ and $m_l = -1$ **cannot** be directly assigned to either $|p_x\rangle$ or $|p_y\rangle$, but rather a combination of $|p_x\rangle$ and $|p_y\rangle$. An alternative description is that $m_l = +1$ might correspond to $(|p_x\rangle + |p_y\rangle)$ and $m_l = -1$ might correspond to $(|p_x\rangle - |p_y\rangle)$.

d-Orbitals (even higher angular momenta wavefunctions)

When $l = 2$, the orbitals are called *d* orbitals and Figure 6.6.4 shows the contours in a plane for a 3*d* orbital and its density distribution. Notice that the density is again zero at the nucleus and that there are now two nodes in the orbital and in its density distribution. As the angular momentum of the electron increases, the density distribution becomes increasingly concentrated along an axis or in a plane in space. Only electrons in s orbitals with **zero angular momentum** give spherical density distributions and in addition place charge density at the position of the nucleus.



Figure 6.6.4 : The appearance of the 3d electron density distribution in three-dimensional space. (CC BY-SA 3.0; I, Sarxos)

As with the p-orbitals, the only d-orbital that a specific m_l can be ascribed is the d_{z^2} orbitals with $m_l = 0$. The rest are linear combinations of the hydrogen atom wavefunctions with complex spherical harmonic angular components.

There seems to be neither rhyme nor reason for the naming of the states corresponding to the different values of ℓ (s, *p*, *d*, *f* for *l* = 0, 1, 2, 3). This set of labels had its origin in the early work of experimental atomic spectroscopy. The letter *s* stood for

sharp, *p* for principal, *d* for diffuse and *f* for fundamental in characterizing spectral lines. From the letter *f* onwards the naming of the orbitals is alphabetical $l = 4, 5, 6 \rightarrow g, h, i, ...$

We have not as yet accounted for the full degeneracy of the hydrogen atom orbitals which we stated earlier to be n^2 for every value of n. For example, when $n = 2$, there are four distinct atomic orbitals. The remaining degeneracy is again determined by the angular momentum of the system. Since angular momentum like linear momentum is a vector quantity, we may refer to the component of the angular momentum vector which lies along some chosen axis. For reasons we shall investigate, the number of values a particular component can assume for a given value of l is $(2l + 1)$. Thus when $l = 0$, there is no angular momentum and there is but a single orbital, an s orbital. When $l = 1$, there are three possible values for the component $(2 \times 1 + 1)$ 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)

11.6: Orbital Angular Momentum and the p-orbitals is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **6.6: Orbital Angular Momentum and the p-Orbitals** is licensed CC BY-NC-SA 4.0.

11.7: The Helium Atom Cannot Be Solved Exactly

Learning Objectives

- Adding electrons to the quantum hydrogen atom results in analytically unsolvable Schrödinger Equations (they exist, we just do not have analytical forms for them)
- A basic aspect of the corresponding multi-electron Hamiltonians is that they are NOT separable with respect to the spatial coordinate of each electron
- The solutions to multi-electron Schrödinger Equations are called multi-electron wavefunctions and they are often approximated as a product of single-electron wavefunctions (called the orbital approximation).

Multi-electron Hamiltonians

The second element in the periodic table provides our first example of a quantum-mechanical problem which *cannot* be solved exactly. Nevertheless, as we will show, approximation methods applied to helium can give accurate solutions in perfect agreement with experimental results. In this sense, it can be concluded that quantum mechanics is correct for atoms more complicated than hydrogen. By contrast, the Bohr theory failed miserably in attempts to apply it beyond the hydrogen atom.

Figure 6.7.1 shows a schematic representation of a helium atom with two electrons whose coordinates are given by the vectors $\boldsymbol{r_1}$ and $\boldsymbol{r_2}$. The electrons are separated by a distance $\boldsymbol{r_{12} = |r_1 - r_2|}$. The origin of the coordinate system is fixed at the nucleus. As with the hydrogen atom, the nuclei for multi-electron atoms are so much heavier than an electron that the nucleus is assumed to be the center of mass. Fixing the origin of the coordinate system at the nucleus allows us to exclude translational motion of the center of mass from our quantum mechanical treatment.

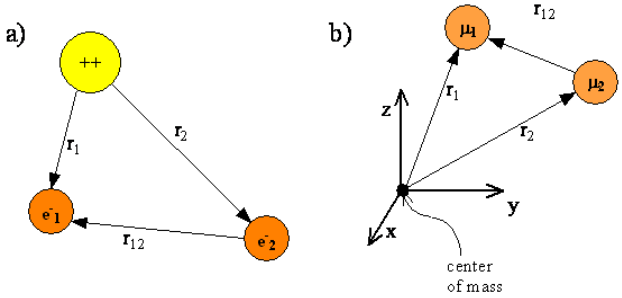


Figure 6.7.1 : (a) The nucleus (++) and electrons (e-) of the helium atom. (b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that μ_1 and $\mu_2 \approx m_e$.

The Hamiltonian operator for the hydrogen atom serves as a reference point for writing the Hamiltonian operator for atoms with more than one electron. Start with the same general form we used for the hydrogen atom Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} \tag{11.7.1}$$

Include a kinetic energy term for each electron and a potential energy term for the attraction of each negatively charged electron for the positively charged nucleus and a potential energy term for the mutual repulsion of each pair of negatively charged electrons. The He atom Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V_1(r_1) + V_2(r_2) + V_{12}(r_{12}) \tag{11.7.2}$$

where

$$V_1(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{11.7.3}$$

$$V_2(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{11.7.4}$$

$$V_{12}(r_{12}) = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{11.7.5}$$

The two-electron Hamiltonian in Equation 11.7.2 can be extended to any atom or ion by replacing the He nuclear charge of +2 with a general charge Z; e.g.

$$V_1(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{11.7.6}$$

and including terms for the additional electrons. The subsequent multi-electron atom with n electron is

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_i^n \nabla_i^2}_{\text{Kinetic Energy}} + \underbrace{\sum_i^n V_i(r_i)}_{\text{Coulombic Attraction}} + \underbrace{\sum_{i\neq j}^{n,n} V_{ij}(r_{ij})}_{\text{electron-electron Repulsion}} \tag{11.7.7}$$

This multi-electron Hamiltonian is qualitatively similar to the 2-electron Hamiltonian (Equation 11.7.1) with each electron having its own kinetic energy and nuclear potential energy terms (Equations 11.7.3 and 11.7.4). The other big difference between single electron systems and multi-electron systems is the presence of the $V_{ij}(r_{ij})$ terms which contain $1/r_{ij}$, where r_{ij} is the distance between electrons i and j. These terms account for the electron-electron repulsion that we expect between like-charged particles.

? Exercise 6.7.1 : Multi-electron atom Hamiltonians

For the generalized multi-electron atom Hamiltonian (Equation 11.7.7):

a. Explain the origin of each of the three summations.
b. What do these summations over (i.e., what is the origin of the summing index)?
c. Write expressions for $V_i(r_i)$ and $V_{ij}(r_{ij})$.

? Exercise 6.7.2 : Boron Atom

Boron is the fifth element of the periodic table (Z=5) and is located in Group 13.

a. Write the multi-electron Hamiltonian for a $^{11}\mathbf{B}$ atom.
b. Would it be any different for a $^{11}\mathbf{B}^+$ ion?
c. Would it be any different for a $^{10}\mathbf{B}$ atom?

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 11.7.7 would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their Coulomb repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends *simultaneously* upon the coordinates of all the electrons; i.e., **a multi-electron wavefunction**,

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \cdots \vec{r}_n)$$

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 11.7.5) make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms and molecules even for two electrons atoms. We have to rely on approximations and the *orbital approximation* is central to basic chemistry concepts.

The Orbital Approximation

The most basic approximations to the exact solutions to a multi-electron atom Hamiltonian, $\hat{H}$, (Equation 11.7.7) involve writing a multi-electron wavefunction ($\psi(r_1, r_2, \cdots, r_n)$) as a simple product of single-electron wavefunctions ($\varphi_i(r_i)$):

$$\psi(r_1, r_2, \cdots, r_n) \approx \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_n(r_n) \tag{11.7.8}$$

or in Dirac notation

$$|\psi(r_1, r_2, \cdots, r_n)\rangle \approx |\varphi_1(r_1)\rangle\,|\varphi_2(r_2)\rangle\cdots|\,\varphi_n(r_n)\rangle \tag{11.7.9}$$

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 11.7.8, 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 11.7.8 or 11.7.9), 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.

11.7: The Helium Atom Cannot Be Solved Exactly is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **6.7: The Helium Atom Cannot Be Solved Exactly** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

11.8: The Hydrogen Atom (Exercises)

Solutions to select questions can be found online.

6.5

$$\int_{-1}^{1} T_n(x) T_m(x) \frac{1}{\sqrt{1-x^2}} dx = \begin{cases} 0, & n \neq m \\ \pi, & n = m = 0 \\ \pi/2, & n = m \neq 0 \end{cases}$$

First 6 Chebyshev Polynomials

$$T_0(x) = 1$$
$$T_1(x) = x$$
$$T_2(x) = 2x^2 - 1$$
$$T_3(x) = 4x^3 - 3x$$
$$T_4(x) = 8x^4 - 8x^2 + 1$$
$$T_5(x) = 16x^5 - 20x^3 + 5x$$

Use the orthogonality of Chebyshev polynomials to determine what the following polynomials are equal to

a. $\int_{-1}^{1} x^2 \frac{dx}{\sqrt{1-x^2}}$
b. $\int_{-1}^{1} 4x^3 - 2x \frac{dx}{\sqrt{1-x^2}}$
c. $\int_{-1}^{1} 1 \frac{dx}{\sqrt{1-x^2}}$
d. $\int_{-1}^{1} 4x^4 - 4x^2 + 1 \frac{dx}{\sqrt{1-x^2}}$

6.6

Use Eq. 6.47 to generate the radial functions $R_{nl}(r)$ for $n = 1, 2$.

6.29

Compare ψ_{310} and ψ_{311}.

Hint: What do the subscripts tell you about the wave function? What do they denote?

6.30

What is the probability density of the 3p orbital by evaluating

$$\left(\sum_{m=-1}^{1} \psi_{31m}^2 \right)$$

6.34

Find the energy, and wavefunction for a single electron located in the 2p orbital of the hydrogen atom. Include all possible wavefunctions.

6.37

The Hamiltonian is given by $\hat{H} = \frac{-\hbar}{2m}\nabla^2 + V$ is an Hermitian Operator. Using this fact, show that

$$\int \psi^* [\hat{H}, \hat{A}] \psi d\tau = 0$$

where $\hat{A}$ is any operator.

6.38

Prove that $\langle \hat{K} \rangle = \langle V \rangle = E/2$ for a harmonic oscillator using the virial theorem

6.41

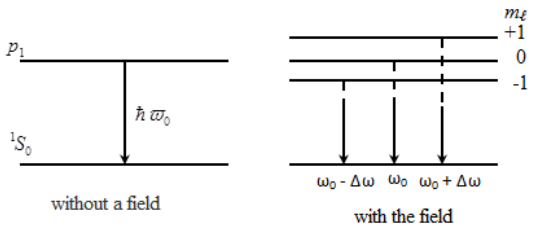
Find the expected values of $1/r$ and $1/r^2$ for a hydrogenlike atom in the $2p_z$ orbital.

6.43

Derive the classical magnetic moment of an electron orbiting a nucleus in terms of charge, mass and angular momentum.

6.46

Find the magnitude of the splitting shown in figure below. The magnetic field in the figure is at 20 T.



6.47

Consider the transition between the $l = 1$ and the $l = 2$ states for atomic hydrogen. Determine the total number of possible allowed transitions between these two states in an external magnetic field given the following selection rules

a. Light whose electric field vector is parallel to the external magnetic field's direction has a selection rule of $\Delta m = 0$ for allowed transitions.
b. Light whose electric field vector is perpendicular to the external magnetic field's direction has a selection rule of $\Delta m = \pm 1$ for allowed transitions.

6.49

Prove that

$$\hat{L_+}\hat{L_-} - \hat{L_-}\hat{L_+} = 2\hbar\hat{L_z}$$

given that

$$\hat{L_+} = \hat{L_x} + i\hat{L_y}$$

and

$$\hat{L_-} = \hat{L_x} - i\hat{L_y}.$$

6.49

Show that the commutative property applies to

$$\hat{L}_-\hat{L}_+$$

Q7.29

Calculate the ground-state energy for particle in the box model using variational method.

6.50

If two functions commute, they have mutual eigenfunctions, such as $\hat{L}^2$ and $\hat{L}_z$. These mutual eigenfunctions are also known as spherical harmonics, $Y_l^m(\theta, \phi)$, however this information is not pertinent in this case. Let

$\psi_{\alpha\beta}$ be a mutual eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ so that

$$\hat{L}_z \psi_{\alpha\beta} = \beta^2 \backslash_{\alpha\beta}$$

and

$$\hat{L}_z \psi_{\alpha\beta} = \alpha\psi_{\alpha\beta}$$

Now let

$$\psi_{\alpha\beta}{}^{+1} = \hat{L}_+ \psi_{\alpha\beta}$$

Show that

$$\hat{L}_z \psi_{\alpha\beta}{}^{+1} = (\alpha + \hbar)\psi_{\alpha\beta}{}^{+1}$$

and

$$\hat{L}^2 \psi_{\alpha\beta}{}^{+1} = \beta^2 \psi_{\alpha\beta}{}^{+1}$$

This proves that if α is an eigenvalue of $\hat{L}_z$, then $\alpha + \hbar$ also is an eigenvalue.

11.8: The Hydrogen Atom (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **6.E: The Hydrogen Atom (Exercises)** is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

12: Approximation Methods

The Schrödinger equation for realistic systems quickly becomes unwieldy, and analytical solutions are only available for very simple systems - the ones we have described as *fundamental systems* in this module. Numerical approaches can cope with more complex problems, but are still (and will remain for a good while) limited by the available computer power. Approximations are necessary to cope with real systems. Within limits, we can use a pick and mix approach, *i.e.* use *linear combinations* of solutions of the fundamental systems to build up something akin to the real system. There are two mathematical techniques, *perturbation* and *variation* theory, which can provide a good approximation along with an estimate of its accuracy. These two approximation techniques are described in this chapter.

12.1: Slater's Rules for Shielding

12.2: The Variational Method

12.3: Linear Variational Method and the Secular Determinant

12.4: Trial Functions Can Be Linear Combinations of Functions with Variational Parameters

12.5: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

12.6: Approximation Methods (Exercises)

12: Approximation Methods is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

12.1: Slater's Rules for Shielding

Learning Objective

- To quantify the shielding effect experienced by atomic electrons.

We have previously described the concepts of electron shielding, orbital penetration and effective nuclear charge, but we did so in a qualitative manner. In this section, we explore one model for quantitatively estimating the impact of electron shielding, and then use that to calculate the effective nuclear charge experienced by an electron in an atom. The model we will use is known as Slater's Rules (J.C. Slater, *Phys Rev* **1930**, *36*, 57).

Slater's Rules

The general principle behind Slater's Rule is that the actual charge felt by an electron is equal to what you'd expect the charge to be from a certain number of protons, but minus a certain amount of charge from other electrons. Slater's rules allow you to estimate the effective nuclear charge Z_{eff} from the real number of protons in the nucleus and the effective shielding of electrons in each orbital "shell" (e.g., to compare the effective nuclear charge and shielding 3d and 4s in transition metals). Slater's rules are fairly simple and produce fairly accurate predictions of things like the electron configurations and ionization energies.

Slater's Rules

- **Step 1**: Write the electron configuration of the atom in the following form:

  (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) . . .

- **Step 2**: Identify the electron of interest, and ignore all electrons in higher groups (to the right in the list from Step 1). These do not shield electrons in lower groups
- **Step 3**: Slater's Rules is now broken into two cases:
  - the shielding experienced by an s- or p- electron,
    - electrons within same group shield **0.35**, except the 1*s* which shield **0.30**
    - electrons within the n-1 group shield **0.85**
    - electrons within the n-2 or lower groups shield **1.00**
  - the shielding experienced by n*d* or n*f* valence electrons
    - electrons within same group shield **0.35**
    - electrons within the lower groups shield **1.00**

These rules are summarized in Figure **12.1.1** and Table **12.1.1**.

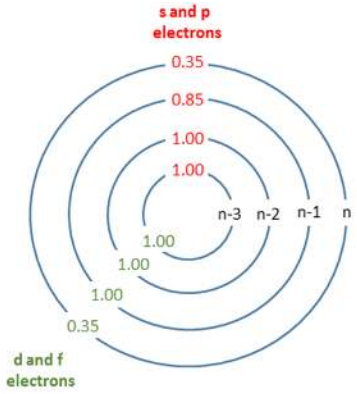


Figure **12.1.1**: Graphical depiction of Slater's rules with shielding constants indicated.

Shielding happens when electrons in lower valence shells (or the same valence shell) provide a repulsive force to valence electrons, thereby "negating" some of the attractive force from the positive nucleus. Electrons really close to the atom (n-2 or lower) pretty

much just look like protons, so they completely negate. As electrons get closer to the electron of interest, some more complex interactions happen that reduce this shielding.

Table **12.1.1**: Slater's Rules for calculating shielding constants

Group	Other electrons in the same group	Electrons in group(s) with principal quantum number n and azimuthal quantum number < l	Electrons in group(s) with principal quantum number n-1	Electrons in all group(s) with principal quantum number < n-1
[1s]	0.30	-	-	-
[*n*s,*n*p]	0.35	-	0.85	1
[*n*d] or [*n*f]	0.35	1	1	1

The shielding numbers in Table **12.1.1** were derived semi-empirically (i.e., derived from experiments) as opposed to theoretical calculations. This is because quantum mechanics makes calculating shielding effects quite difficult, which is outside the scope of this Module.

Calculating *S*

Sum together the contributions as described in the appropriate rule above to obtain an estimate of the shielding constant, S, which is found by totaling the screening by **all electrons** except the one in question.

$$S = \sum n_i S_i \tag{12.1.1}$$

where

- n_i is the number of electrons in a specific shell and subshell and
- S_i is the shielding of the electrons subject to Slater's rules (Table **12.1.1**)

Example 12.1.1: The Shielding of 3*p* Electrons of Nitrogen Atoms

What is the shielding constant experienced by a 2*p* electron in the nitrogen atom?

Given:

Nitrogen (N)

Asked for:

S, the shielding constant, for a 2*p* electron (Equation 12.1.1)

Strategy:

A. Determine the electron configuration of nitrogen, then write it in the appropriate form.

B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Step A

N: $1s^2\ 2s^2\ 2p^3$

N: $(1s^2)(2s^2,2p^3)$

Step B

$$S[2p] = \underbrace{0.85(2)}_{\text{the 1s electrons}} + \underbrace{0.35(4)}_{\text{the 2s and 2p electrons}} = 3.10$$

As Table **12.1.1** indicates,

- the 1s electrons shield the other 2p electron to 0.85 "charges".
- the 2s and 2p electrons shield the other 2p electron equally at 0.35 "charges".

Exercise 12.1.1: The Shielding of valence *p* Electrons of Bromine Atoms

What is the shielding constant experienced by a valence *p*-electron in the bromine atom?

Example 12.1.2: The Shielding of 3*d* Electrons of Bromine Atoms

What is the shielding constant experienced by a 3*d* electron in the bromine atom?

Given:

Bromine (Br)

Asked for:

S, the shielding constant, for a 3*d* electron

Strategy:

A. Determine the electron configuration of bromine, then write it in the appropriate form.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Step A

Br: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

Br: $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^{10})(4s^2,4p^5)$

Ignore the group to the right of the 3d electrons. These do not contribute to the shielding constant.

Step B

$$S[3d] = 1.00(18) + 0.35(9) = 21.15$$

Exercise 12.1.2: The Shielding of 3*d* Electrons of Copper Atoms

What is the shielding constant experienced by a valence *d*-electron in the copper atom?

Calculating Effective Nuclear Charge

Previously, we described Z_{eff} as being less than the actual nuclear charge (Z) because of the repulsive interaction between core and valence electrons. We can quantitatively represent this difference between Z and Z_{eff} as follows:

$$S = Z - Z_{eff} \tag{12.1.2}$$

Rearranging this formula to solve for Z_{eff} we obtain:

$$Z_{eff} = Z - S \tag{12.1.3}$$

We can then substitute the shielding constant obtained using Equation 12.1.3 to calculate an estimate of Z_{eff} for the corresponding atomic electron.

Example 12.1.3: The Effective Charge of p Electrons of Boron Atoms

What is the effective nuclear charge experienced by a valence *p*- electron in boron?

Given:

Boron (B)

Asked for:

Z_{eff} for a valence *p*- electron

Strategy:

A. Determine the electron configuration of boron and identify the electron of interest.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

C. Use the Periodic Table to determine the actual nuclear charge for boron.
D. Determine the effective nuclear constant.

Step A

B: $1s^2\ 2s^2\ 2p^1$. The valence p- electron in boron resides in the $2p$ subshell.

B: $(1s^2)(2s^2,2p^1)$

Step B

$S[2p] = 1.00(0) + 0.85(2) + 0.35(2) = 2.40$

Step C

$Z = 5$

Step D

Using Equation 12.1.3,

$$\begin{aligned} Z_{eff} &= Z - S \\ &= 5 - 2.50 \\ &= 2.60 \end{aligned}$$

Exercise 12.1.3

What is the effective nuclear charge experienced by a valence d-electron in copper?

Summary

Slater's Rules can be used as a model of shielding. This permits us to quantify both the amount of shielding experienced by an electron and the resulting effective nuclear charge. Others performed better optimizations of Z_{eff} using variational Hartree-Fock methods. For example, Clementi and Raimondi published "Atomic Screening Constants from SCF Functions." J Chem Phys (1963) 38, 2686–2689.

References

- James L. Reed, "The Genius of Slater's Rules" , J. Chem. Educ., 1999, 76 (6), p 802
- David Tudela, "Slater's rules and electron configurations", J. Chem. Educ., 1993, 70 (11), p 956
- Kimberley A. Waldron, Erin M. Fehringer, Amy E. Streeb, Jennifer E. Trosky and Joshua J. Pearson, "Screening Percentages Based on Slater Effective Nuclear Charge as a Versatile Tool for Teaching Periodic Trends", J. Chem. Educ., 2001, 78 (5), p 635

12.1: Slater's Rules for Shielding is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **2.6: Slater's Rules** by Brett McCollum is licensed CC BY-NC-SA 4.0.

12.2: The Variational Method

Learning Objectives

- Appreciate the complexity of solving muliti-electron atoms
- Characterize multi-electron interactions within shielding and penetration concepts
- Use the variational method as an approximation to study insolvable problems
- User variational method to evaluate the effective nuclear charge for a specific atom

In this section we introduce the powerful and versatile variational method and use it to improve the approximate solutions we found for the helium atom using the independent electron approximation.

The True (Experimentally Determined) Energy of the Helium Atom

The helium atom has two electrons bound to a nucleus with charge $Z = 2$. The *successive* removal of the two electrons can be considered stepwise:

$$\mathrm{He} \xrightarrow{I_1} \mathrm{He}^+ + e^- \xrightarrow{I_2} \mathrm{He}^{++} + 2e^- \tag{12.2.1}$$

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 12.2.1 is zero (by definition). Therefore the ground-state energy of helium atom is given by

$$\begin{aligned} E_{true} &= -(I_1 + I_2) \\ &= -79.02\ \mathrm{eV}. \end{aligned}$$

which can be expressed in terms of the ***Rydberg*** constant ($R_H = 13.6\ eV$) that also describes the lowest energy of the hydrogen atom

$$E_{true} = -5.8066\, R_H$$

We will attempt to reproduce this **true value**, as close as possible, by different theoretical approaches (all approximations).

The "Ignorance is Bliss" Approximation

The Hamiltonian for the Helium atom is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \cancel{\frac{e^2}{4\pi\epsilon_0 r_{12}}} \tag{12.2.2}$$

If we simply *ignore* the electron-electron repulsion term, then Equation 12.2.2 can be simplified to

$$\hat{H} \approx -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_2} \tag{12.2.3}$$

$$\approx h_1(r_1) + h_2(r_2) \tag{12.2.4}$$

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 12.2.4 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:

$$\Psi_{total} = \psi_{el_1}\psi_{el_2} \tag{12.2.5}$$

or in braket notation

$$|\Psi_{total}\rangle = \hat{H}\left|\psi_{el_1}\psi_{el_2}\right\rangle \tag{12.2.6}$$

With some operator algebra, something important arises - the one electron energies are **additive**:

$$\hat{H}\Psi_{total} = (\hat{H}_{el_1} + \hat{H}_{el_2})\psi_{n\ el_1}\psi_{n\ el_2} = (E_{n_1} + E_{n_2})\psi_{n\ el_1}\psi_{n\ el_2}$$

or in bra-ket notation

$$\begin{aligned}\hat{H}|\Psi_{total}\rangle &= \hat{H}|\psi_{el_1}\psi_{el_2}\rangle \\ &= (E_{n_1} + E_{n_2})|\psi_1\psi_2\rangle\end{aligned}$$

The energy for a ground state Helium atom (both electrons in lowest state) is then

$$\begin{aligned}E_{He_{1s}} &= \underbrace{E_{n_1}}_{\text{energy of single electron in helium}} + \underbrace{E_{n_2}}_{\text{energy of single electron in helium}} \\ &= -R_H\left(\frac{Z^2}{1}\right) - R_H\left(\frac{Z^2}{1}\right) \\ &= -8R_H\end{aligned}$$

This approximation significantly overestimates the true energy of the helium atom $E_{He_{1s}} = -5.8066\ R$. This is a poor approximation and we need to address electron-electron repulsion properly (or better at least).

Shielding and Penetration

One way to take electron-electron repulsion into account is to modify the form of the wavefunction. A logical modification is to change the nuclear charge, Z, in the wavefunctions to an effective nuclear charge (Z_{eff}), from +2 to a smaller value. The rationale for making this modification is that one electron partially shields the nuclear charge from the other electron, as shown in Figure 7.1.1 .

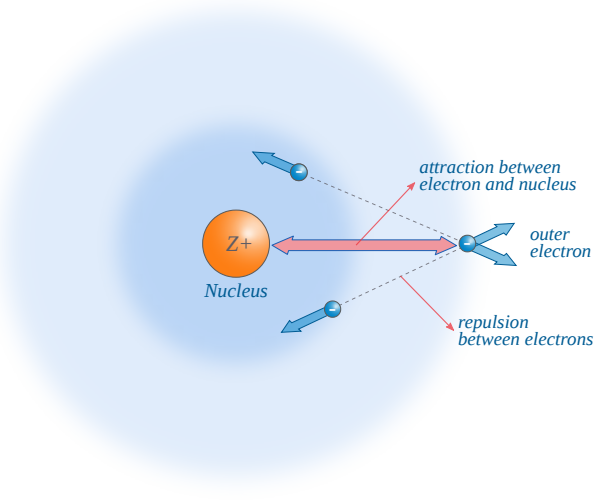


Figure 7.1.1 : Electron-electron shielding leading to a reduced effective nuclear charge. The attractive force of the nucleus on the outer electron is partially countered by the repulsive force between inner electrons and the outer electron. (CC BY-SA; Ümit Kaya via LibreTexts)

A region of negative charge density between one of the electrons and the +2 nucleus makes the potential energy between them more positive (decreases the attraction between them). We can effect this change mathematically by using $\zeta < 2$ in the wavefunction expression. If the shielding were complete, then Z_{eff} would equal 1. If there is no shielding, then $Z_{eff} = 2$. So a way to take into account the electron-electron interaction is by saying it produces a shielding effect. The shielding is not zero, and it is not complete, so the effective nuclear charge varies between one and two.

In general, a theory should be able to make predictions in advance of knowledge of the experimental result. Consequently, a principle and method for choosing the best value for Z_{eff} or any other adjustable parameter that is to be optimized in a calculation is needed. The Variational Principle provides the required criterion and method and says that the best value for any variable parameter in an approximate wavefunction is the value that gives the **lowest energy for the ground state**; i.e., the value that minimizes the energy. The variational method is the procedure that is used to find the lowest energy and the best values for the variable parameters.

A Better Approximation: The Variational Method

The variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. This allows calculating approximate wavefunctions and is the variational principle. The method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an **upper bound** to the ground state energy.

The variational principle means that the expectation value for the binding energy obtained using an approximate wavefunction and the exact Hamiltonian operator will be higher than or equal to the true energy for the system. This idea is really powerful. When implemented, it permits us to find the best approximate wavefunction from a given wavefunction that contains one or more adjustable parameters, called a **trial wavefunction**. A mathematical statement of the variational principle is

$$E_{trial} \geq E_{true} \tag{12.2.7}$$

where

$$E_{trial} = \frac{\langle \psi_{trial} \left| \hat{H} \right| \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{12.2.8}$$

$$= \frac{\int \psi^*_{trial} \hat{H} \psi_{trial} d\tau}{\int \psi^*_{trial} \psi_{trial} d\tau} \tag{12.2.9}$$

Equation 12.2.7 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 12.2.7). Because of this, the variational energy is an upper bound to the true ground state energy of a given molecule. The general approach of this method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible (Figure 7.1.2).

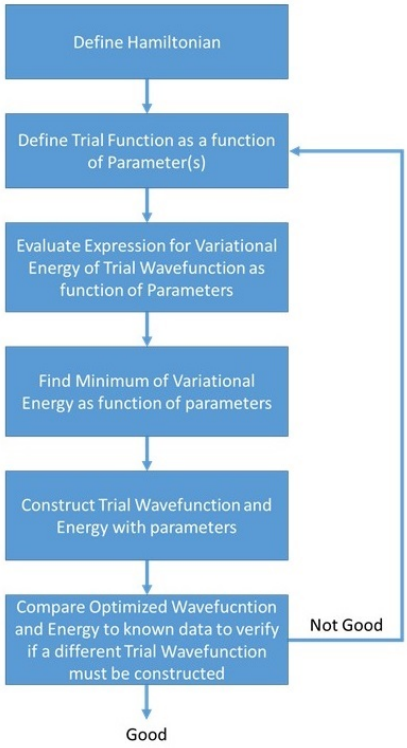


Figure 7.1.2 : Simplified algorithmic flowchart of the Variational Method approximation

> *The variational energy E_{trial} is only equal to the true energy E_{true} when the the corresponding trial wavefunction ψ_{trial} is equal to the true wavefunction ψ_{true}.*

Application to the Helium atom Ground State

Often the expectation values (numerator) and normalization integrals (denominator) in Equation 12.2.9 can be evaluated analytically. For the case of the He atom, let's consider the trial wavefunction as the product wavefunction given by Equation 12.2.10 (this is called the **orbital approximation**),

$$\psi(r_1, r_2) \approx \varphi(r_1)\varphi(r_2) \tag{12.2.10}$$

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).

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{12.2.11}$$

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 12.2.9) is evaluated for helium, the result is a variational energy that depends on the adjustable parameter, ζ.

$$E_{trial}(\zeta) = \frac{\mu e^4}{4\epsilon_0^2 h}\left(\zeta^2 - \frac{27}{8}\zeta\right) \tag{12.2.12}$$

This function is plotted in Figure 7.1.3 as a function of ζ. According to the variational principle (Equation 12.2.7), 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.

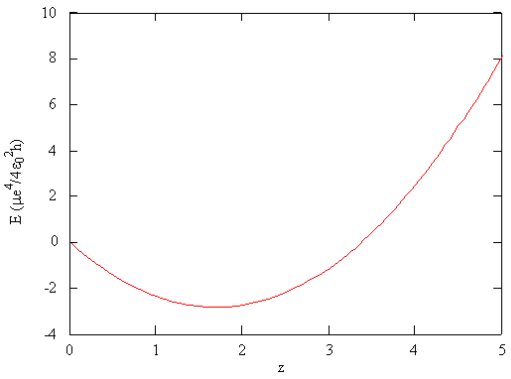


Figure 7.1.3 : Graph of trial energies for helium atom as a function of the adjustable parameter ζ in Equation 12.2.12 that represents the effective nuclear charge felt by the electrons.

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 12.2.10 with the Hamiltonian in Equation 12.2.11. 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 12.2.11.
- Step 2: Define the trial wavefunction as a function of at least one parameter - This is given by Equation 12.2.10.
- Step 3: Evaluate variational energy (E_{trial} integral (Equation 12.2.9) - This procedure was already above in Equation 12.2.12.
- 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.

12.2: The Variational Method is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **7.1: The Variational Method Approximation** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

12.3: 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

$$|\psi_{trial}\rangle = \sum_{j=1}^{N} a_j \Big| \phi_j \rangle \tag{12.3.1}$$

and

$$\langle \psi_{trial}| = \sum_{j=1}^{N} a_j^* \langle \phi_j| \tag{12.3.2}$$

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 12.3.1 and 12.3.2.

As discussed in Section 7.1, the variational energy for a generalized trial wavefunction is

$$E_{trial} = \frac{\langle \psi_{trial} \Big| \hat{H} \Big| \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{12.3.3}$$

Substituting Equations 12.3.1 and 12.3.2 into Equation 12.3.3 involves addressing the numerator and denominator individually. For the numerator, the integral can be expanded thusly:

$$\langle \psi_{trial} | H | \psi_{trial} \rangle = \sum_{i}^{N} \sum_{j}^{N} a_i^* a_j \langle \phi_i | H | \phi_j \rangle. \tag{12.3.4}$$

$$= \sum_{i,j}^{N,N} a_i^* a_j \langle \phi_i | H | \phi_j \rangle. \tag{12.3.5}$$

We can rewrite the following integral in Equation 12.3.5 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 12.3.3 becomes

$$\langle \psi_{trial} | H | \psi_{trial} \rangle = \sum_{i,j}^{N,N} a_i^* a_j H_{ij} \tag{12.3.6}$$

Similarly, the denominator of the right side of Equation 12.3.3 can be expanded

$$\langle \psi_{trial} | \psi_{trial} \rangle = \sum_{i,j}^{N,N} a_i^* a_j \langle \phi_i | \phi_j \rangle \tag{12.3.7}$$

We often simplify the integrals on the right side of Equation 12.3.7 as

$$S_{ij} = \langle \phi_i | \phi_j \rangle$$

where S_{ij} are **overlap integrals** between the different $\{\phi_j\}$ basis functions. Equation 12.3.7 is thus expressed as

$$\langle \psi_{trial} | \psi_{trial} \rangle = \sum_{i,j}^{N,N} a_i^* a_j S_{ij} \tag{12.3.8}$$

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 12.3.6 and 12.3.8 into the variational energy formula (Equation 12.3.3) results in

$$E_{trial} = \frac{\sum_{i,j}^{N,N} a_i^* a_j H_{ij}}{\sum_{i,j}^{N,N} a_i^* a_j S_{ij}} \tag{12.3.9}$$

For such a trial wavefunction as Equation 12.3.1, 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.

Minimizing the Variational Energy

The expression for variational energy (Equation 12.3.9) can be rearranged

$$E_{trial} \sum_{i,j}^{N,N} a_i^* a_j S_{ij} = \sum_{i,j}^{N,N} a_i^* a_j H_{ij} \tag{12.3.10}$$

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).

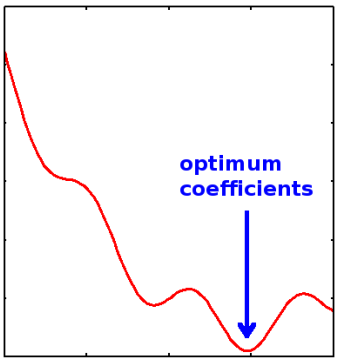


Figure 7.2.1 : Linear Variational Principle in action. Two (or more) wavefunctions are mixed by linear combination. The coefficients a_1, a_2 determine the weight each of them is given. The optimum coefficients are found by searching for minima in the potential landscape spanned by a_1 and a_2. (CC BY-SA-NC; 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 12.3.10 for the kth coefficient gives,

$$\frac{\partial E_{trial}}{\partial a_k} \sum_{i,j}^{N,N} a_i^* a_j S_{ij} + E_{trial} \sum_i \sum_j \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^* \right] S_{ij} \tag{12.3.11}$$
$$= \sum_{i,j}^{N,N} \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^* \right] H_{ij}$$

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 12.3.11 simplifies to

$$\frac{\partial E_{trial}}{\partial a_k} \sum_i \sum_j a_i^* a_j S_{ij} + 2E_{trial} \sum_i a_i S_{ik} = 2 \sum_i a_i H_{ik} \tag{12.3.12}$$

At the minimum variational energy, when

$$\frac{\partial E_{trial}}{\partial a_k} = 0$$

then Equation 12.3.12 gives

$$\sum_i^N a_i (H_{ik} - E_{trial} S_{ik}) = 0 \tag{12.3.13}$$

for all k. The equations in 12.3.13 are called the **Secular Equations**.

Hermitian Operators

Hermitian operators are operators that satisfy the general formula

$$\langle \phi_i \left| \hat{A} \right| \phi_j \rangle = \langle \phi_j \left| \hat{A} \right| \phi_i \rangle \tag{12.3.14}$$

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 12.3.14 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 12.3.13 reduces to the more familiar Eigenvalue form:

$$\sum_i^N H_{ij} a_j = E_{trial} a_i. \tag{12.3.15}$$

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 12.3.1). 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*'.

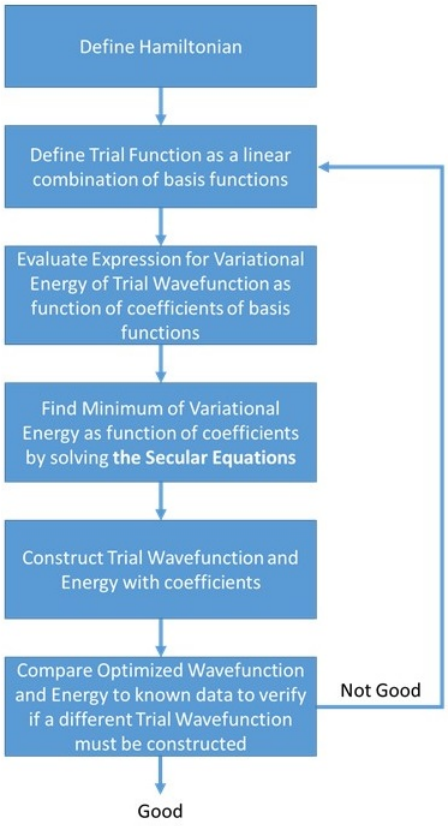


Figure 7.2.2 : Simplified algorithmic flowchart of the linear Variational Method approximation. Compared to the similar algorithmic flowchart for the "normal" Variational Method approximation.

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.

The Secular Determinant

From the secular equations with an orthonormal functions (Equation 12.3.15), 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.

$$|H_{ik}-ES_{ik}| = 0 \tag{12.3.16}$$

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 12.3.16, 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,

$$|\psi_{trial}\rangle = \sum_{n=1}^{N=2} a_n \left| f_n \right\rangle = a_1 |\phi_1\rangle + a_2 |\phi_2\rangle$$

then the secular determinant (Equation 12.3.16), 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

$$a_1^2 H_{11} + 2a_1 a_2 H_{12} + a_2^2 H_{22} = 0$$

and

$$a_1(H_{12} - E_{trial}S_{12}) + a_2(H_{22} - E_{trial}S_{22}) = 0$$

Equation 12.3.16 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 12.3.1). 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

$$|\psi(r)\rangle = \sum_i a_i \left| \phi_i(r) \right\rangle$$

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.

This page titled 12.3: Linear Variational Method and the Secular Determinant is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Claire Vallance via source content that was edited to the style and standards of the LibreTexts platform.

- **7.2: Linear Variational Method and the Secular Determinant** by Claire Vallance is licensed CC BY-NC-SA 4.0. Original source: http://vallance.chem.ox.ac.uk/pdfs/SymmetryLectureNotes.pdf.

12.4: Trial Functions Can Be Linear Combinations of Functions with 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

$$\varphi_{1s}(r_1) = \sum_j c_j e^{-\zeta_j r_j / a_o} \tag{12.4.1}$$

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 12.4.1 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 12.4.1 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 12.4.1 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 12.4.1 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?

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.

12.4: Trial Functions Can Be Linear Combinations of Functions with Variational Parameters is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

12.5: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

Learning Objectives

- Use perturbation theory to approximate the energies of systems as a series of perturbation of a solved system.
- Use perturbation theory to approximate the wavefunctions of systems as a series of perturbation of a solved system.

It is easier to compute the changes in the energy levels and wavefunctions with a scheme of successive corrections to the zero-field values. This method, termed **perturbation theory**, is the single most important method of solving problems in quantum mechanics and is widely used in atomic physics, condensed matter and particle physics. Perturbation theory is another approach to finding approximate solutions to a problem, by starting from the exact solution of a related, simpler problem. A critical feature of the technique is a middle step that breaks the problem into "solvable" and "perturbation" parts. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a "small" term to the mathematical description of the exactly solvable problem.

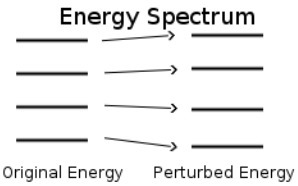


Figure 7.4.1 : Perturbed Energy Spectrum. (CC BY-SA 2.0, Frontier via Wikipedia)

We begin with a Hamiltonian $\hat{H}^0$ having known eigenstates and eigenenergies:

$$\hat{H}^o\,|n^o\rangle = E_n^o|\,n^o\rangle \tag{12.5.1}$$

The task is to find how these eigenstates and eigenenergies change if a small term H^1 (an external field, for example) is added to the Hamiltonian, so:

$$(\hat{H}^0 + \hat{H}^1)\,|n\rangle = E_n|\,n\rangle \tag{12.5.2}$$

That is to say, on switching on $\hat{H}^1$ changes the wavefunctions:

$$\underbrace{|n^o\rangle}_{\text{unperturbed}} \Rightarrow \underbrace{|n\rangle}_{\text{Perturbed}} \tag{12.5.3}$$

and energies (Figure 7.4.1):

$$\underbrace{E_n^o}_{\text{unperturbed}} \Rightarrow \underbrace{E_n}_{\text{Perturbed}} \tag{12.5.4}$$

> *The basic assumption in perturbation theory is that H^1 is sufficiently small that the leading corrections are the same order of magnitude as H^1 itself, and the true energies can be better and better approximated by a successive series of corrections, each of order H^1/H^o compared with the previous one.*

The strategy is to **expand** the true wavefunction and corresponding eigenenergy as series in $\hat{H}^1/\hat{H}^o$. These series are then fed into Equation 12.5.2, and terms of the same order of magnitude in $\hat{H}^1/\hat{H}^o$ on the two sides are set equal. The equations thus generated are solved one by one to give progressively more accurate results.

To make it easier to identify terms of the same order in $\hat{H}^1/\hat{H}^o$ on the two sides of the equation, it is convenient to introduce a dimensionless parameter λ which always goes with $\hat{H}^1$, and then expand both eigenstates and eigenenergies as power series in λ,

$$|n\rangle = \sum_i^m \lambda^i |n^i\rangle \tag{12.5.5}$$

$$E_n = \sum_{i=0}^m \lambda^i E_n^i \tag{12.5.6}$$

where m is how many terms in the expansion we are considering. The ket $|n^i\rangle$ is multiplied by λ^i and is therefore of order $(H^1/H^o)^i$.

> *λ is purely a bookkeeping device: we will set it equal to 1 when we are through! It's just there to keep track of the orders of magnitudes of the various terms.*

For example, in first order perturbation theory, Equations 12.5.5 are truncated at $m = 1$ (and setting $\lambda = 1$):

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{12.5.7}$$

$$E_n \approx E_n^o + E_n^1 \tag{12.5.8}$$

However, let's consider the general case for now. Adding the full expansions for the eigenstate (Equation 12.5.5) and energies (Equation 12.5.6) into the Schrödinger equation for the perturbation Equation 12.5.2 in

$$(\hat{H}^o + \lambda \hat{H}^1)\,|n\rangle = E_n |\,n\rangle \tag{12.5.9}$$

we have

$$(\hat{H}^o + \lambda \hat{H}^1) \left(\sum_{i=0}^m \lambda^i |n^i\rangle \right) = \left(\sum_{i=0}^m \lambda^i E_n^i \right) \left(\sum_{i=0}^m \lambda^i |n^i\rangle \right) \tag{12.5.10}$$

We're now ready to match the two sides term by term in powers of λ. Note that the zeroth-order term, of course, just gives back the unperturbed Schrödinger Equation (Equation 12.5.1).

Let's look at Equation 12.5.10 with the first few terms of the expansion:

$$(\hat{H}^o + \lambda \hat{H}^1)\,(|n^o\rangle + \lambda |n^1\rangle) = \left(E_n^0 + \lambda E_n^1\right)(|n^o\rangle + \lambda |n^1\rangle) \tag{12.5.11}$$

$$\begin{aligned} \hat{H}^o \left|n^o\right\rangle + \lambda \hat{H}^1 \left| n^o\right\rangle + \lambda H^o \left|n^1\right\rangle + \lambda^2 \hat{H}^1 \left| n^1\right\rangle = E_n^0 \left|n^o\right\rangle + \lambda E_n^1 |\,n^o\rangle \\ + \lambda E_n^0 \left|n^1\right\rangle + \lambda^2 E_n^1 |\,n^1\rangle \end{aligned} \tag{12.5.12}$$

Collecting terms in order of λ and coloring to indicate different orders

$$\begin{aligned} &\underset{\text{zero order}}{\hat{H}^o |n^o\rangle} \\ &+ \underbrace{\lambda(\hat{H}^1 |n^o\rangle + \hat{H}^o |n^1\rangle)}_{\text{1st order}} + \underbrace{\lambda^2 \hat{H}^1 |n^1\rangle}_{\text{2nd order}} = \underbrace{E_n^0 |n^o\rangle}_{\text{zero order}} + \underbrace{\lambda(E_n^1 |n^o\rangle + E_n^0 |n^1\rangle)}_{\text{1st order}} + \underbrace{\lambda^2 E_n^1 |n^1\rangle}_{\text{2nd order}} \end{aligned} \tag{12.5.13}$$

If we expanded Equation 12.5.10 further we could express the energies and wavefunctions in higher order components.

Zero-Order Terms ($\lambda = 0$)

Collecting the zero order terms in the expansion (black terms in Equation 12.5.13) results in just the Schrödinger Equation for the unperturbed system

$$\hat{H}^o |n^o\rangle = E_n^o |\,n^o\rangle \tag{12.5.14}$$

First-Order Expression of Energy ($\lambda = 1$)

The summations in Equations 12.5.5, 12.5.6, and 12.5.10 can be truncated at any order of λ. For example, the first order perturbation theory has the truncation at $\lambda = 1$. Matching the terms that linear in λ (red terms in Equation 12.5.13) and setting $\lambda = 1$ on both sides of Equation 12.5.13:

$$\hat{H}^o \left|n^1\right\rangle + \hat{H}^1 \left| n^o\right\rangle = E_n^o \left|n^1\right\rangle + E_n^1 |\,n^o\rangle \tag{12.5.15}$$

Equation 12.5.15 is the key to finding the first-order change in energy E_n^1. Taking the **inner product** of both sides with $\langle n^o|$:

$$\langle n^o \left| \hat{H}^o \right| n^1 \rangle + \langle n^o \left| \hat{H}^1 \right| n^o \rangle = \langle n^o \left| E_n^o \right| n^1 \rangle + \langle n^o \left| E_n^1 \right| n^o \rangle \tag{12.5.16}$$

since operating the zero-order Hamiltonian on the bra wavefunction (this is just the Schrödinger equation; Equation 12.5.14) is

$$\langle n^o | \hat{H}^o = \langle n^o | E_n^o \tag{12.5.17}$$

and via the orthonormality of the unperturbed $|n^o\rangle$ wavefunctions both

$$\langle n^o | n^o \rangle = 1 \tag{12.5.18}$$

and Equation 12.5.8 can be simplified

$$\cancel{E_n^o \langle n^o | n^1 \rangle} + \langle n^o \left| H^1 \right| n^o \rangle = \cancel{E_n^o \langle n^o | n^1 \rangle} + E_n^1 \cancel{\langle n^o | n^o \rangle^1} \tag{12.5.19}$$

since the unperturbed set of eigenstates are orthogonal (Equation 12.5.18) and we can cancel the other term on each side of the equation, we find that

$$E_n^1 = \langle n^o \left| \hat{H}^1 \right| n^o \rangle \tag{12.5.20}$$

> *The first-order change in the energy of a state resulting from adding a perturbing term $\hat{H}^1$ to the Hamiltonian is just the **expectation value** of $\hat{H}^1$ in the **unperturbed** wavefunctions.*

That is, the first order energies (Equation 12.5.15) are given by

$$E_n \approx E_n^o + E_n^1 \tag{12.5.21}$$

$$\approx \underbrace{E_n^o + \langle n^o | H^1 | n^o \rangle}_{\text{First Order Perturbation}} \tag{12.5.22}$$

12.5.1A ✔ Example : A Perturbed Particle in a Box

Estimate the energy of the ground-state and first excited-state wavefunction within first-order perturbation theory of a system with the following potential energy

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

Solution

The first step in any perturbation problem is to write the Hamiltonian in terms of a unperturbed component that the solutions (both eigenstates and energy) are known and a perturbation component (Equation 12.5.2). For this system, the unperturbed Hamilonian and solutions is the particle in an infiinitely high box and the perturbation is a shift of the potential within the box by V_o.

$$\hat{H}^1 = V_o$$

Using Equation 12.5.20 for the first-order term in the energy of the ground-state

$$E_n^1 = \langle n^o \left| H^1 \right| n^o \rangle$$

with the wavefunctions known from the particle in the box problem

$$|n^o\rangle = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right)$$

At this stage we can do two problems independently (i.e., the ground-state with $|1\rangle$ and the first excited-state $|2\rangle$). However, in this case, the first-order perturbation to any particle-in-the-box state can be easily derived.

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

or better yet, instead of evaluating this integrals we can simplify the expression

$$E_n^1 = \langle n^o \left| H^1 \right| n^o \rangle = \langle n^o \left| V_o \right| n^o \rangle = V_o \langle n^o | n^o \rangle = V_o$$

so via Equation 12.5.22, the energy of each perturbed eigenstate is

$$\begin{aligned} E_n &\approx E_n^o + E_n^1 \\ &\approx \frac{h^2}{8mL^2} n^2 + V_o \end{aligned}$$

While this is the first order perturbation to the energy, it is also the exact value.

12.5.1B Example : An Even More Perturbed Particle in a Box

Estimate the energy of the ground-state wavefunction within first-order perturbation theory of a system with the following potential energy

$$V(x) = \begin{cases} V_o & 0 \le x \le L/2 \\ \infty & x < 0 \; and \; x > L \end{cases}$$

Solution

As with Example 7.4.1 , we recognize that unperturbed component of the problem (Equation 12.5.2) is the particle in an infinitely high well. For this system, the unperturbed Hamiltonian and solution is the particle in an infinitely high box and the perturbation is a shift of the potential within half a box by V_o. This is essentially a step function.

Using Equation 12.5.20 for the first-order term in the energy of the any state

$$\begin{aligned} E_n^1 &= \langle n^o \left| H^1 \right| n^o \rangle \\ &= \int_0^{L/2} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) V_o \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) dx + \int_{L/2}^{L} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) 0 \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) dx \end{aligned}$$

The second integral is zero and the first integral is simplified to

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

this is evaluated to

$$\begin{aligned} E_n^1 &= \frac{2V_o}{L} \left[\frac{-1}{2\frac{\pi n}{a}} \cos\left(\frac{n\pi}{L}x\right) \sin\left(\frac{n\pi}{L}x\right) + \frac{x}{2} \right]_0^{L/2} \\ &= \frac{2V_o}{\cancel{L}} \frac{\cancel{L}}{4} = \frac{V_o}{2} \end{aligned}$$

The energy of each perturbed eigenstate, via Equation 12.5.22, is

$$\begin{aligned} E_n &\approx E_n^o + \frac{V_o}{2} \\ &\approx \frac{h^2}{8mL^2} n^2 + \frac{V_o}{2} \end{aligned}$$

First-Order Expression of Wavefunction ($\lambda = 1$)

The general expression for the first-order change in the *wavefunction* is found by taking the inner product of the first-order expansion (Equation 12.5.15) with the bra $\langle m^o |$ with $m \neq n$,

$$\langle m^o \left| H^o \right| n^1 \rangle + \langle m^o \left| H^1 \right| n^o \rangle = \langle m^o \left| E_n^o \right| n^1 \rangle + \langle m^o \left| E_n^1 \right| n^o \rangle \tag{12.5.23}$$

Last term on right side of Equation 12.5.23

The last integral on the right hand side of Equation 12.5.23 is zero, since $m \neq n$ so

$$\langle m^o \left| E_n^1 \right| n^o \rangle = E_n^1 \langle m^o | n^o \rangle \tag{12.5.24}$$

and

$$\langle m^o | n^0 \rangle = 0 \tag{12.5.25}$$

First term on right side of Equation 12.5.23

The first integral is more complicated and can be expanded back into the H^o

$$E_m^o \langle m^o | n^1 \rangle = \langle m^o \left| E_m^o \right| n^1 \rangle = \langle m^o \left| H^o \right| n^1 \rangle \tag{12.5.26}$$

since

$$\langle m^o | H^o = \langle m^o | E_m^o \tag{12.5.27}$$

so

$$\langle m^o | n^1 \rangle = \frac{\langle m^o \left| H^1 \right| n^o \rangle}{E_n^o - E_m^o} \tag{12.5.28}$$

and therefore the wavefunction corrected to first order is:

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{12.5.29}$$

$$\approx \underbrace{|n^o\rangle + \sum_{m \neq n} \frac{|m^o\rangle \langle m^o | H^1 | n^o\rangle}{E_n^o - E_m^o}}_{\text{First Order Perturbation Theory}} \tag{12.5.30}$$

Equation 12.5.30 is essentially is an expansion of the unknown wavefunction correction as a **linear combination** of known unperturbed wavefunctions 12.5.32:

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{12.5.31}$$

$$\approx \left| n^o \rangle + \sum_{m \neq n} c_{m,n} \right| m^o \rangle \tag{12.5.32}$$

with the expansion coefficients determined by

$$c_{m,n} = \frac{\langle m^o \left| H^1 \right| n^o \rangle}{E_n^o - E_m^o} \tag{12.5.33}$$

This is justified since the set of original zero-order wavefunctions forms a **complete basis set** that can describe any function.

