BCU: CH 332 PHYSICAL CHEMISTRY II



Bethune-Cookman University

LibreTexts™

University of California, Davis

UC Davis Chem 110B Physical Chemistry II

Delmar Larsen

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 03/11/2026

TABLE OF CONTENTS

AGENDA

- Rethinking Hybridization

Text

- Licensing
- 10: Bonding in Polyatomic Molecules
  - 10.1: Hybrid Orbitals Account for Molecular Shape
  - 10.2: Different Hybrid Orbitals Used for Bonding in Water
  - 10.3: Why is BeH_2 Linear and H_2O Bent?
  - 10.4: Photoelectron Spectroscopy
  - 10.5: The \(\pi\)-Electron Approximation of Conjugation
  - 10.6: Butadiene is Stabilized by a Delocalization Energy
- 11: Computational Quantum Chemistry
  - 11.0: Overview of Quantum Calculations
  - 11.1: Gaussian Basis Sets
  - 11.2: Extended Basis Sets
  - 11.3: Orbital Polarization Terms
  - 11.4: The Ground-State Energy of H_2
  - 11.5: Quantum Calculations
- 12: Group Theory - Exploiting Symmetry
  - 12.1: Using Symmetry to Simplify Calculations
  - 12.2: The Symmetry of Molecules
  - 12.3: Symmetry Operations Define Groups
  - 12.4: Symmetry Operations can be Represented by Matrices
  - 12.5: The \(C_3V\) Point Group Has a 2-D Irreducible Representation
  - 12.6: Character Tables
  - 12.7: Relations involving Characters
  - 12.8: Using Symmetry to Predict Zero in a Secular Determinant
  - 12.9: Generating Operators for Irreducible Representations
- 13: Molecular Spectroscopy
  - 13.1: The Electromagnetic Spectrum
  - 13.2: Rotational Transitions Accompany Vibrational Transitions
  - 13.3: The Vibration-Rotation Spectrum
  - 13.4: The Pure Rotational Spectrum has Unequal Spacings
  - 13.5: Vibrational Overtones
  - 13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
  - 13.7: The Franck-Condon Principle
  - 13.8: Rotational Spectra of Polyatomic Molecules
  - 13.9: Normal Modes in Polyatomic Molecules
  - 13.10: Irreducible Representation of Point Groups
  - 13.11: Time-Dependent Perturbation Theory
  - 13.12: The Selection Rule for the Rigid Rotator
  - 13.13: The Harmonic Oscillator Selection Rule

- 13.14: Group Theory Determines Infrared Activity
- 13.E: Molecular Spectroscopy (Exercises)
- 14: Nuclear Magnetic Resonance Spectroscopy
  - 14.1: Nuclei Have Intrinsic Spin Angular Momenta
  - 14.2: Magnetic Moments Interact with Magnetic Fields
  - 14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz
  - 14.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded
  - 14.5: Chemical Shifts is Sensitive to Chemical Environment of the Nucleus
  - 14.6: Spin-Spin Coupling Results in Multiplets in NMR Spectra
  - 14.7: Spin-Spin Coupling Between Chemically Equivalent Protons Is Not Observed
  - 14.8: The n+1 Rule Applies Only to First-Order Spectra
  - 14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method
- 15: Lasers, Laser Spectroscopy, and Photochemistry
  - 15.1: Electronically Excited Molecules
  - 15.2: Transitions Modeled as Kinetics
  - 15.3: Two-Level Systems Cannot Form Population Inversions
  - 15.4: Population Inversion via Three-Level Systems
  - 15.5: Laser Fundamentals
  - 15.6: The Helium-Neon Laser
  - 15.7: High-Resolution Laser Spectroscopy
  - 15.8: Photochemical Dynamics
- 16: The Properties of Gases
  - 16.1: All Dilute Gases Behave Ideally
  - 16.2: van der Waals and Redlich-Kwong Equations
  - 16.3: A Cubic Equation of State
  - 16.4: The Law of Corresponding States
  - 16.5: The Second Virial Coefficient
  - 16.6: The Repulsive Term in the Lennard-Jones Potential
  - 16.7: Van der Waals Constants in Terms of Molecular Parameters
  - 16.E: The Properties of Gases (Exercises)
- 17: Boltzmann Factor and Partition Functions
  - 17.1: The Boltzmann Factor Is One of the Most Important Quantities in the Physical Sciences
  - 17.2: The Thermal Boltzman Distribution
  - 17.3: We Postulate That the Average Ensemble Energy Is Equal to the Observed Energy of a System
  - 17.4: The Heat Capacity at Constant Volume
  - 17.5: Express the Pressure in Terms of a Partition Function
  - 17.6: Partition Functions of Systems of Distinguishable Molecules are Products of Molecular Partition Functions
  - 17.7: Partition Function of Indistinguishable Components
  - 17.8: A Molecular Partition Function Can Be Decomposed into Partition Functions for Each Degree of Freedom
  - 17.E: Exercises
- 18: Partition Functions and Ideal Gases
  - 18.1: The Translational Partition Function of a Monatomic Ideal Gas
  - 18.2: Most Atoms Are in the Ground Electronic State at Room Temperature
  - 18.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms
  - 18.4: Most Molecules Are in the Ground Vibrational State at Room Temperature
  - 18.5: Most Molecules Are in Excited Rotational States at Ordinary Temperatures
  - 18.6: Rotational Partition Functions Contain a Symmetry Number
  - 18.7: The Vibrational Partition Function

- 18.8: The Rotational Partition Function Depends on the Shape of the Molecule
- 18.9: Molar Heat Capacities
- 18.E: Partition Functions and Ideal Gases (Exercises)

- Index
- Glossary
- Detailed Licensing
- 6: The Hydrogen Atom
  - 6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly
  - 6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics
  - 6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision
  - 6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers
  - 6.5: s-orbitals are Spherically Symmetric
  - 6.6: Orbital Angular Momentum and the p-Orbitals
  - 6.7: The Helium Atom Cannot Be Solved Exactly
  - 6.E: The Hydrogen Atom (Exercises)
- 7: Approximation Methods
  - 7.1: The Variational Method Approximation
  - 7.2: Linear Variational Method and the Secular Determinant
  - 7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters
  - 7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems
  - 7.E: Approximation Methods (Exercises)
- 8: Multielectron Atoms
  - 8.1: Atomic and Molecular Calculations are Expressed in Atomic Units
  - 8.2: Perturbation Theory and the Variational Method for Helium
  - 8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method
  - 8.4: An Electron Has an Intrinsic Spin Angular Momentum
  - 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
  - 8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants
  - 8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data
  - 8.8: Term Symbols Gives a Detailed Description of an Electron Configuration
  - 8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number
  - 8.E: Multielectron Atoms (Exercises)
  - 8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States
  - 8.11: Using Atomic Term Symbols to Interpret Atomic Spectra
- 9: Chemical Bonding in Diatomic Molecules
  - 9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules
  - 9.2: The H_2^+ Prototypical Species
  - 9.3: The Overlap Integral
  - 9.4: Chemical Bond Stability
  - 9.5: Bonding and Antibonding Orbitals
  - 9.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital
  - 9.7: Molecular Orbitals Can Be Ordered According to Their Energies
  - 9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule
  - 9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle
  - 9.E: Chemical Bond in Diatomic Molecules (Exercises)
  - 9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic
  - 9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals
  - 9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

- 9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently
- 9.14: Molecular Term Symbols Describe Electronic States of Molecules
- 9.15: Molecular Term Symbols Designate Symmetry
- 9.16: Most Molecules Have Excited Electronic States

Homework

- Homework 1
- Solutions 1
- Homework 2
- Solutions 2
- Homework 3
- Solutions 3
- Homework 4
- Solutions 4
- Homework 5
- Solutions 5
- Homework 6
- Solutions 6
- Homework 7
- Solutions 7
- Homework 8
- Solutions 8
- Homework 9
- Solutions 9
- Homework 10
- Solutions 10
- Homework 11
- Solutions 11
- Homework 12
- Solutions 12
- Homework 13
- Solutions 13
- Homework 14
- Solutions 14
- Homework 15
- Solutions 15

Workgroup Activities

- Workgroup 1: Valence Bond Orbitals for Hydrogen
- Workgroup 2: Symmetry and Assigning Point Groups
- Workgroup 3: Using Symmetry to Solve Integrals
- Workgroup 4: Deriving Selection Rules with Symmetry
- Workgroup 5: Translation Partition Function
- Workgroup 6: Rotational Partition Functions

00: Front Matter

- Table of Contents

Licensing

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

CHAPTER OVERVIEW

Front Matter

TitlePage

InfoPage

Table of Contents

Licensing

University of California, Davis

UC Davis Chem 110B Physical Chemistry II

Delmar Larsen

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 03/11/2026

TABLE OF CONTENTS

AGENDA

- Rethinking Hybridization

Text

- Licensing
- 10: Bonding in Polyatomic Molecules
  - 10.1: Hybrid Orbitals Account for Molecular Shape
  - 10.2: Different Hybrid Orbitals Used for Bonding in Water
  - 10.3: Why is BeH_2 Linear and H_2O Bent?
  - 10.4: Photoelectron Spectroscopy
  - 10.5: The \(\pi\)-Electron Approximation of Conjugation
  - 10.6: Butadiene is Stabilized by a Delocalization Energy
- 11: Computational Quantum Chemistry
  - 11.0: Overview of Quantum Calculations
  - 11.1: Gaussian Basis Sets
  - 11.2: Extended Basis Sets
  - 11.3: Orbital Polarization Terms
  - 11.4: The Ground-State Energy of H_2
  - 11.5: Quantum Calculations
- 12: Group Theory - Exploiting Symmetry
  - 12.1: Using Symmetry to Simplify Calculations
  - 12.2: The Symmetry of Molecules
  - 12.3: Symmetry Operations Define Groups
  - 12.4: Symmetry Operations can be Represented by Matrices
  - 12.5: The \(C_3V\) Point Group Has a 2-D Irreducible Representation
  - 12.6: Character Tables
  - 12.7: Relations involving Characters
  - 12.8: Using Symmetry to Predict Zero in a Secular Determinant
  - 12.9: Generating Operators for Irreducible Representations
- 13: Molecular Spectroscopy
  - 13.1: The Electromagnetic Spectrum
  - 13.2: Rotational Transitions Accompany Vibrational Transitions
  - 13.3: The Vibration-Rotation Spectrum
  - 13.4: The Pure Rotational Spectrum has Unequal Spacings
  - 13.5: Vibrational Overtones
  - 13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
  - 13.7: The Franck-Condon Principle
  - 13.8: Rotational Spectra of Polyatomic Molecules
  - 13.9: Normal Modes in Polyatomic Molecules
  - 13.10: Irreducible Representation of Point Groups
  - 13.11: Time-Dependent Perturbation Theory
  - 13.12: The Selection Rule for the Rigid Rotator
  - 13.13: The Harmonic Oscillator Selection Rule

- 13.14: Group Theory Determines Infrared Activity
- 13.E: Molecular Spectroscopy (Exercises)
- 14: Nuclear Magnetic Resonance Spectroscopy
  - 14.1: Nuclei Have Intrinsic Spin Angular Momenta
  - 14.2: Magnetic Moments Interact with Magnetic Fields
  - 14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz
  - 14.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded
  - 14.5: Chemical Shifts is Sensitive to Chemical Environment of the Nucleus
  - 14.6: Spin-Spin Coupling Results in Multiplets in NMR Spectra
  - 14.7: Spin-Spin Coupling Between Chemically Equivalent Protons Is Not Observed
  - 14.8: The n+1 Rule Applies Only to First-Order Spectra
  - 14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method
- 15: Lasers, Laser Spectroscopy, and Photochemistry
  - 15.1: Electronically Excited Molecules
  - 15.2: Transitions Modeled as Kinetics
  - 15.3: Two-Level Systems Cannot Form Population Inversions
  - 15.4: Population Inversion via Three-Level Systems
  - 15.5: Laser Fundamentals
  - 15.6: The Helium-Neon Laser
  - 15.7: High-Resolution Laser Spectroscopy
  - 15.8: Photochemical Dynamics
- 16: The Properties of Gases
  - 16.1: All Dilute Gases Behave Ideally
  - 16.2: van der Waals and Redlich-Kwong Equations
  - 16.3: A Cubic Equation of State
  - 16.4: The Law of Corresponding States
  - 16.5: The Second Virial Coefficient
  - 16.6: The Repulsive Term in the Lennard-Jones Potential
  - 16.7: Van der Waals Constants in Terms of Molecular Parameters
  - 16.E: The Properties of Gases (Exercises)
- 17: Boltzmann Factor and Partition Functions
  - 17.1: The Boltzmann Factor Is One of the Most Important Quantities in the Physical Sciences
  - 17.2: The Thermal Boltzman Distribution
  - 17.3: We Postulate That the Average Ensemble Energy Is Equal to the Observed Energy of a System
  - 17.4: The Heat Capacity at Constant Volume
  - 17.5: Express the Pressure in Terms of a Partition Function
  - 17.6: Partition Functions of Systems of Distinguishable Molecules are Products of Molecular Partition Functions
  - 17.7: Partition Function of Indistinguishable Components
  - 17.8: A Molecular Partition Function Can Be Decomposed into Partition Functions for Each Degree of Freedom
  - 17.E: Exercises
- 18: Partition Functions and Ideal Gases
  - 18.1: The Translational Partition Function of a Monatomic Ideal Gas
  - 18.2: Most Atoms Are in the Ground Electronic State at Room Temperature
  - 18.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms
  - 18.4: Most Molecules Are in the Ground Vibrational State at Room Temperature
  - 18.5: Most Molecules Are in Excited Rotational States at Ordinary Temperatures
  - 18.6: Rotational Partition Functions Contain a Symmetry Number
  - 18.7: The Vibrational Partition Function

- 18.8: The Rotational Partition Function Depends on the Shape of the Molecule
- 18.9: Molar Heat Capacities
- 18.E: Partition Functions and Ideal Gases (Exercises)

- Index
- Glossary
- Detailed Licensing
- 6: The Hydrogen Atom
  - 6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly
  - 6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics
  - 6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision
  - 6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers
  - 6.5: s-orbitals are Spherically Symmetric
  - 6.6: Orbital Angular Momentum and the p-Orbitals
  - 6.7: The Helium Atom Cannot Be Solved Exactly
  - 6.E: The Hydrogen Atom (Exercises)
- 7: Approximation Methods
  - 7.1: The Variational Method Approximation
  - 7.2: Linear Variational Method and the Secular Determinant
  - 7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters
  - 7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems
  - 7.E: Approximation Methods (Exercises)
- 8: Multielectron Atoms
  - 8.1: Atomic and Molecular Calculations are Expressed in Atomic Units
  - 8.2: Perturbation Theory and the Variational Method for Helium
  - 8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method
  - 8.4: An Electron Has an Intrinsic Spin Angular Momentum
  - 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
  - 8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants
  - 8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data
  - 8.8: Term Symbols Gives a Detailed Description of an Electron Configuration
  - 8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number
  - 8.E: Multielectron Atoms (Exercises)
  - 8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States
  - 8.11: Using Atomic Term Symbols to Interpret Atomic Spectra
- 9: Chemical Bonding in Diatomic Molecules
  - 9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules
  - 9.2: The H_2^+ Prototypical Species
  - 9.3: The Overlap Integral
  - 9.4: Chemical Bond Stability
  - 9.5: Bonding and Antibonding Orbitals
  - 9.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital
  - 9.7: Molecular Orbitals Can Be Ordered According to Their Energies
  - 9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule
  - 9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle
  - 9.E: Chemical Bond in Diatomic Molecules (Exercises)
  - 9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic
  - 9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals
  - 9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

- 9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently
- 9.14: Molecular Term Symbols Describe Electronic States of Molecules
- 9.15: Molecular Term Symbols Designate Symmetry
- 9.16: Most Molecules Have Excited Electronic States

Homework

- Homework 1
- Solutions 1
- Homework 2
- Solutions 2
- Homework 3
- Solutions 3
- Homework 4
- Solutions 4
- Homework 5
- Solutions 5
- Homework 6
- Solutions 6
- Homework 7
- Solutions 7
- Homework 8
- Solutions 8
- Homework 9
- Solutions 9
- Homework 10
- Solutions 10
- Homework 11
- Solutions 11
- Homework 12
- Solutions 12
- Homework 13
- Solutions 13
- Homework 14
- Solutions 14
- Homework 15
- Solutions 15

Workgroup Activities

- Workgroup 1: Valence Bond Orbitals for Hydrogen
- Workgroup 2: Symmetry and Assigning Point Groups
- Workgroup 3: Using Symmetry to Solve Integrals
- Workgroup 4: Deriving Selection Rules with Symmetry
- Workgroup 5: Translation Partition Function
- Workgroup 6: Rotational Partition Functions

00: Front Matter

- Table of Contents

Licensing

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

CHAPTER OVERVIEW

10: 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.

10.1: Hybrid Orbitals Account for Molecular Shape

10.2: Different Hybrid Orbitals Used for Bonding in Water

10.3: Why is BeH_2 Linear and H_2O Bent?

10.4: Photoelectron Spectroscopy

10.5: The \(\pi\)-Electron Approximation of Conjugation

10.6: Butadiene is Stabilized by a Delocalization Energy

10: Bonding in Polyatomic Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

10.1: 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

$$V = V_{ee} + V_{en} + V_{nn} \tag{10.1.1}$$

$$= \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{R_{AB}}\right] \tag{10.1.2}$$

But as $R_{AB} \rightarrow \infty$, 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

$$\psi_u(r_1, r_2, s_1, s_2) = \psi_u(x_1, x_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)] \\ [\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.3}$$

$$\psi_g(r_1, r_2, s_1, s_2) = \psi_g(x_1, x_2) = C_g[\psi^A_{1s}(r_1)\psi_{1s}B(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)] \\ [\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.4}$$

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:

$$\psi_{1s}^{A}(r_1) = \psi_{1s}^{B}(r_1) = A \tag{10.1.5}$$

$$\psi_{1s}^{B}(r_2) = \psi_{1s}^{A}(r_2) = A' \tag{10.1.6}$$

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

$$\psi(r_1, r_2, s_1, s_2) = [\psi_{1s}^{H}(1)\psi_{2p_z}^{F}(2) + \psi_{1s}^{H}(2)\psi_{2p_z}^{F}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]) \tag{10.1.7}$$

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

$$\psi_1(1,2) = C_1\left[\psi_{1s}^{H_1}(1)\psi_{2s}^{Be}(2) + \psi_{1s}^{H_1}(2)\psi_{2s}^{Be}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.8}$$

$$\psi_2(1,2) = C_2\left[\psi_{1s}^{H_2}(1)\psi_{2p_z}^{Be}(2) + \psi_{1s}^{H_2}(2)\psi_{2p_z}^{Be}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.9}$$

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 $\mathbf{H}$ 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 $\mathbf{BeH_2}$, the external potential on the electrons in $\mathbf{Be}$ by the two hydrogens changes the energy levels and creates a near degeneracy between the $2s$ and $2p_z$ orbitals, hence, we are now free to combine the into linear combinations that are more suitable to the construction both of valence bond wavefunctions *and* MOs via the LCAO procedure.

sp Hybrid Orbitals

For Be, we now allow the s and p orbitals to mix and create two *hybrid* orbitals known as sp orbitals. The two new hybrid wavefunctions as linear combination of the functions for 2s and $2p_z$ (using Dirac Notation):

$$|\chi_i\rangle = a_1|2s\rangle + b_1|2p_z\rangle \tag{10.1.10}$$

$$|\chi_j\rangle = a_2|2s\rangle + b_2|2p_z\rangle \tag{10.1.11}$$

These two wavefunctions must be orthogonal.

$$\langle\chi_i|\chi_j\rangle = \delta_{ij}$$

Which can be separated into the following relationships:

$$\langle\chi_i|\chi_i\rangle = 1 \tag{10.1.12}$$

and

$$\langle\chi_j|\chi_j\rangle = 1 \tag{10.1.13}$$

and

$$\langle\chi_i|\chi_j\rangle = \langle\chi_j|\chi_i\rangle = 0 \tag{10.1.14}$$

Equations 10.1.12 and 10.1.13 are the **normality requirement** and Equation 10.1.14 is the **orthogonality requirement** for the new hybrid wavefunctions. Substituting 10.1.10 into 10.1.12 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

$$\langle\chi_i|\chi_i\rangle = a_1^2 + b_1^2 = 1 \tag{10.1.15}$$

$$\langle\chi_j|\chi_j\rangle = a_2^2 + b_2^2 = 1 \tag{10.1.16}$$

and

$$\langle\chi_i|\chi_j\rangle = a_1a_2 + b_1b_2 = 0 \tag{10.1.17}$$

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 10.1.15 to 10.1.17 revert to

$$a_1^2 + b_1^2 = 1 \tag{10.1.18}$$

$$a_1^2 + b_2^2 = 1 \tag{10.1.19}$$

$$b_1^2 = b_2^2 \tag{10.1.20}$$

Therefore

$$b_1 = -b_2$$

and

$$a_1 = b_1 \tag{10.1.21}$$

Insert Equation 10.1.21 into 10.1.20 to get

$$a_1 = \frac{1}{\sqrt{2}}$$

and the two hybrid orbitals are

$$\chi_1(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) + \psi_{2p_z}(r)] \tag{10.1.22}$$

$$\chi_2(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) - \psi_{2p_z}(r)] \tag{10.1.23}$$

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

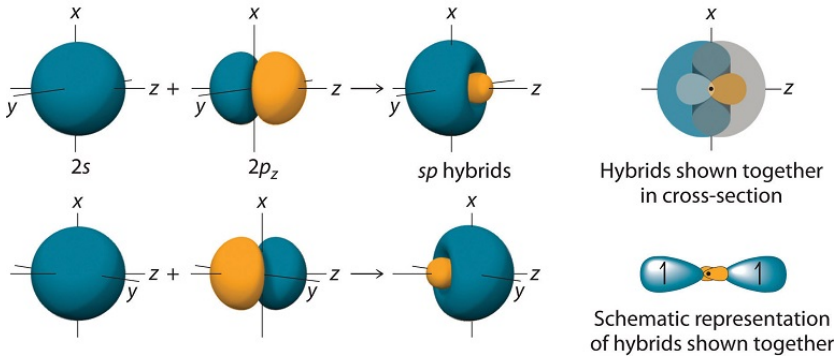


Figure 10.1.3 : The Formation of sp Hybrid Orbitals. Taking the sum and difference of an ns and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

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:

$$\psi_1(1,2) = C_1[\psi_{1s}^{H_1}(1)\chi_1^{Be}(2) + \psi_{1s}^{H_1}(2)\chi_1^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.24}$$

$$\psi_2(1,2) = C_2[\psi_{1s}^{H_2}(1)\chi_2^{Be}(2) + \psi_{1s}^{H_2}(2)\chi_2^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.25}$$

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).

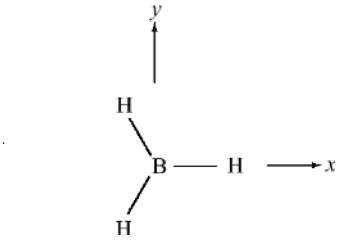


Figure 10.1.4: Geometry of BH_3.

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

$$\psi_{2p_y}^{(rot)} \sim \sin(\phi + 30)$$

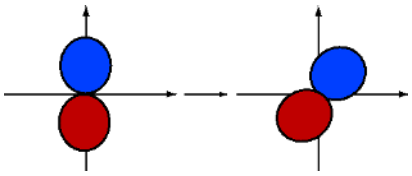


Figure 10.1.5: Rotation of a $2p_y$ orbital by -30 degrees.

Using the fact that

$$\sin(\alpha \pm \beta) = \sin\alpha\cos\beta \pm cos\alpha sin\beta$$

this rotation gives

$$\psi_{2p_y}^{(rot,1)} \sim \sin\phi\cos 30 + \cos\phi\sin 30 \tag{10.1.26}$$

$$\sim \left[\frac{\sqrt{3}}{2}\sin\phi + \frac{1}{2}\cos\phi\right] \tag{10.1.27}$$

$$\sim \left[\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_z}\right] \tag{10.1.28}$$

Similarly, consider rotating $-\psi_{2p_y}$ by $+30$ degrees (Figure 10.1.6). This gives

$$-\psi_{2p_y}^{(rot,2)} \sim -\sin(\phi - 30) \tag{10.1.29}$$

$$\sim -\left[\frac{\sqrt{3}}{2}\sin\phi - \frac{1}{2}\cos\phi\right] \tag{10.1.30}$$

$$\sim -\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_z} \tag{10.1.31}$$

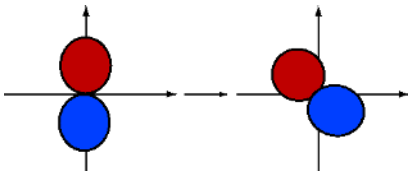


Figure 10.1.6: Rotation of a $-2p_y$ orbital by 30 degrees.

So, we now take the hybrid orbitals to be of the form

$$\chi_1(r) = a\psi_{2s}(r) - b\psi_{2p_x} \tag{10.1.32}$$

$$\chi_2(r) = c\psi_{2s}(r) + d\psi_{2p_y}^{(rot,1)}(r) \tag{10.1.33}$$

$$\chi_3(r) = c\psi_{2s}(r) - d\psi_{2p_y}^{(rot,2)}(r) \tag{10.1.34}$$

The coefficients a, b, and c are determined by requiring that the orbitals are normalized and mutually orthogonal:

$$\int |\chi_1(r)|^2 dV = 1\ ;\ \int \chi_1^*(r)\chi_2(r)dV = 0 \tag{10.1.35}$$

$$\int |\chi_2(r)|^2 dV = 1\ ;\ \int \chi_1^*(r)\chi_3(r)dV = 0 \tag{10.1.36}$$

$$\int |\chi_3(r)|^2 dV = 1\ ;\ \int \chi_2^*(r)\chi_3(r)dV = 0 \tag{10.1.37}$$

Carrying out the algebra, we obtain the following sp^2 hybrid orbitals:

$$\chi_1(r) = \frac{1}{\sqrt{3}}[\psi_{2s}(r) - \sqrt{2}\psi_{2p_x}(r)] \tag{10.1.38}$$

$$\chi_2(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) + \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.39}$$

$$\chi_3(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) - \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.40}$$

The sp^2 hybrids allow bonding at $120°$ degrees, and these orbitals appear as shown in Figure 10.1.7:

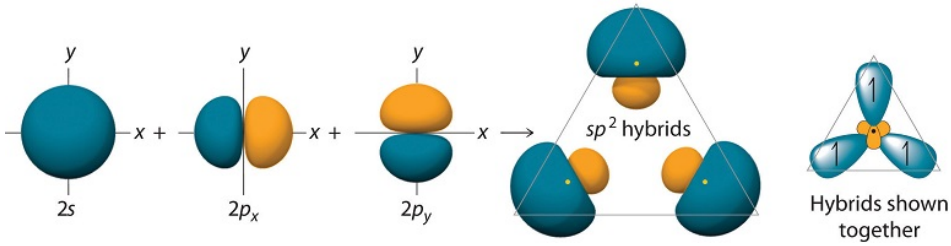


Figure 10.1.7: Formation of sp^2 Hybrid Orbitals. Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

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:

$$\chi_1(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{10.1.41}$$

$$\chi_2(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{10.1.42}$$

$$\chi_3(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{10.1.43}$$

$$\chi_4(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{10.1.44}$$

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.

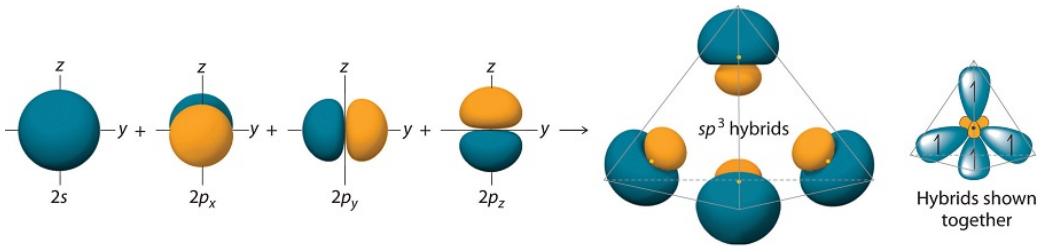


Figure 10.1.8 : Formation of sp^3 Hybrid Orbitals. Combining one ns and three np atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

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.

10.1: 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.

10.2: 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):

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + b_1|2p_y\rangle_O \tag{10.2.1}$$

$$|\chi_2\rangle = a_2|1s\rangle_{H_2} + b_2|2p_z\rangle_O \tag{10.2.2}$$

However, with a $\mathbf{H{-}O{-}H}$ 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.

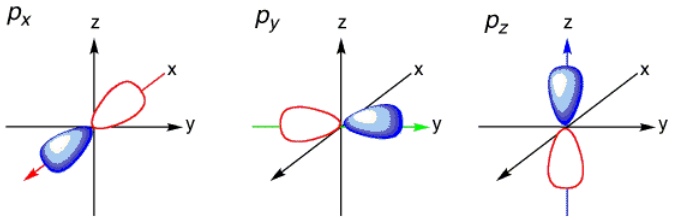


Figure 10.2.1 : The three p-orbitals are aligned along perpendicular axis (CC-SA-BY-NC; Nick Greeves via ChemTube3D);

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.

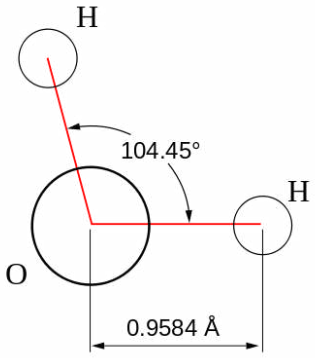


Figure 10.2.2 : Experimentally determined geometry of the water molecule (CC BY-SA 3.0; Booyabazooka).

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).

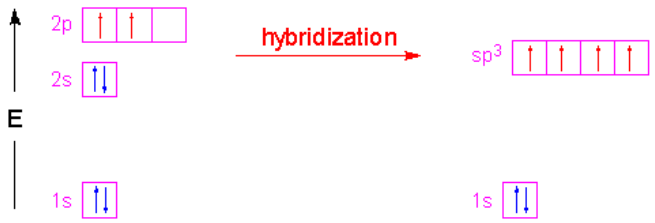


Figure 10.2.4: This would leave the $2s$ and $2p_z$ orbitals of oxygen left over for the two lone pairs on the oxygen.

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°.

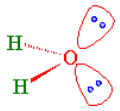


Figure 10.2.4 : Among the four hybrid orbitals, two are half filled and the remaining two are completely filled.

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:

$$|\chi_i\rangle = N(p+\gamma s) \tag{10.2.3}$$

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 10.2.3 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

$$N^2 \int p^2 d\tau + N^2 2\gamma \int sp\, d\tau + N^2\gamma^2 \int s^2 d\tau = 1 \tag{10.2.4}$$

These terms simplify either due to orthogonality or normality of the constitute atomic orbitals. Equation 10.2.4 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 10.2.3) is

$$|\chi_i\rangle = \frac{1}{\sqrt{1+\gamma^2}}(p+\gamma s) \tag{10.2.5}$$

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

$$\left(\frac{1}{\sqrt{1+\gamma^2}}\right)^2 = \frac{1}{1+\gamma^2} \tag{10.2.6}$$

  as $\gamma \rightarrow 0$, then the p character of the hybrid goes to 100%
- The magnitude of s-character is

$$\left(\frac{1}{\sqrt{1+\gamma^2}}\gamma^2\right)^2 = \frac{\gamma^2}{1+\gamma^2} \tag{10.2.7}$$

  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:

$$\cos\theta = -\gamma^2 \tag{10.2.8}$$

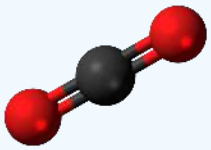
Equation 10.2.8 is an important equation as it related experimentally determined structure to the nature of the bonding and specifically, the composition of the atomic orbitals that create the hybrid orbitals used in the bonding.

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 10.2.8, $\gamma = 1$ since $\cos 180° = -1$. Hence, Equation 10.2.7 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 10.2.7 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 10.2.6, 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 10.2.7).

$$\frac{\gamma^2}{1+\gamma^2} = \frac{0.5^2}{1+0.5^2} = 0.20$$

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 10.2.6 and 10.2.8

- 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)

10.2: 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.

10.3: Why is BeH_2 Linear and H_2O Bent?

In this section, we will construct approximate molecular orbitals for a water molecule by considering a simple linear triatomic of the general form HXH, where X is a second row element. We will take a multi-centered molecular orbital approach instead of the two-centered valence bond/hybrid approach discussed previously. As with previous discussions of Molecular Orbitals, we approximate them as a linear combinations of atomic orbitals (LCAO). In molecular orbital theory linear combinations of **all** available (atomic) orbitals will form molecular orbitals. These are spread over the whole molecule, or delocalized, and in a quantum chemical interpretation they are called canonical orbitals. Since it is absolutely wrong to assume that there are only three types of sp^x hybrid orbitals, it is possible, that there are multiple different types of orbitals involved in bonding for a certain atom.

AH_2 Molecules

We want to construct a reasonable argument for the energetic ordering and structure of the molecular orbitals. We first note that each H will donate a $1s$ orbital in the LCAO scheme, and A will likely donate at least $2s$ and possible $2p$ orbitals, depending on its chemical identity. In general, if we consider only the first row A elements, the molecule orbitals (via the LCAO) can be expressed as combination of $1s$ orbitals on the two Hydrogens (H_1 and H_2) and the four n=2 orbitals ($2s$ $2p_x$ $2p_y$; $2p_z$) on the A atom:

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_2|1s\rangle_{H_2} + a_3|2s\rangle_A + a_4|2p_x\rangle_A + a_5|2p_y\rangle_A + a_6|2p_z\rangle_A \tag{10.3.1}$$

These molecular orbitals were created with six atomic orbitals and hence six different $|\chi\rangle$ molecular orbitals can be created. As with previous molecular orbitals problems, the coefficients of this expansion ($\{a_i\}$) are determined by solving the secular determinant.

If we consider only linear AH_2 molecules, then Equation 10.3.1 can be simplified by ignoring $2p_x$ and $2p_y$ atomic orbitals since they are perpendicular to the bonds and are hence non-bonding (only for linear AH_2 molecules). Moreover, the molecule is symmetric about the center (the position of A), hence the orbitals have to have the same symmetry.

Only the $2p$ orbital of A that will overlap with $1s$ of H is the $2p_z$. Hence, Equation 10.3.1 can be simplified to consider the combination

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A + a_6|2p_z\rangle_A \tag{10.3.2}$$

Note that the two coefficients in front of the $1s$ orbitals of hydrogen are the same by symmetry. This since no hydrogen is "special" and they must have the same contribution to the molecular orbital.

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 10.3.1 are shown in Figure 10.3.1 .

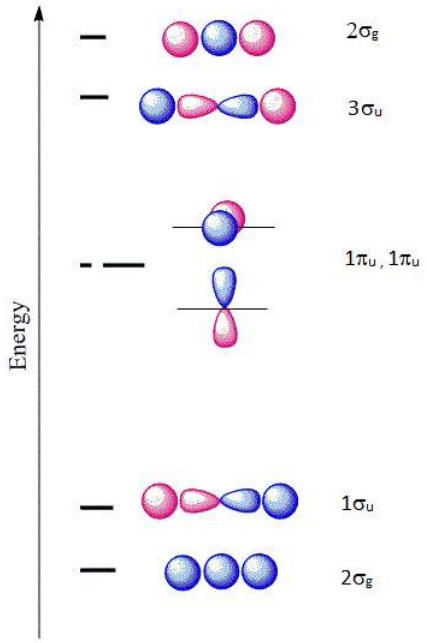


Figure 10.3.1 : The six molecular orbitals for the AH_2 molecule constrained to a linear geometry. The symmetry labels for each molecular orbital are indicated.

The first molecular orbital $|\chi_1\rangle$ constructed from Equation 10.3.1 is purely bonding because the $2s$ orbital is positive near the A nucleus, but becomes negative as we go away from the nucleus. This orbital is also even (*garade symmetry*), so we can denote it as a $2\sigma_g$ orbital signifying that it is constructed from a $2s$ orbital of A combined with the two $1s$ orbitals of H. The only other MO that can be constructed that has the right symmetry is $|\chi_6\rangle$ which is denoted as $2\sigma_u$. This is an antibonding molecular orbital and is also even (*garade symmetry*). The corresponding wavefunctions are:

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A$$

$$|\chi_6\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} - a_3|2s\rangle_A$$

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 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.

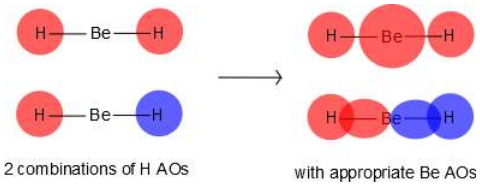


Figure 10.3.2: Forming molecular orbitals for BeH_2.

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.

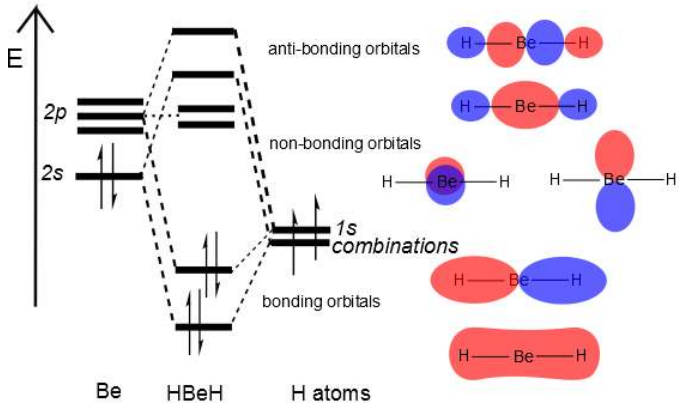


Figure 10.3.3: Molecular orbitals diagram for BeH_2.

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.

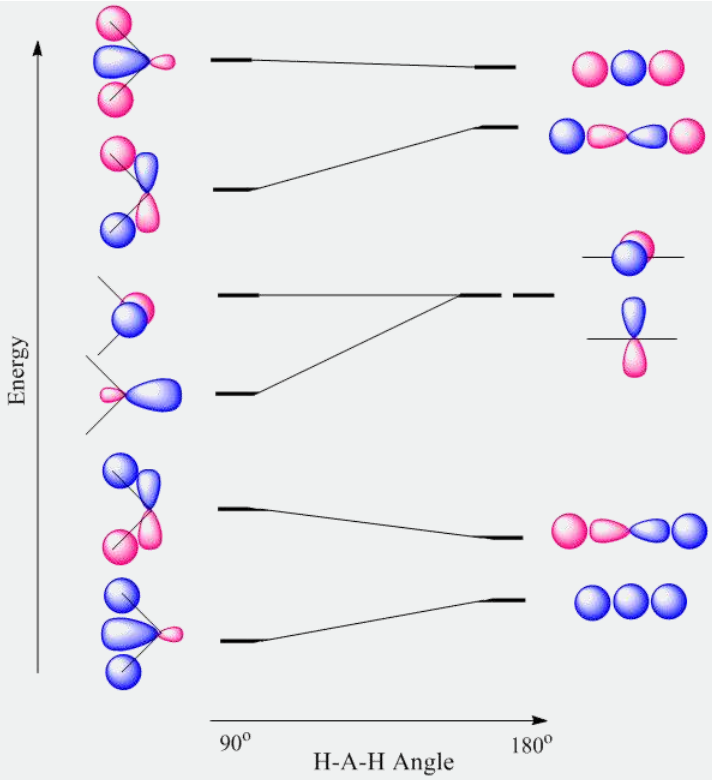


Figure 10.3.4: A Walsh diagram for an $\mathbf{AH_2}$ molecule. (public domain).

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.

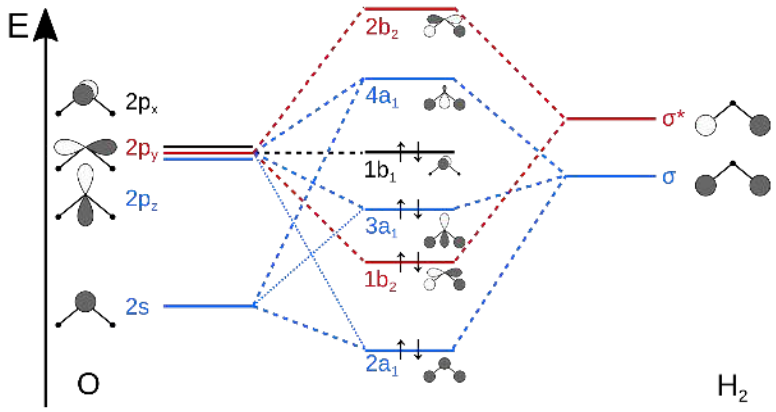


Figure 10.3.5: MO diagram for water. (CC-SA-BY-3.0; Officer781).

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

$$(a_1)^2(b_2)^2(a_1)^2(b_1)^2$$

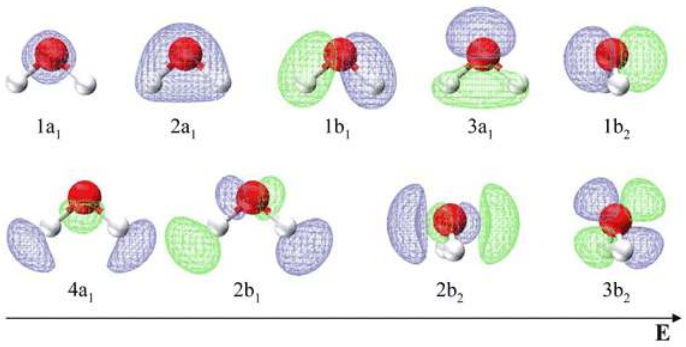


Figure 10.3.5. Image from Anna Krylov (USC)

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.

10.3: 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.

10.4: 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:

$$E = h\nu \tag{10.4.1}$$

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.

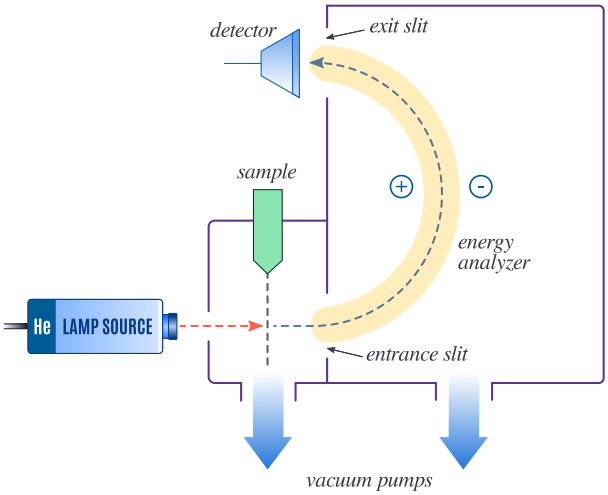


Figure 10.4.1: Diagram of a basic, typical PES instrument used in UPS, where the radiation source is an UV light source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical 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:

$$A + \text{photon} \rightarrow A^+ + e^- \tag{10.4.2}$$

Conservation of energy then requires that (after using Equation 10.4.1):

$$E(A) + h\nu = E(A^+) + E(e^-) \tag{10.4.3}$$

Since the free electron's energy is present solely as kinetic energy (KE) (i.e., there is no internal energy in a free electron)

$$E(e^-) = KE$$

Equation 10.4.3 can then be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - [E(A^+) - E(A)] \tag{10.4.4}$$

The final term in brackets represents the difference in energy between the ionized and neutral species and is generally called the **vertical ionization energy** (IE) of the ejected electron; this then leads to the following commonly quoted equations:

$$KE = h\nu - IE \tag{10.4.5}$$

or

$$IE = h\nu - KE \tag{10.4.6}$$

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 10.4.5 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.

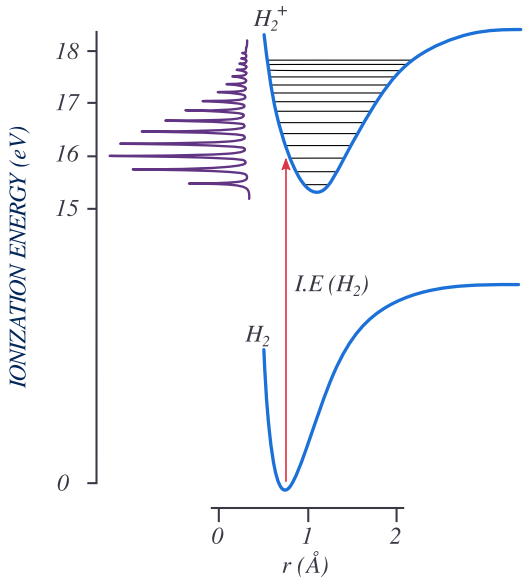


Figure 10.4.2: Vertical ionization process for molecular hydrogen. (CC BY 4.0; Ümit Kaya via LibreTexts)

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states as shown in Equation 10.4.6 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).

$$I_j = -\epsilon_j \tag{10.4.7}$$

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.

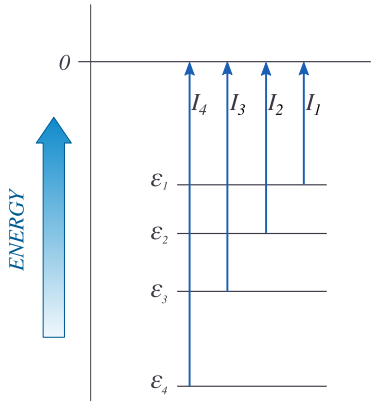


Figure 10.4.3: Within Koopmans' Theorem, the energies of the orbitals ϵ have an attractively simple physical interpretation: they give the amount of energy necessary to remove (ionize) the electron out of the molecular orbital, which corresponds to the negative of the experimentally observable ionization 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.

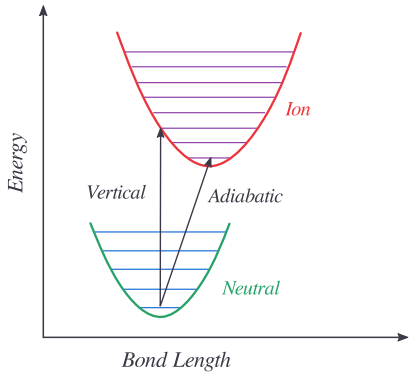


Figure 10.4.4: Difference between vertical and adiabatic ionization energies for a simple harmonic oscillator system. (CC BY 4.0; Ümit Kaya via LibreTexts)

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.

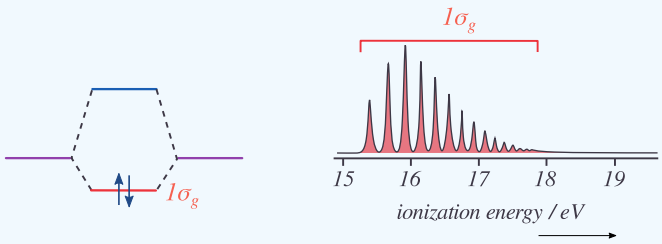
Differing Ionization Energies

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 $1\sigma_g$.



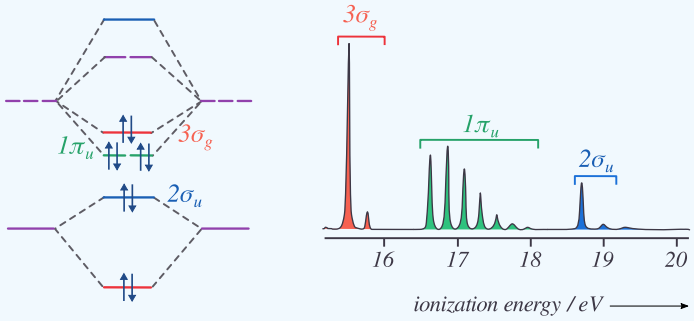
MO diagram and PES spectrum of H_2. (CC BY 4.0; Ümit Kaya via LibreTexts)

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

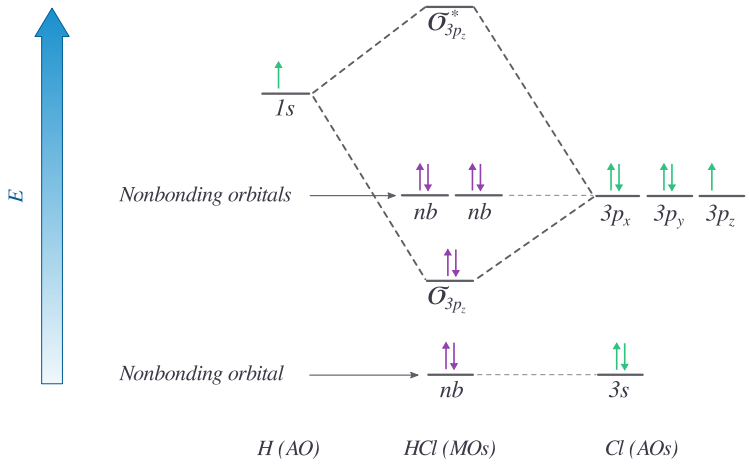


Figure 10.4.5: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts molecular orbitals strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only 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).

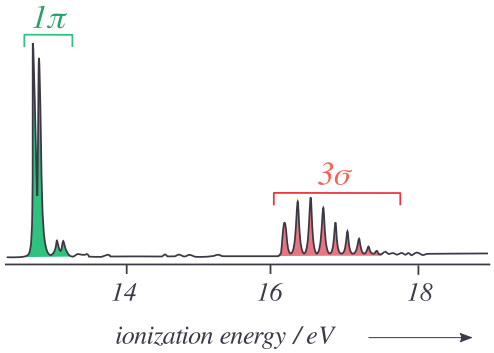


Figure 10.4.6: Photoelectron spectrum **HCl**. (CC BY 4.0; Ümit Kaya via LibreTexts)

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 $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^2$.

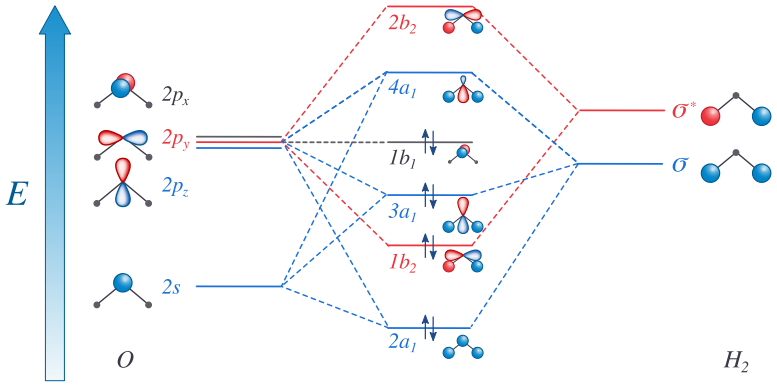


Figure 10.4.7: MO diagram for water. (CC BY 4.0; Ümit Kaya via LibreTexts)

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.

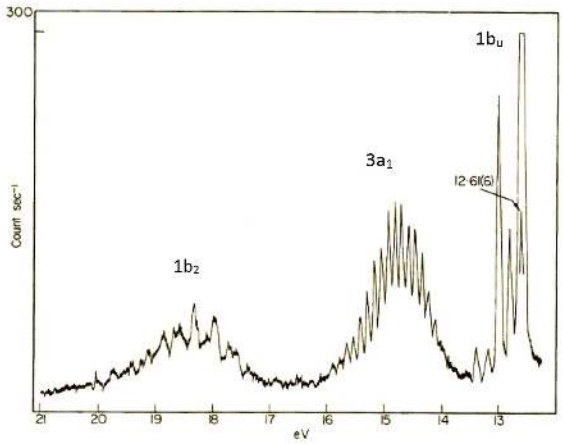


Figure 10.4.8: Photoelectron spectrum of water. Note the energy axes is flipped compared to other spectra on this page. This spectrum does not go to high enough energy to show the deep $2a_1$ molecular orbital.

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.

10.4: 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.

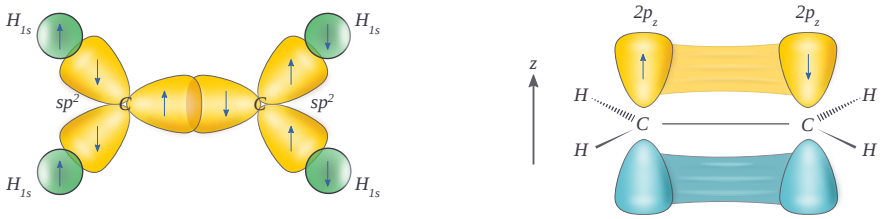
10.5: The π -Electron Approximation of Conjugation

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).

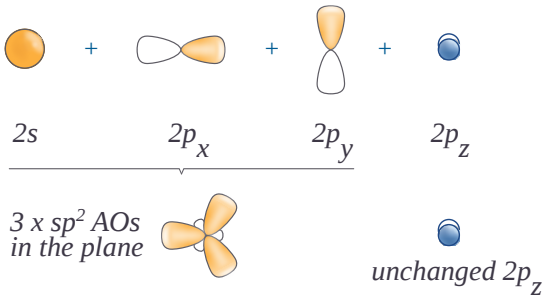


Figure 10.5.2 : Hybridizing of the carbon atomic orbitals to give sp^2 hybrid orbitals for bonding to hydrogen atoms in ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

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 i[th] molecular orbital can be described via hybrid orbitals

$$|\psi_1\rangle = c_1|sp_1^2\rangle + c_2|1s_a\rangle$$

or via atomic orbitals.

$$|\psi_1\rangle = a_1|2s\rangle + a_1|2p_x\rangle + a_1|2p_y\rangle + a_4|1s_a\rangle$$

where $\{a_i\}$ and $\{c_i\}$ are coefficients of the expansion. Either describe will work and both are identical approaches since

$$|sp_1^2\rangle = b_1|2s\rangle + b_1|2p_x\rangle + b_1|2p_y\rangle$$

where $\{c_i\}$ are coefficients describing the hybridized orbital.

The bonding occurs via the mixing of the electrons in the sp^2 hybrid orbitals on carbon and the electrons in the $1s$ atomic orbitals of the four hydrogen atoms (Figure 10.5.1 ; left) resulting in the σ-bonding framework. The π-bonding framework results from the unhybridized $2p_z$ orbitals (Figure 10.5.2 ; right). The independence of these two frameworks is demonstrated in the resulting molecular orbital diagram in Figure 10.5.3 ; Hückel theory is concerned only with describing the molecular orbitals and energies of the π bonding framework.

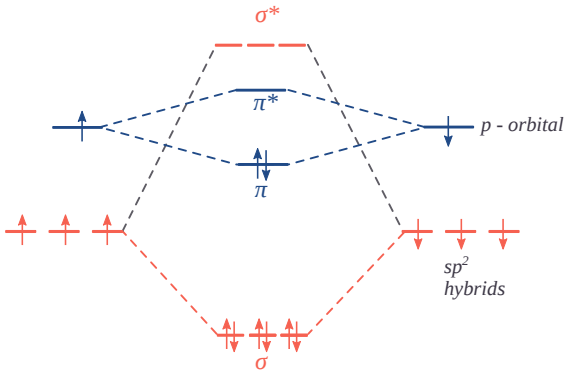


Figure 10.5.3 : Molecular orbitals demonstrating the sigma-pi separability of the π-bonding framework (blue) and the σ-bonding frameworks (red) of ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

> *Hückel treatment is concerned only with describing the molecular orbitals and energies of the π bonding framework.*

Since Hückel theory is a special consideration of molecular orbital theory, the molecular orbitals $|\psi_i\rangle$ can be described as a linear combination of the $2p_z$ atomic orbitals ϕ at carbon with their corresponding $\{c_i\}$ coefficients:

$$|\psi_i\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \tag{10.5.1}$$

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:

$$\hat{H}c_1|\phi_1\rangle + \hat{H}c_2|\phi_2\rangle = Ec_1|\phi_1\rangle + Ec_2|\phi_2\rangle \tag{10.5.2}$$

If Equation 10.5.2 is multiplied by $\langle\phi_1|$ (and integrated), then

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{10.5.3}$$

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 10.5.2 is multiplied by $\langle\phi_2|$ (and integrated), then

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \tag{10.5.4}$$

Both Equations 10.5.3 and 10.5.4 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.

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.5}$$

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 10.5.5 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 10.5.5 will also have a non-trivial solution, if and only if, the secular determinant is zero

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{10.5.6}$$

or in shorthand notation

$$\det(H - ES) = 0$$

Everything in Equation 10.5.6 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 10.5.1). However, if more than two $|\phi\rangle$ atomic orbitals were used, e.g., in a bigger molecule, then more energies would be estimated by solving the secular determinant.

Solving the secular determinant is simplified within Hückel method via the following four assumptions:

1. All overlap integrals S_{ij} are set equal to zero. This is quite reasonable since the $\pi-$ orbitals are directed perpendicular to the direction of their bonds (Figure 10.5.1). This assumption is often call neglect of differential overlap (NDO).

2. All resonance integrals H_{ij} between non-neighboring atoms are set equal to zero.
3. All resonance integrals H_{ij} between neighboring atoms are equal and set to β.
4. All coulomb integrals H_{ii} are set equal to α.

These assumptions are mathematically expressed as

$$H_{11} = H_{22} = \alpha$$

$$H_{12} = H_{21} = \beta$$

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 10.5.5 in two homogeneous equations:

$$\begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.7}$$

if Equation 10.5.7 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

$$x = \frac{\alpha - E}{\beta} \tag{10.5.8}$$

then Equation 10.5.7 simplifies to

$$\begin{bmatrix} x & 1 \\ 1 & x \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.9}$$

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 10.5.8, 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: $E_2 = \alpha - \beta$

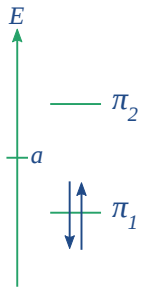


Figure 10.5.4 : π energies of ethylene with occupation. (CC BY-NC; Ümit Kaya via LibreTexts)

To extract the coefficients attributed to these energies, the corresponding x values can be substituted back into the Secular Equations (Equation 10.5.9). 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 10.5.1):

$$|\psi_1\rangle = N_1(|\phi_1\rangle + |\phi_2\rangle) \tag{10.5.10}$$

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 10.5.1):

$$\psi_2\rangle = N_2(|\phi_1\rangle - |\phi_2\rangle) \tag{10.5.11}$$

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.

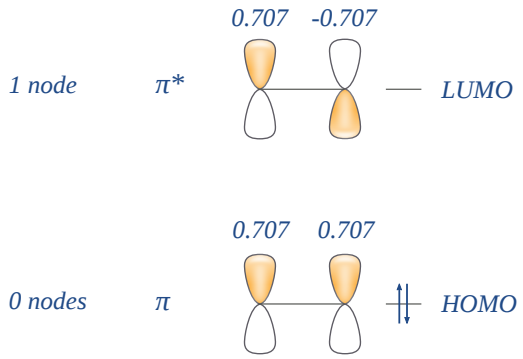


Figure 10.5.5 : Schemetic representation of the π molecular orbitals framework for ethylene . Notice that the antibonding molecular orbital has one more node than the bonding molecular orbital as expected since it is higher in energy. (CC BY-NC; Ümit Kaya via LibreTexts)

> *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 .

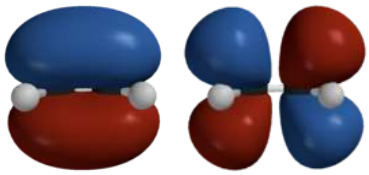


Figure 10.5.6 : Calculated π molecular orbitals for ethylene . (left) the bonding orbital (|\psi_1 \rangle\) and (right) the antibonding ($|\psi_2\rangle$ orbital.

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.

10.5: The π-Electron Approximation of Conjugation is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

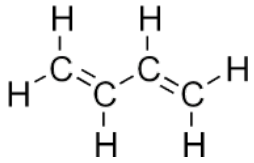
- **10.5: The pi-Electron Approximation of Conjugation (Hückel Theory)** by Seymour Blinder is licensed CC BY-NC-SA 4.0.

10.6: 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:

$$|\psi_i\rangle = \sum_j^4 c_{ij}|p_i\rangle$$

or explicitly

$$|\psi_i\rangle = c_{i1}|p_1\rangle + c_{i2}|p_2\rangle + c_{i3}|p_3\rangle + c_{i4}|p_4\rangle \tag{10.6.1}$$

for the i[th] molecular orbital $|\psi_i\rangle$. The secular equations that need to be solved are

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{10.6.2}$$

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 10.6.2 become

$$\begin{bmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{10.6.3}$$

Solving Equation 10.6.3 for $\{c_i\}$ coefficients and energy secular equation requires extracting the roots of the secular determinant:

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0 \tag{10.6.4}$$

If both sides of Equation 10.6.4 were divided by β^4 and a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{10.6.5}$$

then Equation 10.6.4 simplifies further to

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{10.6.6}$$

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 10.6.6 gives the 4th order polynomial equation

$$x^4 - 3x^2 + 1 = 0 \tag{10.6.7}$$

While solving 4th order equations typically require numerical estimation, Equation 10.6.7 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):

$$E_1 = \alpha + 1.618\beta \tag{10.6.8}$$

$$E_2 = \alpha + 0.618\beta \tag{10.6.9}$$

$$E_3 = \alpha - 0.618\beta \tag{10.6.10}$$

$$E_4 = \alpha - 1.618\beta \tag{10.6.11}$$

This sequence of energies is displayed in the energy diagram of Figure 10.6.1 .

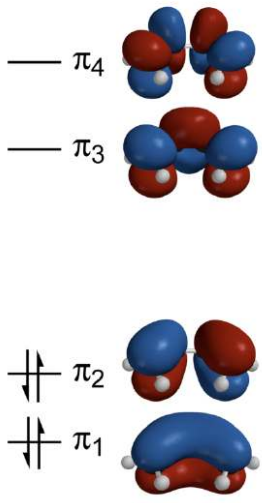


Figure 10.6.1 : The π molecular orbital energies from Hückel theory for butadiene with ground-state configuration. Structures calculated and images produced using HF/6-31G* (Public Domain; Ben Mills).

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 10.6.8-10.6.11 and scaling by their occupations to get

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_1 + 2\times E_2 + 0\times E_3 + 0\times E_4 \\ &= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) \\ &= 4\alpha + 4.472\beta \end{aligned} \tag{10.6.12}$$

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:

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_\pi(\text{ethylene}) \\ &= 2\times 2(\alpha+\beta) \\ &= 4\alpha + 4\beta \end{aligned} \tag{10.6.13}$$

Comparing Equation 10.6.12 with Equation 10.6.12, 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.

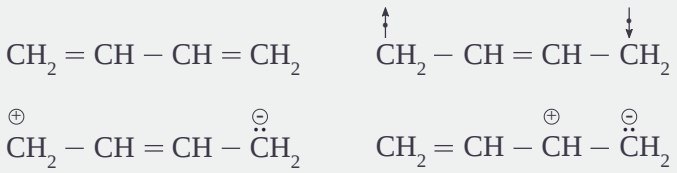


Figure 10.6.2 : Several resonance structures that can be written for 1,3-butadiene. The resonance structure in the upper left dominates, but does not exclusively describe the system since a delocalization energy is experimentally observed compared to two ethylene molecules. (CC BY-NC; Ümit Kaya via LibreTexts)

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 10.6.2) gives the $\{c_{ij}\}$ coefficients for the molecular orbitals in Equation 10.6.1 (not demonstrated):

$$|\psi_1\rangle = 0.37|p_1\rangle + 0.60|p_2\rangle + 0.60|p_3\rangle + 0.37|p_4\rangle \tag{10.6.14}$$

$$|\psi_3\rangle = 0.60|p_1\rangle + 0.37|p_2\rangle - 0.37|p_3\rangle - 0.60|p_4\rangle \tag{10.6.15}$$

$$|\psi_3\rangle = 0.60|p_1\rangle - 0.37|p_2\rangle - 0.37|p_3\rangle + 0.60|p_4\rangle \tag{10.6.16}$$

$$|\psi_4\rangle = 0.37|p_1\rangle - 0.60|p_2\rangle + 0.60|p_3\rangle - 0.37|p_4\rangle \tag{10.6.17}$$

These are depicted in Figure 10.6.3 .

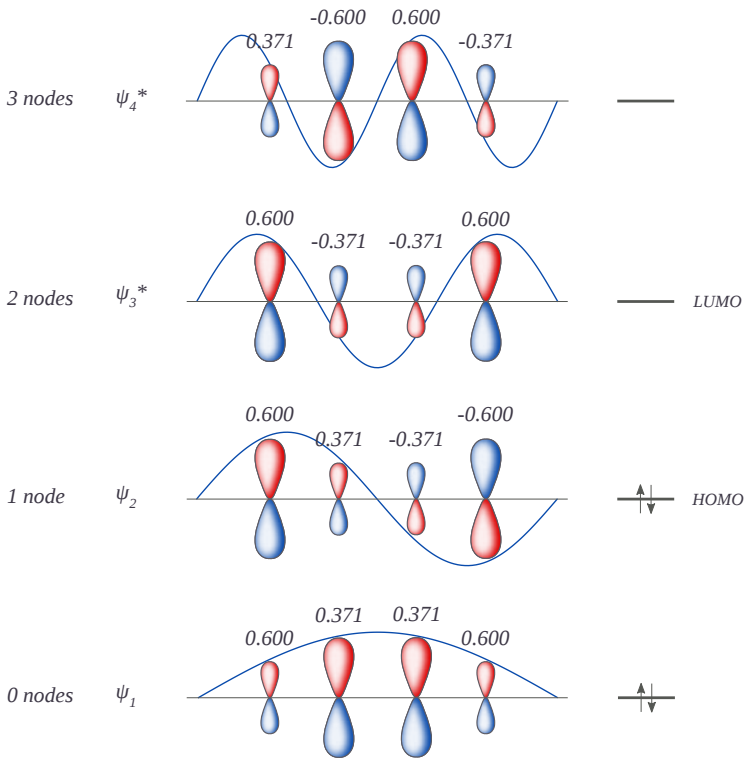


Figure 10.6.3 : Energy level diagram and decomposition of the π molecular orbitals of butadiene. This is view three-dimensionally in Figure 10.6.1 . (CC BY-NC; Ümit Kaya via LibreTexts)

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?

10.6: 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

11: 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.

11.0: Overview of Quantum Calculations

11.1: Gaussian Basis Sets

11.2: Extended Basis Sets

11.3: Orbital Polarization Terms

11.4: The Ground-State Energy of H_2

11.5: Quantum Calculations

11: Computational Quantum Chemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.0: Overview of Quantum Calculations

Multielectron Electronic Wavefunctions

We could symbolically write an approximate two-particle wavefunction as $\psi(r_1, r_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 (r_1) for the coordinates of particle 2 (r_2) and vice versa, to get the new wavefunction $\psi(r_1, r_2)$. This new wavefunction must have the property that

$$|\psi(r_1, r_2)|^2 = \psi(r_2, r_1)^* \psi(r_2, r_1) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{11.0.1}$$

Equation 11.0.1 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

$$\left(e^{-i\varphi} \psi(r_1, r_2)^*\right) \left(e^{i\varphi} \psi(r_1, r_2)^*\right) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{11.0.2}$$

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, $1s^2$.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) \tag{11.0.3}$$

After permutation of the electrons, this becomes

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1) \tag{11.0.4}$$

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 11.0.4 from the right-hand side of Equation 11.0.3 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

$$\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\chi_1(\mathbf{r}_1)\alpha & \chi_1(\mathbf{r}_1)\beta & \cdots & \chi_{N/2}(\mathbf{r}_1)\beta\\ \chi_1(\mathbf{r}_2)\alpha & \chi_2(\mathbf{r}_2)\beta & \cdots & \chi_{N/2}(\mathbf{r}_2)\beta\\ \vdots & \vdots & \ddots & \vdots\\ \chi_1(\mathbf{r}_N)\alpha & \chi_2(\mathbf{r}_N)\beta & \cdots & \chi_{N/2}(\mathbf{r}_N)\beta\end{vmatrix} \tag{11.0.5}$$

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

$$\varphi_j = \sum_k c_{jk}\psi_k \tag{11.0.6}$$

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

$$E = \frac{\int \Psi^* \hat{H}\Psi d\tau}{\int \Psi^*\Psi d\tau} \tag{11.0.7}$$

or in bra-ket notation

$$E = \frac{\left\langle \Psi|\hat{H}|\Psi\right\rangle}{\langle\psi|\psi\rangle}$$

The the optimum coefficients c_{jk} for each molecular orbital in Equation 11.0.6 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 11.0.5). 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 11.0.6. The ground state wavefunction Ψ is written as the Slater Determinant of the five lowest energy molecular orbitals ψ_k. Equation 11.0.7 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.

- $1\pi \approx 0.322p_{xc} + 0.442p_{xo}$ 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.

11.0: 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.

11.1: Gaussian Basis Sets

A basis set in theoretical and computational chemistry is a set of functions (called **basis functions**) which are combined in linear combinations (generally as part of a quantum chemical calculation) to create molecular orbitals. For convenience these functions are typically atomic orbitals centered on atoms, but can theoretically be any function; plane waves are frequently used in materials calculations.

The Variational Method and Basis Sets

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, ψ_i, as a linear combination of other functions, φ_j, which are called basis functions because they provide the basis for representing the molecular orbital.

$$\psi_i = \sum_j c_{ij}\varphi_j \tag{11.1.1}$$

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 11.1.2, 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**.

$$R_{2s}(r) = C_1 re^{-\zeta_1 r} + C_2 re^{-\zeta_2 r} \tag{11.1.2}$$

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 11.1.3. 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.

$$G_{nlm}(r,\theta,\psi) = N_n \underbrace{r^{n-1}e^{-\alpha r^2}}_{\text{radial part}} \underbrace{Y_l^m(\theta,\psi)}_{\text{angular part}} \tag{11.1.3}$$

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).

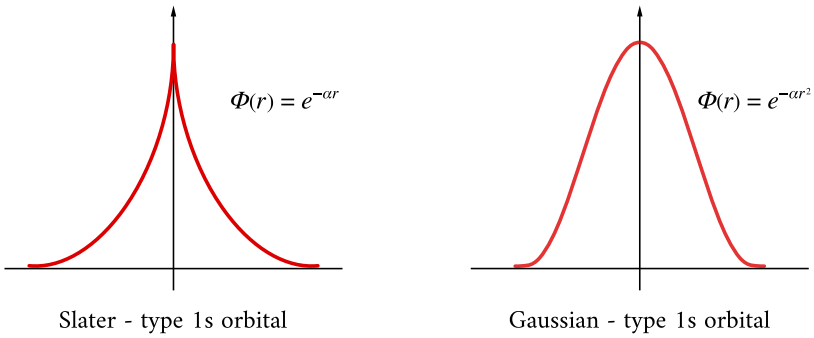


Figure 11.2.1 : Radial Dependence of Slater and Gaussian Basis Functions. (CC BY 4.0; Ümit Kaya via LibreTexts)

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.

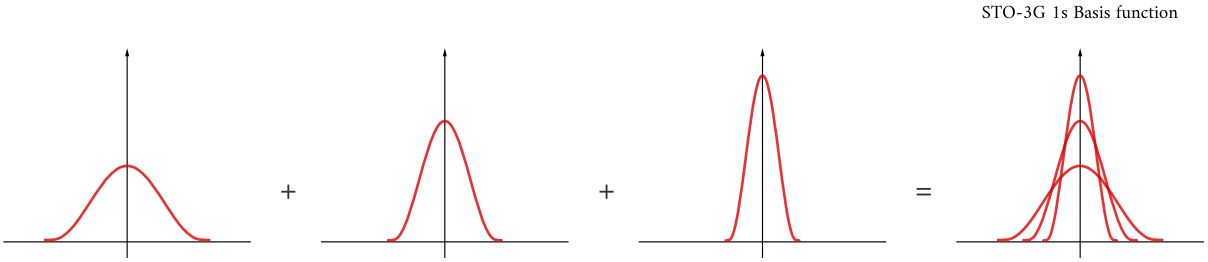


Figure 11.2.2 : To better represent the cusp in the electron density at the nuclei, GTO basis sets are constructed from fixed linear-combinations of Gaussian functions, contracted GTOs (CGTO). The earliest CGTO basis sets, where constructed from N GTOs that best fit the desired STO. These are called 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 11.1.1), 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

11.1: 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.

11.2: Extended Basis Sets

Today, there are hundreds of basis sets composed of Gaussian Type Orbitals (GTOs). The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The largest of these can contain literally dozens to hundreds of basis functions on each atom.

Minimum Basis sets

A minimum basis set is one in which a **single** basis function is used for each orbital in a Hartree-Fock calculation on the atom. However, for atoms such as lithium, basis functions of p type are added to the basis functions corresponding to the 1s and 2s orbitals of each atom. For example, each atom in the first row of the periodic system (Li - Ne) would have a basis set of five functions (two s functions and three p functions).

> *In a minimum basis set, a single basis function is used for each atomic orbital on each constituent atom in the system.*

The most common minimal basis set is STO-nG, where n is an integer. This n value represents the number GTOs used to approximate the Slater Type orbital (STO) for both core and valence orbitals. Minimal basis sets typically give rough results that are insufficient for research-quality publication, but are much cheaper (less calculations requires) than the larger basis sets discussed below. Commonly used minimal basis sets of this type are: STO-3G, STO-4G, and STO-6G.

Two is Often Better than One

Minimal basis sets are not flexible enough for accurate representation of, which requires the use multiple functions to represent each atomic orbital. The distribution of the electron density of valence electrons is better represented by the sum of two orbitals with different "effective charges". This is a double-ζ basis sets and includes split-valence set (inner and valence) and linear combination of two orbitals of same type, but with different effective charges (i.e., ζ). This flexibility can be used to generate atomic orbital of adjustable sizes.

For example, the double-zeta basis set allows us to treat each orbital separately when we conduct the Hartree-Fock calculation.

$$\phi_i = a_1\phi_{2s}^{STO}(r,\zeta_1) + a_2\phi_{2s}^{STO}(r,\zeta_2) \tag{11.2.1}$$

The 2s atomic orbital approximated as a sum of two STOs. The two equations are the same except for the value of ζ which accounts for how large the orbital is. The constants a_1 and a_2 determines how much each STO contributes to the final atomic orbital, which will vary depending on the type of atom that the atomic orbit (i.e., hydrogen and lithium orbitals will have different a_1, a_2, ζ_1, and ζ_2 values).

Extended Basis Sets

The triple and quadruple-zeta basis sets work the same way, except use three and four STOs instead of two like in 11.2.1. 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*			

11.2: 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.

11.3: 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.

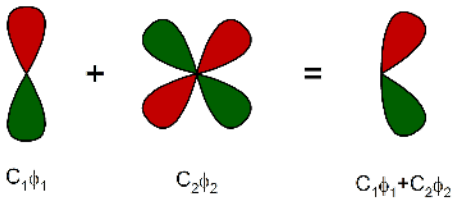


Figure 11.4.1 : A d-polarization function added to a p orbital. (CC-BY-SA-3.0; Rifleman 82)

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.

11.3: 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.

11.4: The Ground-State Energy of H_2

11.05: The Ground-State Energy of H

11.4: The Ground-State Energy of H_2 is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

11.5: Quantum Calculations

11.06: Quantum Calculations

11.5: Quantum Calculations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

12: Group Theory - Exploiting Symmetry

12.1: Using Symmetry to Simplify Calculations
12.2: The Symmetry of Molecules
12.3: Symmetry Operations Define Groups
12.4: Symmetry Operations can be Represented by Matrices
12.5: The \(C_3V\) Point Group Has a 2-D Irreducible Representation
12.6: Character Tables
12.7: Relations involving Characters
12.8: Using Symmetry to Predict Zero in a Secular Determinant
12.9: Generating Operators for Irreducible Representations

12: Group Theory - Exploiting Symmetry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

12.1: Using Symmetry to Simplify Calculations

To a fully understand the math behind group theory one needs to take a look at the theory portion of the Group Theory topic or refer to one of the reference text listed at the bottom of the page. Never the less as Chemist the object in question we are examining is usually a molecule. Though we live in the 21st century and much is known about the physical aspects that give rise to molecular and atomic properties. The number of high level calculations that need to be performed can be both time consuming and tedious. To most experimentalist this task is takes away time and is usually not the integral part of their work. When one thinks of group theory applications one doesn't necessarily associated it with everyday life or a simple toy like a Rubik's cube. A Rubik's cube is an a cube that has a $\mathbf{3 \times 3}$ array of different colored tiles on each of its six surfaces, for a total of 54 tiles. Since the cube exist in 3D space, the three axis are x, y, z. Since the rubik's cube only allows rotation which are called operations, there are three such operations around each of the x, y, z axis.

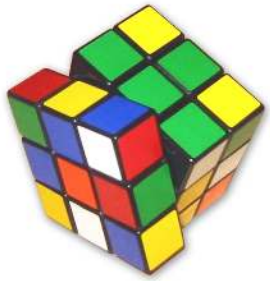


Figure: Reubik's cube. Use with permission from Wikipedia

Of course the ultimate challenge of a Rubik's cube is to place all six colors on each of the six faces. By performing a series of such operations on the Rubik's cube one can arrive at a solution (A link of a person solving a Rubik's cube[1] in 10.4s with operations performed noted, the operations performed will not translate to chemistry applications but it is a good example of how symmetry operations arrive at a solution). The operations shown in the Rubik's cube case are inherent to the make up of the cube, i.e., the only operations allowed are the rotations along the x, y, z axis. Therefore the Rubik's cube only has x,y,z rotation operations. Similarly the operations that are specific to a molecule are dependent on its symmetry.

Using group theory, we can exploit the symmetry of molecules to give us a rich amount of information on the molecular orbitals, rotations, and vibrations of bonds, to name a few. Making symmetry arguments, we can skip complicated quantum calculations to gain qualitatively accurate information.

In section 10.7, we used Hückel theory to explore the π bonding network of benzene by constructing linear combinations of $2p_x$ atomic orbitals on the carbon atoms. In doing so, the roots of the secular equations were found via solving the $\mathbf{6 \times 6}$ secular determinant.

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{12.1.1}$$

Since the secular determinant is a $\mathbf{6 \times 6}$ matrix, there are six solutions or values of x that can be determined after expanding the determinant into the resulting (6th-order) polynomial.

$$x^6 - 6x^4 + 9x^2 - 4 = 0 \tag{12.1.2}$$

Secular determinants are formulated in terms of a specific basis set; i.e., a set of functions that describe the wavefunctions. For the determinnat in Equation 12.1.1, that basis set is the the $\{|2p_z\rangle\}$ orbitals on the carbons. However, any basis set can be used to represent the determinant (long as it span the same space). For example, the following linear combination of $\{|2p_z\rangle\}$ orbitals could also be used:

$$|\phi_1\rangle = \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle\right]$$
$$|\phi_2\rangle = \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle\right]$$
$$|\phi_3\rangle = \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle + \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle - |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle + \frac{1}{2}|2p_{z6}\rangle\right]$$
$$|\phi_4\rangle = \frac{1}{\sqrt{4}}\left[|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle\right]$$
$$|\phi_5\rangle = \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle - \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle + |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle - \frac{1}{2}|2p_{z6}\rangle\right]$$
$$|\phi_6\rangle = \frac{1}{\sqrt{6}}\left[|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle\right]$$

In this new basis set $\{\phi\rangle\}$, the secular determinant Equation 12.1.1 is represented as

$$\begin{vmatrix} x+2 & 0 & 0 & 0 & 0 & 0 \\ 0 & x-2 & 0 & 0 & 0 & 0 \\ 0 & 0 & x+1 & \frac{x+1}{2} & 0 & 0 \\ 0 & 0 & \frac{x+1}{2} & x+1 & 0 & 0 \\ 0 & 0 & 0 & 0 & x-1 & \frac{x-1}{2} \\ 0 & 0 & 0 & 0 & \frac{x-1}{2} & x-1 \end{vmatrix} = 0 \tag{12.1.3}$$

This is the determinant into a bock diagonal form; which can be expanded into a product of smaller determinants to give the polynomial

$$\frac{9}{16}(x+2)(x-2)(x+1)^2(x-1)^2 = 0$$

The roots to this equation are ± 2, ± 1 and ± 1. This is not surprising since these are the same roots obtained from expanding the determinant in the original basis set (Equation 12.1.2). You may remember that the selection of a specific basis set to represent a function does not change the fundamental nature of the function (e.g., a parabola in 2D space is the same curve if represented in terms of Cartesian coordinates (x and y) or polar coordinates (θ and r), which both span 2-D space).

As you recall, Hückel theory (irrespective of the basis set) was used to simplify the general secular determinant (e.g., for benzene)

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} & H_{15}-ES_{15} & H_{16}-ES_{16} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} & H_{25}-ES_{25} & H_{26}-ES_{26} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} & H_{35}-ES_{35} & H_{36}-ES_{36} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} & H_{45}-ES_{45} & H_{46}-ES_{46} \\ H_{51}-ES_{51} & H_{52}-ES_{52} & H_{53}-ES_{53} & H_{54}-ES_{54} & H_{55}-ES_{55} & H_{56}-ES_{56} \\ H_{61}-ES_{61} & H_{62}-ES_{62} & H_{63}-ES_{63} & H_{64}-ES_{64} & H_{65}-ES_{65} & H_{66}-ES_{6} \end{vmatrix} = 0 \tag{12.1.4}$$

where H_{ij} are the Hamiltonian matrix elements

$$H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle\phi_i|\phi_j\rangle = \int \phi_i \phi_j \mathrm{d}v$$

In general, this involves solving 36 Hamiltonian matrix elements (H_{ij}) and 36 overlap integrals (S_{ij}), which can be a daunting task to do by hand without the assumptions of Hückel theory to help out. As with the application of Hückel theory, which was used to set most of these integrals to zero, solving for the energies from Equation 12.1.4 can be simplified by using the intrinsic symmetry of the benzene system to demonstrate (rigorously) that many of these integrals are zero. This is the subject of group theory. Group

theory is used to exploit the symmetry of molecules to quickly gain insights into their properties, such as vibrations and molecular orbitals.

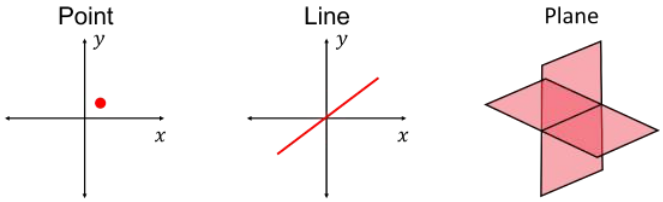
12.1: Using Symmetry to Simplify Calculations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Group Theory and its Application to Chemistry** by Jim Hughes is licensed CC BY-NC-SA 4.0.
- **12.1: The Exploitation of Symmetry Can Help Simplify Numerical Calculations** by Delmar Larsen, Jerry LaRue is licensed CC BY 4.0.

12.2: The Symmetry of Molecules

Symmetry Elements

A *symmetry operation* is an action that leaves an object looking the same after it has been carried out. For example, if we take a molecule of water and rotate it by 180° about an axis passing through the central O atom (between the two H atoms) it will look the same as before. Each symmetry operation has a corresponding *symmetry element*, which is the axis, plane (2-dimensional), line (1-dimensional) or point (0-dimensional) with respect to which the symmetry operation is carried out:



The symmetry element consists of all the points that stay in the same place when the symmetry operation is performed. In a rotation, the line of points that stay in the same place constitute a *symmetry axis*; in a reflection the points that remain unchanged make up a *plane of symmetry*. The symmetry of a molecule or ion can be described in terms of the complete collection of symmetry operations it possesses. The symmetry elements that a molecule (and any other 3-D object) may possess are discussed below.

Symmetry Operations

The symmetry of a molecule or ion can be described in terms of the complete collection of symmetry operations it possesses. There are five types of operations:

1. Identity, E
2. Rotation, C_n
3. Reflection, σ
4. Inversion, i
5. Improper Rotation, S_n

Symmetry Operations

A symmetry operation is a permutation of atoms such that the molecule is transformed into a state **indistinguishable** from the starting state.

Identity Symmetry, E

The identity operator, E, consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule possesses at least this operation. For example, the $\mathrm{CHFClBr}$ molecule in Figure 12.2.1 . The identify symmetry operation is not indicated since all molecule exhibit this symmetry.

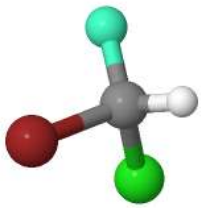


Figure 12.2.1 : Example of Identify Symmetry: The $\mathrm{CHFClBr}$ molecule contain no other symmetry other than identity. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

n-fold Axis of Rotation, C_n

The rotation operation (sometimes called proper rotation), C_n, rotates an object about an axis by $2\pi/n$ radians or $360°/n$. Rotation by C_n leaves the molecule unchanged. The H_2O molecule has a C_2 axis (Figure 12.2.2). Molecules can have more than one C_n

axis, in which case the one with the highest value of n is called the *principal axis*. In some high symmetry systems, there may be more than one principal axis. Note that by convention, rotations are *counterclockwise* about the axis. C_n rotations are indicated via vectors with labels as indicated below.

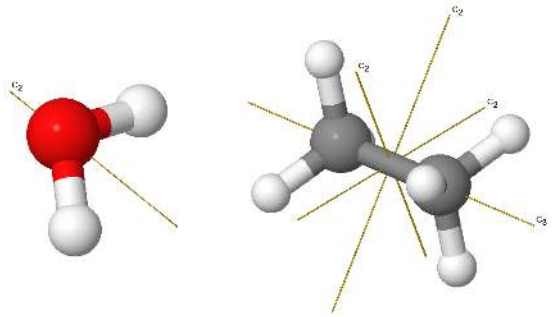


Figure 12.2.2 : Examples of n-fold Axis of Rotation: (left) The water molecule contains a C_2 axis. (right) Ethane contains both C_2 and C_3 axes. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

We always want to express rotations in their simplest equivalent fractions of m/n:

$$C_4^2 = C_2$$

$$C_6^4 = C_3^2$$

$$C_8^6 = C_4^3$$

Rotating an object n times brings the object back to the original object and is equivalent to the identity operation, E:

$$C_n^n = E$$

Linear molecules have a very high rotational symmetry: C_∞. Examples include diatomics such as CO, NO, and $\mathrm{CO_2}$.

Reflection, σ

Reflection, σ, defines the bilateral symmetry about a plane (mirror plane / reflection plane). Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a vertical mirror plane and is labeled σ_v, while one perpendicular to the axis is called a horizontal mirror plane and is labeled σ_h. A vertical mirror plane that bisects the angle between two C_2 axes is called a dihedral mirror plane, σ_d. If no principal axis exist, σ_h is defined as the plane of the molecule. σ symmetry is indicated as a plane on molecules; since they often bisect atoms, which should be clearly indicated.

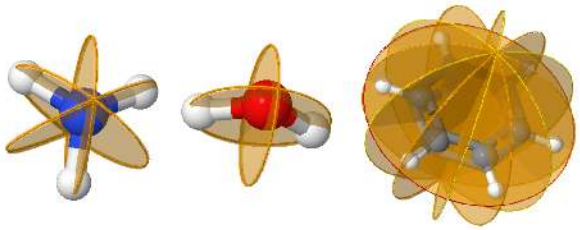


Figure 12.2.3 : Examples of reflection symmetry. (left) The ammonia molecule contains three identical reflection planes. All are designated as vertical symmetry planes (σ_v) because they contain the principle rotation axis.(middle) The water molecule contains two different reflection planes. (right) benzene contains a total of seven reflection planes, one horizontal plane (σ_h) and six vertical planes (σ_v and σ_d). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

For any mirror plane, performing two successive reflections about the same plane brings objects back to their original configuration:

$$\sigma\sigma = \sigma^2 = E$$

Inversion, i

Inversion, i, through the center of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the center of inversion and out to the same distance on the other side of the molecule. If inversion symmetry exists, a line drawn from

any atom through the center will connect with an equivalent atom at an equivalent distance from the center. Examples of molecules with centers of inversion is shown in Figure 12.2.4 . Centers of inversion are indicated via a point, which may or may not overlap with an atoms. The inversion center is always located at the central point of the molecule and there can only be one inversion center in any system. The centers of inversion in the examples below do not overlap with atoms.

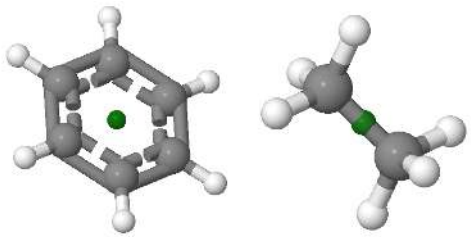


Figure 12.2.4 : Examples of Center of Inversion Symmetry. (left) Benzene and (right) staggard ethane have centers of inversion (green balls). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

Performing inversion twice in succession brings every point back to its original position:

$$ii = i^2 = E$$

Molecules with no inversion symmetry are said to be centrosymmetric.

n-fold Axis of Improper Rotation, S_n

Improper rotations, S_n, are also called rotation-reflections. The rotation-reflection operation consists of rotating by C_n about an axis, followed by reflecting in a plane perpendicular to the same axis. Improper rotation symmetry is indicated with both an axis and a plan as demonstrated in the examples in Figure 12.2.5 .

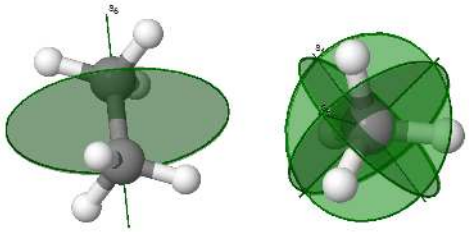


Figure 12.2.5 : Examples of Improper axis of rotation. (left) Staggered ethane contains an S_6 axis of improper rotation. (right) Methane contains three S_4 axes of improper rotation. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

Note

S_1 is the same as reflection and S_2 is the same as inversion.

The lowest-order improper rotation that is not a simpler operation is S_3. The pattern of successive operations depends on if n is even or odd. The general relationships for S_n operations are:

- If n is even, $S_n^n = E$
  - Molecule returns to original orientation configuration after each full rotation
  - There are an even number of rotation operators and reflection operators
- If n is odd, $S_n^n = \sigma$ and $S_n^{2n} = E$
  - First full rotation:
    - Molecular does not return to original configuration after first rotation
    - There are an odd number of rotation operators and reflection operators
  - Second full rotation:
    - Molecule returns to original orientation configuration
    - There are an even number of rotation operators and reflection operators
- When m is even, there is always a corresponding proper rotation (C_n):

- $S_n^m = C_n^m$ when $m < n$
- $S_n^m = C_n^{m-n}$ when $m > n$ (2nd rotation)

- If S_n with even n exists, $C_{n/2}$ exists
- If S_n with odd n exists, then both C_n and σ perpendicular to C_n exist

Summary of Symmetry Operations

The identity E and rotations C_n are symmetry operations that could actually be carried out on a molecule. For this reason they are called *proper symmetry operations*. Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic rearrangement of chemical bonds) and as such, are termed *improper symmetry operations*. These five symmetry operations are tabulated in Table 12.2.1 .

Table 12.2.1 : The five principal symmetry elements and their operators for 3D space

Symbol Elements	Description	Symbol Operator	Symbol
E	identity	$\hat{E}$	no change
C_n	n-fold axis of rotation	$\hat{C}_n$	Rotation by $360°/n$ leaves the molecule unchanged
σ	plane of symmetry	$\hat{\sigma}$	Reflection in the plane leaves the molecule unchanged
i	center of symmetry.	$\hat{i}$	Inversion through the center of symmetry leaves the molecule unchanged.
S_n	n-fold improper rotation	$\hat{S}_n$	The rotary reflection operation consists of rotating through an angle $360°/n$ about the axis, followed by reflecting in a plane perpendicular to the axis.

Defining the Coordinate System

Axis Definitions

Conventionally, when imposing a set of Cartesian axes on a molecule (as we will need to do later on in the course), the z axis lies along the principal axis of the molecule, the x axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the y axis makes up a right handed axis system.

Generally, the following conventions are observed to define the coordinate system:

1. The origin of the coordinate system is located at the central atom or the center of the molecule.
2. The z-axis is collinear with the highest-order rotational axis (principal axis).
3. For planar molecules, if the z-axis is perpendicular to the molecular plane:
   - The x-axis lies in the plane of the molecule and passes through the greatest number of atoms.

   If the z-axis lies in the plane of the molecule:
   - The x-axis stands perpendicular to the plane
4. For non-planar molecules, once the z-axis has been defined, the x-axis is the usually chosen so that the xz plane contains as many atoms as possible.

Molecular Point Groups

It is only possible for certain combinations of symmetry elements to be present in a molecule (or any other object). As a result, we may group together molecules that possess the same symmetry elements and classify molecules according to their symmetry. These

groups of symmetry elements are called *point groups* (due to the fact that there is at least one point in space that remains unchanged no matter which symmetry operation from the group is applied). There are two systems of notation for labeling symmetry groups, called the Schönflies and Hermann-Mauguin (or International) systems. Schönflies notation is used by chemists and spectroscopists, while Crystallographers prefer Hermann-Mauguin notation.The symmetry of individual molecules is usually described using the **Schönflies** notation, which is used below. The common point groups can be categorized into the following:

- Nonrotational groups
- Single-axis rotationa groups
- Dihedral groups
- Cubic groups

Shared Names

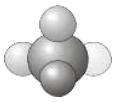
Some of the point groups share their names with symmetry operations, so be careful you do not mix up the two. It is usually clear from the context which one is being referred to.

Nonrotational groups

Nonrotational groups represent the lowest symmetry groups. They include:

C_1 - Contains only the identity (a C_1 rotation is a rotation by 360° and is the same as the identity operation, E). Molecules that belongs to the C_1 group have no symmetry and are therefore asymmetric.

- Example: CHDFCl



C_i - Contains the identity E and a center of inversion i.

- Example: $C_2H_2F_2Cl_2$



C_S - Contains the identity E and a plane of reflection σ.



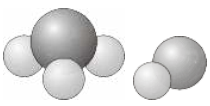
Single-axis rotation groups

Single-axis rotation groups are examples of cyclic groups. In cyclic groups, all of the operators commute (Abelian). In their multiplication tables, elements appear along right-to-left diagonals. Knowing this pattern makes it easy to construct multiplication tables! Single-axis rotational groups include:

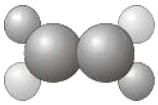
C_n - Contains the identity and an n-fold axis of rotation.



C_{nv} - Contains the identity, an n-fold axis of rotation, and n vertical mirror planes σ_v.



C_{nh} - Contains the identity, an n-fold axis of rotation, and a horizontal reflection plane σ_h (note that in C_{2h} this combination of symmetry elements automatically implies a center of inversion).



S_n - Contains the identity and *one* S_n axis. Note that molecules only belong to S_n if they have not already been classified in terms of one of the preceding point groups (e.g. S_2 is the same as C_i, and a molecule with this symmetry would already have been classified).

Dihedral groups

The dihedral groups have n two-fold axes perpendicular to the principal n-fold axis. These C_2 axis are called dihedral axes. Dihedral groups groups include:

D_n - Contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.

D_{nd} - Contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.



D_{nh} - Contains the same symmetry elements as D_n with the addition of a horizontal mirror plane.

- There are n-fold vertical mirror places (σ_v)
- Includes n-fold improper axis when $n > 2$
- They are centrosymmetric when n is even

$D_{\infty h}$ - Same as D_{nh}, except the principal rotational axis is an infinite-fold C_∞.

- This is the point group for all linear centrosymmetric linear molecules (e.g. H_2, CO_2)

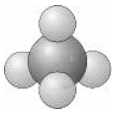


Cubic groups

The following groups are the cubic groups, which contain more than one principal axis. The cubic groups are associated with polyhedra that are geometrically related to the cube. All are characterized by the presence of multiple, intersecting, high-order rotational axes. They separate into the tetrahedral groups (T_d, T_h and T) and the octahedral groups (O and O_h).

T_d - Contains all the symmetry elements of a regular tetrahedron, including the identity, 4 C_3 axes, 3 C_2 axes, 6 dihedral mirror planes, and 3 S_4 axes e.g. CH_4.

- Example: Methane, C_4

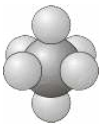


T - Same as for T_d but no planes of reflection.

T_h - Same as for T but contains a center of inversion.

O_h - The group of the regular octahedron.

- Example: Sulfur hexafluoride, SF_6



O - Same as for O_h, but with no planes of reflection.

I_h - Icoshedral, a geometric shape with 20 faces.

- Example: Buckminsterfullerene, (C_{60})

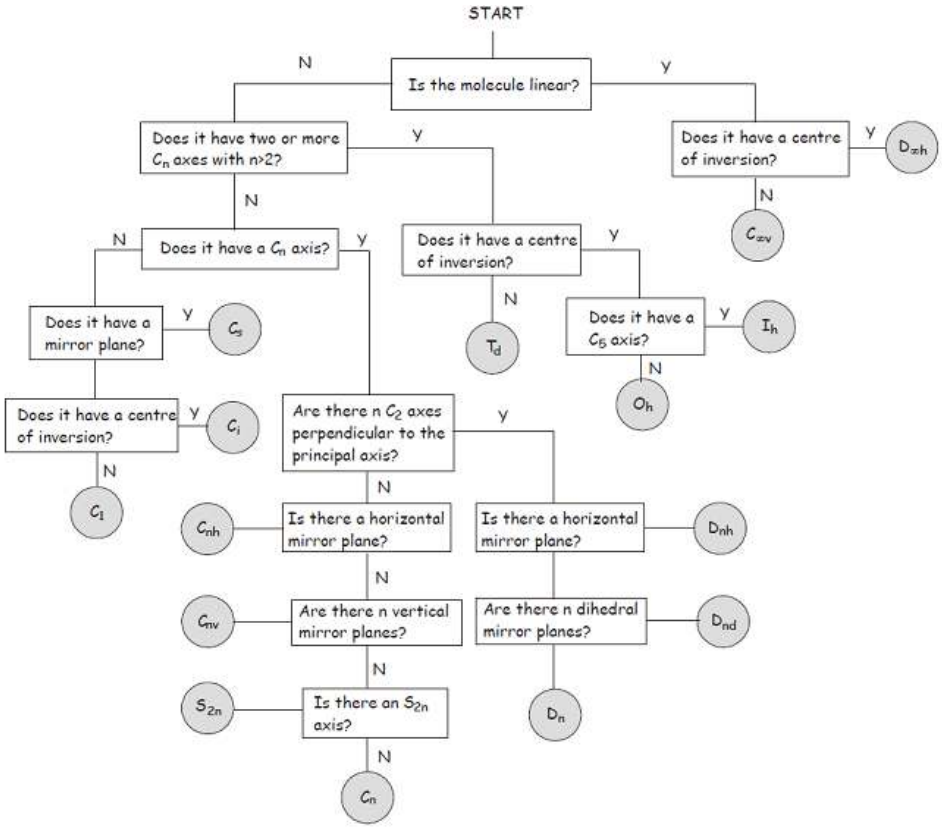
Summary of groups

The final group is the full rotation group R_3, which consists of an infinite number of C_n axes with all possible values of n and describes the symmetry of a sphere. Atoms (but no molecules) belong to R_3, and the group has important applications in atomic quantum mechanics. However, we won't be treating it any further here.