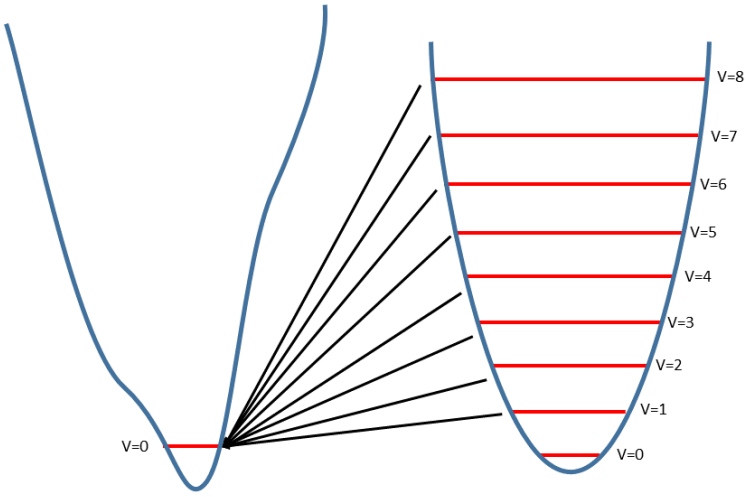


Figure 7.4.2 : The first order perturbation of the ground-state wavefunction for a perturbed (left potential) can be expressed as a linear combination of all excited-state wavefunctions of the unperturbed potential (Equation 12.5.32), shown as a harmonic oscillator in this example (right potential). Note that the ground-state harmonic oscillator wavefunction is not part of this expression and all wavefunctions need to be included in the expression, not just the first eight wavefunctions shown here. (CC BY 4.0; Delmar Larsen)

Calculating the first order perturbation to the wavefunctions is in general an infinite sum of off diagonal matrix elements of $\boldsymbol{H}^1$ (Figure 7.4.2).

- However, the denominator argues that terms in this sum will be weighted by states that are of **comparable energy**. That means in principle, these sum can be truncated easily based off of some criterion.
- Another point to consider is that many of these matrix elements will equal zero depending on the symmetry of the $\{|n^o\rangle\}$ basis and $\boldsymbol{H}^1$ (e.g., some $\langle m^o|\boldsymbol{H}^1|n^o\rangle$ integrals in Equation 12.5.30 could be zero due to the integrand having an odd symmetry; see Example 7.4.3).

> *The denominators in Equation 12.5.30 argues that terms in this sum will be preferentially dictated by states that are of **comparable energy**. That is, eigenstates that have energies significantly greater or lower than the unperturbed eigenstate will weakly contribute to the perturbed wavefunction.*

Example 7.4.2 : A Harmonic Oscillator with a Cubic Perturbation

Estimate the energy of the ground-state wavefunction associated with the Hamiltonian using perturbation theory

$$\hat{H} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \epsilon x^3$$

Solution

The first step in a perturbation theory problem is to identify the reference system with the known eigenstates and energies. For this example, this is clearly the harmonic oscillator model.

Energy

The first steps in flowchart for applying perturbation theory (Figure 7.4.1) is to separate the Hamiltonian of the difficult (or unsolvable) problem into a solvable one with a perturbation. For this case, we can rewrite the Hamiltonian as

$$\hat{H}^o + \hat{H}^1$$

where

- $\hat{H}^o$ is the Hamitonian for the standard Harmonic Oscillator with **known** eigenstates and eigenenergies

$$\hat{H}^{(0)} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

- $\hat{H}^1$ is the pertubtiation

$$\hat{H}^1 = \epsilon x^3$$

The first order perturbation is given by Equation 12.5.20, which for this problem is

$$E_n^1 = \langle n^o \left| \epsilon x^3 \right| n^o \rangle$$

Notice that the integrand has an odd symmetry (i.e., $f(x) = -f(-x)$) with the perturbation Hamiltonian being odd and the ground state harmonic oscillator wavefunctions being even. So

$$E_n^1 = 0$$

This means to first order pertubation theory, this cubic terms does not alter the ground state energy (via Equation 12.5.22). However, this is not the case if second-order perturbation theory were used, which is more accurate (not shown).

Wavefunction

Calculating the first order perturbation to the wavefunctions (Equation 12.5.30) is more difficult than energy since multiple integrals must be evaluated (an infinite number if symmetry arguments are not applicable). The harmonic oscillator wavefunctions are often written in terms of Q, the unscaled displacement coordinate:

$$|\Psi_v(x)\rangle = N_v'' H_v(\sqrt{\alpha}Q)e^{-\alpha Q^2/2}$$

with α

$$\alpha = 1/\sqrt{\beta} = \sqrt{\frac{k\mu}{\hbar^2}}$$

and

$$N_v'' = \sqrt{\frac{1}{2^v v!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

Let's consider only the first six wavefunctions that use these Hermite polynomials $H_v(x)$:

- $H_0 = 1$
- $H_1 = 2x$
- $H_2 = -2 + 4x^2$
- $H_3 = -12x + 8x^3$
- $H_4 = 12 - 48x^2 + 16x^4$
- $H_5 = 120x - 160x^3 + 32x^5$

The first order perturbation to the ground-state wavefunction (Equation 12.5.30)

$$|0^1\rangle = \sum_{m\neq 0}^{5} \frac{|m^o\rangle\langle m^o \left| H^1 \right| 0^o\rangle}{E_0^o - E_m^o} \tag{12.5.34}$$

given these truncated wavefunctions (we should technically use the infinite sum) and that we are considering only the ground state with $n = 0$:

$$|0^1\rangle = \frac{\langle 1^o \left| H^1 \right| 0^o\rangle}{E_0^o - E_1^o}\left|1^o\right\rangle + \frac{\langle 2^o \left| H^1 \right| 0^o\rangle}{E_0^o - E_2^o}\left|2^o\right\rangle + \frac{\langle 3^o \left| H^1 \right| 0^o\rangle}{E_0^o - E_3^o}\left|3^o\right\rangle + \frac{\langle 4^o \left| H^1 \right| 0^o\rangle}{E_0^o - E_4^o}\left|4^o\right\rangle + \frac{\langle 5^o \left| H^1 \right| 0^o\rangle}{E_0^o - E_5^o}\left|5^o\right\rangle$$

We can use symmetry of the perturbation and unperturbed wavefunctions to solve the integrals above. We know that the unperturbed harmonic oscillator wavefunctions $\{|n^0\}\rangle$ alternate between even (when v is even) and odd (when v is odd) as

shown previously. Since the perturbation is an odd function, only when $m = 2k + 1$ with $k = 1, 2, 3$ would these integrals be non-zero (i.e., for $m = 1, 3, 5, ...$).

So of the original five unperturbed wavefunctions, only $|m = 1\rangle$, $|m = 3\rangle$, and $|m = 5\rangle$ mix to make the first-order perturbed ground-state wavefunction so

$$|0^1\rangle = \frac{\langle 1^o | H^1 | 0^o \rangle}{E_0^o - E_1^o} |1^o\rangle + \frac{\langle 3^o | H^1 | 0^o \rangle}{E_0^o - E_3^o} |3^o\rangle + \frac{\langle 5^o | H^1 | 0^o \rangle}{E_0^o - E_5^o} |5^o\rangle$$

At this stage, the integrals have to be manually calculated using the defined wavefuctions above, which is left as an exercise. Notice that each unperturbed wavefunction that can "mix" to generate the perturbed wavefunction will have a reciprocally decreasing contribution (w.r.t. energy) due to the growing denominator in Equation 12.5.34.

? Exercise 7.4.3 : Harmonic Oscillator with a Quartic Perturbation

Use perturbation theory to estimate the energy of the ground-state wavefunction associated with this Hamiltonian

$$\hat{H} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \gamma x^4.$$

Second-Order Terms ($\lambda = 2$)

There are higher energy terms in the expansion of Equation 12.5.5 (e.g., the blue terms in Equation 12.5.13), but are not discussed further here other than noting the whole perturbation process is an infinite series of corrections that ideally converge to the correct answer. It is truncating this series as a finite number of steps that is the approximation. The general approach to perturbation theory applications is giving in the flowchart in Figure 7.4.1 .

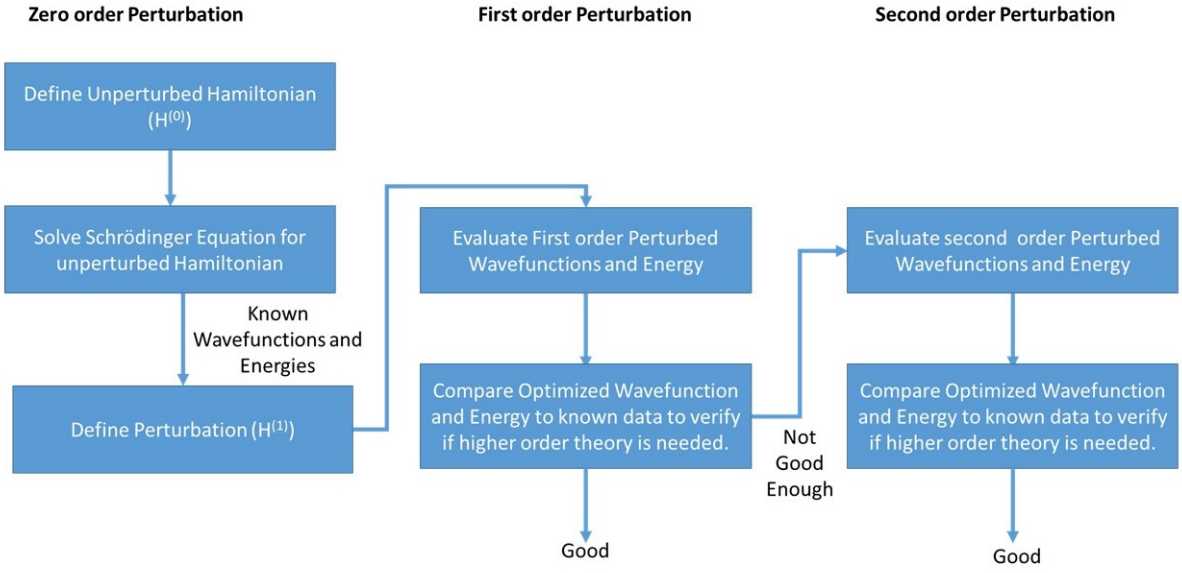


Figure 7.4.1 : Simplified algorithmic flowchart of the Perturbation Theory approximation showing the first two perturbation orders. The process can be continued to third and higher orders. (CC BY 4.0; Delmar Larsen)

Perturbation Theory Does not always Work

It should be noted that there *are* problems that cannot be solved using perturbation theory, even when the perturbation is very weak, although such problems are the exception rather than the rule. One such case is the one-dimensional problem of free particles perturbed by a localized potential of strength λ. Switching on an arbitrarily weak attractive potential causes the $k = 0$ free particle wavefunction to drop below the continuum of plane wave energies and become a localized bound state with binding energy of order λ^2. However, changing the sign of λ to give a repulsive potential there is no bound state, the lowest

> energy plane wave state stays at energy zero. Therefore the energy shift on switching on the perturbation **cannot** be represented as a power series in λ, the strength of the perturbation.

12.5: Perturbation Theory Expresses the Solutions in Terms of Solved Problems is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems** by Delmar Larsen is licensed CC BY-NC-SA 4.0.

12.6: Approximation Methods (Exercises)

Solutions to select questions can be found online.

7.3

Calculate the ground state energy of Harmonic Oscillator using variation method with the following trial wavefunction

$$\phi(x) = |\phi(x)\rangle = \frac{1}{(1+\beta x^2)^2}$$

You may require these definite integrals:

$$\int_{-\infty}^{\infty} \frac{dx}{(1+\beta x^2)^n} = \frac{(2n-3)(2n-5)(2n-7)\ldots(1)}{(2n-2)(2n-4)(2n-6)\ldots(2)} \cdot \pi/\beta^{1/2}$$

$$\int_{-\infty}^{\infty} \frac{dx}{(1-\beta x^2)^n} = \frac{(2n-5)(2n-7)\ldots(1)}{(2n-2)(2n-4)\ldots(2)} \cdot \pi/\beta^{3/2}$$

7.8

What is the variational (trial) energy of the trial function

$$|\phi\rangle = e^{-ax^2}$$

for the ground-state of a harmonic oscillator? Just set up the integral, but do not evaluate. Use

$$\hat{H} = \frac{\hbar^2}{2m}\nabla n^2 + \frac{kx^2}{2}$$

7.9

Use the trial function

$$|\exp^{\frac{-ax^2}{2}}\rangle$$

to set up the integrals to find the ground state energy of a anharmonic oscillator whose potential is $V(x) = cx^5$, but do not evaluate.

7.12

Consider a particle of mass m in a box from $x = -a$ to $x = a$ with $V(x) = -V_0$ for $|x| \geq a$. Assume a trial function of the form

$$|\phi(x)\rangle = l^2 - x^2$$

for $-l < x < l$ and $\psi(x) = 0$ otherwise. l is the parameter. Does the trial function satisfy the requirements of a particle in a box wavefunction?

The result of the variational method was

$$E_\phi(s) = \frac{5}{16}\frac{\hbar^2}{ma^2}\left[\frac{4}{s^2} + \frac{4}{5}\left(8 - \frac{15}{s} + \frac{10}{s^3} - \frac{3}{s^5}\right)\right]$$

Where $s = \frac{l}{a}$ is a new variational parameter for convenience of expression. Derive a polynomial expression for s that can be solved to obtain the value of s that yields the ground state energy, but do not attempt to solve for this value of s.

7.13

Given a trial wavefunction equal to $\sin\lambda(x)$, explain in words a stepwise procedure on how you would go about solving for the energy of this trial wavefunction as well as how to minimize the error.

7.16

Using the variational method approximation, find the ground state energy of a particle in a box using this trial function:

$$|\phi\rangle = N\cos\left(\frac{\pi x}{L}\right)$$

How does is it compare to the true ground state energy?

7.17

For the three-electron detrimental wavefunction

$$\psi = \begin{vmatrix} \phi_A(1) & \phi_A(2) & \phi_A(3) \\ \phi_B(1) & \phi_B(2) & \phi_B(3) \\ \phi_C(1) & \phi_C(2) & \phi_C(3) \end{vmatrix}.$$

confirm that:

a. the interchange of two columns changes the sign of the wavefunction,
b. the interchange of two rows changes the sign of the wavefunction, and
c. the three electrons cannot have the same spin orbital.

7.20

a. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for an oscillator that has a potential of

$$V(x) = (1/2)kx^2 + x^3 + x^4 + x^5?$$

b. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for a particle in a box that has a potential of $V(x) = 0$ between 0<x<L?
c. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for a hydrogenlike atom that has a potential of

$$V(x) = \frac{-e^2}{4\pi\epsilon_o r} + \frac{1}{2}\epsilon r\cos\theta?$$

7.21

Using a harmonic oscillator as the unperturbed problem, calculate the first-order correction to the energy of the $v = 0$ level for the system described as

$$V(x) = \frac{k}{2}x^2 + \frac{m}{6}x^3 + \frac{b}{24}x^4$$

7.22

Using the first order perturbation theory for particle in a box, calculate the ground-state energy for the system

$$V(x) = ax^3 \qquad 0 < x < b$$

7.23

In your chemistry lab you were able to manipulate an external electric field to have the strength κ. You're supervisor wants you to figure out what the first-order correction to the ground state energy of a hydrogen like atom of charge N in this electric field.

7.25A

Use first-order perturbation theory to calculate ground-state energy of a harmonic oscillator with a cx^7 added to the end of the potential.

7.25B

In order to calculate the first-order correction to the ground-state energy of the quartic oscillator, use first-order perturbation theory. The potential energy is $V(x) = cx^4$. For this potential use the harmonic oscillator as the unperturbed system. Solve for the perturbing potential as well.

7.26

Solve the following integrals using this trial wavefunction

$$|\phi\rangle = c_1 x(a-x) + c_2 x^2 (a-x)^2$$

For simplicity purposes, we can assume that a = 1.

$$H_{11} = \frac{\hbar^2}{6m} \; S = \frac{1}{30}$$

$$H_{12} = H_{22} = \frac{\hbar^2}{30m} \; S_{12} = S_{21} = \frac{1}{140}$$

$$H_{22} = \frac{\hbar^2}{105m} \; S_{22} = \frac{1}{630}$$

7.27

Use Perturbation Theory to add cubic and quartic perturbations to the SHO and find the first three SHO energy levels. Do this by expanding the Morse potential:

$$V(x) = D(1 - e^{-Bx})^2$$

into polynomials (i.e., a Taylor expansion). Show that the Hamiltonian can be written as

$$\frac{-h^2\nabla^2}{8\pi^2 m} + ax^2 + bx^3 + cx^4$$

Note which terms can be associated with H^0 and which are the H^1 perturbation. What are the relationships between a, b, c, and D, B? How do the new energy levels compare to the old ones?

7.27

Use the perturbation theory to calculate the first - order corrections to the ground state energy of

a. A harmonic oscillator that arises from a cubic and quartic term.
b. A quartic oscillator that arises from only using a quartic term cx^4

and compare the results.

12.6: Approximation Methods (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

13: Multielectron Atoms

Electrons with more than one atom, such as Helium (He), and Nitrogen (N), are referred to as multi-electron atoms. Hydrogen is the only atom in the periodic table that has one electron in the orbitals under ground state. We will learn how additional electrons behave and affect a certain atom.

13.1: Atomic and Molecular Calculations are Expressed in Atomic Units
13.2: Perturbation Theory and the Variational Method for Helium
13.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method
13.4: An Electron Has An Intrinsic Spin Angular Momentum
13.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
13.6: Antisymmetric Wave Functions can be Represented by Slater Determinants
13.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data
13.8: Term Symbols Gives Detailed Descriptions of an Electron Configuration
13.9: Multi-electron Considerations - A Closer Look at Helium
13.10: The Allowed Values of J - the Total Angular Momentum Quantum Number
13.11: Hund's Rules Determine the Term Symbols of the Ground Electronic States
13.12: Using Atomic Term Symbols to Describe Atomic Spectra
13.13: Multielectron Atoms (Exercises)

Thumbnail: Shell model of Carbon atom. (all right reserved, xponentialdesign).

13: Multielectron Atoms is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

13.1: Atomic and Molecular Calculations are Expressed in Atomic Units

Learning Objectives

- Demonstrate how solving electron structure problems are less cluttered by switching to atomic units instead of SI units.

Atomic units (au or a.u.) form a system of natural units which is especially convenient for atomic physics calculations. Atomic units, like SI units, have a unit of mass, a unit of length, and so on. However, the use and notation is somewhat different from SI. Suppose a particle with a mass of m has 3.4 times the mass of electron. The value of mass m can be written in three ways:

- $m = 3.4\ m_e$: This is the clearest notation (but least common), where the atomic unit is included explicitly as a symbol.
- $m = 3.4\ a.u.$: This notation is ambiguous, but is common. Here, it means that the mass m is 3.4 times the atomic unit of mass. If considering a length L of 3.4 times the atomic unit of length, the equation would look the same, $L = 3.4\ a.u.$ The dimension needs to be inferred from context, which is sloppy.
- $m = 3.4$: This notation is similar to the previous one, and has the same dimensional ambiguity. It comes from formally setting the atomic units to 1 (Table 8.1.1).

This article deals with "Hartree type" of atomic units, where the numerical values of the following four fundamental physical constants are all unity by definition:

Table 8.1.1 : Fundamental atomic units

Dimension	Name	Symbol/Definition	Value in SI units	Value in Atomic Units
mass	electron rest mass	m_e	9.109×10^{-31} kg	1
charge	elementary charge	e	1.602×10^{-19} C	1
action	reduced Planck's constant	$\hbar = \frac{h}{2\pi}$	1.054×10^{-34} J·s	1
electric constant^{-1}	Coulomb force constant	$k_e = \frac{1}{4\pi\epsilon_o}$	8.987 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}	

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

13.1: Atomic and Molecular Calculations are Expressed in Atomic Units is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **8.1: Atomic and Molecular Calculations are Expressed in Atomic Units** by Wikipedia is licensed CC BY-SA 4.0.

13.2: Perturbation Theory and the Variational Method for Helium

Learning Objectives

- Demonstrate that both perturbation theory and variational methods can be used to solve the electron structure of the helium atom.

Both perturbation theory and variation method (especially the linear variational method) provide good results in approximating the energy and wavefunctions of multi-electron atoms. Below we address both approximations with respect to the helium atom.

Perturbation Theory of the Helium Atom

We use perturbation theory to approach the analytically unsolvable helium atom Schrödinger equation by focusing on the Coulomb repulsion term that makes it different from the simplified Schrödinger equation that we have just solved analytically. The electron-electron repulsion term is conceptualized as a correction, or perturbation, to the Hamiltonian that can be solved exactly, which is called a **zero-order Hamiltonian**. The perturbation term corrects the previous Hamiltonian to make it fit the new problem. In this way the Hamiltonian is built as a sum of terms, and each term is given a name. For example, we call the simplified or starting Hamiltonian, $\hat{H}^0$, the zero order term, and the correction term $\hat{H}^1$.

$$\hat{H} = \hat{H}^0 + \hat{H}^1 \tag{13.2.1}$$

The Hamilonian for the helium atom (in atomic units) is:

$$\hat{H}^0 = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}}_{\text{H atom Hamiltonian}} - \underbrace{\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}}_{\text{H atom Hamiltonian}} \tag{13.2.2}$$

$$\hat{H}^1 = \frac{1}{r_{12}} = \frac{1}{|r_1 - r_2|} \tag{13.2.3}$$

The expression for the first-order correction to the energy is

$$\begin{aligned} E^1 &= \langle \psi^0 \left| \hat{H}^1 \right| \psi^0 \rangle \\ &= \int \psi^{0*} \hat{H}^1 \psi^0 \, d\tau \end{aligned}$$

Equation ??? is a general expression for the first-order perturbation energy, which provides an improvement or correction to the zero-order energy we already obtained. Hence, E^1 is the average interaction energy of the two electrons calculated using wavefunctions that assume there is no interaction.

The solution to $\hat{H}^0$ (Equation 13.2.2) is the product of two single-electron hydrogen wavefunctions (scaled by the increased nuclear charge) since $\hat{H}^0$ can be separated into independent functions of each electron (i.e., Separation of Variables).

$$|\psi^0\rangle = |\varphi_{1s}(r_1)\varphi_{1s}(r_2)\rangle$$

So the integral in Equation ??? is

$$E^1 = \iint \varphi_{1s}(r_1)\varphi_{1s}(r_2)\frac{1}{r_{12}}\varphi_{1s}(r_1)\varphi_{1s}(r_2)\, d\tau_1 d\tau_2 \tag{13.2.4}$$

where the double integration symbol represents integration over all the spherical polar coordinates of both electrons $r_1, \theta_1, \varphi_1, r_2, \theta_2, \varphi_2$. The evaluation of these six integrals is lengthy. When the integrals are done, the result is E^1 = +34.0 eV so that the total energy calculated using our second approximation method, first-order perturbation theory, is

$$E_{approx2} = E^0 + E^1 = -74.8eV \tag{13.2.5}$$

The new approximate value for the binding energy represents a substantial (~30%) improvement over the zero-order energy:

$$E^0 = \frac{2}{n^2} + \frac{2}{n^2} = 4 \underbrace{E_h}_{hartrees} = 108.8\, eV$$

so the interaction of the two electrons is an important part of the total energy of the helium atom. We can continue with perturbation theory and find the additional corrections, E^2, E^3, etc. For example,

$$E^0 + E^1 + E^2 = -79.2\,eV.$$

So with two corrections to the energy, the calculated result is within 0.3% of the experimental value of -79.01 eV. It takes thirteenth-order perturbation theory (adding E^1 through E^{13} to E^0) to compute an energy for helium that agrees with experiment to within the experimental uncertainty. Interestingly, while we have improved the calculated energy so that it is much closer to the experimental value, we learn nothing new about the helium atom wavefunction by applying the first-order perturbation theory to the energy above. He need to expand the wavefunctions to first order perturbation theory, which requires more effort. Below, we will employ the variational method approximation to modify zero-order wavefunctions to address one of the ways that electrons are expected to interact with each other.

The Hartree Unit of Energy

The hartree is the atomic unit of energy (named after the British physicist Douglas Hartree) and is defined as

$$E_h = 2R_H hc$$

where R_H is the Rydberg constant, h is the Planck constant and c is the speed of light.

$$\begin{aligned} E_h &= 4.359 \times 10^{-18}\,J \\ &= 27.21\,eV. \end{aligned}$$

The hartree is usually used as a unit of energy in atomic physics and computational chemistry. As discussed before for hydrogen emission, IR, and microwave spectroscopies, experimental measurements prefer the electronvolt (eV) or the wavenumber (cm^{-1}).

Variational Method Applied to the Helium Method

As discussed in Section 6.7, because of the electron-electron interactions, the Schrödinger's Equation cannot be solved exactly for the helium atom or more complicated atomic or ionic species. However, the ground-state energy of the helium atom can be estimated using approximate methods. One of these is the variational method which requires the minimizing of the following variational integral.

$$E_{trial} = \frac{\langle \psi_{trial} \left| \hat{H} \right| \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{13.2.6}$$

$$= \frac{\int_0^\infty \psi_{trial}^* \hat{H} \psi_{trial} d\tau}{\int_0^\infty \psi_{trial}^2 \, d\tau} \tag{13.2.7}$$

The five trial wavefunctions discussions below are equally "valid" trial wavefunctions that describe the probability of finding each electron (technically the wavefunction squared). What separates the "poor" approximations from the "good" approximation is whether the trial wavefunction predicts experimental results. Consequently, for all the approximations used for the rest of this TextMap, it is important to compare the theoretical results to the "true" (i.e., experimental) results. No matter how complicated an approximation is, it is only as good as the accuracy of its predicted values to experimental values.

Trial Wavefunction #1: Simple Orbital Approximation with One Parameter

As is clear from Equation 13.2.6, the variational method approximation requires that a trial wavefunction with one or more adjustable parameters be chosen. A logical first choice for such a multi-electron wavefunction would be to assume that the electrons in the helium atom occupy two identical, but scaled, hydrogen 1s orbitals.

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{13.2.8}$$

$$= \exp\left[-\alpha(r_1 + r_2)\right] \tag{13.2.9}$$

The variational energy obtained after minimizing Equation 13.2.7 after substituting the trial wavefunction (Equation 13.2.9) by varying α is

$$E_{trial} = -2.84766\ E_h$$

and the experimentally determined ground-state energy for the helium atom is the sum of first and second ionization energies

$$E_{\text{exp}} = I_1 + I_2 = -2.90372\ E_h \tag{13.2.10}$$

The deviation of energy for the optimized trial wavefunction from the experimental value is

$$\left|\frac{E_{trial}(\alpha) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.84766\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{13.2.11}$$

$$= 1.93\% \tag{13.2.12}$$

The value of -2.8477 hartrees is within 2% of the known ground-state energy of the helium atom. The error in the calculation is attributed to the fact that the wavefunction is based on the orbital approximation and, therefore, does not adequately take electron-electron interactions into account. In other words, this wavefunction gives the electrons too much independence, given that they have like charges and tend to avoid one another.

Trial Wavefunction #2: Orbital Approximation with Two Parameters

Some electron-electron interactions can be built into the multi-electron wavefunction by assuming that each electron is in an orbital which is a linear combination of two different and scaled hydrogen 1s orbitals.

$$\phi(r_1) = \exp(-\alpha r_1) + \exp(-\beta r_1) \tag{13.2.13}$$

Under the orbital approximation this assumption gives a trial wavefunction of the form

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{13.2.14}$$

$$= \exp(-\alpha r_1)\exp(-\alpha r_2) + \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) + \exp(-\beta r_1)\exp(-\beta r_2) \tag{13.2.15}$$

Inspection of this trial wavefunction indicates that 50% of the time the electrons are in different orbitals, while for the first trial wavefunction the electrons were in the same orbital 100% of the time. Notice the enormous increase in the complexity of the variational expression for the energy for this trial wavefunction (Equation 13.2.7). However, the calculation is very similar to that using the previous trial wavefunction. The differences are that in this case the expression for the energy is more complex and that it is being minimized simultaneously with respect to two parameters (α and β) rather than just one (α).

The variational energy obtained after minimizing Equation 13.2.7 after substituting the trial wavefunction (Equation 13.2.15) by varying α and β is

$$E_{trial} = -2.86035\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 13.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.86035\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{13.2.16}$$

$$= 1.49\% \tag{13.2.17}$$

Clearly introducing some electron-electron interactions into the trial wavefunction has improved the agreement between theory and experiment (Equation 13.2.12 vs. 13.2.17).

Trial Wavefunction #3: Orbital Approximation with Two Parameters

The extent of electron-electron interactions can be increased further by eliminating the first and last term in the second trial wavefunction (Equation 13.2.15). This yields a multi-electron wavefunction of the form,

$$|\psi(1,2)\rangle_{trial} = \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) \tag{13.2.18}$$

This trial wavefunction places the electrons in different scaled hydrogen 1s orbitals 100% of the time this adds further improvement in the agreement with the literature value of the ground-state energy is obtained. The variational energy obtained after

minimizing Equation 13.2.7 after substituting the trial wavefunction (Equation 13.2.18) by varying α and β is

$$E_{trial} = -2.87566\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 13.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.87566\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{13.2.19}$$

$$= 0.97\% \tag{13.2.20}$$

This result is within 1% of the actual ground-state energy of the helium atom.

Trial Wavefunction #4: Approximation with Two Parameters

The third trial wavefunction, however, still rests on the orbital approximation and, therefore, does not treat electron-electron interactions adequately. Hylleraas took the calculation a step further by introducing electron-electron interactions directly into the first trial wavefunction by adding a term, r_{12}, involving the inter-electron separation.

$$|\psi_{trial}(1,2)\rangle = (\exp[-\alpha(r_1 + r_2)])\,(1 + \beta r_{12}) \tag{13.2.21}$$

In the trial multi-electron wavefunction of Equation 13.2.21, if the electrons are far apart, then r_{12} is large and the magnitude of the wavefunction increases to favor that configuration. The variational energy obtained after minimizing Equation 13.2.7 after substituting the trial wavefunction (Equation 13.2.21) by varying α and β is

$$E_{trial} = -2.89112\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 13.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.89112\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{13.2.22}$$

$$= 0.43\% \tag{13.2.23}$$

This modification of the trial wavefunction has further improved the agreement between theory and experiment to within 0.5%.

Fifth Trial Wavefunction #5: Approximation with Three Parameters

Chandrasakar brought about further improvement by adding Hylleraas's r_{12} term to the third trial wavefunction (Equation 13.2.18) as shown here.

$$|\psi(1,2)\rangle_{trial} = [\exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2)]\,[1 + \gamma r_{12}] \tag{13.2.24}$$

Chandrasakar's three parameter wavefunction gives rise to a fairly complicated variational expression for ground-state energy. The variational energy obtained after minimizing Equation 13.2.7 after substituting the trial wavefunction (Equation 13.2.24) by varying α, β and γ is

$$E_{trial} = -2.90143\ E_h$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 13.2.10) is

$$\left|\frac{E_{trial}(\alpha,\beta,\gamma) - E_{\text{exp}}}{E_{\text{exp}}}\right| = \left|\frac{-2.90143 + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{13.2.25}$$

$$= 0.0789\% \tag{13.2.26}$$

Chandrasakar's wavefunction gives a result for helium that is within 0.07% of the experimental value for the ground-state energy.

Summary

The purpose of this section is to examine five trial wavefunctions for the helium atom used within the Perturbation Theory and Variational method approximation. For the Variational method approximation, the calculations begin with an uncorrelated wavefunction in which both electrons are placed in a hydrogenic orbital with scale factor α. The next four trial functions use several methods to increase the amount of electron-electron interactions in the wavefunction. As the summary of results that is appended shows this gives increasingly more favorable agreement with the experimentally determined value for the ground-state

energy of the species under study. The detailed calculations show that the reason for this improved agreement with experiment is due to a reduction in electron-electron repulsion.

Five variational method calculations that have been outlined above for the helium atom ($Z = 2$) can be repeated for two-electron atoms (e.g., H^-, Li^+, Be^{2+}, etc). The hydride anion is a particularly interesting case because the first two trial wavefunctions do not predict a stable ion (i.e., they are poor approximations). This indicates that electron-electron interactions is an especially important issue for atoms and ions with small nuclear charge.

13.2: Perturbation Theory and the Variational Method for Helium is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **8.2: Perturbation Theory and the Variational Method for Helium** by Frank Rioux is licensed CC BY 4.0. Original source: https://faculty.csbsju.edu/frioux/workinprogress.html.

13.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method

Learning Objectives

- Show how the Hartree approximation can be used to solve for the wavefunctions and energies of multi-electron atoms.
- Understand the orbital approach of independent orbitals is an approximation to a mutlti-electron system with the motions of all electrons coupled together.
- Demonstate how the Self-Consistant Field (SCF) calculation is needed to support the Hartree approximation

The Hartree method is used to approximate the wavefunction and the energy of a quantum multi-electron system in a stationary state. This approximation assumes that the exact N-body wavefunction of the system can be approximated by a product of single-electron wavefunctions. By invoking the variational method, one can derive a set of N-coupled equations for the N spin orbitals. A solution of these equations yields the Hartree wavefunction and energy of the system. It is one step better than the "Ignorance is Bliss" approach, discussed previously, but still far from modern state-off-the-art methods.

Unsolvable Systems

The Hamiltonian for a generic multielectron atom includes nucleus-electron attraction terms for the additional electrons with a general charge Z; e.g.

$$V_{\text{nuclear-electron}}(r_1) = -\frac{Z}{|\mathbf{r}-\mathbf{R}|} \tag{13.3.1}$$

in atomic units with $|\mathbf{r}-\mathbf{R}|$ is the distance between the electron and the nucleus, The Hamiltonian must also have terms for electron-electron repulsion (also in atomic units)

$$V_{\text{electron-electron}}(r_{12}) = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

with $|\mathbf{r}-\mathbf{r}'|$ is the distance between electron 1 and electron 2. So the proper multi-electron Hamiltonian can be constructed

$$\hat{H}(r_1, r_2, \ldots r_n) = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V_{\text{nuclear-electron}}(r_i) + \sum_{i\neq j} V_{\text{electron-electron}}(r_{ij}) \tag{13.3.2}$$

Given what we have learned from the previous quantum mechanical systems we've studied, we predict that exact solutions to the multi-electron Schrödinger equation would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their electron-electron repulsion (final term in Equation 13.3.2) means that an exact wavefunction for a multi-electron system would be a single function that depends **simultaneously** upon the coordinates of all the electrons; i.e., a multi-electron wavefunction:

$$|\psi(r_1, r_2, \cdots r_i)\rangle \tag{13.3.3}$$

Unfortunately, the electron-electron repulsion terms make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms.

The Hartree Approximation

The method for finding best possible one-electron wavefunctions that was published by Douglas Hartree in 1948 and improved two years later by Vladimir Fock. For the Schrödinger equation to be analytically solvable, the variables must be separable - the variables are the coordinates of the electrons. To separate the variables in a way that retains information about electron-electron interactions, the electron-electron term (Equation 13.3.1) must be approximated so it depends only on the coordinates of one electron. Such an approximate Hamiltonian can account for the interaction of the electrons in **an average way**. The exact one-

electron eigenfunctions of this approximate Hamiltonian then can be found by solving the Schrödinger equation. These functions are the best possible **one-electron functions**.

The Hartree approximation starts by invoking an initial *ansatz* that the multi-electron wavefunction in Equation 13.3.3 can be expanded as a product of single-electron wavefunctions (i.e., orbitals)

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\rangle \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\ldots\psi_N(\mathbf{r}_N)$$

from which it follows that the electrons are *independent*, and interact only via the mean-field Coulomb potential. This yields one-electron Schrödinger equations of the form

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

or

$$H_e(r)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

where $V(r)$ is the potential in which the electron moves; this includes both the nuclear-electron interaction

$$V_{nucleus}(\mathbf{r}) = -Ze^2\sum_R \frac{1}{|\mathbf{r}-\mathbf{R}|}$$

and the mean field arising from the $N-1$ other electrons. We smear the other electrons out into a smooth negative charge density $\rho(\mathbf{r}')$ leading to a potential of the form

$$V_{electron}(\mathbf{r}) = -e\int d\mathbf{r}'\rho(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

where

$$\rho(\mathbf{r}) = \sum_i^{\text{occupied}} |\psi(\mathbf{r})|^2.$$

The sum over runs over all occupied states; i.e., only the states of electrons that exist in the atom. The wavefunctions that from this approach with the Hamiltonian $H_e(r)$ involve possess three kinds of energies discussed below.

Three Energies within the Hartree Approximation

The total energy ϵ_j of the orbital ϕ_j, is the sum of the above three contributions:

1. **Kinetic Energy:** The Kinetic energy of the electron has an average value is computed by taking the expectation value of the kinetic energy operator

   $$\frac{-\hbar^2}{2m}\nabla^2$$

   with respect to any particular solution $\phi_j(r)$ to the Schrödinger equation:

   $$KE = \langle\phi_j\left|\frac{-\hbar^2}{2m}\nabla^2\right|\phi_j\rangle$$

2. **Nuclear-Electron Coulombic Attraction Energy:** Coulombic attraction energy with the nucleus of charge Z:

   $$\langle\phi_j\left|\frac{-Ze^2}{|\mathbf{r}-\mathbf{R}|}\right|\phi_j\rangle$$

3. **Electron-Electron Coulombic Repulsion Energy:** Coulomb repulsion energies with all of the $N-1$ other electrons, which are assumed to occupy other atomic orbitals denoted ϕ_K, with this energy computed as

   $$\sum_{j\neq k}\langle\phi_j(r)\phi_k(r')\left|\frac{e^2}{|r-r'|}\right|\phi_j(r)\phi_k(r')\rangle. \tag{13.3.4}$$

The Dirac notation $\langle\phi_j(r)\phi_k(r')\left|\frac{e^2}{|r-r'|}\right|\phi_j(r)\phi_k(r')\rangle$ is used to represent the two-electron (six-dimensional) Coulomb integral

$$J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr'$$

that describes the Coulomb repulsion between the charge density $|\phi_j(r)|^2$ for the electron in ϕ_j and the charge density $|\phi_k(r')|^2$ for the electron in ϕ_k. Of course, the sum over k must be limited to exclude $k = j$ to avoid counting a "self-interaction" of the electron in orbital ϕ_j with itself.

Adding these all together to get the total energy ϵ_j of the orbital ϕ_j:

$$\epsilon_J = \langle\phi_j\left|\frac{-\hbar^2}{2m}\nabla^2\right|\phi_j\rangle + \langle\phi_j\left|\frac{-Ze^2}{|\mathbf{r}-\mathbf{R}|}\right|\phi_j\rangle + \sum_{j\neq k}\langle\phi_j(r)\phi_k(r')\left|\frac{e^2}{|r-r'|}\right|\phi_j(r)\phi_k(r')\rangle.$$

This treatment of the electrons and their orbitals is referred to as the **Hartree-level of theory**.

When screened hydrogenic atomic orbitals are used to approximate the ϕ_j and ϕ_K orbitals, the resultant ϵ_J values do **not** produce accurate predictions. For example, the negative of ϵ_J should approximate the ionization energy for removal of an electron from the orbitals ϕ_j. Such ionization potentials (IP s) can be measured, and the measured values do not agree well with the theoretical values when a crude screening approximation is made for the atomic orbitals.

The Self-Consistant Field (SCF) Approach to the Variational Method

The Hartree Equations are nonlinear and must be solved iteratively. This is because if particles interact, that interaction must be in the Hamiltonian. So until we know where the particles are, we cannot write down the Hamiltonian, but until we know the Hamiltonian, we cannot tell where the particles are.

The idea is to solve the Schrödinger equation for an electron moving in the potential of the nucleus and all the other electrons. We start with a guess for the trial electron charge density, solve N/2 one-particle Schrödinger equations (initially identical) to obtain N electron wavefunctions. Then we construct the potential for each wavefunction from that of the nucleus and that of all the other electrons, symmetrize it, and solve the N/2 Schrödinger equations again. This method is ideal for a computer, because it is easily written as an algorithm (Figure 8.3.1).

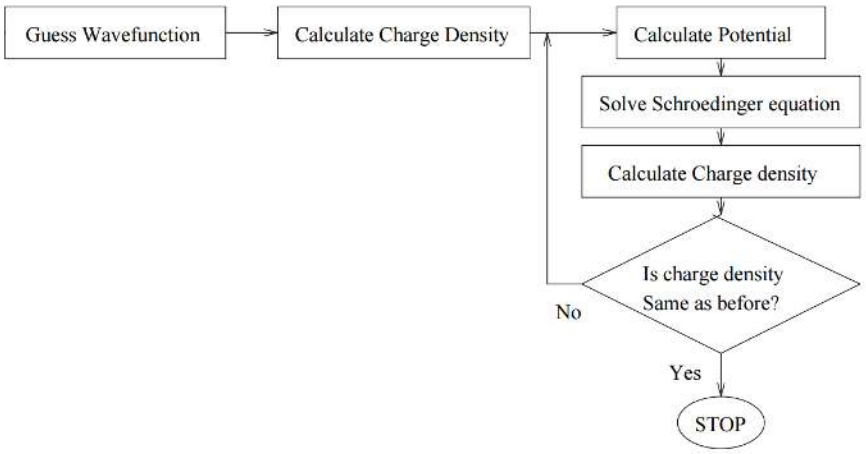


Figure 8.3.1 : Algorithm for Self-consistent field theory.

Although we are concerned here with atoms, the same methodology is used for molecules or even solids (with appropriate potential symmetries and boundary conditions). This is a variational method, so wherever we refer to wavefunctions, we assume that they are expanded in some appropriate basis set.

> *Fock improved on Hartree's method by using proper "antisymmetrized wavefunctions" (called the Hartree-Fock method) instead of simple one-electron wavefunctions.*

Shielding and Effective Charges Concepts are Useful

The hydrogen-like orbitals provide qualitative descriptions of orbitals of atoms with more than a single electron. By introducing the concept of screening as a way to represent the repulsive interactions among the electrons of an atom, an effective nuclear charge Z_{eff} can be used in place of Z in the hydrogenic $\psi_{n,l,m}$ and $E_{n,l}$ formulas to generate approximate atomic orbitals to be filled by electrons in a many-electron atom. For example, in the crudest approximation of a carbon atom, the two $1s$ electrons experience the full nuclear attraction so $Z_{\text{eff}} = 6$ for them, whereas the $2s$ and $2p$ electrons are screened by the two $1s$ electrons, so $Z_{\text{eff}} = 4$ for them. Within this approximation, one then occupies two $1s$ orbitals with $Z = 6$, two $2s$ orbitals with $Z = 4$ and two $2p$ orbitals with $Z = 4$ in forming the full six-electron product wavefunction of the lowest-energy state of carbon

$$|\psi(1,2,\ldots,6)\rangle = |\psi_{1s}(1)\psi_{1s}(2)\psi_{2s}(3)\ldots\psi_{1p}(6)\rangle. \tag{13.3.5}$$

However, such approximate orbitals are not sufficiently accurate to be of use in quantitative simulations of atomic and molecular structure. In particular, their energies do not properly follow the trends in atomic orbital (AO) energies that are taught in introductory chemistry classes (Figure 8.3.2).

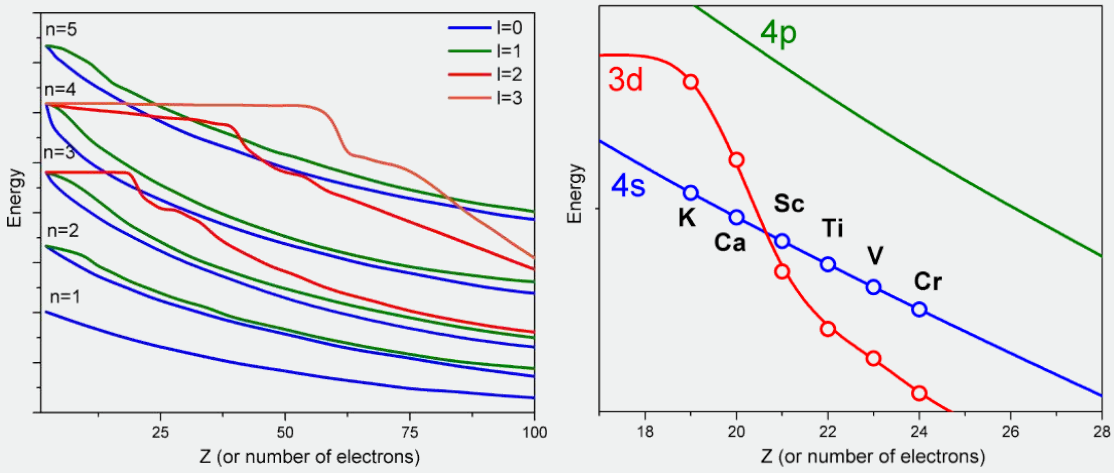


Figure 8.3.2 : Energies of Atomic Orbitals as Functions of the number of electrons in Neutral Atoms. (CC BY 4.0; Delmar Larsen).

For example, the relative energies of the $3d$ and $4s$ orbitals are not adequately described in a model that treats electron repulsion effects in terms of a simple screening factor. So, now it is time to examine how we can move beyond the screening model and take the electron repulsion effects, which cause the inter-electronic couplings that render the Schrödinger equation insolvable, into account in a more reliable manner.

13.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

13.4: An Electron Has An Intrinsic Spin Angular Momentum

Learning Objectives

- Understand the forth quantum number for electrons - spin.
- Understand how spin is connected to magnetic properties of the electrons and atoms.
- Understand how to break degeneracy via externally applied magnetic fields in electrons and atoms.

Imagine doing a hypothetical experiment that would lead to the discovery of electron spin. Your laboratory has just purchased a microwave spectrometer with variable magnetic field capacity. We try the new instrument with hydrogen atoms using a magnetic field of 10^4 Gauss and look for the absorption of microwave radiation as we scan the frequency of our microwave generator (Figure 8.4.1).

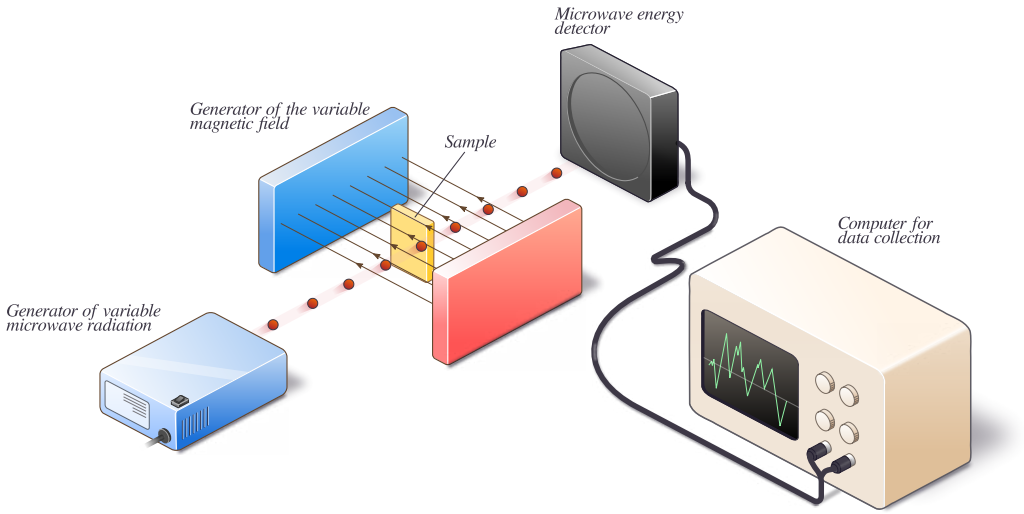


Figure 8.4.1 : Schematic diagram of a microwave spectrometer with the sample in a variable magnetic field. The strength of the magnetic field is set, and the sample's absorption of microwave photons is measured for a range of microwave photon energies (or frequencies). (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Finally we see absorption at a microwave photon frequency of $28 \times 10^9\ Hz$ (28 gigahertz). This result is really surprising from several perspectives. Each hydrogen atom is in its ground state, with the electron in a 1s orbital. The lowest energy electronic transition that we predict based on existing theory (the electronic transition from the ground state (ψ_{100} to ψ_{21m}) requires an energy that lies in the vacuum ultraviolet (the lower Lyman line at 121 nm), not the microwave, region of the spectrum. Furthermore, when we vary the magnetic field we note that the frequency at which the absorption occurs varies in proportion to the magnetic field.

The Zeeman Effect: Breaking Degeneracies with Magnetic Fields

Magnetism results from the circular motion of charged particles. This property is demonstrated on a macroscopic scale by making an electromagnet from a coil of wire and a battery. Electrons moving through the coil produce a magnetic field, which can be thought of as originating from a magnetic dipole or a bar magnet. Electrons in atoms also are moving charges with angular momentum so they too produce a magnetic dipole, which is why some materials are magnetic. A **magnetic dipole** interacts with a magnetic field, and the energy of this interaction is given by the scalar product of the magnetic dipole moment, and the magnetic field, $\vec{B}$.

$$E_B = -\vec{\mu}_m \cdot \vec{B} \tag{13.4.1}$$

Pieter Zeeman was one of the first to observe the splittings of spectral lines in a magnetic field caused by this interaction. Consequently such splittings are known as the Zeeman effect. (Figure 8.4.2). The expectation value calculated for the total energy in this case is the sum of the energy in the absence of the field, E_n, plus the Zeeman energy:

$$\langle E \rangle = E_n + \frac{e\hbar B_z m_l}{2m_e} \tag{13.4.2}$$

$$= E_n + \mu_B B_z m_l \tag{13.4.3}$$

The factor

$$\frac{e\hbar}{2m_e} = -\gamma_e \hbar = \mu_B \tag{13.4.4}$$

defines the constant μ_B, called the **Bohr magneton**, which is taken to be the fundamental magnetic moment. It has units of 9.2732×10^{-21} erg/Gauss or 9.2732×10^{-24} Joule/Tesla. This factor will help you to relate magnetic fields, measured in Gauss or Tesla, to energies, measured in ergs or Joules, for any particle with a charge and mass the same as an electron.

Equation 13.4.3 demonstrates that that m_l quantum number degeneracy of the hydrogen atom is removed by the externally applied magnetic field. For example, the three hydrogen atom eigenstates $|\psi_{211}\rangle$, $|\psi_{21-1}\rangle$, and $|\psi_{210}\rangle$ are degenerate in zero magnetic field, but have different energies in an externally applied magnetic field (Figure 8.4.2).

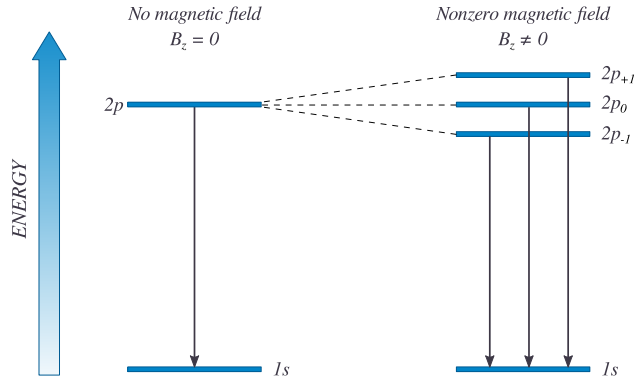


Figure 8.4.2 : The Zeeman effect for the $2s \rightarrow 1s$ transition. Emission when an electron switches from a 2p orbital to a 1s orbital occurs at only one energy in the absence of a magnetic field, but can occur at three different energies in the presence of a magnetic field. (CC BY-NC; Ümit Kaya via LibreTexts)

The $m_l = 0$ state, for which the component of angular momentum and hence also the magnetic moment in the external field direction is zero, experiences no interaction with the magnetic field. The $m_l = +1$ state, for which the angular momentum in the z-direction is +ħ and the magnetic moment is in the opposite direction, against the field, experiences a raising of energy in the presence of a field. Maintaining the magnetic dipole against the external field direction is like holding a small bar magnet with its poles aligned exactly opposite to the poles of a large magnet. It is a higher energy situation than when the magnetic moments are aligned with each other.