Table 12.2.2 : Common Point Groups for Molecules

Nonaxial groups	C_1	C_s	C_i	-	-	-	-	-	-
C_n groups	C_2	C_3	C_4	C_5	C_6	C_7	C_8	-	-
D_n groups	D_2	D_3	D_4	D_5	D_6	D_7	D_8	-	-
C_{nv} groups	C_{2v}	C_{3v}	C_{4v}	C_{5v}	C_{6v}	C_{7v}	C_{8v}	-	-
C_{nh} groups	C_{2h}	C_{3h}	C_{4h}	C_{5h}	C_{6h}	-	-	-	-
D_{nh} groups	D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}	D_{7h}	D_{8h}	-	-
D_{nd} groups	D_{2d}	D_{3d}	D_{4d}	D_{5d}	D_{6d}	D_{7d}	D_{8d}	-	-
S_n groups	S_2	-	S_4	-	S_6		S_8	S_{10}	S_{12}
Cubic groups	T	T_h	T_d	O	O_h	I	I_h	-	-
Linear groups	$C_{\infty v}$	$D_{\infty h}$	-	-	-	-	-	-	-

Once you become more familiar with the symmetry elements and point groups described above, you will find it quite straightforward to classify a molecule in terms of its point group. In the meantime, the flowchart shown below provides a step-by-step approach to the problem.



[1]Though the Hermann-Mauguin system can be used to label point groups, it is usually used in the discussion of crystal symmetry. In crystals, in addition to the symmetry elements described above, translational symmetry elements are very important. Translational symmetry operations leave no point unchanged, with the consequence that crystal symmetry is described in terms of *space groups* rather than *point groups*.

Symmetry and Physical Properties

Carrying out a symmetry operation on a molecule must not change any of its physical properties. It turns out that this has some interesting consequences, allowing us to predict whether or not a molecule may be chiral or polar on the basis of its point group.

For a molecule to have a permanent dipole moment, it must have an asymmetric charge distribution. The point group of the molecule not only determines whether the molecule may have a dipole moment, but also in which direction(s) it may point. If a molecule has a C_n axis with $n > 1$, it **cannot** have a dipole moment perpendicular to the axis of rotation (for example, a C_2 rotation would interchange the ends of such a dipole moment and reverse the polarity, which is not allowed – rotations with higher values of n would also change the direction in which the dipole points). Any dipole must lie parallel to a C_n axis.

Also, if the point group of the molecule contains any symmetry operation that would interchange the two ends of the molecule, such as a σ_h mirror plane or a C_2 rotation perpendicular to the principal axis, then there cannot be a dipole moment along the axis. The only groups compatible with a dipole moment are C_n, C_{nv} and C_s. In molecules belonging to C_n or C_{nv} the dipole must lie along the axis of rotation.

One example of symmetry in chemistry that you will already have come across is found in the isomeric pairs of molecules called enantiomers. Enantiomers are non-superimposable mirror images of each other, and one consequence of this symmetrical relationship is that they rotate the plane of polarized light passing through them in opposite directions. Such molecules are said to be chiral,[2] meaning that they cannot be superimposed on their mirror image. Formally, the symmetry element that precludes a molecule from being chiral is a rotation-reflection axis S_n. Such an axis is often implied by other symmetry elements present in a group.

For example, a point group that has C_n and σ_h as elements will also have S_n. Similarly, a center of inversion is equivalent to S_2. As a rule of thumb, a molecule definitely cannot have be chiral if it has a center of inversion or a mirror plane of any type (σ_h, σ_v or σ_d), but if these symmetry elements are absent the molecule should be checked carefully for an S_n axis before it is assumed to be chiral.

Chirality

The word chiral has its origins in the Greek word for hand ($\chi\epsilon\rho\iota$, pronounced 'cheri' with a soft ch as in 'loch'). A pair of hands is also a pair of non-superimposable mirror images, and you will often hear chirality referred to as 'handedness' for this reason.

Summary

All molecules can be described in terms of their symmetry or lack thereof, which may contain symmetry elements (point, line, plane). Identity, rotation, reflection, and inversion are symmetry operations (movement of the molecules such that after the movement, all the atoms of the molecules is coincidental with equivalent atom of the molecule in original).

12.2: The Symmetry of Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **12.2: Symmetry Elements and Operations Define the Point Groups** by Claire Vallance, Delmar Larsen, Jerry LaRue is licensed CC BY 4.0.

12.3: Symmetry Operations Define Groups

Now that we have explored some of the properties of symmetry operations and elements and their behavior within point groups, we are ready to introduce the formal mathematical definition of a group.

A mathematical group is defined as a set of elements (g_1, g_2, g_3...) together with a rule for forming combinations $g_i g_j$. The number of elements h is called the **order** of the group. For our purposes, the elements are the symmetry operations of a molecule and the rule for combining them is the sequential application of symmetry operations investigated in the previous section. The elements of the group and the rule for combining them must satisfy the following criteria.

1. The group must include the identity E, for which

$$Eg_i = g_i \tag{12.3.1}$$

   for all the elements of the group.
2. The elements must satisfy the **group property** that the combination of any pair of elements is also an element of the group.
3. Each element g_i must have an inverse g_i^{-1}, which is also an element of the group, such that

$$g_i g_i^{-1} = g_i^{-1} g_i = E \tag{12.3.2}$$

   (e.g. in C_{3v} the inverse of C_3^+ is C_3^-, the inverse of (σ_v is σ_v', the inverse g_i^{-1} effectively 'undoes' the effect of the symmetry operation g_i).
4. The rule of combination must be associative i.e.

$$(g_i g_j)(g_k) = g_i(g_j g_k) \tag{12.3.3}$$

The above definition **does not** require the elements to commute, which would require

$$g_i g_k = g_k g_i \tag{12.3.4}$$

As we discovered in the C_{3v} example above, in many groups the outcome of consecutive application of two symmetry operations depends on the order in which the operations are applied.

Note: Commuting is not a Requirement of Group Elements

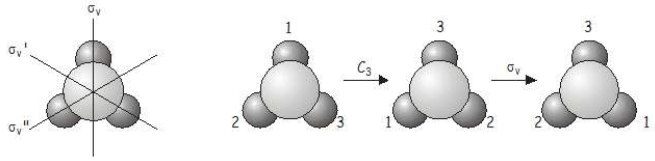
Groups for which the elements do not commute are called *non-Abelian* groups; those for which they elements do commute are *Abelian*.

Group theory is an important area in mathematics, and luckily for chemists the mathematicians have already done most of the work for us. Along with the formal definition of a group comes a comprehensive mathematical framework that allows us to carry out a rigorous treatment of symmetry in molecular systems and learn about its consequences.

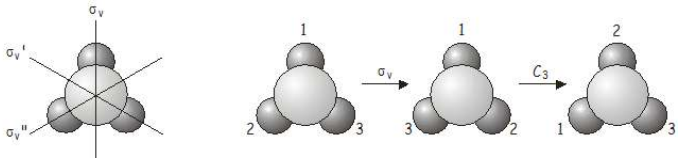
Many problems involving operators or operations (such as those found in quantum mechanics or group theory) may be reformulated in terms of matrices. Any of you who have come across transformation matrices before will know that symmetry operations such as rotations and reflections may be represented by matrices. It turns out that the set of matrices representing the symmetry operations in a group obey all the conditions laid out above in the mathematical definition of a group, and using matrix representations of symmetry operations simplifies carrying out calculations in group theory. Before we learn how to use matrices in group theory, it will probably be helpful to review some basic definitions and properties of matrices.

Group Multiplication

Now we will investigate what happens when we apply two symmetry operations in sequence. As an example, consider the NH_3 molecule, which belongs to the C_{3v} point group. Consider what happens if we apply a C_3rotation followed by a σ_v reflection. We write this combined operation $\sigma_v C_3$ (when written, symmetry operations operate on the thing directly to their right, just as operators do in quantum mechanics – we therefore have to work backwards from right to left from the notation to get the correct order in which the operators are applied). As we shall soon see, the order in which the operations are applied is important.



The combined operation $\sigma_v C_3$ is equivalent to σ_v'', which is also a symmetry operation of the C_{3v} point group. Now let's see what happens if we apply the operators in the reverse order i.e. $C_3\sigma_v$ (σ_v followed by C_3).



Again, the combined operation $C_3\sigma_v$ is equivalent to another operation of the point group, this time σ_v'.

There are two important points that are illustrated by this example:

1. The order in which two operations are applied is important. For two symmetry operations A and B, AB is not necessarily the same as BA, i.e. symmetry operations do not in general commute. In some groups the symmetry elements do commute; such groups are said to be *Abelian*.
2. If two operations from the same point group are applied in sequence, the result will be equivalent to another operation from the point group. Symmetry operations that are related to each other by other symmetry operations of the group are said to belong to the same *class*. In NH_3, the three mirror planes σ_v, σ_v' and σ_v'' belong to the same class (related to each other through a C_3 rotation), as do the rotations C_3^+ and C_3^- (anticlockwise and clockwise rotations about the principal axis, related to each other by a vertical mirror plane

The effects of applying two symmetry operations in sequence within a given point group are summarized in *group multiplication tables*. As an example, the complete group multiplication table for C_{3v} using the symmetry operations as defined in the figures above is shown below. The operations written along the first row of the table are carried out first, followed by those written in the first column (note that the table would change if we chose to name σ_v, σ_v' and σ_v'' in some different order).

C_{3v}	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
E	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
C_3^+	C_3^+	C_3^-	E	σ_v'	σ_v''	σ_v
C_3^-	C_3^-	E	C_3^+	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^-	C_3^+
σ_v'	σ_v'	σ_v	σ_v''	C_3^+	E	C_3^-
σ_v''	σ_v''	σ_v'	σ_v	C_3^-	C_3^+	E

(12.3.5)

Contributors

- Claire Vallance (University of Oxford)

12.3: Symmetry Operations Define Groups is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

12.4: Symmetry Operations can be Represented by Matrices

Matrices can be used to map one set of coordinates or functions onto another set. Matrices used for this purpose are called *transformation matrices*. In group theory, we can use transformation matrices to carry out the various symmetry operations discussed previously. As a simple example, we will investigate the matrices we would use to carry out some of these symmetry operations on a vector in 2D space (x, y).

The Identity Operation

The identity operation leaves the vector unchanged, and as you may already suspect, the appropriate matrix is the identity matrix.

$$(x, y)\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} = (x, y) \tag{12.4.1}$$

Reflection in a plane

The simplest example of a reflection matrix corresponds to reflecting the vector (x, y) in either the x or y axes. Reflection in the x axis maps y to $-y$, while reflection in the y axis maps x to $-x$. The appropriate matrix is very like the identity matrix but with a change in sign for the appropriate element. Reflection in the x axis transforms the vector (x, y) to $(x, -y)$, and the appropriate matrix is

$$(x, y)\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = (x, -y) \tag{12.4.2}$$

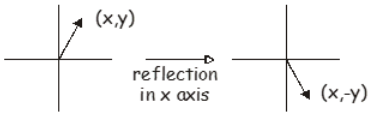


Figure 12.4.1: Reflection across the x-axis in 2D space.

Reflection in the y axis transforms the vector (x, y) to $(-x, y)$, and the appropriate matrix is

$$(x, y)\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix} = (-x, y) \tag{12.4.3}$$

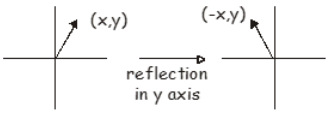


Figure 12.4.2: Reflection across the y-axis *in 2D space.*

More generally, matrices can be used to represent reflections in any plane (or line in 2D). For example, reflection in the 45° axis shown below maps (x, y) onto $(-y, -x)$.

$$(x, y)\begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix} = (-y, -x) \tag{12.4.4}$$

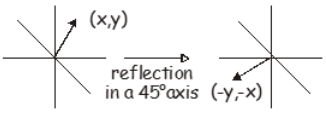


Figure 12.4.3: Reflection across the axis that is rotated 45° with with respect to x-axis *in 2D space.*

Rotation about an Axis

In two dimensions, the appropriate matrix to represent rotation by an angle θ about the origin is

$$R(\theta) = \begin{pmatrix}\cos\theta & -\sin\theta\\ \sin\theta & \cos\theta\end{pmatrix} \tag{12.4.5}$$

In three dimensions, rotations about the x, y and z axes acting on a vector (x, y, z) are represented by the following matrices.

$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \tag{12.4.6}$$

$$R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \tag{12.4.7}$$

$$R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{12.4.8}$$

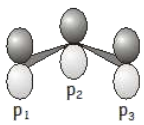
Matrix Representation

The symmetry operations in a group may be represented by a set of transformation matrices $\Gamma(g)$, one for each symmetry element g. Each individual matrix is called a *representative* of the corresponding symmetry operation, and the complete set of matrices is called a *matrix representation* of the group. The matrix representatives act on some chosen *basis set* of functions, and the actual matrices making up a given representation will depend on the basis that has been chosen. The representation is then said to *span* the chosen basis. In the examples above we were looking at the effect of some simple transformation matrices on an arbitrary vector (x, y). The basis was therefore a pair of unit vectors pointing in the x and y directions. In most of the examples we will be considering in this course, we will use sets of atomic orbitals as basis functions for matrix representations. Before proceeding any further, we must check that a matrix representation of a group obeys all of the rules set out in the formal mathematical definition of a group.

1. The first rule is that the group must include the identity operation E (the 'do nothing' operation). We showed above that the matrix representative of the identity operation is simply the identity matrix. As a consequence, every matrix representation includes the appropriate identity matrix.
2. The second rule is that the combination of any pair of elements must also be an element of the group (the *group property*). If we multiply together any two matrix representatives, we should get a new matrix which is a representative of another symmetry operation of the group. In fact, matrix representatives multiply together to give new representatives in exactly the same way as symmetry operations combine according to the group multiplication table. For example, in the C_{3v} point group, we showed that the combined symmetry operation $C_3\sigma_v$ is equivalent to σ_v''. In a matrix representation of the group, if the matrix representatives of C_3 and σ_v are multiplied together, the result will be the representative of σ_v''.
3. The third rule states that every operation must have an inverse, which is also a member of the group. The combined effect of carrying out an operation and its inverse is the same as the identity operation. It is fairly easy to show that matrix representatives satisfy this criterion. For example, the inverse of a reflection is another reflection, identical to the first. In matrix terms we would therefore expect that a reflection matrix was its own inverse, and that two identical reflection matrices multiplied together would give the identity matrix. This turns out to be true, and can be verified using any of the reflection matrices in the examples above. The inverse of a rotation matrix is another rotation matrix corresponding to a rotation of the opposite sense to the first.
4. The final rule states that the rule of combination of symmetry elements in a group must be associative. This is automatically satisfied by the rules of matrix multiplication.

Example: a matrix representation of the C_{2v} point group (the allyl radical)

In this example, we'll take as our basis a p orbital on each carbon atom (p_1, p_2, p_3).



Note that the p orbitals are *perpendicular* to the plane of the carbon atoms (this may seem obvious, but if you're visualizing the basis incorrectly it will shortly cause you a not inconsiderable amount of confusion). The symmetry operations in the C_{2v} point

group, and their effect on the three p orbitals, are as follows:

$$\begin{array}{ll} E & (p_1, p_2, p_3) \rightarrow (p_1, p_2, p_3) \\ C_2 & (p_1, p_2, p_3) \rightarrow (-p_3, -p_2, -p_1) \\ \sigma_v & (p_1, p_2, p_3) \rightarrow (-p_1, -p_2, -p_3) \\ \sigma_v' & (p_1, p_2, p_3) \rightarrow (p_3, p_2, p_1) \end{array} \tag{12.4.9}$$

The matrices that carry out the transformation are

$$\begin{array}{ll} \Gamma(E) & (p_1, p_2, p_3) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = (p_1, p_2, p_3) \\ \Gamma(C_2) & (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} = (-p_3, -p_2, -p_1) \\ \Gamma(\sigma_v) & (p_1, p_2, p_3) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = (-p_1, -p_2, -p_3) \\ \Gamma(\sigma_v') & (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} = (p_3, p_2, p_1) \end{array} \tag{12.4.10}$$

Note

We have written the vectors representing our basis as *row vectors*. This is important. If we had written them as column vectors, the corresponding transformation matrices would be the transposes of the matrices above, and would not reproduce the group multiplication table (try it as an exercise if you need to convince yourself).

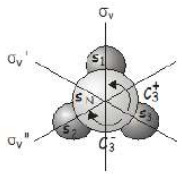
Contributors

- Claire Vallance (University of Oxford)

12.4: Symmetry Operations can be Represented by Matrices is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

12.5: The C_{3v} Point Group Has a 2-D Irreducible Representation

The first thing we need to do before we can construct a matrix representation is to choose a basis. For NH_3, we will select a basis (s_N, s_1, s_2, s_3) that consists of the valence s orbitals on the nitrogen and the three hydrogen atoms. We need to consider what happens to this basis when it is acted on by each of the symmetry operations in the C_{3v} point group, and determine the matrices that would be required to produce the same effect. The basis set and the symmetry operations in the C_{3v} point group are summarized in the figure below.



The effects of the symmetry operations on our chosen basis are as follows:

$$\begin{array}{ll} E & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3) \\ C_3^+ & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1) \\ C_3^- & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2) \\ \sigma_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2) \\ \sigma_v' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3) \\ \sigma_v'' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1) \end{array} \tag{12.5.1}$$

By inspection, the matrices that carry out the same transformations are:

$$\begin{array}{ll} \Gamma(E) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_1, s_2, s_3) \\ \Gamma(C_3^+) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_2, s_3, s_1) \\ \Gamma(C_3^-) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_1, s_2) \\ \Gamma(\sigma_v) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_1, s_3, s_2) \\ \Gamma(\sigma_v') & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_2, s_1, s_3) \\ \Gamma(\sigma_v'') & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_2, s_1) \end{array} \tag{12.5.2}$$

These six matrices therefore form a representation for the C_{3v} point group in the (s_N, s_1, s_2, s_3) basis. They multiply together according to the group multiplication table and satisfy all the requirements for a mathematical group.

Reduced Representations

If we look at the matrices carefully we see that they all take the same block diagonal form (a square matrix is said to be **block diagonal** if all the elements are zero except for a set of submatrices lying along the diagonal).

$$\begin{array}{cccccc} \Gamma(E) & \Gamma(C_3^+) & \Gamma(C_3^-) & \Gamma(\sigma_v) & \Gamma(\sigma_v') & \Gamma(\sigma_v'') \\ \begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix} & \begin{pmatrix}1&0&0&0\\0&0&1&0\\0&0&0&1\\0&1&0&0\end{pmatrix} & \begin{pmatrix}1&0&0&0\\0&0&0&1\\0&1&0&0\\0&0&1&0\end{pmatrix} & \begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix} & \begin{pmatrix}1&0&0&0\\0&0&1&0\\0&1&0&0\\0&0&0&1\end{pmatrix} & \begin{pmatrix}1&0&0&0\\0&0&0&1\\0&0&1&0\\0&1&0&0\end{pmatrix} \\ \chi(E)=4 & \chi(C_3^+)=1 & \chi(C_3^-)=1 & \chi(\sigma_v)=2 & \chi(\sigma_v')=2 & \chi(\sigma_v'')=2 \end{array} \tag{12.5.3}$$

A block diagonal matrix can be written as the *direct sum* of the matrices that lie along the diagonal. In the case of the C_{3v} matrix representation, each of the matrix representatives may be written as the direct sum of a 1×1 matrix and a 3×3 matrix.

$$\Gamma^{(4)}(g) = \Gamma^{(1)}(g) \otimes \Gamma^{(3)}(g) \tag{12.5.4}$$

in which the bracketed superscripts denote the dimensionality of the matrices. Note that a direct sum is very different from ordinary matrix addition since it produces a matrix of higher dimensionality. A direct sum of two matrices of orders n and m is performed by placing the matrices to be summed along the diagonal of a matrix of order $n+m$ and filling in the remaining elements with zeroes.

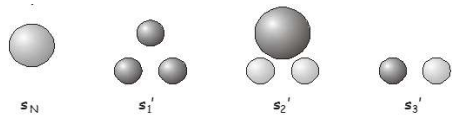
The reason why this result is useful in group theory is that the two sets of matrices $\Gamma^{(1)}(g)$ and $\Gamma^{(3)}(g)$ also satisfy all of the requirements for a matrix representation. Each set contains the identity and an inverse for each member, and the members multiply together associatively according to the group multiplication table[3]. Recall that the basis for the original four-dimensional representation had the s orbitals (s_N, s_1, s_2, s_3) of ammonia as its basis. The first set of reduced matrices, $\Gamma^{(1)}(g)$, forms a one-dimensional representation with (s_N) as its basis. The second set, $\Gamma^{(3)}(g)$ forms a three-dimensional representation with the basis (s_1, s_2, s_3). Separation of the original representation into representations of lower dimensionality is called *reduction* of the representation. The two *reduced representations* are shown below.

g	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''	
$\Gamma^{(1)}(g)$	(1)	(1)	(1)	(1)	(1)	(1)	1D representation spanned by (s_N)
$\Gamma^{(3)}(g)$	$\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}$	$\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}$	$\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}$	$\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix}$	3D representation spanned by (s_1, s_2, s_3)

(12.5.5)

The logical next step is to investigate whether or not the three dimensional representation $\Gamma^{(3)}(g)$ can be reduced any further. As it stands, the matrices making up this representation are not in block diagonal form (some of you may have noted that the matrices representing E and σ_v are block diagonal, but in order for a representation to be reducible *all* of the matrix representatives must be in the *same* block diagonal form) so the representation is not reducible. However, we can carry out a similarity transformation (see **10.1**) to a new representation spanned by a new set of basis functions (made up of linear combinations of (s_1, s_2, s_3)), which *is* reducible. In this case, the appropriate (normalized) linear combinations to use as our new basis functions are

$$\begin{aligned} s_1' &= \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3) \\ s_2' &= \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3) \\ s_3' &= \frac{1}{\sqrt{2}}(s_2 - s_3) \end{aligned} \tag{12.5.6}$$



or in matrix form

$$\begin{array}{ccccc} (s_1', s_2', s_3') & = & (s_1, s_2, s_3) & \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \\ \mathbf{x'} & = & \mathbf{x} & C \end{array} \tag{12.5.7}$$

The matrices in the new representation are found from $\mathbf{\Gamma}'(g) = C^{-1}\mathbf{\Gamma}(g)C$ to be

$$\begin{array}{cccccc} E & C_3^+ & C_3^- & \sigma_v & \sigma_v' & \sigma_v'' \\ \Gamma^{(3),}(g) & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} \end{array} \tag{12.5.8}$$

We see that each matrix is now in block diagonal form, and the representation may be reduced into the direct sum of a 1 x 1 representation spanned by (s_1') and a 2x2 representation spanned by (s_2', s_3'). The complete set of reduced representations obtained from the original 4D representation is:

E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''	
(1)	(1)	(1)	(1)	(1)	(1)	1D representation spanned by (s_N)
(1)	(1)	(1)	(1)	(1)	(1)	1D representation spanned by (s_1')
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	2D representation spanned by (s_2', s_3')

(12.5.9)

This is as far as we can go in reducing this representation. None of the three representations above can be reduced any further, and they are therefore called *irreducible representations*, of the point group. Formally, a representation is an irreducible representation if there is no similarity transform that can simultaneously convert all of the representatives into block diagonal form. The linear combination of basis functions that converts a matrix representation into block diagonal form, allowing reduction of the representation, is called a *symmetry adapted linear combination (SALC)*.

Irreducible Representations

The two one-dimensional irreducible representations spanned by s_N and s_1' are seen to be identical. This means that s_N and s_1' have the 'same symmetry', transforming in the same way under all of the symmetry operations of the point group and forming bases for the same matrix representation. As such, they are said to belong to the same *symmetry species*. There are a limited number of ways in which an arbitrary function can transform under the symmetry operations of a group, giving rise to a limited number of symmetry species. Any function that forms a basis for a matrix representation of a group must transform as one of the symmetry species of the group. The irreducible representations of a point group are labeled according to their symmetry species as follows:

i. 1D representations are labeled A or B, depending on whether they are symmetric (character $+1$) or antisymmetric (character -1) under rotation about the principal axis.
ii. 2D representations are labeled E, 3D representations are labeled T.
iii. In groups containing a center of inversion, g and u labels (from the German *gerade* and *ungerade*, meaning symmetric and antisymmetric) denote the character of the irreducible representation under inversion ($+1$ for g, -1 for u)
iv. In groups with a horizontal mirror plane but no center of inversion, the irreducible representations are given prime and double prime labels to denote whether they are symmetric (character $+1$ or antisymmetric (character -1) under reflection in the plane.
v. If further distinction between irreducible representations is required, subscripts 1 and 2 are used to denote the character with respect to a C_2 rotation perpendicular to the principal axis, or with respect to a vertical reflection if there are no C_2 rotations.

The 1D irreducible representation in the C_{3v} point group is symmetric (has character $+1$) under all the symmetry operations of the group. It therefore belongs to the irreducible representation A_1. The 2D irreducible representation has character 2 under the identity operation, -1 under rotation, and 0 under reflection, and belongs to the irreducible representation E.

Note

Sometimes there is confusion over the relationship between a function f and its irreducible representation, but it is quite important that you understand the connection. There are several different ways of stating the relationship. For example, the following statements all mean the same thing:

- "f has A_2 symmetry"

- "f transforms as A_2"
- "f has the same symmetry

Contributors

- Claire Vallance (University of Oxford)

12.5: The C_3V Point Group Has a 2-D Irreducible Representation is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

12.6: Character Tables

Now that we've learnt how to create a matrix representation of a point group within a given basis, we will move on to look at some of the properties that make these representations so powerful in the treatment of molecular symmetry. The trace of a matrix representative $\Gamma(g)$ is usually referred to as the *character* of the representation under the symmetry operation g. We will soon come to see that the characters of a matrix representation are often more useful than the matrix representatives themselves. Characters have several important properties.

1. The character of a symmetry operation is invariant under a similarity transform
2. Symmetry operations belonging to the same class have the same character in a given representation. Note that the character for a given class may be different in different representations, and that more than one class may have the same character.

Proofs of the above two statements are given in the Appendix.

Character Tables

A character table summarizes the behavior of all of the possible irreducible representations of a group under each of the symmetry operations of the group. The character table for C_{3v} is shown below.

$C_{3v}, 3m$	E	$2C_3$	$3\sigma_v$	$h = 6$
A_1	1	1	1	$z, z^2, x^2 + y^2$
A_2	1	1	−1	R_z
E	2	−1	0	$(x, y), (xy, x^2 + y^2), (xz, yz), (R_x, R_y)$

(12.6.1)

The various sections of the table are as follows:

i. The first element in the table gives the name of the point group, usually in both Schoenflies (C_{3v}) and Hermann-Mauguin ($3m$) notation.
ii. Along the first row are the symmetry operations of the group, E, $2C_3$ and $3\sigma_v$, followed by the order of the group. Because operations in the same class have the same character, symmetry operations are grouped into classes in the character table and not listed separately.
iii. In the first column are the irreducible representations of the group. In C_{3v} the irreducible representations are A_1, A_2 and E (the representation we considered above spans $2A_1$ + E).
iv. The characters of the irreducible representations under each symmetry operation are given in the bulk of the table.
v. The final column of the table lists a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products $(z^2, x^2 + y^2, xy, yz)$, and the rotations (R_x, R_y, R_z).

The functions listed in the final column of the table are important in many chemical applications of group theory, particularly in spectroscopy. For example, by looking at the transformation properties of x, y and z (sometimes given in character tables as T_x, T_y, T_z) we can discover the symmetry of translations along the x, y, and z axes. Similarly, R_x, R_y and R_z represent rotations about the three Cartesian axes. As we shall see later, the transformation properties of x, y, and z can also be used to determine whether or not a molecule can absorb a photon of x-, y-, or z-polarized light and undergo a spectroscopic transition. The Cartesian products play a similar role in determining selection rules for Raman transitions, which involve two photons.

A simple way to determine the characters of a representation

In many applications of group theory, we only need to know the characters of the representative matrices, rather than the matrices themselves. Luckily, when each basis function transforms as a 1D irreducible representation (which is true in many cases of interest) there is a simple shortcut to determining the characters without having to construct the entire matrix representation. All we have to do is to look at the way the individual basis functions transform under each symmetry operation. For a given operation, step through the basis functions as follows:

i. Add 1 to the character if the basis function is unchanged by the symmetry operation (i.e. the basis function is mapped onto itself);
ii. Add −1 to the character if the basis function changes sign under the symmetry operation (i.e the basis function is mapped onto minus itself);

iii. Add 0 to the character if the basis function moves when the symmetry operation is applied (i.e the basis function is mapped onto something different from itself).

Try this for the s orbital basis we have been using for the C_{3v} group. You should find you get the same characters as we obtained from the traces of the matrix representatives.

We can also work out the characters fairly easily when two basis functions transform together as a 2D irreducible representation. For example, in the C_{3v} point group x and y axes transform together as E. If we carry out a rotation about z by an angle θ, our x and y axes are transformed onto new axes x' and y'. However, the new axes can each be written as a linear combination of our original x and y axes. Using the rotation matrices introduced in Section 9, we see that:

$$\begin{aligned} x' &= \cos\theta\, x + \sin\theta\, y \\ y' &= -\sin\theta\, x + \cos\theta\, y \end{aligned} \tag{12.6.2}$$

For one-dimensional irreducible representations we asked if a basis function/axis was mapped onto itself, minus itself, or something different. For two-dimensional irreducible representations we need to ask how much of the 'old' axis is contained in the new one. From the above we see that the x' axis contains a contribution $\cos\theta$ from the x axis, and the y' axis contains a contribution $\cos\theta$ from the y axis. The characters of the x and y axes under a rotation through θ are therefore $\cos\theta$, and the overall character of the E irreducible representation is therefore $\cos\theta + \cos\theta = 2\cos\theta$. For a C_3 rotation through 120 degrees, the character of the E irreducible representation is therefore $2\cos 120^\circ = -1$.

In general, *when an axis is rotated by an angle θ by a symmetry operation, its contribution to the character for that operation is* $\cos\theta$.

Note: Irreducible representations with complex characters

In many cases, the characters for rotations C_n and improper rotations S_n are complex numbers, usually expressed in terms of the quantity $\epsilon = \exp(2\pi i/n)$. It is fairly straightforward to reconcile this with the fact that in chemistry we are generally using group theory to investigate physical problems in which all quantities are real. It turns out that whenever our basis spans an irreducible representation whose characters are complex, it will also span a second irreducible representation whose characters are the complex conjugates of the first irreducible representation i.e. complex irreducible representations occur in pairs. According to the strict mathematics of group theory, each irreducible representation in the pair should be considered as a separate representation. However, when applying such irreducible representations in physical problems, we add the characters for the two irreducible representations together to get a single irreducible representation whose characters are real.

As an example, the 'correct' character table for the group C_3 takes the form:

C_3	E	C_3	C_3^2
A	1	1	1
E	$\begin{Bmatrix}1\\1\end{Bmatrix}$	$\begin{matrix}\epsilon\\ \epsilon*\end{matrix}$	$\begin{matrix}\epsilon*\\ \epsilon\end{matrix}$

(12.6.3)

Where $\epsilon = \exp(2\pi i/3)$. However, as chemists we would usually combine the two parts of the E irreducible representation to give:

C_3	E	C_3	C_3^2
A	1	1	1
E	2	−1	1

(12.6.4)

Contributors

- Claire Vallance (University of Oxford)

12.6: Character Tables is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

12.7: Relations involving Characters

12.7: Relations involving Characters is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

12.8: Using Symmetry to Predict Zero in a Secular Determinant

As we continue with this course, we will discover that there are many times when we would like to know whether a particular integral is necessarily zero, or whether there is a chance that it may be non-zero. We can often use group theory to differentiate these two cases.

You will have already used symmetry properties of functions to determine whether or not a one-dimensional integral is zero. For example, cos(x) is an 'even' function (symmetric with respect to reflection through the origin), and it follows from this that

$$\int_{-\infty}^{\infty} \cos(x)dx = 0$$

In general integral between these limits for any other even function will be also be zero.

In the general case we may have an integral of more than one dimension. The key to determining whether a general integral is necessarily zero lies in the fact that because an integral is just a number, it must be invariant to any symmetry operation. For example, bonding in a diatomic (see next section) depends on the presence of a non-zero overlap between atomic orbitals on adjacent atoms, which may be quantified by an *overlap integral*. You would not expect the bonding in a molecule to change if you rotated the molecule through some angle θ, so the integral must be invariant to rotation, and indeed to any other symmetry operation.

In group theoretical terms, for an integral to be non-zero, *the integrand must transform as the totally symmetric irreducible representation in the appropriate point group*. In practice, the integrand may not transform as a single irreducible representation, but it **must include** the totally symmetric irreducible representation. These ideas should become more clear in the next section.

> It should be noted that even when the irreducible representations spanned by the integrand do include the totally symmetric irreducible representation, it is still possible for the integral to be zero. All group theory allows us to do is identify integrals that are *necessarily* zero based on the symmetry (or lack thereof) of the integrand.

Secular Equations

As we have seen already, any set of linear equations may be rewritten as a matrix equation $\mathbf{Ax} = \mathbf{b}$. Linear equations are classified as *simultaneous linear equations* or *homogeneous linear equations*, depending on whether the vector $\mathbf{b}$ is non-zero or zero. For a set of simultaneous linear equations (non-zero $\mathbf{b}$) it is fairly apparent that if a unique solution exists, it can be found by multiplying both sides by the inverse matrix $\mathbf{A}^{-1}$ (since $\mathbf{A}^{-1}\mathbf{A}$ on the left hand side is equal to the identity matrix, which has no effect on the vector $\mathbf{x}$)

$$\begin{aligned} \mathbf{Ax} &= \mathbf{b} \\ \mathbf{A}^{-1}\mathbf{Ax} &= \mathbf{A}^{-1}\mathbf{b} \\ \mathbf{x} &= \mathbf{A}^{-1}\mathbf{b} \end{aligned} \tag{12.8.1}$$

In practice, there are easier matrix methods for solving simultaneous equations than finding the inverse matrix, but these need not concern us here. We previously argued that in order for a matrix to have an inverse, **it must have a non-zero determinant**. Since $\mathbf{A}^{-1}$ must exist in order for a set of simultaneous linear equations to have a solution, this means that the determinant of the matrix $\mathbf{A}$ must be non-zero for the equations to be solvable.

> *For a matrix to have an inverse, it must have a non-zero determinant.*

The reverse is true for homogeneous linear equations. In this case the set of equations only has a solution if the determinant of $\mathbf{A}$ *is* equal to zero. The secular equations we want to solve are homogeneous equations, and we will use this property of the determinant to determine the molecular orbital energies. An important property of homogeneous equations is that if a vector $\mathbf{x}$ is a solution, so is any multiple of $\mathbf{x}$, meaning that the solutions (the molecular orbitals) can be normalized without causing any problems.

Solving for the orbital energies and expansion coefficients

Recall the secular equations for the A_1 orbitals of NH_3 derived in the previous section

$$\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) &= 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) &= 0 \end{aligned} \tag{12.8.2}$$

where c_1 and c_2 are the coefficients in the linear combination of the SALCs $\phi_1 = s_N$ and $\phi_2 = \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3)$ used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{12.8.3}$$

In order for the equations to have a solution, the determinant of the matrix must be equal to zero. Writing out the determinant will give us a polynomial equation in E that we can solve to obtain the orbital energies in terms of the Hamiltonian matrix elements H_{ij} and overlap integrals S_{ij}. The number of energies obtained by 'solving the secular determinant' in this way is equal to the order of the matrix, in this case two.

The secular determinant for Equation (21.3) is (noting that S_{11} = $S_{22} = 1$ since the SALCs are normalized)

$$(H_{11} - E)(H_{22} - E) - (H_{12} - ES_{12})^2 = 0 \tag{12.8.4}$$

Expanding and collecting terms in E gives

$$E^2(1 - S_{12}^2) + E(2H_{12}S_{12} - H_{11} - H_{22}) + (H_{11}H_{22} - H_{12}^2) = 0 \tag{12.8.5}$$

which can be solved using the quadratic formula to give the energies of the two molecular orbitals.

$$\begin{aligned} E_{\pm} &= \\ &= \frac{-(2H_{12}S_{12} - H_{11} - H_{22}) \pm \sqrt{(2H_{12}S_{12} - H_{11} - H_{22})^2 - 4(1 - S_{12}^2)(H_{11}H_{22} - H_{12}^2)}}{2(1 - S_{12}^2)} \end{aligned} \tag{12.8.6}$$

To obtain numerical values for the energies, we need to evaluate the integrals H_{11}, H_{22}, H_{12}, and S_{12}. This would be quite a challenge to do analytically, but luckily there are a number of computer programs that can be used to calculate the integrals. One such program gives the following values.

$$\begin{aligned} H_{11} &= -26.0000\ eV \\ H_{22} &= -22.2216\ eV \\ H_{12} &= -29.7670\ eV \\ S_{12} &= 0.8167\ eV \end{aligned} \tag{12.8.7}$$

When we substitute these into our equation for the energy levels, we get:

$$\begin{aligned} E_+ &= 29.8336\ eV \\ E_- &= -31.0063\ eV \end{aligned} \tag{12.8.8}$$

We now have the orbital energies and the next step is to find the orbital coefficients. The coefficients for an orbital of energy E are found by substituting the energy into the secular equations and solving for the coefficients c_i. Since the two secular equations are not linearly independent (i.e. they are effectively only one equation), when we solve them to find the coefficients what we will end up with is the *relative* values of the coefficients. This is true in general: in a system with N coefficients, solving the secular equations will allow all N of the coefficients c_i to be obtained in terms of, say, c_1. The absolute values of the coefficients are found by normalizing the wavefunction.

Since the secular equations for the orbitals of energy E_+ and E_- are not linearly independent, we can choose to solve either one of them to find the orbital coefficients. We will choose the first.

$$(H_{11} - E_{\pm})c_1 + (H_{12} - E_{\pm}S_{12})c_2 = 0 \tag{12.8.9}$$

For the orbital with energy E_- = -31.0063 eV, substituting numerical values into this equation gives

$$\begin{aligned} 5.0063c_1 - 4.4442c_2 &= 0 \\ c_2 &= 1.1265c_1 \end{aligned} \tag{12.8.10}$$

The molecular orbital is therefore

$$\Psi = c_1(\phi_1 + 1.1265\phi_2) \tag{12.8.11}$$

Normalizing to find the constant c_1 (by requiring $< \Psi | \Psi >$ = 1) gives

$$\begin{aligned} \Psi_1 &= 0.4933\phi_1 + 0.5557\phi_2 \\ &= 0.4933s_N + 0.3208(s_1 + s_2 + s_3) \quad \text{(substituting the SALCs for } \phi_1 \text{ and } \phi_2) \end{aligned} \tag{12.8.12}$$

For the second orbital, with energy E_+ = 29.8336 eV, the secular equation is

$$\begin{aligned} -55.8336c_1 - 54.1321c_2 &= 0 \\ c_2 &= -1.0314c_1 \end{aligned} \tag{12.8.13}$$

giving

$$\begin{aligned} \Psi_2 &= c_1(\phi_1 - 1.0314\phi_2) \\ &= 1.6242\phi_1 - 1.6752\phi_2 \qquad \text{(after normalization)} \\ &= 1.6242s_N - 0.9672(s_1 + s_2 + s_3) \end{aligned} \tag{12.8.14}$$

These two A_1 molecular orbitals Ψ_1 and Ψ_2, one bonding and one antibonding, are shown below.



The remaining two SALCs arising from the s orbitals of NH_3 ($\phi_3 = \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3)$ and $\phi_4 = \frac{1}{\sqrt{2}}(s_2 - s_3)$), form an orthogonal pair of molecular orbitals of E symmetry. We can show this by solving the secular determinant to find the orbital energies. The secular equations in this case are:

$$\begin{aligned} c_1(H_{33} - ES_{33}) + c_2(H_{34} - ES_{34}) &= 0 \\ c_1(H_{34} - ES_{34}) + c_2(H_{44} - ES_{44}) &= 0 \end{aligned} \tag{12.8.15}$$

Solving the secular determinant gives

$$E_\pm = \frac{-(2H_{34}S_{34} - H_{33} - H_{44}) \pm \sqrt{(2H_{34}S_{34} - H_{33} - H_{44})^2 - 4(1 - S_{34}^2)(H_{33}H_{44} - H_{34}^2)}}{2(1 - S_{34}^2)} \tag{12.8.16}$$

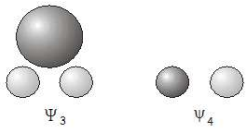
The integrals required are

$$\begin{aligned} H_{33} &= -9.2892\ eV \\ H_{44} &= -9.2892\ eV \\ H_{34} &= 0 \\ S_{34} &= 0 \end{aligned} \tag{12.8.17}$$

Using the fact that H_{34} = $S_{34} = 0$, the expression for the energies reduces to

$$E_\pm = \frac{(H_{33} + H_{44}) \pm (H_{33} - H_{44})}{2} \tag{12.8.18}$$

giving E_+ = H_{33} = -9.2892 eV and E_- = H_{44} = -9.2892 eV. Each SALC therefore forms a molecular orbital by itself, and the two orbitals have the same energy; the two SALCs form an orthogonal pair of degenerate orbitals. These two molecular orbitals of E symmetry are shown below.



Summary of the steps involved in constructing molecular orbitals

1. Choose a basis set of functions f_i consisting of the valence atomic orbitals on each atom in the system, or some chosen subset of these orbitals.
2. With the help of the appropriate character table, determine which irreducible representations are spanned by the basis set using Equation (15.20) to determine the number of times a_k that the kth irreducible representation appears in the representation.

$$a_k = \frac{1}{h}\sum_C n_C \chi(g)\chi_k(g) \tag{12.8.19}$$

3. Construct the SALCs ϕ_i that transform as each irreducible representation using Equation 16.1

$$\phi_i = \sum_g \chi_k(g) g f_i \tag{12.8.20}$$

4. Write down expressions for the molecular orbitals by taking linear combinations of all the irreducible representations of the same symmetry species.
5. Write down the secular equations for the system.
6. Solve the secular determinant to obtain the energies of the molecular orbitals.
7. Substitute each energy in turn back into the secular equations and solve to obtain the coefficients appearing in your molecular orbital expressions in step 4.
8. Normalize the orbitals.

12.8: Using Symmetry to Predict Zero in a Secular Determinant is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **1.21: Solving the Secular Equations** by Claire Vallance is licensed CC BY 4.0. Original source: http://vallance.chem.ox.ac.uk/pdfs/SymmetryLectureNotes.pdf.

12.9: Generating Operators for Irreducible Representations

12.9: Generating Operators for Irreducible Representations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

13: 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.

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

13: Molecular Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

13.1: 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 **13.1.1** shows an example of plane-polarized electromagnetic radiation, consisting of a single oscillating electric field and a single oscillating magnetic field.

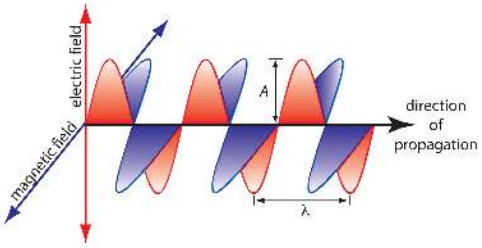


Figure **13.1.1**: Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, A, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation.[2] For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_t = A_e \sin(2\pi\nu t + \phi) \tag{13.1.1}$$

where A_t is the magnitude of the electric field at time t, A_e is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and ϕ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at $t = 0$. The identical equation for the magnetic field is

$$A_t = A_m \sin(2\pi\nu t + \phi) \tag{13.1.2}$$

where A_m is the magnetic field's maximum amplitude.

Units

Other properties also are useful for characterizing the wave behavior of electromagnetic radiation. The **wavelength**, λ, is defined as the distance between successive maxima (Figure **13.1.1**). For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (1 nm = 10^{-9} m), and for infrared radiation it is given in microns (1 μm = 10^{-6} m). The relationship between wavelength and frequency is

$$\lambda = \frac{c}{\nu} \tag{13.1.3}$$

Another unit useful unit is the **wavenumber**, $\tilde{\nu}$, which is the reciprocal of wavelength

$$\tilde{\nu} = \frac{1}{\lambda} \tag{13.1.4}$$

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

Example 13.1.1

In 1817, Josef Fraunhofer studied the spectrum of solar radiation, observing a continuous spectrum with numerous dark lines. Fraunhofer labeled the most prominent of the dark lines with letters. In 1859, Gustav Kirchhoff showed that the D line in the sun's spectrum was due to the absorption of solar radiation by sodium atoms. The wavelength of the sodium D line is 589 nm. What are the frequency and the wavenumber for this line?

Solution

The frequency and wavenumber of the sodium D line are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{589 \times 10^{-9} \text{ m}} = 5.09 \times 10^{14} \text{ s}^{-1} \tag{13.1.5}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{589 \times 10^{-9} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 1.70 \times 10^4 \text{ cm}^{-1} \tag{13.1.6}$$

Exercise 13.1.1

Another historically important series of spectral lines is the Balmer series of emission lines form hydrogen. One of the lines has a wavelength of 656.3 nm. What are the frequency and the wavenumber for this line?

Click here to review your answer to this exercise.

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 **13.1.2**). The boundaries between the regions of the electromagnetic spectrum are not rigid, and overlap between spectral regions is possible.

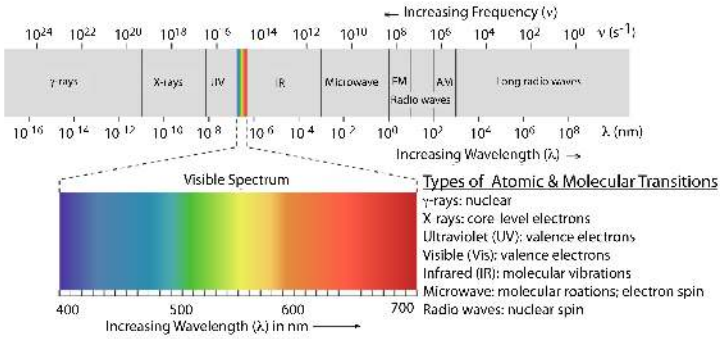


Figure **13.1.2**: The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.wikipedia.org).

Above, we defined several characteristic properties of electromagnetic radiation, including its energy, velocity, amplitude, frequency, phase angle, polarization, and direction of propagation. A spectroscopic measurement is possible only if the photon's interaction with the sample leads to a change in one or more of these characteristic properties. We can divide spectroscopy into two broad classes of techniques. In one class of techniques there is a transfer of energy between the photon and the sample. Table **13.1.1** provides a list of several representative examples.

***Table* 13.1.1**: *Examples of Spectroscopic Techniques Involving an Exchange of Energy Between a Photon and the Sample*

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Techniquea
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis	*UV/Vis spectroscopy* *atomic absorption spectroscopy*
	IR	*infrared spectroscopy* raman spectroscopy
	Microwave	microwave spectroscopy
	Radio wave	electron spin resonance spectroscopy nuclear magnetic resonance spectroscopy
emission (thermal excitation)	UV/Vis	*atomic emission spectroscopy*
photoluminescence	X-ray	X-ray fluorescence
	UV/Vis	*fluorescence spectroscopy* *phosphorescence spectroscopy* atomic fluorescence spectroscopy
chemiluminescence	UV/Vis	chemiluminescence spectroscopy

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 **13.1.3**). The type of transition depends on the photon's energy. The electromagnetic spectrum in Figure **13.1.2**, 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.

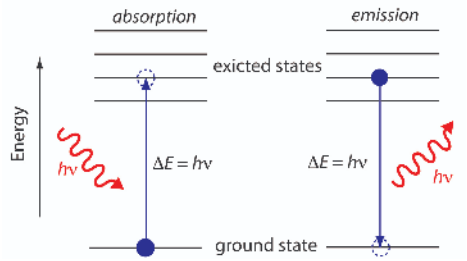


Figure **13.1.3**: Simplified energy diagram showing the absorption and emission of a photon by an atom or a molecule. When a photon of energy hν strikes the atom or molecule, absorption may occur if the difference in energy, ΔE, between the ground state and the excited state is equal to the photon's energy. An atom or molecule in an excited state may emit a photon and return to the ground state. The photon's energy, hν, 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 **13.1.3** 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 **13.1.4**, for example, shows the absorbance spectrum of cranberry juice.