Electron Spin and the Stern-Gerlach Experiment

To discover new things, experimentalists sometimes must explore new areas in spite of contrary theoretical predictions. Our theory of the hydrogen atom at this point gives no reason to look for absorption in the microwave region of the spectrum. By doing the crazy experiment outlines above, we discovered that when an electron is in the $|1s\rangle$ orbital of the hydrogen atom, there are two different states that have the same energy. When a magnetic field is applied, this degeneracy is removed, and microwave radiation can cause transitions between the two states. In the rest of this section, we see what can be deduced from this experimental observation. This experiment actually could be done with electron spin resonance spectrometers available today (Figure 8.4.1). To explain our observations, a new model for the hydrogen atom. Our original model for the hydrogen atom accounted for the motion of the electron and proton in our three-dimensional world; the new model needs something else that can give rise to an additional Zeeman-like effect. We need a charged particle with angular momentum to produce a magnetic moment, just like that obtained by the orbital motion of the electron. We can postulate that our observation results from a motion of the electron that was not considered in the last section - electron spin. We have a charged particle spinning on its axis. We then have charge moving in a circle, angular momentum, and a magnetic moment, which interacts with the magnetic field and gives us the Zeeman-like effect that we observed (Figure 8.4.2).

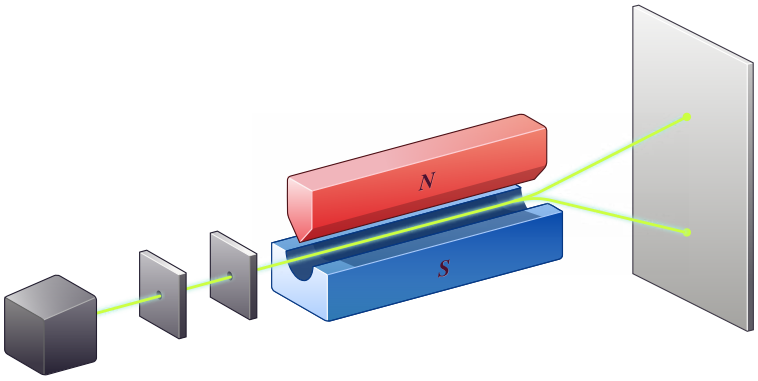


Figure 8.4.2 : Stern–Gerlach experiment: silver atoms travel through an inhomogeneous magnetic field and are deflected up or down depending on their spin. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

In 1920, Otto Stern and Walter Gerlach designed an experiment, which unintentionally led to the discovery that electrons have their own individual, continuous spin even as they move along their orbital of an atom. Today, this electron spin is indicated by the fourth quantum number, also known as the **Electron Spin Quantum Number** and denoted by m_s. In 1925, Samuel Goudsmit and George Uhlenbeck made the claim that features of the hydrogen spectrum that were unexamined might by explained by assuming electrons act as if it has a spin, which can be denoted by an arrow pointing up, which is +1/2, or an arrow pointing down, which is -1/2. The Stern and Gerlach experiment which demonstrated this was done with a beam of vaporized silver atoms that split into two beams after passing through a magnetic field (Figure 8.4.2). An explanation of this is that an electron has a magnetic field due to its spin. When electrons that have opposite spins are put together, there is no net magnetic field because the positive and negative spins cancel each other out. The silver atom used in the experiment has a total of 47 electrons, 23 of one spin type, and 24 of the opposite. Because electrons of the same spin cancel each other out, the *one unpaired electron* in the atom will determine the spin.

Spin Eigenstates and Eigenvalues

To describe electron spin from a quantum mechanical perspective, we must have spin wavefunctions and spin operators. The properties of the spin states are deduced from experimental observations and by analogy with our treatment of the states arising from the orbital angular momentum of the electron. The important feature of the spinning electron is the spin angular momentum vector, which we label $\boldsymbol{S}$ by analogy with the orbital angular momentum $\boldsymbol{L}$. 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:

$$\hat{S}_z \left| \sigma_s^{m_s} \right\rangle = m_s\hbar \left| \sigma_s^{m_s} \right\rangle \tag{13.4.5}$$

Since m_l ranges in integer steps from $-l$ to $+l$, also by analogy m_s ranges in integer steps from $-s$ to $+s$. In our hypothetical experiment, we observed one absorption transition, which means there are two spin states. Consequently, the two values of m_s must

be $+s$ and $-s$, and the difference in m_s for the two states, labeled f and i below, must be the smallest integer step, i.e., 1. The result of this logic is that

$$\begin{aligned} m_{s,f} - m_{s,i} &= 1 \\ (+s) - (-s) &= 1 \\ 2s &= 1 \\ s &= \frac{1}{2} \end{aligned} \tag{13.4.6}$$

Therefore our conclusion is that the magnitude of the spin quantum number is 1/2 and the values for m_s are +1/2 and -1/2. The two spin states correspond to spinning clockwise and counter-clockwise with positive and negative projections of the spin angular momentum onto the z-axis (Figure 8.4.3). The state with a positive projection, m_s = +1/2, is called α; the other is called β. These spin states are arbitrarily labeled α and β, and the associated spin wavefunctions also are designated by $|\alpha\rangle$ and $|\beta\rangle$.

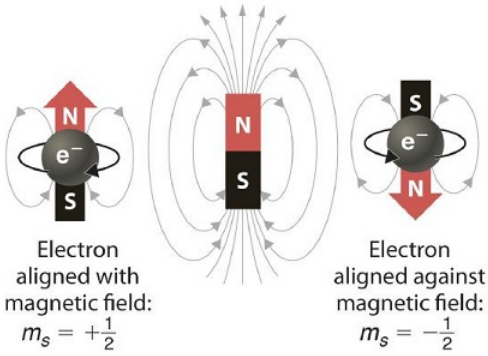


Figure 8.4.3 : Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden. (CC BY-SA-NC 3.0; Anonymous).

From Equation 13.4.5, the magnitude of the z-component of spin angular momentum, S_z, is given by

$$S_z = m_s \hbar \tag{13.4.7}$$

so the value of S_z is $+\hbar/2$ for spin state α and $-\hbar/2$ for spin state β. Hence, we conclude that the α spin state, where the magnetic moment is aligned against the external field direction, has a **greater energy** than the β spin state.

Electrons are not Actually Spinning

Electron's hypothetical surface would have to be moving *faster* than the speed of light for it to rotate quickly enough to produce the observed angular momentum. Hence, an electron is not simply a spinning ball or ring and electron spin appears to be an *intrinsic angular moment* of the particle rather than a consequence of the rotation of a charge particle like Figure 8.4.3 suggests. Despite this, the term "electron spin" persists in quantum vernacular.

Properties of Spin Eigenstates

Even though we do not know their functional forms, the spin wavefunctions are taken to be normalized and orthogonal to each other.

$$\int \alpha^* \alpha \, d\tau_s = \int \beta^* \beta \, d\tau_s = 1 \tag{13.4.8}$$

or in braket notation

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \tag{13.4.9}$$

and

$$\int \alpha^* \beta \, d\tau_s = \int \beta^* \alpha \, d\tau_s = 0 \tag{13.4.10}$$

or in braket notation

$$\langle\alpha|\beta\rangle = \langle\alpha|\beta\rangle = 0 \tag{13.4.11}$$

where the integral is over the spin variable τ_s.

Now let's apply these deductions to the experimental observations in our hypothetical microwave experiment in Figure 8.4.1 . We can account for the frequency of the transition (ν= 28 gigahertz) that was observed in this hypothetical experiment in terms of the magnetic moment of the spinning electron and the strength of the magnetic field. The photon energy, $h\nu$, is given by the difference between the energies of the two states, E_α and E_β

$$\Delta E = h\nu \tag{13.4.12}$$

$$= E_\alpha - E_\beta \tag{13.4.13}$$

The energies of these two states consist of the sum of the energy of an electron in a 1s orbital, E_{1s}, and the energy due to the interaction of the spin magnetic dipole moment of the electron, μ_s, with the magnetic field, B.

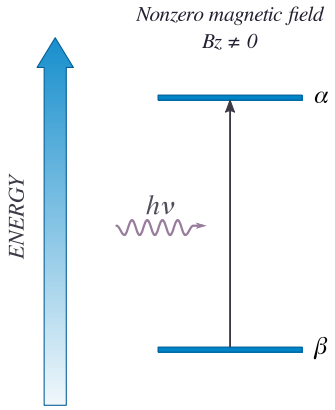


Figure 8.4.4 : Absorption of a photon to cause a transition from the β to the α state. (CC BY-NC; Ümit Kaya via LibreTexts)

The two states with distinct values for spin magnetic moment μ_s are denoted by the subscripts α and β (the spin version of Equation 13.4.1.

$$E_\alpha = E_{1s} - \mu_{s,\alpha} \cdot B$$

$$E_\beta = E_{1s} - \mu_{s,\beta} \cdot B$$

Substituting the two equations above into the expression for the photon (Equation 13.4.13) energy gives

$$h\nu = E_\alpha - E_\beta \tag{13.4.14}$$

$$= (E_{1s} - \mu_{s,\alpha} \cdot B) - (E_{1s} - \mu_{s,\beta} \cdot B) \tag{13.4.15}$$

$$= (\mu_{s,\beta} - \mu_{s,\alpha}) \cdot B \tag{13.4.16}$$

Again by analogy with the orbital angular momentum and magnetic moment discussed above, we take the spin magnetic dipole of each spin state, $\mu_{s,\alpha}$ and $\mu_{s,\beta}$, to be related to the total spin angular momentum of each state, S_α and S_β, by a constant **spin gyromagnetic ratio**, γ_s, as shown below.

$$\mu_s = \gamma_s S$$

or each of the two states

$$\mu_{s,\alpha} = \gamma_s S_\alpha$$

$$\mu_{s,\beta} = \gamma_s S_\beta$$

With the magnetic field direction defined as z, the scalar product in Equation 13.4.16 becomes a product of the z-components of the spin angular momenta, $S_{z,\alpha}$ and $S_{z,\beta}$, with the external magnetic field.

Inserting the values for $S_{z,\alpha} = +\frac{1}{2}\hbar$ and $S_{z,\alpha} = -\frac{1}{2}\hbar$ from Equation 13.4.7 and rearranging Equation 13.4.16 yields

$$\frac{h\nu}{B} = -\gamma_s\hbar$$

Calculating the ratio $\frac{h\nu}{B}$ from our experimental results, $\nu = 28 \times 10^9\ Hz$ when $B = 10^4\ gauss$, gives us a value for

$$-\gamma_s\hbar = 18.5464 \times 10^{-21}\ erg/gauss.$$

This value is about twice the Bohr magneton,$-\gamma_e\hbar$, found in Equation 13.4.4 i.e. $\gamma_s\hbar = 2.0023, \gamma_e\hbar$, or

$$\gamma_s = 2.0023\gamma_e \tag{13.4.17}$$

The factor of 2.0023 is called the **g-factor** and accounts for the deviation of the spin gyromagnetic ratio from the value expected for orbital motion of the electron. In other words, it accounts for the spin transition being observed where it is instead of where it would be if the same ratio between magnetic moment and angular momentum held for both orbital and spin motions. The value 2.0023 applies to a freely spinning electron; the coupling of the spin and orbital motion of electrons can produce other values for g.

? Exercise 8.4.1

Carry out the calculations that show that the g-factor for electron spin is 2.0023.

Interestingly, the concept of electron spin and the value g = 2.0023 follow logically from *Dirac's relativistic quantum theory*, which is beyond the scope of this discussion. Electron spin was introduced here as a postulate to explain experimental observations. Scientists often introduce such postulates parallel to developing the theory from which the property is naturally deduced.

13.4: An Electron Has An Intrinsic Spin Angular Momentum is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **8.4: An Electron has an Intrinsic Spin Angular Momentum** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0. Original source: https://web.archive.org/web/20200619182410/http://www.chemeddl.org.

13.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

Learning Objectives

- Interprete the consequence of exchanging two electrons in a multi-electron atom on the wavelengths
- Connect the Pauli's Exclusion Principle to the permutation symmetry of multi-electron atoms

Quantum mechanics allows us to predict the results of experiments. If we conduct an experiment with indistinguishable particles a correct quantum description cannot allow anything which distinguishes between them. For example, if the wavefunctions of two particles overlap, and we detect a particle, which one is it? The answer to this is not only that we do not know, but that we cannot know. Quantum mechanics can only tell us the probability of finding a particle in a given region. The wavefunction must therefore describe both particles.

The Schrödinger equation for the helium atom is then:

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_1^2)-V(\mathbf{r}_1)-V(\mathbf{r}_2)+V_{12}(\mathbf{r}_1,\mathbf{r}_2)\right]\psi(\mathbf{r}_1,\mathbf{r}_2)=E\psi(\mathbf{r}_1,\mathbf{r}_2)$$

where the subscripts label each particle, and there are six coordinates, three for each particle. While $|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ is a six dimensional wavefunction (three for each electron) and contains all the information we can measure (a Postulate of Quantum Mechanics), it only provide the probability of finding the electron at a specific volume element, and does **not** tell us which particle is which (e.g., is it electon 1 or electron 2?).

What basis states would be appropriate for $|\psi\rangle$? If we consider the orbital approximation that uses a product wavefunction

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle=|\varphi_a(\mathbf{r}_1)\rangle|\varphi_b(\mathbf{r}_2)\rangle$$

where $|\varphi_a(\mathbf{r}_1)\rangle$ and $|\varphi_b(\mathbf{r}_2)\rangle$ are one-particle spin-orbitals (with both spin and spatial components) of atoms 1 and 2. This approximation allows us to separate the two particle equation into two one-electron equations:

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2+V(\mathbf{r}_1)\right]|\varphi_a(\mathbf{r}_1)\rangle=E|\,\varphi_a(\mathbf{r}_1)\rangle$$

$$\left[-\frac{\hbar^2}{2m}\nabla_2^2+V(\mathbf{r}_2)\right]|\varphi_b(\mathbf{r}_2)\rangle=E|\,\varphi_a(\mathbf{r}_2)\rangle$$

provided that the particles do not interact (e.g., ∇_1^2 does not act on $|\varphi_b(\mathbf{r}_2)\rangle$ and $V_{12}=0$).

Unfortunately, by doing this we have introduced unphysical *labels* to the indistinguishable particles. And this is wrong: the effect of it is that the particles do not interfere with each other because they are in different dimensions (six dimensional space - remember?). When we construct a two particle wavefunction out of two one-particle wavefunctions we must be ensure that the probability density (the measurable quantity $|\psi|^2$) is independent of the **artificial** labels.

The Exchange Operator

We can deepen our understanding of the quantum mechanical description of multi-electron atoms by examining the concepts of electron indistinguishability and the Pauli Exclusion Principle in detail. We will use the following statement as a guide to keep our explorations focused on the development of a clear picture of the multi-electron atom: "When a multi-electron wavefunction is built as a product of single-electron wavefunctions, the corresponding concept is that exactly one electron's worth of charge density is described by each atomic spin-orbital."

A subtle, but important part of the conceptual picture, is that the electrons in a multi-electron system are not distinguishable from one another by any experimental means. Since the electrons are indistinguishable, the probability density we calculate by squaring the modulus of our multi-electron wavefunction also cannot change when the electrons are interchanged (permuted) between different orbitals. In general, if we interchange two identical particles, the world does not change. As we will see below, this requirement leads to the idea that the world can be divided into two types of particles based on their behavior with respect to permutation or interchange.

In order for the probability density to remain unchanged when two particles are permuted, the wavefunction itself can change only by a factor of $e^{i\varphi}$, which represents a complex number, when the particles described by that wavefunction are permuted. As we will show below, the $e^{i\varphi}$ factor is possible because the probability density depends on the absolute square of the function and all expectation values involve $\psi\psi^*$. Consequently $e^{i\varphi}$ disappears in any calculation that relates to the real world because $e^{i\varphi}e^{-i\varphi} = 1$.

We could symbolically write an approximate two-particle wavefunction as $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 ($\mathbf{r}_1$) for the coordinates of particle 2 ($\mathbf{r}_2$) and vice versa, to get the new wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This new wavefunction must have the property that

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = \psi(\mathbf{r}_2, \mathbf{r}_1)^*\psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{13.5.1}$$

since the probability density of the electrons in the atom does **not** change upon permutation of the electrons.

Exercise 8.5.1

Permute the electrons the product function for He wavefunction:

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = |\varphi_{1s}(\mathbf{r}_1)\rangle|\,\varphi_{1s}(\mathbf{r}_2)\rangle$$

Equation 13.5.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{13.5.2}$$

so that

$$\left(e^{-i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right)\left(e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2)^*\right) = \psi(\mathbf{r}_1, \mathbf{r}_2)^*\psi(\mathbf{r}_1, \mathbf{r}_2) \tag{13.5.3}$$

If we exchange or permute two identical particles twice, we are (by definition) back to the original situation. If each permutation changes the wavefunction by $e^{i\varphi}$, the double permutation must change the wavefunction by $e^{i\varphi}e^{i\varphi}$. Since we then are back to the original state, the effect of the double permutation must equal 1; i.e.,

$$e^{i\varphi}e^{i\varphi} = e^{i2\varphi} = 1 \tag{13.5.4}$$

which is true only if $\varphi = 0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature.

Exercise 8.5.2

Use Euler's Equality

$$e^{i\pi} + 1 = 0$$

to show that $e^{i2\varphi} = 1$ when $\varphi = 0$ or $n\pi$ and consequently $e^{i\varphi} = \pm 1$.

We can introduce the *exchange operator* $\hat{P}_{12}$: an operator which permutes the labels of the particles in a multi-particle wavefucntion. This is a rather strange operator, because it only changes the *unphysical* labels which we have attached to the one-particle wavefunctions in order to make the maths more easy. For a meaningful solution we must have a wavefunction which has a probability amplitude unchanged by $\hat{P}_{12}$: it must be either symmetric or antisymmetric with respect to exchange:

$$\hat{P}_{12}\,|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \pm|\,\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle \tag{13.5.5}$$

Bosons and femions

Physical solutions must be eigenfunctions of $\hat{P}_{12}$ (i.e., $\hat{H}$ and $\hat{P}_{12}$ commute). Moveover, Equation 13.5.5 argues that the eigenvalues of the Exchange Operator are either +1 (bosons) or −1 (fermions).

Bosons

https://chem.libretexts.org/@go/page/287059

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

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \cdots r_i)\rangle \approx \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\cdots\varphi_i(r_i) \tag{13.5.6}$$

? Exercise 8.5.4

What is meant by the term permutation symmetry?

? Exercise 8.5.5

Explain why the product function $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ could describe two bosons (deuterium nuclei), but can not describe two fermions (e.g. electrons).

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 13.5.6 does **not** satisfy this (unless $\varphi_a = \varphi_b$). A **linear combination of all permutations** is required to satisfy indistinguishability constraints.

For a two particle system (e.g., Helium) there is the asymmetric combination

$$|\psi^-\rangle = \frac{1}{\sqrt{2}}\Big|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{13.5.7}$$

and symmetric combination

$$|\psi^+\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle + C_{aa}\,|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle + C_{bb}|\,\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{13.5.8}$$

where the C_{ab} terms are expansion and normalization parameters.

> *Note that the antisymmetric combination (Equation 13.5.7) **cannot** include terms where both particles are in the same state (spin-orbital), but there are three possibilities for the symmetric state (Equation 13.5.8).*

Although any linear combinations of C_{ab}, C_{bb}, and C_{aa} in Equation 13.5.8 is possible, there are three limiting expressions for possible symmetric combinations:

$$|\psi_1^{+i}\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{13.5.9}$$

$$|\psi_2^{+i}\rangle = C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle \tag{13.5.10}$$

$$|\psi_3^{+i}\rangle = C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{13.5.11}$$

If $\varphi_a(\mathbf{r}_1) = \varphi_a(\mathbf{r}_2)$, then $|\varphi^{-i}\rangle = 0$. Thus there is no possible antisymmetric combination involving electrons in the same state (spin-orbit). This is the **Pauli exclusion principle**.

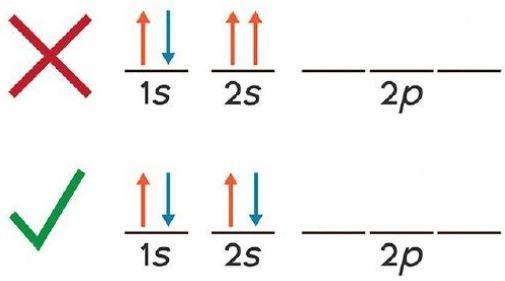


Figure 8.5.1 : The 1s and 2s subshells for beryllium atoms can hold only two electrons and when filled, since each electrons is described by a specific spin-orbital and each orbital (spatial) can hold either an α or a β electron (i.e., they must have opposite spins). Otherwise they will have the same four quantum numbers, in violation of the Pauli Exclusion Principle.

The Pauli Exclusion Principle argues that two electrons **could not** be described by the same spin-orbital. To see the relationship between this statement and the requirement that the wavefunction be antisymmetric for electrons, try to construct an anti-symmetric wavefunction for two electrons that are described by the same spin-orbital

$$|\varphi_b(\mathbf{r}_1)\rangle = \varphi_a(\mathbf{r}_2)\rangle$$

For example, if this were the case for the anti-symmetric combination for helium (Equation 13.5.7), then the wavefunction collapses to zero. We can only constructs wavefunctions that are antisymmetric with respect to permutation symmetry only if each electron is described by a different function.

> *The Pauli Exclusion Principle is simply the requirement that the wavefunction be antisymmetric for electrons, since they are fermions.*

13.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

13.6: Antisymmetric Wave Functions 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).

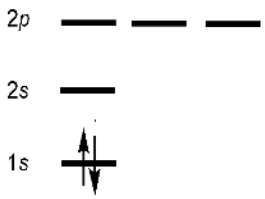


Figure 8.6.1 : Electron configuration for ground state of the helium atom.

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, $1s^2$.

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \varphi_{1s}\alpha(\mathbf{r}_1)\varphi_{1s}\beta(\mathbf{r}_2) \tag{13.6.1}$$

After permutation of the electrons, this becomes

$$|\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle = \varphi_{1s}\alpha(\mathbf{r}_2)\varphi_{1s}\beta(\mathbf{r}_1) \tag{13.6.2}$$

which is different from the starting function since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are different spin-orbital functions. Hence, the simple product wavefunction in Equation 13.6.1 does not satisfy the indistinguishability requirement since an antisymmetric function must produce the same function multiplied by (–1) after permutation of two electrons, and that is not the case here. We must try something else.

To avoid getting a totally different function when we permute the electrons, we can make **a linear combination of functions**. A very simple way of taking a linear combination involves making a new function by simply adding or subtracting functions. The function that is created by subtracting the right-hand side of Equation 13.6.2 from the right-hand side of Equation 13.6.1 has the desired antisymmetric behavior. The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s}\alpha(\mathbf{r}_1)\varphi_{1s}\beta(\mathbf{r}_2) - \varphi_{1s}\alpha(\mathbf{r}_2)\varphi_{1s}\beta(\mathbf{r}_1)] \tag{13.6.3}$$

In this orbital approximation, a single electron is held in a single s*pin-orbital* with an orbital component (e.g., the $1s$ orbital) determined by the n, l, m_l quantum numbers and a spin component determined by the m_s quantum number.

The wavefunction in Equation 13.6.3 can be decomposed into spatial and spin components:

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{1s}(2)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}_{\text{spin component}} \tag{13.6.4}$$

Example 8.6.1 : Symmetry to Electron Permutation

Show that the linear combination of spin-orbitals in Equation 13.6.3 is antisymmetric with respect to permutation of the two electrons.

Hint

Replace the minus sign with a plus sign (i.e. take the positive linear combination of the same two functions) and show that the resultant linear combination is symmetric.

Solution

First a reminder of permutation symmetries:

- If the wavefunction is symmetric with respect to permutation of the two electrons then

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = |\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$

- If the wavefunction is antisymmetric with respect to permutation of the two electrons then

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = -|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle$$

We start with the original wavefunction

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

and flip the position of electron 1 with electron 2 and vice versa

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1) - \varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)] \tag{13.6.5}$$

We then we ask if we can rearrange the left side of Equation 13.6.5 to either become $+|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ (symmetric to permutation) or $-|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ (antisymmetric to permutation).

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = \frac{1}{\sqrt{2}}[-\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) + \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

or

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = -\frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

This is just the negative of the original wavefunction, therefore

$$|\psi(\mathbf{r}_2,\mathbf{r}_1)\rangle = -|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$$

The wavefunction is antisymemtric.

Exercise 8.6.1 : Symmetry

Is this linear combination of spin-orbitals

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) + \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)]$$

symmetric or antisymmetric with respect to permutation of the two electrons?

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.

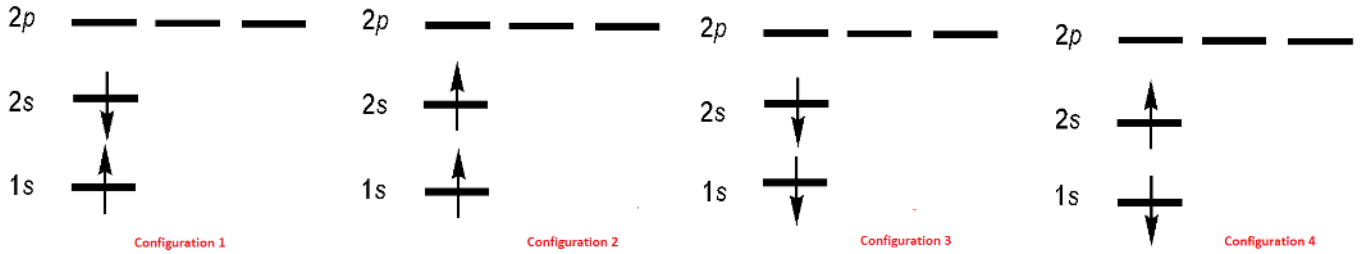


Figure 8.6.2 : Electron configurations for first-excited state of the helium atom.

These electron configurations are used to construct four possible excited-state two-electron wavefunctions (but not necessarily in a one-to-one correspondence):

$$|\psi_1(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)+\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)-\alpha(2)\beta(1)]}_{\text{spin component}} \tag{13.6.6}$$

$$|\psi_2(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\alpha(2)]}_{\text{spin component}} \tag{13.6.7}$$

$$|\psi_3(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)+\alpha(2)\beta(1)]}_{\text{spin component}} \tag{13.6.8}$$

$$|\psi_4(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\beta(1)\beta(2)]}_{\text{spin component}} \tag{13.6.9}$$

All four wavefunctions are antisymmetric as required for fermionic wavefunctions (which is left to an exercise). Wavefunctions $|\psi_2\rangle$ and $|\psi_4\rangle$ correspond to the two electrons both having spin up or both having spin down (Configurations 2 and 3 in Figure 8.6.2 , respectively). Wavefunctions $|\psi_1\rangle$ and $|\psi_3\rangle$ are more complicated and are antisymmetric (Configuration 1 - Configuration 4) and symmetric combinations (Configuration 1 + 4). That is, a single electron configuration does not describe the wavefunction. For many electrons, this ad hoc construction procedure would obviously become unwieldy. However, there is an elegant way to construct an antisymmetric wavefunction for a system of N identical particles.

Determinantal Wavefunctions

A linear combination that describes an appropriately antisymmetrized multi-electron wavefunction for any desired orbital configuration is easy to construct for a two-electron system. However, interesting chemical systems usually contain more than two electrons. For these multi-electron systems a relatively simple scheme for constructing an antisymmetric wavefunction from a product of one-electron functions is to write the wavefunction in the form of a determinant. John Slater introduced this idea so the determinant is called a **Slater determinant**.

> John C. Slater introduced the determinants in 1929 as a means of ensuring the antisymmetry of a wavefunction, however the determinantal wavefunction first appeared three years earlier independently in Heisenberg's and Dirac's papers.

The Slater determinant for the two-electron ground-state wavefunction of helium is

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2)\end{vmatrix} \tag{13.6.10}$$

A shorthand notation for the determinant in Equation 13.6.10 is then

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = 2^{-\frac{1}{2}}Det\left|\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)\right| \tag{13.6.11}$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is $(N!)^{-\frac{1}{2}}$ for N electrons.

The generalized Slater determinant for a multi-electrom atom with N electrons is then

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \varphi_2(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_1) \\ \varphi_1(\mathbf{r}_2) & \varphi_2(\mathbf{r}_2) & \cdots & \varphi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(\mathbf{r}_N) & \varphi_2(\mathbf{r}_N) & \cdots & \varphi_N(\mathbf{r}_N) \end{vmatrix} \tag{13.6.12}$$

Example 8.6.2 : Helium Atom

Expand the Slater determinant in Equation 13.6.10 for the **He** atom.

Solution

To expand the Slater determinant of the Helium atom, the wavefunction in the form of a two-electron system:

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) \end{vmatrix}$$

This is a simple expansion exercise of a $\mathbf{2 \times 2}$ determinant

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} [\varphi_{1s}(1)\alpha(1)\varphi_{1s}(2)\beta(2) - \varphi_{1s}(2)\alpha(2)\varphi_{1s}(1)\beta(1)]$$

It is not unexpected that the determinant wavefunction in Equation 13.6.10 is the same as the form for the helium wavefunction that is given in Equation 13.6.3.

Exercise 8.6.2 : Lithium Atom

Write and expand the Slater determinant for the ground-state **Li** 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 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

$$|\phi_a(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} \tag{13.6.13}$$

$$|\phi_b(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \tag{13.6.14}$$

$$|\phi_c(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \tag{13.6.15}$$

$$|\phi_d(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} \tag{13.6.16}$$

Slater determinants are constructed by arranging spinorbitals in columns and electron labels in rows and are normalized by dividing by $\sqrt{N!}$, where N is the number of occupied spinorbitals. As you can imagine, the algebra required to compute integrals involving Slater determinants is extremely difficult. It is therefore most important that you realize several things about these states so that you can avoid unnecessary algebra:

- A Slater determinant corresponds to a single electron configuration diagram (Figure 8.6.2). Furthermore, recall that for the excited states of helium we had a problem writing certain stick diagrams as a (space)x(spin) product and had to make linear combinations of certain states to force things to separate (Equation 13.6.7 and 13.6.9). Because of the direct correspondence of configuration diagrams and Slater determinants, the same pitfall arises here: Slater determinants sometimes may not be representable as a (space)x(spin) product, in which case a linear combination of Slater determinants must be used instead. This generally only happens for systems with unpaired electrons (like several of the Helium excited-states).
- A Slater determinant is anti-symmetric upon exchange of any two electrons. We recall that if we take a matrix and interchange two its rows, the determinant changes sign.

The wavefunctions in 13.6.6-13.6.9 can be expressed in term of the four determinants in Equations 13.6.13-13.6.16.

$$\begin{aligned}|\psi_2\rangle &= |\phi_b\rangle \\ &= \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix}\end{aligned}$$

$$\begin{aligned}|\psi_4\rangle &= |\phi_d\rangle \\ &= \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix}\end{aligned}$$

but the wavefunctions that represent combinations of spinorbitals and hence combinations of electron configurations (e.g., igure 8.6.2) are combinations of Slater determinants (Equation 13.6.13-13.6.15)

$$\begin{aligned}|\psi_1\rangle &= |\phi_a\rangle - |\phi_c\rangle \\ &= \frac{1}{2}\left(\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix} - \begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix}\right)\end{aligned}$$

$$\begin{aligned}|\psi_3\rangle &= |\phi_a\rangle + |\phi_c\rangle \\ &= \frac{1}{2}\left(\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2)\end{vmatrix} + \begin{vmatrix}\varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2)\end{vmatrix}\right)\end{aligned}$$

Note the expected change in the normalization constants.

✓ Example 8.6.3 : Carbon Atom

Write the Slater determinant for the ground-state carbon atom. If you expanded this determinant, how many terms would be in the linear combination of functions?

Solution

Carbon has 6 electrons which occupy the 1s 2s and 2p orbitals. Each row in the determinant represents a different electron and each column a unique spin-obital where the electron could be found. There are 6 rows, 1 for each electron, and 6 columns, with the two possible p orbitals both alpha (spin up), in the determinate. There are two columns for each s orbital to account for the alpha and beta spin possibilities. There are two different p orbitals because the electrons in their ground state will be in the different p orbitals and both spin up. N=6 so the normalization constant out front is 1 divided by the square-root of 6!

$$\psi(1,2,3,4,5,6) = \frac{1}{6!^{1/2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) & \varphi_{2px}(1)\alpha(1) & \varphi_{2py}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) & \varphi_{2px}(2)\alpha(2) & \varphi_{2py}(2)\alpha(2) \\ \varphi_{1s}(3)\alpha(3) & \varphi_{1s}(3)\beta(3) & \varphi_{2s}(3)\alpha(3) & \varphi_{2s}(3)\beta(3) & \varphi_{2px}(3)\alpha(3) & \varphi_{2py}(3)\alpha(3) \\ \varphi_{1s}(4)\alpha(4) & \varphi_{1s}(4)\beta(4) & \varphi_{2s}(4)\alpha(4) & \varphi_{2s}(4)\beta(4) & \varphi_{2px}(4)\alpha(4) & \varphi_{2py}(4)\alpha(4) \\ \varphi_{1s}(5)\alpha(5) & \varphi_{1s}(5)\beta(5) & \varphi_{2s}(5)\alpha(5) & \varphi_{2s}(5)\beta(5) & \varphi_{2px}(5)\alpha(5) & \varphi_{2py}(5)\alpha(5) \\ \varphi_{1s}(6)\alpha(6) & \varphi_{1s}(6)\beta(6) & \varphi_{2s}(6)\alpha(6) & \varphi_{2s}(6)\beta(6) & \varphi_{2px}(6)\alpha(6) & \varphi_{2py}(6)\alpha(6)\end{vmatrix}$$

Expanding this determinant would result in a linear combination of functions containing 720 terms. An expanded determinant will contain N! factorial terms, where N is the dimension of the matrix.

13.6.3A Exercise : Excited-State of Helium Atom

Write the Slater determinant for the $1s^1 2s^1$ excited state orbital configuration of the helium atom.

13.6.3B 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!)

13.6: Antisymmetric Wave Functions can be Represented by Slater Determinants is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

13.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

Learning Objectives

- Understand how the Hartree method is expanded to include symmetrized mulit-electron determential wavefunctions via the Hartree-Fock equations.
- Understand how to calculate the orbital energies from HF theory.
- Apply HF theory with Koopman's theory to estimate ionization energies and electron affinities.

The Hartree method discussed previously is useful as an introduction to the solution of many-particle system and to the concepts of self-consistency and of the self-consistent-field calculations, but its importance is confined to the history of physics. In fact the Hartree method is not just approximate, it is fundamentally wrong since its wavefunction is not antisymmetric to electron permutation! The Hartree-Fock approach discussed below is a better approach, which correctly takes into account the antisymmetric character of the trial wavefunctions.

Although the *Hartree equations* are numerically tractable via the self-consistent field method, it is not surprising that such a crude approximation fails to capture elements of the essential physics. The Pauli exclusion principle demands that the many-body wavefunction be antisymmetric with respect to interchange of any two electron coordinates, e.g.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) \tag{13.7.1}$$

which clearly cannot be satisfied by the multi-electron wavefunctions of the form used in the Hartree Approximation, i.e., the orbital approximation (Equation 13.7.2).

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_N(\mathbf{r}_N) \tag{13.7.2}$$

This indistinguishability condition can be satisfied by forming a Slater determinant of single-particle orbitals

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N}} |\psi(\mathbf{r}_1)\psi(\mathbf{r}_2)\dots\psi(\mathbf{r}_N)| \tag{13.7.3}$$

This decouples the electrons resulting in N single-particle **Hartree-Fock** equations:

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r})}_{\text{kinetic energy}} + \underbrace{V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{electron-nucleus potential}} + \underbrace{V_{electron}(\mathbf{r})\psi_i(\mathbf{r})}_{\text{Hartree Term}} - \sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = \epsilon_i\psi_i(\mathbf{r}). \tag{13.7.4}$$

As with the *Hartree equations*, the first term is the kinetic energy of the ith electron

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r})$$

and the second term is the electron-nucleus potential between the ith electron and nucleus

$$V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r})$$

The third term (sometimes called the “Hartree” term) is the electrostatic potential between the ith electron and the **average** charge distribution of the other $N-1$ electrons.

$$V_{electron}(\mathbf{r})\psi_i(\mathbf{r}) = J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr' \tag{13.7.5}$$

These three terms are identical to Hartree Equations with the product wavefunction ansatz (i.e., orbital approximation). The fourth term of Equation 13.7.4 is not in the Hartree Equations:

$$\sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

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 13.7.3). Physically, the effect of exchange is for like-spin electrons to avoid each other. The exchange term adds considerably to the complexity of these equations.

The Hartree-Fock Equations in Equation 13.7.4 can be recast as series of Schrödinger-like equations:

$$\hat{F}\left|\varphi_i\right\rangle = \epsilon_i\left|\varphi_i\right\rangle \tag{13.7.6}$$

where $\hat{F}$ is called the **Fock operator** and $\{|\varphi_i\rangle\}$ are the Hatree-Fock orbitals with corresponding energies ϵ_i.

The Fock operator is a one-electron operator and solving a Hartree-Fock equation gives the energy and Hartree-Fock orbital for one electron. For a system with 2N electrons, the variable i will range from 1 to N; i.e there will be one equation for each orbital. The reason for this is that only the spatial wavefunctions are used in Equation 13.7.6. Since the spatial portion of an orbital can be used to describe two electrons, each of the energies and wavefunctions found by solving Equation 13.7.6 will be used to describe two electrons.

The nature of the Fock operator reveals how the Hartree-Fock (HF) or Self-Consistent Field (SCF) Method accounts for the electron-electron interaction in atoms and molecules while preserving the idea of **independent atomic orbitals**. The wavefunction written as a Slater determinant of spin-orbitals is necessary to derive the form of the Fock operator, which is

$$\begin{aligned}\hat{F} &= \hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) \\ &= -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j)\end{aligned} \tag{13.7.7}$$

As shown by the expanded version on the far right, the first term in this equation, $\hat{H}^0$, is the familiar hydrogen-like operator that accounts for the kinetic energy of an electron and the potential energy of this electron interacting with the nucleus. The next term accounts for the potential energy of one electron in an average field created by all the other electrons in the system. The $\hat{J}$ and $\hat{K}$ operators result from the electron-electron repulsion terms in the full Hamiltonian for a multi-electron system. These operators involve the one-electron orbitals as well as the electron-electron interaction energy.

The Fock operator (Equation 13.7.7) depends on **all occupied** orbitals (because of the exchange and Coulomb operators). Therefore, a specific orbital can only be determined if all the others are known. One must use iterative methods to solve the HF equations like the Self-consistent field method discussed previously for the Hartree Approximation.

Exchange Energy

The exchange interaction is a quantum mechanical effect that only occurs between identical particles. Despite sometimes being called an exchange force in analogy to classical force, **it is not a true force**, as it lacks a force carrier. The effect is due to the wavefunction of indistinguishable particles being subject to exchange symmetry, that is, either remaining unchanged (symmetric) or changing its sign (antisymmetric) when two particles are exchanged. Both bosons and fermions can experience the exchange interaction. For fermions, it is sometimes called Pauli repulsion and related to the Pauli exclusion principle. For bosons, the exchange interaction takes the form of an effective attraction that causes identical particles to be found closer together, as in Bose–Einstein condensation.

Example 8.7.1 : Hartree-Fock Energy of Helium

For example, the electron 1 in helium (with $Z = 2$), then

$$\hat{H}^0(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}$$

The Fock operator is couched in terms of the coordinates of the one electron whose perspective we are taking (which we will call electron 1 throughout the following discussion), and the **average field created by all the other electrons** in the system is built in

terms of the coordinates of a generic “other electron” (which we’ll call electron 2) that is considered to occupy each orbital in turn during the summation over the N spatial orbitals. The best possible one-electron wavefunctions, by definition, will give the **lowest possible total energy** for a multi-electron system used with the complete multielectron Hamiltonian to calculate the expectation value for the total energy of the system. These wavefunctions are called the **Hartree-Fock wavefunctions** and the calculated total energy is the Hartree-Fock energy of the system.

As with the Hartree Equations, solving the Hartree-Fock Equations is mathematically equivalent to assuming each electron interacts only with the average charge cloud of the other electrons. This is how the electron-electron repulsion is handled. This also why this approach is also called the **Self-Consistant Field (SCF)** approach.

Hartree-Fock Energy

The Hartree-Fock equations $h_e\phi_i = \epsilon_i\phi_i$ imply that the orbital energies ϵ_i can be written as:

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

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)

$$E_{N-1} - E_N = -\epsilon_k \tag{13.7.8}$$

- and for electron attachment (electron affinities)

$$E_N - E_{N+1} = -\epsilon_k. \tag{13.7.9}$$

The Hartree-Fock equations deal with exchange exactly; however, the equations neglect more detailed correlations due to many-body interactions. The effects of electronic correlations are not negligible; indeed the failure of Hartree-Fock theory to successfully incorporate correlation leads to one of its most celebrated failures.

Example 8.7.2 : Electron Affinity

Let's derive this result for the case in which an electron is added to the $N+1^{st}$ spin-orbital. The energy of the N-electron determinant with spin-orbitals ϕ_1 through f_N occupied is

$$E_N = \sum_{i=1}^{N} \langle \phi_i | T + V | \phi_i \rangle + \sum_{i=1}^{N} [J_{i,j} - K_{i,j}]$$

which can also be written as

$$E_N = \sum_{i=1}^{N} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N} [J_{i,j} - K_{i,j}].$$

Likewise, the energy of the $N+1$-electron determinant wavefunction is

$$E_{N+1} = \sum_{i=1}^{N+1} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N+1} [J_{i,j} - K_{i,j}].$$

The difference between these two energies is given by

$$\begin{aligned} E_N - E_{N+1} = & - \langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \frac{1}{2} \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ & - \frac{1}{2} \sum_{j=1}^{N+1} [J_{N+1,j} - K_{N+1,j}] \\ & = - \langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ & = -\epsilon_{N+1}. \end{aligned}$$

That is, the energy difference is equal to minus the expression for the energy of the $N+1^{st}$ spin-orbital, which was given earlier.

Advanced: Electron Correlation and the "Exchange Hole"

In the Copenhagen Interpretation, the squared modulus of the wavefunction gives the probability of finding a particle in a given place. The many-body wavefunction gives the N-particle distribution function, i.e. $|\Phi(r_1, ..., r_N)|^2$ is the probability density that particle 1 is at r_1, ..., and particle N is at r_N. However, when trying to work out the interaction between electrons, what we want to know is the probability of finding an electron at r, given the positions of all the other electrons $\{r_i\}$. This implies that the electron behaves quantum mechanically when we evaluate its wavefunction, but as a classical point particle when it contributes to the potential seen by the other electrons.

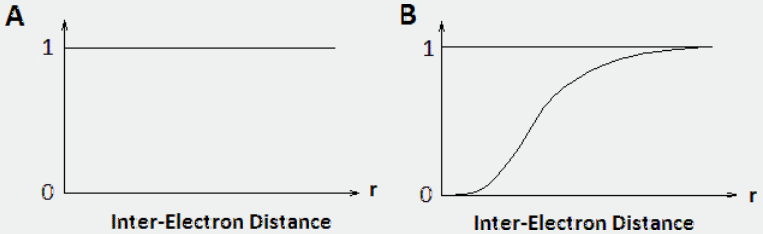


Figure 8.7.2 : Normalized Conditional Probability for from electron-electron interactions (excluding coulomb effects) in (A) the Hartree approximation and (B) the Hartree-Fock approximation.

The contributions of electron-electron interactions in N-electron systems within the Hartree and Hartree-Fock methods are shown in Figure 8.7.2 . The conditional electron probability distributions $n(r)$ of $N-1$ electrons around an electron with given spin situated at $r=0$. Within the Hartree approximation, all electrons are treated as independent, therefore $n(r)$ is structureless. However, within the Hartree-Fock approximation, the N-electron wavefunction reflects the Pauli exclusion principle and near the electron at $r=0$ the exchange hole can be seen where the the density of spins equal to that of the central electron is reduced. Electrons with opposite spins are **unaffected** (not shown).

Summary

So, within the limitations of the HF, frozen-orbital model, the ionization potentials (IPs) and electron affinities (EAs) are given as the negative of the occupied and virtual spin-orbital energies, respectively. This statement is referred to as Koopmans' theorem; it is used extensively in quantum chemical calculations as a means of estimating ionization potentials (Equation 13.7.8) and Electron Affinities (Equation 13.7.9) and often yields results that are qualitatively correct (i.e., ± 0.5 eV). In general Hartree-Fock theory gives a great first order solution (99%) to describing multi-electron systems, but that last 1% is still too great for quantitatively describing many aspects of chemistry and more sophisticated approaches are necessary. These are discussed elsewhere.

13.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

13.8: Term Symbols Gives Detailed Descriptions of an Electron Configuration

Learning Objectives

- Understand how electron configurations results in different manifestations of angular momenta (both oribital and spin)
- Describe the manifestations in atoms via atomic term symbols

Atoms have quantum numbers that are directly analogous to the electronic quantum numbers.

The Total Orbital Angular Momentum Quantum Number: L

One might naively think that you could get the total angular momentum of an atom (L) by simply adding up the l values of the individual electrons. The problem with this idea is that the angular momenta of the various electrons are not necessarily pointing in the same direction. Let's consider the case of adding two 2p-orbitals together (i.e., with $l = 1$ quantum numbers).

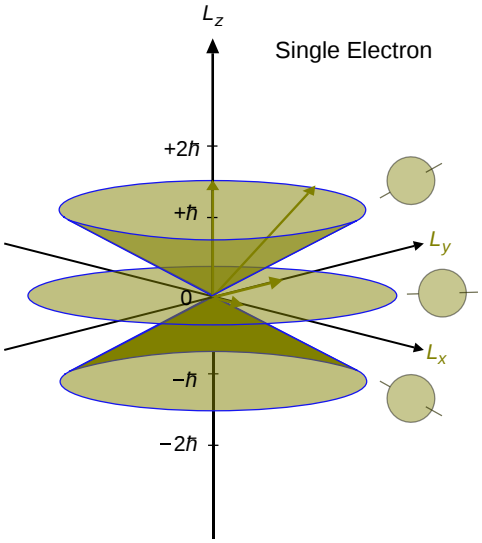


Figure 8.8.1 : The three possible angular momenta vectors for a p-orbital.

As discussed in Section 6.3, each of these electrons has $\sqrt{2}\hbar$ of angular momentum, but oriented in three different directions given by three different m_l values of 1, 0, and -1 (Figure 8.8.1).

$$L = \sum_{i}^{n} l_i \tag{13.8.1}$$

However, we must recognize that while the magnitude of angular momentum is a scalar (represented by l), angular momenta are really vector quantities and to add them together will require vector addition (vs. scalar addition) to do properly and must address all possible orientations of l for each electron.

For example, if two electrons are revolving in the same direction as each other (i.e., same m_l values), one would add just their l values together

$$L(\text{same direction}) = \sqrt{2}\hbar + \sqrt{2}\hbar = 2\hbar$$

If the two elections were revolving in opposites direction (e.., opposite m_l values, you subtract their values.

$$L(\text{same direction}) = \sqrt{2}\hbar - \sqrt{2}\hbar = 0$$

If they are revolving at some off-angle relative to each other (one revolving in a plane and one off plane), you would partially subtract them.

$$L(\text{same direction}) = \sqrt{2}\hbar + 0 = \sqrt{2}\hbar$$

To figure out all of the possible combinations of l for a pair of electrons, simply add them together to get the co-aligned case, subtract them to get the opposing case, and then fill in all the numbers in between to get the off-angle cases. For the two p-orbital case, there are no other possibilities (remember that l and hence L must be non-negative since they represent the magnitude of angular momenta (addressing the m_l values is a different story as we discuss below).

If you prefer to have a formula for the possibilities of L, you can use this:

$$L = |l_1 + l_2|, |l_1 + l_2\text{-}1|, \ldots, |l_1\text{-}l_2| \tag{13.8.2}$$

Technically, Equation 13.8.2 should include all electrons in a system, not just two, to account for all possible combinations of orbital angular momenta, however, there are some tricks that aid in applying this equations to address larger multi-electron atoms. First, electrons in s-orbitals have no orbital angular momentum, so they can be ignored. Second, if block of orbitals are completely filled (e.g., all six p-block spin-orbitals or all 10 d-block spin-orbitals), then the orbital angular momentum vector of each electron will be countered by another electron in the system; these are called **closed-shell** systems. Systems with partially unfilled blocks are called **open-shell** systems.

Hence, conveniently for chemists, an atom's electronic state depends entirely on its unfilled sub shells. Because electrons distribute themselves in a symmetric manner, the inner shell electrons end up canceling out each other's momenta. For an atom in the configuration $1s^2 2s^2 p^2$, only the two p-electrons matter. For an atom in the configuration $1s^2 2s^1 2p^1$, we have to examine only the 2s and 2p electrons (and can ignore the s electrons too).

Example 8.8.1 : Total Orbital Angular Momentum of Carbon

What are the possible L values for the electrons in the $1s^2 2s^2 2p^2$ configuration of carbon?

Solution

Both open-shell electrons (i.e., the 2p electrons) are $l = 1$. The possible combinations are 2, 1, 0.

Example 8.8.2 : Total Orbital Angular Momentum of Unknown Species

What are the possible L values for the electrons in the $[Xe]6s^2 4f^1 5d^1$?

Solution

We can ignore the electrons in the $[Xe]$ core and the electrons in the $6s$ block. So all we have to consider is the f electron $l = 3$ and d electron $l = 2$.

The two extremes possible (Equation 13.8.2) are

$$3 + 2 = 5$$

and

$$3\text{-}2 = 1$$

The possible combinations are thus 5, 4, 3, 2, and 1.

The Total Magnetic Quantum Number: M_l

The Total Magnetic Quantum Number M_l is the total z-component of all of the relevant electrons' orbital momentum. Where L told you how much total angular momentum there is in the system, M_l tells you which direction it is pointing. Like L, a given configuration can have several possible values of M_l, depending on the electrons' relative orientation. Unlike L, M_l is allowed to have negative values. To list the possible M_l values for a two electron system, take the case where both m_l are positive, then take the case where they are both negative, and then fill in the numbers in between (Figure 8.8.1).

$$M_l = m_{l1} + m_{l2}, m_{l1} + m_{l2}\text{-}1, \ldots, \text{-}m_{l1}\text{-}m_{l2} \tag{13.8.3}$$

Note that there is no absolute value function in Equation 13.8.3 like in Equation 13.8.2.

Example 8.8.3 : Total Magnetic Quantum Number of the Zirconium Ground State

What are the possible values M_l of a zirconium atom with the $[Kr]5s^24d^2$ electron configuration?

Solution

Both open-shell electrons (i.e., the 4d electrons) are $l = 2$, so the values are 4, 3, 2, 1, 0, -1, -2, -3, -4.

The Total Spin Magnetic Quantum Number: M_s

M_s is the sum total of the z-components of the electrons' inherent spin. Do not confuse it with M_l, which is the sum total of the z-component of the **orbital angular momentum**. It is easily computed by finding all of the possible combinations of m_s. Since m_s for each individual electron can only be +1/2 or - 1/2, this isn't too complicated.

$$M_s = m_{s1} + m_{s2}, m_{s1} + m_{s2}\text{-}1, ..., m_{s1}\text{-}m_{s2} \tag{13.8.4}$$

Example 8.8.4 : Total Spin Magnetic Quantum Number of the Carbon Ground State

What are the M s values for $1s^22s^22p^2$?

Solution

$M_s = 1, 0, \text{-}1$

The Total Intrinsic Spin Quantum Number: S

The sum total of the spin vectors of all of the electrons is called S. The difference between S and M_s is subtle, but vital for understanding multiplicity. M_s measures the total z-component of the electrons' spins, while S measures the entire resultant vector. The values of S are computing in a manner very similar to M_s. Because S measures the magnitude of a vector, it cannot ever be negative.

$$S = |s_1 + s_2|, |s_1 + s_2\text{-}1|, ..., |s_1\text{-}s_2| \tag{13.8.5}$$

Example 8.8.5 : The Hydrogen Ground State

Find S for $1s^1$.

Solution

S clearly has to be ½ since that's the spin of a single electron and there's only one electron to worry about.

Example 8.8.6 : The Beryllium Excited State

Find S for $1s^22s^12p^1$.

Solution

$S = 1, 0$

Example 8.8.7 : The Carbon Ground State

Find S for carbon atoms with the $1s^22s^22p^2$ electron configuration.

Solution

$S = 1, 0$ This is the same as the previous problem. Notice that S is not affected by which orbitals the electrons are in. S only cares about how many **open-shell electrons** (i.e., unpaired electrons) there are, not about where they are. This is because S measures an inherent property of the electrons themselves

Example 8.8.8

Find S for nitrogen atoms with the $1s^2 2s^2 2p^3$ electron configuration.

Solution

We have not done a three electron case yet, but they are not hard. Find all the combinations for a single pair first, and then factor in the third electron. For two electrons, we already know that the two possible S values are S=1,0. A third electron can either add or subtract ½ from these values, so the final S can be $S = 3/2, 1, 1/2$.