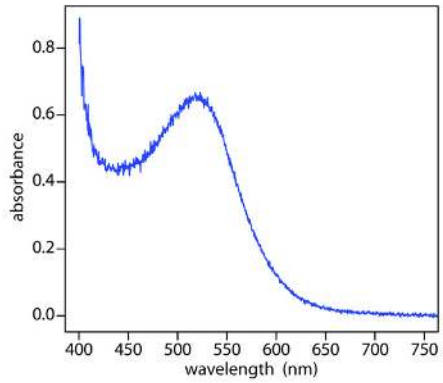


Figure **13.1.3**). As a result, the juice appears red.

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 **13.1.4**). 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 **13.1.5**.

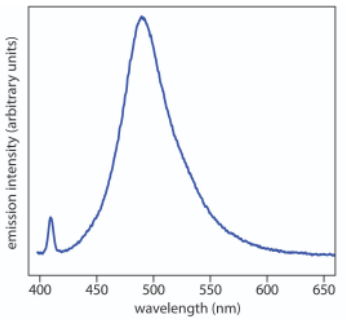


Figure **13.1.5**: Photoluminescence spectrum of the dye coumarin 343, which is incorporated in a reverse micelle suspended in cyclohexanol. The dye's absorbance spectrum (not shown) has a broad peak around 400 nm. The sharp peak at 409 nm is from the laser source used to excite coumarin 343. The broad 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)

13.1: The Electromagnetic Spectrum is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

13.2: 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

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{13.2.1}$$

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 13.2.1) 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).

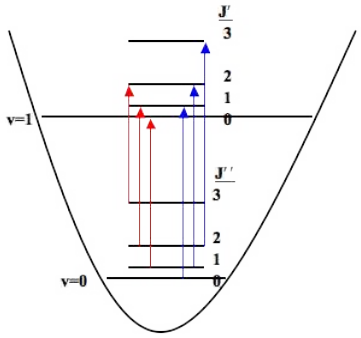


Figure 13.2.1 : Rotation-Vibration Transitions. Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels.

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:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{13.2.2}$$
$$= h\nu_0 + hB\left[(J+1)(J+2) - J(J+1)\right] \tag{13.2.3}$$
$$= h\nu_0 + 2hB(J+1) \tag{13.2.4}$$

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:

$$\Delta E = h\nu_0 + hB\left[J(J+1) - J'(J'+1)\right] \tag{13.2.5}$$
$$= h\nu_0 + hB\left[J(J-1) - J(J+1)\right] \tag{13.2.6}$$
$$= h\nu_0 - 2hBJ \tag{13.2.7}$$

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:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \tag{13.2.8}$$
$$= h\nu_0 \tag{13.2.9}$$

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.

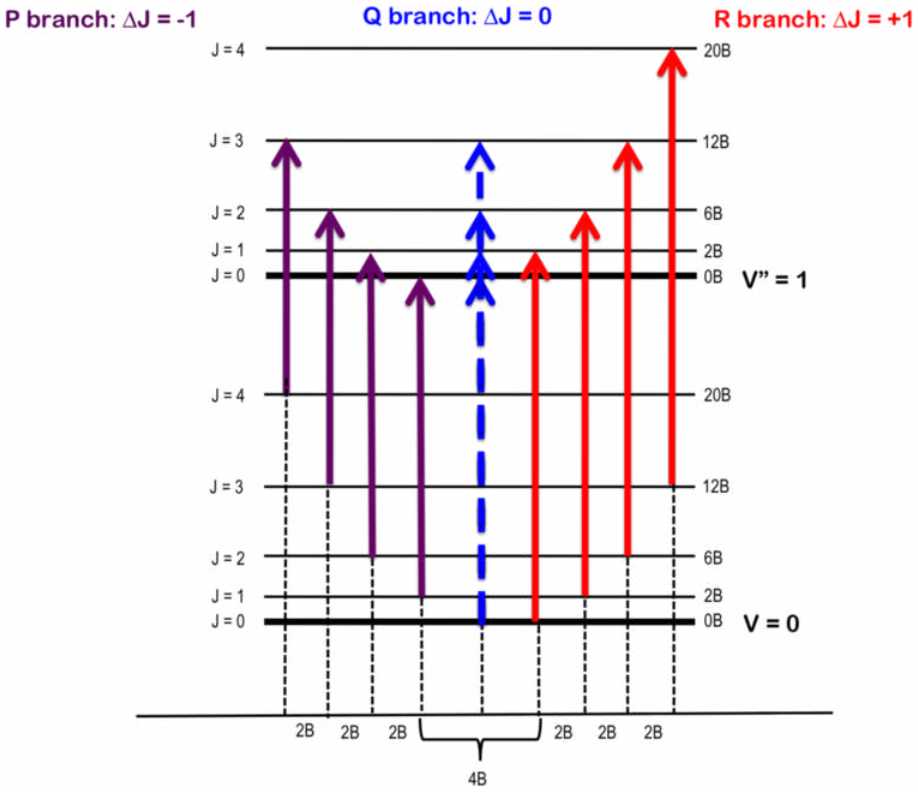


Figure 13.2.3 : Cartoon depiction of rotational energy levels, J, imposed on vibrational energy levels, v. The transitions between levels that would result in the P- and R-branches are depicted in purple and red, respectively, in addition to the theoretical Q-branch line in blue.

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.

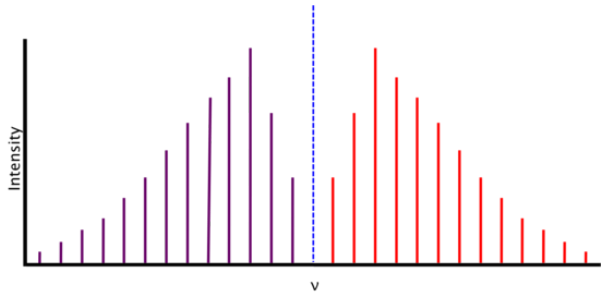


Figure 13.2.3 : A cartoon depiction of an ideal rovibrational spectrum.

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.

13.2: 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.

13.3: 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.

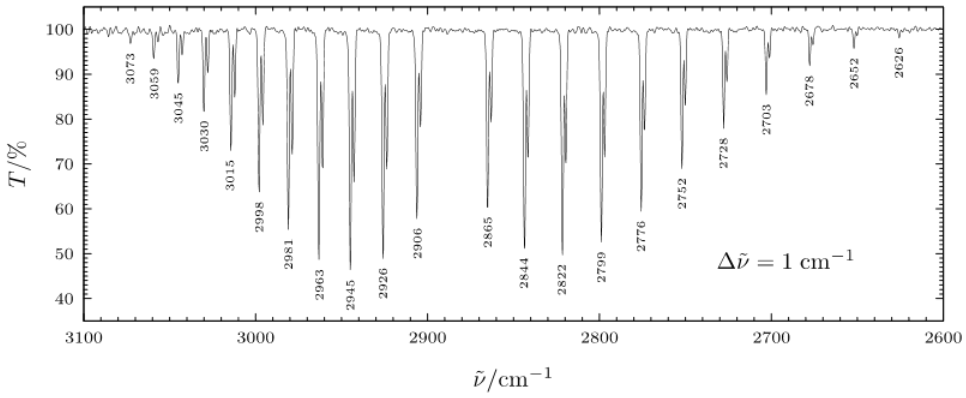


Figure used with permission from Wikipedia.

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.

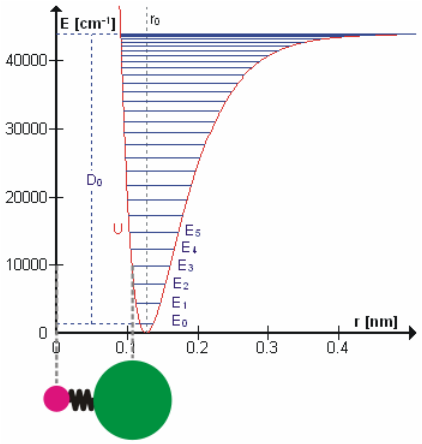


Figure used with permission from Wikipedia.

So far, there are two relationship established above

$$\tilde{B} \propto R_e^2 \tag{13.3.1}$$

(inversely proportional)

and

$$R_e^2 \propto v \tag{13.3.2}$$

(i.e., directly proportional). Therefore,

$$\tilde{B} \propto v \tag{13.3.3}$$

(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

$$\tilde{E}_{v,J} = G(v) + F(J) = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}J(J+1) \tag{13.3.4}$$

or in term of $\tilde{B}_v$

$$\tilde{E}_{v,J} = \tilde{\nu}(v + \frac{1}{2}) + \tilde{B}_v J(J+1) \tag{13.3.5}$$

Frequencies of vibrational transition from $v = 0 \rightarrow 1$ can be calculated from the equation above as the following:

For R branch, allowed $J = 0, 1, 2, ...$

$$\tilde{\nu}_R(\Delta J = +1) = \tilde{E}_{1,J+1} - \tilde{E}_{0,J} \tag{13.3.6}$$

$$= \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1) \tag{13.3.7}$$

$$= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.8}$$

For P branch, allowed $J = 1, 2, 3, ...$

$$\tilde{\nu}_P(\Delta J = -1) = \tilde{E}_{1,J-1} - \tilde{E}_{0,J} \tag{13.3.9}$$

$$= \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.10}$$

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

$$\tilde{\nu}_R = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.11}$$

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,

$$\tilde{\nu}_P = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.12}$$

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

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}(v = \frac{1}{2}) \tag{13.3.13}$$

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

13.3: The Vibration-Rotation Spectrum is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

13.4: 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.

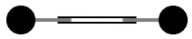


Figure **13.4.1**: This animation can serve as an illustration of one of the aspects of the conservation of angular momentum. The animation is a schematic representation of two weights that are connected to each other. The two weights are circling around their common center of mass, the center of mass is stationary. The connection between the weight consists of pistons. When the connecting pistons contract, the rotation rate goes up. When the inward force exerted by the pistons relaxes the weight slide outwards, and the rotation rate goes down. (Public domain; Cleonis).

Centrifugal force,

$$F_c = \mu r_c \omega^2 = L^2/\mu \text{mtd} \tag{13.4.1}$$

Equating the restoring force to the centrifugal force, one gets

$$k(r_c - r_e) = \frac{L^2}{\mu {r_c}^3} \tag{13.4.2}$$

$$r_c - r_e = \frac{L^2}{k\mu {r_c}^3} \cong \frac{L^2}{k\mu {r_e}^3} \tag{13.4.3}$$

Total energy, on adding kinetic energy, as expressed in Equation 13.4.3 to the potential energy,

$$\frac{1}{2}k(r_c - r_e)^2 \tag{13.4.4}$$

is given by

$$E_r = \frac{L^2}{2\mu {r_c}^2} + \frac{1}{2}k\,(r_c - r_e)^2 \tag{13.4.5}$$

Using $(r_c - r_e) = \Delta r$ and eliminating r_c from equation 13.4.5, one gets

$$E_r = \frac{L^2}{2\mu\ {r_e}^2(1 + \Delta r/r_e)^2} + \frac{1}{2}k\Delta r^2 \tag{13.4.6}$$

$$= \frac{L^2(1 - 2\Delta r/r_e)}{2\mu\ {r_e}^2} + \frac{1}{2}k\Delta r^2 \tag{13.4.7}$$

using

$$(1 + \Delta r/r_e)^{-2} \approx (1 - 2\Delta r/r_e) \tag{13.4.8}$$

$$E_r = \frac{L^2}{2\mu {r_e}^2} - \frac{L^4}{k\mu^2 {r_e}^6} + \frac{1}{2}k\frac{L^4}{k^{2\mu 2}{r_e}^6} \tag{13.4.9}$$

$$= \frac{L^2}{2\mu {r_e}^2} - \frac{1}{2}\frac{L^4}{k\mu^2 {r_e}^6} \tag{13.4.10}$$

$$= \frac{\hbar^2\, J(J+1)}{2\mu {r_e}^2} - \frac{\hbar^4\, J^2(J+1)^2}{2k\mu^2 {r_e}^6} \tag{13.4.11}$$

Use of Equation 13.4.3 and of the relation regarding angular momentum of a rotor

$$L = \hbar\sqrt{J(J+1)} \tag{13.4.12}$$

has been made to obtain relation in Equation 13.4.11, which may be expressed in cm^{-1} as

$$F(J) = \underbrace{\tilde{B}J(J+1)}_{\text{rigid rotator term}} - \underbrace{\tilde{D}J^2(J+1)^2 cm^{-1}}_{\text{centrifugal stretching}} \tag{13.4.13}$$

where

$$\tilde{B} = \frac{\hbar}{4\pi\,\mu\, {r_e}^2 c}\ (\text{in cm}^{-1}) \tag{13.4.14}$$

and

$$\tilde{D} = \frac{\hbar^3}{4\pi k\,\mu^2\, {r_e}^6\, c}\ (\text{in cm}^{-1}) \tag{13.4.15}$$

First term in the Equation 13.4.13 is same as for the rigid rotator; second term is the consequence of the centrifugal stretching. Recall Equation 13.4.3 wherein k is the spring constant that, as we will see in the following section, plays the same role as in the vibrational motion. In other words, centrifugal stretching constant $\tilde{D}$ is not only measures the influence of centrifugal force, but also hints upon the interaction between the rotational and vibrational motions.

Since $\tilde{D}$ is positive, it is clear from Equation 13.4.13 that the energy levels for the non-rigid rotator are slightly lower on energy scale than those of rigid rotator for the corresponding J values; the magnitude of decrease in energy of the non-rigid rotator states increases with J as shown in the Figure 13.4.2.

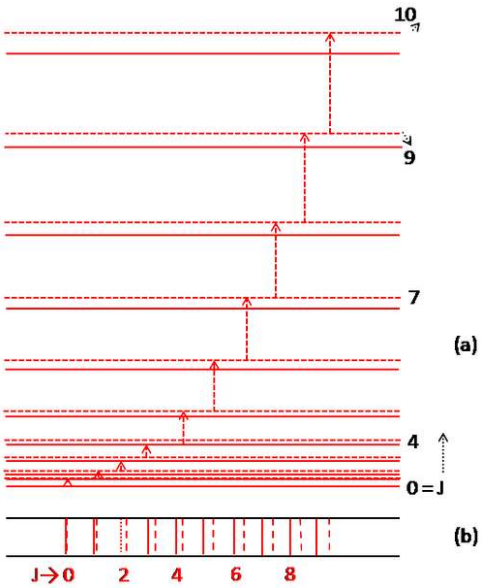


Figure 13.4.2: Energy levels and the transitions of rigid rotator (broken red lines) & of non-rigid rotator (solid red lines). (b) resulting spectra from both the models

Consequently, on applying the selection rule $\Delta J = \pm 1$, rotational spectrum of a non-rigid rotator consists of a series of lines (red lines) wherein separation, unlike the case of spectral series (broken red lines) of a rigid rotator, between the consecutive rotational

lines decreases with increase in J , as shown in the Figure **13.4.2**. It may be noted that value of D is very small compared to B with the result that the influence of D is significant only for very large J values.

For example, for HCl the values are $B \sim 10.4 \ \ cm^{-1}$ and $D \sim 0.0004\, cm^{-1}$. Usually, D is ignored in the calculations. Figure **13.4.2** exaggerates the decrease in energy to visualize its effect. Nevertheless, non-rigid rotator is the model that describes the rotational motion more accurately and hence explains the spectral experimental observations not only in the microwave region but also the rotation-vibration spectra and the rotational structure of the electronic bands discussed in the later sections.

Contributors

- http://202.141.40.218/wiki/index.php...r_Spectroscopy

13.4: The Pure Rotational Spectrum has Unequal Spacings is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

13.5: 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 **13.5.1**). 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.

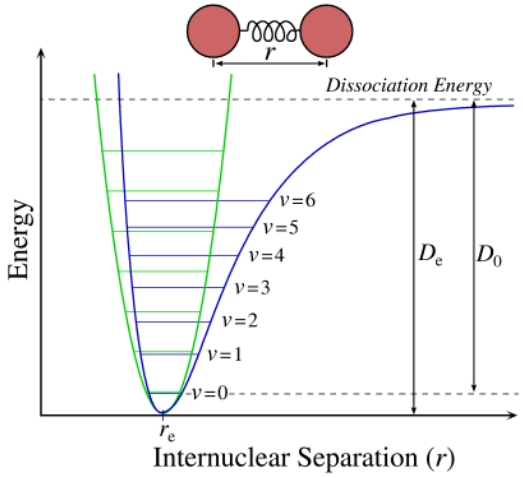


Figure **13.5.1** : Pictured above is the Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left is compression of the bond, towards the right is extension. (CC BY-SA 3.0; Created by Mark Somoza March 26 2006).

As you can see in Figure **13.5.1** , the harmonic oscillator potential 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.

$$V(R) = V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}(R-R_e)^4 + \ldots \tag{13.5.1}$$

This expansion was discussed in detail previously. The first term in the expansion is ignored since the derivative of the potential at R_e is zero (i.e., at the bottom of the well). The Harmonic Oscillator approximation only uses the next term, the quadratic term, in the series

$$V_{HO}(R) \approx V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2$$

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 13.5.1 can be shortened to the cubic term

$$V(x) = \frac{1}{2}kr^2 + \frac{1}{6}\gamma r^3 \tag{13.5.2}$$

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.

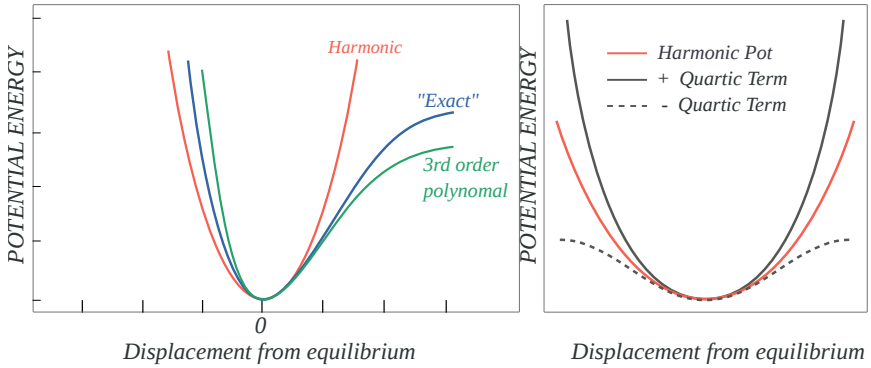


Figure **13.5.2** : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

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 13.5.2) 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 13.5.1.

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?

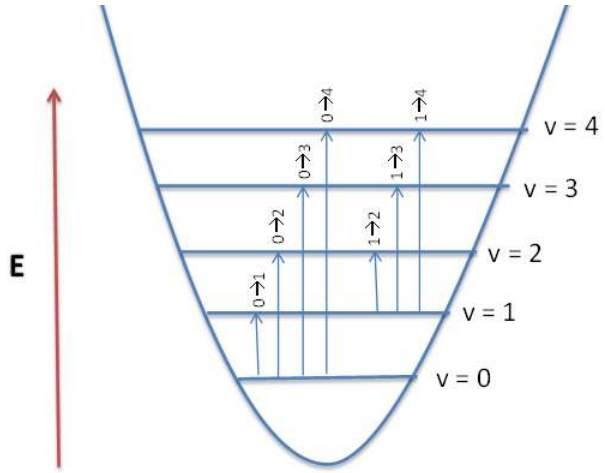


Figure **13.5.3** : A diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potential energy for the harmonic (quadratic) oscillator. The transition $0 \rightarrow 1$ is the fundamental, transitions $0 \rightarrow n$ (n>1) are called overtones, and 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, $v = 0 \rightarrow 1$.

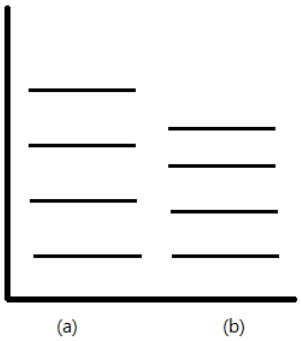


Figure **13.5.4** : An exaggerated view of the energy levels. (a) would be the harmonic oscillator, with the evenly spaced out energy levels. (b) would be the anharmonic, with the energy levels compressing until they converge.

The levels are not equally spaced, like in the harmonic oscillator, but decrease as v increases, until it ultimately converges, as implied by Figure **13.5.4**. Also as a result of anharmonicity, the $\Delta v = \pm 1$ selection rule is no longer valid and v can be any number. This leads to the observation of higher order transitions, or **overtones**, which result from the transition of the ground state to higher energy levels.

Anharmonic Oscillator Selection Rules

For the anharmonic oscillator, the selection rule is $\Delta V = \text{any number}$. That is, there are no selection rules (for state to state transitions)

Overtones occur when a vibrational mode is excited from $v = 0$ to $v = 2$ (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 **13.5.1** : HCl vibrational spectrum.

Transition	$\tilde{\nu}_{obs}$ [cm^{-1}]	$\tilde{\nu}_{obs}$ Harmonic [cm^{-1}]	$\tilde{\nu}_{obs}$ Anharmonic [cm^{-1}]
$0 \rightarrow 1$ (fundamental)	2885.9	2885.9	2,885.3
$0 \rightarrow 2$ (first overtone)	5668.0	5771.8	5,665.0
$0 \rightarrow 3$ (second overtone)	8347.0	8657.7	8,339.0
$0 \rightarrow 4$ (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 **13.5.1** that the anharmonic frequencies correspond much better with the observed frequencies, especially as the vibrational levels increase. Because the energy levels and overtones are closer together in the anharmonic model, they are also more easily reached. This means that there is a higher chance of that level possibly being occupied, meaning it can show up as additional, albeit weaker intensity lines (the weaker intensity indicates a smaller probability of 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.

13.5: 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.

13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information

Molecules can also undergo changes in electronic transitions during microwave and infrared absorptions. The energy level differences are usually high enough that it falls into the visible to UV range; in fact, most emissions in this range can be attributed to electronic transitions.

Electron Transitions are not Purely Electronic

We have thus far studied *rovibrational transitions*--that is, transitions involving both the vibrational and rotational states. Similarly, electronic transitions tend to accompany both rotational and vibrational transitions. These are often portrayed as an electronic potential energy cure with the vibrational level drawn on each curve. Additionally, each vibrational level has a set of rotational levels associated with it.

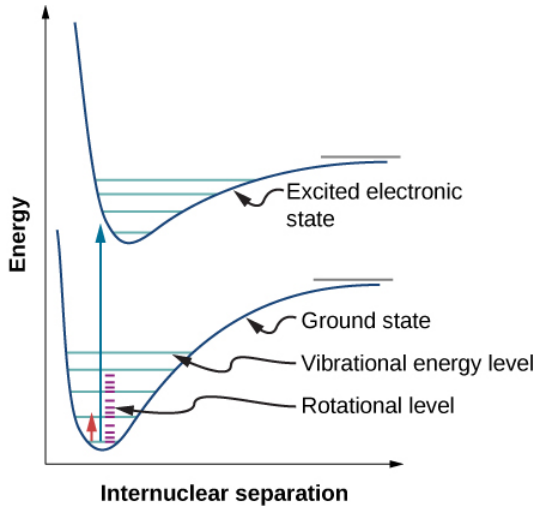


Figure **13.6.1** : Three types of energy levels in a diatomic molecule: electronic, vibrational, and rotational. If the vibrational quantum number (n) changes by one unit, then the rotational quantum number (l) changes by one unit. (CC BY 3.0; OpenStax).

Recall that in the Born-Oppenheimer approximation, nuclear kinetic energies can be ignored (e.g., fixed) to solve for electronic wavefunctions and energies, which are much faster than rotation or vibration. As such, it is important to note that unlike rovibrational transitions, electronic transitions aren't dependent on rotational or transitional terms and are assumed to be separate. Therefore, when using an anharmonic oscillator-nonrigid rotator approximation (and excluding translation energy), the total energy of a diatomic is:

$$\tilde{E}_{total} = \tilde{\nu}_{el} + G(v) + F(J) \tag{13.6.1}$$

where $\tilde{\nu}_{el}$ is the electronic transition energy change in wavenumbers, $G(n)$ is the vibrational energy with energy level v (assuming anharmonic oscillator), and $F(J)$ is the rotational energy, assuming a nonrigid rotor. Equation 13.6.1 can be expanded accordingly:

$$\tilde{E}_{total} = \underbrace{\tilde{\nu}_{el}}_{\text{electronic}} + \underbrace{\tilde{\nu}_e\left(v+\frac{1}{2}\right) - \tilde{\chi}_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^2}_{\text{vibrational}} + \underbrace{\tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2}_{\text{rotational}} \tag{13.6.2}$$

Notice that both the vibration constant ($\tilde{\nu}_e$) and anharmonic constant ($\tilde{\chi}_e$) are electronic state dependent (and hence the rotational constants would be too, but are ignored here). Since rotational energies tend to be so small compared to electronic, their effects are minimal and are typically ignored when we do calculations and are referred to as *vibronic* transitions.

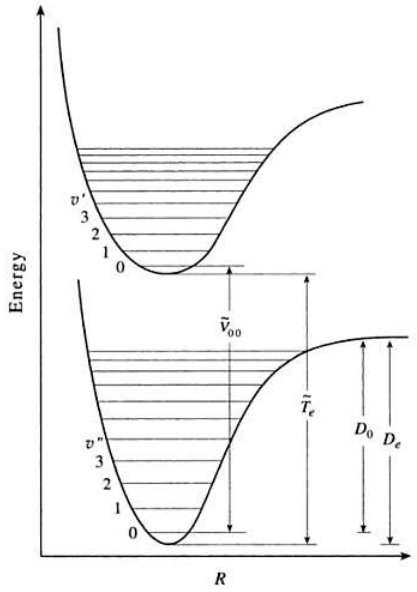


Figure **13.6.2** : As you can see, electronic transitions involve two energy potential wells! The vibrational levels are included, but rotational levels are excluded.

The eigenstate-to-eigenstate transitions (e.g., $\mathbf{1 \rightarrow 2}$) possible are numerous and have absorption lines at

$$\tilde{\nu}_{obs} = \tilde{E}_2 - \tilde{E}_1 \tag{13.6.3}$$

and for simplification, we refer to constants associated with these states as $|'\rangle$ and $|''\rangle$, respectively. So Equation 13.6.3 is

$$\tilde{\nu}_{obs} = E''\tilde{(v'')} - E'\tilde{(v')}$$

Also important to note that typically vibronic transitions are usually the result of the vibrational $v' = 0$ vibratonal state. Within this assumption and excluding the rotational contributions (due to their low energies), Equation 13.6.2 can be used with Equation 13.6.3 to get

$$\tilde{\nu}_{obs} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right) + \tilde{\nu}'_e v'' - \tilde{\chi}'_e\tilde{\nu}'_e v''(v''+1) \tag{13.6.4}$$

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 13.6.4 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.

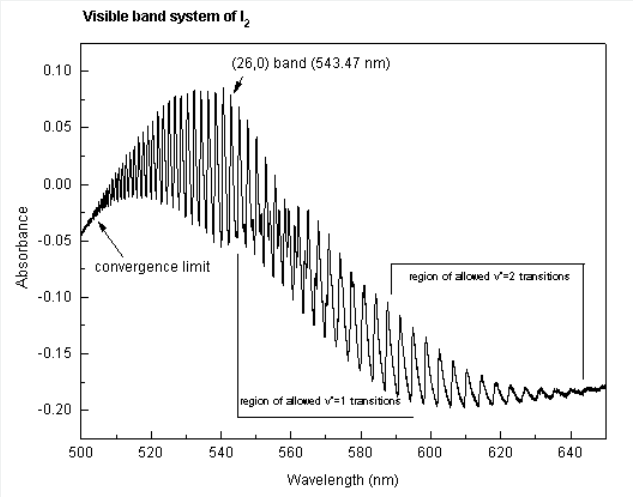
Iodine

The absorption spectrum of iodine yields information about the excited state well rather than the ground state well (notice that equation 13.6.4 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.

13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information** is licensed CC BY-SA 4.0.

13.7: 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.

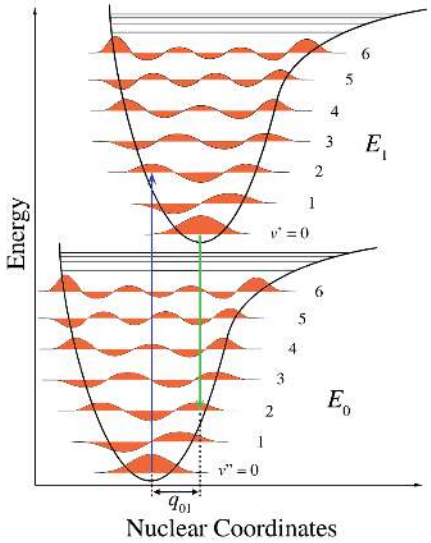


Figure 13.7.1 : Franck–Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v' = 2$. (CC-SA-BY-3.0; Samoza).

In Figure 13.7.1 , the nuclear axis shows a consequence of the internuclear separation and the vibronic transition is indicated by the blue and green vertical arrows. This figure demonstrates three things:

1. An absorption leads to a higher energy state,
2. fluorescence leads to a lower energy state, and
3. the shift in nuclear coordinates between the ground and excited state is indicative of a new equilibrium position for nuclear interaction potential. The fact that the fluorescence arrow is shorter than the absorption indicates that it has less energy, or that its wavelength is longer.

The Classical Condon approximation

Condon approximation is the assumption that the electronic transition occurs on a time scale short compared to nuclear motion so that the transition probability can be calculated at a fixed nuclear position.

This change in vibration is maintained during a state termed the **rapid electronic excitation**. The resulting Coulombic forces produce an equilibrium as shown in the figure for the nuclei termed a turning point. The turning point can be mapped by drawing a vertical line from the minimum of the lower curve to the intersection of the higher electronic state. This procedure is termed a **vertical transition** and was discussed before in the context of photoelectron spectroscopy (another electronic spectroscoy).

The Franck-Condon Principle explains the relative intensities of vibronic transitions by relating the probability of a vibrational transition to the overlap of the vibrational wavefunctions. It states that the probability of a vibrational transition occurring is weighted by the Franck-Condon overlap integral:

$$\begin{aligned} _{i\rightarrow f} &= |\langle \psi^*_{final}|\mu|\psi_{initial}\rangle|^2 \\ &= \left|\int \psi^*_{final}\mu\psi_{initial}d\tau\right|^2 \end{aligned}$$

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 **13.7.1**).

The Quantum Franck-Condon Principle

The Franck-Condon Principle has both a Classical and Quantum application. Classically, the Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

The Franck-Condon principle is based on the Born-Oppenheimer approximation, which allows separation of the electronic q and nuclear Q wavefunctions given the total wavefunction.

$$|\psi_{total}(Q,q) = |\psi_{nuc}(Q)\rangle\psi_{el}(Q;q)\rangle$$

Since the transition operator, $\hat{\mu}(q)$, is dependent only on the electronic component, the nuclear components can be separated from the transition moment integral that dictates the probability of the transition occurring:

$$\langle\psi^*_{total,f}|\hat{\mu}|\psi_{total,i}\rangle = \langle\psi^*_{nuc,f}|\langle\psi^*_{el,f}|\mu|\psi_{el,i}\rangle|\psi_{nuc,i}\rangle \quad (13.7.1)$$

$$= \underbrace{\langle\psi^*_{nuc,f}|\psi_{nuc,i}\rangle}_{\text{nuclear overlap}}\langle\psi^*_{el,f}|\mu|\psi_{el,i}\rangle \quad (13.7.2)$$

If the nuclear overlap integral is zero for this transition, then the transition will not be observed, irrespective of the magnitude of the electronic factor.

S_{00} Transition Evaluated within Harmonic Oscillator Model

The nuclear overlap for the zero-zero transition S_{00} can be calculated quite simply using the definition of the Gaussian form of the harmonic oscillator wavefunctions.

The zero-point wavefunction in the ground electronic state is

$$|\psi(R)\rangle = |\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2}\rangle$$

The zero-point wavefunction in the excited electronic state is

$$|\psi(R)\rangle = |\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-Q_e)^2/2}\rangle$$

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

$$S_{00} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} e^{-\alpha(R-Q_e)^2/2} dR \tag{13.7.3}$$

The exponent in Equation 13.7.3 can be expanded as

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(2R^2 - RR_e - 2RQ_e + R_e^2 + Q_e^2)/2} dR \tag{13.7.4}$$

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 13.7.4 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

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \frac{1}{\sqrt{\alpha}} \int_{-\infty}^{\infty} e^{z^2} dz \tag{13.7.5}$$

this integral has been solved already, from a table of integrals, Equation 13.7.5 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 $x = \sqrt{\alpha}(R - Q_e)$.

$$S_{01} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle \tag{13.7.6}$$

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 13.7.6) 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.

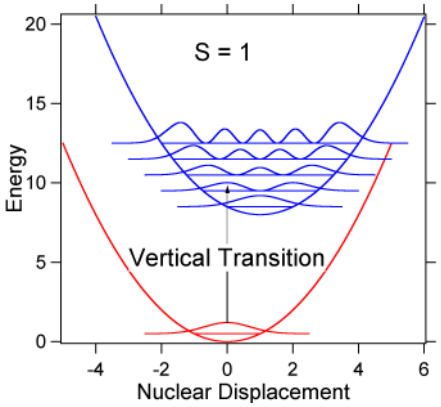


Figure **13.7.2** : Wavefunctions transitions for a harmonic oscillator model system with moderate displacement (S=1).

According to the above model for the Franck-Condon factor we would generate a "stick" spectrum (Figure **13.7.3**) where each vibrational transition is infinitely narrow and transition can only occur when $E = h\nu$ exactly. For example, the potential energy surfaces were given for S = 1 and the transition probability at each level is given by the sticks (black) in the figure below.

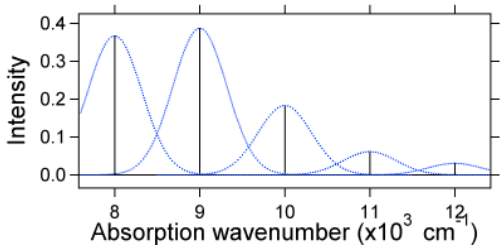


Figure **13.7.3** : Stick spectrum, dressed with Gaussians, for the moderate displacement (S=1) harmonic oscillator system from Figure **13.7.2** .

The dotted Gaussians that surround each stick give a more realistic picture of what the absorption spectrum should look like. In this first place each energy level (stick) will be given some width by the fact that the state has a finite lifetime. Such broadening is called homogeneous broadening since it affects all of the molecules in the ensemble in a similar fashion. There is also broadening due to small differences in the environment of each molecule. This type of broadening is called inhomogeneous broadening. Regardless of origin the model above was created using a Gaussian broadening

The nuclear displacement between the ground and excited state determines the shape of the absorption spectrum. Let us examine both a smaller and a large excited state displacement. If $S = ½$ and the potential energy surfaces in this case are:

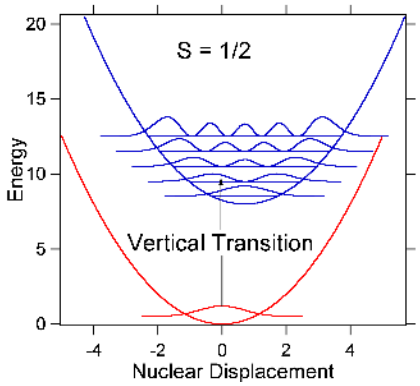


Figure **13.7.4** : Wavefunctions transitions for a harmonic oscillator model system with small displacement (S=1/2).

For this case the "stick" spectrum has the appearance in Figure **13.7.5**

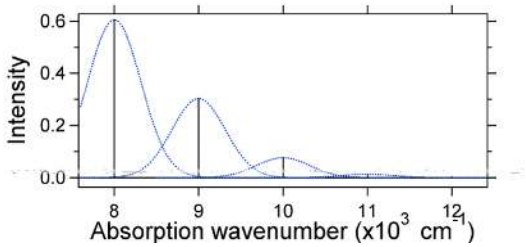


Figure **13.7.5** : Stick spectrum, dressed with Gaussians, for the small displacement (S=1/2) harmonic oscillator system from Figure **13.7.4**.

Note that the zero-zero or $S_{0,0}$ vibrational transition is much large in the case where the displacement is small.

> As a general rule of thumb the S constant gives the ratio of the intensity of the $v = 2$ transition to the $v = 1$ transition. In this case since $S = 0.5$, the $v = 2$ transition is 0.5 the intensity of $v = 1$ transition.

As an example of a larger displacement the disposition of the potential energy surfaces for S = 2 is shown below.

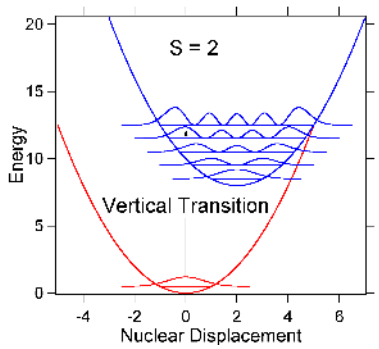


Figure **13.7.6** : Wavefunctions transitions for a harmonic oscillator model system with strong displacement (S=2).

The larger displacement results in decreased overlap of the ground state level with the v = 0 level of the excited state. The maximum intensity will be achieved in higher vibrational levels as shown in the stick spectrum.

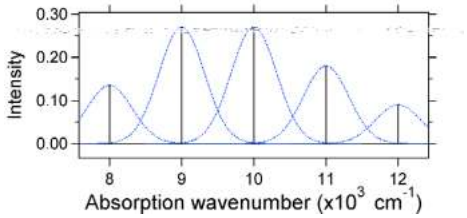


Figure **13.7.7** : Stick spectrum, dressed with Gaussians, for the large displacement (S=2) harmonic oscillator system from Figure **13.7.6**.

The absorption spectra plotted below all have the same integrated intensity, however their shapes are altered because of the differing extent of displacement of the excited state potential energy surface.

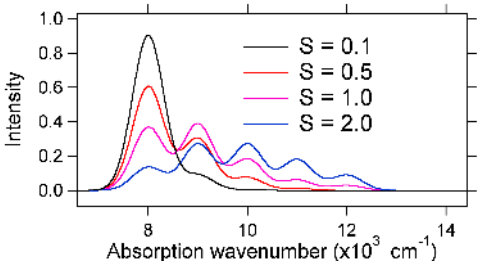


Figure **13.7.8** : Stick spectra, dressed with Gaussians, for the small to large displacements in harmonic oscillator system described above.

So the nature of the relative vibronic band intensities can tell us whether there is a displacement of the equilibrium nuclear coordinate that accompanied a transition. When will there be an increase in bond length (i.e., $Q_e > R_e$)? This occurs when an electron is promoted from a bonding molecular orbital to a non-bonding or anti-bonding molecular orbitals (i.e., when the bond order is less in the excited state than the ground state).

- Non-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ non-bonding molecular orbital

In short, when the bond order is lower in the excited state than in the ground state, then $Q_e > R_e$; an increase in bond length will occur when this happens.

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

13.7: 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.

13.8: Rotational Spectra of Polyatomic Molecules

Quick Review of Diatomic Rotation

As discussed previously, the Schrödinger equation for the angular motion of a rigid (i.e., having fixed bond length R) diatomic molecule is

$$\frac{\hbar^2}{2\mu}\left[\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{R^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\psi\rangle = E|\psi\rangle$$

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:

$$E_J = \frac{\hbar^2 J(J+1)}{2\mu R^2} = BJ(J+1) \tag{13.8.1}$$

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 13.8.1 can be expressed in terms of the moment of inertia I

$$I = \sum_i m_i R_i^2 \tag{13.8.2}$$

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 13.8.1:

$$E_J = \frac{\hbar^2 J(J+1)}{2I} = BJ(J+1) \tag{13.8.3}$$

Rotation of Polyatomic Molecules

In contrast to diatomic molecules (Equation 13.8.2), 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.

$$I = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{xx} & I_{xy} & I_{zz} \end{bmatrix} \tag{13.8.4}$$

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 13.8.4) 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

$$H_{rot} = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} \tag{13.8.5}$$

The components of the quantum mechanical angular momentum operators along the three principal axes are:

$$J_a = -i\hbar \cos\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \sin\chi \frac{\partial}{\partial\theta} \tag{13.8.6}$$

$$J_b = i\hbar \sin\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \cos\chi \frac{\partial}{\partial\theta} \tag{13.8.7}$$

$$J_c = -\frac{ih\partial}{\partial\chi} \tag{13.8.8}$$

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

$$J^2 = J_a^2 + J_b^2 + J_c^2 \tag{13.8.9}$$

$$= -\frac{\partial^2}{\partial\theta^2} - \cot\theta \frac{\partial}{\partial\theta} - \left(\frac{1}{\sin\theta} \right) \left(\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial\chi^2} - 2\cos\theta \frac{\partial^2}{\partial\varphi\partial\chi} \right) \tag{13.8.10}$$

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 13.8.5 can be expressed in terms of the total angular momentum operator J^2

$$H_{rot} = \frac{J^2}{2I}$$

As a result, the eigenfunctions of H_{rot} are those of J^2 (and J_a as well as J_Z both of which commute with J_2 and with one another; J_Z is the component of J along the lab-fixed Z-axis and commutes with J_a because

$$J_Z = -ih\frac{\partial}{\partial\varphi}$$

and

$$J_a = -ih\frac{\partial}{\partial\chi}$$

act on different angles. The energies associated with such eigenfunctions are

$$E(J,K,M) = \frac{\hbar^2 J(J+1)}{2I^2}$$

for all K (i.e., J a quantum numbers) ranging from -J to J in unit steps and for all M (i.e., J Z quantum numbers) ranging from -J to J. Each energy level is therefore $(2J+1)^2$ degenarate because there are $2J+1$ possible K values and $2J+1$ possible M values for each J. The eigenfunctions of J^2, J_Z and J_a, $|J,M,K>$ are given in terms of the set of rotation matrices $D_{J,M,K}$:

$$|J,M,K\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D^*_{J,M,K}(\theta,\varphi,\chi)$$

which obey

$$J^2|J,M,K\rangle = \hbar^2 J(J+1)|J,M,K\rangle$$

$$J_a|J,M,K\rangle = \hbar K|J,M,K\rangle$$

$$J_Z|J,M,K\rangle = \hbar M|J,M,K\rangle$$

Symmetric Tops

Symmetrical tops are molecules with two rotational axes that have the same inertia and one unique rotational axis with a different inertia. Symmetrical tops can be divided into two categories based on the relationship between the inertia of the unique axis and the inertia of the two axes with equivalent inertia. If the unique rotational axis has a greater inertia than the degenerate axes the molecule is called an **oblate symmetrical top** (Figure 13.8.1). If the unique rotational axis has a lower inertia than the degenerate axes the molecule is called a **prolate symmetrical top**. For simplification think of these two categories as either frisbees for oblate tops or footballs for prolate tops.

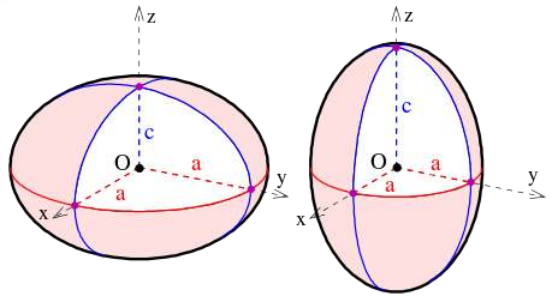


Figure 13.8.1 : The assignment of semi-axes on a spheroid. It is oblate if $c < a$ (left) and prolate if $c > a$ (right). (CC BY-SA 4.0; Ag2gaeh)

Again, the rotational kinetic energy, which is the full rotational Hamiltonian, can be written in terms of the total rotational angular momentum operator J^2 and the component of angular momentum along the axis with the unique principal moment of inertia.

For prolate tops, Equation 13.8.5 becomes

$$H_{rot} = \frac{J^2}{2I} + J_a^2\left(\frac{1}{2I_a} - \frac{1}{2I}\right)$$

For oblate tops, Equation 13.8.5 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 13.8.5 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.

13.8: 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.

13.9: Normal Modes in Polyatomic Molecules

Normal modes are used to describe the different vibrational motions in molecules. Each mode can be characterized by a different type of motion and each mode has a certain symmetry associated with it. Group theory is a useful tool in order to determine what symmetries the normal modes contain and predict if these modes are IR and/or Raman active. Consequently, IR and Raman spectroscopy is often used for vibrational spectra.

Degrees of Freedom

In general, a normal mode is an independent motion of atoms in a molecule that occurs without causing movement to any of the other modes. Normal modes, as implied by their name, are orthogonal to each other. In order to discuss the quantum-mechanical equations that govern molecular vibrations it is convenient to convert Cartesian coordinates into so called normal coordinates. Vibrations in polyatomic molecules are represented by these normal coordinates.

A molecule can have three types of degrees of freedom and a total of 3N degrees of freedom, where N equals the number of atoms in the molecule. These degrees of freedom can be broken down into three categories.

- **Translational**: These are the simplest of the degrees of freedom. These entail the movement of the entire molecule's center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.
- **Rotational**: These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational**: These are any other types of movement not assigned to rotational or translational movement and thus there are 3N – 6 degrees of vibrational freedom for a nonlinear molecule and 3N – 5 for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Table 13.9.1 : Overview of degrees of freedom

	Total Degrees of Freedom	Translational degrees of freedom	Rotational degrees of freedom	Vibrational degrees of freedom
Nonlinear Molecules	3N	3	3	3N **-6**
Linear Molecules	3N	3	2	3N - 5

Each of these degrees of freedom is able to store energy. However, In the case of rotational and vibrational degrees of freedom, energy can only be stored in discrete amounts. This is due to the quantized break down of energy levels in a molecule described by quantum mechanics. In the case of rotations the energy stored is dependent on the rotational inertia of the gas along with the corresponding quantum number describing the energy level.

Example 13.9.1 : Ethane vs. Carbon Dioxide

Ethane, C_2H_6 has eight atoms ($N = 8$) and is a nonlinear molecule so of the $3N = 24$ degrees of freedom, three are translational and three are rotational. The remaining 18 degrees of freedom are internal (vibrational). This is consistent with:

$$3N - 6 = 3(8) - 6 = 18$$

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.

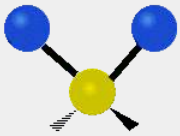
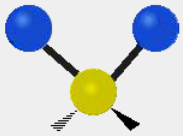
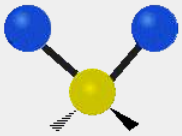
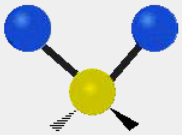
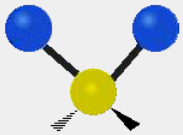
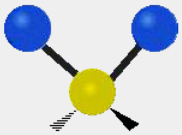
Symmetricical Stretching	Asymmetrical Stretching	Wagging
		
Twisting	**Scissoring**	**Rocking**
		

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:

$$\Delta V = V(q_1, q_2, q_3, ..., q_n) - V(0, 0, 0, ..., 0) \tag{13.9.1}$$

$$= \frac{1}{2}\sum_{i=1}^{N_{vib}}\sum_{j=1}^{N_{vib}}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right) q_i q_j \tag{13.9.2}$$

$$= \frac{1}{2}\sum_{i=1}^{N_{vib}}\sum_{j=1}^{N_{vib}} f_{ij} q_i q_j \tag{13.9.3}$$

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

$$\Delta V = \frac{1}{2}\sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{13.9.4}$$

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:

$$\hat{H}_{vib} = -\sum_{j=1}^{N_{vib}} \frac{\hbar^2}{2\mu_i}\frac{d^2}{dQ_j^2} + \frac{1}{2}\sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{13.9.5}$$

The total wavefunction is a product of the individual wavefunctions and the energy is the sum of independent energies. This leads to:

$$\hat{H}_{vib} = \sum_{j=1}^{N_{vib}} \hat{H}_{vib,j} = \sum_{j=1}^{N_{vib}} \left(\frac{-\hbar^2}{2\mu_j}\frac{d^2}{dQ_i^2} + \frac{1}{2}\sum_{j=1}^{N_{vib}} F_j Q_j^2\right) \tag{13.9.6}$$

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

$$E_{vib} = \sum_{j=1}^{N_{vib}} h\nu_j \left(v_j + \frac{1}{2}\right) \tag{13.9.7}$$

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.

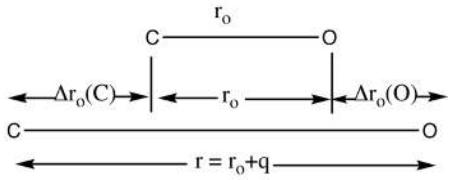


Figure 13.9.2 : The Normal coordinate for CO is equation to $\Delta r(C) + \Delta r(O)$

13.9: 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.

13.10: Irreducible Representation of Point Groups

There exists an important fact about normal coordinates. Each of these coordinates belongs to an irreducible representation of the point the molecule under investigation. Vibrational wavefunctions associated with vibrational energy levels share this property as well. The normal coordinates and the vibration wavefunction can be categorized further according to the point group they belong to. From the character table predictions can be made for which symmetries can exist. The irreducible representation offers insight into the IR and/or Raman activity of the molecule in question.