The Total Angular Momentum Quantum Number J

The total orbital angular momentum of an atom (measured in terms of l), and the total spin angular momentum of an atom (measure in S) combine to form total angular momentum, a number that is quantized by the number J. L and S do not necessarily have to be pointing in the same direction (Figure 8.8.1), so J can range from $L + S$ to $|L–S|$.

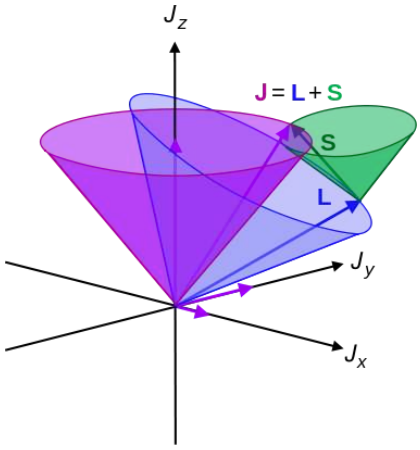


Figure 8.8.1 : Illustration of L-S coupling. Total angular momentum J is purple, orbital L is blue, and spin S is green.

Table 8.8.1 : Quantum Numbers and associated ranges

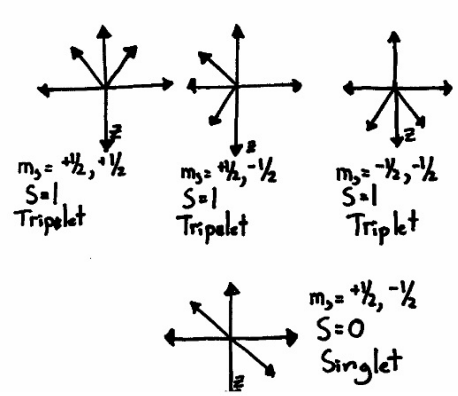
Symbol	Name	Allowed Range
l	Total orbital angular momentum	$\|l_1 + l_2\|, ..., \|l_1 - l_2\|$
M_l	Magnet Quantum number	$[m_{l1} + m_{l2}, ..., -m_{l1} - m_{l2}]$
M_s	Spin Magnetic Quantum Number	$\|m_{s1} + m_{s2}\|, ..., \|m_{s1} - m_{s2}\|$
S	Inherent Spin Number	$\|s_1 + s_2\|, ..., \|s_1 - s_2\|$
M	Multiplicity	2S+1
J	Total Angular Momentum	$L + S, ..., \|L - S\|$

Multiplicity

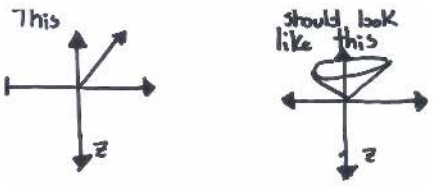
Multiplicity is a simple - sounding concept that defies simple explanations. You know from your first - year education that a singlet is when the net spin (S) is equal to zero (e.g. all the electrons are spin paired), and a triplet happens when the net spin is equal to 1 (e.g. two electrons are pointing in the same direction). They are called “singlet” and “triplet” because there are 3 ways to combine a pair of electron spins to get S=1, but only one way to get $S = 0$. If you draw a picture of the possible ways that two electrons can arrange their spins, you get something like this:



Figure 8.8.1 : When we call an electron spin “up,” what we really mean is that it has a positive z-component (e.g. $m_s = +½$).



While this picture is an improvement over the simple up-down model, it is still misleading. The three spin axes of an electron share a Heisenberg Uncertainty Principle. The more you know about S_x, the less you can know about either S_y or S_z. The same is true for all other combinations of x, y and z. Since we have defined S_z as a known and fixed value, the values of S_x and S_y must be **completely unknown**. This causes the x and y orientations of the electrons to become smeared out across all possible values:



Constructing Term Symbols

Atomic term symbols contain two pieces of information. They tell you the total orbital angular momentum of the atom (l), and they tell you the multiplicity (M). l is denoted by a simple code, similar to the code used to delineate the types of atomic orbitals:

- $L = 0 \rightarrow S$
- $L = 1 \rightarrow P$
- $L = 2 \rightarrow D$
- $L = 3 \rightarrow F$

Note that while the notation is similar, L does NOT say anything about what types of orbitals the electrons are in. A state that has the term symbol P does NOT necessarily have an open p-shell. The multiplicity is indicated by appending a number to the upper left of the symbol. A $L = 2$, $M = 3$ state would be represented by ^3D. The secret to writing the term symbols for an atom is to discover what combinations of l and M are possible for that atom with that specific electronic configuration. An atom that only has closed shells will always be $1S$.

Each term symbol represents a discrete energy level. We can place these levels in the correct order by using these simple rules:

- 1: High multiplicity values mean low energy
- 2: If there is a tie, high l values mean low energy
- 3a: If there is still a tie and the shell is less than half full, then low J means low energy
- 3b: If the shell is more than half full, then high J means low energy

These rules reliably predict the ground state. They have only erratic agreement with experiment when ordering the other levels.

Example 8.8.9 : Hydrogen Ground State

What are the term symbols for the microstates possible for $1s^1$ electronic configuration of hydrogen?

Solution

Since there is only one electron, this is a simple problem. $L = 0$ and $M = 1$, so the only possible term symbol is ^2S. With only one electron, $S = ½$, so $J = 0 + ½ = ½$. Only one microstate exists for this configuration and it has a term symbol of $^2S_{½}$.

Example 8.8.10 : Boron

What are the term symbols for the microstates possible for $1s^2 2s^2 2p^1$ electronic configuration of boron?

Solution

There still only one open shell electron, so $L = 1$, $M = 1$ and $S = ½$. We get a term symbol of the type ^2P, which gets split into separate symbols because $J = 3/2$ and $1/2$. Two possible microstates exist for this system with term symbols of $^2P_{3/2}$ and $^2P_{1/2}$.

Example 8.8.11 : Beryllium Excited State

What are the term symbols for the microstates possible for the $1s^2 2s^1 2p^1$ excited-state electronic configuration of Beryllium?

Solution

Now we have two electrons to worry about. Since $l_1 = 0$ and $l_2 = 1$, the only possible combination is $L = 1$. The possible combinations of S are: $S = 1, 0$. This means that $M = 3$ or $M = 1$. The term symbols will be of the form ^1P and ^3P. For the ^1P state, $L = 1$ and $S = 0$, so $J = 1$. For the second state, $L = 1$ and $S = 1$, so $J = 2, 1, 0$. There are four microstates for this configuration with term symbols of $^1P_1$ and $^3P_2$, $^3P_1$, and $^3P_0$.

Example 8.8.12 : Zirconium

What are the term symbols for the microstates possible for the $[Kr]5s^2 4d^2$ ground-state electronic configuration of zirconium?

Solution

This is a much harder problem. We will need to use a special technique to disentangle all of the possible combinations of l and M. Let's start be listing the relevant quantum numbers for the two open-shell electrons:

$l_1 = 2$	$l_2 = 2$
$m_{l1} = 2, 1, 0, -1, -2$	$m_{l2} = 2, 1, 0, -1, -2$
$m_{s1} = ½, -½$	$m_{s1} = ½, -½$

Let's combine these numbers to generate the atomic quantum numbers:

$$L = 4, 3, 2, 1, 0$$

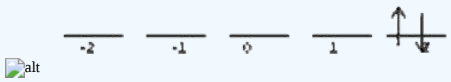
$$M_l = 4, 3, 2, 1, 0, -1, -2, -3, -4$$

$$M_s = 1, 0$$

We know that there will at least one each of S, P, D, F and G. It isn't immediately clear which of these will be singlets and which will be triplets. To figure this out, we need to systematically examine the possible microstates. It turns out that there are **45** possible ways to put distribute two electrons between 5 d orbitals. That's a lot! The easiest way to list the states is to organize them into a chart:

$M_s = -1$	$M_s = 0$	$M_s = +1$

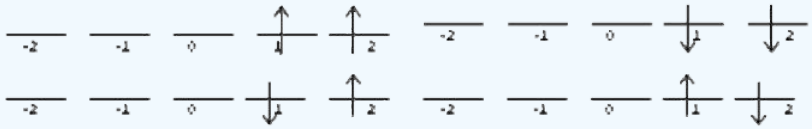
Attacking the chart one row at a time. Ask yourself, how many ways can I arrange the two electrons to give me $M_l = 4$? It turns out there is only one possible combination that does this:



This state is has $M_s = 0$. This means that there is only 1 microstate that corresponds to $M_l = 4$ and $M_s = 0$, and none that correspond to $M_l = 4$ and $M_s = \pm 1$. We add this microstate to the chart like this:

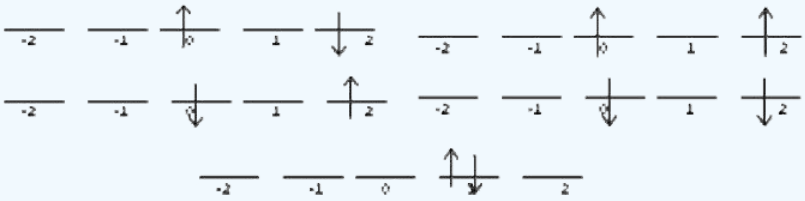
M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0

Now, how many ways are there to get $M_l = 3$?



M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1

For $M_l = 2$, we find the following states:



M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1

You should be able to draw the microstates on your own by now. You should find 8 states, four of which are singlet and four of which are triplets.

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1
1	2	4	2

There are only nine possible ways to arrange the electrons to get $M_l = 0$

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2

The rest of the chart will be symmetric to the first half, so we do not need to do any more work:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
-4	0	1	0

Now that we have a listing of all of the microstates, we need to figure out how to divide them up between the term symbols. It turns out that each term symbol can have, at most, one microstate from each box on the chart. The term symbols always end up claiming a “box” of microstates, centered on the middle of the chart. This is easier shown than said.

Attacking the chart from the top, we can see that the $M_l = 4\ M_s = 0$ state clearly belongs to a ^1G symbol. The $M_l = -4\ M_s = 0$ box also clearly belongs to this symbol. If I connect these states with a "box," I get this:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
~~4~~	~~0~~	~~1~~	~~0~~
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
~~-4~~	~~0~~	~~1~~	~~0~~

The strickthough configurations all belong to the ^1G state. Let's subtract them from the chart to indicate that they are not available for other term symbols.

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1

The next row indicates a $L = 3$ state. Because there are three M_s values available, this is a **triplet**. The term symbol will be ^3F, which reduces the chart down to

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	2	4	2
0	2	5	2
-1	2	4	2

The next state will be ^1D. Leaving us with

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	1	1	1
0	1	2	1
-1	1	1	1

Next is a ^3P state. The chart is getting pretty small now wtih

M_l	$M_s = 0$
	0

The last remaining microstate comprises the ^1S term symbol.

The total listing is

$$^1G, \, ^3F, \, ^1D, \, ^3P, \, ^1S.$$

Assigning J values, we get

$$^1G_4, \, ^3F_4, \, ^3F_3, \, ^3F_2, \, ^1D_2, \, ^3P_2, \, ^3P_1, \, ^3P_0, \, ^1S_0$$

If you can do this problem, you can do almost any atomic term symbol.

Note

The secret to writing the term symbols for an atom is to discover what combinations of l and M are possible for that atom with that specific electronic configuration.

Shortcuts

There is a deep symmetry that connects different electronic configurations. It turns out that a p^1 configuration has the same term symbols as a p^5. Similarly, $p^2 = p^4$. A similar relationship can be used to figure out high electron number term symbols for the d and f orbitals.

13.8: Term Symbols Gives Detailed Descriptions of an Electron Configuration is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **8.8: Term Symbols Gives a Detailed Description of an Electron Configuration** by Mattanjah de Vries is licensed CC BY 4.0.

13.9: Multi-electron Considerations - A Closer Look at Helium

If we have two identical fermions of spin $1/2$, confined in the same region, what is the appropriate wavefunction? In the scattering case we could measure spins far from the interaction, and if we knew that the total spins is conserved, spins can be associated with each particle. In the bound state we cannot tell which particle we are measuring, so the ket must contain both spin and spatial wavefunctions of both particles.

Assuming the spins do not interact, we can separate the two-particle spin-only (ignoring the spatial part) wavefunction into $\sigma(1,2) = \sigma_1\sigma_2$. We also know the appropriate one particle basis states $\uparrow 1$, $\downarrow 1$, $\uparrow 2$, $\downarrow 2$, where $\uparrow 1$ represents "particle 1" in spin up. The ONLY combinations for **indistinguishable particles** are then:

$$\uparrow 1 \uparrow 2 \tag{13.9.1}$$

$$\downarrow 1 \downarrow 2 \tag{13.9.2}$$

$$\frac{1}{\sqrt{2}}(\uparrow 1 \downarrow 2 + \downarrow 1 \uparrow 2) \tag{13.9.3}$$

$$\frac{1}{\sqrt{2}}(\uparrow 1 \downarrow 2 - \downarrow 1 \uparrow 2) \tag{13.9.4}$$

- Operating these four possible spin-only wavefunctions with $\hat{P}_{12}$ yields the eigenvalues: 1, 1, 1 and -1 respectively.
- $S^2 = S(S+1)$ on yields: 2, 2, 2 and 0,
- S_z yields: 1, -1, 0 and 0.

Thus the demands of indistinguishability couples the spins of two identical particles into a triplet ($S = 1$) and a singlet ($S = 0$). The spin-1 vector (i.e., $S = 1$) has **three** possible M_s component values (wavefunctions 13.9.1, 13.9.2, and 13.9.3). This is reflected in its $2S + 1$ multiplicity and is why it is called a triplet state.

The *overall* wavefunction describing fermions must be antisymmetric with respect to exchange, i.e.

$$\hat{P}_{12}|\psi\rangle = -|\psi\rangle \tag{13.9.5}$$

Therefore in an atom or molecule where Φ includes both spin and spatial parts, the spin and spatial parts of a fermionic wavefunction must have opposite exchange symmetry. Spin must be considered even if the energy (Coulomb potential) depends explicitly only on the spatial part. As discussed in the next section, the expectation value of the potential energy is different for symmetric and antisymmetric spatial combinations.

The Exchange Interaction

Since the *overall* wavefunction describing fermions must be antisymmetric with respect to exchange, i.e.

$$\hat{P}_{12}|\psi\rangle = -|\psi\rangle, \tag{13.9.6}$$

therefore in an atom or molecule where Φ includes both spin and spatial parts, the spin and spatial parts of a fermionic wavefunction must have opposite exchange symmetry. Spin must be considered even if the energy (Coulomb potential) depends explicitly only on the spatial part. However, the expectation value of the potential energy is different for symmetric and antisymmetric spatial combinations.

For helium, there asymmetric combination is

$$|\Phi^-\rangle = \frac{1}{\sqrt{2}}\Big|\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)\rangle \tag{13.9.7}$$

and symmetric combination is

$$|\Phi^+\rangle = C_{ab}\big|\phi_a(r_1)\phi_b(r_2) + \phi_a(r_2)\phi_b(r_1)\rangle + C_{aa}\,|\phi_a(r_2)\phi_a(r_1)\rangle + C_{bb}|\,\phi_b(r_2)\phi_b(r_1)\rangle \tag{13.9.8}$$

For convenience, let's consider only the $|\Phi^{\pm}\rangle$ combinations with $C_{aa} = C_{bb} = 1$). The corresponding energy associated with the inter-electron interaction potential V can be expanded

$$\langle \psi^{\pm} \left| \hat{V} \right| \psi^{\mp} \rangle = \langle \phi_a(r_1)\phi_b(r_2) \left| V(r) \right| \phi_a(r_1)\phi_b(r_2) \rangle \pm \langle \phi_a(r_1)\phi_b(r_2) \left| V(r) \right| \phi_a(r_2)\phi_b(r_1) \rangle \tag{13.9.9}$$

The first term is called the **Coulomb interaction (*J*)** and the second term is known as **the exchange interaction (\K\))**: a measurable contribution to the energy comparable in size to the first, which has no classical analog.

Now notice something strange. The exchange interaction has split the $S = 1$ states from the $S = 0$ states. We could write the potential as

$$\hat{V} = J_{nl} - (2\hat{S} - 1)K_{nl} \tag{13.9.10}$$

even though the Hamiltonian does not act on the spin! This is because the sign of the exchange integral depends on the (anti)symmetry of the spatial wavefunction. Thus we can write the matrix element as

$$\langle \psi \left| J_{nl} - (2S - 1)K_{nl} \right| \psi \rangle \tag{13.9.11}$$

> *This 'exchange interaction' depends on the spin; the triplet states have lower energy than the singlet (this is one of Hund's rules for determining energy levels in atoms).*

Helium

Helium is the simplest system for which we are unable to accurately calculate the energy. For a single electron moving in the field of a helium nucleus, the spatial wavefunctions are similar to those of hydrogen $|\phi_{n,l,m_s}\rangle$. When a second electron is added, a reasonable basis set is exchange-symmetrized wavefunctions consisting of spin states multiplying hydrogenic spatial parts:

$$(\phi_{n,l,m}(r_1)\phi_{n',l',m_l'}(r_2) \pm \phi_{n,l,m}(r_2)\phi_{n',l',m_l'}(r_1)) \tag{13.9.12}$$

The **overall wavefunction** must be antisymmetric so:

- the singlet spin states (exchange-antisymmetric) must combine with symmetric spatial states and
- the triplet spin states (exchange-symmetric) must combine with antisymmetric spatial states.

If both electrons were in the **same spatial state (orbital)**, the antisymmetric spatial wavefunction would be:

$$|(a(r_1)a(r_2) - a(r_2)a(r-1))\rangle = 0 \tag{13.9.13}$$

Hence, there is no **triplet** for the ground state.

Electron-electron interaction - ground state by perturbation theory

The hydrogen wavefunctions are only a choice of basis set: the hydrogenic potential ignores the electron-electron repulsion. A simple approach is to treat this as a perturbation and to use degenerate perturbation theory. The perturbation potential is just

$$V = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{13.9.14}$$

where $r_{12} = |r_1 - r_2|$. For helium, the **unperturbed** spatial ground state is just a product of the $1s$ hydrogenic ones with $Z = 2$:

$$\phi_{n=1,l=0,m_l=0}(r_1)\phi_{n=1,l=0,m_l=0}(r_2) = \frac{Z^3}{\pi a_0^3}\exp[-Zr_1/a_0]\exp[-Zr_2/a_0] \tag{13.9.15}$$

The zero-order energy (i.e., unperturbed energy) associated with this wavefunction is

$$E^0 = \frac{4Ze^4}{\hbar^2} \tag{13.9.16}$$

Via first-order perturbation theory, the energy shift from the perturbed energy of any state is

$$\langle \phi \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| \phi \rangle \tag{13.9.17}$$

and for the ground state fo Helium, Equation 13.9.17 is given by:

$$\langle \phi_{n=1,l=0,m_l=0}(r_1)\phi_{n=1,l=0,m_l=0}(r_2) \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| \phi_{n=1,l=0,m_l=0}(r_1)\phi_{n=1,l=0,m_l=0}(r_2)\rangle \tag{13.9.18}$$

Comparison of the zero-order energy and the measured energy show that electron-electron repulsion is over 30% of the unperturbed energy (Equation 13.9.16), so perturbation theory may seem inappropriate (although higher order perturbation theory may be used). Strictly, Equation 13.9.18 is not even the right integral, as it neglects electron correlation effects (discussed elsewhere), but the value of this integral

$$\frac{5Ze^4}{8\hbar^2} \tag{13.9.19}$$

is within 5% of the actual energy.

> *Note also that the radial wavefunctions are different for* $2s$ *and* $2p$*, so the electron-electron interaction splits the degeneracy between* $1s2s$ *and* $1s2p$ *configurations.*

Multiplicity and Degeneracy of Excited States

Ignoring electron-electron interaction (e.g., in the hydrogen atom), all $1s2s$ and $1s2p$ states have the same energy. However, the electron-electron perturbation

$$H^1 = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{13.9.20}$$

lifts that degeneracy, which we can treat with **degenerate** perturbation theory (this is outside the scope of this class). Rather than evaluating resulting perturbation theory integral exactly, we can use a physical argument about the nature of the perturbation. Since $(e^2/4\pi\epsilon_0 r_{12})$ is **not** an externally applied potential, it applies no net torque nor force on the electrons. The perturbation cannot change the angular momentum, so it cannot mix states with different l or m_l (i.e., the perturbed wavefunctions does not have components of differing angular momentum quantum numbers). Integrating over θ results in $\delta_{ll'}$ and integrating over ϕ give $\delta_{m_l m_l'}$, so **total orbital angular momentum** remains a good quantum number, hence:

$$L = \sum_{i=1}^{2} l_i = 0 + 0 = 0 \tag{13.9.21}$$

for the $1s^1 2s^1$ electron configuration (promoting a 1s electron to the 2s orbital) or

$$L = \sum_{i=1}^{2} l_i = 0 + 1 = 1 \tag{13.9.22}$$

for the $1s^1 2p^1$ electron configuration (promoting a 1s electron to the 2p orbital).

> *Different electron configurations will have different total orbital angular momentum and spin angular momentum amplitudes.*

Since the 2s electron is less well screened from the nuclear charge by the $1s$ that the $2p$ electron due to its closer radial distribution function, it will have lower energy (see Slater's Rules). As wth the helium ground-state, for a given spatial excited state, the possible normalized spin-orbital wavefunction combinations, consistent with the antisymmetry requirement are a triplet ($S = 1$) and a singlet ($S = 0$).

The spin-orbital wavefunctions for the triplet state are

$$\Phi_3 = \frac{1}{\sqrt{2}}[\phi_{n,l,m_l,n',l',m_l'} - \phi_{n',l',m_l',n,l,m_l}](\uparrow\uparrow) \tag{13.9.23}$$

and

$$\frac{1}{\sqrt{2}}[\phi_{n,l,m_l,n',l',m_l'} - \phi_{n',l',m_l',n,l,m_l}](\downarrow\downarrow) \tag{13.9.24}$$

and

$$\frac{1}{2}[\phi_{n,l,m_l,n',l',m_l'} - \phi_{n',l',m_l',n,l,m_l}](\downarrow\uparrow + \downarrow\uparrow) \tag{13.9.25}$$

The spin-orbital wavefunction for the singlet state is

$$\Phi_1 = \frac{1}{2}[\phi_{n,l,m_l,n',l',m_l'} + \phi_{n',l',m_l',n,l,m_l}](\downarrow\uparrow - \downarrow\uparrow) \tag{13.9.26}$$

where $\phi_{n,l,m_l,n',l',m_l'}\rangle$ represents electron 1 in a hydrogenic state with quantum numbers n, l and m_l and electron 2 with n', l', and m_l. The subscripts on the Φ label spin *multiplicity*

$$2S + 1 \tag{13.9.27}$$

Again, whole effect of the potential is contained in the spatial part, the spin integral will be $\delta_{\sigma,\sigma'}$. So off-diagonal matrix elements are all zero. We need to evaluate two types of integrals to compute the energies of these states:

- the **Coulomb integral**

$$J_{nl} = \langle\phi_{n,l,m_l,n',l',m_l'}\left|\frac{e^2}{4\pi\epsilon_0 r_{12}}\right|\phi_{n,l,m_l,n',l',m_l'}\rangle \tag{13.9.28}$$

- and the **Exchange integral**

$$K_{nl} = \langle\phi_{n,l,m_l,n',l',m_l'}\left|\frac{e^2}{4\pi\epsilon_0 r_{12}}\right|\phi_{n',l',m_l',n,l,m_l}\rangle \tag{13.9.29}$$

Within first-order perturbation theory, an energy shift can be calculated by Equation 13.9.17. Apply this expression to the $1s^1 2s^1$ singlet state wavefunction (Equation 13.9.26) results in:

$$\begin{aligned} E^1 = \frac{1}{2}\frac{e^2}{4\pi\epsilon_o}\Big(&\langle\phi_{100,200}\left|\frac{1}{r_{12}}\right|\phi_{100,200}\rangle + \langle\phi_{200,100}\left|\frac{1}{r_{12}}\right|\phi_{200,100}\rangle \\ &\pm\langle\phi_{100,200}\left|\frac{1}{r_{12}}\right|\phi_{200,100}\rangle \pm \langle\phi_{200,100}\left|\frac{1}{r_{12}}\right|\phi_{100,200}\rangle\Big) \end{aligned} \tag{13.9.30}$$

which in terms of the integrals defined above can be rewritten

$$E^1 = \frac{1}{2}\left(J_{1,2} + J_{2,1} \pm K_{1,2} \pm K_{2,1}\right) \tag{13.9.31}$$

since $J_{1,2} = J_{2,1}$ and $K_{1,2} = k_{2,1}$, then

$$E^1 = J \pm K \tag{13.9.32}$$

where the + applies to the singlet state (the 1s and 2s electrons have opposing spin) and the − to the triplet (the electrons aligned). The Coulomb integral as a measure of the electron-electron repulsion, increases the energy of the state. However, the exchange integral can either increase (for singlets) or decrease energy (for triplets). This means that electron-electron repulsion lifts the degeneracy two-fold:

- the energy levels are split by different direct interactions into $L = 0$ and $L = 1$ and
- the energy levles are again split through exchange interaction into singlet and triplet.

The final degeneracies of states of helium with one electron excited to $n = 2$ are 3, 1, 9 and 3 (Figure 13.9.1).

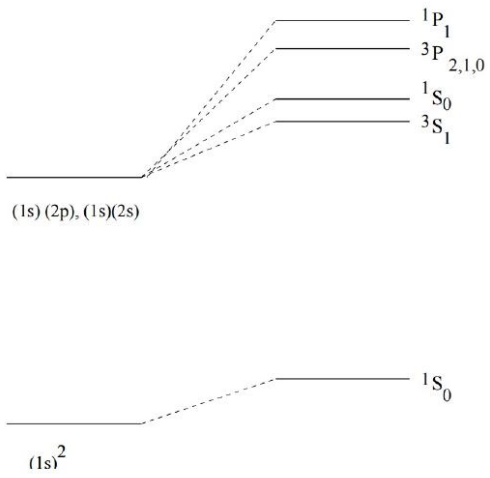


Figure* 13.9.1*: *Ground and Excited-states of Helium. (left) underperturned energies from* $\boldsymbol{H^0}$ *and (right) perturbed energies due to electron-electron repulsion.*

The spectroscopic notation in Figure **13.9.1** is called a term symbol and expresses the quantum numbers as:

$$^{2S+1}L_J \tag{13.9.33}$$

where J is the total angular moment.

> *The 'exchange force' selects preferred spin state via the requirement of overall antisymmetry of the wavefunction.*

Contributors

- Graeme Ackland (University of Edinburgh)

13.9: Multi-electron Considerations - A Closer Look at Helium is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

13.10: The Allowed Values of J - the Total Angular Momentum Quantum Number

Learning Objectives

- Compate two spin-orbit coupling schemes that couple the total spin angular momenta and total orbital angular momenta of a multi-electron spectra

We need to be able to identify the electronic states that result from a given electron configuration and determine their relative energies. An electronic state of an atom is characterized by a specific energy, wavefunction (including spin), electron configuration, total angular momentum, and the way the orbital and spin angular momenta of the different electrons are coupled together. There are two descriptions for the coupling of angular momentum. One is called **j-j coupling**, and the other is called **L-S coupling**. The j-j coupling scheme is used for heavy elements (z > 40) and the L-S coupling scheme is used for the lighter elements. Only L-S coupling is discussed below.

L-S Coupling of Angular Momenta

L-S coupling also is called R-S or Russell-Saunders coupling. In L-S coupling, the orbital and spin angular momenta of all the electrons are combined separately

$$L = \sum_i l_i \tag{13.10.1}$$

$$S = \sum_i s_i \tag{13.10.2}$$

The total angular momentum vector then is the sum of the total orbital angular momentum vector and the total spin angular momentum vector.

$$J = L + S \tag{13.10.3}$$

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.

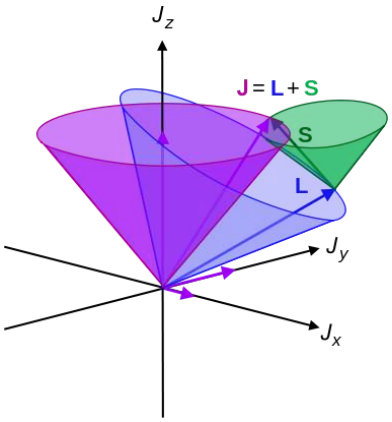


Figure 8.9.1 : "Vector cones" of total angular momentum $\boldsymbol{J}$ (purple), orbital $\boldsymbol{L}$ (blue), and spin $\boldsymbol{S}$ (green). The cones arise due to quantum uncertainty between measuring angular momentum components (see vector model of the atom). (Public Domain; Maschen).

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:

$$m_\ell \in \{-\ell, -(\ell-1) \cdots \ell-1, \ell\}, \quad \ell \in \{0, 1 \cdots n-1\} \tag{13.10.4}$$
$$m_s \in \{-s, -(s-1) \cdots s-1, s\}, \tag{13.10.5}$$
$$m_j \in \{-j, -(j-1) \cdots j-1, j\}, \tag{13.10.6}$$
$$m_j = m_\ell + m_s, \quad j = |\ell + s| \tag{13.10.7}$$

and the magnitudes are:

$$|\mathbf{J}| = \hbar\sqrt{j(j+1)} \tag{13.10.8}$$
$$|\mathbf{J}_1| = \hbar\sqrt{j_1(j_1+1)} \tag{13.10.9}$$
$$|\mathbf{J}_2| = \hbar\sqrt{j_2(j_2+1)} \tag{13.10.10}$$

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.

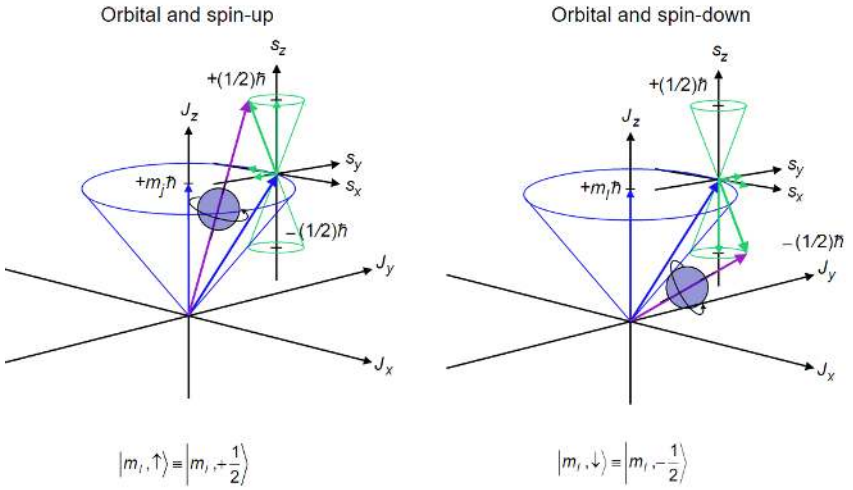


Figure 8.9.2 : Vector model of total angular momentum: spin and orbital coupling (spin-1/2 particles). (Public Domain; Maschen).

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

---

13.10: The Allowed Values of J - the Total Angular Momentum Quantum Number is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

13.11: Hund's Rules Determine the Term Symbols of the Ground Electronic States

Learning Objectives

- Define Hund three rules
- Use Hunds three rules to predict the lowest energy configuration and term symbols for multi-electron systems

The Aufbau section discussed how that electrons fill the lowest energy orbitals first, and then move up to higher energy orbitals only after the lower energy orbitals are full. However, there a problem with this rule. Certainly, 1s orbitals should be filled before 2s orbitals, because the 1s orbitals have a lower value of n, and thus a lower energy. What about the three different 2p orbitals? In what order should they be filled? The answer to this question involves Hund's rule, which make a lot more sense in the context of generated term symbols that are used to combine the various L and S values represent vector additions of possible microstates.

Hund's Rules

1. State with the largest value of S is most stable and stability decreases with decreasing S.
2. For states with same values of S, the state with the largest value of L is the most stable.
3. If states have same values of L and S then, for a subshell that is less than half filled, state with smallest J is most stable; for subshells that are more than half filled, state with largest value of J is most stable.

Example 8.10.1

Rank these terms associated with an electronic configuration of an atom based on energy (via Hund's rules):

$$^3D,\ ^3P,\ ^3S,\ ^1D,\ ^1P,\ ^1S$$

Hund's First Rule (Maximize Spin Multiplicity)

According to the first rule, electrons always enter an empty orbital before they pair up. Electrons are negatively charged and, as a result, they repel each other. Electrons tend to minimize repulsion by occupying their own orbitals, rather than sharing an orbital with another electron. Furthermore, quantum-mechanical calculations have shown that the electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus.

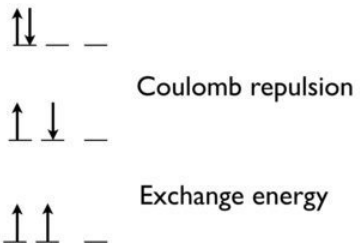


Figure 8.10.1 : Origin of Hund's First Rule. Hund's first rule is that for a given electron configuration, a state in which the spins are unpaired has lower total energy than one in which the spins are paired.

There's a Coulomb repulsion between two electrons to put them in the same orbital (a spin pairing energy often discussed in Crystal Field Theory). However, there's also a quantum mechanical effect. The *exchange energy* (which is favorable) increases with the number of possible exchanges between electrons with the same spin and energy. In transitioning from the top state to the middle state of Figure 8.10.1 , we remove the Coulomb repulsion between electrons in the same orbital. Moreover, In transitioning from the middle state to the bottom state (most stable state predicted by Hund's first rule), we *gain* the *exchange energy*, because these two electrons are indistinguishable.

Hund's Second Rule (Maximize Orbital Angular Multiplicity)

What matters is the total (scalar) angular momentum, not the direction. The negative and positive signs refer only to the direction of the angular momentum, not the magnitude. The direction is furthermore arbitrary (except in, say, a magnetic or electric field). So is the spin direction, incidentally. By convention we usually draw the first electron in each orbital as "up" (positive spin). However we could just as easily draw it "down". It makes no difference - in the absence of an external EM field, the energy is the same, if

only because molecules/atoms are rotating with respect to the lab frame anyway. "Up" and "down", in other words, is artificial. What matters is the *relative* momentum vectors of the various electrons in the system, and hence their sum total.

Hund's Third Rule (Minimize less than half filled or maximize greater than half filled shells)

A long time ago someone offering a reasonably simple explanation related to the fact that when the shell is more than half full, it's easier to visualize the system as an interaction between the spin and orbital momenta of holes rather than electrons, in which case the energetic stabilization term is reversed in sign. This would be because the spin angular momentum of a single hole would be opposite in sign compared to the spin angular momentum of a single electron. Taking as an example - the three p-orbitals. A situation with 1 electron and 5 electrons are functionally similar, except that one has a single electron and one has a single hole. All things being equal, the total spin angular momentum of the 1 electron system would be opposite in sign to whatever the total spin angular momentum of the 5 electron system is. So the expectations for Hund's rules would be switched. You can kind of see this if you draw out all the microstates of the 1-electron and 5-electron configurations: the everything is pretty much changed in sign in the latter case.

Example 8.10.2

What terms and levels can arise from an atom with the ground-state configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^1 3d^1$? Which is the most stable (lowest in energy) state?

Solution

Possible states include:

$$^1F_3,\ ^1D_2,\ ^1P_1,\ ^3F_4,\ ^3F_3,\ ^3F_2,\ ^3D_3,\ ^3D_2,\ ^3D_1,\ ^3P_2,\ ^3P_1,\ ^3P_0.$$

There are two unpaired electrons in this system from the electron configuration.

- Rule 1 predicts that the ground state will be a triplet with $S = 1$ so $2S + 1 = 3$. So the ground state is from this more narrowed list: $^3F_4,\ ^3F_3,\ ^3F_2,\ ^3D_3,\ ^3D_2,\ ^3D_1,\ ^3P_2,\ ^3P_1,\ ^3P_0$.
- Rule 2 predicts a F state since that is the highest multiplicity with $L = 3$: So the ground state is from this more narrowed list: $^3F_4,\ ^3F_3,\ ^3F_2$
- Rule 3 predicts the lowest J term since the d shell is less than half full. That is the $J = 2$ state.

Therefore for this system, the atom will have a ground-state structure of

$$^3F_2$$

Example 8.10.3 : Titanium cation

The ground configuration of a Ti^{2+} ion is $[Ar]3d^2$. What is the term of lowest energy state?

Solution

- Rule 1: two unpaired electrons ⇒ highest S = 1 ⇒ 2S + 1 = 3
- Rule 2: two in d in parallel spin ⇒ highest L = 1 + 2 = 3 ⇒ 3F
- Rule 3:.L = 3, S = 1 ⇒ J = 4, 3, 2; less than half-filled ⇒ $^3F_2$

Exercise 8.10.3

What is the term of lowest energy state for the following atoms and ions.

- C: $[He]2s^2 2p^2$
- N: $[He]2s^2 2p^3$
- O: $[He]2s^2 2p^4$
- Cr^{3+}: $[Ar]3d^3$
- Mn^{3+}: $[Ar]3d^4$
- Fe^{3+}: $[Ar]3d^5$

13.11: Hund's Rules Determine the Term Symbols of the Ground Electronic States is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States** by Delmar Larsen is licensed CC BY-NC-SA 4.0.

13.12: Using Atomic Term Symbols to Describe 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 $\mathbf{He}^+$.

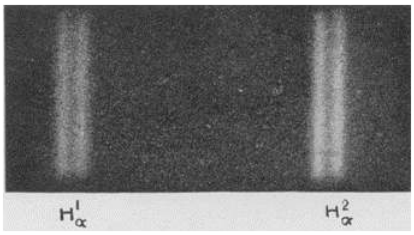


Figure 8.11.1 : Photograph of the first line in the Balmer series for atomic hydrogen and deuterium. These lines are identified as H_α^1 (hydrogen) and H_α^2 (deuterium), respectively. From H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) p. 132 and G.N. Lewis and F.H. Spedding, 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.

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.

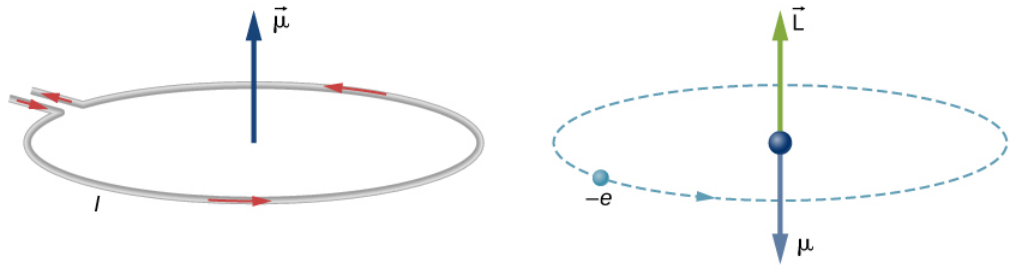
$$E_{s-o} \propto S \cdot L$$

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).

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:

$$\Delta S = 0 \tag{13.12.1}$$
$$\Delta L = 0, \pm 1 \tag{13.12.2}$$
$$\Delta J = 0, \pm 1, \tag{13.12.3}$$

but the $J = 0$ to $J = 0$ transition is forbidden

$$\Delta m_J = 0, \pm 1 \tag{13.12.4}$$

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 13.12.2 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 13.12.2.

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 13.12.1) 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 .

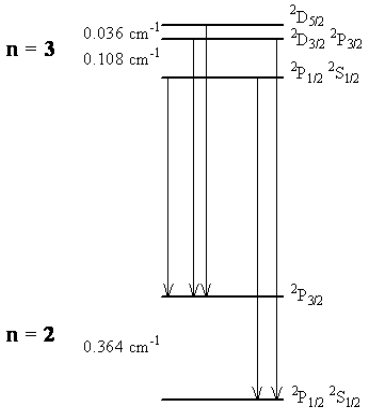


Figure 8.11.2 : Energy level diagram for the electronic states of hydrogen corresponding to an electron with the principal quantum number n = 3 and n = 2. While the relative energies of the terms are drawn to scale, the energy of n = 3 relative to n = 2 is not. Transitions to the $2P_{3/2}$ and ($2P_{1/2}$ 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.

13.12: Using Atomic Term Symbols to Describe Atomic Spectra is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **8.11: Using Atomic Term Symbols to Interpret Atomic Spectra** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

13.13: Multielectron Atoms (Exercises)

Solutions to select questions can be found online.

8.4

Prove the speed of electron in first Bohr orbit is $e^2/4\pi\epsilon_0\hbar = 2.188 \times 10^6 m \bullet s^{-1}$. The speed is in atomic units.

8.15

Explain why:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1dr_2d\sigma_1d\sigma_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1dr_2d\sigma_1d\sigma_2}$$

can be rewritten as:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1dr_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1dr_2}$$

8.16

Why must you distinguish the two electrons in separated hydrogen atoms?

8.17

In both the Hartree-Fock approximation and hydrogen atomic wavefunction, why is the angular dependence the same?

8.20

Given the two electron determinate wavefunction below, determine if the spin component of the system is symmetric, anti-symmetric, or neither.

$$\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\alpha(2) \end{vmatrix}$$

8.23

Given $\hat{S}_z\alpha = \frac{\hbar}{2}\alpha$ and $\hat{S}_z\alpha = \frac{-\hbar}{2}\beta$, show that Ψ_{200} is an eigenfunction of $S_{z,total} = \hat{S}_{za} + \hat{S}_{zB}$.

8.24

For the wavefunction:

$$\psi = \begin{vmatrix} \psi_A(1) & \psi_A(2) \\ \psi_B(1) & \psi_B(2) \end{vmatrix}$$

discuss the effect on the wavefunction of (a) swapping rows of the matrix and (b) swapping columns of the matrix.

8.27

What are the term symbols for carbon and oxygen atoms in the ground state?

8.28

Show that the number of sets of magnetic quantum number (m_l) and spin quantum number (m_s) associated with any term symbol is equal to $(2L+1)(2S+1)$. Apply this result to the np^2 case and show that symbol ^1S, ^3P and ^1D account for all the possible sets of magnetic quantum numbers and spin quantum numbers

8.29

Calculate all possible numbers of term symbol for an np^1 electron configuration.

8.30

Determine the ground state term symbol for the electron configuration of the Halogens.

8.33

^2P, ^2D, and ^4S are the term symbols for an atom with the np^3 electron configuration. Using the term symbols for the np^3 electron configuration, calculate the J values associated with each of the term symbol. Then find out which term symbol represent the ground state.

8.34

What are the ground state electron configuration and term symbol for Calcium?

8.34

Find the ground state term symbol for Ca.

8.36

Write the electron configuration for vanadium and use this information to find the ground-state term symbol for V.

8.36

What is the ground-state term symbol for Ne.

8.37

Looking at the $1s2p$ electron configuration for He. Solve for the term symbols (states) of the Helium configuration and the degeneracies. If electron spin orbit coupling is included, what effect will this have?

13.13: Multielectron Atoms (Exercises) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

14: Bonding in Polyatomic Molecules

Valence bond (VB) theory is one of two basic bonding theories, along with molecular orbital (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory, which will be discussed elsewhere, predict wavefunctions that cover the entire molecule.

14.1: Hybrid Orbitals Account for Molecular Shape

14.2: Different Hybrid Orbitals Used for Bonding in Water

14.3: Why is BeH_2 Linear and H_2O Bent?

14.4: Photoelectron Spectroscopy

14.5: The \(\pi\)-Electron Approximation of Conjugation

14.6: Butadiene is Stabilized by a Delocalization Energy

14: Bonding in Polyatomic Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

14.1: Hybrid Orbitals Account for Molecular Shape

Learning Objectives

- Introduce hybrid orbital to explain non-linear molecular structure

Valence bond (VB) theory is one of two basic theories, along with **molecular orbital** (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory, which will be discussed elsewhere, predict wavefunctions that cover the entire molecule.

Review of Diatomics

Let us consider H_2. Recall that the Lewis structure for a single H atom is $H\cdot$ and for H_2, it is $H:H$. Thus, each hydrogen brings one unpaired electron to the bond. Let the two protons be denoted A and B and the two electrons 1 and 2. Now, consider the potential energy

$$V = V_{ee} + V_{en} + V_{nn} \tag{14.1.1}$$

$$= \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{R_{AB}}\right] \tag{14.1.2}$$

But as $R_{AB} \rightarrow \infty$, the $1/r_{12}$, $1/r_{1B}$, $1/r_{2A}$, and $1/R_{AB}$ terms vanish and the potential energy becomes simply that of two noninteracting hydrogen atoms

$$V \rightarrow -\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{1A}} + \frac{1}{r_{2B}}\right]$$

Since the potential energy becomes a simple sum of separate energies for electrons 1 and 2, the wavefunction should simply be a product $\psi_{1s}(r_1 - r_A)\psi_{1s}(r_2 - r_B)$. But as we let $R_{AB} \rightarrow R_e$, where R_e is the equilibrium bond length, the electrons mix, and we can no longer tell if electron 1 belongs to atom A or atom B and the same for electron 2. Thus, we need to construct a combination of products that is consistent with the Pauli exclusion principle. If we just consider the coordinates r_1 and r_2 of the electrons, then the only wavefunction we can construct from a product of 1s orbitals is

$$\psi_u(r_1, r_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)]$$

where the u designator indicates that this is an odd function. The constant C_u is the overall noramlization constant. Unfortunately, like in the LCAO method, such a wavefunction is antibonding and is not a good representation of the ground state. If, however, we construct the wavefunction

$$\psi_g(r_1, r_2) = C_g[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)]$$

where g designates that this is an even function (even in German is *gerade*), we violate the Pauli exclusion principle, even though such a wavefunction leads to a stable chemical bond.

What is missing here is the fact that we have not considered the spins of the electrons. Since the electrons are identical, if we exchange coordinates *and* spins, then the wavefunction should change sign. Thus, we can make both wavefunctions above consistent with the Pauli exclusion principle by multiplying by an appropriate spin wavefunction. We obtain

$$\psi_u(r_1, r_2, s_1, s_2) = \psi_u(x_1, x_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)] \\ [\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{14.1.3}$$

$$\psi_g(r_1, r_2, s_1, s_2) = \psi_g(x_1, x_2) = C_g[\psi^A_{1s}(r_1)\psi_{1s}B(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)] \\ [\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{14.1.4}$$

where s_1 and s_2 are the z-components of spin for electrons 1 and 2, respectively. We can now use ψ_g as an approximate 2-electron wavefunction that leads to a stable chemical bond in H_2.

The fact that ψ_u is antibonding can be easily determined by looking for a nodal plane between the two atoms, in this case, in the plane that exactly bisects the line joining the two atoms, midway between them. That this is, indeed, a nodal plane can be seen by

considering two points r_1 and r_2 for the two electrons that are taken to lie in this plane. By symmetry, the functions $\psi_{1s}^{A}(r_1)$ and $\psi_{1s}^{B}(r_1)$ have the same value for r_1 in this plane, and the same for $\psi_{1s}^{B}(r_2)$ and $\psi_{1s}^{A}(r_2)$. Let us assign the following values:

$$\psi_{1s}^{A}(r_1) = \psi_{1s}^{B}(r_1) = A \tag{14.1.5}$$

$$\psi_{1s}^{B}(r_2) = \psi_{1s}^{A}(r_2) = A' \tag{14.1.6}$$

Substituting these into $\psi_u(x_1, x_2)$, we obtain

$$\psi_u(x_1, x_2) = C_u[AA' - A'A][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] = 0$$

Since the wavefunction has a node midway between the two atoms, it is clearly antibonding and should have a *higher energy* than the corresponding bonding wavefunction ψ_g.

A similar argument can be used for the molecule F_2. Each F has an electronic configuration

$$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$$

and the Lewis structure of $\mathbf{F_2}$ is



Figure 10.1.1 : Lewis structure of F_2.

Most of the electrons are in lone pairs, but the $2p_z$ electrons, which are unpaired in each $\mathbf{F}$ atom come together to form the bond. Thus, the bonding wavefunction should be a **2-electron wavefunction** constructed from $2p_z$ orbitals. The bonding wavefunction takes the "gerade" form as in $\mathbf{H_2}$:

$$\psi_g(r_1, r_2, s_1, s_2) = C_g[\psi_{2p_z}^{A}(r_1)\psi_{2p_z}^{B}(r_2) + \psi_{2p_z}^{A}(r_2)\psi_{2p_z}^{B}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]$$

For $\mathbf{HF}$, the $2p_z$ orbital on $\mathbf{F}$ and $1s$ orbital on $\mathbf{H}$ come together to form the bonding wavefunction. To be consistent with the Pauli principle, we need a wavefunction of the form

$$\psi(r_1, r_2, s_1, s_2) = [\psi_{1s}^{H}(1)\psi_{2p_z}^{F}(2) + \psi_{1s}^{H}(2)\psi_{2p_z}^{F}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]) \tag{14.1.7}$$

Looking at the $\mathbf{HF}$ example, it becomes clear how much valence bond theory attempts to appear as a "quantum version" of the Lewis dot structure model. Valence bond theory attempts to construct very approximate wavefunctions for the bonding electrons in a Lewis structure, leaving the orbitals unused in the construction of the valence bond wavefunctions for the lone pair electrons. In the case of $\mathbf{HF}$, we use the $2p_z$ orbitals of $\mathbf{F}$, which leaves the $2s$, $2p_x$ and $2p_y$ orbitals unused. Since there are three lone pairs, these three orbitals are sufficient to hold each of the lone pairs as spin-up/spin-down couples.

Hybridization

For polyatomic molecules, the valence bond theory becomes a very poor approximation because the directionalities of the $2s$ and $2p$ orbitals is too restrictive to describe molecules with steric numbers ranging between 2 and 4. The example considered above of $\mathbf{H_2O}$ illustrates this rather dramatically! Let us consider an even simpler molecule, $\mathbf{BeH_2}$, which has a steric number of 2 and is linear. Let the atoms lie entirely along the z-axis in the arrangement $\mathbf{H{-}Be{-}H}$.

Although the $\mathbf{Be}$ atom has a ground-state electronic configuration of $1s^2 2s^2$, but if we "promote" one of the $2s$ electrons to a state with higher energy and allow its electronic structure to be $1s^2 2s 2p_z$, then the unpaired electrons in the $2s$ and $2p_z$ orbitals can combine with the unpaired electrons in each of the hydrogen atoms to form bonds. The energy needed to excite the electron in Be would be "repaid" by the energy gained in the formation of stable bonds. The two valence-bond wavefunctions we would construct would be

$$\psi_1(1,2) = C_1\left[\psi_{1s}^{H_1}(1)\psi_{2s}^{Be}(2) + \psi_{1s}^{H_1}(2)\psi_{2s}^{Be}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{14.1.8}$$

$$\psi_2(1,2) = C_2\left[\psi_{1s}^{H_2}(1)\psi_{2p_z}^{Be}(2) + \psi_{1s}^{H_2}(2)\psi_{2p_z}^{Be}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{14.1.9}$$

Unfortunately, even this simple scheme does not work entirely because the two $\mathbf{Be{-}H}$ bonds would be different due to their construction from different combinations of orbitals. By symmetry, however, we can see that the two $\mathbf{Be{-}H}$ bonds should be

equivalent. A solution to this problem was proposed by Linus Pauling in the 1930s in the form of **orbital hybridization**, a scheme that we still use today.