Symmetry of normal modes

It is important to realize that every normal mode has a certain type of symmetry associated with it. Identifying the point group of the molecule is therefore an important step. With this in mind it is not surprising that every normal mode forms a basis set for an irreducible representation of the point group the molecule belongs to. For a molecule such as water, having a structure of $\mathbf{XY_2}$, 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:

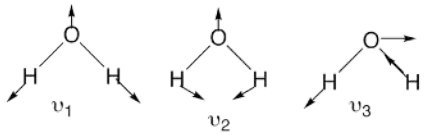


Figure 13.10.1 : Three normal modes of water

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:

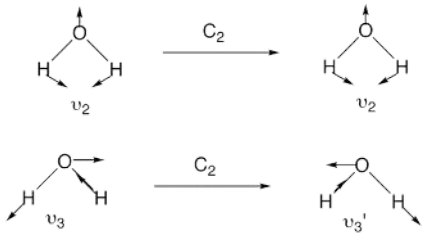


Figure 13.10.2 : Symmetry operations on the symmetric and asymmetric stretches of water

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).

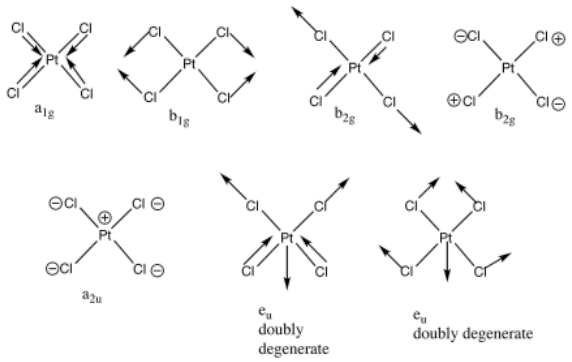


Figure 13.10.3 : A_{1g}, b_{1g} and e_u are stretching vibrations whereas b_{2g}, a_{2u}, b_{2u} and e_u are bending vibrations.

13.10: 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.

13.11: 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)

$$|j(t)\rangle = e^{-iE_j t/\hbar}|j\rangle$$

Now, introduce a time-dependent perturbing Hamiltonian $H_1(t)$. The Hamiltonian of the perturbed system is

$$H = H_0 + H_1(t)$$

Let $|\psi(t)\rangle$ denote the quantum state of the perturbed system at time t and obeys the time-dependent Schrödinger equation,

$$H|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$

The quantum state at each instant can be expressed as a linear combination of the complete eigenbasis of $|n\rangle$:

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}|n\rangle$$

where the $c_n(t)$ coefficients are to be determined complex functions of t which we will refer to as **amplitudes**

We have explicitly extracted the exponential phase factors $\exp(-iE_n t/\hbar)$ on the right hand side. This is only a matter of convention, and may be done without loss of generality. The reason we go to this trouble is that when the system starts in the state $|j\rangle$ and no perturbation is present, the amplitudes have the convenient property that, for all t, $c_j(t) = 1$ and $c_n(t) = 0$ if $n \neq j$.

The square of the absolute amplitude $c_n(t)$ is the probability that the system is in state n at time t, since

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}|n\rangle$$

Plugging into the Schrödinger equation and using the fact that $\partial/\partial t$ acts by a chain rule, one obtains

$$\sum_n \left(i\hbar\frac{\partial c_n}{\partial t} - c_n(t)V(t)\right)e^{-iE_n t/\hbar}|n\rangle = 0\ .$$

By resolving the identity in front of V, this can be reduced to a set of partial differential equations for the amplitudes,

$$\frac{\partial c_n}{\partial t} = \frac{-i}{\hbar}\sum_k \langle n|H_1(t)|k\rangle\, c_k(t)\, e^{-i(E_k - E_n)t/\hbar}\ .$$

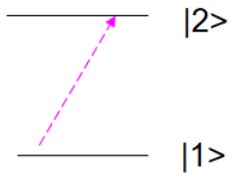
The matrix elements of H_1 play a similar role as in time-independent perturbation theory, being proportional to the rate at which amplitudes are shifted between states. Note, however, that the direction of the shift is modified by the exponential phase factor. Over times much longer than the energy difference $E_k - E_n$, the phase winds around 0 several times. If the time-dependence of H_1

is sufficiently slow, this may cause the state amplitudes to oscillate (e.g., such oscillations are useful for managing radiative transitions in a laser).

Two-Level System

Consider the two level system (i.e. $n = 1, 2$)

$$|\psi\rangle = \sum_{n=1,2} c_n(t)|n\rangle_o$$



Solution of time-dependent perturbation for two level system:

$$i\hbar\frac{\partial c_1(t)}{\partial t} = c_1(t)H_{11}(t) + c_2 e^{-i\omega_o t}H_{12}(t)$$

$$i\hbar\frac{\partial c_2(t)}{\partial t} = c_2(t)H_{22}(t) + c_1 e^{+i\omega_o t}H_{21}(t)$$

where the matrix elements of the permutation (in terms of the eigenstates of $H(0)$) are

$$\langle m|H_1(t)|n\rangle = H_{mn}(t)$$

Assume initial state is $n = 1$, and $H_{11} = H_{22} = 0$

$$|\psi(t = 0)\rangle = |1\rangle$$

Probability of particle at $n = 2$ at time t after the perturbation is turned on (i.e., incident light):

$$c_2(t) = \frac{-i}{\hbar}\int_o^t e^{i\omega_o t}dt' H_{21}(t') \tag{13.11.1}$$

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 13.11.1 can be simplified to

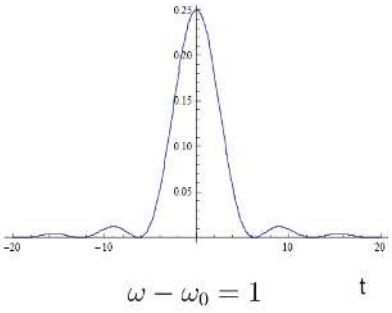
$$c_2(t) = -\frac{2i}{\hbar}\frac{\sin(\omega - \omega_o)t/2}{(\omega - \omega_o)t}e^{i(\omega_0 - \omega)t/2}H_{21}$$

Transition Probability

Assume initial state is $n = 1$, and probability of transition from $n = 1$ state to $n = 2$ state is:

$$P_{12}(t) = |c_2(t)|^2 = \frac{4}{\hbar^2}|\frac{\sin(\omega - \omega_o)t/2}{(\omega - \omega_o)t}|^2|H_{21}|^2$$

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.

13.11: 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.

13.12: 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 ($\Delta l = \pm 1$, $\Delta m = 0$).

13.12: 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.

13.13: The Harmonic Oscillator Selection Rule

Selection rules are a very important concept in spectroscopy and physical chemistry, as they directly complement the concept that systems on the atomic level are quantized. Quantization tells us how electrons, neutrons, and protons are set up, and selection rules tell us how, energetically speaking, they may move about. For example, the principal quantum number, n, determines the energy state of particles in the Particle in a Box model. With respect to real systems, the quantum number n describes electronic transitions, such as the excitation of an electron. There are other transitions, such as the rotational transition, which applies to the rigid rotator model and occurs where there are spherical harmonics. Vibrational transitions occur where there is a system that can be visualized as two masses connected by a spring, such as a diatomic molecule.

Selection rules can be very useful in spectroscopy for obtaining information about an unknown substance; any given substance has properties and behaviors that operate within the selection rules and determine the wavelengths of electromagnetic radiation (light) that cause transitions. By tracking these properties, chemists can use techniques like IR spectroscopy to determine the chemical structure of a molecule. For example, a selection rule might govern how a quantum number changes during a transition. That quantum number appears in equations that determine the energy transition based on the mass and other structural properties of a molecule. Thus, if one knows the selection rules and the energy transition, he or she can determine other properties about the molecule, such as its mass or its bond strength.

Example: Evaluating vibrational transitions using a transition moment integral.

Vibrational systems are described by the harmonic oscillator wavefunctions, which look like

$$\Psi_v(x) = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

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.

13.13: 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.

13.14: 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:

$$M(v \rightarrow v') = \langle \textbf{final wavefunction}|\vec{\mu}|\textbf{initial wavefunction} \rangle$$

or in terms of vibrational wavefunctions for a specific normal mode $|\phi(v)\rangle$

$$M(v \rightarrow v') = \langle \phi(v' \neq 0)|\vec{\mu}|\phi(v = 0)\rangle \tag{13.14.1}$$

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 13.14.1 becomes

$$M(v \rightarrow v') = \vec{\mu}\langle \phi(v' \neq 0)|\phi(v = 0)\rangle \tag{13.14.2}$$

Since $|\phi(v = 0)\rangle$ and $|\phi(v =\neq 0)\rangle$ are mutually orthogonal to each other, the integral in Equation 13.14.1 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):

$$M(v \rightarrow v') = \langle \phi(v' \neq 0)|\alpha|\phi(v = 0)\rangle \tag{13.14.3}$$

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 $\mathbf{\Gamma}_{tot}$ - $\mathbf{\Gamma}_{trans}$ - $\mathbf{\Gamma}_{rot}$.

$$\Gamma_{vib}(H_2O) = (3a_1 + a_2 + 2b_1 + 3b_2) - (a_1 + b_1 + b_2) - (a_2 + b_1 + b_2) = 2a_1 + b_2$$

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 $\mathbf{\Gamma}_{vib}$ is necessary. If they contain the same irreducible representation, the mode is IR

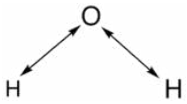
active.

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)	
$\mathbf{\Gamma_{stretch}}$	2	0	0	2	$= \mathbf{a_1 + b_2}$

$$\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch} = 2a_1 + b_2 - a_1 - b_2 = a_1$$

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 $\mathbf{\Gamma}_{stretch}$ has been worked out, $\mathbf{\Gamma}_{bend}$ can be determined by $\mathbf{\Gamma}_{bend} = \mathbf{\Gamma}_{vib} - \mathbf{\Gamma}_{stretch}$.

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.

13.14: 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.

13.E: Molecular Spectroscopy (Exercises)

These are homework exercises to accompany Chapter 13 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q13.1

1. Calculate the energy difference for radiation wavenumber of, $\nu = 1.00 cm^{-1}$ including the type of molecular process that absorbs of this radiation corresponding to.
2. Given the wavelength of 3.4 x 10^{-4}, which molecular process does it fall into?
3. What are other advantages of knowing the spectroscopy of molecules?
4. Do you think the spectroscopy and molecular processes of the molecules have relationship to temperature? Explain.
5. What is other form that you can express in above equation?

Q13.20

The vibrational term of a diatomic molecule is

$$G(v) = (v + \frac{1}{2})\nu_e - (v + \frac{1}{2})^2 \chi_e \nu_e \tag{13.E.1}$$

Show that the spacing between adjacent levels is given by

$$\Delta G = G(v+1) - G(v) = \nu_e - 2\chi_e \nu_e (v+1)$$

Show that the maximum vibrational quantum number, v_{max} is given by

$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{13.E.2}$$

Use this result to show that the dissociation energy of the diatomic molecule can be written as

$$D_e = \frac{\nu_e - \nu_e \chi_e^2}{4\chi_e} \approx \frac{\nu_e}{4\chi_e} \tag{13.E.3}$$

Explain how the constants ν_e and χ_e can be evaluated from a plot of ΔG versus $v + 1$, called a Birge-Sponer plot. After finding these constants, determine the dissociation energy of the molecule. Use the following experimental data of H_2 to determine the dissociation energy of the molecule.

v	G(v) / cm^{-1}
0	4161.12
1	8087.11
2	11782.35
3	15250.36
4	18497.92
5	21505.65
6	24287.83
7	26830.97
8	29123.93
9	31150.19
10	32886.65
11	34301.83
12	35351.01
13	35972.97

Explain why your plot is not linear for high values of v. How does this dissocation energy differ with the experimental value of $38269.48 cm^{-1}$.

S13.20

$$\Delta G = G(v+1) - G(v) = \left(v+\frac{3}{2}\right)\nu_e - \left(v+\frac{3}{2}\right)^2 \chi_e\nu_e - \left(v+\frac{1}{2}\right)\nu_e + \left(v+\frac{1}{2}\right)^2 \chi_e\nu_e = \nu_e - \chi_e\nu_e(2v+2) = \nu_e - 2\chi_e\nu_e(v+1)$$

In the limit that $\Delta G \to 0, v \to v_{max}$, solving for v_{max} gives

$$0 = \nu_e - 2\chi_e\nu_e(v_{max}+1) \tag{13.E.4}$$

$$2\chi_e(v_{max}+1) = 1 \tag{13.E.5}$$

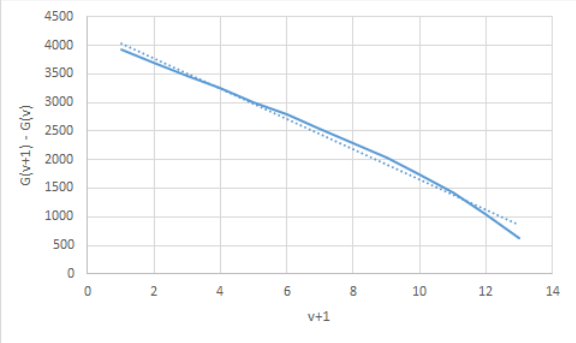
$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{13.E.6}$$

The molecule dissociates in the limit $\Delta G \to 0$, so the dissociation energy is given by

$$D_e = G(v_{max}) = (\frac{1}{2\chi_e} - \frac{1}{2})\nu_e - (\frac{1}{2\chi_e} - \frac{1}{2})^2\chi_e\nu_e = \frac{\nu_e}{2\chi_e}(1-\chi_e) - \frac{\nu_e}{4\chi_e}(1-\chi_e)^2 \tag{13.E.7}$$
$$= \frac{\nu_e}{4\chi_e}(2-2\chi_e-1+2\chi_e-\chi_e^2) = \frac{\nu_e}{4\chi_e}(1-\chi_e^2) \approx \frac{\nu_e}{4\chi_e}$$

The final step can be made if we assume χ_e to be very small.

Looking at the equation for ΔG, we conclude that a plot of ΔG versus $v+1$ will have an intercept of ν_e and a slope of $-2\chi_e\nu_e$. The experimental data points for H_2 can be plotted as such:



If we use a best linear fit, we determine that the intercept is $\nu_e = 4164.4 cm^{-1}$ and the slope is $-2\chi_e\nu_e = -232.01 cm^{-1}$. Thus, $\chi_e = 0.0279$. Then, the dissociation energy is

$$D_e = \frac{\nu_e}{4\chi_e} = 37400 cm^{-1} \tag{13.E.8}$$

The plot is not linear for large values of v because the potential curve is not well described by the anharmonic potential energy function.

Q13.21

An analysis of the vibrational spectrum of the ground-state homonuclear diatomic molecule Na_2 gives $\tilde{\nu}_e = 159.125\ cm^{-1}$ and $\tilde{\nu}_e\tilde{x}_e = 0.7255\ cm^{-1}$. Suggest an experimental method that can be used to determine there spectroscopic parameters. Use $\nu_{max} = \frac{1}{2\tilde{x}_e} - 1$ to determine the number of bound vibrational levels for ground state of Na_2.

S13.21

First solve for $\tilde{x}$:

$$\tilde{x} = \frac{0.7255\ cm^{-1}}{159.125\ cm^{-1}} = 4.5593 \times 10^{-3}\ cm^{-1} \tag{13.E.9}$$

Then plug it in to the equation:

$$\nu_{max} = \frac{1}{2 \times 4.5593 \times 10^{-3}\ cm^{-1}} - 1 = 109.67\ cm^{-1} \tag{13.E.10}$$

There are 109 bound vibrational levels for the ground state of Ne_2.

Q13.22

A Morse potential is a decent representation of internuclear potential and is modeled by

$$U(q) = D_e(1 - e^{-/betaq})^2 \tag{13.E.11}$$

where $q = R - R_e$. Prove the force constant for the Morse Potential is evaluated

$$k = 2D_e\beta^2 \tag{13.E.12}$$

If $D_e = 6.23 \times 10^{-19} J \cdot Molecule^{-1}$ and $\beta = 1.37 \times 10^{10} m^{-1}$ for a given compound, calculate the force constant for that compound.

S13.22

Using a Maclaurin series expansion of the Morse potential, the formula can be rewritten

$$U(q) = D_e(1 - e^{-\beta q})^2 = D_e(1 - (1 - \beta q + \frac{\beta^2 q^2}{2} O(q)^3))^2 = D_e(\beta^2 q^2 + O(q)^3) \tag{13.E.13}$$

We know that

$$U(q) = \frac{kq^2}{2} \tag{13.E.14}$$

assuming that $O(q)^3$ approaches zero, we get

$$\frac{kq^2}{2} = D_e(\beta^2 q^2 + O(q)^3) \implies k = 2D_e\beta^2 \tag{13.E.15}$$

Plugging in our given values, we get

$$l = 2(6.23 \times 10^{-19} J \cdot Molecule^{-1})(1.37 \times 10^{10})^2 = 234 N \cdot m^{-1} \tag{13.E.16}$$

Q13.23

Given that $D_e = 7.33 \times 10^{-19} J \cdot molecule^{-1}, \tilde{v}_e = 1580.0 cm^{-1}, and R_e = 121 pm$, find k and β for $^{16}O_2$.

S13.23

Assuming a a harmonic oscillator model, we can use the equation:

$$\tilde{v}_e = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{13.E.17}$$

We can find k from the parameters given in the problem. Solving for k gives

$$k = (2\pi c\tilde{v}_e)^2 \mu \tag{13.E.18}$$

$$= [2\pi(3 \times 10^{10} cm \cdot s^{-1})(1580.0 cm^{-1})]^2 \\ (7.9975 amu)(1.661 x 10^{-27} kg \cdot amu^{-1}) \tag{13.E.19}$$

$$= 1176.3 N \cdot m^{-1} \tag{13.E.20}$$

Using the equation:

$$\beta = \left(\frac{k}{2D_e}\right)^{1/2} \tag{13.E.21}$$

We can solve for β using the information above

$$\beta = \left[\frac{1176.3 N \cdot m^{-1}}{2(7.33 \times 10^{-19} J)}\right]^{1/2} \tag{13.E.22}$$

$$= 2.84 \times 10^{10} m^{-1} \tag{13.E.23}$$

Q13.24

The fundamental line in the IR spectrum of $^{12}C^{16}O\ cm^{-1}$, and the first overtone occurs at 4260.0 cm^{-1}. Find $\tilde{v}_e$ and $\tilde{x}_e\tilde{v}_e$ for $^{12}C^{16}O$.

S13.24

The equations for the fundamental frequency and the overtone are

$$\tilde{v} = \tilde{v}_e - 2\tilde{x}_e\tilde{v}_e \tag{13.E.24}$$

and

$$\tilde{v} = 2\tilde{v}_e - 6\tilde{x}_e\tilde{v}_e, \tag{13.E.25}$$

respectively.

We can set the fundamental frequency equal to $2143.0\ cm^{-1}$ and the first overtone equal to $4260.0\ cm^{-1}$ which is given from the problem statement. Then, we want to solve for $\tilde{x}_e\tilde{v}_e$.

Multiply the fundamental frequency by 3 and subtract the overtone.

$$\tilde{v}_e = [3(2143.0) - 4260.0] cm^{-1} = 2169.0 cm^{-1} \tag{13.E.26}$$

Then multiply the fundamental frequency by 2 and subtract from the overtone.

$$\tilde{x}_e\tilde{v}_e = 13.0cm^{-1} \tag{13.E.27}$$

Q13.24

Which of the following molecules exhibit a microwave rotational absorption spectrum: BF_2,SO_2,C_2F_2,NO_3^-

S13.24

SO_2

notes: microwave rotational absorption correlates to the rotation of polyatomic molecules. Would BF_2 and NO_3^- also fall in this range?

Q13-25 Slightly Incorrect

Calculate the fundamental and the first two overtones of

$$H^{35}Cl \tag{13.E.28}$$

given

$$\tilde{v_e} = 2990.946cm^{-1} \tag{13.E.29}$$

$$\tilde{x_e}\tilde{v_e} = 52.819cm^{-1} \tag{13.E.30}$$

S13-25

Use equation,

$$\tilde{v_{obs}} = \tilde{v_e}\nu - \tilde{x_e}\tilde{v_e}\nu(\nu+1) \tag{13.E.31}$$

with v =1,2...

The fundamental frequency is given by v=1 and the first two overtones are given by v=2 and v=3.

Fundamental:

$$\tilde{v_{obs}} = \tilde{v_e} - 2\tilde{x_e}\tilde{v_e} = 2990.946cm^{-1} - 2(52.819cm^{-1}) = 2885.308cm^{-1} \tag{13.E.32}$$

First overtone:

$$\tilde{v_{obs}} = 2\tilde{v_e} - 6\tilde{x_e}\tilde{v_e} = 2990.946cm^{-1} - 6(52.819cm^{-1}) = 5664.978cm^{-1} \tag{13.E.33}$$

Second overtone:

$$\tilde{v_{obs}} = 3\tilde{v_e} - 12\tilde{x_e}\tilde{v_e} = 3(2990.946cm^{-1}) - 12(52.819cm^{-1}) = 8339.01cm^{-1} \tag{13.E.34}$$

Q13.26

Plot the

$$\frac{\nu_{obs}}{\nu} \tag{13.E.35}$$

versus

$$(\nu+1) \tag{13.E.36}$$

for the anharmonic oscillator approximation and use it to determine the values of

$$\nu_e \tag{13.E.37}$$

and

$$x_e\nu_e \tag{13.E.38}$$

for

$$H^{3}5Cl \tag{13.E.39}$$

. Use the information in Table13.4.

S13.26

$$\nu_{obs} = \nu_{obs}\nu - x_e\nu_e\nu(\nu+1) \tag{13.E.40}$$

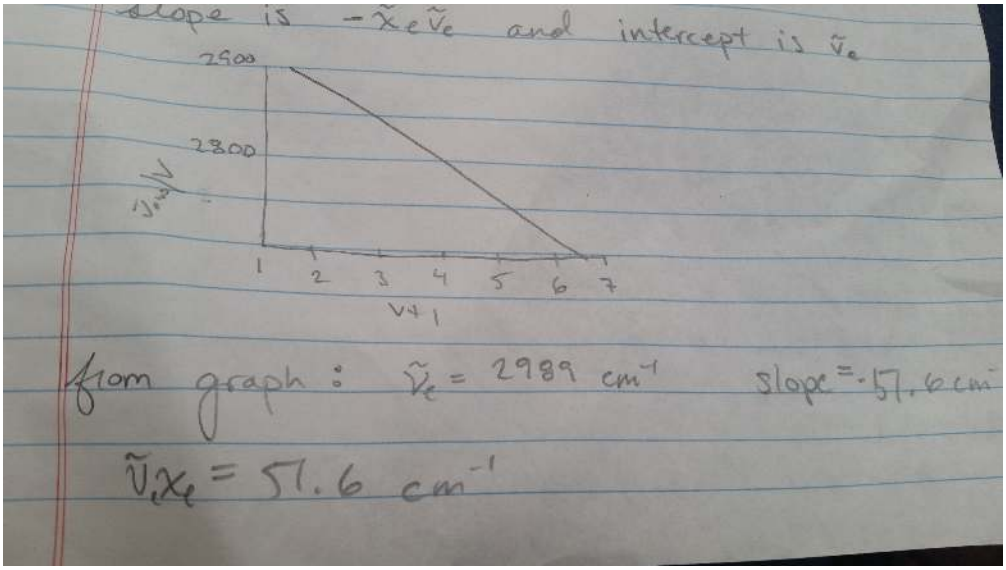
$$\frac{\nu_{obs}}{\nu} = \nu_e - x_e\nu_e(\nu+1) \tag{13.E.41}$$

The slope is

$$-x_e\nu_e \tag{13.E.42}$$

and the intercept is

$$\nu_e \tag{13.E.43}$$



The problem is nice and straight forward. It would be great for an explanation of why the slope is negative for an insight of the graph

Q13.31

Phosphorus nitride (PN) is a heteronuclear diatomic molecule that is a similar to N_2 with a triple bond, although is substantially weaker because P is a larger atomic radius than N. Using the following data, calculate $\tilde{\nu_e}'$ and $\tilde{\chi_e}'\ \tilde{\nu_e}'$ for PN.

IR Transition	$\tilde{\nu_{abs}}\ [cm^{-1}]$
$0 \rightarrow 0$	39,699.10
$0 \rightarrow 1$	40,786.80
$0 \rightarrow 2$	41,858.90

S13.31

We will use the following equation:

$$\tilde{\nu_{abs}} = \tilde{\nu_{0,0}}' + \tilde{\nu_e}'\tilde{\nu}' - \tilde{\chi_e}'\tilde{\nu_e}'\tilde{\nu}'(\nu'+1) \tag{13.E.44}$$

Plugging in the appropriate values of ν', we get:

According to your table $\tilde{\nu_{0,0}}'$ should be 39,699.10 not 29,699.10.

- $\nu' = 0$:

$$\tilde{\nu_{0,0}}' = 29,699.10\ cm^{-1} \quad (1)$$

- $\nu' = 1$:

$$\tilde{\nu_{0,0}}' + \tilde{\nu_e}' - 2\tilde{\chi_e}'\tilde{\nu_e}' = 40,786.80\ cm^{-1} \quad (2)$$

- $\nu' = 2$:

$$\tilde{\nu_{0,0}}' + 2\tilde{\nu_e}' - 6\tilde{\chi_e}'\tilde{\nu_e}' = 41,858.90\ cm^{-1} \quad (3)$$

Solving as a system of equations, we subtract:

(2) - (1) = (4), (3) - (1) = (5), and finally (5) - 2x(4) = (6)

Equation (6) can be solved for $\tilde{\chi_e}'\tilde{\nu_e}'$, and then plugged back in to equation (4) or equation (5) to solve for $\tilde{\nu_e}'$. The answer is:

$$\tilde{\chi_e}'\tilde{\nu_e}' = 1103.3\ cm^{-1} \quad (13.E.45)$$

and

$$\tilde{\nu_e}' = 7.80\ cm^{-1} \quad (13.E.46)$$

from my calculations $\tilde{\nu_e}' = 1103.3$ and $\tilde{\chi_e}'\tilde{\nu_e}' = 7.80$ it looks like you had them switched

Q13.32

The frequencies of the first few vibronic transitions to an excited state of NaCl* are as follows:

Vibronic Transitions	$0 \rightarrow 0$	$0 \rightarrow 1$	$0 \rightarrow 2$
$\tilde{\nu}_{obs}/cm^{-}1$	12376	89706	15219

*not accurate values for NaCl

Use these data to calculate the values of $\tilde{\nu}_e$ and $\tilde{\nu}_e\tilde{x}_e$ for the excited state of NaCl

S13.32

$A = \tilde{\nu}'_e, B = \tilde{\nu}'_e\tilde{x}'_e$

$12376 = \tilde{\nu}_0, 0$

$89706 = \tilde{\nu}_0, 0 + \tilde{\nu}'_e - 2\tilde{\nu}'_e\tilde{x}'_e - 12376 = \tilde{\nu}_0, 0 = 77330 = +\tilde{\nu}'_e - 2\tilde{\nu}'_e\tilde{x}'_e$ (1)

$15219 = \tilde{\nu}_0, 0 + 2\tilde{\nu}'_e - 6\tilde{\nu}'_e\tilde{x}'_e - 12376 = \tilde{\nu}_0, 0 = 2843 = 2\tilde{\nu}'_e - 6\tilde{\nu}'_e\tilde{x}'_e$ (2)

77330 + 2B = A (1a)

2843 = 2A - 6B (2a)

77330+2B = A

2843 - 154660 = -2B

B = 75908.5 cm^{-1} = $\tilde{\nu}'_e$

A = 229147 cm^{-1} = $\tilde{\nu}'_e\tilde{x}'_e$

Q13.33

Determine the number of translational, rotational, and vibrational degrees of freedom in

a. Xe
b. HCl

c. CS_2

d. hemoglobin containing 9272 molecules

The total number of degrees of freedom is 3N, where N is the number of atoms in the molecule. All molecules have three translational degrees of freedom. A nonlinear molecule has three rotational degrees of freedom and a linear molecule has two rotational degrees of freedom. A linear molecule has $3N-5$ vibrational degrees of freedom and a nonlinear molecule has 3N — 6 vibrational degrees of freedom.

S13.33

The number of translational degrees of freedom is 3, the number of rotational degrees of freedom is 2 for linear molecules and 3 for non-linear molecules. Therefore, the remaining degrees of freedom, which is equal to 3N-5 for linear molecules or 3N-6 for non-linear molecules, is equal to the number of vibrational degrees of freedom.

	Translation	Rotation	Vibration	Total
Xe	3	0	0	3
HCl	3	2	1	6
CS_2	3	2	4	9
hemoglobin	3	3	27810	27816

Q13.36

Classify each of the following molecules as either a prolate or an oblate symmetric top: XeF_4, $ClCH_3$, NH_3, and C_6H_6.

S13.36

- XeF_4 :oblate
- $ClCH_3$:prolate
- NH_3:prolate
- C_6H_6:oblate

Q13.37

Solve for the components of the moment of inertia of a trigonal planar molecule if all the masses are m, the bond lengths are unit length, and all bond angles are $120°$.

S13.37

$$I_{xx} = \sum m_j y_j^2 = m(1)^2 + 2m(sin^2 30°) = \frac{3}{2}m \tag{13.E.47}$$

$$I_{yy} = \sum m_j x_j^2 = m(0)^2 + 2m(cos^2 30°) = \frac{3}{2}m \tag{13.E.48}$$

$$I_{zz} = \sum m_j x_j^2 + \sum m_j y_j^2 = 3m \tag{13.E.49}$$

Q13.38

This problem illustrates how the principal moments of inertia can be obtained as an eigenvalue problem. Consider a molecule where all the masses are unit masses and the long and short bond lengths are 2 and 1, respectively.

Show that

$$I_{xx} = 2\cos^2\theta + 8\sin^2\theta \tag{13.E.50}$$

$$I_{yy} = 8\cos^2\theta + 2\sin^2\theta \tag{13.E.51}$$

$$I_{xy} = -6\cos\theta\sin\theta \tag{13.E.52}$$

Solve the secular determinant equation for λ

$$\begin{vmatrix} I_{xx} - \lambda & I_{xy} \\ I_{xy} & I_{yy} - \lambda \end{vmatrix} = 0 \tag{13.E.53}$$

and compare the result with the values of I_{xx} and I_{yy} that you would obtain if you align the "molecule" and coordinate system such that $\theta = 180°$. What does this comparison tell you? What are the values of I_{xx} and I_{yy} if $\theta = 90$?

S13.38

We use trigonometric functions to find the x and y components

$$I_{xx} = \sum m_i y_i^2 = 2(1)(2\sin\theta)^2 + 2(1)\left[\sin\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\sin^2\theta + 2\cos^2\theta \tag{13.E.54}$$

$$I_{yy} = \sum m_i x_i^2 = 2(1)(2\cos\theta)^2 + 2(1)\left[\cos\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\cos^2\theta + 2\sin^2\theta \tag{13.E.55}$$

$$\begin{aligned} I_{xy} = -\sum m_i x_i y_i &= -(2\cos\theta)(2\sin\theta) - 2\left[\cos(\pi) + \theta\right]\left[\sin(\pi) + \theta\right] \\ &\quad - \left[\sin\left(\frac{\pi}{2}\right) - \theta\right]\left[\cos\left(\frac{\pi}{2}\right) - \theta\right] - \left[\cos\left(\frac{\pi}{2}\right) + \theta\right]\left[\sin\left(\frac{\pi}{2}\right) + \theta\right] \\ &= -6\cos\theta\sin\theta \end{aligned} \tag{13.E.56}$$

The secular determinantal equation becomes

$$\begin{vmatrix} 8\sin^2\theta + 2\cos^2\theta - \lambda & -6\cos\theta\sin\theta \\ -6\cos\theta\sin\theta & 8\cos^2\theta + 2\sin^2\theta - \lambda \end{vmatrix} = 0 \tag{13.E.57}$$

Expanding the determinant gives

$$0 = \lambda^2 - \lambda(10)(\sin\theta^2 + \cos\theta^2) + 16(\sin\theta^2 + \cos\theta^2)^2 \tag{13.E.58}$$

$$0 = \lambda^2 - 10\lambda + 16 \tag{13.E.59}$$

$$\lambda = 5 \pm 3 \tag{13.E.60}$$

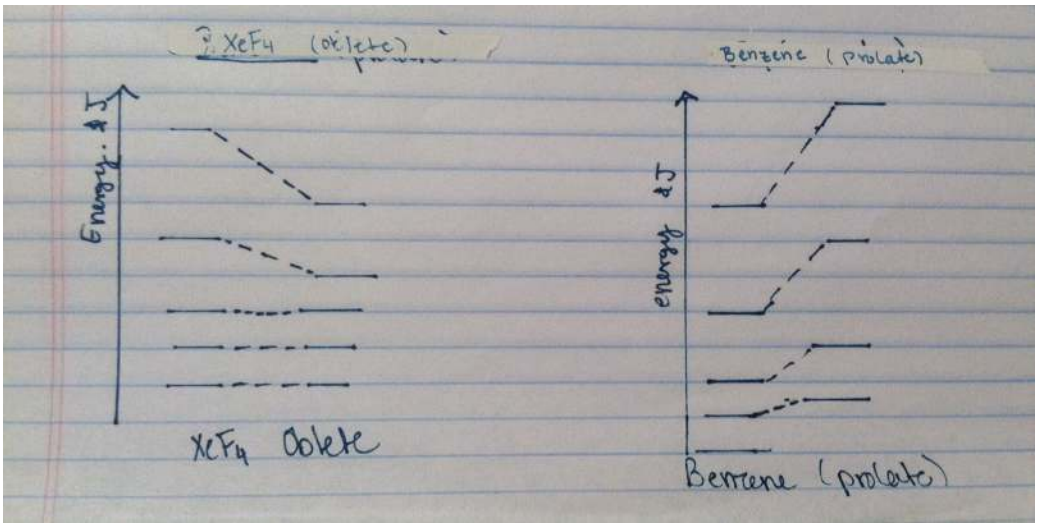
If $\theta = 180°$ then $I_{xx} = 2, I_{yy} = 8, and I_{xy} = 0$. If $\theta = 90°$ then $I_{xx} = 8, I_{yy} = 2, and I_{xy} = 0$. This tells us that the coordinate system does not affect the values of the principal momentum of inertia.

Q13.39

Sketch the energy level diagram of NH_3 (a prolate symmetric top molecule) and XeF_4 (an oblate symmetric top). How do they differ?

S13.39

The energies increase as the J levels increases for the prolate symmetry and the energies decrease as J increases for the oblate symmetry



13.E: Molecular Spectroscopy (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

14: Nuclear Magnetic Resonance Spectroscopy

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Chem 110A ● Chem 110B ● Chem 110C ● **Agenda** ● **Homework** ● **Worksheet Activities**

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).

Topic hierarchy

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

14: Nuclear Magnetic Resonance Spectroscopy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

14.1: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.1.1}$$

You can see from Equation 14.1.1 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 14.1.1

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.

14.1: 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.

14.2: Magnetic Moments Interact with Magnetic Fields

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.2.1}$$

You can see from Equation 14.2.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 14.2.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

14.2: 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.

14.3: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.3.1}$$

You can see from Equation 14.3.1 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 14.3.1

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.

14.3: 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.

14.4: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.4.1}$$

You can see from Equation 14.4.1 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 14.4.1

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.

14.4: 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.

14.5: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.5.1}$$

You can see from Equation 14.5.1 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 14.5.1

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.

14.5: 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.

14.6: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.6.1}$$

You can see from Equation 14.6.1 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 14.6.1

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.

14.6: 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.

14.7: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.7.1}$$

You can see from Equation 14.7.1 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 14.7.1

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.

14.7: 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.

14.8: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.8.1}$$

You can see from Equation 14.8.1 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 14.8.1

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.

14.8: 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.

14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.9.1}$$

You can see from Equation 14.9.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 14.9.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

14.9: 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

15: 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.

15.1: Electronically Excited Molecules
15.2: Transitions Modeled as Kinetics
15.3: Two-Level Systems Cannot Form Population Inversions
15.4: Population Inversion via Three-Level Systems
15.5: Laser Fundamentals
15.6: The Helium-Neon Laser
15.7: High-Resolution Laser Spectroscopy
15.8: Photochemical Dynamics

15: Lasers, Laser Spectroscopy, and Photochemistry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

15.1: 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 15.1.1. 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.

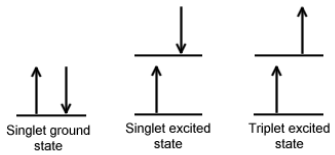


Figure 15.1.1: Spin in the ground and excited states (Tyler Matthews - Paint Shop Pro, Public Domain, https://commons.wikimedia.org/w/inde...curid=64926546)

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.

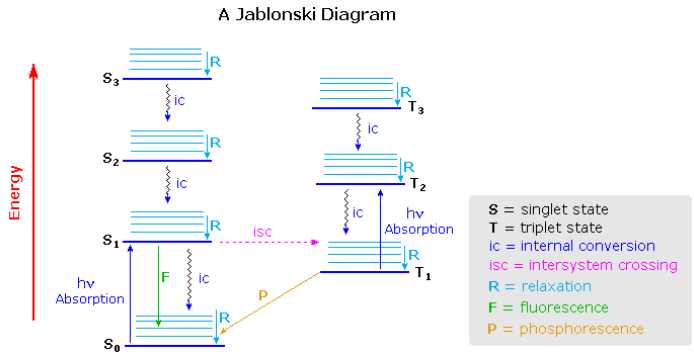


Figure **15.1.2**: Partial Jablonski Diagram for Absorption, Fluorescence, and Phosphorescence. (Bill Reusch, Michigan State University).

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 **15.1.2**.The deactivation process of fluorescence and phosphorescence involve an emission of a photon radiation as shown by the straight arrow in Figure **15.1.2**. The wiggly arrows in Figure **15.1.2** are deactivation processes without the use of radiation. The favored deactivation process is the route that is most rapid and spends 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 **15.1.3**).

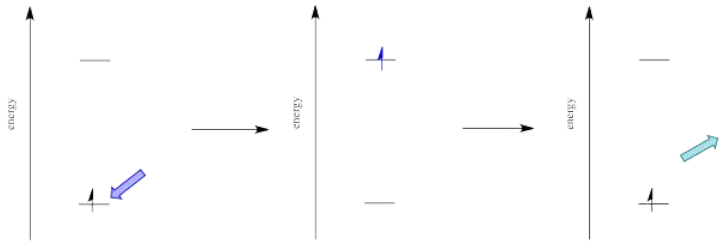


Figure 15.1.3: The absorption of purple light by a ground state particle, leading to the creation of an excited state particle. This excited state particle then emits blue light as it returns to the ground state.

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 15.1.4). Vibrational energy, however, is not exchanged exclusively by means of photons. It can be gained or lost through molecular collisions and heat transfer.

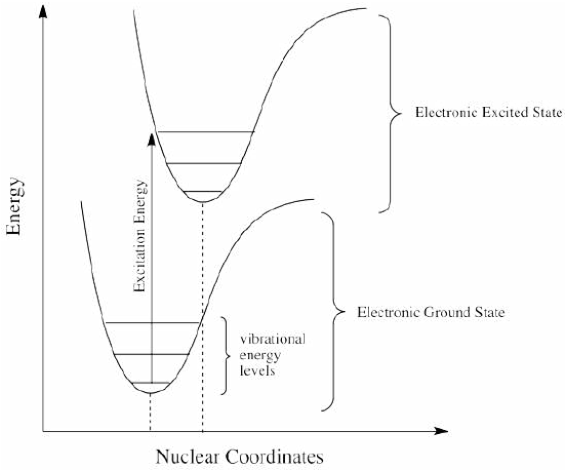


Figure 15.1.4: Transition from the ground state to an excited vibrational state within the excited electronic state.

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 15.1.5.

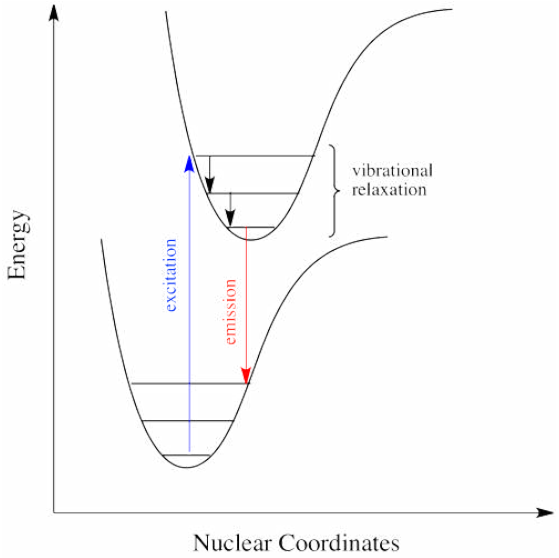


Figure 15.1.5: Excitation, followed by vibrational relaxation, and then emission.

Figure 15.1.6 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.

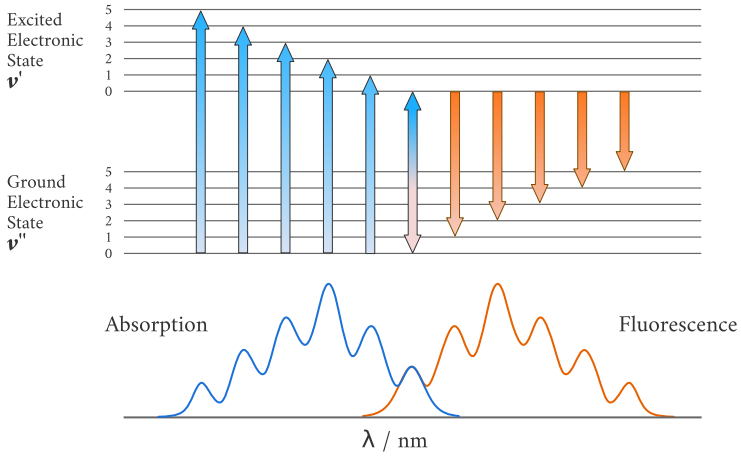


Figure 15.1.6: Absorption and fluorescence transitions in a hypothetical diatomic molecule in which the equilibrium bond length of the ground state is equal to the equilibrium bond length of the excited state. (CC BY-NC; Ümit Kaya, via LibreTexts)

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 15.1.7 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.

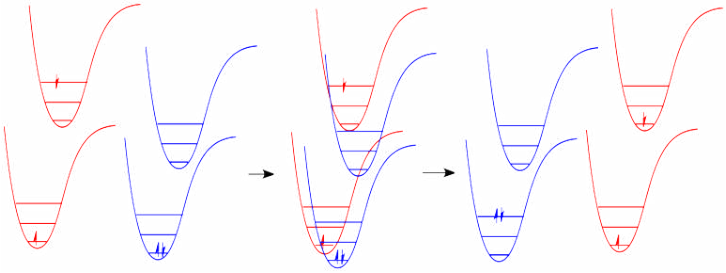


Figure **15.1.7**: The transfer of vibrational energy (heat) through a collision.

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 15.1.1

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 15.1.2

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 **15.1.1**, 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}).

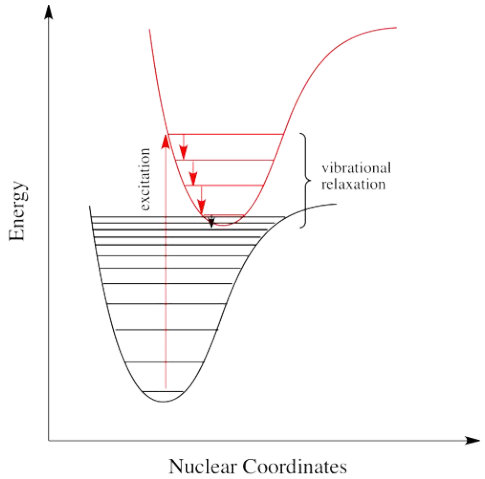


Figure **15.1.8**: Relaxation of an excited state particle to the ground state through the nonradiative process of internal conversion.

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 **15.1.9**: 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 **15.1.9**, 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 **15.1.10**. 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.

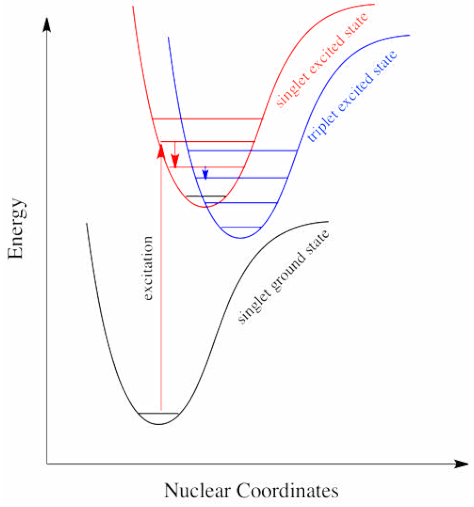


Figure **15.1.10**: Intersystem crossing from a singlet excited state to a triplet excited state.

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}).

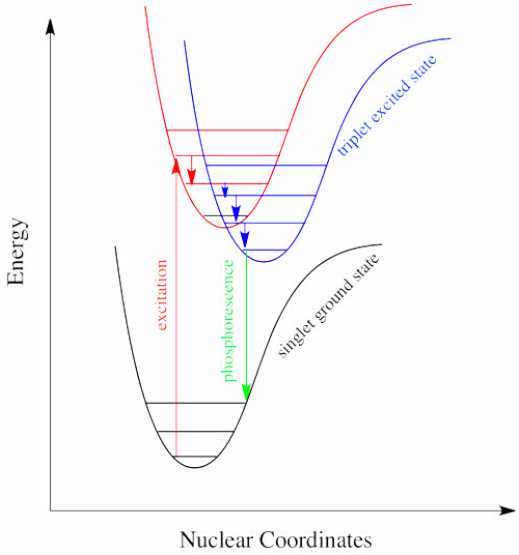


Figure **15.1.11**: The process of phosphorescence - excitation, followed by vibrational relaxation, intersystem crossing, and phosphorescence.

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)

15.1: 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.

15.2: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{15.2.1}$$

You can see from Equation 15.2.1 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 15.2.1

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.

15.2: 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.

15.3: 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.

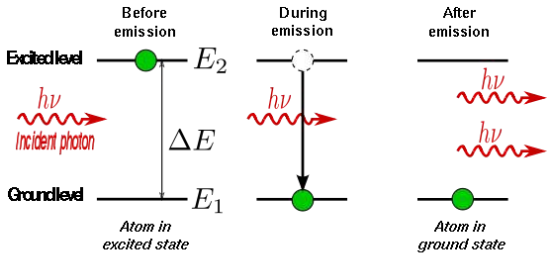
Lasing in Two-Level Systems

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.



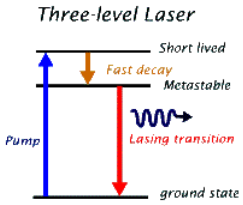
$$E_2 - E_1 = \Delta E = h\nu$$

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

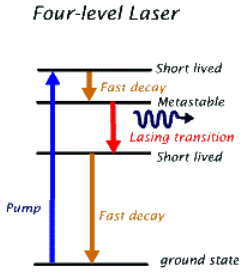
In fact, the first laser that was demonstrated to operate was a three-level laser, Maiman's ruby laser.



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.

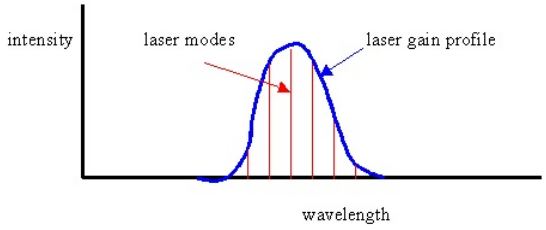
There are three different laser pumps: electromagnetic, optical, and chemical. Most lasers are pumped electro-magnetically, meaning via collisions with either electrons or ions. Dye lasers and many solid state lasers are pumped optically; however, solid state lasers are typically pumped with a broad 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)

15.3: 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.

15.4: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{15.4.1}$$

You can see from Equation 15.4.1 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 15.4.1

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.

15.4: 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.

15.5: 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.

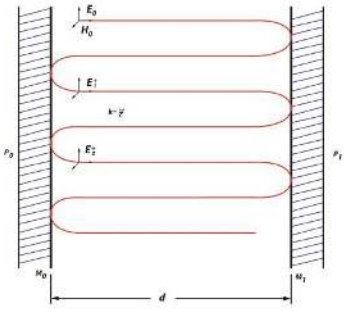


Figure 2. an optical cavity where the light inside moves back and forth between two mirrors

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.

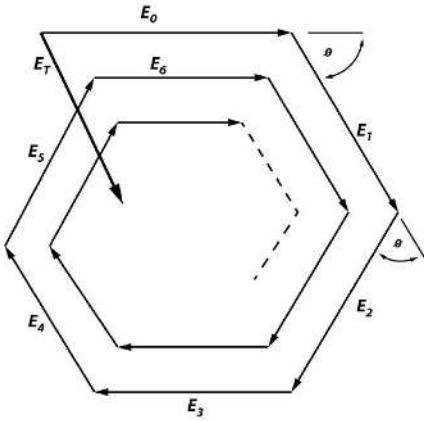


Figure 3. Totle field E_T

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.