Pauling used the fact that in the first and second periods, the $2s$ and $2p$ orbitals have similar energies. Indeed, for the **H** atom, the energies are exactly the same. Given that these energies are not that different, we can combine s and p orbitals and still have a valid solution of the Schrödinger equation. That is, a general orbital

$$\chi(r) = C_1\psi_{2s}(r) + C_2\psi_{2p_z}(r) + C_3\psi_{2p_y}(r) + C_4\psi_{2p_x}(r)$$

is also a solution of the Schrödinger equation with the same energy as a $2s$ or $2p$ orbitals individually (this is exactly true for H). In the case of BeH_2, the external potential on the electrons in **Be** by the two hydrogens changes the energy levels and creates a near degeneracy between the $2s$ and $2p_z$ orbitals, hence, we are now free to combine the into linear combinations that are more suitable to the construction both of valence bond wavefunctions *and* MOs via the LCAO procedure.

sp Hybrid Orbitals

For Be, we now allow the s and p orbitals to mix and create two *hybrid* orbitals known as sp orbitals. The two new hybrid wavefunctions as linear combination of the functions for 2s and $2p_z$ (using Dirac Notation):

$$|\chi_i\rangle = a_1|2s\rangle + b_1|2p_z\rangle \tag{14.1.10}$$

$$|\chi_j\rangle = a_2|2s\rangle + b_2|2p_z\rangle \tag{14.1.11}$$

These two wavefunctions must be orthogonal.

$$\langle\chi_i|\chi_j\rangle = \delta_{ij}$$

Which can be separated into the following relationships:

$$\langle\chi_i|\chi_i\rangle = 1 \tag{14.1.12}$$

and

$$\langle\chi_j|\chi_j\rangle = 1 \tag{14.1.13}$$

and

$$\langle\chi_i|\chi_j\rangle = \langle\chi_j|\chi_i\rangle = 0 \tag{14.1.14}$$

Equations 14.1.12 and 14.1.13 are the **normality requirement** and Equation 14.1.14 is the **orthogonality requirement** for the new hybrid wavefunctions. Substituting 14.1.10 into 14.1.12 results in

$$\langle\chi_i|\chi_i\rangle = a_1^2\cancelto{1}{\langle 2s|2s\rangle} + a_1b_1\cancelto{0}{\langle 2s|2p_z\rangle} + a_1b_1\cancelto{0}{\langle 2p_z|2s\rangle} + b_1^2\cancelto{1}{\langle 2p_z|2p_z\rangle} = 1$$

and similarly for $\langle\chi_j|\chi_j\rangle$

$$\langle\chi_j|\chi_j\rangle = a_2^2\cancelto{1}{\langle 2s|2s\rangle} + a_2b_2\cancelto{0}{\langle 2s|2p_z\rangle} + a_2b_2\cancelto{0}{\langle 2p_z|2s\rangle} + b_2^2\cancelto{1}{\langle 2p_z|2p_z\rangle} = 1$$

results in the following relationships

$$\langle\chi_i|\chi_i\rangle = a_1^2 + b_1^2 = 1 \tag{14.1.15}$$

$$\langle\chi_j|\chi_j\rangle = a_2^2 + b_2^2 = 1 \tag{14.1.16}$$

and

$$\langle\chi_i|\chi_j\rangle = a_1a_2 + b_1b_2 = 0 \tag{14.1.17}$$

These are four unknowns and three equations. The fourth "constraint" is that we assume contribution of $|s\rangle$ is the same for both hybrid orbitals.

$$a_1 = a_2$$

Equations 14.1.15 to 14.1.17 revert to

$$a_1^2 + b_1^2 = 1 \tag{14.1.18}$$

$$a_1^2 + b_2^2 = 1 \tag{14.1.19}$$

$$b_1^2 = b_2^2 \tag{14.1.20}$$

Therefore

$$b_1 = -b_2$$

and

$$a_1 = b_1 \tag{14.1.21}$$

Insert Equation 14.1.21 into 14.1.20 to get

$$a_1 = \frac{1}{\sqrt{2}}$$

and the two hybrid orbitals are

$$\chi_1(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) + \psi_{2p_z}(r)] \tag{14.1.22}$$

$$\chi_2(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) - \psi_{2p_z}(r)] \tag{14.1.23}$$

Note that these orbitals are both normalized and orthogonal:

$$\int |\chi_1(r)|^2 dV = 1\ ;\ \int |\chi_2(r)|^2 dV = 1\ ;\ \int \chi_1^*(r)\chi_2(r) dV = 0$$

These orbitals appear as shown in Figure 10.1.3

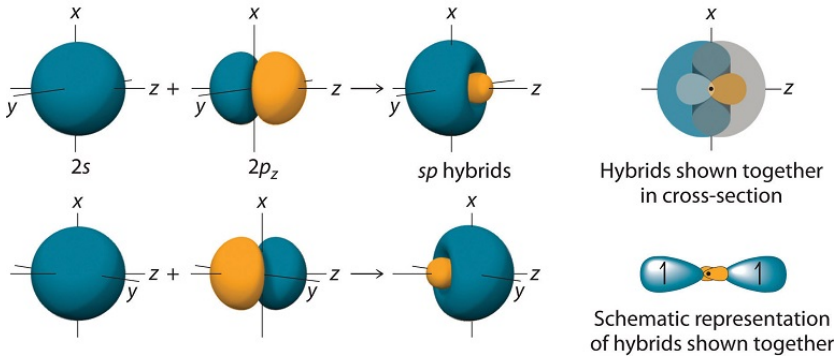


Figure 10.1.3 : The Formation of sp Hybrid Orbitals. Taking the sum and difference of an ns and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

Given that the two sp hybrid orbitals are mirror images of each other, they can overlap with the $1s$ orbital of H (shown in the figure) and create two equal bonds, as needed for BeH_2. Using the valence bond formulation, now, one of the BeH bonds will be described by a wavefunction of the form:

$$\psi_1(1,2) = C_1[\psi_{1s}^{H_1}(1)\chi_1^{Be}(2) + \psi_{1s}^{H_1}(2)\chi_1^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{14.1.24}$$

$$\psi_2(1,2) = C_2[\psi_{1s}^{H_2}(1)\chi_2^{Be}(2) + \psi_{1s}^{H_2}(2)\chi_2^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{14.1.25}$$

In the above wavefunctions, it is clear that H_1 is on the right and H_2 is on the left, based on the directionalities of χ_1 and χ_2.

sp^2 Hybrid Orbitals

For trigonal planar molecules such as BH_3, we start with the electronic configuration of B, which is $1s^2 2s^2 2p_x$, and we promote one of the $2s$ electrons to a $2p_y$ orbital, so that we have $1s^2 2s 2p_x 2p_y$. Suppose the geometry of BH_3 is such that one of the hydrogen atoms lies along the positive x axis. The remaining hydrogen atoms would be in the 3rd and 4th quadrants, respectively (Figure 10.1.4).

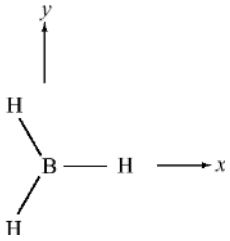


Figure 10.1.4: Geometry of BH_3.

If we simply combine the $2s$ with the $2p_x$ and $2p_y$ orbitals of boron, the resulting hybrid orbitals will not point in the correct direction. For this reason, we will create rotated versions of the p_x and p_y orbitals, which, as we will see are tantamount to taking new combinations of $2p_x$ and $2p_y$ orbitals to combine with the $2s$. Since the rotation occurs in the xy plane, the coordinate that controls this is the azimuthal angle ϕ. For the p_x and p_y orbitals, the ϕ dependence is

$$\psi_{2p_x} \sim \cos\phi \; ; \; \psi_{2p_y} \sim \sin\phi$$

If we rotate $2p_y$ by -30 degrees (Figure 10.1.5 ; blue is positive and red is negative), the ϕ dependence becomes

$$\psi_{2p_y}^{(rot)} \sim \sin(\phi + 30)$$

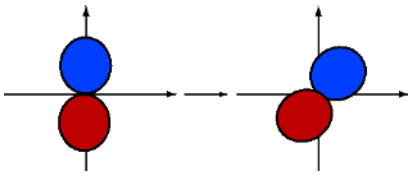


Figure 10.1.5: Rotation of a $2p_y$ orbital by -30 degrees.

Using the fact that

$$\sin(\alpha \pm \beta) = \sin\alpha\cos\beta \pm cos\alpha sin\beta$$

this rotation gives

$$\psi_{2p_y}^{(rot,1)} \sim \sin\phi\cos 30 + \cos\phi\sin 30 \tag{14.1.26}$$

$$\sim \left[\frac{\sqrt{3}}{2}\sin\phi + \frac{1}{2}\cos\phi\right] \tag{14.1.27}$$

$$\sim \left[\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_z}\right] \tag{14.1.28}$$

Similarly, consider rotating $-\psi_{2p_y}$ by $+30$ degrees (Figure 10.1.6). This gives

$$-\psi_{2p_y}^{(rot,2)} \sim -\sin(\phi - 30) \tag{14.1.29}$$

$$\sim -\left[\frac{\sqrt{3}}{2}\sin\phi - \frac{1}{2}\cos\phi\right] \tag{14.1.30}$$

$$\sim -\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_z} \tag{14.1.31}$$

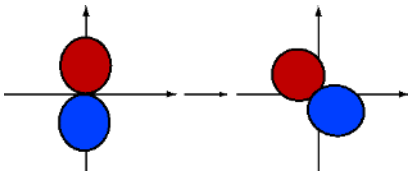


Figure 10.1.6: Rotation of a $-2p_y$ orbital by 30 degrees.

So, we now take the hybrid orbitals to be of the form

$$\chi_1(r) = a\psi_{2s}(r) - b\psi_{2p_x} \tag{14.1.32}$$

$$\chi_2(r) = c\psi_{2s}(r) + d\psi_{2p_y}^{(rot,1)}(r) \tag{14.1.33}$$

$$\chi_3(r) = c\psi_{2s}(r) - d\psi_{2p_y}^{(rot,2)}(r) \tag{14.1.34}$$

The coefficients a, b, and c are determined by requiring that the orbitals are normalized and mutually orthogonal:

$$\int |\chi_1(r)|^2 dV = 1\ ;\ \int \chi_1^*(r)\chi_2(r)dV = 0 \tag{14.1.35}$$

$$\int |\chi_2(r)|^2 dV = 1\ ;\ \int \chi_1^*(r)\chi_3(r)dV = 0 \tag{14.1.36}$$

$$\int |\chi_3(r)|^2 dV = 1\ ;\ \int \chi_2^*(r)\chi_3(r)dV = 0 \tag{14.1.37}$$

Carrying out the algebra, we obtain the following sp^2 hybrid orbitals:

$$\chi_1(r) = \frac{1}{\sqrt{3}}[\psi_{2s}(r) - \sqrt{2}\psi_{2p_x}(r)] \tag{14.1.38}$$

$$\chi_2(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) + \sqrt{3}\psi_{2p_y}(r)] \tag{14.1.39}$$

$$\chi_3(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) - \sqrt{3}\psi_{2p_y}(r)] \tag{14.1.40}$$

The sp^2 hybrids allow bonding at $120°$ degrees, and these orbitals appear as shown in Figure 10.1.7:

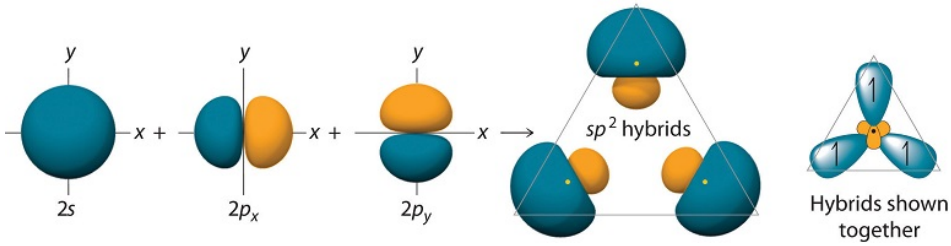


Figure 10.1.7: Formation of sp^2 Hybrid Orbitals. Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

The figure also shows the overlaps of these orbitals with the $1s$ orbitals of H.

sp^3 Hybrid Orbitals

Finally, we consider the case of methane CH_4. The electronic configuration of C is $1s^2 2s^2 2p_x 2p_y$. We now promote one of the $2s$ orbitals to the $2p_z$ orbital and write C as $1s^2 2s 2p_x 2p_y 2p_z$. We can now hybridize the $2s$ orbital with each of the $2p$ orbitals to create four hybrids:

$$\chi_1(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{14.1.41}$$

$$\chi_2(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{14.1.42}$$

$$\chi_3(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{14.1.43}$$

$$\chi_4(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{14.1.44}$$

The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 10.1.8). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

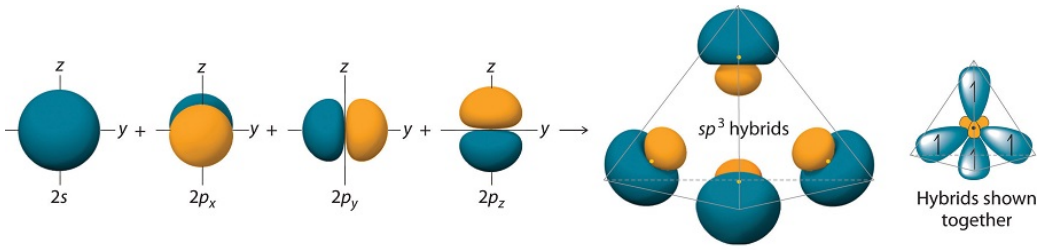


Figure 10.1.8 : Formation of sp^3 Hybrid Orbitals. Combining one ns and three np atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

Are hybrid orbitals Real?

Hybridization is an often misconceived concept. It only is a mathematical interpretation, which explains a certain bonding situation (in an intuitive fashion). In a molecule the equilibrium geometry will result from various factors, such as steric and electronic interactions, and further more interactions with the surroundings like a solvent or external field. The geometric arrangement will not be formed because a molecule is hybridized in a certain way, it is the other way around, i.e. a result of the geometry or more precise and interpretation of the wavefunction for the given molecular arrangement.

The justification we gave for invoking hybridization in molecules such as BeH_2, BF_3 and CH_4 was that the bonds in each are geometrically and chemically equivalent, whereas the atomic *s*- and *p*-orbitals on the central atoms are not. By combining these into new orbitals of *sp*, sp^2 and sp^3 types we obtain the required number of completely equivalent orbitals. This seemed easy enough to do on paper; we just drew little boxes and wrote "sp^2" or whatever below them. But what is really going on here?

The full answer is beyond the scope of this course, so we can only offer the following very general explanation. First, recall what we mean by "orbital": a mathematical function ψ having the character of a standing wave whose square ψ^2 is proportional to the probability of finding the electron at any particular location in space. The latter, the *electron density distribution*, can be observed (by X-ray scattering, for example), and in this sense is the only thing that is "real".

A given standing wave (ψ-function) can be synthesized by combining all kinds of fundamental wave patterns (that is, atomic orbitals) in much the same way that a color we observe can be reproduced by combining different sets of primary colors in various proportions. In neither case does it follow that these original orbitals (or colors) are actually present in the final product. So one could well argue that hybrid orbitals are not "real"; they simply turn out to be convenient for understanding the bonding of simple molecules at the elementary level, and this is why we use them.

Summary

The shape and bonding valecies of polyatomic molecules can be accounted for by hybrid orbitals. Molecular orbitals are formed from linear combinations of atomic orbitals which are similar in energy. These atomic orbitals could come from different atoms, or from the same atom. For example, the 2 sand 2patomic orbitals are very close energetically. When a linear combo of more than one atomic orbital from the **same atom** is formed, we have a hybrid orbital.

14.1: Hybrid Orbitals Account for Molecular Shape is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **10.1: Hybrid Orbitals Account for Molecular Shape** by Mark E. Tuckerman is licensed CC BY-NC-SA 4.0.

14.2: Different Hybrid Orbitals Used for Bonding in Water

The goal of applying Valence Bond Theory to water is to describe the bonding in $\mathbf{H_2O}$ and account for its structure (i.e., appropriate bond angle and two lone pairs predicted from VSEPR theory).

The ground state electronic configuration of atomic oxygen atom is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ and of course the ground state electronic configuration of atomic hydrogen atom is $1s^1$, i.e., a spherical atomic orbital with no preferential orientation. If only the unfilled $2p_y$ and $2p_z$ atomic orbitals of the oxygen were used as bonding orbitals, then two bonds would be predicted. These bonding wavefunctions would be mixture of only $|2p_y\rangle$ and $|2p_z\rangle$ orbitals on oxygen and the $|1s\rangle$ orbitals on the hydrogens (H_1 and H_2):

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + b_1|2p_y\rangle_O \tag{14.2.1}$$

$$|\chi_2\rangle = a_2|1s\rangle_{H_2} + b_2|2p_z\rangle_O \tag{14.2.2}$$

However, with a $\mathbf{H{-}O{-}H}$ bond angle for these bonds would be expected to be 90° since $2p_y$ and $2p_z$ are oriented 90° with respect to each other. Note that $|\chi_1\rangle$ and $|\chi_2\rangle$ are two-center bonding orbitals common to Valence Bond theory.

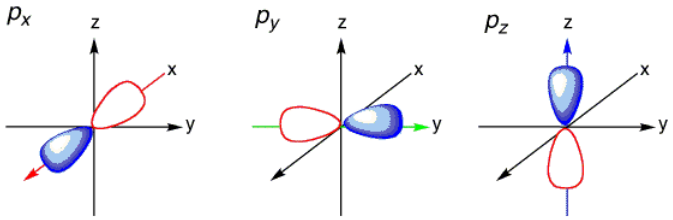


Figure 10.2.1 : The three p-orbitals are aligned along perpendicular axis (CC-SA-BY-NC; Nick Greeves via ChemTube3D);

Using the oxygen atomic orbitals directly is obviously not a good model for describing bonding in water, since we know from experiment that the bond angle for water is 104.45° (Figure 10.2.2), which is also in agreement with VSEPR theory. Since the $2s$ orbital is spherical, mixing some $2s$ character into the $2p_z$ orbitals can adjust the bond angle as discussed previously by creating new hybrid orbitals.

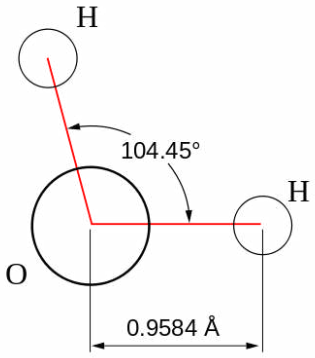


Figure 10.2.2 : Experimentally determined geometry of the water molecule (CC BY-SA 3.0; Booyabazooka).

Historically, Valence Bond theory was used to explain bend angles in small molecules. Of course, it was only qualitatively correct in doing this, as the following example shows. Let us construct the Valence Bond wavefunctions for the two bonding pairs in H_2O by mixing the $|2s\rangle$, $|2p_x\rangle$, $|2p_y\rangle$, and $|2p_z\rangle$ into four new sp^3 hybrid orbitals:

$$\chi_1(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right]$$
$$\chi_2(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right]$$
$$\chi_3(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right]$$
$$\chi_4(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right]$$

Hence, the three $2p$ orbitals of the oxygen atom combined with the $2s$ orbitals of the oxygen to form four sp^3 hybrid orbitals (Figure 10.2.3).

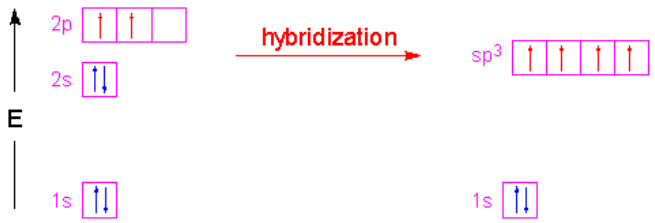


Figure 10.2.4: This would leave the $2s$ and $2p_z$ orbitals of oxygen left over for the two lone pairs on the oxygen.

The bond angle for four groups of electrons around a central atom is 109.5 degrees. However, for water the experimental bond angle is 104.45°. The VSPER picture (general chemistry) for this is that the smaller angle can be explained by the presence of the two lone-pairs of electrons on the oxygen atom. Since they take up more volume of space compared to a bonding pair of electrons the repulsions between lone pairs and bonding pairs is expected to be greater causing the H-O-H bond angle to be smaller than the ideal 109.5°.

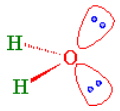


Figure 10.2.4 : Among the four hybrid orbitals, two are half filled and the remaining two are completely filled.

We can rationalize this by thinking about the s and p characters of the hybrids. In a perfectly sp^3 hybridized set of hybrid orbitals, each sp^3 orbital should have: 25% s character and and 75% p character. Since the bond angle is not 109.5° in water, the hybrid orbitals cannot have exactly this ratio of s and p character. So there there is uneven distribution of s and p character between the 4 hybrid orbitals. First we will write down the wavefunction and see what this means and then we will rationalize it.

Estimating Character of Hybrid Orbitals

The terminology we use for hybridization actually is just an abbreviation:

$$\mathrm{sp}^x = \mathrm{s}^{\frac{1}{x+1}}\mathrm{p}^{\frac{x}{x+1}}$$

In theory x can have any value, hence any of the following combinations constitute valid hybridization schemes for 1 s orbital and 3 p orbitals:

$$\begin{aligned} 1\times\mathrm{s}, 3\times\mathrm{p} &\rightsquigarrow 4\times\mathrm{sp}^3 \\ &\rightsquigarrow 3\times\mathrm{sp}^2, 1\times\mathrm{p} \\ &\rightsquigarrow 2\times\mathrm{sp}, 2\times\mathrm{p} \\ &\rightsquigarrow 2\times\mathrm{sp}^3, 1\times\mathrm{sp}, 1\times\mathrm{p} \\ &\rightsquigarrow \text{etc. pp.} \\ &\rightsquigarrow 2\times\mathrm{sp}^4, 1\times\mathrm{p}, 1\times\mathrm{sp}^{(2/3)} \end{aligned}$$

There are virtually infinite possibilities of combinations. Which one is "valid" is only determined by experiment (e.g., structure or spectroscopy). The generic sp^x hybrid orbitals wavefunction can be roughly written in terms of atomic orbital character:

$$|\chi_i\rangle = N(p+\gamma s) \tag{14.2.3}$$

where N is a normalization constant and γ is the relative contribution of s character to the hybrid orbital. For a pure sp^3 hybrid, γ would be 0.25 and for a pure sp hybrid, γ would be 1. The question is how to determine γ to get a better picture of the hybridization of water. Starting with the normalization criteria for wavefunctions:

$$\langle\chi_i|\chi_i\rangle = 1$$

and substituting Equation 14.2.3 into to get

$$\langle N(p+\gamma s)|N(p+\gamma s)\rangle = 1$$

which in integral notation is

$$\int N^2(p+\gamma s)^2 d\tau = 1$$

where $d\tau$ represents all space. This is then expanded to

$$N^2 \cancelto{1}{\int p^2 d\tau} + N^2 2\gamma \cancelto{0}{\int sp\, d\tau} + N^2\gamma^2 \cancelto{1}{\int s^2 d\tau} = 1 \tag{14.2.4}$$

These terms simplify either due to orthogonality or normality of the constitute atomic orbitals. Equation 14.2.4 simplifies to

$$N^2 + N^2\gamma^2 = 1$$

and thus the normalization factor can be expressed in terms of γ

$$N = \frac{1}{\sqrt{1+\gamma^2}}$$

and the generic normalized sp^x hybrid orbital (Equation 14.2.3) is

$$|\chi_i\rangle = \frac{1}{\sqrt{1+\gamma^2}}(p+\gamma s) \tag{14.2.5}$$

The s and p characters to a hybrid orbital are now easy to obtain by squaring $|\chi_i\rangle$

- The magnitude of p-character is

$$\left(\frac{1}{\sqrt{1+\gamma^2}}\right)^2 = \frac{1}{1+\gamma^2} \tag{14.2.6}$$

  as $\gamma \rightarrow 0$, then the p character of the hybrid goes to 100%
- The magnitude of s-character is

$$\left(\frac{1}{\sqrt{1+\gamma^2}}\gamma^2\right)^2 = \frac{\gamma^2}{1+\gamma^2} \tag{14.2.7}$$

  as $\gamma \rightarrow 1$, then the s character of the hybrid goes to 50%

As mentioned above, the geometric arrangement will **not** be formed because a molecule is hybridized in a certain way, it is the other way around. How do we choose the correct value of γ for the hybrid orbitals? The mixing coefficient γ is clearly related to the bond angle θ. Using some simple trigonometric relationships, it can be proven that:

$$\cos\theta = -\gamma^2 \tag{14.2.8}$$

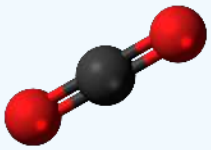
Equation 14.2.8 is an important equation as it related experimentally determined structure to the nature of the bonding and specifically, the composition of the atomic orbitals that create the hybrid orbitals used in the bonding.

✔ Example 10.2.1 : Carbon Dioxide

What is the s-character in the hybrid orbitals for CO_2.

Solution

We know from simple VSEPR theory that the geometry of CO_2 is a linear triatomic molecule.



Thus $\theta = 180°$ and via Equation 14.2.8, $\gamma = 1$ since $\cos 180° = -1$. Hence, Equation 14.2.7 argues that the hybrid orbitals used in the bonding of CO_2 have 50% character; i.e., they are sp hybrid orbitals

$$|\chi_1\rangle = \frac{1}{\sqrt{2}}(s+p)$$

and

$$|\chi_2\rangle = \frac{1}{\sqrt{2}}(s-p)$$

Now, let's apply Equation 14.2.7 to water to find the character of the hybrid orbitals in water. The bond angle in water is 104.45° (Figure 10.2.2) hence

$$\cos 104.5° = -0.25$$

and

$$\gamma = \sqrt{0.25} = 0.5$$

From Equation 14.2.6, then the amount of p character in the hybrid orbitals are

$$\frac{1}{1+\gamma^2} = \frac{1}{1+0.5^2} = 0.80\%$$

which leave 20% for s character (Equation 14.2.7).

$$\frac{\gamma^2}{1+\gamma^2} = \frac{0.5^2}{1+0.5^2} = 0.20$$

The two hybridized atomic orbitals of oxygen involved in bonding are each 80% p and 20% s character. This are not perfect sp^3 hybrid orbitals, as expected. Actually, the orbitals involved in the bonds would be better described as sp^4 hybridized. It does not mean that there are 4 p-orbitals in the hybrid orbital, but that each hybrid consists of 20% of s and 80% of p atomic orbitals.

Lone Pairs

Water has two sets of non-bonding electron pairs (Figure 10.2.4). Without a bond angle to start from, we cannot derive γ that describes the nonbonding hybrid orbitals that they occupy. However, we do know that the O atom has three p orbitals. So the TOTAL absolute p-character in all hybrid orbitals must be 3.

Let x be the p-character in the lone pairs hybrid orbitals:

$$0.8 + 0.8 + x + x = 3$$

This is assuming the lone pairs are **identical**. Solving for this, x = 0.7 (i.e. 70% p and 30% s). From this we can estimate the angle between the lone pair using Equations 14.2.6 and 14.2.8

- p-character:

$$\frac{1}{1+\gamma^2} = 0.7$$

so

$$-\gamma^2 = \frac{1}{0.7-1} = -0.42$$

and $\theta = 115°$.

The angle between the lone pairs is greater (115°) than the bond angle (104.5°). The sp^3 hybrid atomic orbitals of the lone pairs have > 25% s-character. These hybrid orbitals are less directional and held more tightly to the O atom. The sp^3 hybrid atomic orbitals of the bonding pairs have < 25% s-character. They are more directional (i.e., more p-character) and electron density found in the bonding region between O and H.

Warning

> It should be noted that the valence bond theory application described above predicts that the two lone electron pairs are in the same hybrid orbitals and hence have the same energies. As discussed in the next sections, that is not experimentally observed in photoelectron spectroscopy, which is a shortcoming of valence bond theory's application to water.

Contributors and Attributions

- Andrew Wolff (Adjunct Professor of Chemistry)
- Martin (Stackexchange)

14.2: Different Hybrid Orbitals Used for Bonding in Water is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **10.2: Hybrid Orbitals in Water** by LibreTexts is licensed CC BY-NC-SA 4.0.

14.3: Why is BeH_2 Linear and H_2O Bent?

In this section, we will construct approximate molecular orbitals for a water molecule by considering a simple linear triatomic of the general form HXH, where X is a second row element. We will take a multi-centered molecular orbital approach instead of the two-centered valence bond/hybrid approach discussed previously. As with previous discussions of Molecular Orbitals, we approximate them as a linear combinations of atomic orbitals (LCAO). In molecular orbital theory linear combinations of **all** available (atomic) orbitals will form molecular orbitals. These are spread over the whole molecule, or delocalized, and in a quantum chemical interpretation they are called canonical orbitals. Since it is absolutely wrong to assume that there are only three types of sp^x hybrid orbitals, it is possible, that there are multiple different types of orbitals involved in bonding for a certain atom.

AH_2 Molecules

We want to construct a reasonable argument for the energetic ordering and structure of the molecular orbitals. We first note that each H will donate a $1s$ orbital in the LCAO scheme, and A will likely donate at least $2s$ and possible $2p$ orbitals, depending on its chemical identity. In general, if we consider only the first row A elements, the molecule orbitals (via the LCAO) can be expressed as combination of $1s$ orbitals on the two Hydrogens (H_1 and H_2) and the four n=2 orbitals ($2s$ $2p_x$ $2p_y$; $2p_z$) on the A atom:

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_2\,|1s\rangle_{H_2} + a_3|\,2s\rangle_A + a_4\,|2p_x\rangle_A + a_5|\,2p_y\rangle_A + a_6|2p_z\rangle_A \tag{14.3.1}$$

These molecular orbitals were created with six atomic orbitals and hence six different $|\chi\rangle$ molecular orbitals can be created. As with previous molecular orbitals problems, the coefficients of this expansion ($\{a_i\}$) are determined by solving the secular determinant.

If we consider only linear AH_2 molecules, then Equation 14.3.1 can be simplified by ignoring $2p_x$ and $2p_y$ atomic orbitals since they are perpendicular to the bonds and are hence non-bonding (only for linear AH_2 molecules). Moreover, the molecule is symmetric about the center (the position of A), hence the orbitals have to have the same symmetry.

Only the $2p$ orbital of A that will overlap with $1s$ of H is the $2p_z$. Hence, Equation 14.3.1 can be simplified to consider the combination

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_1\,|1s\rangle_{H_2} + a_3|\,2s\rangle_A + a_6|2p_z\rangle_A \tag{14.3.2}$$

Note that the two coefficients in front of the $1s$ orbitals of hydrogen are the same by symmetry. This since no hydrogen is "special" and they must have the same contribution to the molecular orbital.

Mixing Amplitudes

How big should the $2s$ orbital contributors of A be compared to the $1s$ orbital of H?

This depends on several things. First, is the nuclear charge on A and the second is the **electronegativity** difference between H and A. The first determines how quickly the $2s$ orbitals, remembering that the exponential part is $exp(-Zr/a_0)$, and the electronegativity difference determines the relative magnitude of H_1 compared to H_2.

The six $|\chi\rangle$ molecular orbitals from Equation 14.3.1 are shown in Figure 10.3.1 .

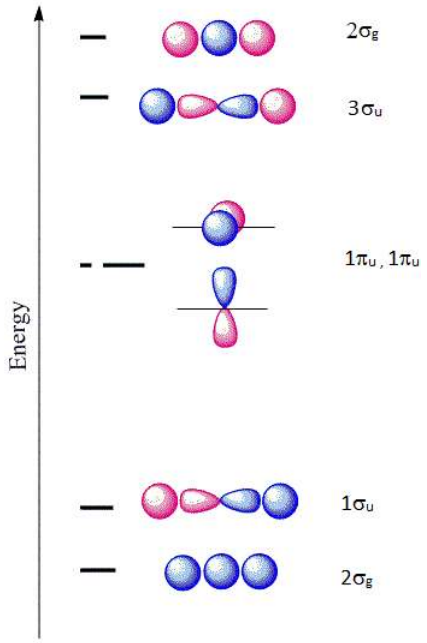


Figure 10.3.1 : The six molecular orbitals for the AH_2 molecule constrained to a linear geometry. The symmetry labels for each molecular orbital are indicated.

The first molecular orbital $|\chi_1\rangle$ constructed from Equation 14.3.1 is purely bonding because the $2s$ orbital is positive near the A nucleus, but becomes negative as we go away from the nucleus. This orbital is also even (*garade symmetry*), so we can denote it as a $2\sigma_g$ orbital signifying that it is constructed from a $2s$ orbital of A combined with the two $1s$ orbitals of H. The only other MO that can be constructed that has the right symmetry is $|\chi_6\rangle$ which is denoted as $2\sigma_u$. This is an antibonding molecular orbital and is also even (*garade symmetry*). The corresponding wavefunctions are:

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A$$

$$|\chi_6\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} - a_3|2s\rangle_A$$

Next, if we combine a $2p_z$ orbital of A with the $1s$ of H, there are two possibilities that have the right symmetry. The first is

$$|\chi_2\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A$$

which is a bonding orbital and denoted as $1\sigma_u$. This is purely antibonding and has an odd symmetry (*ungarede*). The other combination is

$$|\chi_5\rangle = a_1|1s\rangle_{H_1} - a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A$$

Hence, we denote this as $2\sigma_g$. The orbitals $2p_x$ and $2p_y$ from X are nonbonding and become π_{2p_x} and π_{2p_y} nonbonding orbitals and designated as $1\pi_u$ orbitals:

$$|\chi_3\rangle = |2p_x\rangle_A$$

$$|\chi_4\rangle = |2p_y\rangle_A$$

Beryllium Hydride (BeH_2) is Linear

Consider the $\mathbf{BeF_2}$ molecule: Be has a $1s^2\,2s^2$ electron configuration with is no unpaired electrons available for bonding. From a perspective of using only atomic orbitals to generate the bonding orbitals, we would conclude that the molecule could not exist since no free orientals exist on **Be** atom to bond. Clearly, atomic orbitals are not adequate to describe orbitals in molecules, but this can be solved by allowing the 2s and one 2p orbital on **Be** to mix to form sp hybrid orbitals. The experimental **H–Be–H** bond angle is 180°. Presumably, one electron from Be is shared with each unpaired electrons from **H**. We could promote and electron from the

2s orbital on Be to the 2p orbital to get two unpaired electrons for bonding (predicting 90° bond angles, not 180°). Thus the geometry is still not explained with atomic orbitals alone.

Be has 2s and 2p orbitals, and it is in the middle. **H** has 1s orbitals; there are two **H** atoms on the outside. We initially make combinations of the **H** atomic orbitals that we previously used to make diatomic hydrogen, except there is no overlap (i.e., $S = 0$). These combinations will mix with the 2s and $2p_z$ on Be, as shown in Figure 10.3.2.

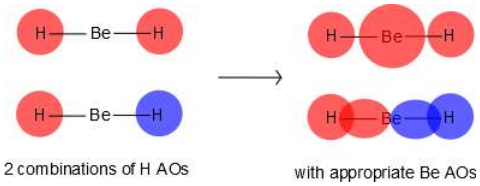


Figure 10.3.2: Forming molecular orbitals for BeH_2.

Then we can put the Molecular Orbital diagram together, starting with the outside, drawing in bonding, non-bonding and anti-bonding MOs, and filling the electrons (Figure 10.3.3). The bond order is 2.

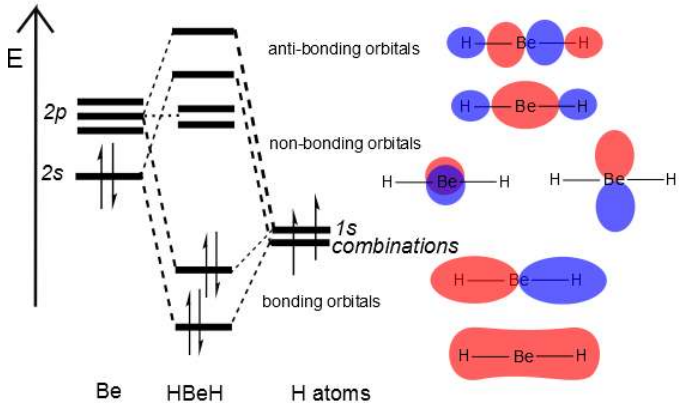


Figure 10.3.3: Molecular orbitals diagram for BeH_2.

Walsh diagrams, often called angular coordinate diagrams or correlation diagrams, are representations of calculated orbital energies of a molecule versus a distortion coordinate, used for making quick predictions about the geometries of small molecules. By plotting the change in molecular orbital levels of a molecule as a function of geometrical change, Walsh diagrams explain why molecules are more stable in certain spatial configurations (i.e. why water adopts a bent conformation).

Walsh Correlation Diagrams

A major application of Walsh diagrams is to explain the regularity in structure observed for related molecules having identical numbers of valence electrons (i.e. why H_2O and H_2S look similar), and to account for how molecules alter their geometries as their number of electrons or spin state changes. Additionally, Walsh diagrams can be used to predict distortions of molecular geometry from knowledge of how the LUMO (Lowest Unoccupied Molecular Orbital) affects the HOMO (Highest Occupied Molecular Orbital) when the molecule experiences geometrical perturbation. Walsh's rule for predicting shapes of molecules states that a molecule will adopt a structure that best provides the most stability for its HOMO. If a particular structural change does not perturb the HOMO, the closest occupied molecular orbital governs the preference for geometrical orientation.

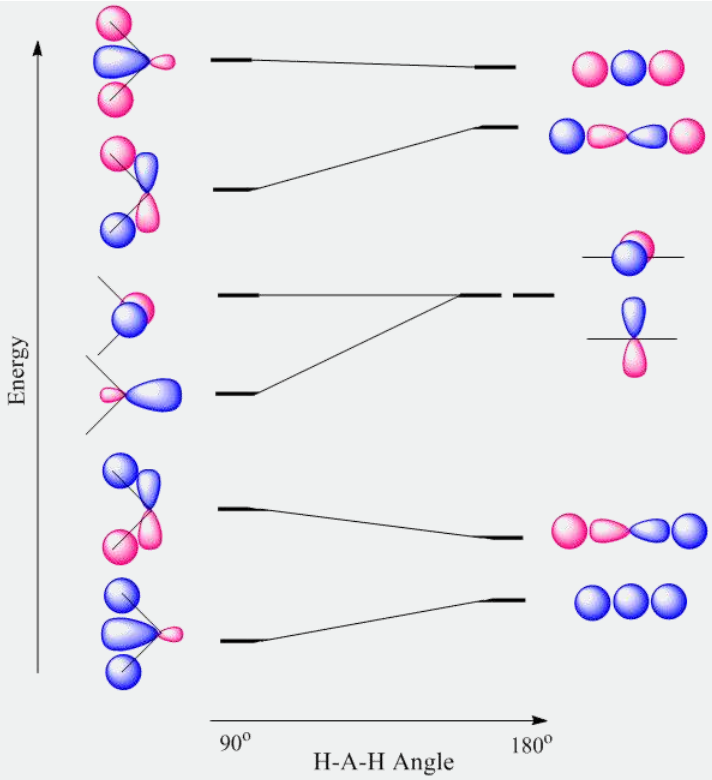


Figure 10.3.4: A Walsh diagram for an $\mathbf{AH_2}$ molecule. (public domain).

For the $\mathbf{AH_2}$ molecular system, Walsh produced the first angular correlation diagram by plotting the orbital energy curves for the canonical molecular orbitals while changing the bond angle from 90° to 180° (Figure 10.3.4). As the bond angle is distorted, the energy for each of the orbitals can be followed along the lines, allowing a quick approximation of molecular energy as a function of conformation.

A typical prediction result for water is an bond angle of 90°, which is not even close to the experimental value of 104°. At best, the method is able to differentiate between a bent and linear molecule.

> *Walsh's rule for predicting shapes of molecules states that a molecule will adopt a structure that best provides the most stability for its HOMO. If a particular structural change does not perturb the HOMO, the closest occupied molecular orbital governs the preference for geometrical orientation.*

Figure 10.3.4 illustrates the difference between the actual linear case we just analyzed and the truly bent molecule, e.g. $\mathbf{H_2O}$. The geometry changes the ordering somewhat, but the qualitative picture we obtain from the linear case makes it a useful construction. The oxygen atomic orbitals are labeled according to their symmetry (Figure 10.3.5) as a_1 for the 2s orbital and b_1 ($2p_x$), b_2 ($2p_y$) and a_1 ($2p_z$) for the three 2p orbitals. The two hydrogen 1s orbitals are premixed to form a_1 and b_2 molecular orbitals.

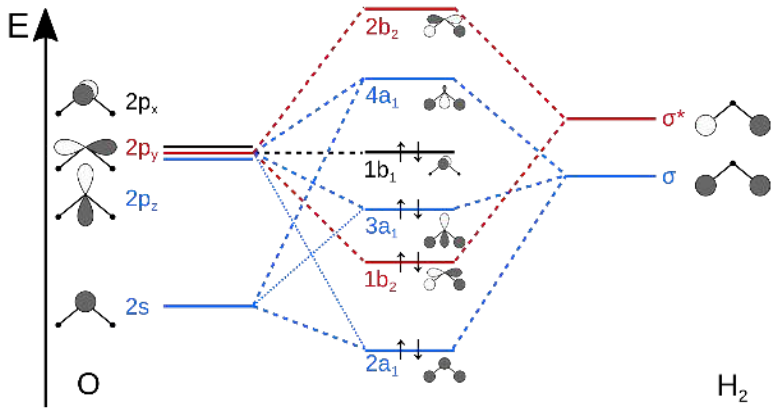


Figure 10.3.5: MO diagram for water. (CC-SA-BY-3.0; Officer781).

Mixing takes place between same-symmetry orbitals of comparable energy resulting a new set of MO's for water:

- $2a_1$ MO from mixing of the oxygen 2s atomic orbital and the hydrogen σ MO. Small oxygen $2p_z$ atomic orbital admixture strengthens bonding and lowers the orbital energy.
- $1b_2$ MO from mixing of the oxygen $2p_y$ atomic orbital and the hydrogen σ* MO.
- $3a_1$ MO from mixing of the oxygen $2p_z$ atomic orbital and the hydrogen σ MO. Small oxygen 2s atomic orbital admixture weakens bonding and raises the orbital energy.
- $1b_1$ nonbonding MO from the oxygen $2p_x$ atomic orbital (the p-orbital perpendicular to the molecular plane).

In the water molecule the highest occupied orbital, $(\mathbf{1b_1})$ is non-binding and highly localized on the oxygen atom, similar to the non-bonding orbitals of hydrogen fluoride. The next lowest orbital $(\mathbf{2a_1})$ can be thought of as a non-bonding orbital, as it has a lobe pointing away from the two hydrogens. From the lower energy bonding orbitals, it is possible to see that oxygen also takes more than its "fair share" of the total electron density. The electronic configuration of water in the ground state (Figure 10.3.5) is therefore

$$(a_1)^2(b_2)^2(a_1)^2(b_1)^2$$

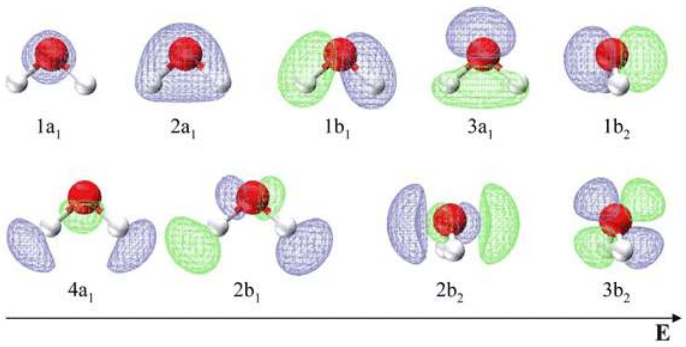


Figure 10.3.5. Image from Anna Krylov (USC)

Table 10.3.1 list the respective LCAO coefficients for the six atomic orbitals. Table 10.3.1 combines the energy values with the description derived from the character table for molecules of point group C_{2v}

Table 10.3.1: LCAO Coefficients of first six molecular orbitals of water

Energy	Symbol	s(H)	s(O)	p_x(O)	p_y(O)	p_z(O)	s(H)
6.728	$2b_2$	0.525	0	0	-0.669	0	-0.525
5.440	$3a_1$	-0.553	0.306	0	0	-0.544	0.553
-12.191	$1b_1$	0	0	-1.000	0	0	0
-14.467	$2a_1$	-0.309	0.354	0	0	0.827	-0.309
-19.113	$1b_2$	-0.473	0	0	-0.743	0	0.473
-40.032	$1a_1$	0.315	0.884	0	0	-0.143	0.315

Note in contrast to the valence bond theory discussed previous for water, the two lone electron pairs are **not in identical orbitals**. The $1b_1$ MO is a lone pair, while the $3a_1$, $1b_2$ and $2a_1$ MO's can be localized to give two O−H bonds and an in-plane lone pair. This is in agreement with the experimentally measured photoelectron spectrum discussed in the next section.

Summary

Walsh correlation diagram is a plot of molecular orbital energy as a function of some systematic change in molecular geometry. For example, the correlation between orbital energies and bond angle for an $\mathbf{AH_2}$ molecule. The geometry of a molecule is determined by which possible structure is lowest in energy. We can use the Walsh diagram to determine the energy trends based on which orbitals are occupied.

14.3: Why is BeH_2 Linear and H_2O Bent? is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **10.3: BeH_2 is Linear and H_2O is Bent** by Emily V Eames, Mark Tuckerman is licensed CC BY-NC-SA 4.0.

14.4: Photoelectron Spectroscopy

Learning Objectives

- Demonstrate how photoelectron spectroscopy can be used to resolve the absolute energies of molecular orbitals.

Photoelectron spectroscopy (PES) utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample.

- **X-ray Photoelectron Spectroscopy** (XPS) uses soft x-rays (with a photon energy of 200-2000 eV) to examine electrons in *core*-levels.
- **Ultraviolet Photoelectron Spectroscopy** (UPS) using vacuum UV radiation (with a photon energy of 10-45 eV) to examine electrons in *valence* levels.

Both photoelectron spectroscopies are based upon a single photon in/electron out process. The energy of a photon of all types of electromagnetic radiation is given by the Planck–Einstein relation:

$$E = h\nu \tag{14.4.1}$$

where h is Planck constant and ν is the frequency (Hz) of the radiation. UPS is a powerful technique to exam molecular electron structure since we are interested in the molecular orbitals from polyatomic molecules (especially the valence orbitals) and is the topic of this page.

Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy). In UPS the photon interacts with valence levels of the molecule or solid, leading to ionization by removal of one of these valence electrons. The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.

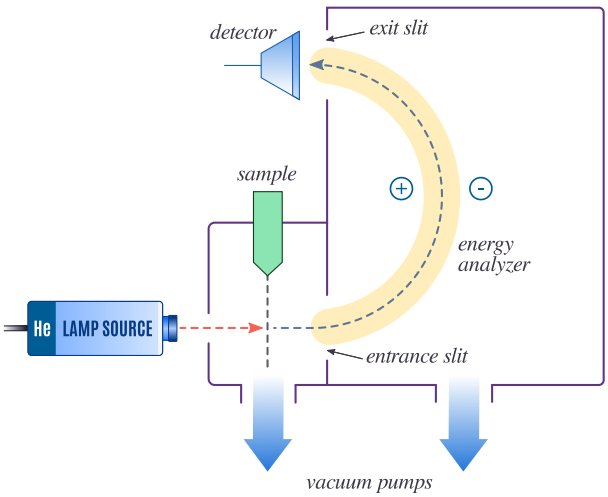


Figure 10.4.1: Diagram of a basic, typical PES instrument used in UPS, where the radiation source is an UV light source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit. (CC BY 4.0; Ümit Kaya via LibreTexts)

The process of photoionization can be considered in several ways. One way is to look at the overall process for a species A:

$$A + \text{photon} \rightarrow A^+ + e^- \tag{14.4.2}$$

Conservation of energy then requires that (after using Equation 14.4.1):

$$E(A) + h\nu = E(A^+) + E(e^-) \tag{14.4.3}$$

Since the free electron's energy is present solely as kinetic energy (KE) (i.e., there is no internal energy in a free electron)

$$E(e^-) = KE$$

Equation 14.4.3 can then be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - [E(A^+) - E(A)] \tag{14.4.4}$$

The final term in brackets represents the difference in energy between the ionized and neutral species and is generally called the **vertical ionization energy** (IE) of the ejected electron; this then leads to the following commonly quoted equations:

$$KE = h\nu - IE \tag{14.4.5}$$

or

$$IE = h\nu - KE \tag{14.4.6}$$

The vertical ionization energy is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (i.e., a free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

Note

Equation 14.4.5 may look familiar to you as it the same equation Einstein used to describe the photoelectric effect except the vertical ionization energy (IE) is substituted for workfunction Φ. Both vertical ionization energy and workfunctions are metrics for the binding energy of an electron in the sample.

At a fundamental level, ionization energies are well-defined thermodynamic quantities related to the heats of protonation, oxidation/reduction chemistry, and ionic and covalent bond energies. Ionization energies are closely related to the concepts of electronegativity, electron-richness, and the general reactivity of molecules. The energies and other characteristic features of the ionization bands observed in photoelectron spectroscopy provide some of the molecular orbitals detailed and specific quantitative information regarding the electronic structure and bonding in molecules.

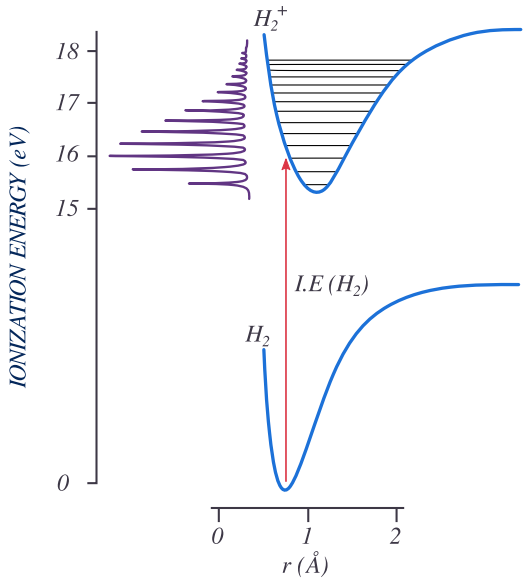


Figure 10.4.2: Vertical ionization process for molecular hydrogen. (CC BY 4.0; Ümit Kaya via LibreTexts)

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states as shown in Equation 14.4.6 and as illustrated in the Figure 10.4.2. Nonetheless, the information obtained from photoelectron spectroscopy is typically discussed in terms of the electronic structure and bonding in the ground states of neutral molecules, with ionization of electrons

occurring from bonding molecular orbitals, lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals by Koopmans' theorem, which states that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the *vertical ionization energy* to the ion state formed by removal of an electron from that orbital (Figure 10.4.3), provided the distributions of the remaining electrons do not change (i.e., frozen).

$$I_j = -\epsilon_j \tag{14.4.7}$$

There are many limitations to Koopmans' theorem, but in a first order approximation each ionization of a molecule can be considered as removal of an electron from an individual orbital. The ionization energies can then be considered as measures of orbital stabilities, and shifts can be interpreted in terms of orbital stabilizations or destabilizations due to electron distributions and bonding. Koopmans' theorem is implicated whenever an orbital picture is involved, but is not necessary when the focus is on the total electronic states of the positive ions.

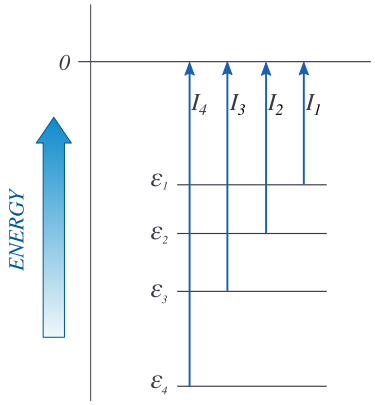


Figure 10.4.3: Within Koopmans' Theorem, the energies of the orbitals ϵ have an attractively simple physical interpretation: they give the amount of energy necessary to remove (ionize) the electron out of the molecular orbital, which corresponds to the negative of the experimentally observable ionization potential (I). (CC BY 4.0; Ümit Kaya via LibreTexts)

Koopmans' Theorem

Koopmans' theorem argues that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the vertical ionization energy to the ion state formed by removal of an electron from that orbital.

Several different ionization energies can be defined, depending on the degree of vibrational excitation of the cations. In general, the following two types of ionization energies are considered (Figure 10.4.4):

- Adiabatic ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v''=0) + h\nu \rightarrow M^+(x, v'=0) + e^-$$

  Adiabatic ionization energy that is, the minimum energy required to eject an electron from a molecule in its ground vibrational state and transform it into a cation in the lowest vibrational level of an electronic state x of the cation.
- Vertical ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v''=0) + h\nu \rightarrow M^+(x, v'=n) + e^-$$

  where, the value n of the vibrational quantum number v' corresponds to the vibrational level whose wavefunction gives the largest overlap with the v" = 0 wavefunction. This is the most probable transition and usually corresponds to the vertical transition where the internuclear separations of the ionic state are similar to those of the ground state.

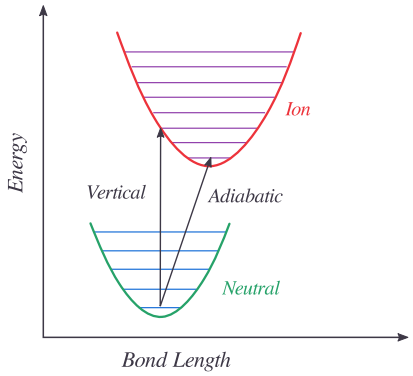


Figure 10.4.4: Difference between vertical and adiabatic ionization energies for a simple harmonic oscillator system. (CC BY 4.0; Ümit Kaya via LibreTexts)

The geometry of an ion may be different from the neutral molecule. The measured ionzation energy in a PES experiment can refer to the vertical ionization energy, in which case the ion is in the same geometry as the neutral, or to the adiabatic ionzaiton energy, in which case the ion is in its lowest energy, relaxed geometry (mostly the former though). This is illustrated in the Figure 10.4.4. For a diatomic the only geometry change possible is the bond length. The figure shows an ion with a slightly longer bond length than the neutral. The harmonic potential energy surfaces are shown in green (neutral) and red (ion) with vibrational energy levels. The vertical ionzation energy is **always greater** than the adiabatic ionzation energy.

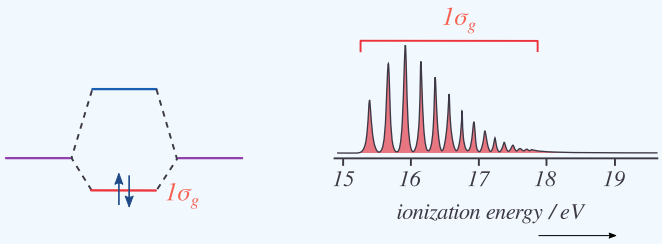
Differing Ionization Energies

You have been exposed to three metrics of ionization energies already, which are similar, but with distinct differences:

- The *ionization energy* (also called *adiabatic ionization energy*) is the lowest energy required to effect the removal of an electron from a molecule or atom, and corresponds to the transition from the lowest electronic, vibrational and rotational level of the isolated molecule to the lowest electronic, vibrational and rotational level of the isolated ion.
- The *binding energy* (also called *vertical ionization energy*) is the energy change corresponding to an ionization reaction leading to formation of the ion in a configuration which is the same as that of the equilibrium geometry of the ground state neutral molecule.
- The *workfunction* is the minimum energy needed to remove an electron from a (bulk) solid to a point in the vacuum.