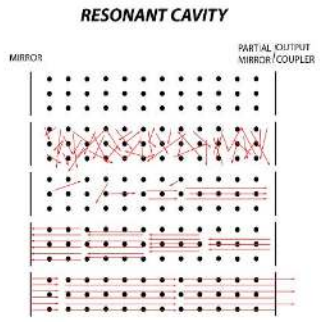


Figure 4. The first stage shows that all molecules present are in the ground state since there is no excitation energy present in the cavity. In the second stage, molecules become excited causing spontaneous emission of photons. In the third stage, photons collide with excited molecules causing an amplification 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.

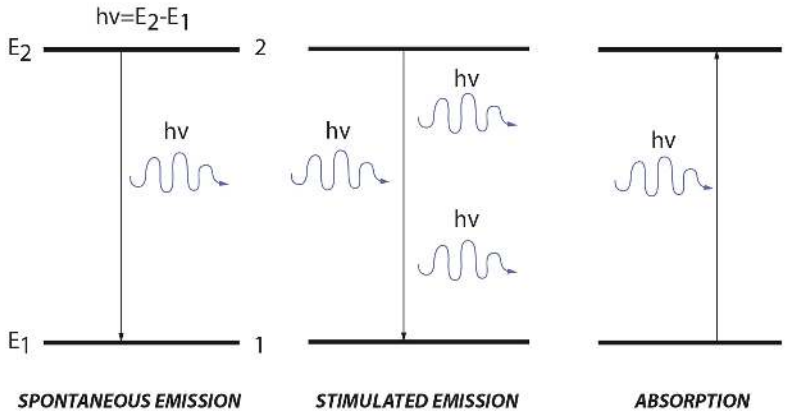


Figure 5. Diagram of spontaneous emission, stimulated emission and absorption in a two energy level system

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**).

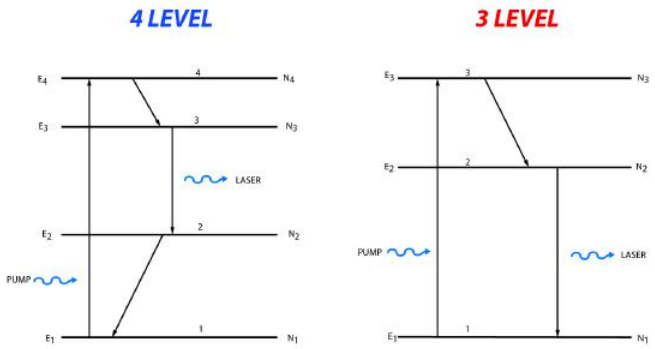


Figure 6. Three and four level energy system

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):

$$\langle W_p \rangle = \eta_p (P/(VN_g \hbar\omega_p))$$

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.

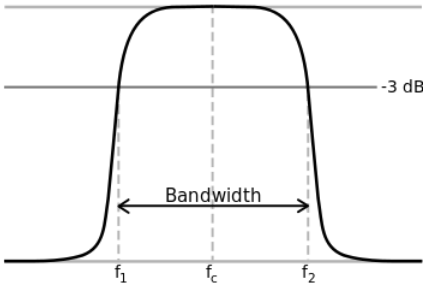


Figure 7. The bandwidth, Δf , or f1 to f2, of a damped oscillator is shown on a graph of energy versus frequency. The Q factor of the damped oscillator, or filter, is $f_c/\Delta f$. The higher the Q, the narrower and 'sharper' the peak is.

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.

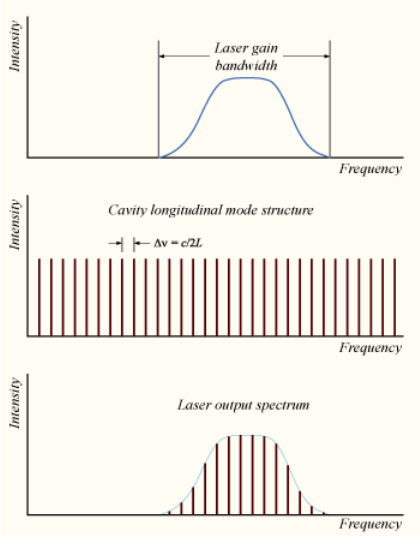


FIgure 8:Laser mode structure

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.

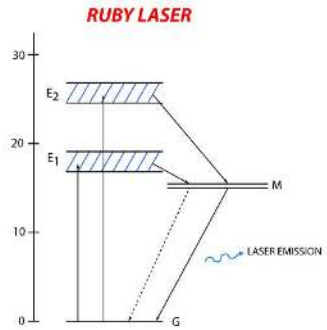


Figure 9. Schematic of Ruby laser

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.

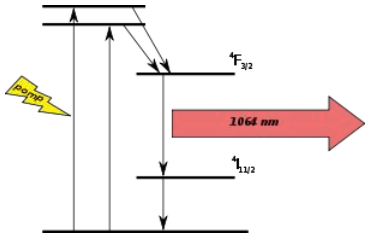


Figure 10. Simplified energy level diagram of the $^4F_{3/2}$---$4I_{11/2}$ laser transition in Nd:YAG showing the four- level nature of the system

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.

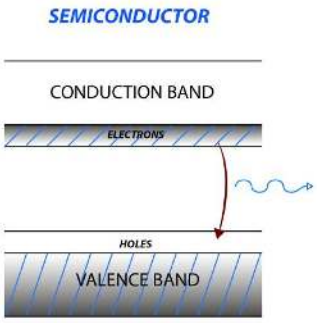


Figure 11. Schematic of semicondecor laser

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**).

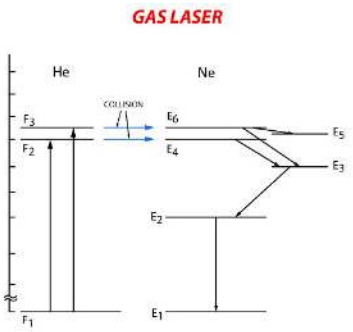


Figure 12. Schematic of gas laser

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.

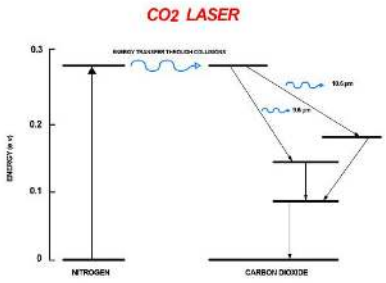


Figure 13. Schematic of carbondioxide laser

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.

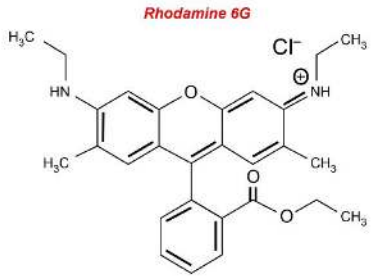


Figure 14. Rhodamine 6G molecule

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)

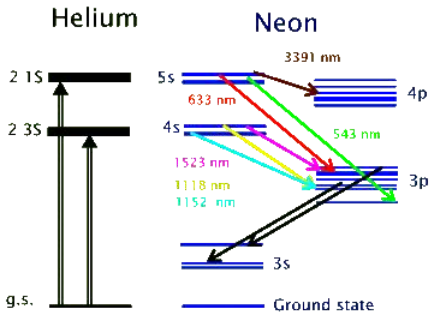
15.5: Laser Fundamentals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Overview of Lasers** is licensed CC BY-NC-SA 4.0.

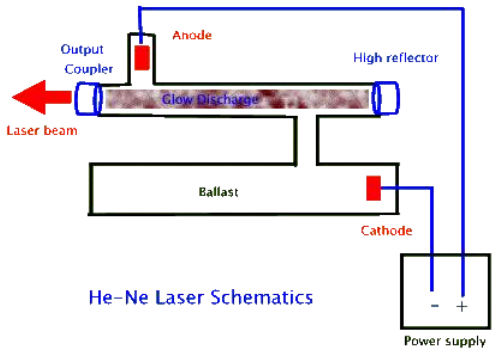
15.6: The Helium-Neon Laser

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.

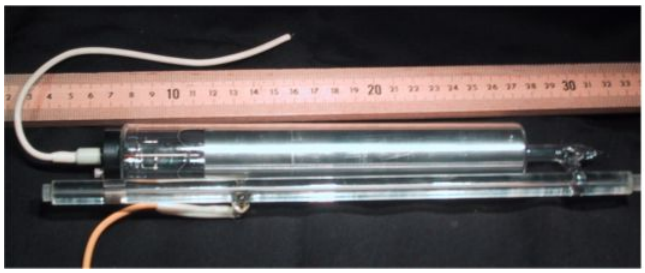


The above energy level diagram shows the two excited states of helium atom, the 2 3S and 2 1S, that get populated as a result of the electromagnetic pumping in the discharge. Both of these states are metastable and do not allow de-excitations via radiative transitions. Instead, the helium atoms give 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.

15.6: 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.

15.7: High-Resolution Laser Spectroscopy

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{15.7.1}$$

You can see from Equation 15.7.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 15.7.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

15.7: 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.

15.8: 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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{15.8.1}$$

You can see from Equation 15.8.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 15.8.1

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.

15.8: 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

16: The Properties of Gases

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

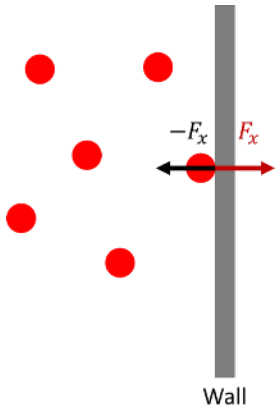
Template:HideTOC

16.1: All Dilute Gases Behave Ideally
16.2: van der Waals and Redlich-Kwong Equations
16.3: A Cubic Equation of State
16.4: The Law of Corresponding States
16.5: The Second Virial Coefficient
16.6: The Repulsive Term in the Lennard-Jones Potential
16.7: Van der Waals Constants in Terms of Molecular Parameters
16.E: The Properties of Gases (Exercises)

16: The Properties of Gases is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

16.1: All Dilute Gases Behave Ideally

Ideal gases have no interactions between the particles, hence, the particles do not exert forces on each other. However, particles do experience a force when they collide with the walls of the container. Let us assume that each collision with a wall is elastic. Let us assume that the gas is in a cubic box of length a and that two of the walls are located at $x = 0$ and at $x = a$. Thus, a particle moving along the x direction will eventually collide with one of these walls and will exert a force on the wall when it strikes it, which we will denote as F_x. Since every action has an equal and opposite reaction, the wall exerts a force $-F_x$ on the particle.



According to Newton's second law, the force $-F_x$ on the particle in this direction gives rise to an acceleration via

$$-F_x = ma_x = m\frac{\Delta v_x}{\Delta t} \tag{16.1.1}$$

Here, t represents the time interval between collisions with the same wall of the box. In an elastic collision, all that happens to the velocity is that it changes sign. Thus, if v_x is the velocity in the x direction before the collision, then $-v_x$ is the velocity after, and $\Delta v_x = -v_x - v_x = -2v_x$, so that

$$-F_x = -2m\frac{v_x}{\Delta t} \tag{16.1.2}$$

Since the particles have no forces acting upon them, except for when they collide iwht the wall container, the particles move at constant speed. Thus, a collision between a particle and, say, the wall at $x = 0$ will not change the particle's speed. Before it strikes this wall again, it will proceed to the wall at $x = a$ first, bounce off that wall, and then return to the wall at $x = 0$. The total distance in the x direction traversed is $2a$, and since the speed in the x direction is always v_x, the interval $\Delta t = \frac{2a}{v_x}$. Consequently, the force is:

$$-F_x = -\frac{mv_x^2}{a} \tag{16.1.3}$$

Thus, the force that the particle exerts on the wall is:

$$F_x = \frac{mv_x^2}{a} \tag{16.1.4}$$

The mechanical definition of pressure is the average force over area:

$$P = \frac{\langle F \rangle}{A} \tag{16.1.5}$$

where $\langle F \rangle$ is the average force exerted by all N particles on a wall of the box of area A. Here $A = a^2$. If we use the wall at $x = 0$ we have been considering, then

$$P = \frac{N\langle F_x \rangle}{a^2} \tag{16.1.6}$$

because we have N particles hitting the wall. Hence:

$$P = \frac{Nm\langle v_x^2 \rangle}{a^3} \tag{16.1.7}$$

from our study of the Maxwell-Boltzmann distribution, we found that:

$$\langle v_x^2 \rangle = \frac{k_B T}{m} \tag{16.1.8}$$

Hence, since $a^3 = V$:

$$\begin{aligned} P &= \frac{Nk_B T}{V} \\ &= \frac{nRT}{V} \end{aligned} \tag{16.1.9}$$

which is the ideal gas law. It relates the pressure, volume, and temperature of an ideal gas and is referred to as an equation of state. An equation of state is a relation between variables and describes the state of matter under a set of given physical conditions. One way to visualize any equation of state is to plot *isotherms*, which are graphs of P vs. V at fixed values of T . For the ideal-gas equation of state, some of the isotherms are shown in the figure below (left panel): If we plot P vs. T at fixed volume (called the *isochores*), we obtain the plot in the right panel. What is important to note, here, is that an ideal gas can exist *only* as a gas. It is not possible for an ideal gas to condense into some kind of "ideal liquid". In other words, a phase transition from gas to liquid can be modeled only if interparticle interactions are properly accounted for.

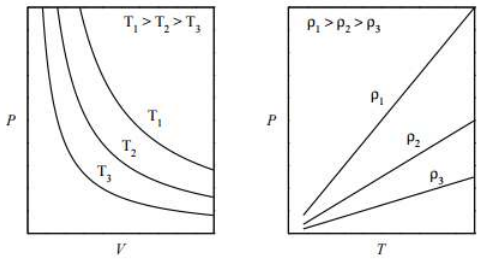


Figure 16.1.1 : (Left) Pressure vs. volume for different temperatures (isotherms of the ideal-gas equation of state. (Right) Pressure vs. temperature for different densities $\rho = N/V$.

We can rearrange the ideal gas equation of state to put all the constants and variables on one side:

$$\frac{PV}{nRT} = 1 = Z \tag{16.1.10}$$

Z is called the *compressibility* of the gas. In an ideal gas, if we compress the gas by increasing P , the volume decreases as well so as to keep $Z = 1$. For a real gas, Z, therefore, gives us a measure of how much the gas deviates from ideal-gas behavior.

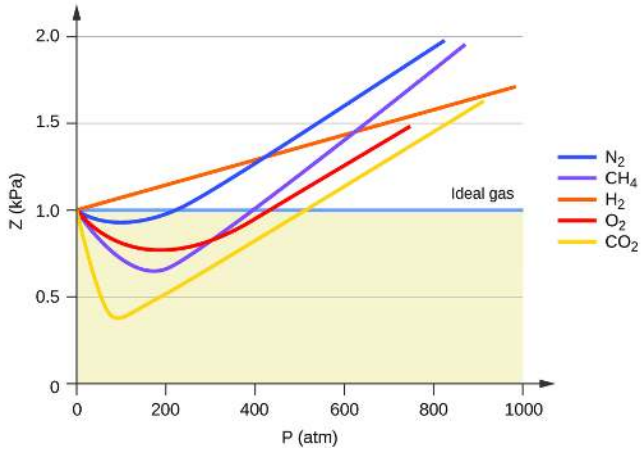


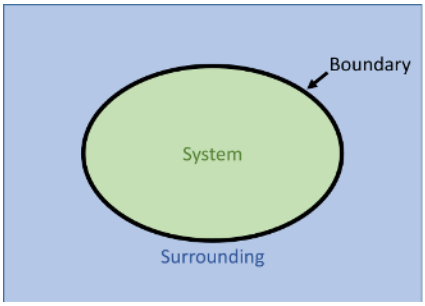
Figure 16.1.2 : A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law. from Openstax (CC-BY)

Figure 16.1.2 shows a plot of Z vs. P for several real gases and for an ideal gas. The plot shows that for sufficiently low pressures (hence, low densities), each gas approaches ideal-gas behavior, as expected.

Extensive and Intensive Properties in Thermodynamics

Before we discuss ensembles and how we construct them, we need to introduce an important distinction between different types of thermodynamic properties that are used to characterize the ensemble. This distinction is *extensive* and *intensive* properties.

Thermodynamics always divides the universe into a *system* and its *surroundings* with a *boundary* between them. The unity of all three of these is the thermodynamic *universe*.



Now suppose we allow the system to grow in such a way that both the number of particles and the volume grow with the ratio N/V remaining constant. Any property that increases as we grow the system in this way is called an *extensive* property. Any property that remains the same as we grow the system in this way is called *intensive*.

The ideal gas equation of state can be written in an extensive form:

$$\begin{aligned} PV &= nRT \\ P\bar{V} &= RT \\ P &= \rho RT \end{aligned} \tag{16.1.11}$$

where $\bar{V} = V/n$ is called the molar volume and $\rho = N/V$ is called density. Unlike V , which increases as the number of moles increases (an *extensive* quantity, $\bar{V}$ and ρ do not exhibit this dependence and, therefore, are called *intensive*. Compressibility can also be written in an intensive form:

$$\begin{aligned} Z &= \frac{PV}{nRT} \\ &= \frac{P\bar{V}}{RT} \\ &= \frac{P}{\rho RT} \end{aligned}$$

Some examples of intensive and extensive properties include:

- Extensive: number of particles (N), moles (n), volume (V), mass (m), energy, free energy
- Intensive: pressure (P), density (ρ), molar heat capacity (C), temperature (T)

Contributors and Attributions

- Mark Tuckerman (New York University)
- Jerry LaRue (Chapman University)

16.1: All Dilute Gases Behave Ideally is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **16.1: All Dilute Gases Behave Ideally** is licensed CC BY-NC-SA 4.0.

16.2: van der Waals and Redlich-Kwong Equations

The ideal gas law is valid for low pressures, where the finite volume of particles and intermolecular attractions do not have a large impact. At higher pressures, we must account for these factors. The van der Waals and Redlich-Kwong equations of states are equations of state that attempt to account for real gas behavior by modifying the ideal gas law with two additional parameters.

The Van der Waals Equation of State

The van der Waals Equation of State is an equation relating the density of gases and liquids to the pressure, volume, and temperature conditions (i.e., it is a thermodynamic equation of state). It can be viewed as an adjustment to the ideal gas law that takes into account the non-zero volume of gas molecules and inter-particle attraction using correction terms a and b. It was derived in 1873 by Johannes Diderik van der Waals, who received the Nobel Prize in 1910 for this work. The van der Waals equation of state is:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{16.2.1}$$

Equation 16.2.1 can also be rewritten as

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

If the correction terms a and b go to zero, the equation reduces to the ideal gas equation of state:

$$PV = nRT$$

Let's first look first at the correction term b, which represents the volumes of the particles and assumes a hard-wall potential, $u_o(r)$. This potential energy term describes a system of hard sphere "billiard balls" of diameter σ. Figure 16.2.1 shows two of these billiard ball type particles at the point of contact (i.e, the distance of closest approach). At this point, they undergo a collision and separate, so they cannot be closer than that distance.

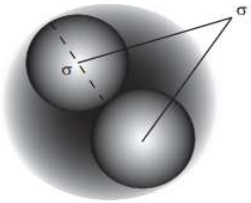


Figure 16.2.1 : Two hard spheres of diameter σ at closest contact. The distance between their centers is also σ. A sphere of radius σ just containing the two particles is shown in cross-section.

The distance between their centers is also σ. Because of this distance of closest approach, the total volume available to the particles is not the volume of the container, V, but some volume less than V. This reduction in volume can be calculated. Figure 16.2.1 shows a shaded sphere that just contains the pair of billiard ball particles. The volume of this sphere is the volume excluded from any two particles. The radius of the sphere is σ and the excluded volume for the two particles is $4\pi\sigma^3/3$, which is the volume of the shaded sphere. From this, we see that the excluded volume for any *one* particle is just half of this or $\frac{2}{3}\pi\sigma^3$. The excluded volume for a mole of such particles is the parameter b:

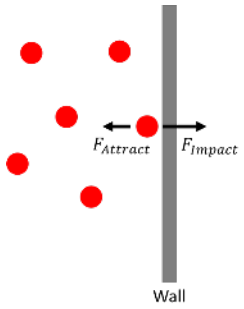
$$b = \frac{2}{3}\pi\sigma^3 N_0$$

Given n moles of gas, the total excluded volume is then nb, so that the total *available* volume is $V - nb$.

Let's turn our attention the a, which represents the intermolecular attractions of the particles. Molecular attractions tend to make the P exerted by the gas less than that predicted by the ideal gas law at low pressures. P is force over area:

$$P = \frac{F}{A}$$

Pressure is proportion to the net force on the wall of the container:



The net force is the force of the molecules impacting the container wall minus the intermolecular attraction of the molecules:

$$\bar{F}_{Net} = \bar{F}_{Impact} - \bar{F}_{Attract}$$

Therefore, the pressure will be less for the real gas than the ideal gas. We can add a correction term to pressure to account for intermolecular attractions:

$$P_{VDW} = P_{Real} + a\,(?)$$

V does influence the amount of intermolecular attraction because P is reduced as V is increased:

$$P \propto \frac{1}{V}$$

And pressure is proportional to the number of attractive interactions:

of molecular interactions $\propto P^2$

of molecular interactions $\propto \frac{1}{V^2}$

We now have an expression for the van der Waals P:

$$P = P_{Real} + \frac{an^2}{V^2}$$

The constants a and b depend on the substance. Some typical values are:[1]

Molecule	a $\left(\frac{L^2 \cdot bar}{mol^2}\right)$	b $\left(\frac{L}{mole}\right)$
H_2O	5.536	0.03049
N_2	1.43	0.03913
CH_4	2.283	0.04278
C_2H_6	5.562	0.0638

1. *R. C. Weast (1972). Handbook of Chemistry and Physics 53rd Edition. Chemical Rubber Pub.*

Redlich-Kwong Equation of State

The van der Waals Equation of State had to wait almost 100 years before a real, successful improvement was introduced to it. This progress occurred once researchers committed themselves to finding the empirical temperature dependency of the attraction parameter a proposed by van der Waals. In contrast, very little attention has been paid to modifying the parameter b for co-volume. It makes a lot of sense that b would not be modified by temperature, because it represents the *volume* of the molecules, which should not be affected by their kinetic energy (measured in terms of temperature). The very first noteworthy successful modification to the attraction parameter came with the publication of the equation of state of Redlich-Kwong in 1949.

The Redlich–Kwong equation of state is an empirical, algebraic equation that relates temperature, pressure, and volume of gases. It is generally more accurate than the van der Waals and the ideal gas equations of state at temperatures above the critical temperature. It was formulated by Otto Redlich and Joseph Neng Shun Kwong in 1949, who showed that a simple two-parameter

equation of state could well reflect reality in many situations. Redlich and Kwong revised the van der Waals Equation of State (Equation 16.2.1) and proposed the following expressions:

$$\left(P+\frac{a}{\sqrt{T}\bar{V}(\bar{V}+b)}\right)(\bar{V}-b)=RT \tag{16.2.2}$$

The fundamental change they introduced was to the functional form of $\partial P_{\text{attraction}}$. Additionally, they introduced the co-volume b into the denominator of this functional form. The important concept here is that the attraction parameter a of van der Waals needed to be made a function of temperature to do a better job of quantitatively matching experimental data. This was a realization that van der Waals had suggested, but no actual functional dependency had been introduced until the Redlich-Kwong equation.

We know what follows at this point. To come up with an expression for a and b of Equation 16.2.2, we apply the criticality conditions to this equation of state. As we recall, imposing the criticality conditions allows us to relate the coefficients a and b to the critical properties (P_c, T_c) of the substance. Once we have done that, we obtain the definition of a and b for the Redlich-Kwong equation of state:

$$a=0.42780\frac{R^2T_c^{2.5}}{P_c} \tag{16.2.3}$$

$$b=0.086640\frac{RT_c}{P_c} \tag{16.2.4}$$

The Redlich-Kwong equation of state radically improved, in a quantitative sense, the predictions of the van der Waals equation of state. We now recall that van der Waals-type equations are cubic because they are cubic polynomials in molar volume and compressibility factor. It comes as no surprise then, that we can transform Equation 16.2.2 into:

$$\bar{v}^3-\left(\frac{RT}{P}\right)\bar{v}^2+\frac{1}{P}\left(\frac{1}{T^{0.5}}-bRT-Pb^2\right)\bar{v}-\frac{ab}{PT^{0.5}}=0 \tag{16.2.5}$$

and, by defining the following parameters:

$$A=\frac{aP}{R^2T^{2.5}} \tag{16.2.6}$$

$$B=\frac{bP}{RT} \tag{16.2.7}$$

and introducing the compressibility factor definition:

$$Z=\frac{P\bar{v}}{RT}$$

we get:

$$Z^3-Z^2+(A-B-B^2)Z-AB=0 \tag{16.2.8}$$

We may also verify the two-parameter corresponding state theory by introducing Equations 16.2.3, 16.2.4, and 16.2.5 into Equation 16.2.8:

$$Z^3-Z^2+\frac{P_r}{T_r}\left(\frac{0.42748}{T_r^{1.5}}-0.08664-0.007506\frac{P_r}{T_r}\right)Z-0.03704\frac{P_r^2}{T_r^{3.5}}=0 \tag{16.2.9}$$

Where:

$$P_r=\frac{P}{P_c}$$

$$T_r=\frac{T}{T_c}$$

P_r and T_r are the pressure and temperature at the reduced state. See Section 16.4 for more information on reduced states. In Equation 16.2.9, we can observe the same thing that we saw with the van der Waals equation of state: gases at corresponding states

have the same properties. Equation 16.2.9 is particularly clear about it: any two different gases at the same P_r, T_r condition have the same compressibility factor.

Just as any other cubic equation of state, Equations 16.2.2 through 16.2.9, as they stand, are to be applied to pure substances. For mixtures, however, we apply *the same equation*, but we impose certain mixing rules to obtain a and b, which are functions of the properties of the pure components. Strictly speaking, we create a new "pseudo" pure substance that has the average properties of the mixture. Redlich-Kwong preserved the same mixing rules that van der Waals proposed for his eqution of state:

$$a_m = \sum_i \sum_j y_i y_j a_{ij}$$

with

$$a_{ij} = \sqrt{a_i a_j}$$

and

$$b_m = \sum_i y_i b_i$$

Naturally, Redlich and Kwong did not have the last word on possible improvements to the van der Waals equation of state. The Redlich-Kwong equation of state, as shown here, is no longer used in practical applications. Research continued and brought with it new attempts to improve the Redlich-Kwong equation of state. After more than two decades, a modified Redlich-Kwong equation of state with very good potential was developed.

Contributors and Attributions

- Mark Tuckerman (New York University)
- Michael Adewumi (The Pennsylvania State University) Vice Provost for Global Program, Professor of Petroleum and Natural Gas Engineering
- Jerry LaRue (Chapman University)

16.2: van der Waals and Redlich-Kwong Equations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **16.2: van der Waals and Redlich-Kwong Equations of State** is licensed CC BY-NC-SA 4.0.

16.3: A Cubic Equation of State

Isotherms

Isotherms are plots of the pressure of a gas as a function of volume at a fixed constant temperature. The isotherms for an ideal gas are hypberbolas:

$$P = \frac{RT}{\bar{V}}$$

where $\bar{V}$ is the molar volume V/n. We know that at sufficiently low temperatures, any real gas, when compressed, must undergo a transition from gas to liquid. The signature of such a transition is a discontinuous change in the volume, signifying the condensation of the gas into a liquid that occupies a significantly lower volume.

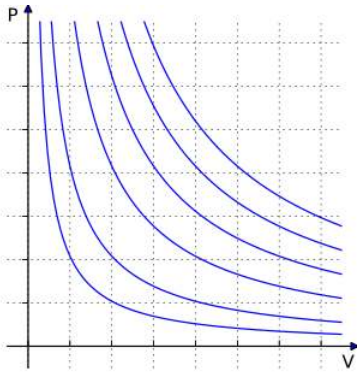


Figure 16.3.1 : Ideal gas isotherms for one mole of the gas and at select temperatures. (public domain).

CO_2 isotherms for the van der Waals Equation of state are shown in Figure 16.3.2 . At sufficiently high temperatures, the isotherms approach those of an ideal gas. At lower temperatures, the fluid obeys approximately the ideal gas law $PV = nRT$ at large volumes when the pressures are low. If we decrease the volume (go to the left in the figure along an isotherm), the pressure rises. Consider the (blue) isotherm of 10 °C, which is below the critical temperature. Decrease the volume until we reach the point B, where condensation (formation of liquid CO_2) starts. At this point the van der Waals curve is no longer physical (excluding the possibility of the occurrence of an oversaturated, metastable gas) because P and V increase together. It should be clear that many approximations and assumptions go into the derivation of the van der Waals equation so that some of the important physics is missing from the model. Hence, we should not be surprised if the van der Waals equation has some unphysical behavior buried in it. In reality, the pressure stays constant between the region A and B and the real physical behavior is given by the dashed blue line, called the *tie line*. This lines represents the gas-liquid coexistence and the pressure is equal to the vapor pressure of the liquid.

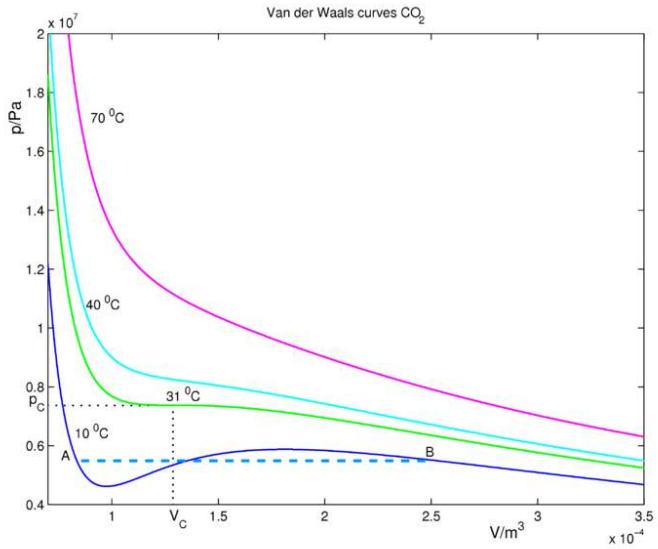


Figure 16.3.2 : Different isotherms (curves of constant temperature) of the van der Waals equation of state using parameters a and b computed for carbon dioxide. The dashed line from A to B is drawn in accordance with Maxwell's equal area rule. The carbon dioxide molecule (CO_2) has p_C = 7.37 MPa and T_C = 304.1 K = 31 ˚C , which gives a = 0.366 m^6 Pa and b = 42.9 10^{-6} m^3. The critical pressure is at 73.7 bar = 7370 kPa.

The tie line must be added in *ad hoc* by drawing a horizontal line through the isotherm (Figure 16.3.2). The vertical position of the line is chosen so that the area above the line (between the line and the isotherm) and below the line (again between the line and the isotherm) is exactly the same. This is known as *Maxwell's construction*. In this way, we entirely remove the artifact of the unphysical increase of P with V when we compute the compressional work on the gas from $\int P(V)\, dV$, to be discussed in our section on thermodynamics. Although the van der Waals curves have regions where they are not physical, the equation for these curves, derived by van der Waals in 1873, was a great scientific achievement.

Note

Even today it is not possible to give a *single* equation that describes correctly the gas-liquid phase transition.

Critical Point

Looking to the left of point A on the 10 °C isotherm (blue curve), the system is in the liquid state. Increasing the volume to point A leads to a rapid drop in the pressure of the system because the compressibility of a liquid is considerable smaller than that of a gas. The system is still in the liquid state at point A, but as we increase the volume further, we enter the gas-liquid coexistence line and the liquid begins to transition to gas. As we move along this line to the right, there is less liquid and more gas in the system until we reach point B, at which point the system will be completely in the gas phase. The areas, bounded by the 10 °C isotherm (blue curve) below and above the coexistence line are equal. Any further increase in the volume will lead to an expansion of the gas.There is exactly one isotherm along which the van der Waals equation correctly predicts the gas-to-liquid phase transition. If one follows the 31 °C isotherm (green curve in Figure 16.3.2) of critical temperature, the volume discontinuity captured by the tie line is shrunken down to a single point (so that there is no possibility of an increase of P with V!). This point is called the critical point and it exists at only one temperature, called the **critical temperature**, denoted T_c. The critical isotherm at the critical temperature corresponds to the highest possible temperature at which a gas-liquid transition can occur. Isotherms at higher temperatures have no liquid-gas phase transitions. Along those isotherms, the higher pressure fluid, called a supercritical fluid, resembles a liquid, while at lower pressures the fluid is more gas-like.

The critical point exists at an inflection where the first and second derivatives of P with respect to V are zero:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

Substituting the van der Waals equation into these two conditions, we find the following:

$$-\frac{nRT_c}{(V_c - nb)^2} + \frac{2an^2}{V_c^3} = 0$$
$$\frac{2nRT_c}{(V_c - nb)^3} - \frac{6an^2}{V_c^4} = 0$$

Hence, we have two equations in two unknowns V_c and T_c for the critical temperature and critical volume. Once these are determined, the van der Waals equation, itself, allows us to determine the critical pressure, P_c. To solve the equations, first divide one by the other. This gives us a simple condition for the volume:

$$\frac{V_c - nb}{2} = \frac{V_c}{3}$$
$$3V_c - 3nb = 2V_c$$
$$V_c = 3nb$$

This is the **critical volume**. Now use either of the two conditions to obtain the critical temperature, T_c. If we use the first one, we find:

$$\frac{nRT_c}{(V_c - nb)^2} = \frac{2an^2}{V_c^3}$$
$$\frac{nRT_c}{(3nb - nb)^2} = \frac{2an^2}{(3nb)^3}$$
$$\frac{nRT_c}{4n^2b^2} = \frac{2an^2}{27n^3b^3}$$
$$RT_c = \frac{8a}{27b}$$

Finally, plugging the critical temperature and volume into the van der Waals equation, we obtain the critical pressure:

$$P_c = \frac{nRT_c}{V_c - nb} - \frac{an^2}{V_c^2}$$
$$= \frac{8an/27b}{3nb - nb} - \frac{an^2}{(3nb)^2}$$
$$= \frac{a}{27b^2}$$

It comes as no surprise that cubic equations of state like the van der Waals (and Redlich-Kwong) equations of state yield three different roots for volume and compressibility factor. This is simply because they are algebraic equations, and any nth order algebraic equation will always yield “n” roots. However, those “n” roots are not required to be distinct, and that is not all: they are not required be real numbers, either. A quadratic expression (n = 2) may have zero real roots (e.g., $x^2 + 1 = 0$); this is because those roots are complex numbers. In the case of cubic expressions (n = 3), we will either have one or three real roots; this is because complex roots always show up in pairs (i.e., once you have a complex root, its conjugate must also be a solution). In our case, and because we are dealing with physical quantities (densities, volumes, compressibility factors), only real roots are of interest. More specifically, we look for real, positive roots such that $\bar{V} > b$ in the case of molar volume and $Z > \frac{Pb}{RT}$ in the case of compressibility factor.

In a cubic equation of state, the possibility of three real roots is restricted to the case of sub-critical conditions ($T < T_c$), because the S-shaped behavior, which represents the vapor-liquid transition, takes place only at temperatures below critical. This restriction is mathematically imposed by the criticality conditions. Anywhere else, beyond the S-shaped curve, we will only get one real root of the type $\bar{V} > b$. Figure 16.3.3 illustrates this point.

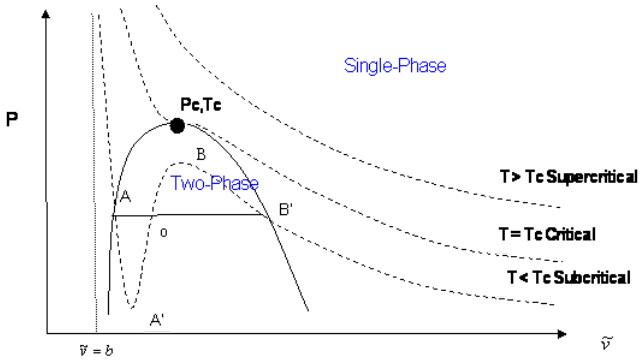


Figure 16.3.3 : Multiple Roots in Cubic EOS

The shape of the critical isotherm at the critical point allows us to determine the exact temperature, pressure, and volume at which the phase transitions from gas to liquid will occur. If we draw a curve through the isotherms joining all points of these isotherms at which the tie lines begin, continue the curve up to the critical isotherm, and down the other side where the tie lines end, this curve reaches a maximum at the critical point. The region inside this curve is when the gas and liquid phases coexist.

Let us summarize the three cases presented in Figure 16.3.3 :

1. Supercritical isotherms ($T > T_c$: At temperatures beyond critical, the cubic equation will have only one real root (the other two are imaginary complex conjugates). In this case, there is no ambiguity in the assignment of the volume root since we have single-phase conditions. The occurrence of a unique real root remains valid at any pressure: any horizontal (isobaric) line cuts the supercritical isotherm just once in Figure 16.3.3 .
2. Critical isotherm ($T = T_c$): At the critical point ($P = P_c$), vapor and liquid properties are the same. Consequently, the cubic equation predicts three real and equal roots at this special and particular point. However, for any other pressure along the critical isotherm ($P < P_c$ or $P > P_c$,) the cubic equation gives a unique real root with two complex conjugates.
3. Subcritical isotherm ($T < T_c$): Predictions for pressures within the pressure range for metastability ($P'_A < P < P'_B$) or for the saturation condition ($P = P^{sat}$) will always yield three real, different roots. In fact, this is the only region where an isobar cuts the same isotherm more than once. The smallest root is taken as the specific volume of the liquid phase; the largest is the specific volume of the vapor phase; the intermediate root is not computed as it is physically meaningless. However, do not get carried away. Subcritical conditions will not always yield three real roots of the type $\bar{v} > b$. If the pressure is higher than the maximum of the S-shaped curve, P_B, we will only have one (liquid) real root that satisfies $\bar{v} > b$. By the same token, pressures between $0 < P < P'_A$ yield only one (vapor) root. In the case of P'_A being a negative number, three real roots are to be found even for very low pressures when the ideal gas law applies. The largest root is always the correct choice for the gas phase molar volume of pure components.

Most of these considerations apply to the cubic equation of state in Z (compressibility factor). The most common graphical representation of compressibility factor is the well-known chart of Standing and Katz, where compressibility, Z, is plotted against pressure (Figure 16.3.4). Standing and Katz presented their chart for the compressibility factor of sweet natural gases in 1942. This chart was based on experimental data. Graphical determination of properties was widespread until the advent of computers, and thus the Standing and Katz Z-chart became very popular in the natural gas industry. Typical Standing and Katz charts are given for high temperature conditions ($T > T_c$ or $T_r > 1$).

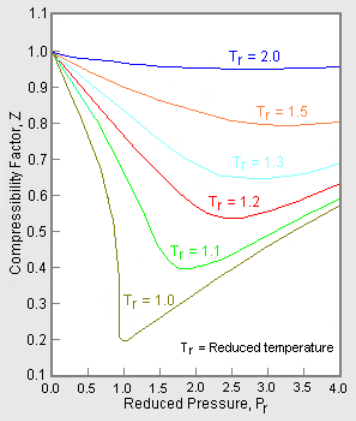


Figure 16.3.4 : Compressibility Factor versus Pressure

16.3: A Cubic Equation of State is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **16.3: A Cubic Equation of State** by Jerry LaRue, Michael Adewumi is licensed CC BY-NC-SA 4.0.

16.4: The Law of Corresponding States

Johannes Diderik van der Waals modified the ideal gas law to better describe the behavior of real gases by introducing corrections to account for the finite size of molecules and the intermolecular forces between them, leading to the well-known van der Waals equation.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \tag{16.4.1}$$

This expression for the van der Waal gas involves two phenomenological constants, a and b. Van der Waals postulated that all real gases at corresponding states should behave similarly and he focused on applying Equation 16.4.1 at the critical point of difference gases—the unique temperature, pressure, and volume at which the distinction between liquid and gas disappears.

The corresponding state that van der Waals chose to use is called the **reduced state**, which is based on the deviation of the conditions of a substance from its own critical conditions. We can define reduced quantities:

$$P_r = \frac{P}{P_c}$$
$$V_r = \frac{V}{V_c}$$
$$T_r = \frac{T}{T_c}$$

By substitution into Equation 16.4.1, the Van der Waal equations can be expressed differently

$$\left(P_r + \frac{3}{\bar{V}_r^2}\right)\left(\bar{V}_r - \frac{1}{3}\right) = \frac{8}{3}T_r \tag{16.4.2}$$

Equation 16.4.2 means the critical parameters for a gas can be expressed in terms of a and b parameters:

$$V_c = 3b$$
$$P_c = \frac{a}{27b^2}$$
$$T_c = \frac{8a}{27bR}$$

Hence, when gases are expressed in terms of their **reduced variables**, the van der Waals equation takes on a universal form (Equation 16.4.2) that applies to all gases, regardless of their chemical identity. This discovery led van der Waals to formulate the **Law of Corresponding State**s, which states that different gases at the same reduced temperature and reduced pressure will exhibit similar thermodynamic behavior. This principle provided a unifying framework for understanding real-gas behavior and laid the foundation for generalized equations of state and compressibility charts used in modern thermodynamics.

Although the actual pressures and volumes may differ, two gases are said to be in corresponding states if their reduced pressure, volume, and temperature are the same. What it says is that the behavior of all gases (and liquids!!) is pretty much the same, except for a scaling factor that is related to the critical point of the substance. The compressibility value (Z) of 3/8 at the critical point for the van der Waals equation is actually not in such good agreement with measurement. This is why the more complicated Redlich-Kwong and Peng-Robertson expressions are better, although the idea is the same. Hence, all one needs to know to describe any fluid's behavior is its critical point. For example, argon behaves much the same at 300 K as ethane does at 600 K because these temperatures correspond to twice their respective critical temperatures (150.72 K and 305.4 K, respectively) so $T_r = 2.0$.

Compressibility

The Compressibility provides a useful way to compare the behavior of real gases with that predicted by the ideal gas law, and it connects directly to the critical ratios first introduced by van der Waals.

$$Z = \frac{PV}{RT}$$

Over the past 150 years, researchers have collected extensive experimental data on a wide variety of fluids, allowing the Law of Corresponding States to be tested and validated. When the pressure, temperature, and volume of different fluids are expressed in terms of their reduced values, their measurements can be superimposed on the same compressibility chart (Figure **16.4.1**). This overlap shows that most "normal" fluids, despite having different molecular structures, follow a common pattern of behavior when scaled by their critical properties.

We can rewrite the universal expression for compressibility Z using reduced variables and plot measured values of Z versus the reduced pressure, P_r (Figure **16.4.1**). As you can see, very different gases/liquids like nitrogen and water can be made to coincide if their properties are plotted relative to there critical points rather than in absolute terms. The compressibility factor Z can also be cast into the form of corresponding states showing that Z also can be expressed as a universal function of V_r and T_r or any other two reduced quantities:

$$Z = \frac{\bar{V}_r}{\bar{V}_r - \frac{1}{3}} - \frac{9}{8\bar{V}_r T_r}$$

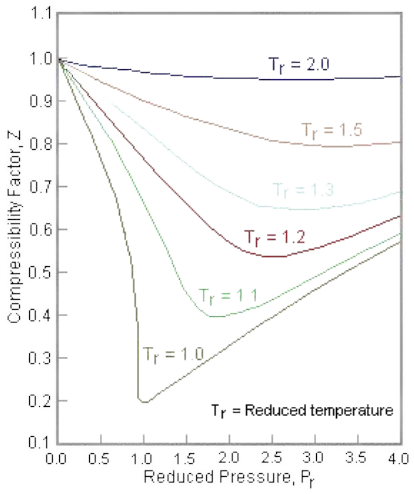


Figure **16.4.1**: Example of a generalized compressibility factor graph (Public domain; Milton Beychok)

These charts show that most "normal" fluids, such as simple hydrocarbons, noble gases, and diatomic molecules, conform closely to the predictions of the Law of Corresponding States. Deviations occur mainly in more complex or strongly associating fluids—such as water, ammonia, or hydrogen fluoride—where strong polarity or hydrogen bonding introduces additional interactions not accounted for by van der Waals' simple model. Nevertheless, the overall success of the law demonstrates its power: by scaling thermodynamic variables to the critical constants, we can describe the behavior of a wide variety of substances with a single framework. This insight not only validated van der Waals' pioneering theory but also provided a foundation for modern equations of state and practical tools in chemical engineering and physical chemistry.

Van der Waals did not stop here. He went on to describe the root cause of condensation of gases into liquids at lower temperatures: the attractive interactions between the molecules.

16.4: The Law of Corresponding States is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **16.4: The Law of Corresponding States** by Delmar Larsen, Jerry LaRue, Stefan Franzen is licensed CC BY-NC-SA 4.0.

16.5: The Second Virial Coefficient

The second virial coefficient describes the contribution of the pair-wise potential to the pressure of the gas. The third virial coefficient depends on interactions between three molecules, and so on and so forth.

Introduction

As the density is increased the interactions between gas molecules become non-negligible. Deviations from the ideal gas law have been described in a large number of equations of state. The *virial equation of state* expresses the deviation from ideality in terms of a power series in the density:

$$\frac{P}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + ...$$

- $B_2(T)$ is the second virial coefficient,
- $B_3(T)$ is called the third virial coefficient, etc.

The j[th] virial coefficient can be calculated in terms of the interaction of j molecules in a volume V. The second and third virial coefficients give most of the deviation from ideal (P/rkT) up to 100 atm.

The **second virial coefficient** is usually written as B or as B_2. The second virial coefficient represents the initial departure from ideal-gas behavior. The second virial coefficient, in three dimensions, is given by:

$$B_2(T) = -\frac{1}{2}\int \left(\exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right) - 1\right) 4\pi r^2 dr$$

where $\Phi_{12}(\mathbf{r})$ is the intermolecular pair potential, T is the temperature, and k_B is the Boltzmann constant. Notice that the expression within the parenthesis of the integral is the *Mayer f-function*. In practice, the integral is often *very hard* to integrate analytically for anything other than, say, the hard sphere model, thus one numerically evaluates:

$$B_2(T) = -\frac{1}{2}\int \left(\left\langle \exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right)\right\rangle - 1\right) 4\pi r^2 dr$$

calculating:

$$\left\langle \exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T}\right)\right\rangle$$

for each r using the numerical integration scheme proposed by Harold Conroy [1][2].

Calculation of virial coefficients

The configuration integrals for Z_1, Z_2, and Z_3 are:

- $Z_1 = \int dr_1 = V$
- $Z_2 = \int e^{-U_2/kT} dr_1\ dr_2$
- $Z_3 = \int e^{-U_3/kT} dr_1\ dr_2\ dr_3$

The series method allows the calculation of a number of virial coefficients. Recall that the second and third virial coefficient can account for the properties of gases up to hundreds of atmospheres. We will discuss the calculation of the second virial coefficient for a monatomic gas to illustrate the procedure. To calculate $B_2(T)$ we need U_2. For monatomic particles it is reasonable to assume that the potential depends only on the separation of the two particles so $U_2 = u(r_{12})$, where $r_{12} = |r_2 - r_1|$. Using a change of variables we can write this integral $r_{12} = r_2 - r_1$ and after integration over r_1 we can transform variables from dr_{12} to $4\pi r^2 dr$. The result is:

$$B_2(T) = -2\pi \int [e^{-\beta u(r)} - 1] r^2\ dr$$

This expression can be used to obtain parameters from experiment. The second virial coefficient is tabulated for a number of gases. For a hard-sphere potential there is an infinite repulsive wall at a particle radius σ. There is no attractive part.

$$B_2(T) = -2\pi \int_0^\sigma [-1] r^2 \, dr$$
$$= \frac{2\pi\sigma^3}{3}$$

The Lennard-Jones potential cannot be calculated analytically, but the integral can be computed numerically. The second virial coefficient was a useful starting point for obtaining Lennard-Jones parameters that were used in simulations.

Isihara-Hadwiger Formula

The Isihara-Hadwiger formula was discovered simultaneously and independently by Isihara and the Swiss mathematician Hadwiger in 1950. The second virial coefficient for any hard convex body is given by the exact relation:

$$B_2 = RS + V$$

or:

$$\frac{B_2}{V} = 1 + 3\alpha$$

where:

$$\alpha = \frac{RS}{3V}$$

where V is the volume, S, the surface area, and R the mean radius of curvature.

Hard spheres

For the hard sphere model one has:[9]

$$B_2(T) = -\frac{1}{2} \int_0^\sigma \left(\langle 0 \rangle - 1 \right) 4\pi r^2 dr$$

leading to

$$B_2 = \frac{2\pi\sigma^3}{3}$$

Note that B_2 for the hard sphere is independent of temperature.

Van der Waals equation of state

For the Van der Waals equation of state one has:

$$B_2(T) = b - \frac{a}{RT}$$

Excluded volume

The second virial coefficient can be computed from the expression:

$$B_2 = \frac{1}{2} \iint v_{\text{excluded}}(\Omega, \Omega') f(\Omega) f(\Omega') \, \mathrm{d}\Omega \mathrm{d}\Omega'$$

where v_{excluded} is the excluded volume.

References

1. Reid, B. P. J. Chem. Educ. 1996, 73, 612-615.
2. Harold Conroy "Molecular Schrödinger Equation. VIII. A New Method for the Evaluation of Multidimensional Integrals", Journal of Chemical Physics **47** pp. 5307 (1967)
3. I. Nezbeda, J. Kolafa and S. Labík "The spherical harmonic expansion coefficients and multidimensional integrals in theories of liquids", Czechoslovak Journal of Physics **39** pp. 65-79 (1989)

4. Akira Isihara "Determination of Molecular Shape by Osmotic Measurement", Journal of Chemical Physics **18** pp. 1446-1449 (1950)
5. Akira Isihara and Tsuyoshi Hayashida "Theory of High Polymer Solutions. I. Second Virial Coefficient for Rigid Ovaloids Model", Journal of the Physical Society of Japan **6** pp. 40-45 (1951)
6. Akira Isihara and Tsuyoshi Hayashida "Theory of High Polymer Solutions. II. Special Forms of Second Osmotic Coefficient", Journal of the Physical Society of Japan **6** pp. 46-50 (1951)
7. H. Hadwiger "Einige Anwendungen eines Funkticnalsatzes fur konvexe Körper in der räumichen Integralgeometrie" Mh. Math. **54** pp. 345- (1950)
8. H. Hadwiger "Der kinetische Radius nichtkugelförmiger Moleküle" Experientia **7** pp. 395-398 (1951)
9. H. Hadwiger "Altes und Neues über Konvexe Körper" Birkäuser Verlag (1955)
10. Donald A. McQuarrie "Statistical Mechanics", University Science Books (2000) ISBN 978-1-891389-15-3 Eq. 12-40
11. I. Amdur and E. A. Mason "Properties of Gases at Very High Temperatures", Physics of Fluids **1** pp. 370-383 (1958)

Related reading

- W. H. Stockmayer "Second Virial Coefficients of Polar Gases", Journal of Chemical Physics **9** pp. 398- (1941)
- G. A. Vliegenthart and H. N. W. Lekkerkerker "Predicting the gas–liquid critical point from the second virial coefficient", Journal of Chemical Physics **112** pp. 5364-5369 (2000)

16.5: The Second Virial Coefficient is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **16.5: The Second Virial Coefficient** by SklogWiki, Stefan Franzen is licensed CC BY 4.0.

16.6: The Repulsive Term in the Lennard-Jones Potential

Proposed by Sir John Edward Lennard-Jones, the Lennard-Jones potential describes the potential energy of interaction between two non-bonding atoms or molecules based on their distance of separation. The potential equation accounts for the difference between attractive forces (dipole-dipole, dipole-induced dipole, and London interactions) and repulsive forces.

Introduction

Imagine two rubber balls separated by a large distance. Both objects are far enough apart that they are not interacting. The two balls can be brought closer together with minimal energy, allowing interaction. The balls can continuously be brought closer together until they are touching. At this point, it becomes difficult to further decrease the distance between the two balls. To bring the balls any closer together, increasing amounts of energy must be added. This is because eventually, as the balls begin to invade each other's space, they repel each other; the force of repulsion is far greater than the force of attraction.

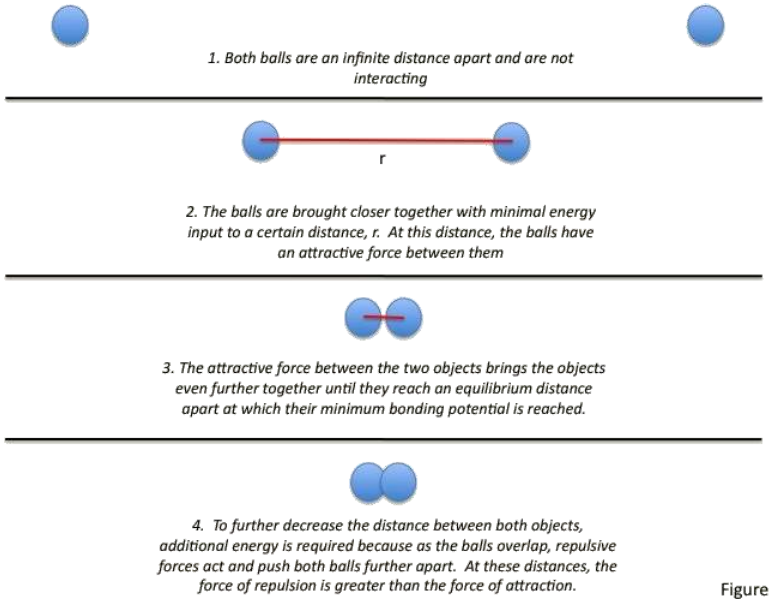


Figure A

This scenario is similar to that which takes place in neutral atoms and molecules and is often described by the **Lennard-Jones potential**.

The Lennard-Jones Potential

The Lennard-Jones model consists of two 'parts'; a steep repulsive term, and smoother attractive term, representing the London dispersion forces. Apart from being an important model in itself, the Lennard-Jones potential frequently forms one of 'building blocks' of many force fields. It is worth mentioning that the 12-6 Lennard-Jones model is not the most faithful representation of the potential energy surface, but rather its use is widespread due to its computational expediency. The Lennard-Jones Potential is given by the following equation:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{16.6.1}$$

or is sometimes expressed as:

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} \tag{16.6.2}$$

where

- V is the intermolecular potential between the two atoms or molecules.
- ϵ is the well depth and a measure of how strongly the two particles attract each other.

- σ is the distance at which the intermolecular potential between the two particles is zero (Figure **16.6.1**). σ gives a measurement of how close two nonbonding particles can get and is thus referred to as the *van der Waals radius*. It is equal to one-half of the internuclear distance between nonbonding particles.
- r is the distance of separation between both particles (measured from the center of one particle to the center of the other particle).
- $A = 4\epsilon\sigma^{12}$, $B = 4\epsilon\sigma^{6}$
- Minimum value of $\Phi_{12}(r)$ at $r = r_{min}$.

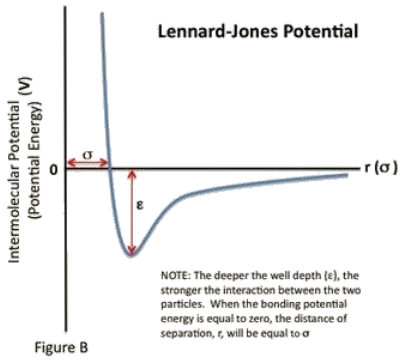


Figure B

Figure **16.6.1**: The Lennard-Jones potential describes both the attraction and repulsion between nonionic particles. The first part of the equation, the short-ranged $\sigma/r)^{12}$ term describes the repulsive forces between particles while the latter part of the equation and the longer-ranged σ/r^{6} term denotes the attraction.

Example 16.6.1: The van der Waals Radius

The ϵ and σ values for Xenon (**Xe**) are found to be 1.77 kJ/mol and 4.10 Angstroms, respectively. Determine the van der Waals radius for the Xenon atom.

Solution

Recall that the van der Waals radius is equal to one-half of the internuclear distance between nonbonding particles. Because σ gives a measure of how close two non-bonding particles can be, the van der Waals radius for Xenon (Xe) is given by:

$$r = \sigma/2 = 4.10 \text{ Angstroms}/2 = 2.05 \text{ Angstroms}$$

Bonding Potential

The Lennard-Jones potential is a function of the distance between the centers of two particles. When two non-bonding particles are an infinite distance apart, the possibility of them coming together and interacting is minimal. For simplicity's sake, their bonding potential energy is considered zero. However, as the distance of separation decreases, the probability of interaction increases. The particles come closer together until they reach a region of separation where the two particles become bound; their bonding potential energy decreases from zero to a negative quantity. While the particles are bound, the distance between their centers continue to decrease until the particles reach an equilibrium, specified by the separation distance at which the minimum potential energy is reached.

If the two bound particles are further pressed together, past their equilibrium distance, repulsion begins to occur: the particles are so close together that their electrons are forced to occupy each other's orbitals. Repulsion occurs as each particle attempts to retain the space in their respective orbitals. Despite the repulsive force between both particles, their bonding potential energy increases rapidly as the distance of separation decreases.

Example 16.6.2

Calculate the intermolecular potential between two Argon (Ar) atoms separated by a distance of 4.0 Angstroms (use ϵ=0.997 kJ/mol and σ=3.40 Angstroms).

Solution

To solve for the intermolecular potential between the two Argon atoms, we use equation 2.1 where V is the intermolecular potential between two non-bonding particles.

$$V = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The data given are:

- $\epsilon = 0.997\ \text{kJ/mol}$,
- $\sigma = 3.40\ \text{Angstroms}$, and
- the distance of separation, $r = 4.0\ \text{Angstroms}$.

We plug these values into Equation 16.6.1 and solve as follows:

$$\begin{aligned} V &= 4(0.997\ \text{kJ/mol})\left[\left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{12} - \left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{6}\right] \\ &= 3.988(0.14 - 0.38) \\ &= 3.988(-0.24) \\ &= -0.96 kJ/mol \end{aligned}$$

Stability and Force of Interactions

Like the bonding potential energy, the stability of an arrangement of atoms is a function of the Lennard-Jones separation distance. As the separation distance decreases below equilibrium, the potential energy becomes increasingly positive (indicating a repulsive force). Such a large potential energy is energetically unfavorable, as it indicates an overlapping of atomic orbitals. However, at long separation distances, the potential energy is negative and approaches zero as the separation distance increases to infinity (indicating an attractive force). This indicates that at long-range distances, the pair of atoms or molecules experiences a small stabilizing force. Lastly, as the separation between the two particles reaches a distance slightly greater than σ, the potential energy reaches a minimum value (indicating zero force). At this point, the pair of particles is most stable and will remain in that orientation until an external force is exerted upon it.

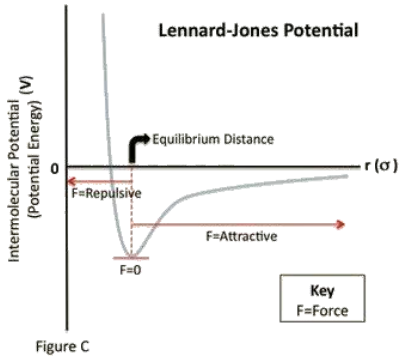


Figure C

Example 16.6.3

Two molecules, separated by a distance of 3.0 angstroms, are found to have a σ value of 4.10 angstroms. By decreasing the separation distance between both molecules to 2.0 angstroms, the intermolecular potential between the molecules becomes more negative. Do these molecules follow the Lennard-Jones potential? Why or why not?

Solution

Recall that σ is the distance at which the bonding potential between two particles is zero. On a graph of the Lennard-Jones potential, then, this value gives the x-intersection of the graph. According to the Lennard-Jones potential, any value of r greater than σ should yield a negative bonding potential and any value of r smaller than σ should yield a positive bonding potential. In this scenario, as the separation between the two molecules decreases from 3.0 angstroms to 2.0 angstroms, the bonding potential is becomes more negative. In essence however, because the starting separation (3.0 angstroms) is already less than σ

(4.0 angstroms), decreasing the separation even further (2.0 angstroms) should result in a more positive bonding potential. Therefore, these molecules do not follow the Lennard-Jones potential.

? Exercise 16.6.1

The second part of the Lennard-Jones equation is $(\sigma/r)^6$ and denotes attraction. Name at least three types of intermolecular interactions that represent attraction.

Answer

From section 2.1, dipole-dipole, dipole-induced dipole, and London interactions are all attractive forces.

? Exercise 16.6.2

At what separation distance in the Lennard-Jones potential does a species have a repulsive force acting on it? An attractive force? No force?

Answer

See Figure C. A species will have a repulsive force acting on it when r is less than the equilibrium distance between the particles. A species will have an attractive force acting on it when r is greater than the equilibrium distance between the particles. Lastly, when r is equal to t↑he equilibrium distance between both particles, the species will have no force acting upon it.

References

1. Atkins, Peter and de Paula, Julio. *Physical Chemistry for the Life Sciences*. New York, N.Y. W. H. Freeman Company, 2006. (469-472).
2. Royer, Donald J. *Bonding Theory*. New York, NY.:McGraw-Hill, Inc., 1968.
3. Chang, Raymond. *Physical Chemistry for the Biosciences.* Sausalito, CA. University Science Books, 2005. (498-500)

16.6: The Repulsive Term in the Lennard-Jones Potential is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Lennard-Jones Potential** by Rabia Naeem is licensed CC BY 4.0.

16.7: Van der Waals Constants in Terms of Molecular Parameters

The van der Waals equation can be written as:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

Using the binomial expansion:

$$\frac{1}{1-x} = 1 + x + x^2 + \cdots$$

We can write the van der Waals equation of state as:

$$\begin{aligned} P &= \frac{RT}{\bar{V}}\left[1 + \frac{b}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \cdots\right] - \frac{a}{\bar{V}^2} \\ &= \frac{RT}{\bar{V}} + (RTb - a)\frac{1}{\bar{V}^2} + \frac{RTb^2}{\bar{V}^3} + \cdot \end{aligned}$$

Rearranging in terms of compressibility, Z:

$$Z = \frac{P\bar{V}}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \cdots$$

Comparing to the Viral equation of state, we can see that the second Viral coefficient is related to the van der Waals coefficients:

$$B_{2V}(T) = b - \frac{a}{RT}$$

Using a combination of the hard sphere model and the Lennard-Jones potential, we obtain:

$$u(r) = \begin{cases} \infty & r \leq \sigma \\ -\dfrac{C_6}{r^6} & r > \sigma \end{cases} \tag{16.7.1}$$

We can write the second Virial coefficient as

$$B_2(T) = \frac{2}{3}\pi N_0 \sigma^3 \left[1 - \frac{C_6}{3k_B T \sigma^6}\right] \tag{16.7.2}$$

Let us introduce to simplifying variables

$$b = \frac{2}{3}\pi N_0 \sigma^3 \tag{16.7.3}$$

$$a = \frac{2\pi N_0^2 C_6}{9\sigma^3} \tag{16.7.4}$$

In which the second Virial coefficient becomes:

$$B_2(T) = b - \frac{a}{RT} \tag{16.7.5}$$

From these equations, we can see that a is directly proportional to c_6, the intermolecular attraction between particles with a force proportional to r^{-6}. Likewise, b is equivalent to four times the volume of the particle. In other words, the van der Waals equations assumes the hard sphere model at small distances and weak interactions (attractive forces) at larger distances.

16.7: Van der Waals Constants in Terms of Molecular Parameters is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **16.7: Van der Waals Constants in Terms of Molecular Parameters** is licensed CC BY-NC-SA 4.0.

16.E: The Properties of Gases (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 16 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q16.10

One liter of N_2 (g) at 2.1 bar and two liters of Ar(g) at 3.4 bar are mixed in a 4.0-L flask to form an ideal-gas mixture. Calculate the value of the final pressure of the mixture if the initial and final temperature of the gases are the same. Then, repeat this calculation if the initial temperatures of the N_2 (g) and Ar(g) are 304 K and 402 K, respectively, and the final temperature of the mixture is 377 K. (Assume ideal-gas behavior.)

S16.10

Using the ideal gas law, we can find the number of moles of each gas.

$$n_{N_2} = \frac{P_{N_2}V_{N_2}}{RT} = \frac{(2.1x10^5 Pa) * (1x10^{-3}m^3)}{RT} = \frac{210Pa * m^3}{RT}$$

$$n_{Ar} = \frac{P_{Ar}V_{Ar}}{RT} = \frac{(3.4x10^5 Pa) * (2x10^{-3}m^3)}{RT} = \frac{680Pa * m^3}{RT}$$

The total moles of gas in the final mixture is the sum of the moles of each gas in the mixture, which is

$$\frac{210Pa * m^3}{RT} + \frac{680Pa * m^3}{RT} = \frac{890Pa * m^3}{RT}$$

Therefore,

$$P = \frac{nRT}{V} = \frac{890Pa * m^3}{0.0040m^3} = 2.2x10^5 Pa = 2.2bar$$

Now, considering the initial temperatures of the gases are different from each other and from the final temperature of the mixture, we calculate the total number of moles to be

$$n_{total} = n_{N_2} + n_{Ar} = \frac{210Pa * m^3}{R * (304K)} + \frac{680Pa * m^3}{R * (402K)}$$

Substituting this into the ideal gas law, we get the final pressure to be

$$P = [\frac{210Pa * m^3}{R * (304K)} + \frac{680Pa * m^3}{R * (402K)}] * \frac{R * (377K)}{0.0040m^3} = 2.2x10^5 Pa = 2.2bar$$

Q16.12

What is the molar Gas Constant in units of cm^3 torr K^{-1} mol^{-1}.

S16.12

We know $R = 0.082058L \cdot atm \cdot mol^{-1}K^{-1}$

using dimensional analysis:

$$R = 0.082058L \cdot atm \cdot mol^{-1}K^{-1} \times \frac{760torr}{1atm} \times \frac{1dm^3}{1L} \times \frac{1dm^3}{1000cm^3} \tag{16.E.1}$$

$$R = 0.0623639cm^3 \cdot atm \cdot mol^{-1}K^{-1} \tag{16.E.2}$$

Q16.13

Use the van der Waals equation to plot the compressibility factor, Z, against P for methane for T = 180 K, 189 K, 190 K, 200 K, and 250 K.

S16.13

First, calculate Z as a function of $\bar{V}$ and P as a function of $\bar{V}$ and plot Z versus P

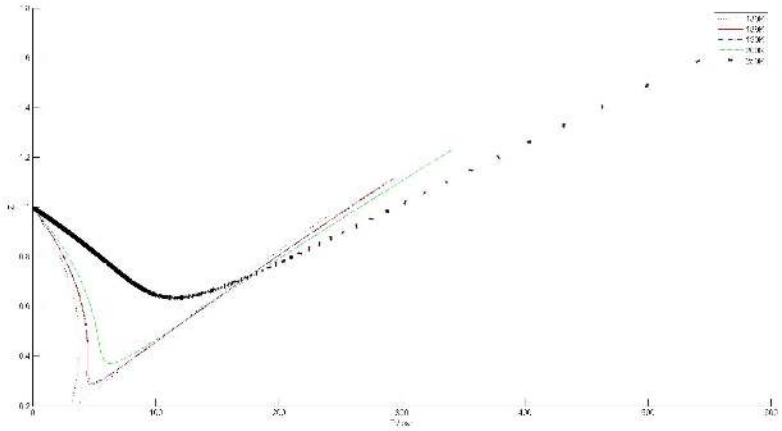
For methane, a = 2.3026 $dm^6 \cdot bar \cdot mol^{-2}$ and b = 0.043067 $dm^3 \cdot mol^{-1}$

$$Z = \frac{P\bar{V}}{RT} \tag{16.E.3}$$

and the van der Waals equation of state is:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \tag{16.E.4}$$

Then create a parametric plot of Z versus P for the suggested temperatures as shown below.



Q16-15

Define the equation that could be solved by using the Netwon-Raphson method to find the molar volume of O2 at 300K and 200atm. Use the van der Waals anf Redlich-Kwong equations.

Constants:

- van der Waals:

$$a = 1.3820 dm^6 * bar * mol, b = 0.031860 dm^3 * mol^{-1} \tag{16.E.5}$$

- Redlich-Kwong:

$$A = 17.411 dm^6 * bar * mol^{-2} * K^{1/2}, B = 0.022082 dm^3 * mol^{-1} \tag{16.E.6}$$

S16.15

Solving van der Waals equation for volume produces:

$$\bar{V}^{3} - (b + \dfrac{RT}{P})\bar{V}^{2} + \dfrac{a}{P}\bar{V} - \dfrac{ab}{P}=0$$

Plugging in constants gives:

$$\bar{V}^{3} - 0.15486\bar{V}^{2} + 0.00691\bar{V} - 0.00022015=0$$

which can be solved numerically to find molar volume.

The Redlich-Kwong equation can be written as a cubic in volume:

$$\bar{V}^{3} - \dfrac{RT}{P}\bar{V}^{2} - \left(B^{2} + \dfrac{BRT}{P} - \dfrac{A}{T^{1/2}P}\right)\bar{V} - \dfrac{AB}{T^{1/2}P} = 0\]

Plugging in constants gives:

$$\bar{V}^{3} - 0.123\bar{V}^{2} + 0.001822\bar{V} - 0.00011099 = 0\]

which can be solved numerically to find molar volume.

Q16.16

Compare the Redlich-Kwong and the van der Waals equations for ethane. Take the molar volume to be 0.09416 .

S16.16

van der Waals:

$$P = \dfrac{RT}{\bar{V}-b}-\dfrac{a}{(\bar{V})^2}\]

Reference Table 16.3 for a, b

$$P = \dfrac{0.083145*400}{.09416-0.065144}-\dfrac{5.5818}{(0.09416)^2}\]

Redlich-Kwong equation of state improved the accuracy of the van der Waals equation by adding a temperature dependence for the attractive term:

$$P = \dfrac{RT}{\bar{V}-B} - \dfrac{A}{T^(\dfrac{1}{2})\bar{V}(\bar{V}+B)}\]

Reference Table 16.4 for A, B

$$P = \dfrac{0.083145*400}{0.09416-0.045153} - \dfrac{98.831}{400^(\dfrac{1}{2})0.09416*(0.09416+0.62723)}\]

Q16.17

$$p = \frac{RT}{\frac{V}{n} - b} - \frac{a}{\sqrt{T}\frac{V}{n}\left(\frac{V}{n} + b\right)} \tag{16.E.7}$$

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{16.E.8}$$

Use the equations above to calculate the temperature of a system with $1.5\ mol$ of methane at $300\ K$ confined to a volume of $100\ cm^3$. Compare the two calculated pressures.

S16.17

$R = 82.057338 \frac{cm^2\ atm}{K\ mol}$

Redlich-Kwong constants: $a = 31.59 \times 10^6\ (atm)(K^{\frac{1}{2}})\left(\frac{cm^3}{mol}\right)^2$ and $b = 29.6\ \frac{cm^3}{mol}$

Van der Waals constants: $a = 2.25 \times 10^6\ (atm)\left(\frac{cm^3}{mol}\right)^2$ and $b = 42.8\ \frac{cm^3}{mol}$

Redlich-Kwong equation: $p = \frac{82.057338\frac{cm^2\ atm}{K\ mol}\ 300\ K}{\frac{100\ cm^3}{1.5\ mol} - 29.6\ \frac{cm^3}{mol}} - \frac{31.59 \times 10^6\ (atm)(K^{\frac{1}{2}})\left(\frac{cm^3}{mol}\right)^2}{\sqrt{300\ K}\frac{100\ cm^3}{1.5\ mol}\left(\frac{100\ cm^3}{1.5\ mol} + 29.6\ \frac{cm^3}{mol}\right)} = 379.95\ atm$

Van der Waals equation: $p = \frac{(1.5\ mol)(82.057338\frac{cm^2\ atm}{K\ mol})(300\ K)}{(100\ cm^3) - (1.5\ mol)(42.8\ \frac{cm^3}{mol})} - \frac{(1.5\ mol)^2(2.25 \times 10^6\ (atm)\left(\frac{cm^3}{mol}\right)^2)}{(100\ cm^3)^2} = 525.2\ atm$

There is a $145.25\ atm$ difference in the calculated pressures.

Q16.20

The following equation can be used to relate the pressure of propane to its density at temperatures below 400 K:

$$P = 33.258\rho - 7.5884\rho^2 + 1.0306\rho^3 - 0.058757\rho^4 - 0.0033566\rho^5 + 0.00060696\rho^6 \tag{16.E.9}$$

where the pressure (P) is in bar and the density (ρ) is in $\frac{mol}{L}$ and ranges from $0\frac{mol}{L} \leq \rho \leq 12.3\frac{mol}{L}$.

Calculate and plot the pressure for the given density range using:

a. the equation given above
b. the Van der Waals equation of state
c. the Redlich-Kwong equation of state

Compare your results from the above parts.

S16.20

a.) Straight forward to calculate.

Even though straight forward, should still put solution for students.



graph plotted using matlab.

b.) The following constants were used in the equation below:

$$a = 9.3919\frac{L^2 bar}{mol^2} \text{ and } b = 0.09049\frac{L}{mol}$$

$$P_{VDW} = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2} \tag{16.E.10}$$

c.) The following constants were used in the equation below:

$$a = 183.01\frac{L^2 bar}{mol^2} \text{ and } b = 0.06272\frac{L}{mol}$$

$$P_{RK} = \frac{RT}{\overline{V} - b} - \frac{a}{\sqrt{T}\overline{V}(\overline{V} + b)} \tag{16.E.11}$$



As can be seen by the plot, the Van der Waals equation of state deviates greatly from the empirical fit at higher densities. The Redlich-Kwong equation provides a reasonable approximation to the empirical data. (All calculations were done in MATLAB, and the above plot was produced by me)

Q16.21

Use the data below to evaluate the van der waals and Redlich Kwong constants for benzene.

Species	T_c/K	P_c/bar	P_c/atm	V_{nc}/L mol^{-1}*	P_cV_{nc}/RT_c
Benzene	561.75	48.758	48.120	0.256	0.26724

*n to indicate molar volume

Van Der Waals

$$a = \frac{27(RT_c)^2}{64P_c} \; and \; b = \frac{RT_c}{8P_c}$$

Redlich-Kwong

$$A = 0.42748\frac{R^2T_c^{\frac{5}{2}}}{P_c} \; and \; B = 0.08664\frac{RT_c}{P_c}$$

S16.21

Van Der Waals

$$\text{a} = \frac{27 * (0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^2}{64 * 48.758 bar} = \mathbf{18.8754\,dm^6 \cdot atm \cdot mol^{-2}}$$

$$\text{b} = \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^2}{8 * 48.758 bar} = \mathbf{5.5927\,dm^3 \cdot mol^{-1}}$$

Redlich-Kwong

$$A = 0.42748 * \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^{\frac{5}{2}}}{48.758 bar} = \mathbf{453.315\,dm^6 \cdot atm \cdot mol^{-2} \cdot K^{\frac{1}{2}}}$$

$$B = 0.42748 * \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^2}{48.758 bar} = \mathbf{19.126\,dm^3 \cdot mol^{-1}}$$

Q16.22

Show that the van der Waals equation for argon at T = 142.69 K and P = 35.00 atm can be written as

$$\overline{V}^3 - 0.3664\overline{V}^2 + 0.001210 = 0 \qquad (16.E.12)$$

where, for convenience, we have suppressed the units in the coefficients. Use the Newton-Raphson method (MathChapter G) to find the three roots to this equation, and calculate the values of the density of liquid and vapor in equilibrium with each other under

these conditions.

S16.22

Using Table 16.3, we can get the values of a and b for argon to use in Van der Waals equation of state.

By doing this, you can isolate $\overline{V}$ in van der Waals equation of state. Next, by applying the Newton-Raphson method to the function given by van der Waals equation (which is only dependent on $\overline{V}$), and the derivative of the function, we find the roots to the equation. On the case here, the smallest root represents the molar volume of liquid argon, and the largest root represents the molar volume of vapor argon.

Q16.23

Calculate the Volume occupied by $50\ kg$ of propane at $50°C$ and $35\ bar$, using the Redlich-Kwong equation of state and the Peng-Robinson equation of state.

S16.23

Redlich-Kwong equation of state:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{16.E.13}$$

v is volume of gas per mole.

we have $T = 50°C = 323\ K$, $P = 35\ bar = 35 \times (10^5) Pa$

For propane, we have $P_c = 42.4924\ bar = 42.4924 \times 10^5 Pa$ and $T_c = 369.522\ K$

so we have $a = \frac{0.42748 R^2 T_c^{2.5}}{P_c T^{0.5}}$;

$b = \frac{0.08664 * R * T_c}{P_c}$

so, $a = \frac{0.42748(8.314^2)369.522^{2.5}}{42.4924\times10^5(323^{0.5})} = 1.015603$

$b = \frac{(0.08664)(8.314)(369.522)}{42.4924\times10^5} = 6.2640829 \times 10^{-5}$

so, $P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$

$(35 * (10^5)) = \frac{(8.314)(323)}{v-(6.2640829\times10^{-5})} - \frac{1.015603}{v(v+6.2640829\times10^{-5})}$

The only real solution is

$v = 0.00010933 \frac{m^3}{mol}$

so In $50\ Kg$ propane, number of moles = $\frac{50*1000}{44.10} = 1133.78684$

total volume occupied by $50\ Kg$ propane at the specified conditions = $(1133.78684)(0.00010933) = 0.1239569 m^3 = 123.9569$ Liters is the answer.

Peng - Robinson's equation of state:

$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}$

$a = 0.45724 R^2 * T_c^2 * \frac{\alpha}{P_c}$

$b = 0.0778 R \frac{T_c}{P_c}$

$\alpha = 1 + S(1 - \sqrt{T_r})$

$S = 0.37464 + 1.54226w - 0.26992w^2$

$T_r = \frac{T}{T_c}$

we have $P = 35 \times 10^5 Pa$ and $T = 323\ K$

$P_c = 42.4924\ bar = 42.4924 \times 10^5 Pa$ and $T_c = 369.522\ K$

we have accentric factor = $w = 0.152$.

$T_r = \frac{T}{T_c} = \frac{323}{369.522} = 0.87410$

$S = 0.37464 + (1.54226)(0.152) - (0.26992)(0.152^2) = 0.602827$

$\alpha = 1 + 0.602827 * (1 - \sqrt{0.87410}) = 1.0392240523$

$a = (0.45724)(8.314^2)(369.522^2)\frac{1.0392240523}{42.4924 \times 10^5} = 1.055462444$

$b = (0.0778)(8.314)\frac{369.522}{42.4924 \times 10^5} = 0.0000562494$

so, by the equation of state:

$(35 \times 10^5) = \frac{(8.314)(323)}{v - 0.0000562494} - \frac{1.055462444}{v(v + 0.0000562494 + 0.0000562494(v - 0.0000562494)}$

$v = 0.0000988504 \frac{m^3}{mol}$

so In $50\ Kg$ propane, number of moles = $\frac{(50)(1000)}{44.10} = 1133.78684$

total volume occupied by $50\ Kg$ propane at the specified conditions = $(1133.78684)(0.0000988504) = 0.1120752 m^3 = 112.0752$ Liters is the answer.

Q16.25

A way to obtain the expressions for the van der Waals constants is to make $(\frac{\partial P}{\partial \bar{V}})_T$ and $(\frac{\partial^2 P}{\partial \bar{V}^2})_T$ zero at the critical point, but why do they equal to zero at critical point? Obtain the equation $\bar{V}_c = 3b$from this procedure.

S16.25

$$(\frac{\partial P}{\partial \bar{V}})_T = 0$$

$$(\frac{\partial^2 P}{\partial \bar{V}^2})_T = 0$$

$$(\frac{\partial P}{\partial \bar{V}})_T = \frac{\partial}{\partial \bar{V}} (\frac{RT}{\bar{V} - b} - \frac{a}{T^2})_T$$

$$= RT (-\frac{1}{(\bar{V} - b)^2}) - a (\frac{-2}{\bar{V}^3})$$

$$= -\frac{RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3}$$

At critical point,

$\frac{RT_c}{(\bar{V}_c - b)^2} = \frac{2a}{\bar{V}_c^3}$ by equating $(\frac{\partial P}{\partial \bar{V}})_T = 0$.

By differentiating the equation $RT (-\frac{1}{(\bar{V} - b)^2}) - a (\frac{-2}{\bar{V}^3})$ with respect to $\bar{V}$,

$$(\frac{\partial^2 P}{\partial \bar{V}^2})_T = \frac{\partial}{\partial \bar{V}} (-\frac{RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3})_T$$

$$= RT (-\frac{2}{(\bar{V} - b)^3}) + 2a (\frac{-3}{\bar{V}^4})$$

$$= \frac{2RT}{(\bar{V} - b)^3} - \frac{6a}{\bar{V}^4}$$

At critical point,

$\frac{2RT_c}{(\bar{V}_c - b)^3} = \frac{6a}{\bar{V}_c^4}$ by equating $(\frac{\partial^2 P}{\partial \bar{V}^2})_T = 0$.

Now,

$$\frac{\frac{2a}{\bar{V}_c^3}}{\frac{6a}{\bar{V}_c^4}} = \frac{\frac{RT_c}{(\bar{V}_c - b)^2}}{\frac{2RT_c}{(\bar{V}_c - b)^3}}$$

$$\frac{\bar{V}_c}{3} = \frac{(\bar{V}_c - b)}{2}$$

$$\bar{V}_c = 3b$$

Q16.26

Show that the Redlich-Kwong equation can be rewritten in the following form:

$$\bar{(V)}^3 - \frac{RT}{P}\bar{V}^2 - (B^2 + \frac{BRT}{P} - \frac{A}{PT^{1/2}})\bar{V} - \frac{AB}{PT^{1/2}} = 0 \qquad (16.E.14)$$

S16.26

Starting with the Redlich-Kwong equation and manipulating it we get the following:

$$P = \frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} \tag{16.E.15}$$

$$P(\bar{V} - B)T^{1/2}\bar{V}(\bar{V} + B) = RT^{3/2}\bar{V}(\bar{V} + B) - A(\bar{V} - B) \tag{16.E.16}$$

$$PT^{1/2}\bar{V}(\bar{V}^2 - B^2) = RT^{3/2}\bar{V}^2 + RT^{3/2}\bar{V}B - A\bar{V} + AB \tag{16.E.17}$$

$$\bar{(V)}^3 - \frac{RT}{P}\bar{V}^2 - (B^2 + \frac{BRT}{P} - \frac{A}{PT^{1/2}})\bar{V} - \frac{AB}{PT^{1/2}} = 0 \tag{16.E.18}$$

Q16.27

Use the results of the previous question, Q16.26, to derive Equations 16.14.

$(a)\bar{V}_c = 3.8473B$, $(b)P_c = .029894\frac{A^{2/3}R^{1/3}}{B^{5/3}}$, and $(c)T_c = .34504\left(\frac{A}{BR}\right)^{2/3}$

The following are solved from Q16.26 and are necessary to solve for Equation 16.14:

$$1)B = .25992\bar{V}_c \tag{16.E.19}$$

$$2)A = 0.42748\frac{R^2T_c^{5/2}}{P_c} \tag{16.E.20}$$

$$3)\frac{P_c\bar{V}_C}{RT_c} = \frac{1}{3} \tag{16.E.21}$$

S16.27

From equation (1) we see that solving for $\bar{V}_c$ yields the first equation

$$\bar{V}_c = 3.8473B \tag{16.E.22}$$

.

From equation (2) we can rewrite the expression with some manipulation as

$$A = .42748RT_c^{3/2}\left(\frac{RT_c}{P_c\bar{V}_c}\right)\bar{V}_c \tag{16.E.23}$$

Substituting equation (3) and 16.14a into the previous equation gives the expression

$$A = 3(.42748)RT_c^{3/2}(3.8473B) \tag{16.E.24}$$

Lastly, solving for T_c gives the equation for 16.14c

$$T_c = .34504\left(\frac{A}{BR}\right)^{2/3} \tag{16.E.25}$$

Finally, solving for equation 16.14b we must substitute the previously solved 16.14c into equation (2),solving for P_c

$$P_c = 0.42748\frac{R^2T_c^{5/2}}{A} \tag{16.E.26}$$
$$= \left(\frac{.42748}{A}\right)R^2\left[.34504\left(\frac{A}{BR}\right)^{2/3}\right]^{5/2} = .029894\frac{A^{2/3}R^{1/3}}{B^{5/3}}$$

which is equation 16.14b.

Q16.28

Derive the Van der Waals cubic equation of state from

$$\left(P+\frac{a}{\bar{V}^2}\right)\left(\bar{V}-b\right)=RT \tag{16.E.27}$$

S16.28

The Van der Waal equation can be rewritten in terms of Z:

$$Z=\frac{P\bar{V}}{RT}=\frac{\bar{V}}{\bar{V}-b}-\frac{a}{RT\bar{V}} \tag{16.E.28}$$

solving for $\bar{V}$

$$\bar{V}^3-\left(b+\frac{RT}{P}\right)\bar{V}^2+\frac{a}{P}\bar{V}-\frac{ab}{P}=0 \tag{16.E.29}$$

16.E: The Properties of Gases (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

17: Boltzmann Factor and Partition Functions

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Chem 110A ● Chem 110B ● Chem 110C ● **Agenda ● Homework ● Worksheet Activities**

Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc. Statistical Mechanics provides the microscopic basis for thermodynamics, which, otherwise, is just a phenomenological theory. Microscopic basis allows calculation of a wide variety of properties not dealt with in thermodynamics, such as structural properties, using distribution functions, and dynamical properties – spectra, rate constants, etc., using time correlation functions. Because a statistical mechanical formulation of a problem begins with a detailed microscopic description, microscopic trajectories can, in principle and in practice, be generated providing a window into the microscopic world. This window often provides a means of connecting certain macroscopic properties with particular modes of motion in the complex dance of the individual atoms that compose a system, and this, in turn, allows for interpretation of experimental data and an elucidation of the mechanisms of energy and mass transfer in a system.

17.1: The Boltzmann Factor Is One of the Most Important Quantities in the Physical Sciences

17.2: The Thermal Boltzman Distribution

17.3: We Postulate That the Average Ensemble Energy Is Equal to the Observed Energy of a System

17.4: The Heat Capacity at Constant Volume

17.5: Express the Pressure in Terms of a Partition Function

17.6: Partition Functions of Systems of Distinguishable Molecules are Products of Molecular Partition Functions

17.7: Partition Function of Indistinguishable Components

17.8: A Molecular Partition Function Can Be Decomposed into Partition Functions for Each Degree of Freedom

17.E: Exercises

17: Boltzmann Factor and Partition Functions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

17.1: The Boltzmann Factor Is One of the Most Important Quantities in the Physical Sciences

Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc.

The Microscopic Laws of Motion

Consider a system of N classical particles. The particles are confined to a particular region of space by a container of volume V. In classical mechanics, the state of each particle is specified by giving its position and its velocity, i.e., by telling where it is and where it is going. The position of particle i is simply a vector of three coordinates $r_i = (x_i, y_i, z_i)$, and its velocity $\mathbf{v}_i$ is also a vector $(v_{x_i}, v_{y_i}, v_{z_i})$ of the three velocity components. Thus, if we specify, at any instant in time, these six numbers, we know everything there is to know about the state of particle i.

The particles in our system have a finite kinetic energy and are therefore in constant motion, driven by the forces they exert on each other (and any external forces which may be present). At a given instant in time t, the Cartesian positions of the particles are $\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t)$, and the velocities at t are related to the positions by differentiation:

$$\mathbf{v}_i(t) = \frac{d\mathbf{r}_i}{dt} = \dot{\mathbf{r}}_i \tag{17.1.1}$$

In order to determine the positions and velocities as function of time, we need the classical laws of motion, particularly, Newton's second law. Newton's second law states that the particles move under the action of the forces the particles exert on each other and under any forces present due to external fields. Let these forces be denoted $\mathbf{F}_1, \mathbf{F}_2, \ldots, \mathbf{F}_N$. Note that these forces are functions of the particle positions:

$$\mathbf{F}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{17.1.2}$$

which is known as a force field (because it is a function of positions). Given these forces, the time evolution of the positions of the particles is then given by Newton's second law of motion:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

where $\mathbf{F}_1, \ldots, \mathbf{F}_N$ are the forces on each of the N particles due to all the other particles in the system. The notation $\ddot{\mathbf{r}}_i = d^2\mathbf{r}_i/dt^2$.

N Newton's equations of motion constitute a set of $3N$ coupled second order differential equations. In order to solve these, it is necessary to specify a set of appropriate initial conditions on the coordinates and their first time derivatives, $\{\mathbf{r}_1(0), \ldots, \mathbf{r}_N(0), \dot{\mathbf{r}}_1(0), \ldots, \dot{\mathbf{r}}_N(0)\}$. Then, the solution of Newton's equations gives the complete set of coordinates and velocities for all time t.

The Ensemble Concept (Heuristic Definition)

For a typical macroscopic system, the total number of particles is $N \sim 10^{23}$. Since an essentially infinite amount of precision is needed in order to specify the initial conditions (due to exponentially rapid growth of errors in this specification), the amount of information required to specify a trajectory is essentially infinite. Even if we content ourselves with quadrupole precision, however, the amount of memory needed to hold just one phase space point would be about 128 bytes $= 2^7 \sim 10^2$ bytes for each number or $10^2 \times 6 \times 10^{23} \sim 10^{17}$ gigabytes which is also 10^2 yottabytes! The largest computers we have today have perhaps 10^6 gigabytes of memory, so we are off by 11 orders of magnitude just to specify 1 classical state.

Fortunately, we do not need all of this detail. There are enormous numbers of microscopic states that give rise to the same macroscopic observable. Let us again return to the connection between temperature and kinetic energy:

$$\frac{3}{2}NkT = \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2 \tag{17.1.3}$$

which can be solved to give:

$$T = \frac{2}{3k}\left(\frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}m_i v_i^2\right) \tag{17.1.4}$$

Here we see that T is related to the average kinetic energy of all of the particles. We can imagine many ways of choosing the particle velocities so that we obtain the same average. One is to take a set of velocities and simply assign them in different ways to the N particles, which can be done in $N!$ ways. Apart from this, there will be many different choices of the velocities, themselves, all of which give the same average.

Since, from the point of view of macroscopic properties, precise microscopic details are largely unimportant, we might imagine employing a construct known as the *ensemble concept* in which a large number of systems with different microscopic characteristics but similar macroscopic characteristics is used to "wash out" the microscopic details via an averaging procedure. This is an idea developed by individuals such as Gibbs, Maxwell, and Boltzmann.

Consider a large number of systems each described by the same set of microscopic forces and sharing a common set of macroscopic thermodynamic variables (e.g. the same total energy, number of moles, and volume). Each system is assumed to evolve under the microscopic laws of motion from a different initial condition so that the time evolution of each system will be different from all the others. Such a collection of systems is called an *ensemble*. The ensemble concept then states that macroscopic observables can be calculated by performing averages over the systems in the ensemble. For many properties, such as temperature and pressure, which are time-independent, the fact that the systems are evolving in time will not affect their values, and we may perform averages at a particular instant in time.

The questions that naturally arise are:

1. How do we construct an ensemble?
2. How do we perform averages over an ensemble?
3. How do we determine which thermodynamic properties characterize an ensemble?
4. How many different types of ensembles can we construct, and what distinguishes them?

These questions will be addresses in the sections ahead.

Thermal energy

A confined monatomic gas can be seen as a box with a whole bunch of atoms in it. Each of these particles can be in one of the states given by the last formula. If all of them have large n values there is obviously a lot of kinetic energy in the system. The lowest energy is when all atoms have 1,1,1 as quantum numbers. Boltzmann realized that this should relate to temperature. When we add energy to the system (by heating it up without changing the volume of the box), the temperature goes up. At higher temperatures we would expect higher quantum numbers, and at lower T, lower ones. But how exactly are the atoms distributed over the various states?

This is a good example of a problem involving a discrete probability distribution. The probability that a certain level (e.g., $n = (n_1, n_2, n_3)$ with energy E_i) is occupied should be a function of temperature: $P_i(T)$. Boltzmann postulated that you could look at temperature as a form of energy. The thermal energy of a system is directly proportional to an absolute temperature.

$$E_{thermal} = kT$$

The proportionality constant k (or k_B) is named after him: the Boltzmann constant. It plays a central role in all statistical thermodynamics. The Boltzmann factor is used to approximate the fraction of particles in a large system. The Boltzmann factor is given by:

$$e^{-\beta E_i} \tag{17.1.5}$$

where:

- E_i is the energy in the state i,
- T is the kelvin temperature, and
- k is Boltzmann constant.

As the following section demonstrates, the term β in Equation 17.1.5 is expressed as:

$$\beta = \frac{1}{kT}$$

The rates of many physical processes are also determined by the Boltzmann factor. For a random particle, its thermal energy of a particle is a small multiple of the energy kT. An increase in temperature results in more particles crossing the energy barrier characteristic of activation processes. If this is to occur, particles need to carry sufficient energy. This energy is needed for the particles to successfully cross the energy barrier and is usually called activation energy. The fraction of molecules that have sufficient energy to escape the original material surface is approximately proportional to the Boltzmann factor.

References

1. Hakala, R.W. (1961). A new derivation of the Boltzmann distribution law. *Journal of Chemical Education.* **doi:** 10.1021/ed038p33.
2. Claudio Fazio, Onofrio R Battaglia, Ivan Guastella. (2012).Two experiments to approach the Boltzmann factor: chemical reaction and viscous flow. *European Journal of Physics*, *33*, *2*, *359*.doi:10.1088/0143-0807/33/2/359.

Problems

1. How are temperature and the average energy per particle for a system related?
2. What does the Boltzmann factor tell you? Why is it important?
3. When is it possible for particles to get extra energy?
4. Give three examples of activation processes.
5. What do "separate arrangements" mean? What are the differences between these arrangements?

17.1: The Boltzmann Factor Is One of the Most Important Quantities in the Physical Sciences is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System** by Mark Tuckerman is licensed CC BY 4.0.

17.2: The Thermal Boltzman Distribution

Consider a N-particle ensemble. The particles are not necessarily indistinguishable and possibly have mutual potential energy. Since this is a large system, there are many different ways to arrange its particles and yet yield the same thermodynamic state. Only one arrangement can occur at a time. The sum of the probabilities of each separate arrangement equals the total number of separate arrangements. Then the probability of a system is:

$$p_N = W_N p_i$$

where p_N is the probability of the system, W_N is the total number of different possible arrangements of the N particles in the system, and p_i is the probability of each separate arrangement. Heisenberg's uncertainty principle states that it is impossible to simultaneously know the momentum and the position of an object with complete precision. In agreement with the uncertainty principle, the total possible number of combinations can be defined as the total number of distinguishable rearrangements of the N particles.

The most practical ensemble is the canonical ensemble with N, V, and T fixed. We can imagine a collection of boxes with equal volumes and number of particles with the entire collection kept in thermal equilibrium. Based on the Boltzmann factor, we know that for a system that has states with energies e_1, e_2, e_3..., the probability p_j that the system will be in the state j with energy E_j is exponentially proportional to the energy of state j. The partition functions of the state places a very important role in calculating the properties of a system, for example, it can be used to calculate the probability, as well as the energy, heat capacity, and pressure.

The Boltzmann Distribution

We are ultimately interested in the probability that a given distribution will occur. The reason for this is that we must have this information in order to obtain useful thermodynamic averages. Let's consider an ensemble of A systems. We will define a_j as the number of systems in the ensemble that are in the quantum state j. For example, a_1 represents the number of systems in the quantum state 1. The total number of possible microstates is:

$$W(a_1, a_2, ...) = \frac{A!}{a_1! a_2! ...}$$

The overall probability that P_j that a system is in the jth quantum state is obtained by averaging a_j/A over all the allowed distributions. Thus, P_j is given by:

$$P_j = \frac{\langle a_j \rangle}{A}$$
$$= \frac{1}{A} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)}$$

where the angle brackets indicate an ensemble average. Using this definition we can calculate any average property (i.e. any thermodynamic property):

$$\langle M \rangle = \sum_j M_j P_j \tag{17.2.1}$$

The method of the most probable distribution is based on the idea that the average over P_j is **identical** to the most probable distribution. Physically, this results from the fact that we have so many particles in a typical system that the fluctuations from the mean are extremely (immeasurably) small. The equivalence of the average probability of an occupation number and the most probable distribution is expressed as follows:

$$P_j = \frac{\langle a_j \rangle}{A} = \frac{a_j}{A}$$

The probability function is subject to the following constraints:

- Constraint 1: Conservation of energy requires:

$$E_{total} = \sum_j a_j e_j \tag{17.2.2}$$

where e_j is the energy of the jth quantum state.

- Constraint 2: Conservation of mass requires:

$$A = \sum_j a_j \tag{17.2.3}$$

which says only that the total number of all of the systems in the ensemble is A.

As we will learn in later chapters, the system will tend towards the distribution of a_j that maximizes the total number of microstates. This can be expressed as:

$$\sum_j \left(\frac{\partial \ln W}{\partial a_j} \right) = 0$$

Our constraints becomes:

$$\sum_j e_j da_j = 0$$

$$\sum_j da_j = 0$$

The method of Lagrange multipliers (named after Joseph Louis Lagrange is a strategy for finding the local maxima and minima of a function subject to equality constraints. Using the method of LaGrange undetermined multipliers we have:

$$\sum_j \left[\left(\frac{\partial \ln W}{\partial a_j} \right) da_j + \alpha da_j - \beta e_j da_j \right] = 0$$

We can use Stirling's approximation:

$$\ln x! \approx x \ln x – x$$

to evaluate:

$$\left(\frac{\partial \ln W}{\partial a_j} \right)$$

to get:

$$\left(\frac{\partial A!}{\partial a_j} \right) - \sum_i \left(\frac{\partial \ln a_i}{\partial a_j} \right) = 0$$

as outlined below.