Example 10.4.1: Molecular Hydrogen

As you remember, the molecular orbital description of molecular hydrogen involves two $|1s\rangle$ atomic orbitals generating a bonding $1\sigma_g$ and antibonding $2\sigma_u^*$ molecular orbitals. The two electrons that are responsible for the H_2 bond are occupied in the $1\sigma_g$.



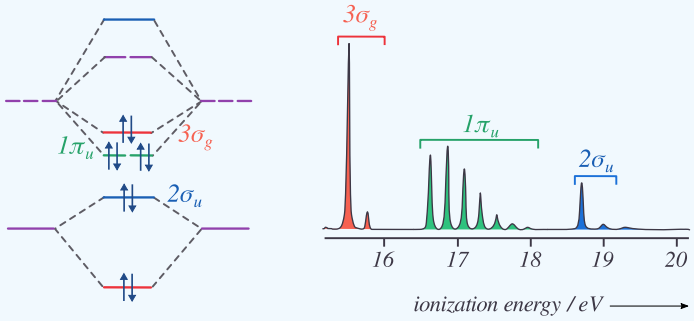
MO diagram and PES spectrum of H_2. (CC BY 4.0; Ümit Kaya via LibreTexts)

The PES spectrum has a single band that corresponds to the ionization of a $1\sigma_g$ electron. The multiple peaks are due to electrons ejecting from a range of stimulated vibrational energy levels. When extensive vibrational structure is resolved in a

PES molecular orbital, then the removal of an electron from that molecular orbital induces a significant change in the bonding (in this case an increase in the bond length since the bond order has been reduced).

Example 10.4.2: Molecular Nitrogen

Diatomic nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Four molecular orbitals are occupied (the two $1\pi_u$ orbitals are both occupied). The UV photoelectron spectrum of N_2, has three bands corresponding to $3\sigma_g$, $1\pi_u$ and $2\sigma_u$ occupied molecular orbitals. Both $3\sigma_g$ and $2\sigma_u$ are weakly bonding and antibonding. The $1\sigma_g$ orbital is not resolved in this spectrum since the incident light $h\nu$ used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital.



MO diagram and PES spectrum of N_2. (CC BY 4.0; Ümit Kaya via LibreTexts)

Note that extensive vibrational structure for the $1\pi_u$ band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.

Hydrogen Chloride

The molecular energy level diagram for HCl is reproduced in Figure 10.4.5

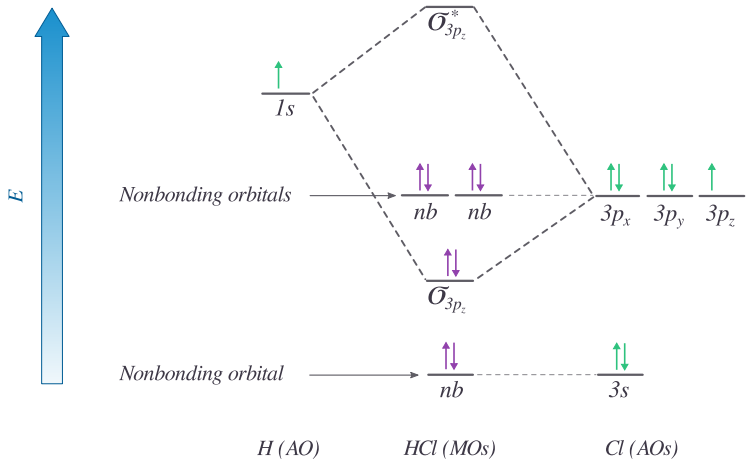


Figure 10.4.5: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts molecular orbitals strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1. (CC BY 4.0; Ümit Kaya via LibreTexts)

Important aspects of molecular orbital diagram in Figure 10.4.5:

- The H 1*s* energy lies well above the Cl 2*s* and 2*p* atomic orbitals;
- The valence electron configuration can be written $3\sigma^2 1\pi^4$;

- The H 1*s* orbital contributes only to the σ molecular orbitals, as does one of the Cl 2*p* orbitals (hence the lines in Figure 10.4.5 connecting these atomic orbitals and the 3σ and 4σ molecular orbitals);
- The remaining Cl 2*p* orbitals (ie those perpendicular to the bond axis) are unaffected by bonding, and these form the 1π molecular orbitals;
- The 1π orbitals are nonbonding - they are not affected energetically by the interaction between the atoms, and are hence neither bonding nor antibonding;
- The 3σ orbital is weakly bonding, and largely Cl 2*p*;
- The 3σ* orbital is antibonding, and primarily of H 1*s* character;

Figure 10.4.6 shows the analogous MO diagram and photoelectron spectrum for **HCl**. The spectrum has two bands corresponding to non-bonding 1*p* (or 1π) molecular orbitals (with negligible vibrational structure) and the 3*s* bonding molecular orbital (vibrational structure).

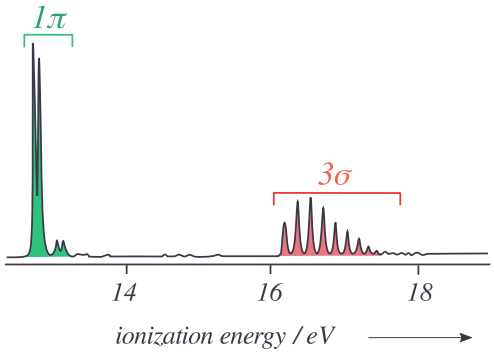


Figure 10.4.6: Photoelectron spectrum **HCl**. (CC BY 4.0; Ümit Kaya via LibreTexts)

The higher energy (more stabilized) core molecular orbitals are not observed since the incident photon energy $h\nu$ is below their ionization energies.

Water

In the simplified valence bond theory perspective of the water molecule, the oxygen atom form four sp^3 hybrid orbitals. Two of these are occupied by the two lone pairs on the oxygen atom, while the other two are used for bonding. Within the molecular orbital picture, the electronic configuration of the H_2O^+ molecule is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ where the symbols a_1, b_2 and b_1 are orbital labels based on molecular symmetry that will be discussed later (Figure 10.4.7). Within Koopmans' theorem:

- The energy of the $1b_1$ HOMO corresponds to the ionization energy to form the H_2O^+ ion in its ground state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1$.
- The energy of the second-highest molecular orbitals $3a_1$ refers to the ion in the excited state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^2$.

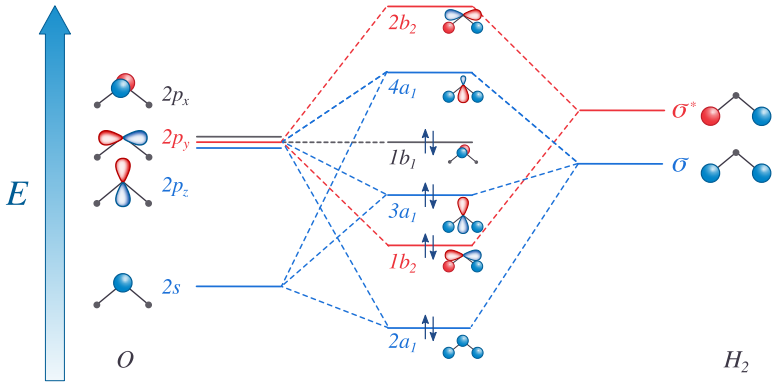


Figure 10.4.7: MO diagram for water. (CC BY 4.0; Ümit Kaya via LibreTexts)

The Hartree–Fock orbital energies (with sign changed) of these orbitals are tabulated below and compared to the experimental ionization energies.

Molecular orbital	Hartree–Fock orbital Energies (eV)	Experimental Ionization Energies (eV)
$2a_1$	36.7	32.2
$1b_2$	19.5	18.5
$3a_1$	15.9	14.7
$1b_1$	13.8	12.6

As explained above, the deviations between orbital energy and ionization energy is small and due to the effects of orbital relaxation as well as differences in electron correlation energy between the molecular and the various ionized states.

The molecular orbital perspective has the lone pair in different orbitals (one in a non-bonding orbital ($1b_1$ and one in the bonding orbitals). We tern to the photoelectron spectroscopy to help identify which theory is more accurate (i.e., describes reality better). The photoelectron spectrum of water in Figure 10.4.6 can be interpreted as having three major peaks with some fine structure arises from vibrational energy changes. The light source used in this experiment is not sufficiently energetic to ionize electrons from the lowest lying molecular orbitals.

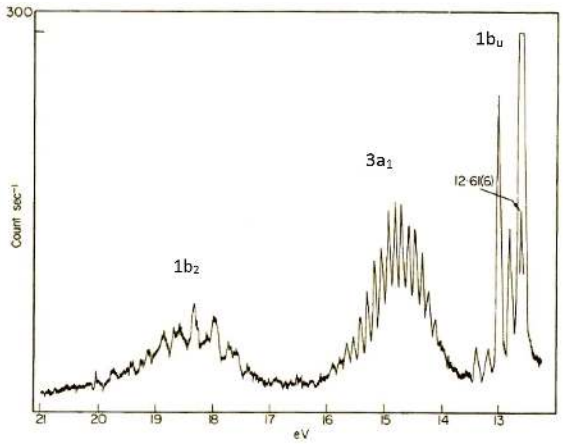


Figure 10.4.8: Photoelectron spectrum of water. Note the energy axes is flipped compared to other spectra on this page. This spectrum does not go to high enough energy to show the deep $2a_1$ molecular orbital.

If water was formed two identical O-H bonds and two lone pairs on the oxygen atom line valence bond theory predicts, then the PES in Figure 10.4.8 would have two (degenerate) peaks, one for the two bonds and one for the two lone pairs. The photoelectron spectrum clearly shows three peaks in the positions expected for the molecular orbitals in Figure 10.4.8.

If the molecular orbitals in Figure 10.4.7 represent the real electronic structure, how do we view the bonding? These molecular orbitals are delocalized and bare little relationship to the familiar 2-center bonds used in valence bond theory. For example, the $2a_1$ $1b_1$ and $3a_1$ molecular orbitals all have contributions from all three atoms, they are really 3-centered molecular orbitals. The bonds however can be thought of as representing a build up of the total electron density which loosely put is a total of all the orbital contributions. Despite this, we keep the ideas of hybridization and 2-center bonds because they are useful NOT because they represent reality

Summary

A photoelecton spectrum can show the relative energies of occupied molecular orbitals by ionization. (i.e. ejection of an electron). A photoelectron spectrum can also be used to determine energy spacing between vibrational levels of a given electronic state. Each orbital energy band has a structure showing ionization to different vibrational levels.

14.4: Photoelectron Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **10.4: Photoelectron Spectroscopy** by Roger Nix is licensed CC BY 4.0.

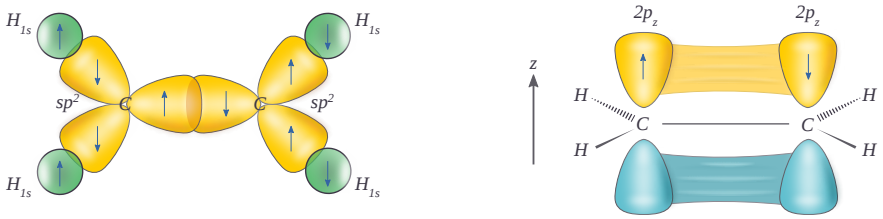
14.5: The π -Electron Approximation of Conjugation

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.

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).

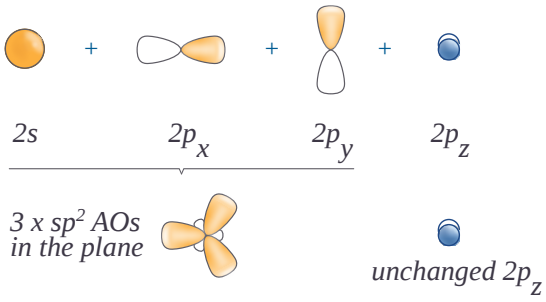


Figure 10.5.2 : Hybridizing of the carbon atomic orbitals to give sp^2 hybrid orbitals for bonding to hydrogen atoms in ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

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 ith molecular orbital can be described via hybrid orbitals

$$|\psi_1\rangle = c_1|sp_1^2\rangle + c_2|1s_a\rangle$$

or via atomic orbitals.

$$|\psi_1\rangle = a_1|2s\rangle + a_1\,|2p_x\rangle + a_1|\,2p_y\rangle + a_4|1s_a\rangle$$

where $\{a_i\}$ and $\{c_i\}$ are coefficients of the expansion. Either describe will work and both are identical approaches since

$$|sp_1^2\rangle = b_1|2s\rangle + b_1\,|2p_x\rangle + b_1|\,2p_y\rangle$$

where $\{c_i\}$ are coefficients describing the hybridized orbital.

The bonding occurs via the mixing of the electrons in the sp^2 hybrid orbitals on carbon and the electrons in the $1s$ atomic orbitals of the four hydrogen atoms (Figure 10.5.1 ; left) resulting in the σ-bonding framework. The π-bonding framework results from the unhybridized $2p_z$ orbitals (Figure 10.5.2 ; right). The independence of these two frameworks is demonstrated in the resulting molecular orbital diagram in Figure 10.5.3 ; Hückel theory is concerned only with describing the molecular orbitals and energies of the π bonding framework.

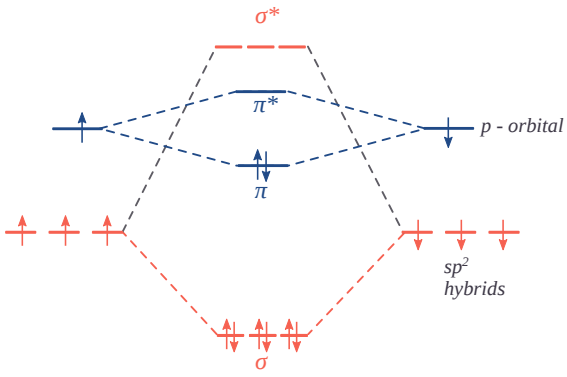


Figure 10.5.3 : Molecular orbitals demonstrating the sigma-pi separability of the π-bonding framework (blue) and the σ-bonding frameworks (red) of ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

> *Hückel treatment is concerned only with describing the molecular orbitals and energies of the π bonding framework.*

Since Hückel theory is a special consideration of molecular orbital theory, the molecular orbitals $|\psi_i\rangle$ can be described as a linear combination of the $2p_z$ atomic orbitals ϕ at carbon with their corresponding $\{c_i\}$ coefficients:

$$|\psi_i\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \tag{14.5.1}$$

This equation is substituted in the Schrödinger equation:

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$$

with $\hat{H}$ the Hamiltonian and E_i the energy corresponding to the molecular orbital to give:

$$\hat{H}c_1|\phi_1\rangle + \hat{H}c_2|\phi_2\rangle = Ec_1|\phi_1\rangle + Ec_2|\phi_2\rangle \tag{14.5.2}$$

If Equation 14.5.2 is multiplied by $\langle\phi_1|$ (and integrated), then

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{14.5.3}$$

where H_{ij} are the Hamiltonian matrix elements (see note below)

$$H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle\phi_i|\phi_j\rangle = \int \phi_i \phi_j \mathrm{d}v$$

If Equation 14.5.2 is multiplied by $\langle\phi_2|$ (and integrated), then

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \tag{14.5.4}$$

Both Equations 14.5.3 and 14.5.4 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.

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{14.5.5}$$

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 14.5.5 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 14.5.5 will also have a non-trivial solution, if and only if, the secular determinant is zero

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{14.5.6}$$

or in shorthand notation

$$\det(H - ES) = 0$$

Everything in Equation 14.5.6 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 14.5.1). However, if more than two $|\phi\rangle$ atomic orbitals were used, e.g., in a bigger molecule, then more energies would be estimated by solving the secular determinant.

Solving the secular determinant is simplified within Hückel method via the following four assumptions:

1. All overlap integrals S_{ij} are set equal to zero. This is quite reasonable since the $\pi-$ orbitals are directed perpendicular to the direction of their bonds (Figure 10.5.1). This assumption is often call neglect of differential overlap (NDO).

2. All resonance integrals H_{ij} between non-neighboring atoms are set equal to zero.
3. All resonance integrals H_{ij} between neighboring atoms are equal and set to β.
4. All coulomb integrals H_{ii} are set equal to α.

These assumptions are mathematically expressed as

$$H_{11} = H_{22} = \alpha$$

$$H_{12} = H_{21} = \beta$$

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 14.5.5 in two homogeneous equations:

$$\begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{14.5.7}$$

if Equation 14.5.7 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

$$x = \frac{\alpha - E}{\beta} \tag{14.5.8}$$

then Equation 14.5.7 simplifies to

$$\begin{bmatrix} x & 1 \\ 1 & x \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{14.5.9}$$

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 14.5.8, 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: $E_2 = \alpha - \beta$

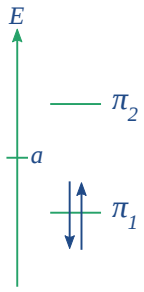


Figure 10.5.4 : π energies of ethylene with occupation. (CC BY-NC; Ümit Kaya via LibreTexts)

To extract the coefficients attributed to these energies, the corresponding x values can be substituted back into the Secular Equations (Equation 14.5.9). 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 14.5.1):

$$|\psi_1\rangle = N_1(|\phi_1\rangle + |\phi_2\rangle) \tag{14.5.10}$$

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 14.5.1):

$$\psi_2\rangle = N_2(|\phi_1\rangle - |\phi_2\rangle) \tag{14.5.11}$$

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.

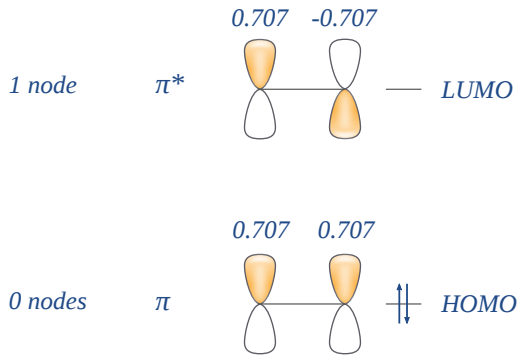


Figure 10.5.5 : Schemetic representation of the π molecular orbitals framework for ethylene . Notice that the antibonding molecular orbital has one more node than the bonding molecular orbital as expected since it is higher in energy. (CC BY-NC; Ümit Kaya via LibreTexts)

> *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 .

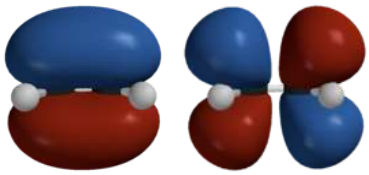


Figure 10.5.6 : Calculated π molecular orbitals for ethylene . (left) the bonding orbital (|\psi_1 \rangle\) and (right) the antibonding ($|\psi_2\rangle$ orbital.

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.

14.5: The π-Electron Approximation of Conjugation is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

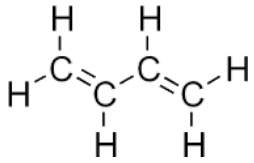
- **10.5: The pi-Electron Approximation of Conjugation (Hückel Theory)** by Seymour Blinder is licensed CC BY-NC-SA 4.0.

14.6: 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

$$|\psi_i\rangle = c_{i1}|p_1\rangle + c_{i2}\,|p_2\rangle + c_{i3}|\,p_3\rangle + c_{i4}|p_4\rangle \tag{14.6.1}$$

for the ith molecular orbital $|\psi_i\rangle$. The secular equations that need to be solved are

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{14.6.2}$$

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 14.6.2 become

$$\begin{bmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{14.6.3}$$

Solving Equation 14.6.3 for $\{c_i\}$ coefficients and energy secular equation requires extracting the roots of the secular determinant:

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0 \tag{14.6.4}$$

If both sides of Equation 14.6.4 were divided by β^4 and a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{14.6.5}$$

then Equation 14.6.4 simplifies further to

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{14.6.6}$$

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 14.6.6 gives the 4th order polynomial equation

$$x^4 - 3x^2 + 1 = 0 \tag{14.6.7}$$

While solving 4th order equations typically require numerical estimation, Equation 14.6.7 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):

$$E_1 = \alpha + 1.618\beta \tag{14.6.8}$$

$$E_2 = \alpha + 0.618\beta \tag{14.6.9}$$

$$E_3 = \alpha - 0.618\beta \tag{14.6.10}$$

$$E_4 = \alpha - 1.618\beta \tag{14.6.11}$$

This sequence of energies is displayed in the energy diagram of Figure 10.6.1 .

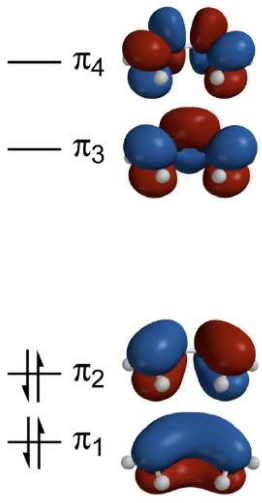


Figure 10.6.1 : The π molecular orbital energies from Hückel theory for butadiene with ground-state configuration. Structures calculated and images produced using HF/6-31G* (Public Domain; Ben Mills).

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 14.6.8-14.6.11 and scaling by their occupations to get

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_1 + 2\times E_2 + 0\times E_3 + 0\times E_4 \\ &= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) \\ &= 4\alpha + 4.472\beta \end{aligned} \tag{14.6.12}$$

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:

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_\pi(\text{ethylene}) \\ &= 2\times 2(\alpha+\beta) \\ &= 4\alpha + 4\beta \end{aligned} \tag{14.6.13}$$

Comparing Equation 14.6.12 with Equation 14.6.12, 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.

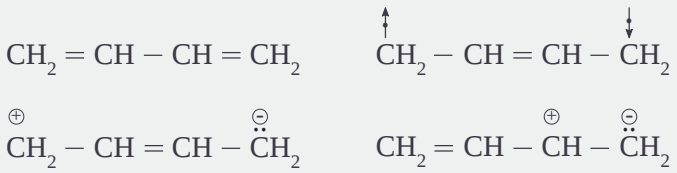


Figure 10.6.2 : Several resonance structures that can be written for 1,3-butadiene. The resonance structure in the upper left dominates, but does not exclusively describe the system since a delocalization energy is experimentally observed compared to two ethylene molecules. (CC BY-NC; Ümit Kaya via LibreTexts)

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 14.6.2) gives the $\{c_{ij}\}$ coefficients for the molecular orbitals in Equation 14.6.1 (not demonstrated):

$$|\psi_1\rangle = 0.37|p_1\rangle + 0.60\,|p_2\rangle + 0.60|\,p_3\rangle + 0.37|p_4\rangle \tag{14.6.14}$$

$$|\psi_3\rangle = 0.60|p_1\rangle + 0.37\,|p_2\rangle - 0.37|\,p_3\rangle - 0.60|p_4\rangle \tag{14.6.15}$$

$$|\psi_3\rangle = 0.60|p_1\rangle - 0.37\,|p_2\rangle - 0.37|\,p_3\rangle + 0.60|p_4\rangle \tag{14.6.16}$$

$$|\psi_4\rangle = 0.37|p_1\rangle - 0.60\,|p_2\rangle + 0.60|\,p_3\rangle - 0.37|p_4\rangle \tag{14.6.17}$$

These are depicted in Figure 10.6.3 .

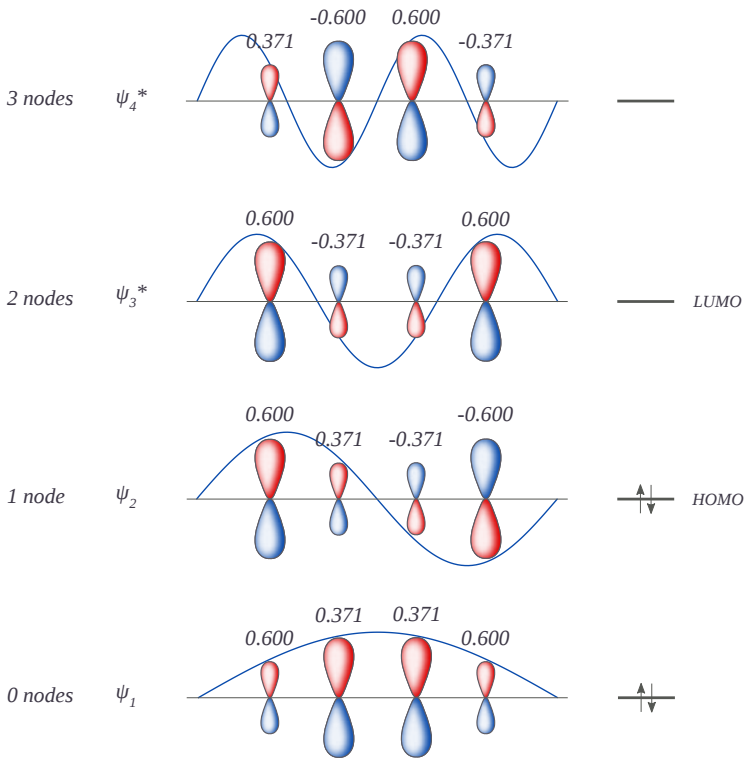


Figure 10.6.3 : Energy level diagram and decomposition of the π molecular orbitals of butadiene. This is view three-dimensionally in Figure 10.6.1 . (CC BY-NC; Ümit Kaya via LibreTexts)

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?

14.6: Butadiene is Stabilized by a Delocalization Energy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **10.6: Butadiene is Stabilized by a Delocalization Energy** by Delmar Larsen is licensed CC BY-SA 4.0.

CHAPTER OVERVIEW

15: Computational Quantum Chemistry

Computational chemistry is a branch of chemistry that uses computer simulation to assist in solving chemical problems. It uses methods of theoretical chemistry, incorporated into efficient computer programs, to calculate the structures and properties of molecules and solids. Its necessity arises from the fact that — apart from relatively recent results concerning the hydrogen molecular ion (see references therein for more details) — the quantum many-body problem cannot be solved analytically, much less in closed form. While computational results normally complement the information obtained by chemical experiments, it can in some cases predict hitherto unobserved chemical phenomena. It is widely used in the design of new drugs and materials.

15.1: Overview of Quantum Calculations
15.2: Gaussian Basis Sets
15.3: Extended Basis Sets
15.4: Orbital Polarization Terms
15.5: The Ground-State Energy of H_2
15.6: Quantum Calculations

15: Computational Quantum Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

15.1: Overview of Quantum Calculations

Multielectron Electronic Wavefunctions

We could symbolically write an approximate two-particle wavefunction as $\psi(r_1, r_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 (r_1) for the coordinates of particle 2 (r_2) and vice versa, to get the new wavefunction $\psi(r_1, r_2)$. This new wavefunction must have the property that

$$|\psi(r_1, r_2)|^2 = \psi(r_2, r_1)^* \psi(r_2, r_1) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{15.1.1}$$

Equation 15.1.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(r_1, r_2) = e^{i\varphi} \psi(r_1, r_2)$$

so that

$$\left(e^{-i\varphi} \psi(r_1, r_2)^*\right) \left(e^{i\varphi} \psi(r_1, r_2)^*\right) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{15.1.2}$$

If we exchange or permute two identical particles twice, we are (by definition) back to the original situation. If each permutation changes the wavefunction by $e^{i\varphi}$, the double permutation must change the wavefunction by $e^{i\varphi} e^{i\varphi}$. Since we then are back to the original state, the effect of the double permutation must equal 1; i.e.,

$$e^{i\varphi} e^{i\varphi} = e^{i2\varphi} = 1$$

which is true only if $\varphi = 0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature, but the behavior of elections is that the wavefunction be antisymmetric with respect to permutation ($e^{i\varphi} = -1$). A wavefunction that is antisymmetric with respect to electron interchange is one whose output changes sign when the electron coordinates are interchanged, as shown below.

$$\psi(r_2, r_1) = e^{i\varphi} \psi(r_1, r_2) = -\psi(r_1, r_2)$$

Blindly following the first statement of the Pauli Exclusion Principle, that each electron in a multi-electron atom **must** be described by a different spin-orbital, we try constructing a simple product wavefunction for helium using two different spin-orbitals. Both have the 1s spatial component, but one has spin function α and the other has spin function β so the product wavefunction matches the form of the ground state electron configuration for He, $1s^2$.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) \tag{15.1.3}$$

After permutation of the electrons, this becomes

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1) \tag{15.1.4}$$

which is different from the starting function since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are different spin-orbital functions. However, an antisymmetric function must produce the same function multiplied by (–1) after permutation, and that is not the case here. We must try something else.

To avoid getting a totally different function when we permute the electrons, we can make a linear combination of functions. A very simple way of taking a linear combination involves making a new function by simply adding or subtracting functions. The function that is created by subtracting the right-hand side of Equation 15.1.4 from the right-hand side of Equation 15.1.3 has the desired antisymmetric behavior. The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1)]$$

A linear combination that describes an appropriately antisymmetrized multi-electron wavefunction for any desired orbital configuration is easy to construct for a two-electron system. However, interesting chemical systems usually contain more than two electrons. For these multi-electron systems a relatively simple scheme for constructing an antisymmetric wavefunction from a

product of one-electron functions is to write the wavefunction in the form of a determinant. John Slater introduced this idea so the determinant is called a Slater determinant.

The Slater determinant for the two-electron wavefunction for the ground state H_2 system (with the two electrons occupying the σ_{1s} molecular orbital)

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\sigma_{1s}(1)\alpha(1) & \sigma_{1s}(1)\beta(1)\\ \sigma_{1s}(2)\alpha(2) & \sigma_{1s}(2)\beta(2)\end{vmatrix}$$

We can introduce a shorthand notation for the arbitrary **spin-orbital**

$$\chi_{i\alpha}(\mathbf{r}) = \varphi_i\alpha$$

or

$$\chi_{i\beta}(\mathbf{r}) = \varphi_i\beta$$

as determined by the m_s quantum number. A shorthand notation for the determinant in Equation 8.6.4 is then

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = 2^{-\frac{1}{2}}Det|\chi_{1s\alpha}(\mathbf{r}_1)\alpha\chi_{1s\beta}(\mathbf{r}_2)\beta|$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is

$$(N!)^{-\frac{1}{2}}$$

for a system of N electrons.

The generalized Slater determinant for a multe-electrom atom with N electrons is then

$$\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\chi_1(\mathbf{r}_1)\alpha & \chi_1(\mathbf{r}_1)\beta & \cdots & \chi_{N/2}(\mathbf{r}_1)\beta\\ \chi_1(\mathbf{r}_2)\alpha & \chi_2(\mathbf{r}_2)\beta & \cdots & \chi_{N/2}(\mathbf{r}_2)\beta\\ \vdots & \vdots & \ddots & \vdots\\ \chi_1(\mathbf{r}_N)\alpha & \chi_2(\mathbf{r}_N)\beta & \cdots & \chi_{N/2}(\mathbf{r}_N)\beta\end{vmatrix} \tag{15.1.5}$$

In a modern *ab initio* electronic structure calculation on a closed shell molecule, the electronic Hamiltonian is used with a single determinant wavefunction. This wavefunction, Ψ, is constructed from molecular orbitals, ψ that are written as linear combinations of contracted Gaussian basis functions, φ

$$\varphi_j = \sum_k c_{jk}\psi_k \tag{15.1.6}$$

The contracted Gaussian functions are composed from primitive Gaussian functions to match Slater-type orbitals. The exponential parameters in the STOs are optimized by calculations on small molecules using the nonlinear variational method and then those values are used with other molecules. The problem is to calculate the electronic energy from

$$E = \frac{\int \Psi^*\hat{H}\Psi d\tau}{\int \Psi^*\Psi d\tau} \tag{15.1.7}$$

or in bra-ket notation

$$E = \frac{\left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle}{\langle\psi|\psi\rangle}$$

The the optimum coefficients c_{jk} for each molecular orbital in Equation 15.1.6 by using the Self Consistent Field Method and the Linear Variational Method to minimize the energy as was described previously for atoms.

The variational principle says an approximate energy is an upper bound to the exact energy, so the lowest energy that we calculate is the most accurate. At some point, the improvements in the energy will be very slight. This limiting energy is the lowest that can be obtained with a single determinant wavefunction (e.g., Equation 15.1.5). This limit is called the *Hartree-Fock limit*, the energy is

the *Hartree-Fock energy*, the molecular orbitals producing this limit are called *Hartree-Fock orbitals*, and the determinant is the *Hartree-Fock wavefunction*.

Hartree-Fock Calculations

You may encounter the terms *restricted* and *unrestricted* Hartree-Fock. The above discussion pertains to a restricted HF calculation. In a restricted HF calculation, electrons with α spin are restricted or constrained to occupy the same spatial orbitals as electrons with β spin. This constraint is removed in an unrestricted calculation. For example, the spin orbital for electron 1 could be $\psi_A(r_1)\alpha(1)$, and the spin orbital for electron 2 in a molecule could be $\psi_B(r_2)\beta(2)$, where both the spatial molecular orbital and the spin function differ for the two electrons. Such spin orbitals are called *unrestricted*. If both electrons are constrained to have the same spatial orbital, e.g. $\psi_A(r_1)\alpha(1)$ and $\psi_A(r_2)\beta(2)$, then the spin orbital is said to be *restricted*. While unrestricted spin orbitals can provide a better description of the electrons, twice as many spatial orbitals are needed, so the demands of the calculation are much higher. Using unrestricted orbitals is particular beneficial when a molecule contains an odd number of electrons because there are more electrons in one spin state than in the other.

Example 11.1.1 : Carbon Monoxide

It is well known that carbon monoxide is a poison that acts by binding to the iron in hemoglobin and preventing oxygen from binding. As a result, oxygen is not transported by the blood to cells. Which end of carbon monoxide, carbon or oxygen, do you think binds to iron by donating electrons? We all know that oxygen is more electron-rich than carbon (8 vs 6 electrons) and more electronegative. A reasonable answer to this question therefore is *oxygen*, but experimentally it is carbon that binds to iron.

A quantum mechanical calculation done by Winifred M. Huo, published in J. Chem. Phys. 43, 624 (1965), provides an explanation for this counter-intuitive result. The basis set used in the calculation consisted of 10 functions: the ls, 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of C and O. Ten molecular orbitals (mo's) were defined as linear combinations of the ten atomic orbitals (Equation 15.1.6. The ground state wavefunction Ψ is written as the Slater Determinant of the five lowest energy molecular orbitals ψ_k. Equation 15.1.7 gives the energy of the ground state, where the denominator accounts for the normalization requirement. The coefficients C_{kj} in the linear combination are determined by the variational method to minimize the energy. The solution of this problem gives the following equations for the molecular orbitals. Only the largest terms have been retained here. These functions are listed and discussed in order of increasing energy.

- $1s \approx 0.941s_o$. The 1 says this is the first σ orbital. The σ says it is symmetric with respect to reflection in the plane of the molecule. The large coefficient, 0.94, means this is essentially the 1s atomic orbital of oxygen. The oxygen 1s orbital should have a lower energy than that of carbon because the positive charge on the oxygen nucleus is greater.
- $2s \approx 0.921s_c$. This orbital is essentially the 1s atomic orbital of carbon. Both the 1σ and 2σ are "nonbonding" orbitals since they are localized on a particular atom and do not directly determine the charge density between atoms.
- $3s \approx (0.722s_o + 0.182p_{zo}) + (0.282s_c + 0.162p_{zc})$. This orbital is a "bonding" molecular orbital because the electrons are delocalized over C and O in a way that enhances the charge density between the atoms. The 3 means this is the third σ orbital. This orbital also illustrates the concept of hybridization. One can say the 2s and 2p orbitals on each atom are hybridized and the molecular orbital is formed from these hybrids although the calculation just obtains the linear combination of the four orbitals directly without the *à priori* introduction of hybridization. In other words, hybridization just falls out of the calculation. The hybridization in this bonding LCAO increases the amplitude of the function in the region of space between the two atoms and decreases it in the region of space outside of the bonding region of the atoms.
- $4s \approx (0.372s_c + 0.12p_{zc}) + (0.542p_{zo} - 0.432s_0)$. This molecular orbital also can be thought of as being a hybrid formed from atomic orbitals. The hybridization of oxygen atomic orbitals, because of the negative coefficient with $2s_O$, decreases the electron density between the nuclei and enhances electron density on the side of oxygen facing away from the carbon atom. If we follow how this function varies along the internuclear axis, we see that near carbon the function is positive whereas near oxygen it is negative or possibly small and positive. This change means there must be a node between the two nuclei or at the oxygen nucleus. Because of the node, the electron density between the two nuclei is low so the electrons in this orbital do not serve to shield the two positive nuclei from each other. This orbital therefore is called an "antibonding"

molecular orbital and the electrons assigned to it are called antibonding electrons. This orbital is the antibonding partner to the 3σ orbital.

- $1\pi \approx 0.322p_{xc} + 0.442p_{xo} \text{and} 2\pi \approx 0.322p_{yc} + 0.442p_{yo}$. These two orbitals are degenerate and correspond to bonding orbitals made up from the p_x and p_y atomic orbitals from each atom. These orbitals are degenerate because the x and y directions are equivalent in this molecule. π tells us that these orbitals are antisymmetric with respect to reflection in a plane containing the nuclei.
- $5\sigma \approx 0.382_{sC} - 0.382_{pC} - 0.292p_{zO}$. This orbital is the sp hybrid of the carbon atomic orbitals. The negative coefficient for $2p_C$ puts the largest amplitude on the side of carbon away from oxygen. There is no node between the atoms. We conclude this is a nonbonding orbital with the nonbonding electrons on carbon. This is not a “bonding” orbital because the electron density between the nuclei is lowered by hybridization. It also is not an antibonding orbital because there is no node between the nuclei. When carbon monoxide binds to Fe in hemoglobin, the bond is made between the C and the Fe. This bond involves the donation of the 5σ nonbonding electrons on C to empty d orbitals on Fe. Thus molecular orbital theory allows us to understand why the C end of the molecule is involved in this electron donation when we might naively expect O to be more electron-rich and capable of donating electrons to iron.

15.1: Overview of Quantum Calculations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **11.1: Overview of Quantum Calculations** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

15.2: Gaussian Basis Sets

A basis set in theoretical and computational chemistry is a set of functions (called **basis functions**) which are combined in linear combinations (generally as part of a quantum chemical calculation) to create molecular orbitals. For convenience these functions are typically atomic orbitals centered on atoms, but can theoretically be any function; plane waves are frequently used in materials calculations.

The Variational Method and Basis Sets

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, ψ_i, as a linear combination of other functions, φ_j, which are called basis functions because they provide the basis for representing the molecular orbital.

$$\psi_i = \sum_j c_{ij}\varphi_j \tag{15.2.1}$$

The linear variational method is used to find values for parameters in the basis functions and for the constant coefficients in the linear combination that optimize these functions, i.e. make them as good as possible. The criterion for quality in the variational method is making the ground state energy of the molecule as low as possible. Here and in the rest of this chapter, the following notation is used: σ is a general spin function (can be either α or β), φ is the basis function (this usually represents an atomic orbital), ψ is a molecular orbital, and Ψ is the electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. For example, an active area of research in industry involves calculating changes in chemical properties of pharmaceutical drugs as a result of changes in chemical structure.

> *Selecting the ab initio model for a chemical system is almost always involves a trade-off between accuracy and computational cost. More accurate methods and larger basis sets make jobs run longer.*

In modern computational chemistry, quantum chemical calculations are typically performed using a finite set of basis functions. In these cases, the wavefunctions of the system in question are represented as vectors, the components of which correspond to coefficients in a linear combination of the basis functions in the basis set used.

The molecular spin-orbitals that are used in the Slater determinant usually are expressed as a linear combination of some chosen functions, which are called *basis functions*. This set of functions is called the *basis set*. The fact that one function can be represented by a linear combination of other functions is a general property. All that is necessary is that the basis functions *span-the-space*, which means that the functions must form a complete set and must be describing the same thing. For example, spherical harmonics cannot be used to describe a hydrogen atom radial function because they do not involve the distance r, but they can be used to describe the angular properties of anything in three-dimensional space.

This span-the-space property of functions is just like the corresponding property of vectors. The unit vectors $(\vec{x}, \vec{y}, \vec{z})$ describe points in space and form a complete set since any position in space can be specified by a linear combination of these three unit vectors. These unit vectors also could be called basis vectors.

? Exercise 11.2.1 : "Spanning the Space"

Explain why the unit vectors $(\vec{x}, \vec{y})$ do not form a complete set to describe your (three-dimensional) classroom.

Just as we discussed for atoms, parameters in the basis functions and the coefficients in the linear combination can be optimized in accord with the Variational Principle to produce a self-consistent field (SCF) for the electrons. This optimization means that the ground state energy calculated with the wavefunction is minimized with respect to variation of the parameters and coefficients

defining the function. As a result, that ground state energy is larger than the exact energy, but is the best value that can be obtained with that wavefunction.

Slater Type Orbitals (STOs)

Intuitively one might select hydrogenic atomic orbitals as the basis set for molecular orbitals. After all, molecules are composed of atoms, and hydrogenic orbitals describe atoms exactly if the electron-electron interactions are neglected. At a better level of approximation, the nuclear charge that appears in these functions can be used as a variational parameter to account for the shielding effects due to the electron-electron interactions. Also, the use of atomic orbitals allows us to interpret molecular properties and charge distributions in terms of atomic properties and charges, which is very appealing since we picture molecules as composed of atoms. As described in the previous chapter, calculations with hydrogenic functions were not very efficient so other basis functions, **Slater-type atomic orbitals (STOs)**, were invented.

A minimal basis set of STOs for a molecule includes only those STOs that would be occupied by electrons in the atoms forming the molecule. As with most variational method calculations, a larger basis set improves the accuracy of the calculations by providing more variable parameters to produce a better approximate wavefunction. However, this is at the expense of increased computational time (i.e., calculation "cost" or "expense"). STOs have the following radial part (the spherical harmonic functions are used to describe the angular part)

$$R(r) = Nr^{n-1}e^{-\zeta r}$$

where

- n is a natural number that plays the role of principal quantum number, $n = 1, 2, \ldots$,
- N is a normalizing constant,
- r is the distance of the electron from the atomic nucleus, and ζ is a constant related to the effective charge of the nucleus, the nuclear charge being partly shielded by electrons. Historically, the effective nuclear charge was estimated by Slater's rules.

Double-zeta basis Sets

One can use more than one STO to represent one atomic orbital, as shown in Equation 15.2.2, and rather than doing a nonlinear variational calculation to optimize each ζ value, use two STOs with different ζ variables. The linear variation calculation then will produce the coefficients (C_1 and C_2) for these two functions in the linear combination that **best** describes the charge distribution in the molecule (for the ground state). The function with the large zeta accounts for charge near the nucleus, while the function with the smaller zeta accounts for the charge distribution at larger values of the distance from the nucleus. This expanded basis set is called a **double-zeta basis set**.

$$R_{2s}(r) = C_1 re^{-\zeta_1 r} + C_2 re^{-\zeta_2 r} \tag{15.2.2}$$

The use of double zeta functions in basis sets is especially important because without them orbitals of the same type are constrained to be identical even though in the molecule they may be chemically inequivalent. For example, in acetylene the p_z orbital along the internuclear axis is in a quite different chemical environment and is being used to account for quite different bonding than the p_x and p_y orbitals. With a double zeta basis set the p_z orbital is not constrained to be the same size as the p_x and p_y orbitals.

Example 11.2.1

Explain why the p_x, p_y, and p_z orbitals in a molecule might be constrained to be the same in a single-zeta basis set calculation, and how the use of a double-zeta basis set would allow the p_x, p_y, and p_z orbitals to differ.

Gaussian Orbitals

Although any basis set that sufficiently spans the space of electron distribution could be used, the concept of Molecular Orbitals as **Linear Combinations of Atomic Orbitals** **(LCAO)** suggests a very natural set of basis functions: AO-type functions centered on each nuclei. One obvious choice are the exact hydrogen AO's, known as **Slater-type orbitals (STO)** -describing the radial component of the functions. However, the computation of the integrals is greatly simplified by using **Gaussian-type orbitals (GTO)** for basis functions.

While the STO basis set was an improvement over hydrogenic orbitals in terms of computational efficiency, representing the STOs with Gaussian functions produced further improvements that were needed to accurately describe molecules. A Gaussian basis function has the form shown in Equation 15.2.3. Note that in all the basis sets, only the radial part of the orbital changes, and the spherical harmonic functions are used in all of them to describe the angular part of the orbital.

$$G_{nlm}(r,\theta,\psi) = N_n \underbrace{r^{n-1}e^{-\alpha r^2}}_{\text{radial part}} \underbrace{Y_l^m(\theta,\psi)}_{\text{angular part}} \tag{15.2.3}$$

Unfortunately Gaussian functions do not match the shape of an atomic orbital very well. In particular, they are flat rather than steep near the atomic nucleus at $r = 0$, and they fall off more rapidly at large values of r (Figure 11.2.1).

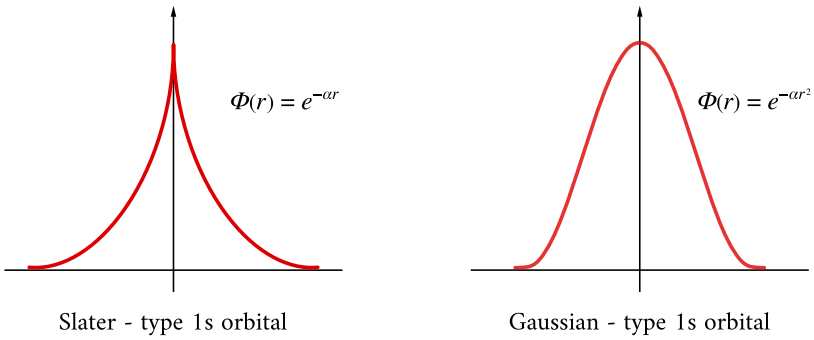


Figure 11.2.1 : Radial Dependence of Slater and Gaussian Basis Functions. (CC BY 4.0; Ümit Kaya via LibreTexts)

To compensate for this problem, each STO is replaced with a number of Gaussian functions with different values for the exponential parameter. These Gaussian functions form a *primitive Gaussian basis set*. Linear combinations of the primitive Gaussians are formed to approximate the radial part of an STO. This linear combination is not optimized further in the energy variational calculation, but rather is frozen and treated as a single function. The linear combination of **primitive Gaussian functions** is called a **contracted Gaussian function**. Although more functions and more integrals now are part of the calculation, the integrals involving Gaussian functions are quicker to compute than those involving exponentials, so there is a net gain in the efficiency of the calculation.

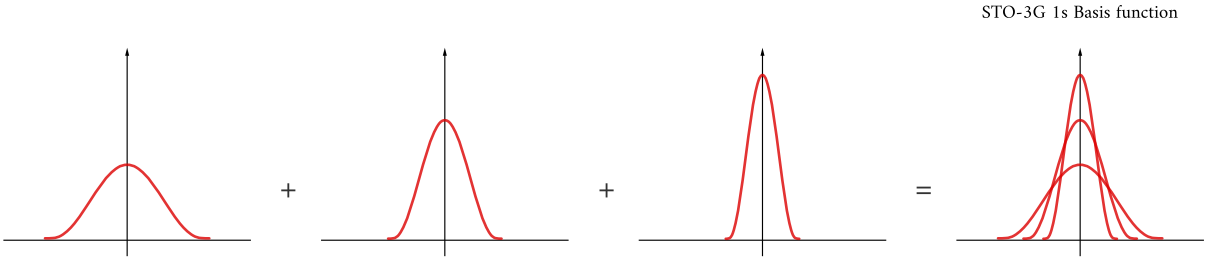


Figure 11.2.2 : To better represent the cusp in the electron density at the nuclei, GTO basis sets are constructed from fixed linear-combinations of Gaussian functions, contracted GTOs (CGTO). The earliest CGTO basis sets, where constructed from N GTOs that best fit the desired STO. These are called STO-NG basis sets. (CC BY 4.0; Ümit Kaya via LibreTexts)

Gaussian basis sets are identified by abbreviations such as N-MPG*. N is the number of Gaussian primitives used for each inner-shell orbital. The hyphen indicates a split-basis set where the valence orbitals are double zeta. The M indicates the number of primitives that form the large zeta function (for the inner valence region), and P indicates the number that form the small zeta function (for the outer valence region). G identifies the set a being Gaussian. The addition of an asterisk to this notation means that a single set of Gaussian 3d polarization functions (discussed elsewhere) is included. A double asterisk means that a single set of Gaussian 2p functions is included for each hydrogen atom.

For example, 3G means each STO is represented by a linear combination of three primitive Gaussian functions. 6-31G means each inner shell (1s orbital) STO is a linear combination of 6 primitives and each valence shell STO is split into an inner and outer part (double zeta) using 3 and 1 primitive Gaussians, respectively (see Table 11.2.1 for other examples).

Table 11.2.1 : Different Gaussian Basis sets

Basis set	# functions		Basis set	# functions		Basis set	# functions
STO-3G	5		6-31G	9		6-311G	13
3-21G	9		6-31G*	15		6-311G*	18*
4-31G	9		6-31+G*	19		6-311+G*	22*

Example 11.2.2

The 1s Slater-type orbital $S_1(r) = \sqrt{4\zeta_1 e^{-\zeta_1 r}}$ with $\zeta_1 = 1.24$ is represented as a sum of three primitive Gaussian functions,

$$S_G(r) = \sum_{j=1}^{3} C_j e^{-\alpha_j r^2}$$

This sum is the contracted Gaussian function for the STO.

a. Make plots of the STO and the contracted Gaussian function on the same graph so they can be compared easily. All distances should be in units of the Bohr radius. Use the following values for the coefficients, C, and the exponential parameters, α.

index j	α_j	C_j
1	0.1688	0.4
2	0.6239	0.7
3	3.425	1.3

b. Change the values of the coefficients and exponential parameters to see if a better fit can be obtained.

c. Comment on the ability of a linear combination of Gaussian functions to accurately describe a STO.

Summary

When molecular calculations are performed, it is common to use a basis composed of a finite number of atomic orbitals (Equation 15.2.1), centered at each atomic nucleus within the molecule (linear combination of atomic orbitals ansatz). These atomic orbitals are well described with Slater-type orbitals (STOs), as STOs decay exponentially with distance from the nuclei, accurately describing the long-range overlap between atoms, and reach a maximum at zero, well describing the charge and spin at the nucleus. STOs are computationally difficult and it was later realized by Frank Boys that these Slater-type orbitals could in turn be approximated as linear combinations of Gaussian orbitals instead. Because it is easier to calculate overlap and other integrals with Gaussian basis functions, this led to huge computational savings

15.2: Gaussian Basis Sets is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **11.2: Gaussian Basis Sets** by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski is licensed CC BY-NC-SA 4.0.

15.3: Extended Basis Sets

Today, there are hundreds of basis sets composed of Gaussian Type Orbitals (GTOs). The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The largest of these can contain literally dozens to hundreds of basis functions on each atom.

Minimum Basis sets

A minimum basis set is one in which a **single** basis function is used for each orbital in a Hartree-Fock calculation on the atom. However, for atoms such as lithium, basis functions of p type are added to the basis functions corresponding to the 1s and 2s orbitals of each atom. For example, each atom in the first row of the periodic system (Li - Ne) would have a basis set of five functions (two s functions and three p functions).

> *In a minimum basis set, a single basis function is used for each atomic orbital on each constituent atom in the system.*

The most common minimal basis set is STO-nG, where n is an integer. This n value represents the number GTOs used to approximate the Slater Type orbital (STO) for both core and valence orbitals. Minimal basis sets typically give rough results that are insufficient for research-quality publication, but are much cheaper (less calculations requires) than the larger basis sets discussed below. Commonly used minimal basis sets of this type are: STO-3G, STO-4G, and STO-6G.

Two is Often Better than One

Minimal basis sets are not flexible enough for accurate representation of, which requires the use multiple functions to represent each atomic orbital. The distribution of the electron density of valence electrons is better represented by the sum of two orbitals with different "effective charges". This is a double-ζ basis sets and includes split-valence set (inner and valence) and linear combination of two orbitals of same type, but with different effective charges (i.e., ζ). This flexibility can be used to generate atomic orbital of adjustable sizes.

For example, the double-zeta basis set allows us to treat each orbital separately when we conduct the Hartree-Fock calculation.

$$\phi_i = a_1\phi_{2s}^{STO}(r,\zeta_1) + a_2\phi_{2s}^{STO}(r,\zeta_2) \tag{15.3.1}$$

The 2s atomic orbital approximated as a sum of two STOs. The two equations are the same except for the value of ζ which accounts for how large the orbital is. The constants a_1 and a_2 determines how much each STO contributes to the final atomic orbital, which will vary depending on the type of atom that the atomic orbit (i.e., hydrogen and lithium orbitals will have different a_1, a_2, ζ_1, and ζ_2 values).

Extended Basis Sets

The triple and quadruple-zeta basis sets work the same way, except use three and four STOs instead of two like in 15.3.1. The typical trade-off applies here as well, better accuracy, however with more expensive calculations. There are several different types of **extended basis sets** including: n split-valence, n polarized sets, n diffuse sets, and n correlation consistent sets. The notation of this sort of basis set (with a Gaussian basis) is

$$N-MPG$$

for describing split-valence basis set. N is the number of Gaussian functions describing inner-shell orbitals, while the hyphen denotes a split-valence set. M and P designate the number of Gaussian functions used to fit the two orbitals of the valence shell:

- M corresponds to number of Gaussian functions used to describe the smaller orbital
- P corresponds to number of Gaussian functions used to describe the larger orbital (e.g., 6-31G and 3-21G).

A minimal basis set is when one basis function for each atomic orbital in the atom, while a double-ζ, has two two basis functions for each atomic orbital. Correspondingly, a triple and quadruple-ζ set had three and four basis functions for each atomic orbital, respectively. Higher order basis set have been constructed too, e.g., 5Z, 6Z,)..

There are hundreds of basis sets composed of Gaussian-type orbitals (Figure Figure 11.3.1). The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The largest of these can contain dozens to hundreds of basis functions on each atom.

Figure 11.3.1 : Commonly used split-valence basis sets

3-21G	3-21G	3-21G	3-21G* - Polarized	3-21+G - Diffuse functions	3-21+G* - With polarization and diffuse functions
4-21G	4-31G	4-31G	4-31G	4-31G	
6-21G	6-31G	6-31G*	6-31+G*	6-31G(3df, 3pd)	6-311G
6-311G	6-311G*	6-311+G*			

15.3: Extended Basis Sets is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **11.3: Extended Basis Sets** is licensed CC BY-NC-SA 4.0.

15.4: Orbital Polarization Terms

Polarization functions denoted in Pople's sets by an asterisk. Two asterisks, indicate that polarization functions are also added to light atoms (hydrogen and helium). n Polarization functions have one additional node. For example, the only basis function located on a hydrogen atom in a minimal basis set would be a function approximating the 1 s atomic orbital. When polarization is added to this basis set, a p -function is also added to the basis set. The 6-31G** is synonymous to 6-31 G(d,p).

The use of a minimal basis set with fixed zeta parameters severely limits how much the electronic charge can be changed from the atomic charge distribution to describe molecules and chemical bonds. This limitation is removed if STOs with larger n values and different spherical harmonic functions, the $Y_l^m(\theta, \varphi)$ in the definition of STO's are included. Adding such functions is another way to expand the basis set and obtain more accurate results. Such functions are called polarization functions because they allow for charge polarization away form the atomic distribution to occur.

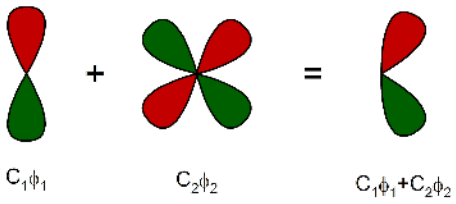


Figure 11.4.1 : A d-polarization function added to a p orbital. (CC-BY-SA-3.0; Rifleman 82)

The most common addition to minimal basis sets is probably the addition of polarization functions, denoted (in the names of basis sets developed by Pople) by an asterisk, *. Two asterisks, **, indicate that polarization functions are also added to light atoms (hydrogen and helium). These are auxiliary functions with one additional node. For example, the only basis function located on a hydrogen atom in a minimal basis set would be a function approximating the 1s atomic orbital. When polarization is added to this basis set, a p-function is also added to the basis set. This adds some additional needed flexibility within the basis set, effectively allowing molecular orbitals involving the hydrogen atoms to be more asymmetric about the hydrogen nucleus.

This is an important result when considering accurate representations of bonding between atoms, because the very presence of the bonded atom makes the energetic environment of the electrons spherically asymmetric. Similarly, d-type functions can be added to a basis set with valence p orbitals, and f-functions to a basis set with d-type orbitals, and so on. Another, more precise notation indicates exactly which and how many functions are added to the basis set, such as (d, p).

Diffuse Functions

Another common addition to basis sets is the addition of **diffuse functions**, denoted in Pople-type sets by a plus sign, +, and in Dunning-type sets by "aug" (from "augmented"). Two plus signs indicate that diffuse functions are also added to light atoms (hydrogen and helium). These are very shallow Gaussian basis functions, which more accurately represent the "tail" portion of the atomic orbitals, which are distant from the atomic nuclei. These additional basis functions can be important when considering anions and other large, "soft" molecular systems.

15.4: Orbital Polarization Terms is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **11.4: Orbital Polarization Terms in Basis Sets** by Wikipedia is licensed CC BY-NC-SA 4.0.

15.5: The Ground-State Energy of H_2

11.05: The Ground-State Energy of H

15.5: The Ground-State Energy of H_2 is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

15.6: Quantum Calculations

11.06: Quantum Calculations

15.6: Quantum Calculations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

16: MathChapters

16.1: Complex Numbers
16.2: Probability and Statistics
16.3: Vectors
16.4: Spherical Coordinates
16.5: Determinants
16.6: Matrices
16.7: Numerical Methods
16.8: Partial Differentiation
16.9: Series and Limits
16.10: The Binomial Distribution and Stirling's Appromixation

16: MathChapters is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

16.1: Complex Numbers

Real Numbers

Let us think of the ordinary numbers as set out on a line which goes to infinity in both positive and negative directions. We could start by taking a stretch of the line near the origin (that is, the point representing the number zero) and putting in the integers as follows:

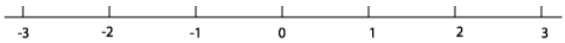


Figure **16.1.1**: Integers on number line

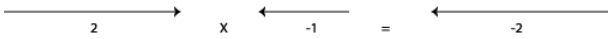
Next, we could add in rational numbers, such as ½, 23/11, etc., then the irrationals like $\sqrt{2}$, then numbers like π, and so on, so any number you can think of has its place on this line. Now let's take a slightly different point of view, and think of the numbers as represented by a *vector* from the origin to that number, so 1 is



and, for example, –2 is represented by:



Note that if a number is multiplied by –1, the corresponding vector is turned through 180 degrees. In pictures,



The "vector" 2 is turned through π, or 180 degrees, when you multiply it by –1.

Example 16.1.1

What are the square roots of 4?

Solving Quadratic Equations

In solving the standard quadratic equation

$$ax^2 + bx + c = 0 \tag{16.1.1}$$

we find the solution to be:

$$x = \frac{-b \pm \sqrt{b^2 - ac}}{2a} \tag{16.1.2}$$

The problem with this is that sometimes the expression inside the square root is negative. What does that signify? For some problems in physics, it means there is no solution. For example, if I throw a ball directly upwards at 10 meters per sec, and ask when will it reach a height of 20 meters, taking g = 10 m per sec^2, the solution of the quadratic equation for the time t has a negative number inside the square root, and that means that the ball doesn't get to 20 meters, so the question didn't really make sense.

We shall find, however, that there are other problems, in wide areas of physics, where negative numbers inside square roots have an important physical significance. For that reason, we need to come up with a scheme for interpreting them.

The simplest quadratic equation that gives trouble is:

$$x^2 + 1 = 0 \tag{16.1.3}$$

the solutions being

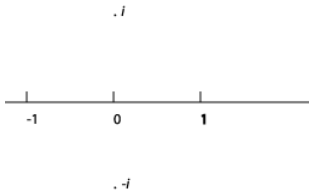
$$x = \pm\sqrt{-1} \tag{16.1.4}$$

What does that mean? We've just seen that the square of a positive number is positive, and the square of a negative number is also positive, since multiplying one negative number, which points backwards, by another, which turns any vector through 180º, gives a

positive vector. Another way of saying the same thing is to regard the minus sign itself, -, as an operator which turns the number it is applied to through 180º. Now $(-2) \times (-2)$ has two such rotations in it, giving the full 360º back to the positive axis.

To make sense of the square root of a negative number, we need to find something which when multiplied by itself gives a negative number. Let's concentrate for the moment on the square root of –1, from the quadratic equation above. Think of –1 as the operator – acting on the vector 1, so the – turns the vector through 180º. We need to find the square root of this operator, the operator which applied *twice* gives the rotation through 180º. Put like that, it is pretty obvious that the operator we want rotates the vector 1 through 90º.

But if we take a positive number, such as 1, and rotate its vector through 90º only, it isn't a number at all, at least in our original sense, since we put all known numbers on one line, and we've now rotated 1 away from that line. The new number created in this way is called a pure imaginary number, and is denoted by i.



Once we've found the square root of –1, we can use it to write the square root of any other negative number—for example, $2i$ is the square root of -4. Putting together a real number from the original line with an imaginary number (a multiple of *i*) gives a *complex number*. Evidently, complex numbers fill the entire two-dimensional plane. Taking ordinary Cartesian coordinates, any point P in the plane can be written as (x, y) where the point is reached from the origin by going x units in the direction of the positive real axis, then y units in the direction defined by i, in other words, the y axis.

Thus the point *P* with coordinates (*x*, *y*) can be identified with the complex number z, where

$$z = x + iy. \tag{16.1.5}$$

The plane is often called the *complex plane*, and representing complex numbers in this way is sometimes referred to as an **Argand Diagram** (Figure 16.1.2).

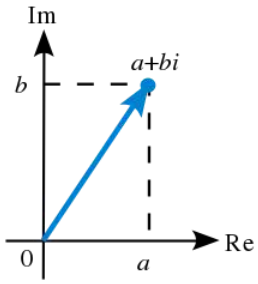


Figure 16.1.2: A complex number can be visually represented as a pair of numbers (a, b) forming a vector on a diagram called an Argand diagram, representing the complex plane. "Re" is the real axis, "Im" is the imaginary axis, and i satisfies $i^2 = -1$. Image used with permission (Cc BY-SA 4.0; Wolfkeeper).

Visualizing the complex numbers as two-dimensional vectors, it is clear how to *add* two of them together. If $z_1 = x_1 + iy_1$, and $z_2 = x - 2 + iy_2$, then $z_1 + z_2 = (x_1 + x_2) + i(y_1 + y_2)$. The real parts and imaginary parts are added separately, just like vector components.

Multiplying two complex numbers together does not have quite such a simple interpretation. It is, however, quite straightforward—ordinary algebraic rules apply, with i^2 replaced where it appears by -1. So for example, to multiply $z_1 = x_1 + iy_1$ by $z_2 = x_2 + iy_2$,

$$z_1 z_2 = (x_1 + iy_1)(x_2 + iy_2) \tag{16.1.6}$$

$$= (x_1 x_2 - y_1 y_2) + i(x_1 y_2 + x_2 y_1). \tag{16.1.7}$$

Polar Coordinates

Some properties of complex numbers are most easily understood if they are represented by using the polar coordinates r, θ instead of (x, y) to locate z in the complex plane (Figure 16.1.3).

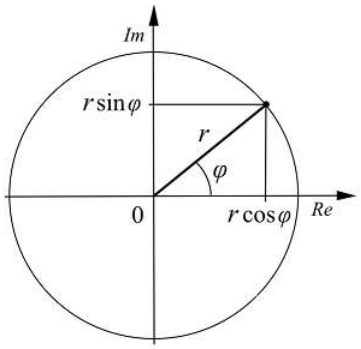


Figure 16.1.3: Polar Argand diagram. Image used with permission (CC BY-SA 4.0; Svjo).

Note that $z = x + iy$ can be written $r(\cos\theta + i\sin\theta)$ from Figure 16.1.3. In fact, this representation leads to a clearer picture of multiplication of two complex numbers:

$$z_1 z_2 = [r_2(\cos(\theta_1 + i\sin\theta_1)][r_2(\cos(\theta_2 + i\sin\theta_2)] \tag{16.1.8}$$

$$= r_1 r_2\,[(\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2) + i(\sin\theta_1\cos\theta_2 + \cos\theta_1\sin\theta_2)] \tag{16.1.9}$$

$$= r_1 r_2\,[\cos(\theta_1 + \theta_2) + i\sin(\theta_1 + \theta_2)] \tag{16.1.10}$$

So, if

$$z = r(\cos\theta + i\sin\theta) \tag{16.1.11}$$

$$= z_1 z_2 \tag{16.1.12}$$

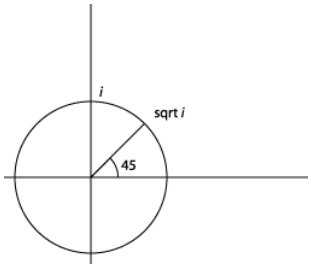
then

$$r = r_1 r_2 \tag{16.1.13}$$

and

$$\theta = \theta_1 \theta_2 \tag{16.1.14}$$

That is to say, to multiply together two complex numbers, we *multiply* the r's – called the *moduli* – and *add* the phases, the θ's. The modulus r is often denoted by \(|z|\), and called **mod** z, the phase θ is sometimes referred to as **arg** z. For example, $|i| = 1$, **arg** $i = \pi/2$.

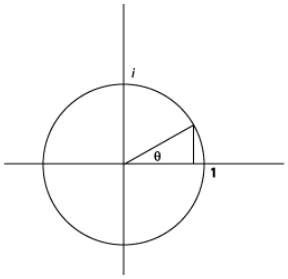


We can now see that, although we had to introduce these complex numbers to have a $\sqrt{-1}$, we do not need to bring in new types of numbers to get $\sqrt{-1}$, or $\sqrt{i}$. Clearly, $|\sqrt{i}| = 1$, $arg\sqrt{i} = 45°$. It is on the circle of unit radius centered at the origin, at 45°, and squaring it just doubles the angle.

The Unit Circle

In fact this circle—called the *unit circle*—plays an important part in the theory of complex numbers and every point on the circle has the form

$$z = \cos\theta + i\sin\theta = Cis(\theta) \tag{16.1.15}$$



Since all points on the unit circle have $|z| = 1$, by definition, multiplying any two of them together just amounts to adding the angles, so our new function $Cis(\theta)$ satisfies

$$Cis(\theta_1)Cis(\theta_2) = Cis(\theta_1 + \theta_2). \tag{16.1.16}$$

But that is just how multiplication works for exponents! That is,

$$a^{\theta_1}a^{\theta_2} = a^{\theta_1+\theta_2} \tag{16.1.17}$$

for a any constant, which strongly suggests that maybe our function $Cis(\theta$ is nothing but some constant a raised to the power θ, that is,

$$Cis(\theta) = a^{\theta} \tag{16.1.18}$$

It turns out to be convenient to write $a^{\theta} = e^{\ln a)\theta} = e^{A\theta}$, where $A = \ln a$. This line of reasoning leads us to write

$$\cos\theta + i\sin\theta = e^{A\theta} \tag{16.1.19}$$

Now, for the above "addition formula" to work for multiplication, A must be a constant, *independent* of θ. Therefore, we can find the value of A by choosing θ for which things are simple. We take θ to be very small—in this limit

$$\cos\theta \approx 1$$
$$\sin\theta \approx \theta$$

and

$$e^{A\theta} \approx 1 + A\theta \tag{16.1.20}$$

after dropping terms of order θ^2 and higher.

Substituting these values into Equation 16.1.19 givesθ

So we find:

$$(\cos\theta + i\sin\theta)e^{i\theta} \tag{16.1.21}$$

To test this result, we expand $e^{i\theta}$:

$$e^{i\theta} = 1 + i\theta + \frac{(i\theta)^2}{2!} + \frac{(i\theta)^3}{3!} + \frac{(i\theta)^4}{4!} + \frac{(i\theta)^5}{5!} + \ldots \tag{16.1.22}$$

$$= 1 + i\theta - \frac{\theta^2}{2!} - \frac{i\theta^3}{3!} + \frac{\theta^4}{4!} + \frac{i\theta^5}{5!} + \ldots \tag{16.1.23}$$

$$= \left(1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!}\right) + i\left(\theta - \frac{i\theta^3}{3!} + \frac{i\theta^5}{5!}\right) \tag{16.1.24}$$

$$= \cos\theta + i\sin\theta \tag{16.1.25}$$

We write $= \cos\theta + i\sin\theta$ in the last line because the series in the brackets are precisely the Taylor series for $\cos\theta$ and $\sin\theta$ confirming our equation for $e^{i\theta}$. Changing the sign of θ it is easy to see that

$$e^{-i\theta} = \cos\theta - i\sin\theta \tag{16.1.26}$$

so the two trigonometric functions can be expressed in terms of exponentials of complex numbers:

$$\cos(\theta) = \frac{1}{2}\left(e^{i\theta} + e^{-i\theta}\right) \tag{16.1.27}$$

$$\sin(\theta) = \frac{1}{2i}\left(e^{i\theta} - e^{-i\theta}\right) \tag{16.1.28}$$

Euler Formula

The Euler formula states that any complex number can be written (Equation 16.1.25):

$$e^{i\theta} = \cos\theta + i\sin\theta$$

Contributors

- Michael Fowler (Beams Professor, Department of Physics, University of Virginia)

16.1: Complex Numbers is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

16.2: Probability and Statistics

A random variable X can have more than one value x as an outcome. Which value the variable has in a particular case is a matter of *chance* and cannot be predicted other than that we associate a probability to the outcome. **Probability** p is a number between 0 and 1 that indicates the likelihood that the variable X has a particular outcome x. The set of outcomes and their probabilities form a ***probability distribution***. There are two kinds of distributions:

1. discrete ones
2. continuous ones

Total probability should always add up to unity.

Discrete Distributions

A good example of a discrete distribution is a *true coin*. The random variable X can have two values:

1. heads (0)
2. tails (1)

Both have equal probability and as the sum must equal unity, the probability must be ½ for each. 'The probability that X=heads' is written formally as:

$$Pr(X = heads) = Pr(X = 0) = 0.5$$

The random function is written as a combination of three statements.

- Pr(X=0) = ½
- Pr(X=1) = ½
- elsewhere Pr = 0

Continuous Distributions

Now consider a spherical die. One could say it has an infinite number of facets that it can land on. Thus the number of outcomes $n = \infty$, this make each probability

$$p = 1/\infty = 0.$$

This creates a bit of a mathematical problem, because how can we get a total probability of unity by adding up zeros? Also, if we divide the sphere in a northern and a southern hemisphere clearly the probability that it lands on a point in say, the north should be ½. Still, p = 0 for all points. We introduce a new concept: **probability density** over which we *integrate* rather than *sum*. We assign an equal density to each point of the sphere and make sure that if we integrate over a hemisphere we get ½. (This involves two angles θ and φ and an integration over them and I won't go into that).

A bit simpler example of a continuous distribution than the spherical die is the 1D ***uniform*** distribution. It is the one that the Excel function =RAND() produces to good approximation. Its probability density is defined as

- f(x) = 1 for 0<1>
- f(x) = 0 elsewhere

The figure shows a (bivariate) uniform distribution.

The probability that the outcome is smaller than 0.5 is written as Pr(X<0.5) and is found by integrating from 0 to 0.5 over f(x).

Notice that in each individual outcome b the probability is indeed zero because an integral from b to b is always zero, even if the probability density f(b) is not zero. Clearly the probability and the probability density are not the same. Unfortunately the distinction between probability and probability density is often not properly made in the physical sciences. Moments can also be computed for continuous distributions by integrating over the probability density 

Another well-known continuous distribution is the ***normal*** (or ***Gaussian***) distribution, defined as:

\[f(x) = 1/[√(2π)σ] * exp(-½[(x-μ)/σ]^2) \nonumber \]

(Notice the normalization factor 1/[√(2π)σ])

We can also compute moments of continuous distribution. Instead of using a summation we now have to evaluate an integral:

$$\langle X \rangle = \int [f(x)^* x] dx$$

$$\langle X^2 \rangle = \int [f(x)^* x^2] dx$$

For the normal distribution $\langle X \rangle = \mu$

? Exercise

Compute $^2>$ and $^3>$ for the uniform distribution. answer>

Indistinguishable Outcomes

When flipping two coins we could get four outcomes: two heads (0), heads plus tails (1), tails plus heads (1), two tails (2)

Each outcome is equally likely, this implies a probability of ¼ for each:

The probability of a particular outcome is often abbreviated simply to p. The two middle outcomes collapse into one with p=¼+¼= ½ if the coins are **indistinguishable**. We will see that this concept has very important consequences in statistical thermodynamics.

If we cannot distinguish the two outcomes leading to X_{tot}=1 we get the following random function:

Notice that it is quite possible to have a distribution where the probabilities differ from outcome to outcome. Often the p values are given as f(x), a function of x. An example:

X3 defined as:

The factor 1/6 makes sure the probabilities add up to unity. Such a factor is known as a **normalization factor**. Again this concept is of prime importance in statistical thermodynamics.

Another example of a discrete distribution is a die. If it has 6 sides (the most common die) there are six outcomes, each with p= 1/6. There are also dice with n=4, 12 or 20 sides. Each outcome will then have p= 1/n.

Moments of Distributions

In important aspect of probability distributions are the **moments** of the distribution. They are values computed by summing over the whole distribution.

The **zero** order moment is simply the sum of all p and that is unity:

The **first** moment multiplies each outcome with its probability and sums over all outcomes:

This moment is known as the ***average*** or ***mean***. (It is what we have done to your grades for years...)

For one coin is ½, for two coins is 1. (Exercise: verify this)

The **second** moment is computed by summing the product of the square of X and p:

The notation is used a lot in quantum mechanics, often in the form <ψ*ψ> or <ψ*|h|ψ>. The <.. part is known as the ***bra***, the ..> part as the ***ket***. (Together ***bra***(c)***ket***)

Intermezzo: The strange employer

You have a summer job but your employer likes games of chance. At the end of every day he rolls a die and pays you the square of the outcome in dollars per hour. So on a lucky day you'd make $36.- per hour, but on a bad day $1.-. Is this a bad deal? What would you make on the average over a longer period?

To answer this we must compute the second moment $^2>$ of the distribution:

(I have taken p=1/6 out of brackets because the value is the same for all six outcomes)

As you see in the intermezzo, the value of the second moment is in this case what you ***expect*** to be making on the long term. Moments are examples of what is know as **expectation values**. Another term you may run into that of a **functional**. A functional is a *number* computed by some operation (such as summation or integration) over a whole function. Moments are clearly an example of that too.

16.2: Probability and Statistics is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **32.2: Probability and Statistics** is licensed CC BY-NC-SA 4.0.

16.3: Vectors

In this chapter we will review a few concepts you probably know from your physics courses. This chapter does not intend to cover the topic in a comprehensive manner, but instead touch on a few concepts that you will use in your physical chemistry classes.

A vector is a quantity that has both a magnitude and a direction, and as such they are used to specify the position, velocity and momentum of a particle, or to specify a force. Vectors are usually denoted by boldface symbols (e.g. $\mathbf{u}$) or with an arrow above the symbol (e.g. $\vec{u}$). A tilde placed above or below the name of the vector is also commonly used in shorthand ($\tilde{u}$,$\underset{\sim}{u}$).

If we multiply a number a by a vector $\mathbf{v}$, we obtain a new vector that is parallel to the original but with a length that is a times the length of $\mathbf{v}$. If a is negative $a\mathbf{v}$ points in the opposite direction than $\mathbf{v}$. We can express any vector in terms of the so-called unit vectors. These vectors, which are designated $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$, have unit length and point along the positive x, y and z axis of the cartesian coordinate system (Figure 16.3.1). The symbol $\hat{\mathbf{i}}$ is read "i-hat". Hats are used to denote that a vector has unit length.

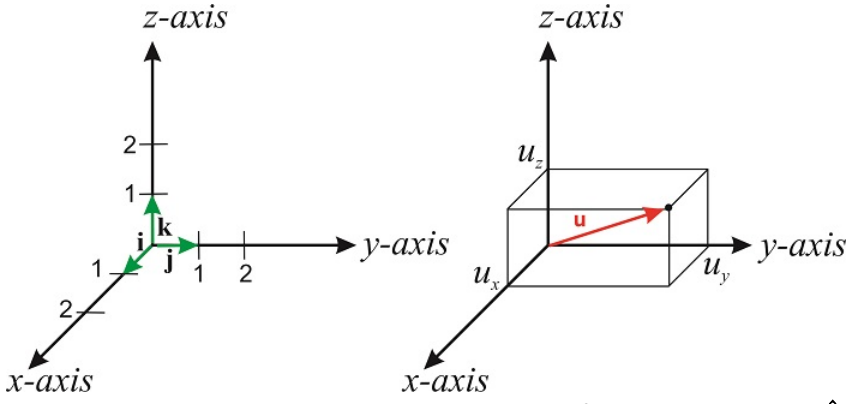


Figure 16.3.1: Left: The unit vectors. Right: A vector $\mathbf{u}$ can be expressed in terms of the unit vectors as $\mathbf{u} = u_x\hat{\mathbf{i}} + u_y\hat{\mathbf{j}} + u_z\hat{\mathbf{k}}$ (CC BY-NC-SA; Marcia Levitus)

The length of $\mathbf{u}$ is its magnitude (or modulus), and is usually denoted by u:

$$u = |u| = (u_x^2 + u_y^2 + u_z^2)^{1/2} \tag{16.3.1}$$

If we have two vectors $\mathbf{u} = u_x\hat{\mathbf{i}} + u_y\hat{\mathbf{j}} + u_z\hat{\mathbf{k}}$ and $\mathbf{v} = v_x\hat{\mathbf{i}} + v_y\hat{\mathbf{j}} + v_z\hat{\mathbf{k}}$, we can add them to obtain

$$\mathbf{u} + \mathbf{v} = (u_x + v_x)\hat{\mathbf{i}} + (u_y + v_y)\hat{\mathbf{j}} + (u_z + v_z)\hat{\mathbf{k}}$$

or subtract them to obtain:

$$\mathbf{u} - \mathbf{v} = (u_x - v_x)\hat{\mathbf{i}} + (u_y - v_y)\hat{\mathbf{j}} + (u_z - v_z)\hat{\mathbf{k}}$$

When it comes to multiplication, we can perform the product of two vectors in two different ways. The first, which gives a scalar (a number) as the result, is called scalar product or dot product. The second, which gives a vector as a result, is called the vector (or cross) product. Both are important operations in physical chemistry.

The Scalar Product

The scalar product of vectors $\mathbf{u}$ and $\mathbf{v}$, also known as the dot product or inner product, is defined as (notice the dot between the symbols representing the vectors)

$$\mathbf{u} \cdot \mathbf{v} = |\mathbf{u}|\,|\mathbf{v}| \cos\theta$$

where θ is the angle between the vectors. Notice that the dot product is zero if the two vectors are perpendicular to each other, and equals the product of their absolute values if they are parallel. It is easy to prove that

$$\mathbf{u} \cdot \mathbf{v} = u_x v_x + u_y v_y + u_z v_z$$

Example 16.3.1

Show that the vectors

$$\mathbf{u_1} = \frac{1}{\sqrt{3}}\hat{\mathbf{i}} + \frac{1}{\sqrt{3}}\hat{\mathbf{j}} + \frac{1}{\sqrt{3}}\hat{\mathbf{k}}$$
$$\mathbf{u_2} = \frac{1}{\sqrt{6}}\hat{\mathbf{i}} - \frac{2}{\sqrt{6}}\hat{\mathbf{j}} + \frac{1}{\sqrt{6}}\hat{\mathbf{k}}$$
$$\mathbf{u_3} = -\frac{1}{\sqrt{2}}\hat{\mathbf{i}} + \frac{1}{\sqrt{2}}\hat{\mathbf{k}}$$

are of unit length and are mutually perpendicular.

Solution

The length of the vectors are:

$$|\mathbf{u_1}| = \left[\left(\frac{1}{\sqrt{3}}\right)^2 + \left(\frac{1}{\sqrt{3}}\right)^2 + \left(\frac{1}{\sqrt{3}}\right)^2\right]^{1/2} = \left[\frac{1}{3} + \frac{1}{3} + \frac{1}{3}\right]^{1/2} = 1$$
$$|\mathbf{u_2}| = \left[\left(\frac{1}{\sqrt{6}}\right)^2 + \left(-\frac{2}{\sqrt{6}}\right)^2 + \left(\frac{1}{\sqrt{6}}\right)^2\right]^{1/2} = \left[\frac{1}{6} + \frac{4}{6} + \frac{1}{6}\right]^{1/2} = 1$$
$$|\mathbf{u_3}| = \left[\left(-\frac{1}{\sqrt{2}}\right)^2 + \left(\frac{1}{\sqrt{2}}\right)^2\right]^{1/2} = \left[\frac{1}{2} + \frac{1}{2}\right]^{1/2} = 1$$

To test if two vectors are perpendicular, we perform the dot product:

$$\mathbf{u_1} \cdot \mathbf{u_2} = \left(\frac{1}{\sqrt{3}}\frac{1}{\sqrt{6}} - \frac{1}{\sqrt{3}}\frac{2}{\sqrt{6}} + \frac{1}{\sqrt{3}}\frac{1}{\sqrt{6}}\right) = 0$$
$$\mathbf{u_1} \cdot \mathbf{u_3} = \left(-\frac{1}{\sqrt{3}}\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{3}}\frac{1}{\sqrt{2}}\right) = 0$$
$$\mathbf{u_2} \cdot \mathbf{u_3} = \left(-\frac{1}{\sqrt{6}}\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{6}}\frac{1}{\sqrt{2}}\right) = 0$$

Therefore, we just proved that the three pairs are mutually perpendicular, and the three vectors have unit length. In other words, these vectors are the vectors $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$ rotated in space.

If the dot product of two vectors (of any dimension) is zero, we say that the two vectors are orthogonal. If the vectors have unit length, we say they are normalized. If two vectors are both normalized and they are orthogonal, we say they are orthonormal. The set of vectors shown in the previous example form an orthonormal set.[vectors:orthonormal] These concepts also apply to vectors that contain complex entries, but how do we perform the dot product in this case?

In general, the square of the modulus of a vector is

$$|\mathbf{u}|^2 = \mathbf{u} \cdot \mathbf{u} = u_x^2 + u_y^2 + u_z^2.$$

However, this does not work correctly for complex vectors. The square of i is -1, meaning that we risk having non-positive absolute values. To address this issue, we introduce a more general version of the dot product:

$$\mathbf{u} \cdot \mathbf{v} = u_x^* v_x + u_y^* v_y + u_z^* v_z,$$

where the "$*$" refers to the complex conjugate. Therefore, to calculate the modulus of a vector $\mathbf{u}$ that has complex entries, we use its complex conjugate:

$$|\mathbf{u}|^2 = \mathbf{u}^* \cdot \mathbf{u}$$

Example 16.3.2: Calculating the Modulus of a vector

Calculate the modulus of the following vector:

$$\mathbf{u} = \hat{\mathbf{i}} + i\hat{\mathbf{j}}$$

Solution

$$|\mathbf{u}|^2 = \mathbf{u}^* \cdot \mathbf{u} = (\hat{\mathbf{i}} - i\hat{\mathbf{j}})(\hat{\mathbf{i}} + i\hat{\mathbf{j}}) = (1)(1) + (-i)(i) = 2 \rightarrow |\mathbf{u}| = \sqrt{2}$$

Analogously, if vectors contain complex entries, we can test whether they are orthogonal or not by checking the dot product $\mathbf{u}^* \cdot \mathbf{v}$.

Example 16.3.3: Confirming orthogonality

Determine if the following pair of vectors are orthogonal (do not confuse the irrational number i with the unit vector $\hat{\mathbf{i}}$!)

$$\mathbf{u} = \hat{\mathbf{i}} + (1 - i)\hat{\mathbf{j}}$$

and

$$\mathbf{v} = (1 + i)\hat{\mathbf{i}} + \hat{\mathbf{j}}$$

Solution

$$\mathbf{u}^* \cdot \mathbf{v} = (\hat{\mathbf{i}} + (1 + i)\hat{\mathbf{j}})((1 + i)\hat{\mathbf{i}} + \hat{\mathbf{j}}) = (1)(1 + i) + (1 + i)(1) = 2 + 2i \neq 0$$

Therefore, the vectors are not orthogonal.

The Vector Product

The vector product of two vectors is a vector defined as

$$\mathbf{u} \times \mathbf{v} = |\mathbf{u}|\,|\mathbf{v}|\,\mathbf{n}\sin\theta$$

where θ is again the angle between the two vectors, and $\mathbf{n}$ is the unit vector perpendicular to the plane formed by $\mathbf{u}$ and $\mathbf{v}$. The direction of the vector $\mathbf{n}$ is given by the right-hand rule. Extend your right hand and point your index finger in the direction of $\mathbf{u}$ (the vector on the left side of the $\times$ symbol) and your forefinger in the direction of $\mathbf{v}$. The direction of $\mathbf{n}$, which determines the direction of $\mathbf{u} \times \mathbf{v}$, is the direction of your thumb. If you want to revert the multiplication, and perform $\mathbf{v} \times \mathbf{u}$, you need to point your index finger in the direction of $\mathbf{v}$ and your forefinger in the direction of $\mathbf{u}$ (still using the right hand!). The resulting vector will point in the opposite direction (Figure 16.3.1).

The magnitude of $\mathbf{u} \times \mathbf{v}$ is the product of the magnitudes of the individual vectors times $\sin\theta$. This magnitude has an interesting geometrical interpretation: it is the area of the parallelogram formed by the two vectors (Figure 16.3.1).

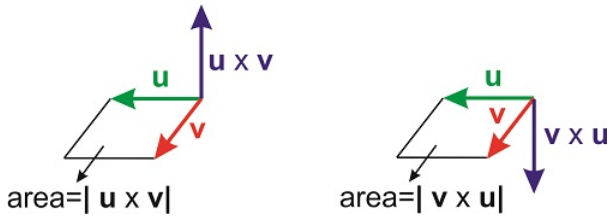


Figure 16.3.1: The vector product (CC BY-NC-SA; Marcia Levitus)

The cross product can also be expressed as a determinant:

$$\mathbf{u} \times \mathbf{v} = \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ u_x & u_y & u_z \\ v_x & v_y & v_z \end{vmatrix}$$

Example 16.3.1:

Given $\mathbf{u} = -2\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}}$ and $\mathbf{v} = 3\hat{\mathbf{i}} - \hat{\mathbf{j}} + \hat{\mathbf{k}}$, calculate $\mathbf{w} = \mathbf{u} \times \mathbf{v}$ and verify that the result is perpendicular to both $\mathbf{u}$ and $\mathbf{v}$.

Solution

$$\mathbf{u} \times \mathbf{v} = \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ u_x & u_y & u_z \\ v_x & v_y & v_z \end{vmatrix} = \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ -2 & 1 & 1 \\ 3 & -1 & 1 \end{vmatrix}$$

$$= \hat{\mathbf{i}}(1+1) - \hat{\mathbf{j}}(-2-3) + \hat{\mathbf{k}}(2-3)$$

$$= 2\hat{\mathbf{i}} + 5\hat{\mathbf{j}} - \hat{\mathbf{k}}$$

To verify that two vectors are perpendicular we perform the dot product:

$$\mathbf{u} \cdot \mathbf{w} = (-2)(2) + (1)(5) + (1)(-1) = 0$$

$$\mathbf{v} \cdot \mathbf{w} = (3)(2) + (-1)(5) + (1)(-1) = 0$$

An important application of the cross product involves the definition of the angular momentum. If a particle with mass m moves a velocity $\mathbf{v}$ (a vector), its (linear) momentum is $\mathbf{p} = m\mathbf{v}$. Let $\mathbf{r}$ be the position of the particle (another vector), then the angular momentum of the particle is defined as

$$\mathbf{l} = \mathbf{r} \times \mathbf{p}$$

The angular momentum is therefore a vector perpendicular to both $\mathbf{r}$ and $\mathbf{p}$. Because the position of the particle needs to be defined with respect to a particular origin, this origin needs to be specified when defining the angular momentum.

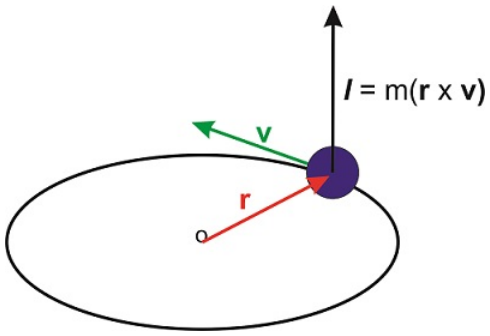


Figure 16.3.2: The angular momentum of a particle of position $\mathbf{r}$ from the origin and momentum $\mathbf{p} = m\mathbf{v}$ (CC BY-NC-SA; Marcia Levitus)

Vector Normalization

A vector of any given length can be divided by its modulus to create a unit vector (i.e. a vector of unit length). We will see applications of unit (or normalized) vectors in the next chapter.

For example, the vector

$$\mathbf{u} = \hat{\mathbf{i}} + \hat{\mathbf{j}} + i\hat{\mathbf{k}}$$

has a magnitude:

$$|\mathbf{u}|^2 = 1^2 + 1^2 + (-i)(i) = 3 \rightarrow |\mathbf{u}| = \sqrt{3}$$

Therefore, to normalize this vector we divide all the components by its length:

$$\hat{\mathbf{u}} = \frac{1}{\sqrt{3}}\hat{\mathbf{i}} + \frac{1}{\sqrt{3}}\hat{\mathbf{j}} + \frac{i}{\sqrt{3}}\hat{\mathbf{k}}$$

Notice that we use the “hat” to indicate that the vector has unit length.

Need help? The links below contain solved examples.

Operations with vectors: http://tinyurl.com/mw4qmz8

External links:

- The dot product: http://patrickjmt.com/vectors-the-dot-product/
- The cross product: http://patrickjmt.com/the-cross-product/
- The dot and cross product: http://www.youtube.com/watch?v=enr7JqvehJs

---

16.3: Vectors is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **14.1: Introduction to Vectors** by Marcia Levitus is licensed CC BY-NC-SA 4.0. Original source: https://www.public.asu.edu/~mlevitus/chm240/book.pdf.
- **32.5: Vectors** by Marcia Levitus is licensed CC BY-NC-SA 4.0. Original source: https://www.public.asu.edu/~mlevitus/chm240/book.pdf.
- **14.2: The Scalar Product** by Marcia Levitus is licensed CC BY-NC-SA 4.0. Original source: https://www.public.asu.edu/~mlevitus/chm240/book.pdf.
- **14.3: The Vector Product** by Marcia Levitus is licensed CC BY-NC-SA 4.0. Original source: https://www.public.asu.edu/~mlevitus/chm240/book.pdf.
- **14.4: Vector Normalization** by Marcia Levitus is licensed CC BY-NC-SA 4.0. Original source: https://www.public.asu.edu/~mlevitus/chm240/book.pdf.

16.4: Spherical Coordinates

Objectives

- Understand the concept of area and volume elements in cartesian, polar and spherical coordinates.
- Be able to integrate functions expressed in polar or spherical coordinates.
- Understand how to normalize orbitals expressed in spherical coordinates, and perform calculations involving triple integrals.

Coordinate Systems

The simplest coordinate system consists of coordinate axes oriented perpendicularly to each other. These coordinates are known as cartesian coordinates or rectangular coordinates, and you are already familiar with their two-dimensional and three-dimensional representation. In the plane, any point P can be represented by two signed numbers, usually written as (x, y), where the coordinate x is the distance perpendicular to the x axis, and the coordinate y is the distance perpendicular to the y axis (Figure **16.4.1**, left). In space, a point is represented by three signed numbers, usually written as (x, y, z) (Figure **16.4.1**, right).

Often, positions are represented by a vector, $\vec{r}$, shown in red in Figure **16.4.1**. In three dimensions, this vector can be expressed in terms of the coordinate values as $\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$, where $\hat{i} = (1, 0, 0)$, $\hat{j} = (0, 1, 0)$ and $\hat{z} = (0, 0, 1)$ are the so-called unit vectors.

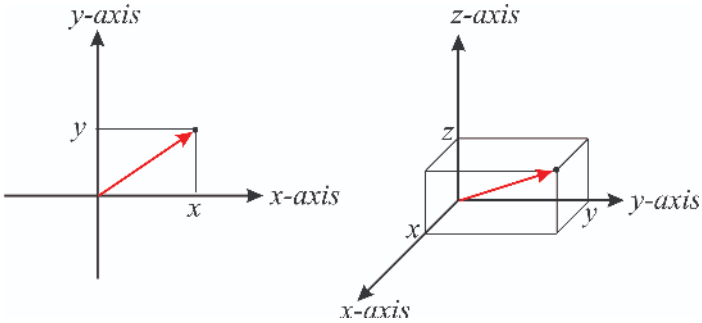


Figure **16.4.1**: Cartesian coordinates (CC BY-NC-SA; Marcia Levitus)

We already know that often the symmetry of a problem makes it natural (and easier!) to use other coordinate systems. In two dimensions, the polar coordinate system defines a point in the plane by two numbers: the distance r to the origin, and the angle θ that the position vector forms with the x-axis. Notice the difference between $\vec{r}$, a vector, and r, the distance to the origin (and therefore the modulus of the vector). Vectors are often denoted in bold face (e.g. $\mathbf{r}$) without the arrow on top, so be careful not to confuse it with r, which is a scalar.

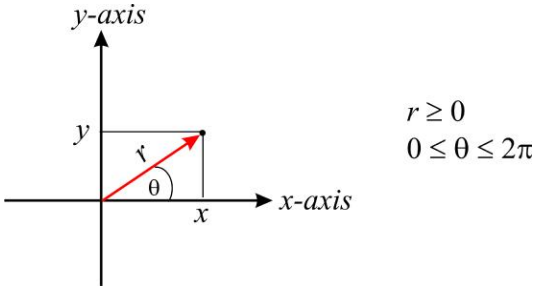


Figure **16.4.2**: Plane polar coordinates (CC BY-NC-SA; Marcia Levitus)

While in cartesian coordinates x, y (and z in three-dimensions) can take values from $-\infty$ to ∞, in polar coordinates r is a positive value (consistent with a distance), and θ can take values in the range $[0, 2\pi]$.

The relationship between the cartesian and polar coordinates in two dimensions can be summarized as:

$$x = r\cos\theta \tag{16.4.1}$$

$$y = r\sin\theta \tag{16.4.2}$$

$$r^2 = x^2 + y^2 \tag{16.4.3}$$

$$\tan\theta = y/x \tag{16.4.4}$$

In three dimensions, the spherical coordinate system defines a point in space by three numbers: the distance r to the origin, a polar angle ϕ that measures the angle between the positive x-axis and the line from the origin to the point P projected onto the xy-plane, and the angle θ defined as the is the angle between the z-axis and the line from the origin to the point P:

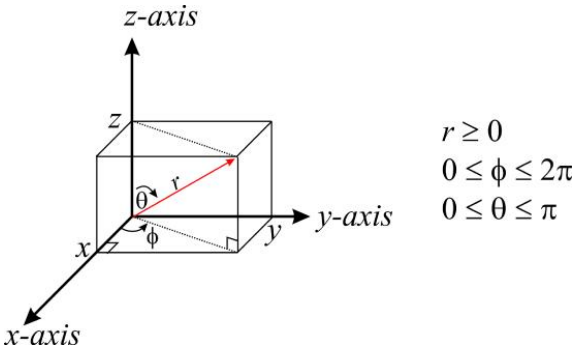


Figure **16.4.3**: Spherical coordinates (CC BY-NC-SA; Marcia Levitus)

Before we move on, it is important to mention that depending on the field, you may see the Greek letter θ (instead of ϕ) used for the angle between the positive x-axis and the line from the origin to the point P projected onto the xy-plane. That is, θ and ϕ may appear interchanged. This can be very confusing, so you will have to be careful. When using spherical coordinates, it is important that you see how these two angles are defined so you can identify which is which.

Spherical coordinates are useful in analyzing systems that are symmetrical about a point. For example a sphere that has the cartesian equation $x^2 + y^2 + z^2 = R^2$ has the very simple equation $r = R$ in spherical coordinates. Spherical coordinates are the natural coordinates for physical situations where there is spherical symmetry (e.g. atoms). The relationship between the cartesian coordinates and the spherical coordinates can be summarized as:

$$x = r\sin\theta\cos\phi \tag{16.4.5}$$

$$y = r\sin\theta\sin\phi \tag{16.4.6}$$

$$z = r\cos\theta \tag{16.4.7}$$

These relationships are not hard to derive if one considers the triangles shown in Figure **16.4.4**:

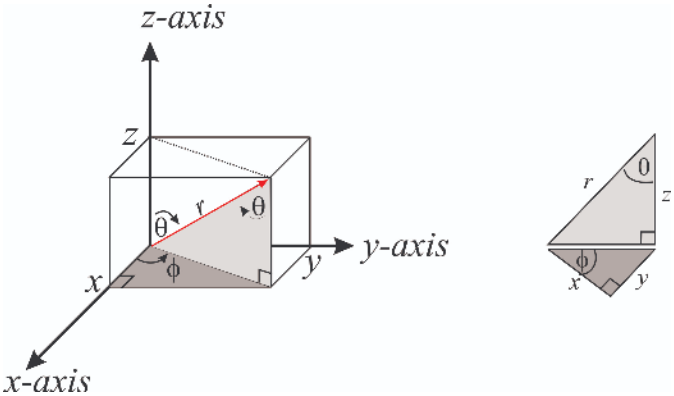


Figure **16.4.4**: Spherical coordinates (CC BY-NC-SA; Marcia Levitus)

Area and Volume Elements

In any coordinate system it is useful to define a differential area and a differential volume element. In cartesian coordinates the differential area element is simply $dA = dx\,dy$ (Figure **16.4.1**), and the volume element is simply $dV = dx\,dy\,dz$.

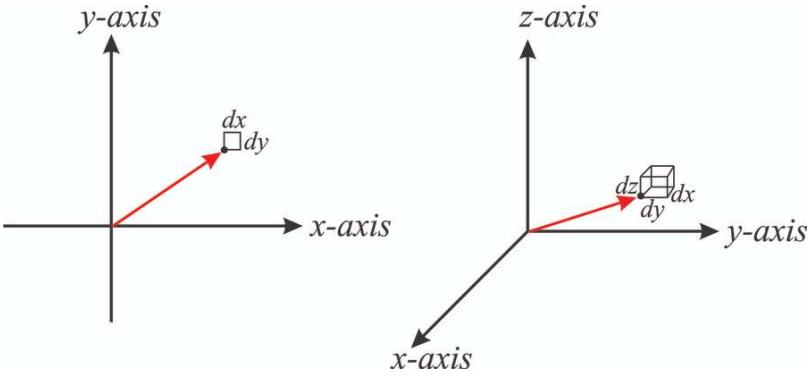


Figure 16.4.1: Area and volume elements in cartesian coordinates (CC BY-NC-SA; Marcia Levitus)

We already performed double and triple integrals in cartesian coordinates, and used the area and volume elements without paying any special attention. For example, in example [c2v:c2vex1], we were required to integrate the function $|\psi(x,y,z)|^2$ over all space, and without thinking too much we used the volume element $dx\ dy\ dz$ (see page). We also knew that "all space" meant $-\infty \leq x \leq \infty$, $-\infty \leq y \leq \infty$ and $-\infty \leq z \leq \infty$, and therefore we wrote:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x,y,z)|^2\ dx\ dy\ dz = 1$$

But what if we had to integrate a function that is expressed in spherical coordinates? Would we just replace $dx\ dy\ dz$ by $dr\ d\theta\ d\phi$? The answer is no, because the volume element in spherical coordinates depends also on the actual position of the point. This will make more sense in a minute. Coming back to coordinates in two dimensions, it is intuitive to understand why the area element in cartesian coordinates is $dA = dx\ dy$ independently of the values of x and y. This is shown in the left side of Figure 16.4.2. However, in polar coordinates, we see that the areas of the gray sections, which are both constructed by increasing r by dr, and by increasing θ by $d\theta$, depend on the actual value of r. Notice that the area highlighted in gray increases as we move away from the origin.

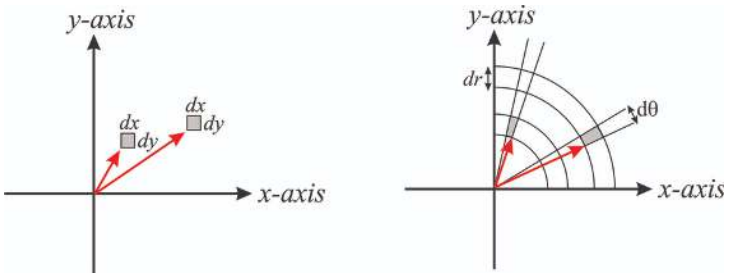


Figure 16.4.2: Differential of area in cartesian and polar coordinates (CC BY-NC-SA; Marcia Levitus)

The area shown in gray can be calculated from geometrical arguments as

$$dA = \left[\pi(r+dr)^2 - \pi r^2\right]\frac{d\theta}{2\pi}.$$

Because $dr << 0$, we can neglect the term $(dr)^2$, and $dA = r\ dr\ d\theta$ (see Figure 10.2.3).

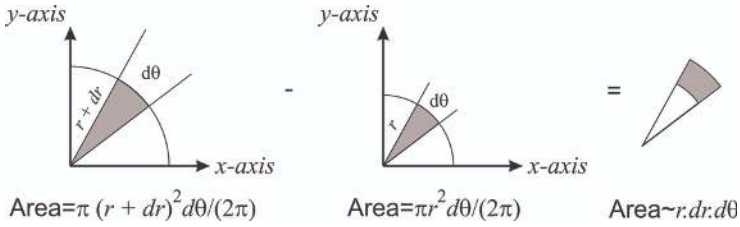


Figure 16.4.3: Differential of area in polar coordinates (CC BY-NC-SA; Marcia Levitus)

Let's see how this affects a double integral with an example from quantum mechanics. The wave function of the ground state of a two dimensional harmonic oscillator is: $\psi(x,y) = Ae^{-a(x^2+y^2)}$. We know that the quantity $|\psi|^2$ represents a probability density, and as such, needs to be normalized:

$$\int_{\text{all space}} |\psi|^2 \, dA = 1$$

This statement is true regardless of whether the function is expressed in polar or cartesian coordinates. However, the limits of integration, and the expression used for dA, will depend on the coordinate system used in the integration.

In cartesian coordinates, "all space" means $-\infty < x < \infty$ and $-\infty < y < \infty$. The differential of area is $dA = dxdy$:

$$\int_{\text{all space}} |\psi|^2 \, dA = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} A^2 e^{-2a(x^2+y^2)} \, dxdy = 1$$

In polar coordinates, "all space" means $0 < r < \infty$ and $0 < \theta < 2\pi$. The differential of area is $dA = r \; drd\theta$. The function $\psi(x, y) = Ae^{-a(x^2+y^2)}$ can be expressed in polar coordinates as: $\psi(r, \theta) = Ae^{-ar^2}$

$$\int_{\text{all space}} |\psi|^2 \, dA = \int_{0}^{\infty} \int_{0}^{2\pi} A^2 e^{-2ar^2} r \, d\theta dr = 1$$

Both versions of the double integral are equivalent, and both can be solved to find the value of the normalization constant (A) that makes the double integral equal to 1. In polar coordinates:

$$\int_0^{\infty} \int_0^{2\pi} A^2 e^{-2ar^2} r \, d\theta dr = A^2 \int_0^{\infty} e^{-2ar^2} r \, dr \int_0^{2\pi} d\theta = A^2 \times \frac{1}{4a} \times 2\pi = 1$$

Therefore[1], $A = \sqrt{2a/\pi}$. The same value is of course obtained by integrating in cartesian coordinates.

It is now time to turn our attention to triple integrals in spherical coordinates. In cartesian coordinates, the differential volume element is simply $dV = dx \, dy \, dz$, regardless of the values of x, y and z. Using the same arguments we used for polar coordinates in the plane, we will see that the differential of volume in spherical coordinates is not $dV = dr \, d\theta \, d\phi$. The geometrical derivation of the volume is a little bit more complicated, but from Figure 16.4.4 you should be able to see that dV depends on r and θ, but not on ϕ. The volume of the shaded region is

$$dV = r^2 \sin\theta \, d\theta \, d\phi \, dr \tag{16.4.8}$$

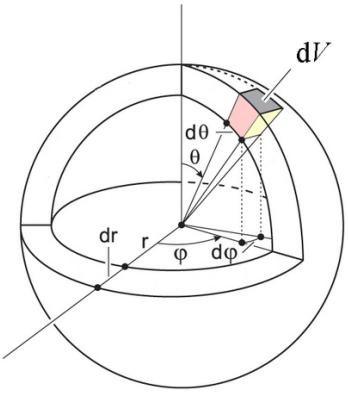


Figure 16.4.4: Differential of volume in spherical coordinates (CC BY-NC-SA; Marcia Levitus)

We will exemplify the use of triple integrals in spherical coordinates with some problems from quantum mechanics. We already introduced the Schrödinger equation, and even solved it for a simple system in Section 5.4. We also mentioned that spherical coordinates are the obvious choice when writing this and other equations for systems such as atoms, which are symmetric around a point.

As we saw in the case of the particle in the box (Section 5.4), the solution of the Schrödinger equation has an arbitrary multiplicative constant. Because of the probabilistic interpretation of wave functions, we determine this constant by normalization. The same situation arises in three dimensions when we solve the Schrödinger equation to obtain the expressions that describe the possible states of the electron in the hydrogen atom (i.e. the orbitals of the atom). The Schrödinger equation is a partial differential

equation in three dimensions, and the solutions will be wave functions that are functions of r, θ and ϕ. The lowest energy state, which in chemistry we call the 1s orbital, turns out to be:

$$\psi_{1s} = Ae^{-r/a_0}$$

This particular orbital depends on r only, which should not surprise a chemist given that the electron density in all s-orbitals is spherically symmetric. We will see that p and d orbitals depend on the angles as well. Regardless of the orbital, and the coordinate system, the normalization condition states that:

$$\int_{all\ space} |\psi|^2\, dV = 1$$

For a wave function expressed in cartesian coordinates,

$$\int_{all\ space} |\psi|^2\, dV = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^*(x,y,z)\psi(x,y,z)\, dxdydz$$

where we used the fact that $|\psi|^2 = \psi^*\psi$.

In spherical coordinates, "all space" means $0 \le r \le \infty$, $0 \le \phi \le 2\pi$ and $0 \le \theta \le \pi$. The differential dV is $dV = r^2 \sin\theta\, d\theta\, d\phi\, dr$, so

$$\int_{all\ space} |\psi|^2\, dV = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, r^2 \sin\theta\, drd\theta d\phi = 1$$

Let's see how we can normalize orbitals using triple integrals in spherical coordinates.

Example 16.4.1

When solving the Schrödinger equation for the hydrogen atom, we obtain $\psi_{1s} = Ae^{-r/a_0}$, where A is an arbitrary constant that needs to be determined by normalization. Find A.

Solution

In spherical coordinates,

$$\int_{all\ space} |\psi|^2\, dV = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, r^2 \sin\theta\, drd\theta d\phi = 1$$

because this orbital is a real function, $\psi^*(r,\theta,\phi)\psi(r,\theta,\phi) = \psi^2(r,\theta,\phi)$. In this case, $\psi^2(r,\theta,\phi) = A^2e^{-2r/a_0}$.

Therefore,

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, r^2 \sin\theta\, drd\theta d\phi = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} A^2e^{-2r/a_0}\, r^2 \sin\theta\, drd\theta d\phi = 1$$

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} A^2e^{-2r/a_0}\, r^2 \sin\theta\, drd\theta d\phi = A^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} e^{-2r/a_0}\, r^2\, dr$$

The result is a product of three integrals in one variable:

$$\int_0^{2\pi} d\phi = 2\pi$$

$$\int_0^{\pi} \sin\theta\, d\theta = -\cos\theta\Big|_0^{\pi} = 2$$

$$\int_0^\infty e^{-2r/a_0}\, r^2\, dr = ?$$

From the formula sheet:

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}},$$

where $a > 0$ and n is a positive integer.

In this case, $n = 2$ and $a = 2/a_0$, so:

$$\int_0^\infty e^{-2r/a_0}\, r^2\, dr = \frac{2!}{(2/a_0)^3} = \frac{2}{8/a_0^3} = \frac{a_0^3}{4}$$

Putting the three pieces together:

$$A^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^\infty e^{-2r/a_0}\, r^2\, dr = A^2 \times 2\pi \times 2 \times \frac{a_0^3}{4} = 1$$

$$A^2 \times \pi \times a_0^3 = 1 \rightarrow A = \frac{1}{\sqrt{\pi a_0^3}}$$

The normalized 1s orbital is, therefore:

$$\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

This page titled 16.4: Spherical Coordinates is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Marcia Levitus via source content that was edited to the style and standards of the LibreTexts platform.

- **32.6: Spherical Coordinates** is licensed CC BY-NC-SA 4.0.
- **10.1: Coordinate Systems** by Marcia Levitus is licensed CC BY-NC-SA 4.0. Original source: https://www.public.asu.edu/~mlevitus/chm240/book.pdf.
- **10.2: Area and Volume Elements** by Marcia Levitus is licensed CC BY-NC-SA 4.0. Original source: https://www.public.asu.edu/~mlevitus/chm240/book.pdf.

16.5: Determinants

The concept of determinants has its origin in the solution of simultaneous linear equations. In physical chemistry, they are an important tool in quantum mechanics

Suppose you want to solve the following system of two equations with two unknowns (x and y):

$$a_1x + b_1y = c_1$$

$$a_2x + b_2y = c_2$$

In order to find y, we could use the following general procedure: we multiply the first equation by a_2 and the second by a_1, and subtract one line from the other to cancel the term in x:

$$a_1x + b_1y = c_1 \overset{\times a_2}{\rightarrow} a_1a_2x + b_1a_2y = c_1a_2$$

$$a_2x + b_2y = c_2 \overset{\times a_1}{\rightarrow} a_1a_2x + b_2a_1y = c_2a_1$$

$$\left.\begin{aligned} a_1a_2x + b_1a_2y &= c_1a_2 \\ a_1a_2x + b_2a_1y &= c_2a_1 \end{aligned}\right\} \rightarrow (b_2a_1 - b_1a_2)y = a_1c_2 - a_2c_1 \rightarrow y = \frac{a_1c_2 - a_2c_1}{b_2a_1 - b_1a_2}$$

We can follow the same strategy to find x: we multiply the first equation by b_2 and the second by b_1, and subtract one line from the other to cancel the term in y:

$$a_1x + b_1y = c_1 \overset{\times b_2}{\rightarrow} a_1b_2x + b_1b_2y = c_1b_2$$

$$a_2x + b_2y = c_2 \overset{\times b_1}{\rightarrow} b_1a_2x + b_2b_1y = c_2b_1$$

$$\left.\begin{aligned} a_1b_2x + b_1b_2y &= c_1b_2 \\ b_1a_2x + b_2b_1y &= c_2b_1 \end{aligned}\right\} \rightarrow (b_2a_1 - b_1a_2)x = b_2c_1 - b_1c_2 \rightarrow x = \frac{b_2c_1 - b_1c_2}{b_2a_1 - b_1a_2}$$

We define a 2×2 determinant as:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - cb$$

The determinant, which is denoted with two parallel bars, is a number. For example,

$$\begin{vmatrix} 3 & -1 \\ 1/2 & 2 \end{vmatrix} = 3 \times 2 - (-1) \times 1/2 = 13/2$$

Let's look at the expressions we obtained for x and y, and write them in terms of determinants:

$$x = \frac{b_2c_1 - b_1c_2}{b_2a_1 - b_1a_2} = \frac{\begin{vmatrix} c_1 & b_1 \\ c_2 & b_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}$$

$$y = \frac{a_1c_2 - a_2c_1}{b_2a_1 - b_1a_2} = \frac{\begin{vmatrix} a_1 & c_1 \\ a_2 & c_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}$$

Let's look at our equations, and see how these determinants are constructed from the coefficients.

$$a_1x + b_1y = c_1$$

$$a_2x + b_2y = c_2$$

The determinant in the denominator of both x and y is the determinant of the coefficients on the left-side of the equal sign:

$$\left.\begin{aligned} a_1x + b_1y &= c_1 \\ a_2x + b_2y &= c_2 \end{aligned}\right\} \begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}$$

The numerator in the expression of y is built by replacing the coefficients in the y-column with the coefficients on the right side of the equation:

$$\left.\begin{aligned} a_1x + b_1y &= c_1 \\ a_2x + b_2y &= c_2 \end{aligned}\right\} \begin{vmatrix} a_1 & c_1 \\ a_2 & c_2 \end{vmatrix}$$

The numerator in the expression of x is built by replacing the coefficients in the x-column with the coefficients on the right side of the equation:

$$\left.\begin{aligned} a_1x + b_1y &= c_1 \\ a_2x + b_2y &= c_2 \end{aligned}\right\} \begin{vmatrix} c_1 & b_1 \\ c_2 & b_2 \end{vmatrix}$$

We can extend this idea to n equations with n unknowns $(x_1, x_2, x_3, ..., x_n)$.

$$\begin{array}{ccccccc} a_{11}x_1 & + & a_{12}x_2 & + & \cdots & + & a_{1n}x_n & = b_1 \\ a_{21}x_1 & + & a_{22}c_2 & + & \cdots & + & a_{2n}x_n & = b_2 \\ \vdots & & \vdots & & \ddots & & \vdots & \vdots \\ a_{n1}x_1 & + & a_{n2}c_2 & + & \cdots & + & a_{nn}x_n & = b_n \end{array}$$

Note that we use two subscripts to identify the coefficients. The first refers to the row, and the second to the column. Let's define the determinant D as the determinant of the coefficients of the equation (the ones on the left side of the equal sign):

$$D = \begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{vmatrix}$$

and let's define the determinant D_k as the one obtained from D by replacement of the kth column of D by the column with elements $b_1, b_2 ... b_n$. For example, D_2 is

$$D_2 = \begin{vmatrix} a_{11} & b_1 & \cdots & a_{1n} \\ a_{21} & b_2 & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & b_n & \cdots & a_{nn} \end{vmatrix}$$

The unknowns of the system of equations are calculated as:

$$x_1 = \frac{D_1}{D}, x_2 = \frac{D_2}{D}, ..., x_n = \frac{D_n}{D}$$

For example, let's say we want to find x, y and z in the following system of equations:

$$2x + 3y + 8z = 0$$

$$x - \frac{1}{2}y - 3z = \frac{1}{2}$$

$$-x - y - z = \frac{1}{2}$$

We can calculate the unknowns as;

$$x = \frac{D_1}{D}, y = \frac{D_2}{D}, z = \frac{D_3}{D}$$

where

$$D = \begin{vmatrix} 2 & 3 & 8 \\ 1 & -1/2 & -3 \\ -1 & -1 & -1 \end{vmatrix}$$

$$D_1 = \begin{vmatrix} 0 & 3 & 8 \\ 1/2 & -1/2 & -3 \\ 1/2 & -1 & -1 \end{vmatrix}$$

$$D_2 = \begin{vmatrix} 2 & 0 & 8 \\ 1 & 1/2 & -3 \\ -1 & 1/2 & -1 \end{vmatrix}$$

$$D_3 = \begin{vmatrix} 2 & 3 & 0 \\ 1 & -1/2 & 1/2 \\ -1 & -1 & 1/2 \end{vmatrix}$$

In order to do this, we need to learn how to solve 3×3 determinants, or in general, $n \times n$ determinants.

This page titled 16.5: Determinants is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Marcia Levitus via source content that was edited to the style and standards of the LibreTexts platform.

- **13.1: The Solutions of Simultaneous Linear Equations** by Marcia Levitus is licensed CC BY-NC-SA 4.0. Original source: https://www.public.asu.edu/~mlevitus/chm240/book.pdf.

16.6: Matrices

Definitions

An $n \times m$ matrix is a two dimensional array of numbers with n rows and m columns. The integers n and m are called the *dimensions* of the matrix. If $n = m$ then the matrix is *square*. The numbers in the matrix are known as *matrix elements* (or just elements) and are usually given subscripts to signify their position in the matrix e.g. an element a_{ij} would occupy the ith row and j^{th} column of the matrix. For example:

$$M = \begin{pmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{pmatrix} \tag{16.6.1}$$

is a 3×3 matrix with $a_{11} = 1$, $a_{12} = 2$, $a_{13} = 3$, $a_{21} = 4$ etc

In a square matrix, *diagonal* elements are those for which i=j (the numbers 1, 5, and 9 in the above example). *Off-diagonal* elements are those for which $i \neq j$ (2, 3, 4, 6, 7, and 8 in the above example). If all the off-diagonal elements are equal to zero then we have a *diagonal* matrix. We will see later that diagonal matrices are of considerable importance in group theory.

A *unit matrix* or *identity matrix* (usually given the symbol I) is a diagonal matrix in which all the diagonal elements are equal to 1. A unit matrix acting on another matrix has no effect – it is the same as the identity operation in group theory and is analogous to multiplying a number by 1 in everyday arithmetic.

The *transpose* A^T of a matrix A is the matrix that results from interchanging all the rows and columns. A *symmetric* matrix is the same as its transpose ($A^T = A$ i.e. $a_{ij} = a_{ji}$ for all values of i and j). The transpose of matrix M above (which is not symmetric) is

$$M^T = \begin{pmatrix} 1 & 4 & 7 \\ 2 & 5 & 8 \\ 3 & 6 & 9 \end{pmatrix} \tag{16.6.2}$$

The sum of the diagonal elements in a square matrix is called the *trace* (or *character*) of the matrix (for the above matrix, the trace is $\chi = 1 + 5 + 9 = 15$). The traces of matrices representing symmetry operations will turn out to be of great importance in group theory.

A *vector* is just a special case of a matrix in which one of the dimensions is equal to 1. An $n \times 1$ matrix is a *column vector*; a $1 \times m$ matrix is a *row vector*. The components of a vector are usually only labeled with one index. A *unit vector* has one element equal to 1 and the others equal to zero (it is the same as one row or column of an identity matrix). We can extend the idea further to say that a single number is a matrix (or vector) of dimension 1×1.

Matrix Algebra

i. Two matrices with the same dimensions may be added or subtracted by adding or subtracting the elements occupying the same position in each matrix. e.g.

$$A = \begin{pmatrix} 1 & 0 & 2 \\ 2 & 2 & 1 \\ 3 & 2 & 0 \end{pmatrix} \tag{16.6.3}$$

$$B = \begin{pmatrix} 2 & 0 & -2 \\ 1 & 0 & 1 \\ 1 & -1 & 0 \end{pmatrix} \tag{16.6.4}$$

$$A + B = \begin{pmatrix} 3 & 0 & 0 \\ 3 & 2 & 2 \\ 4 & 1 & 0 \end{pmatrix} \tag{16.6.5}$$

$$A - B = \begin{pmatrix} -1 & 0 & 4 \\ 1 & 2 & 0 \\ 2 & 3 & 0 \end{pmatrix} \tag{16.6.6}$$

ii. A matrix may be multiplied by a constant by multiplying each element by the constant.

$$4B = \begin{pmatrix} 8 & 0 & -8 \\ 4 & 0 & 4 \\ 4 & -4 & 0 \end{pmatrix} \tag{16.6.7}$$

$$3A = \begin{pmatrix} 3 & 0 & 6 \\ 6 & 6 & 3 \\ 9 & 6 & 0 \end{pmatrix} \tag{16.6.8}$$

iii. Two matrices may be multiplied together provided that the number of columns of the first matrix is the same as the number of rows of the second matrix i.e. an $n \times m$ matrix may be multiplied by an $m \times l$ matrix. The resulting matrix will have dimensions $n \times l$. To find the element a_{ij} in the product matrix, we take the dot product of row i of the first matrix and column j of the second matrix (i.e. we multiply consecutive elements together from row i of the first matrix and column j of the second matrix and add them together i.e. $c_{ij} = \Sigma_k\, a_{ik}b_{jk}$ e.g. in the 3×3 matrices A and B used in the above examples, the first element in the product matrix $C = AB$ is $c_{11} = a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31}$

$$AB = \begin{pmatrix} 1 & 0 & 2 \\ 2 & 2 & 1 \\ 3 & 2 & 0 \end{pmatrix} \begin{pmatrix} 2 & 0 & -2 \\ 1 & 0 & 1 \\ 1 & -1 & 0 \end{pmatrix} = \begin{pmatrix} 4 & -2 & -2 \\ 7 & -1 & -2 \\ 8 & 0 & -4 \end{pmatrix} \tag{16.6.9}$$

An example of a matrix multiplying a vector is

$$A\mathbf{v} = \begin{pmatrix} 1 & 0 & 2 \\ 2 & 2 & 1 \\ 3 & 2 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} = \begin{pmatrix} 7 \\ 9 \\ 7 \end{pmatrix} \tag{16.6.10}$$

> *Matrix multiplication is not generally commutative, a property that mirrors the behavior found earlier for symmetry operations within a point group.*

Direct Products

The direct product of two matrices (given the symbol $\otimes$) is a special type of matrix product that generates a matrix of higher dimensionality if both matrices have dimension greater than one. The easiest way to demonstrate how to construct a direct product of two matrices A and B is by an example:

$$A \otimes B = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \otimes \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \tag{16.6.11}$$

$$= \begin{pmatrix} a_{11}B & a_{12}B \\ a_{21}B & a_{22}B \end{pmatrix} \tag{16.6.12}$$

$$= \begin{pmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{21} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{pmatrix} \tag{16.6.13}$$

Though this may seem like a somewhat strange operation to carry out, direct products crop up a great deal in group theory.

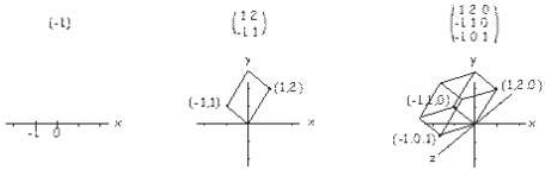
Inverse Matrices and Determinants

If two square matrices A and B multiply together to give the identity matrix I (i.e. $AB = I$) then B is said to be the *inverse* of A (written A^{-1}). If B is the inverse of A then A is also the inverse of B. Recall that one of the conditions imposed upon the symmetry operations in a group is that each operation must have an inverse. It follows by analogy that any matrices we use to represent symmetry elements must also have inverses. It turns out that a square matrix only has an inverse if its determinant is non-zero. For this reason (and others which will become apparent later on when we need to solve equations involving matrices) we need to learn a little about matrix determinants and their properties.

For every square matrix, there is a unique function of all the elements that yields a single number called the determinant. Initially it probably won't be particularly obvious why this number should be useful, but matrix determinants are of great importance both in

pure mathematics and in a number of areas of science. Historically, determinants were actually around before matrices. They arose originally as a property of a system of linear equations that 'determined' whether the system had a unique solution. As we shall see later, when such a system of equations is recast as a matrix equation this property carries over into the matrix determinant.

There are two different definitions of a determinant, one geometric and one algebraic. In the geometric interpretation, we consider the numbers across each row of an $n \times n$ matrix as coordinates in n-dimensional space. In a one-dimensional matrix (i.e. a number), there is only one coordinate, and the determinant can be interpreted as the (signed) length of a vector from the origin to this point. For a 2×2 matrix we have two coordinates in a plane, and the determinant is the (signed) area of the parallelogram that includes these two points and the origin. For a 3×3 matrix the determinant is the (signed) volume of the parallelepiped that includes the three points (in three-dimensional space) defined by the matrix and the origin. This is illustrated below. The idea extends up to higher dimensions in a similar way. In some sense then, the determinant is therefore related to the size of a matrix.



The algebraic definition of the determinant of an nxn matrix is a sum over all the possible products (permutations) of n elements taken from different rows and columns. The number of terms in the sum is $n!$, the number of possible permutations of n values (i.e. 2 for a 2×2 matrix, 6 for a 3×3 matrix etc). Each term in the sum is given a positive or a negative sign depending on whether the number of *permutation inversions* in the product is even or odd. A permutation inversion is just a pair of elements that are out of order when described by their indices. For example, for a set of four elements (a_1, a_2, a_3, a_4), the permutation $a_1a_2a_3a_4$ has all the elements in their correct order (i.e. in order of increasing index). However, the permutation $a_2a_4a_1a_3$ contains the permutation inversions a_2a_1, a_4a_1, a_4a_3.

For example, for a two-dimensional matrix

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \tag{16.6.14}$$

where the subscripts label the row and column positions of the elements, there are 2 possible products/permutations involving elements from different rows and column, $a_{11}a_{22}$ and $a_{12}a_{21}$. In the second term, there is a permutation inversion involving the column indices 2 and 1 (permutation inversions involving the row and column indices should be looked for separately) so this term takes a negative sign, and the determinant is $a_{11}a_{22}$ - $a_{12}a_{21}$.

For a 3×3 matrix

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{16.6.15}$$

the possible combinations of elements from different rows and columns, together with the sign from the number of permutations required to put their indices in numerical order are:

$$\begin{aligned} a_{11}a_{22}a_{33} &\quad (0 \text{ inversions}) \\ -a_{11}a_{23}a_{32} &\quad (1 \text{ inversion - } 3 > 2 \text{ in the column indices}) \\ -a_{12}a_{21}a_{33} &\quad (1 \text{ inversion - } 2 > 1 \text{ in the column indices}) \\ a_{12}a_{23}a_{31} &\quad (2 \text{ inversions - } 2 > 1 \text{ and } 3 > 1 \text{ in the column indices}) \\ a_{13}a_{21}a_{32} &\quad (2 \text{ inversions - } 3 > 1 \text{ and } 3 > 2 \text{ in the column indices}) \\ -a_{13}a_{22}a_{31} &\quad (3 \text{ inversions - } 3 > 2, 3 > 1, \text{ and } 2 > 1 \text{ in the column indices}) \end{aligned} \tag{16.6.16}$$

and the determinant is simply the sum of these terms.

This may all seem a little complicated, but in practice there is a fairly systematic procedure for calculating determinants. The determinant of a matrix A is usually written $\det(A)$ or $|a|$.

For a 2×2 matrix

$$A = \begin{pmatrix} a & b \\ c & d \end{pmatrix}; det(A) = |A| = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc \tag{16.6.17}$$

For a 3×3 matrix

$$B = \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix}; det(B) = a\begin{vmatrix} e & f \\ h & i \end{vmatrix} - b\begin{vmatrix} d & f \\ g & i \end{vmatrix} + c\begin{vmatrix} d & e \\ g & h \end{vmatrix} \tag{16.6.18}$$

For a $4x4$ matrix

$$C = \begin{pmatrix} a & b & c & d \\ e & f & g & h \\ i & j & k & l \\ m & n & o & p \end{pmatrix}; \tag{16.6.19}$$

$$det(C) = a\begin{vmatrix} f & g & h \\ j & k & l \\ n & o & p \end{vmatrix} - b\begin{vmatrix} e & g & h \\ i & k & l \\ m & o & p \end{vmatrix} + c\begin{vmatrix} e & f & h \\ i & j & l \\ m & n & p \end{vmatrix} - d\begin{vmatrix} e & f & g \\ i & j & k \\ m & n & o \end{vmatrix}$$

and so on in higher dimensions. Note that the submatrices in the 3×3 example above are just the matrices formed from the original matrix B that don't include any elements from the same row or column as the premultiplying factors from the first row.

Matrix determinants have a number of important properties:

i. The determinant of the identity matrix is 1.

$$e.g. \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} = 1 \tag{16.6.20}$$

ii. The determinant of a matrix is the same as the determinant of its transpose i.e. det(a) = det(A^T)

$$e.g. \begin{vmatrix} a & b \\ c & d \end{vmatrix} = \begin{vmatrix} a & c \\ b & d \end{vmatrix} \tag{16.6.21}$$

iii. The determinant changes sign when any two rows or any two columns are interchanged

$$e.g. \begin{vmatrix} a & b \\ c & d \end{vmatrix} = -\begin{vmatrix} b & a \\ d & c \end{vmatrix} = -\begin{vmatrix} c & d \\ a & b \end{vmatrix} = \begin{vmatrix} d & c \\ b & a \end{vmatrix} \tag{16.6.22}$$

iv. The determinant is zero if any row or column is entirely zero, or if any two rows or columns are equal or a multiple of one another.

$$e.g. \begin{vmatrix} 1 & 2 \\ 0 & 0 \end{vmatrix} = 0, \begin{vmatrix} 1 & 2 \\ 2 & 4 \end{vmatrix} = 0 \tag{16.6.23}$$

v. The determinant is unchanged by adding any linear combination of rows (or columns) to another row (or column).

vi. The determinant of the product of two matrices is the same as the product of the determinants of the two matrices i.e. det(AB) = det(A)det(B).

The requirement that in order for a matrix to have an inverse it must have a non-zero determinant follows from property vi). As mentioned previously, the product of a matrix and its inverse yields the identity matrix I. We therefore have:

$$\begin{aligned} det(A^{-1}A) = det(A^{-1})det(A) &= det(I) \\ det(A^{-1}) &= det(I)/det(A) = 1/det(A) \end{aligned} \tag{16.6.24}$$

It follows that a matrix A can only have an inverse if its determinant is non-zero, otherwise the determinant of its inverse would be undefined.

16.6: Matrices is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **1.8: Review of Matrices** by Claire Vallance is licensed CC BY 4.0. Original source: http://vallance.chem.ox.ac.uk/pdfs/SymmetryLectureNotes.pdf.

https://chem.libretexts.org/@go/page/287088

16.7: Numerical Methods

16.7: Numerical Methods is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

16.8: Partial Differentiation

The development of thermodynamics would have been unthinkable without calculus in more than one dimension (multivariate calculus) and partial differentiation is essential to the theory.

'Active' Variables

When applying partial differentiation it is very important to keep in mind, which symbol is the variable and which ones are the constants. Mathematicians usually write the variable as x or y and the constants as a, b or c but in Physical Chemistry the symbols are different. It sometimes helps to replace the symbols in your mind.

For example the van der Waals equation can be written as:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2} \tag{16.8.1}$$

Suppose we must compute the partial differential

$$\left(\frac{\partial P}{\partial \overline{V}}\right)_T$$

In this case molar volume is the variable 'x' and the pressure is the function $f(x)$, the rest is just constants, so Equation 16.8.1 can be rewritten in the form

$$f(x) = \frac{c}{x - b} - \frac{a}{x^2} \tag{16.8.2}$$

When calculating

$$\left(\frac{\partial P}{\partial T}\right)_{\overline{V}}$$

should look at Equation 16.8.1 as:

$$f(x) = cx - d$$

The active variable 'x' is now the temperature T and all the rest is just constants. It is useful to train your eye to pick out the one active one from all the inactive ones. Use highlighters, underline, rewrite, do whatever helps you best.

Cross Derivatives

As shown in Equations H.5 and H.6 there are also higher order partial derivatives versus T and versus V. A very interesting derivative of second order and one that is used extensively in thermodynamics is the mixed second order derivative.

$$\left(\frac{\partial^2 P}{\partial T\, \partial \overline{V}}\right) = \left(\frac{\partial^P}{\partial \overline{V}\, \partial T}\right) \tag{16.8.3}$$

Of course here the 'active' variable is first T, then V. The interesting thing about it is that it does not matter whether you first take T and then V or the other way around.

Example H-2 shows an example of how mixed derivatives can be used to translate one quantity into the other. This trick is used over and over again in thermodynamics because it allows you to replace a quantity that is really hard to measure by one (or more) that are much easier to get good experimental values for.

For example:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

This expression is not obvious at all. It tells you that if you study the pressure P when heating up while keeping the volume the same (which is doable) you're measuring how the entropy changes with volume under isothermal conditions. Entropy will be discussed later, suffice it to say that nobody has ever constructed a working 'entropometer'! So that is an impossible quantity to measure directly.

The Decomposition of Changes

A very important result of multivariate calculus is that if a quantity Q is a function of more than one variable, say A and B that we can decompose any infinitesimal change dQ into infinitesimal changes in A and B in a very simple linear way:

$$dQ = \alpha\, dA + \beta dB \tag{16.8.4}$$

dq is sometimes referred to as the total differential. The coefficients α and β are the partial derivatives of first order versus A and B. This mathematical fact is something we will be using over and over.

Exact and Inexact differentials: State and path functions

The car trip

Suppose you drive your car up and down a mountain. You perform two measurements: you have a barometer that measures the air pressure and you keep an eye on your gas gage. Even though the barometer will show lower values on top of the mountain, its value will return to its initial value when you return home (barring weather changes). You might wish the same would hold for your gas gage particularly at current gas prices!

Pressure is a good example of a **state function** (it returns to its old value if you go back to a previous state). The other (the gas gage) is a path function. (Make a detour and your bank account will tell you difference!).

The difference between state and path functions has its roots deep in mathematics and it comes in as soon as a function has two of more variables.

The gas law is a good example. The pressure depends on both temperature T and (molar) volume V. When changing the pressure a little bit, say by dP we can show that we can write that out in the two possible components dT and dV as:

$$dP = pdT + qdV \tag{16.8.5}$$

$$= \left(\frac{\partial S}{\partial V}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \tag{16.8.6}$$

At first, I wrote arbitrary coefficients p and q in Equation 16.8.5, but as you can see they are really partial derivatives (Equation 16.8.6). This is another way that thermodynamics exploits multivariate calculus: it shows how total changes can be built up of various contributions.

The interesting thing is that ***if*** the function P is a ***state*** function (and your barometer will testify to that) then Equation 16.8.3 **must** hold. However, if the function is a ***path*** function, then this equality does ***not*** hold.

Thermodynamics is largely based upon exploiting the above facts:

- It tries to define state functions to describe energy changes
- It tries to decompose changes into well-defined contributions
- It uses partial differentials to link known quantities to unknown ones

---

16.8: Partial Differentiation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **32.3: Partial Differentiation** is licensed CC BY-NC-SA 4.0.

16.9: Series and Limits

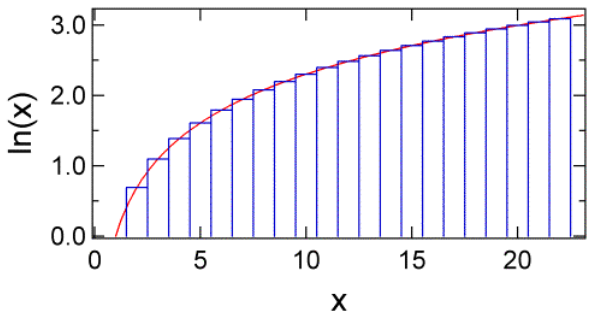
16.9: Series and Limits is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

16.10: The Binomial Distribution and Stirling's Appromixation

Stirling's approximation is named after the Scottish mathematician James Stirling (1692-1770). In confronting statistical problems we often encounter factorials of very large numbers. The factorial $N!$ is a product $N(N-1)(N-2)...(2)(1)$. Therefore, $\ln N!$ is a sum

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + ... + \ln N = \sum_{k=1}^{N} \ln k. \tag{16.10.1}$$

where we have used the property of logarithms that $\log(abc) = \log(a) + \log(b) + \log(c)$. The sum is shown in figure below.



Using **Euler-MacLaurin** formula one has

$$\sum_{k=1}^{N} \ln k = \int_1^N \ln x\, dx + \sum_{k=1}^{p} \frac{B_{2k}}{2k(2k-1)} \left(\frac{1}{n^{2k-1}} - 1 \right) + R, \tag{16.10.2}$$

where $B_1 = -1/2$, $B_2 = 1/6$, $B_3 = 0$, $B_4 = -1/30$, $B_5 = 0$, $B_6 = 1/42$, $B_7 = 0$, $B_8 = -1/30$, ... are the **Bernoulli numbers**, and \(R\) is an error term which is normally small for suitable values of \(p\).

Then, for large N,

$$\ln N! \sim \int_1^N \ln x\, dx \approx N \ln N - N. \tag{16.10.3}$$

after some further manipulation one arrives at (apparently Stirling's contribution was the prefactor of $\sqrt{2\pi}$)

$$N! = \sqrt{2\pi N}\, N^N e^{-N} e^{\lambda_N} \tag{16.10.4}$$

where

$$\frac{1}{12N+1} < \lambda_N < \frac{1}{12N}. \tag{16.10.5}$$

The sum of the area under the blue rectangles shown below up to N is $\ln N!$. As you can see the rectangles begin to closely approximate the red curve as m gets larger. The area under the curve is given the integral of $\ln x$.

$$\ln N! = \sum_{m=1}^{N} \ln m \approx \int_1^N \ln x\, dx \tag{16.10.6}$$

To solve the integral use integration by parts

$$\int u\, dv = uv - \int v\, dy \tag{16.10.7}$$

Here we let $u = \ln x$ and $dv = dx$. Then $v = x$ and $du = \frac{dx}{x}$.

$$\int_0^N \ln x\, dx = x \ln x \Big|_0^N - \int_0^N x \frac{dx}{x} \tag{16.10.8}$$

Notice that $x/x = 1$ in the last integral and $x \ln x$ is 0 when evaluated at zero, so we have

$$\int_0^N \ln x\, dx = N \ln N - \int_0^N dx \tag{16.10.9}$$

Which gives us Stirling's approximation: $\ln N! = N \ln N – N$. As is clear from the figure above Stirling's approximation gets better as the number N gets larger (Table **16.10.1**).

Table **16.10.1**: Evaluation of Approximation with absolute values

N	N!	ln N!	N ln N – N	Error
10	3.63×10^{6}	15.1	13.02	13.8%
50	3.04×10^{64}	148.4	145.6	1.88%
100	9.33×10^{157}	363.7	360.5	0.88%
150	5.71×10^{262}	605.0	601.6	0.56%

Calculators often overheat at 200!, which is all right since clearly result are converging. In thermodynamics, we are often dealing very large N (i.e., of the order of Avagadro's number) and for these values Stirling's approximation is excellent.

References

1. J. Stirling "Methodus differentialis, sive tractatus de summation et interpolation serierum infinitarium", London (1730). English translation by J. Holliday "The Differential Method: A Treatise of the Summation and Interpolation of Infinite Series" (1749)

16.10: The Binomial Distribution and Stirling's Appromixation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- **Stirling's Approximation** by SklogWiki, Stefan Franzen is licensed CC BY-NC-SA 4.0. Original source: http://www.sklogwiki.org/SklogWiki/index.php/Stirling%27s_approximation.

Index

A

Anharmonicity
- 7.5: Vibrational Overtones
- 10.3: The Harmonic Oscillator is an Approximation

Argand diagram
- 16.1: Complex Numbers

B

beating
- 8.4: The Quantum Mechanical Free Particle

C

catalytic efficiency
- 4.2: The Equations of Enzyme Kinetics

centrifugal force
- 7.4: The Pure Rotational Spectrum has Unequal Spacings

collision theory
- 1.7: Theories of Reaction Rates

Commuting Operators
- 9.6: Heisenburg Uncertainy Principle III - Commuting Operators

competitive inhibition
- 4.5: Enzyme Inhibition

CONDON APPROXIMATION
- 7.7: The Franck-Condon Principle

Consecutive Reactions (Kinetics)
- 1.4: More Complex Reactions

Continuous Flow
- 1.10: Fast Reactions in Solution

cooperativity
- 4.6: Allosteric Interactions

correspondence principle
- 8.3: The Schrödinger Equation is an Eigenvalue Problem

Coulomb integral
- 14.5: The \(\pi\)-Electron Approximation of Conjugation

cyclic boundary condition
- 10.8: The Energy Levels of a Rigid Rotor

D

degeneracy
- 8.12: A Particle in a Three-Dimensional Box

delocalization energy
- 14.6: Butadiene is Stabilized by a Delocalization Energy

denaturation
- 4.8: The Effect of Temperature on Enzyme Kinetics

Determinants
- 16.5: Determinants

Diatomic Vibration
- 10.5: The Harmonic Oscillator and Infrared Spectra

double reciprocal plot
- 4.2: The Equations of Enzyme Kinetics

E

eigenfunction
- 8.3: The Schrödinger Equation is an Eigenvalue Problem

eigenvalue problem
- 8.3: The Schrödinger Equation is an Eigenvalue Problem
- 9.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators

envelope function
- 8.4: The Quantum Mechanical Free Particle

exact differential
- 16.8: Partial Differentiation

expectation value
- 8.8: The Average Momentum of a Particle in a Box is Zero

extended basis sets
- 15.3: Extended Basis Sets

F

Flash Photolysis
- 1.10: Fast Reactions in Solution

free particle
- 8.4: The Quantum Mechanical Free Particle

G

Gaussian Type Orbitals
- 15.2: Gaussian Basis Sets

Gaussian Wavepacket
- 8.4: The Quantum Mechanical Free Particle

H

Hückel theory
- 14.5: The \(\pi\)-Electron Approximation of Conjugation

Hamiltonian
- 9.2: Quantum Operators Represent Classical Variables

Harmonic oscillator
- 10.1: A Harmonic Oscillator Obeys Hooke's Law
- 10.3: The Harmonic Oscillator is an Approximation
- 10.4: The Harmonic Oscillator Energy Levels
- 10.5: The Harmonic Oscillator and Infrared Spectra

Heisenberg uncertainty principle
- 8.10: The Uncertainty Principle Redux - Estimating Uncertainties from Wavefunctions

Hermite polynomials
- 10.6: The Harmonic-Oscillator Wavefunctions Involve Hermite Polynomials
- 10.7: Hermite Polynomials are either Even or Odd Functions

Hermitian operators
- 9.5: The Eigenfunctions of Operators are Orthogonal

hill equation
- 4.6: Allosteric Interactions

Hooke's Law
- 10.1: A Harmonic Oscillator Obeys Hooke's Law

hybridization (water)
- 14.2: Different Hybrid Orbitals Used for Bonding in Water

I

inexact differential
- 16.8: Partial Differentiation

inhibitor
- 4.5: Enzyme Inhibition

IR spectra
- 10.5: The Harmonic Oscillator and Infrared Spectra

K

KIE
- 1.8: Isotope Effects in Chemical Reactions

Koopmans' Theorem
- 14.4: Photoelectron Spectroscopy

L

laplacian
- 9.2: Quantum Operators Represent Classical Variables

M

Michaelis constant
- 4.2: The Equations of Enzyme Kinetics

microwave spectroscopy
- 10.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

molecularity
- 1.3: Molecularity of a Reaction

Morse potential
- 10.3: The Harmonic Oscillator is an Approximation
- 10.5: The Harmonic Oscillator and Infrared Spectra

N

nodes
- 8.8: The Average Momentum of a Particle in a Box is Zero

Noncompetitive Inhibition
- 4.5: Enzyme Inhibition

Nonstationary States
- 9.4: The Time-Dependent Schrödinger Equation

O

Operators
- 8.2: Linear Operators in Quantum Mechanics
- 9.2: Quantum Operators Represent Classical Variables

Orthonormality
- 8.6: The Energy of a Particle in a Box is Quantized

overtones
- 7.5: Vibrational Overtones

P

Parallel Reactions (Kinetics)
- 1.4: More Complex Reactions

Particle in a 3D Box
- 8.12: A Particle in a Three-Dimensional Box

Particle in a box
- 8.6: The Energy of a Particle in a Box is Quantized

perturbation theory
- 12.5: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

Perturbation Theory for Helium
- 13.2: Perturbation Theory and the Variational Method for Helium

physical
7.1: The Electromagnetic Spectrum
7.2: Rotational Transitions Accompany Vibrational Transitions
7.3: The Vibration-Rotation Spectrum
7.5: Vibrational Overtones
Polarization Terms
15.4: Orbital Polarization Terms
Principle of Superposition
8.4: The Quantum Mechanical Free Particle
Probabilistic Interpretation
8.5: Wavefunctions Have a Probabilistic Interpretation

Q
quenched flow
1.10: Fast Reactions in Solution

R
reduced mass
10.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule
reducing agent
10.5: The Harmonic Oscillator and Infrared Spectra
resonance integral
14.5: The \(\pi\)-Electron Approximation of Conjugation
Reversible Reactions (Kinetics)
1.4: More Complex Reactions
Rigid rotor
10.8: The Energy Levels of a Rigid Rotor
10.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule

S
Schmidt orthogonalization theorem
9.5: The Eigenfunctions of Operators are Orthogonal
Schrödinger equation
8.1: The Schrödinger Equation
Selection rules
10.5: The Harmonic Oscillator and Infrared Spectra
Slater Type Orbitals
15.2: Gaussian Basis Sets
specificity constant
4.2: The Equations of Enzyme Kinetics
stationary state
9.4: The Time-Dependent Schrödinger Equation
stopped flow
1.10: Fast Reactions in Solution

T
Temperature Jump
1.10: Fast Reactions in Solution
The Hill Equation
4.6: Allosteric Interactions
Total Differentials
16.8: Partial Differentiation
Transition Energies
10.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule
transition state theory
1.7: Theories of Reaction Rates
turnover number
4.2: The Equations of Enzyme Kinetics

U
Uncompetitive Inhibition
4.5: Enzyme Inhibition

V
Variational Method for Helium
13.2: Perturbation Theory and the Variational Method for Helium

W
Walsh diagrams
14.3: Why is BeH_2 Linear and H_2O Bent?
Wavefunction Normalization
8.7: Wavefunctions Must Be Normalized
wavepackets
8.4: The Quantum Mechanical Free Particle

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: Chem 322: Physical Chemisty II

Webpages: 172

Applicable Restrictions: Noncommercial

All licenses found:

- Undeclared: 55.8% (96 pages)
- CC BY-NC-SA 4.0: 43% (74 pages)
- CC BY-SA 4.0: 1.2% (2 pages)

By Page

- Chem 322: Physical Chemisty II - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Chemical Kinetics - *Undeclared*
    - 1.1: Reaction Rates - *Undeclared*
    - 1.2: Reaction Order - *Undeclared*
    - 1.3: Molecularity of a Reaction - *Undeclared*
    - 1.4: More Complex Reactions - *Undeclared*
    - 1.5: The Effect of Temperature on Reaction Rates - *Undeclared*
    - 1.6: Potential Energy Surfaces - *Undeclared*
    - 1.7: Theories of Reaction Rates - *Undeclared*
    - 1.8: Isotope Effects in Chemical Reactions - *Undeclared*
    - 1.9: Reactions in Solution - *Undeclared*
    - 1.10: Fast Reactions in Solution - *Undeclared*
    - 1.11: Oscillating Reactions - *Undeclared*
    - 1.12: Chemical Kinetics (Exercises) - *Undeclared*
  - 2: Chemical Kinetics II - *Undeclared*
    - 2.1: The Rates of Chemical Reactions - *Undeclared*
    - 2.2: Integrated Rate Laws - *Undeclared*
    - 2.3: Reactions Approaching Equilibrium - *Undeclared*
    - 2.4: The Arrhenius Equation - *Undeclared*
    - 2.5: Reaction Mechanisms - *Undeclared*
    - 2.6: Examples of Reaction Mechanisms - *Undeclared*
    - 2.7: Photochemistry - *Undeclared*
    - 2.8: Enzymes - *Undeclared*
  - 3: Reaction Dynamics - *Undeclared*
    - 3.1: Collision Theory - *Undeclared*
    - 3.2: Diffusion-controlled Reactions - *Undeclared*
    - 3.3: Transition-state Theory - *Undeclared*
    - 3.4: The Dynamics of Molecular Collisions - *Undeclared*
    - 3.5: Electron Transfer in Homogeneous Systems - *Undeclared*
    - 3.6: Processes at Electrodes - *Undeclared*
  - 4: Enzyme Kinetics - *Undeclared*
    - 4.1: General Principles of Catalysis - *Undeclared*
    - 4.2: The Equations of Enzyme Kinetics - *Undeclared*
    - 4.3: Chymotrypsin- A Case Study - *Undeclared*
    - 4.4: Multisubstrate Systems - *Undeclared*
    - 4.5: Enzyme Inhibition - *Undeclared*
    - 4.6: Allosteric Interactions - *Undeclared*
    - 4.7: The Effect of pH on Enzyme Kinetics - *Undeclared*
    - 4.8: The Effect of Temperature on Enzyme Kinetics - *CC BY-SA 4.0*
    - 4.9: Exercises - *Undeclared*
  - 5: Lasers, Laser Spectroscopy, and Photochemistry - *Undeclared*
    - 5.1: Electronically Excited Molecules - *Undeclared*
    - 5.2: Transitions Modeled as Kinetics - *Undeclared*
    - 5.3: Two-Level Systems Cannot Form Population Inversions - *Undeclared*
    - 5.4: Population Inversion via Three-Level Systems - *Undeclared*
    - 5.5: Laser Fundamentals - *Undeclared*
    - 5.6: The Helium-Neon Laser - *Undeclared*
    - 5.7: High-Resolution Laser Spectroscopy - *Undeclared*
    - 5.8: Photochemical Dynamics - *Undeclared*
  - 6: Nuclear Magnetic Resonance Spectroscopy - *Undeclared*

- 6.1: Nuclei Have Intrinsic Spin Angular Momenta - *Undeclared*
- 6.2: Magnetic Moments Interact with Magnetic Fields - *Undeclared*
- 6.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz - *Undeclared*
- 6.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded - *Undeclared*
- 6.5: Chemical Shifts is Sensitive to Chemical Environment of the Nucleus - *Undeclared*
- 6.6: Spin-Spin Coupling Results in Multiplets in NMR Spectra - *Undeclared*
- 6.7: Spin-Spin Coupling Between Chemically Equivalent Protons Is Not Observed - *Undeclared*
- 6.8: The n+1 Rule Applies Only to First-Order Spectra - *Undeclared*
- 6.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method - *Undeclared*

7: Molecular Spectroscopy - *Undeclared*

- 7.1: The Electromagnetic Spectrum - *Undeclared*
- 7.2: Rotational Transitions Accompany Vibrational Transitions - *Undeclared*
- 7.3: The Vibration-Rotation Spectrum - *Undeclared*
- 7.4: The Pure Rotational Spectrum has Unequal Spacings - *Undeclared*
- 7.5: Vibrational Overtones - *Undeclared*
- 7.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information - *Undeclared*
- 7.7: The Franck-Condon Principle - *Undeclared*
- 7.8: Rotational Spectra of Polyatomic Molecules - *Undeclared*
- 7.9: Normal Modes in Polyatomic Molecules - *Undeclared*
- 7.10: Irreducible Representation of Point Groups - *Undeclared*
- 7.11: Time-Dependent Perturbation Theory - *CC BY-SA 4.0*
- 7.12: The Selection Rule for the Rigid Rotator - *Undeclared*
- 7.13: The Harmonic Oscillator Selection Rule - *Undeclared*
- 7.14: Group Theory Determines Infrared Activity - *Undeclared*
- 7.15: Molecular Spectroscopy (Exercises) - *Undeclared*

8: The Schrödinger Equation and a Particle in a Box - *CC BY-NC-SA 4.0*

- 8.1: The Schrödinger Equation - *CC BY-NC-SA 4.0*
- 8.2: Linear Operators in Quantum Mechanics - *CC BY-NC-SA 4.0*
- 8.3: The Schrödinger Equation is an Eigenvalue Problem - *CC BY-NC-SA 4.0*
- 8.4: The Quantum Mechanical Free Particle - *CC BY-NC-SA 4.0*
- 8.5: Wavefunctions Have a Probabilistic Interpretation - *CC BY-NC-SA 4.0*
- 8.6: The Energy of a Particle in a Box is Quantized - *CC BY-NC-SA 4.0*
- 8.7: Wavefunctions Must Be Normalized - *CC BY-NC-SA 4.0*
- 8.8: The Average Momentum of a Particle in a Box is Zero - *CC BY-NC-SA 4.0*
- 8.9: Particle in a Finite Box and Tunneling (optional) - *CC BY-NC-SA 4.0*
- 8.10: The Uncertainty Principle Redux - Estimating Uncertainties from Wavefunctions - *CC BY-NC-SA 4.0*
- 8.11: A Particle in a Two-Dimensional Box - *CC BY-NC-SA 4.0*
- 8.12: A Particle in a Three-Dimensional Box - *CC BY-NC-SA 4.0*
- 8.13: The Schrödinger Equation and a Particle in a Box (Exercises) - *CC BY-NC-SA 4.0*

9: Postulates and Principles of Quantum Mechanics - *CC BY-NC-SA 4.0*

- 9.1: The Wavefunction Specifies the State of a System - *CC BY-NC-SA 4.0*
- 9.2: Quantum Operators Represent Classical Variables - *CC BY-NC-SA 4.0*
- 9.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators - *CC BY-NC-SA 4.0*
- 9.4: The Time-Dependent Schrödinger Equation - *CC BY-NC-SA 4.0*
- 9.5: The Eigenfunctions of Operators are Orthogonal - *CC BY-NC-SA 4.0*
- 9.6: Heisenburg Uncertainy Principle III - Commuting Operators - *CC BY-NC-SA 4.0*
- 9.7: Postulates and Principles of Quantum Mechanics (Exercises) - *CC BY-NC-SA 4.0*

10: The Harmonic Oscillator and the Rigid Rotor - *CC BY-NC-SA 4.0*

- 10.1: A Harmonic Oscillator Obeys Hooke's Law - *CC BY-NC-SA 4.0*
- 10.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule - *CC BY-NC-SA 4.0*

- 10.3: The Harmonic Oscillator is an Approximation - *CC BY-NC-SA 4.0*
- 10.4: The Harmonic Oscillator Energy Levels - *CC BY-NC-SA 4.0*
- 10.5: The Harmonic Oscillator and Infrared Spectra - *CC BY-NC-SA 4.0*
- 10.6: The Harmonic-Oscillator Wavefunctions Involve Hermite Polynomials - *CC BY-NC-SA 4.0*
- 10.7: Hermite Polynomials are either Even or Odd Functions - *CC BY-NC-SA 4.0*
- 10.8: The Energy Levels of a Rigid Rotor - *CC BY-NC-SA 4.0*
- 10.9: The Rigid Rotator is a Model for a Rotating Diatomic Molecule - *CC BY-NC-SA 4.0*
- 10.10: The Harmonic Oscillator and the Rigid Rotor (Exercises) - *CC BY-NC-SA 4.0*

- 11: The Hydrogen Atom - *CC BY-NC-SA 4.0*
  - 11.1: The Schrödinger Equation for the Hydrogen Atom Can Be Solved Exactly - *CC BY-NC-SA 4.0*
  - 11.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics - *CC BY-NC-SA 4.0*
  - 11.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision - *CC BY-NC-SA 4.0*
  - 11.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers - *CC BY-NC-SA 4.0*
  - 11.5: s Orbitals are Spherically Symmetric - *CC BY-NC-SA 4.0*
  - 11.6: Orbital Angular Momentum and the p-orbitals - *CC BY-NC-SA 4.0*
  - 11.7: The Helium Atom Cannot Be Solved Exactly - *CC BY-NC-SA 4.0*
  - 11.8: The Hydrogen Atom (Exercises) - *CC BY-NC-SA 4.0*
- 12: Approximation Methods - *CC BY-NC-SA 4.0*
  - 12.1: Slater's Rules for Shielding - *CC BY-NC-SA 4.0*
  - 12.2: The Variational Method - *CC BY-NC-SA 4.0*
  - 12.3: Linear Variational Method and the Secular Determinant - *CC BY-NC-SA 4.0*
  - 12.4: Trial Functions Can Be Linear Combinations of Functions with Variational Parameters - *CC BY-NC-SA 4.0*
  - 12.5: Perturbation Theory Expresses the Solutions in Terms of Solved Problems - *CC BY-NC-SA 4.0*
  - 12.6: Approximation Methods (Exercises) - *CC BY-NC-SA 4.0*
- 13: Multielectron Atoms - *CC BY-NC-SA 4.0*
  - 13.1: Atomic and Molecular Calculations are Expressed in Atomic Units - *CC BY-NC-SA 4.0*
  - 13.2: Perturbation Theory and the Variational Method for Helium - *CC BY-NC-SA 4.0*
  - 13.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method - *CC BY-NC-SA 4.0*
  - 13.4: An Electron Has An Intrinsic Spin Angular Momentum - *CC BY-NC-SA 4.0*
  - 13.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons - *CC BY-NC-SA 4.0*
  - 13.6: Antisymmetric Wave Functions can be Represented by Slater Determinants - *CC BY-NC-SA 4.0*
  - 13.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data - *CC BY-NC-SA 4.0*
  - 13.8: Term Symbols Gives Detailed Descriptions of an Electron Configuration - *CC BY-NC-SA 4.0*
  - 13.9: Multi-electron Considerations - A Closer Look at Helium - *CC BY-NC-SA 4.0*
  - 13.10: The Allowed Values of J - the Total Angular Momentum Quantum Number - *CC BY-NC-SA 4.0*
  - 13.11: Hund's Rules Determine the Term Symbols of the Ground Electronic States - *CC BY-NC-SA 4.0*
  - 13.12: Using Atomic Term Symbols to Describe Atomic Spectra - *CC BY-NC-SA 4.0*
  - 13.13: Multielectron Atoms (Exercises) - *CC BY-NC-SA 4.0*
- 14: Bonding in Polyatomic Molecules - *Undeclared*
  - 14.1: Hybrid Orbitals Account for Molecular Shape - *Undeclared*
  - 14.2: Different Hybrid Orbitals Used for Bonding in Water - *Undeclared*
  - 14.3: Why is BeH_2 Linear and H_2O Bent? - *Undeclared*
  - 14.4: Photoelectron Spectroscopy - *Undeclared*
  - 14.5: The \(\pi\)-Electron Approximation of Conjugation - *Undeclared*
  - 14.6: Butadiene is Stabilized by a Delocalization Energy - *Undeclared*
- 15: Computational Quantum Chemistry - *Undeclared*
  - 15.1: Overview of Quantum Calculations - *Undeclared*
  - 15.2: Gaussian Basis Sets - *Undeclared*
  - 15.3: Extended Basis Sets - *Undeclared*
  - 15.4: Orbital Polarization Terms - *Undeclared*
  - 15.5: The Ground-State Energy of H_2 - *Undeclared*
  - 15.6: Quantum Calculations - *Undeclared*
- 16: MathChapters - *CC BY-NC-SA 4.0*
  - 16.1: Complex Numbers - *CC BY-NC-SA 4.0*
  - 16.2: Probability and Statistics - *CC BY-NC-SA 4.0*

- 16.3: Vectors - *CC BY-NC-SA 4.0*
- 16.4: Spherical Coordinates - *CC BY-NC-SA 4.0*
- 16.5: Determinants - *CC BY-NC-SA 4.0*
- 16.6: Matrices - *CC BY-NC-SA 4.0*
- 16.7: Numerical Methods - *CC BY-NC-SA 4.0*
- 16.8: Partial Differentiation - *CC BY-NC-SA 4.0*
- 16.9: Series and Limits - *CC BY-NC-SA 4.0*
- 16.10: The Binomial Distribution and Stirling's Appromixation - *CC BY-NC-SA 4.0*

Back Matter - *Undeclared*

- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*