Application of Stirling's Approximation

First step is to note that:

$$\ln W = \ln A! - \sum_j \ln a_j ! a \approx A \ln A – A - \sum_j a_j \ln a_j - \sum_j a_j$$

Since (from Equation 17.2.3):

$$A = \sum_j a_j$$

these two cancel to give:

$$\ln W = A \ln A - \sum_j a_j \ln a_j$$

The derivative is:

$$\left(\frac{\partial \ln W}{\partial a_j}\right) = \frac{\partial A \ln A}{\partial a_j} - \sum_i \frac{\partial a_i \ln a_i}{\partial a_j}$$

Therefore we have:

$$\left(\frac{\partial A \ln A}{\partial a_j}\right) = \frac{\partial A}{\partial a_j}\ln A - \frac{\partial A}{\partial a_j} = \ln A - 1$$

$$\left(\frac{\partial a_i \ln a_i}{\partial a_j}\right) = \frac{\partial a_i}{\partial a_j}\ln a_i - \frac{\partial a_i}{\partial a_j} = \ln a_j + 1$$

These latter derivatives result from the fact that:

$$\left(\frac{\partial a_i}{\partial a_i}\right) = 1$$

$$\left(\frac{\partial a_j}{\partial a_i}\right) = 0$$

The simple expression that results from these manipulations is:

$$-\ln\left(\frac{a_j}{A}\right) + \alpha - \beta e_j = 0$$

The most probable distribution is:

$$\frac{a_j}{A} = e^{\alpha}\sum_j e^{-\beta e_j} \tag{17.2.4}$$

Now we need to find the undetermined multipliers α and β.

The left hand side of Equation 17.2.4 is 1. Thus, we have:

$$P_j = \frac{a_j}{A} = \frac{e^{-\beta e_j}}{\sum_j e^{-\beta e_j}}$$

This determines α and defines the Boltzmann distribution. We will show that β from the optimization procedure of method of Lagrange multipliers is:

$$\beta = \frac{1}{kT}$$

This identification will show the importance of temperature in the Boltzmann distribution. The distribution represents a thermally equilibrated most probable distribution over all energy levels (Figure 17.2.1).

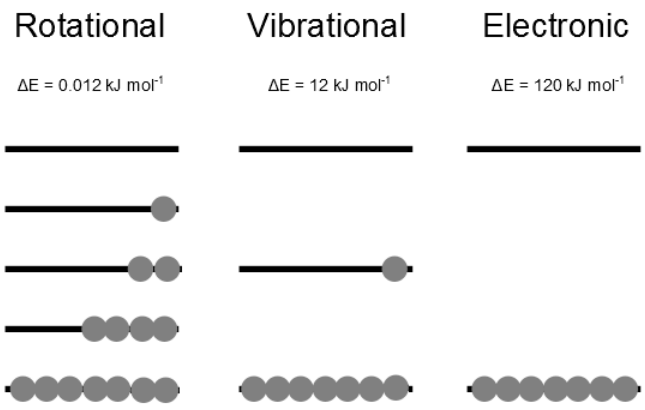


Figure 17.2.1 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. k_BT 2.5 $kJ\ mol^{-1}$ at 300 K. (CC SA-BY 3.0; Mysterioso via Wikiversity).

Boltzmann Distribution

The Boltzmann distribution represents a thermally equilibrated **most probable** distribution over all energy levels. There is always a **higher** population in a state of lower energy than in one of higher energy.

Once we know the probability distribution for energy, we can calculate thermodynamic properties like the energy, entropy, free energies and heat capacities, which are all average quantities (Equation 17.2.1). To calculate P_j, we need the energy levels of a system (i.e., $\{e_i\}$). The energy ("levels") of a system can be built up from the quantum energy levels

> *It must always be remembered that no matter how large the energy spacing is, there is always a non-zero probability of the upper level being populated. The only exception is a system that is at absolute zero. This situation is however hypothetical as absolute zero can be approached but not reached.*

Partition Function

The sum over all factors $e^{-\beta e_j}$ is given a name. It is called the molecular partition function, q:

$$q = \sum_j e^{-\beta e_j}$$

The molecular partition function q gives an indication of the average number of states that are thermally accessible to a molecule at the temperature of the system. The partition function is a sum over states (of course with the Boltzmann factor β multiplying the energy in the exponent) and is a number. Larger the value of q, larger the number of states which are available for the molecular system to occupy (Figure 17.2.2).

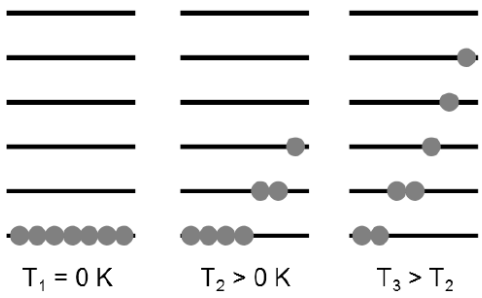


Figure 17.2.2 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. (CC SA-BY 3.0; Mysterioso via Wikiversity).

We distinguish here between the partition function of the ensemble, Q and that of an individual molecule, q. Since Q represents a sum over all states accessible to the system it can written as:

$$Q(N,V,T) = \sum_{i,j,k\ldots} e^{-\beta(e_i+e_j+e_k\ldots)}$$

where the indices i, j, k represent energy levels of **different** particles.

Regardless of the type of particle the molecular partition function, q represents the energy levels of one individual molecule. We can rewrite the above sum as:

$$Q = q_i q_j q_k \ldots$$

or:

$$Q = q^N$$

for N particles. Note that q_i means a sum over states or energy levels accessible to molecule i and q_j means the same for molecule j. The molecular partition function, q counts the energy levels accessible to molecule i only. Q counts not only the states of all of the

molecules, but all of the possible combinations of occupations of those states. However, if the particles are not distinguishable then we will have counted $N!$ states too many. The factor of $N!$ is exactly how many times we can swap the indices in $Q(N,V,T)$ and get the same value (again provided that the particles are not distinguishable). See this video for more information.

References

1. Hakala, R.W. (1967). Simple justification of the form of Boltzmann's distribution law. *Journal of Chemical Education. 44(11), 657.* **doi:** 10.1021/ed044p657
2. Grigorenko, I, Garcia, M.E. (2002). Calculation of the partition function using quantum genetic algorithms. Physica A: Satistical Mechanics and its Applications. 313. 463-470. Retrieved from http://www.sciencedirect.com/science...78437102009883

Problems

1. Complete the justification of Boltzmann's distribution law by computing the proportionality constant a.
2. A system contains two energy levels E_1, E_2. Using Boltzmann statistics, express the average energy of the system in terms of E_1, E_2.
3. Consider a system contains N energy levels. Redo problem #2.
4. Use the property of exponential function, derive equation (17.9).
5. What are the uses of partition functions?

17.2: The Thermal Boltzman Distribution is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution** by Jerry LaRue is licensed CC BY 4.0.

17.3: We Postulate That the Average Ensemble Energy Is Equal to the Observed Energy of a System

We will be restricting ourselves to the canonical ensemble (constant temperature and constant pressure). Consider a collection of N molecules. The probability of finding a molecule with energy E_i is equal to the fraction of the molecules with energy E_i. That is, in a collection of N molecules, the probability of the molecules having energy E_i:

$$P_i = \frac{n_i}{N}$$

This is the directly obtained from the Boltzmann distribution, where the fraction of molecules n_i/N having energy E_i is:

$$P_i = \frac{n_i}{N} = \frac{e^{-E_i/kT}}{Q} \tag{17.3.1}$$

The average energy is obtained by multiplying E_i with its probability and summing over all i:

$$\langle E \rangle = \sum_i E_i P_i \tag{17.3.2}$$

> Equation 17.3.2 is the standard average over a distribution commonly found in quantum mechanics as expectation values. The quantum mechanical version of this Equation is
>
> $$\langle \psi | \hat{H} | \psi \rangle$$
>
> where Ψ^2 is the distribution function that the Hamiltonian operator (e.g., energy) is averaged over; this equation is also the starting point in the Variational method approximation.

Equation 17.3.2 can be solved by plugging in the Boltzmann distribution (Equation 17.3.1):

$$\langle E \rangle = \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{17.3.3}$$

Where Q is the partition function:

$$Q = \sum_i e^{-\frac{E_i}{kT}}$$

We can take the derivative of $\ln Q$ with respect to temperature, T:

$$\left(\frac{\partial \ln Q}{\partial T}\right) = \frac{1}{kT^2} \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{17.3.4}$$

Comparing Equation 17.3.3 with 17.3.4, we obtain:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)$$

It is common to write these equations in terms of β, where:

$$\beta = \frac{1}{kT}$$

The partition function becomes:

$$Q = \sum_i e^{-\beta E_i}$$

We can take the derivative of $\ln Q$ with respect to β:

$$\left(\frac{\partial \ln Q}{\partial \beta}\right) = -\sum_i \frac{E_i e^{-\beta E_i}}{Q}$$

And obtain:

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

Replacing $1/kT$ with β often simplifies the math and is easier to use.

> It is not uncommon to find the notation changes: Z instead of Q and $\bar{E}$ instead of $\langle E \rangle$.

17.3: We Postulate That the Average Ensemble Energy Is Equal to the Observed Energy of a System is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.3: The Average Ensemble Energy is Equal to the Observed Energy of a System** by Jerry LaRue is licensed CC BY 4.0.

17.4: The Heat Capacity at Constant Volume

The heat capacity at constant volume (C_V) is defined to be the change in internal energy with respect to temperature:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{17.4.1}$$

Since:

$$E = -\frac{\partial \ln Q(N,V,\beta)}{\partial \beta} \tag{17.4.2}$$

We see that:

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T} \\ &= \frac{\partial U}{\partial \beta}\frac{\partial \beta}{\partial T} \\ &= \frac{1}{kT^2}\frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \\ &= k\beta^2\frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \end{aligned} \tag{17.4.3}$$

where k is the Boltzmann constant. Energy can be stored in materials/gases via populating the specific degrees of freedom that exist in the sample. Understanding how this occurs requires the usage of Quantum Mechanics.

Dulong-Petit Law on the Heat Capacities of Solids

Pierre Louis Dulong and Alexis Thèrèse Petit conducted experiments in 1819 on three dimensional solid crystals to determine the heat capacities of a variety of these solids (Heat capacity is the solids ability to absorb and retain heat). Dulong and Petit discovered that all investigated solids had a heat capacity of approximately 2.49 x 10^4 J kilomole^{-1} K^{-1} at around 298 K or room temperature. The result from their experiment was explained by considering every atom inside the solid as an oscillator with six degrees of freedom (an oscillator can be thought of as a spring connecting all the atoms in the solid lattice). These springs extend into three dimensional space. The more energy that is added to the solid the more these springs vibrate. Each atom has an energy of $\frac{1}{2}kT$, where k is the Boltzmann constant and T is the absolute temperature. Thus,

$$C_V = \frac{6R}{2} = 3R \qquad \text{(Dulong-Petit Law)}$$

The number 6 in this equation is the number of degrees of freedom for the molecule. Petit and Dulong suggested that these results supported their foundation for the heat capacity of solids. The explanation for Petit and Dulong's experiment was not sufficient when it was discovered that heat capacity decreased as temperature approached absolute zero. The degrees of freedom do not slow down or cease to move when the solid reaches a sufficiently cold temperature. An additional model was proposed to explain this deviance. Two main theories were developed to explain this puzzling deviance in the heat capacity experiments. The first was constructed by Einstein and the second was authored by Debye.

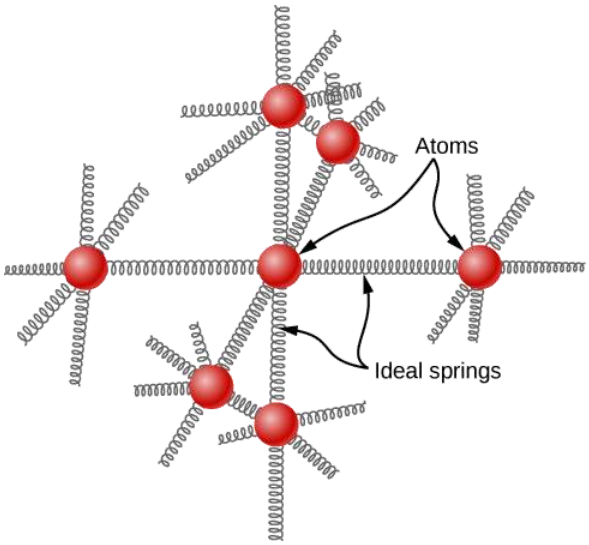


Figure 17.4.1 : In a simple model of a solid element, each atom is attached to others by six springs, two for each possible motion: x, y, and z. Each of the three motions corresponds to two degrees of freedom, one for kinetic energy and one for potential energy. (CC BY-SA 4.0; OpenStax).

Einstein's Theory on the Heat Capacities of Solids

Einstein assumed three things when he investigated the heat capacity of solids. First, he assumed that each solid was composed of a lattice structure consisting of N atoms. Each atom was treated as moving independently in three dimensions within the lattice (3 degrees of freedom). This meant that the entire lattice's vibrational motion could be described by a total of $3N$ motions, or degrees of freedom. Secondly, he assumed that the atoms inside the solid lattice did not interact with each other and thirdly, all of the atoms inside the solid vibrated at the same frequency. The third point highlights the main difference in Einstein's and Debye's two models.

Einstein's first point is accurate because the experimental data supported his hypothesis, however his second point is not because if atoms inside a solid could not interact, sound could not propagate through it. For example, a tuning fork's atoms, when struck, interact with one another to create sound which travels through air to the listener's ear. Atoms also interact in a solid when they are heated. Take for example a frying pan. If the pan is heated on one side, the heat transfers throughout the metal effectively warming the entire pan. Molecules that make up the frying pan interact to transfer heat. Much in the same way the oscillators in a solid interact when energy is added to the system. The extent of these interactions lead to the physically observed heat capacity.

The heat capacity of a solid at a constant volume is

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= 3Nk\left(\frac{\theta_E}{T}\right)^2 \\ &= \frac{\exp\left(\frac{\theta_E}{T}\right)}{\left(\exp\frac{\theta_E}{T}-1\right)^2} \end{aligned}$$

where

- $\theta_E = \frac{h\nu}{k}$ is the **Einstein temperature**,
- h is Planck's constant,
- k is Boltzmann's constant, and
- ν is the oscillator frequency of the atoms inside the solid.

The Einstein temperature's accessibility of the vibrational energy inside of a solid molecule determines the heat capacity of that solid. The greater the accessibility the greater the heat capacity. If the vibrational energy is easily accessible the collisions in the molecule have a greater probability of exciting the atom into an upper vibrational level. This is displayed below.

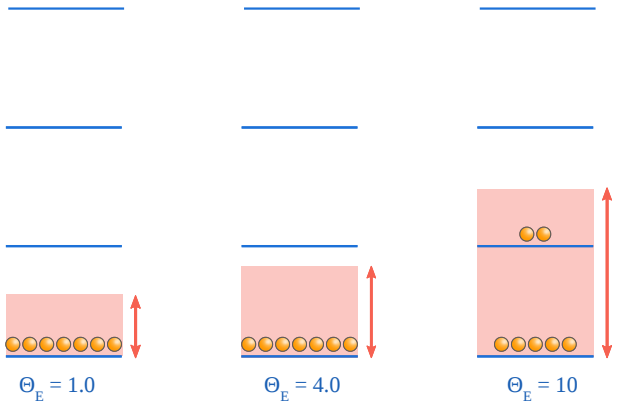


Figure 17.4.2 : This Figure illustrates the effect of the Einstein temperature on the likelihood of an oscillator absorbing energy from a collision and transferring that energy into stored heat or heat capacity. As the Einstein temperature increases, the greater the probability of an oscillator being excited to the next vibrational state. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

So the Einstein temperature specifically indicates the probability that a molecule has in its degrees of freedom to store energy in its atomic oscillators (or bonds). Comparing the Einstein temperature to the traditional classical values of Heat capacity will illustrate the differences the specific strengths (high temperature) and weaknesses (low temperature) of the Einstein model.

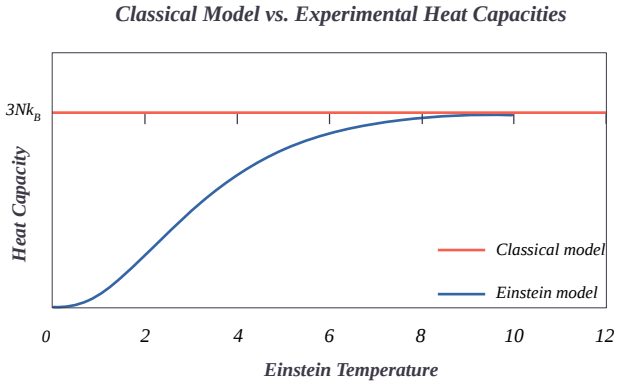


Figure 17.4.3 :This graph shows the accuracy of the of the Einstein temperature at low temperatures. The classical model is effective at temperatures above 10 Einstein Temperatures. (Cc BY-NC; Ümit Kaya via LibreTexts)

Thus, in the high temperature limit ($\frac{\theta_E}{T} \ll 1$) (i.e., the temperature is very large compared to the Einstein temperature) then

$$C_V \approx 3Nk = 3nR. \tag{17.4.4}$$

Einstein's model reveals the accuracy of the Petit and Dulong model and models high temperatures accurately. However, just as Petit and Dulong's model decreased in accuracy as the temperature decreased, so followed Einstein's.

When examining the extremely low temperature limit: $\frac{\theta_E}{T} \gg 1$, it can be seen:

$$C_V = 3Nk\left(\frac{\theta_E}{T}\right)^2 e^{\frac{-\theta_E}{T}} \tag{17.4.5}$$

As temperature (T) goes to zero, the exponential portion of the above equation goes to zero and therefore C_V also approaches zero. This supports the experimental values as temperature approaches zero the heat capacity of the solid likewise decreases to zero.

Einstein's theory also explains solids that exhibit a low heat capacity even at relatively high temperatures. An example of such a solid is diamond. The heat capacity of diamond approaches $3Nk$ as temperature greatly increases. Einstein's model supports this through the definition of an Einstein temperature. As the Einstein temperature increases, ν must increase likewise. This is the

equivalent of each atom possessing more energy and therefore vibrating more rapidly within the solid itself. The oscillator frequency, ν, can be written as:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}} \tag{17.4.6}$$

where κ is the force constant and μ is the reduced mass. This formula better predicts solids with high force constants or low reduced masses. This corrects deviations from the Petit and Dulong model.

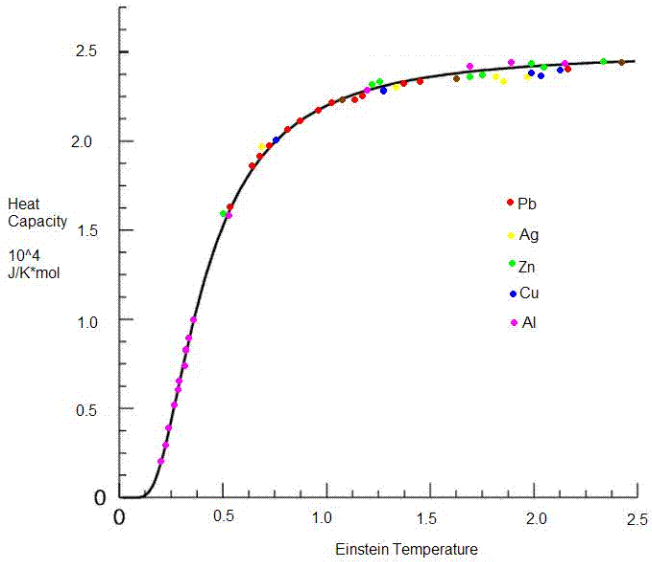


Figure 17.4.4 . This graph indicates the heat capacity of several solid metals as a function of the Einstein temperature: $\theta_E = \frac{h\nu}{k_B}$.

Essentially the Einstein temperature allows for the heat capacity equation and the vibrational frequencies in the solid to change as the temperature changes. This effectively adjusts for the deviations seen in the Petit/Dulong model. As the temperature increases or decreases, the Einstein temperature increases or decreases likewise to mirror the actual physical activity within the solid.

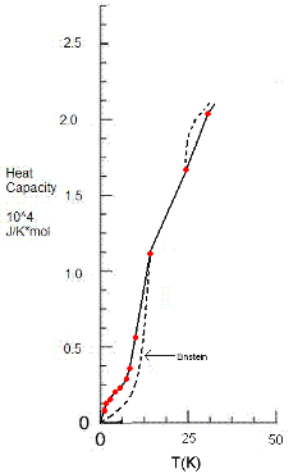


Figure 17.4.5 . This plot shows the heat capacity of lead compared to the expected values calculated from Einstein's model.

Einstein's model predicts relatively low temperatures well. However, when decreasing from approximately 15 K, Einstein's model deviates from experimental values. Also, this can be observed, although not as dramatically, for temperatures from 25 K to 30 K. Clearly a term or correction is still missing from Einstein's model to increase its accuracy.

17.4: The Heat Capacity at Constant Volume is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.4: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature** by Jerry LaRue is licensed CC BY-NC-SA 4.0.

17.5: Express the Pressure in Terms of a Partition Function

Pressure can also be derived from the canonical partition function. The average pressure is the sum of the probability times the pressure:

$$\langle P \rangle = \sum_i P_i(N,V,T) P_i(N,V)$$

The pressure of a macroscopic system is:

$$P(N,V) = -\left(\frac{\partial E_i}{\partial V}\right)_N$$

So we can write the average pressure as:

$$\begin{aligned}\langle P \rangle &= \sum_i P_i(N,V,\beta)\left(-\frac{\partial E_i}{\partial V}\right)_N \\ &= \sum_i \left(-\frac{\partial E_i}{\partial V}\right)_N \frac{e^{-E_i(N,V)/kT}}{Q(N,V,T)}\end{aligned}$$

In a few steps we can show that the temperature can be expressed in terms of the partition function:

$$Q(N,V,T) = \sum_i e^{-E_i(N,V)/kT}$$

Writing in terms of β instead of temperature:

$$Q(N,V,\beta) = \sum_i e^{-\beta E_i(N,V)}$$

The derivative of the partition function with respect to volume is:

$$\left(\frac{\partial Q}{\partial V}\right)_{N,\beta} = -\beta \sum_i \left(\frac{\partial E_i}{\partial V}\right)_N e^{-\beta E_i(N,V)}$$

The average pressure can then be written as:

$$\langle P \rangle = \frac{kT}{Q(N,V,\beta)}\left(\frac{\partial Q}{\partial V}\right)_{N,\beta}$$

Which shows that the pressure can be expressed solely terms of the partition function:

$$\langle P \rangle = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

We can use this result to derive the ideal gas law. For N particles of an ideal gas:

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!}$$

where:

$$q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V$$

is the translational partition function. The utility of expressing the pressure as a logarithm is clear from the fact that we can write:

$$\begin{aligned}\ln Q &= N \ln q - \ln N! \\ &= -\frac{3N}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right) + N \ln V - \ln N!\end{aligned}$$

We have used the property of logarithms that $\ln(AB) = \ln(A) + \ln(B)$ and $\ln(X^Y) = Y \ln(X)$. Only one term in the ln Q depends on V. Taking the derivative of $N \ln V$ with respect to V gives:

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N}{V}$$

Substituting this into the above equation for the pressure gives:

$$P = \frac{NkT}{V}$$

which is the ideal gas law. Recall that $Nk = nR$ where N is the number of molecules and n is the number of moles. R is the universal gas constant (8.314 J/mol-K) which is nothing more than k multiplied by Avagadro's number. $N_A k = R$ converts the constant from a "per molecule" to a "per mole" basis.

Gas Compressed by a Piston

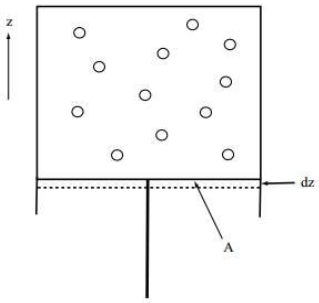


Figure 17.5.1 : Illustration of a thought experiment in which a system is compressed via a piston pushed into the system along the positive z axis.

Let us consider a simple thought experiment, which is illustrated in the figure above: A system of N particles is compressed by a piston pushing in the positive z direction. Since this is a classical thought experiment, we think in terms of forces. The piston exerts a constant force of magnitude F on the system. The direction of the force is purely in the positive z direction, so that we can write the force vector $\mathbf{F}$ as $\mathbf{F} = (0, 0, F)$. At equilibrium (the piston is not moving), the system exerts an equal and opposite force on the piston of the form $(0, 0, -F)$. If the energy of the system is E, then the force exerted by the system on the piston will be given by the negative change in E with respect to z:

$$-F = -\frac{dE}{dz} \tag{17.5.1}$$

or:

$$F = \frac{dE}{dz} \tag{17.5.2}$$

The force exerted by the system on the piston is manifest as an observable pressure P equal to the force F divided by the area A of the piston, $P = F/A$. Given this, the observed pressure is just:

$$P = \frac{dE}{Adz} \tag{17.5.3}$$

Since the volume decreases when the system is compressed, we see that $Adz = -dV$. Hence, we can write the pressure as $P = -dE/dV$.

Of course, the relation $P = -dE/dV$ is a thermodynamic one, but we need a function of x that we can average over the ensemble. The most natural choice is:

$$p(x) = -\frac{d\mathcal{E}(x)}{dV} \tag{17.5.4}$$

so that $P = \langle p(x) \rangle$. Setting up the average, we obtain:

$$P = -\frac{C_N}{Q(N,V,T)} \int \frac{\partial \mathcal{E}}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{17.5.5}$$

$$= \frac{C_N}{Q(N,V,T)} \frac{1}{\beta} \int \frac{\partial}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{17.5.6}$$

$$= \frac{kT}{Q(N,V,T} \frac{\partial}{\partial V} C_N \int e^{-\beta \mathcal{E}(x)} \tag{17.5.7}$$

$$= kT \left(\frac{\partial \ln Q(N,V,T)}{\partial V} \right) \tag{17.5.8}$$

Ideal Gas in the Canonical Ensemble

Recall that the mechanical energy for an ideal gas is:

$$\mathcal{E}(x) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \tag{17.5.9}$$

where all particles are identical and have mass m. Thus, the expression for the canonical partition function $Q(N,V,T)$ is:

$$Q(N,V,T) = \frac{1}{N! h^{3N}} \int dx \, e^{-\beta \sum_{i=1}^{N} \mathbf{p}_i^2 / 2m}$$

Note that this can be expressed as:

$$Q(N,V,T) = \frac{1}{N! h^{3N}} V^N \left[\int dp \, e^{-\beta p^2 / 2m} \right]^{3N}$$

Evaluating the Gaussian integral gives us the final result immediately:

$$Q(N,V,T) = \frac{1}{N!} \left[\frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} \right]^N$$

The expressions for the energy:

$$E = -\frac{\partial}{\partial \beta} \ln Q(N,V,T)$$

which gives:

$$E = \frac{3}{2} NkT = \frac{3}{2} nRT \tag{17.5.10}$$

and pressure:

$$P = kT \left(\frac{\partial \ln Q(N,V,T)}{\partial V} \right)$$

giving:

$$P = \frac{NkT}{V} = \frac{nRT}{V} \tag{17.5.11}$$

which is the ideal gas law.

17.5: Express the Pressure in Terms of a Partition Function is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.5: Pressure can be Expressed in Terms of the Canonical Partition Function** by Jerry LaRue, Mark Tuckerman, Stefan Franzen is licensed CC BY-NC-SA 4.0.

17.6: Partition Functions of Systems of Distinguishable Molecules are Products of Molecular Partition Functions

A system, such as a container of gas, can consist of a large number of subsystems. How is the partition function of the system built up from those of the subsystems? This depends on whether the subsystems are distinguishable or indistinguishable. Let's start with energy. Energy is additive so that:

$$E_{tot}(N,V) = \epsilon_1(V) + \epsilon_2(V) + \epsilon_3(V) + \cdots$$

Each of the molecules can have their energy distributed over their respective energy states (e.g., vibrations, rotations, etc.). This means that each ϵ_i is already a summation over the states of the molecule. Let us assume that we can somehow distinguish all the molecules as: a, b, c, d… and denote the energy state they are in by i, j, k:

$$E_l(N,V) = \epsilon_i^a(V) + \epsilon_j^b(V) + \epsilon_k^c(V) + \cdots$$

A good example would be the molecules in a molecular crystal. They only move around a fixed site and so we can distinguish by how far molecule 'a' is from a given corner of the crystal. The systems partition function becomes:

$$Q(N,V,\beta) = \sum_i e^{-\beta E_l} = \sum_{i,j,k,\ldots} e^{-\beta(\epsilon_i^a + \epsilon_j^b + \epsilon_k^c)}$$

So far, we have done little effort to distinguish between the partition function of a molecular system q and the whole ensemble Q (e.g. the gas). If the entities that we called systems are **distinguishable** and independent, the whole ensemble partition function is the product of the molecular system partition functions. We get:

$$Q(N,V,\beta) = \prod_i q_i$$

for N distinguishable systems. We can split up the summation into a product of molecular partition functions:

$$Q(N,V,\beta) = \prod_i^N q_i(V,\beta) = q_a(V,\beta)q_b(V,\beta)q_c(V,\beta)\cdots$$

This results in each molecular system partition function being summed over independently:

$$Q(N,V,\beta) = \sum_i e^{-\beta\epsilon_i^a} \sum_j e^{-\beta\epsilon_i^b} \sum_k e^{-\beta\epsilon_i^c} \ldots$$

If the energy states of all the particles are the same, then the equation simplifies to:

$$Q(N,V,\beta) = [q(V,\beta)]^N$$

We can do this if, for example, the particles are embedded in a crystal where we can distinguish them by their location. We will see in the next chapter that for indistinguishable particles, such as those in a gas, we get a different result.

17.6: Partition Functions of Systems of Distinguishable Molecules are Products of Molecular Partition Functions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.6: The Partition Function of Distinguishable, Independent Molecules is the Product of the Molecular Partition Functions** by Jerry LaRue is licensed CC BY 4.0.

17.7: Partition Function of Indistinguishable Components

In the previous section, the definition of the the partition function involves a sum of state formulism:

$$Q = \sum_i e^{-\beta E_i}. \tag{17.7.1}$$

However, under most conditions, full knowledge of each member of an ensemble is missing and hence we have to operate with a more reduced knowledge. This is demonstrated via a simple model of two particles in a two-energy level system in Figure 17.7.1. Each particle (red or blue) can occupy either the $E_1 = 0$ energy level or the $E_2 = \epsilon$ energy level resulting in four possible states that describe the system. The corresponding partition function for this system is then (via Equation 17.7.1):

$$Q_{\text{distinguishable}} = e^0 + e^{-\beta\epsilon} + e^{-\beta\epsilon} + e^{-2\beta\epsilon} = q^2 \tag{17.7.2}$$

and is just the molecular partition function (q) squared.

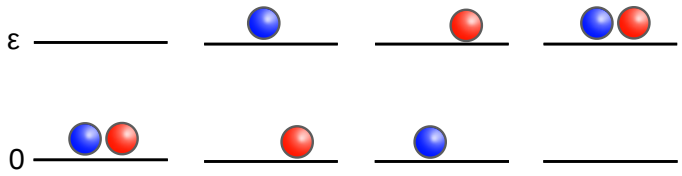


Figure 17.7.1: Four different states can exist for a two-level system with two distinguishable particles (red and blue balls). (CC BY 4.0; Delmar Larsen via LibreTexts)

However, if the two particles are indistinguishable (e.g., both the same color as in Figure 17.7.2) then while four different combinations can be generated like in Figure 17.7.1, there is no discernible way to separate the two middle states. Hence, there are effectively only three states observable for this system.

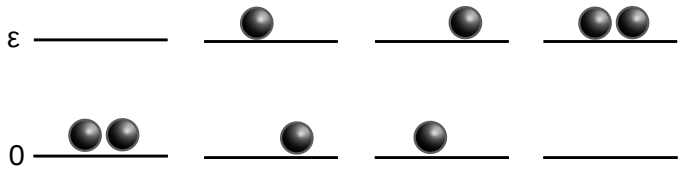


Figure 17.7.2: Three different states can exist for a two-level system with two indistinguishable particles (black balls). The two middle states are indescernable and represent a single state with one particle exited and the other in the ground state. (CC BY 4.0; Delmar Larsen via LibreTexts)

The corresponding partition function for this system (again using Equation 17.7.1) can be constructed:

$$Q(N,V,\beta) = e^0 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} \neq q^2 \tag{17.7.3}$$

and this is not equal to the square of the molecular partition function. If Equation 17.7.2 were used to describe the indistinguishable particle case, then it would overestimate the number of observable states. From combinatorics, using q^N for a large N-particle system of indistinguishable particles will overestimate the number of states by a factor of $N!$. Therefore Equation 17.7.1 requires a slight modification to account for this over counting.

$$Q(N,V,\beta) = \frac{\sum_i e^{-\beta E_i}}{N!} \tag{17.7.4}$$

If we have N molecules, we can perform $N!$ permutations that should not affect the outcome. To avoid over counting (making sure we do not count each state more than once), the partition function becomes:

$$Q(N,V,\beta) = \frac{q(V,\beta)^N}{N!}$$

Note

As you may have noticed, using Equation 17.7.4 to estimate of Q for the two-indistinguishable particle discussed case above with $N = 2$ is incorrect (i.e., Equation 17.7.4 is not equal to Equation 17.7.3). That is because the $N!$ factor is only applicable for large N.

17.7: Partition Function of Indistinguishable Components is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.7: Partition Functions of Indistinguishable Molecules Must Avoid Over Counting States** by Delmar Larsen, Jerry LaRue is licensed CC BY 4.0.

17.8: A Molecular Partition Function Can Be Decomposed into Partition Functions for Each Degree of Freedom

From the previous sections, the partition function for a system of N indistinguishable and independent molecules is:

$$Q(N,V,\beta) = \frac{\sum_i e^{-\beta E_i}}{N!} \tag{17.8.1}$$

And the average energy of the system is:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \tag{17.8.2}$$

We can combine these two equations to obtain:

$$\begin{aligned} \langle E \rangle &= kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \\ &= NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \\ &= N \sum_i \epsilon_i \frac{e^{-\epsilon_i/kT}}{q(V,T)} \end{aligned} \tag{17.8.3}$$

The average energy is equal to:

$$\langle E \rangle = N \langle \epsilon \rangle \tag{17.8.4}$$

where $\langle \epsilon \rangle$ is the average energy of a single particle. If we compare Equation 17.8.2 with Equation 17.8.2, we can see:

$$\langle \epsilon \rangle = \sum_i \epsilon_i \frac{e^{-\epsilon_i/kT}}{q(V,T)}$$

The probability that a particle is in state i, π_i, is given by:

$$\langle \epsilon \rangle = \frac{e^{-\epsilon_i/kT}}{q(V,T)} = \frac{e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}}$$

The energy of a particle is a sum of the energy of each degree of freedom for that particle. In the case of a molecule, the energy is:

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elec}}$$

The molecular partition function is the product of the degree of freedom partition functions:

$$q(V,T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

The partition function for each degree of freedom follows the same is related to the Boltzmann distribution. For example, the vibrational partition function is:

$$q_{\text{vib}} = \sum_i e^{-\epsilon_i/kT}$$

The average energy of each degree of freedom follows the same pattern as before. For example, the average vibrational energy is:

$$\langle \epsilon_{\text{vib}} \rangle = kT^2 \frac{\partial \ln q_{\text{vib}}}{\partial t} = -\frac{\partial \ln q_{\text{vib}}}{\partial \beta}$$

17.8: A Molecular Partition Function Can Be Decomposed into Partition Functions for Each Degree of Freedom is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **17.8: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom** by Jerry LaRue is licensed CC BY 4.0.

17.E: Exercises

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.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{17.E.1}$$

You can see from Equation 17.E.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 17.*E*.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.

17.E: Exercises 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

18: Partition Functions and Ideal Gases

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Chem 110A ● Chem 110B ● Chem 110C ● **Agenda** ● **Homework** ● **Worksheet Activities**

In chemistry, we are typically concerned with a collection of molecules. However, if the molecules are reasonably far apart as in the case of a dilute gas, we can approximately treat the system as an ideal gas system and ignore the intermolecular forces. The present chapter deals with systems in which intermolecular interactions are ignored. In ensemble theory, we are concerned with the ensemble probability density, i.e., the fraction of members of the ensemble possessing certain characteristics such as a total energy E, volume V, number of particles N or a given chemical potential μ and so on. The molecular partition function enables us to calculate the probability of finding a collection of molecules with a given energy in a system. The equivalence of the ensemble approach and a molecular approach may be easily realized if we treat part of the molecular system to be in equilibrium with the rest of it and consider the probability distribution of molecules in this subsystem (which is actually quite large compared to systems containing a small number of molecules of the order of tens or hundreds).

18.1: The Translational Partition Function of a Monatomic Ideal Gas

18.2: Most Atoms Are in the Ground Electronic State at Room Temperature

18.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms

18.4: Most Molecules Are in the Ground Vibrational State at Room Temperature

18.5: Most Molecules Are in Excited Rotational States at Ordinary Temperatures

18.6: Rotational Partition Functions Contain a Symmetry Number

18.7: The Vibrational Partition Function

18.8: The Rotational Partition Function Depends on the Shape of the Molecule

18.9: Molar Heat Capacities

18.E: Partition Functions and Ideal Gases (Exercises)

18: Partition Functions and Ideal Gases is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

18.1: The Translational Partition Function of a Monatomic Ideal Gas

Let us consider the translational partition function of a monatomic gas particle confined to a cubic box of length L. The particle inside the box has translational energy levels given by:

$$E_{\text{trans}} = \frac{h^2\left(n_x^2 + n_y^2 + n_z^2\right)}{8mL^2}$$

where n_x, n_y and n_z are the quantum numbers in the three directions. The translational partition function is given by:

$$q_{\text{trans}} = \sum_i e^{-\epsilon_i/kT}$$

which is the product of translational partition functions in the three dimensions. We can write the translation partition function as the product of the translation partition function for each direction:

$$q_{\text{trans}} = q_x q_y q_z \tag{18.1.1}$$

$$= \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \sum_{n_y=1}^{\infty} e^{-\epsilon_y/kT} \sum_{n_z=1}^{\infty} e^{-\epsilon_z/kT} \tag{18.1.2}$$

Since the levels are very closely spaced (continuous), we can replace each sum in Equation 18.1.2 with an integral. For example:

$$q_x = \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{18.1.3}$$

$$\approx \int_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{18.1.4}$$

and after substituting the energy for the relevant dimension:

$$\epsilon_x = \frac{h^2 n_x^2}{8mL^2}$$

we can extend the lower limit of integration in the approximation of Equation 18.1.4:

$$q_x = \int_1^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2 kT}} \approx \int_0^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2 kT}}$$

We then use the following solved Gaussian integral:

$$\int_o^{\infty} e^{-an^2} dn = \sqrt{\frac{\pi}{4a}}$$

with the following substitution:

$$a = \frac{h^2}{8mL^2 kT}$$

we get:

$$q_x = \frac{1}{2}\sqrt{\frac{\pi}{a}} = \frac{1}{2}\sqrt{\frac{\pi 8mkT}{h^2}} L$$

or more commonly presented as:

$$q_x = \frac{L}{\Lambda}$$

where Λ is the **de Broglie wavelength** and is given by

$$\Lambda = \frac{h}{\sqrt{2\pi 8mkT}}$$

Multiplying the expressions for q_x, q_y and q_z (Equation 18.1.1) and using V as the volume of the box L^3, we arrive at:

$$q_{trans} = \left(\frac{\sqrt{2\pi 8mkT}}{h} \right)^{3/2} V = \frac{V}{\Lambda^3} \tag{18.1.5}$$

This is usually a very large number (10^{20}) for volumes of 1 cm^3 for small molecular masses. This means that such a large number of translational states are accessible and available for occupation by the molecules of a gas. This result is very similar to the result of the classical kinetic gas theory that said that the observed energy of an ideal gas is:

$$U = \frac{3}{2} nRT$$

We postulate therefore that the observed energy of a macroscopic system should equal the statistical average over the partition function as shown above. In other words: if you know the particles your system is composed of and their energy states you can use statistics to calculate what you should observe on the whole ensemble.

Example

Calculate the translational partition function of an I_2 molecule at 300K. Assume V to be 1 liter.

Solution

Mass of I_2 is $2 \times 127 \times 1.6606 \times 10^{-27} kg$

$$\begin{aligned} 2\pi mkT &= 2 \times 3.1415 \times (2 \times 127 \times 1.6606 \times 10^{-27}\, kg) \times 1.3807 \times 10^{-23}\, J/K \times 300K \\ &= 1.0969 \times 10^{-44}\, J\, kg \end{aligned}$$

$$\begin{aligned} \Lambda &= \frac{h}{\sqrt{2\pi mkT}} \\ &= \frac{6.6262 \times 10^{-34}\, J\, s}{\sqrt{1.0969 \times 10^{-44}\, J\, kg}} = 6.326 \times 10^{-12}\, m \end{aligned}$$

The via Equation 18.1.5

$$q_{trans} = \frac{V}{\Lambda^3} = \frac{1000 \times 10^{-6} m^3}{(6.326 \times 10^{-12}\, m)^3} = 3.95 \times 10^{30}$$

This means that 3.95×10^{30} quantum states are thermally accessible to the molecular system

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

18.1: The Translational Partition Function of a Monatomic Ideal Gas is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.1: Translational Partition Functions of Monotonic Gases** is licensed CC BY-NC-SA 4.0.

18.2: Most Atoms Are in the Ground Electronic State at Room Temperature

Writing the electronic energies as $E_1, E_2, E_3, ...$ with corresponding degeneracies $g_1, g_2, g_3, ...$ The electronic partition function is then given by the following summation:

$$q_{el}(T) = g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + ... \tag{18.2.1}$$

Usually, the differences in electronic energies are significantly greater than thermal energy kT:

$$kT \ll E_1 < E_2 < E_3$$

If we treat the lowest energy electronic state E_1 as the reference value of zero of energy, the electronic partition function (Equation 18.2.1) can be approximated as:

$$q_{elec}(T) = g_1 + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + ... \tag{18.2.2}$$

Typically electronic states are tens of thousands of wave numbers above the ground state. For example, the first excited electronic state of nitric oxide (NO) is ~40,000 cm^{-1}. Using this value:

$$\frac{E_2}{kT} = \frac{40000 \text{ cm}^{-1}}{kT} = \frac{10^4 \text{ K}}{T}$$

That means, that even at 1,000 K, the value of the second term in {\reference{3.24}} is:

$$g_2 e^{-10} = g_2 4.5 \times 10^{-5}$$

The result is that the higher electronic states are not accessible under ordinary temperatures. There are some cases, however, where the first excited state lies much closer to the ground state, but these are the exception rather than the rule.

Example 18.2.1

Find the electronic partition of H_2 at 300 K.

Solution

The lowest electronic energy level of H_2 is near $-32\ eV$ and the next level is about $5\ eV$ higher. Taking -32 eV as the zero (or reference value of energy), then

$$q_{el} = e_0 + e^{-5eV/kT} + ...$$

At 300 K, T = 0.02\; eV and

$$q_{el} = 1 + e^{-200} + ...$$
$$\approx 1.0$$

Where all terms other than the first are essentially 0. This implies that $q_{el} = 1$.

The physical meaning of the result from Example 18.2.1 is that only the ground electronic state is generally thermally accessible at room temperature.

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

18.2: Most Atoms Are in the Ground Electronic State at Room Temperature is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.2: Most Atoms are in the Ground Electronic State** is licensed CC BY-NC-SA 4.0.

18.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms

A monatomic gas has three degrees of freedom per molecule, all of them translational:

1. movement in x-direction
2. movement in y-direction
3. movement in z-direction

A polyatomic gas, including diatomic molecules, has other levels that you can 'stuff' energy into. Polyatomic molecules can rotate and vibrate, and if enough energy is available you could also excite the electrons involved in the σ and π bonds. A reasonable approximation of the partition function of the molecule would become:

$$q_{\text{tot}}(V,T) = q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}$$

The partition function of a molecular idea gas is then:

$$Q(N,V,T) = \frac{(q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}})^N}{N!}$$

The total energy of the molecule is then the sum of the translation, vibrational, rotational, and electronic energies:

$$E_{tot} = E_{\text{trans}} E_{\text{vib}} E_{\text{rot}} E_{\text{elec}}$$

We will only scratch the surface of the additional degrees of freedom and their partition functions.

Electronic

At room temperature the system is usually in its ground electronic state. This means that the **electronic partition function** $q_{\text{elec}} = 1$. Usually we do not have to worry about these degrees of freedom. If we do, there are usually just a few levels to worry about. This includes their **degeneracy g**. If there is a single state at a certain energy ($g = 1$), two states ($g = 2$), or more states, we must multiply the Boltzmann factor by this degeneracy number.

If there are more than one state to worry about, we could follow the same procedure as we did for the translational states:

1. Define the energy states and their degeneracies
2. Compose the partition function q for the molecule and Q for the gas
3. Use the (β or T) derivative of $\ln Q$ to determine $\langle E \rangle$
4. Use the T derivative of $U \approx \langle E \rangle$ to find the contribution to the heat capacity

---

18.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.3: The Energy of a Diatomic/Polyatomic Molecule Can Be Approximated as a Sum of Separate Terms** is licensed CC BY-NC-SA 4.0.

18.4: Most Molecules Are in the Ground Vibrational State at Room Temperature

The vibrational energy levels of a diatomic are given by:

$$E_v = (v + 1/2)h\nu$$

where is ν the vibrational frequency and v is the vibrational quantum number. In this case, it is easy to sum the geometric series shown below:

$$\begin{aligned} q_{\text{vib}} &= \sum_{v=0}^{\infty} e^{-(v+1/2)h\nu/kT} \\ &= e^{-h\nu/2kT}\left(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + ...\right) \end{aligned}$$

or rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(1 + x + x^2 + x^3 + ...\right) \tag{18.4.1}$$

where $x = e^{-h\nu/kT}$. Given the following power series expansion:

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + ...$$

Equation 18.4.1 can be rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(\frac{1}{1-x}\right)$$

or:

$$q_{\text{vib}} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \tag{18.4.2}$$

If the zero of energy scale is at $h\nu/2kT$, then Equation 18.4.2 can be rewritten as:

$$q_{\text{vib}} \approx \frac{1}{1 - e^{-h\nu/kT}} \tag{18.4.3}$$

A vibrational temperature Θ_{vib} may be defined as:

$$\Theta_{\text{vib}} = \frac{hc\tilde{\nu}}{k}$$

where $\tilde{\nu}$ is the vibrational frequency in cm^{-1}. Θ_{vib} is a good way to express the *stiffness* of the vibrating bond in units of the Boltzmann constant. Because the stiffness obviously depends on what bond your are talking about, this is a good way to do the same thing we did for the critical temperature of the non-ideal gases.

Table **18.4.1** : Representative molecular data for a few diatomics

Molecule	g	Bond Length (pm)	ω (cm^{-1})	Θ_{vib} (K)	$\tilde{B}$ (cm^{-1})	Θ_{rot} (K)	Force constant k (dynes/cm)	D_0 (kcal/mol)
H_2	1	0.7474	4400	6332	60.9	87.6	5.749	103.2
D_2	1	0.7415	3118	4487	30.45	43.8	5.77	104.6
N_2	1	1.097	2358	3393	2.001	2.99	22.94	225.1
O_2	3	1.207	1580	2274	1.446	2.08	11.76	118.0
Cl_2	1	1.987	560	805	0.244	0.351	3.2	57.0
CO	1	1.128	2170	3122	1.931	2.78	19.03	255.8
NO	2	1.15	190	2719	1.695	2.45	15.7	150.0
HCl	1	1.275	2938	4227	10.44	15.02	4.9	102.2
HI	1	1.609	2270	3266	6.46	9.06	3.0	70.5
Na_2	1	3.096	159	229	0.154	0.221	0.17	17.3
K_2	1	3.979	92.3	133	0.0561	0.081	0.10	11.8

Example 18.4.1

The vibrational frequency of of I_2 is $214.57\ cm^{-1}$. Calculate the vibrational partition function of I_2 at 300 K.

Solution:

$$\frac{h\nu}{kT} = \frac{214.57}{209.7} = 1.0232$$

so

$$e^{-h\nu/kT} = 0.3595$$

and

$$q_{vib} = \frac{1}{1 - 0.3595} = 1.561$$

This implies, as before, that very few vibrational states are accessible and much less than rotation states and many orders less than translation states.

Vibrational Heat Capacity

The vibrational energy is given by the above expression and the molar heat capacity at constant volume, $\bar{C}_V$ is given by:

$$\bar{C}_V = \left(\frac{\partial E}{\partial T}\right)_V$$

We have:

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta} \tag{18.4.4}$$

$$= \frac{-1}{kT^2}\frac{\partial}{\partial \beta} \tag{18.4.5}$$

$$= (-k\beta^2)\left(\frac{\partial}{\partial \beta}\right) \tag{18.4.6}$$

Therefore:

$$\bar{C}_V = (-k\beta^2)\left(\frac{\partial \varepsilon_{\text{vib}}}{\partial \beta}\right)$$

and when the vibrational partition function (Equation 18.4.3) is introduced:

$$q_{\text{vib}} = -k\beta^2 \frac{\left[(1-e^{-hc\nu/kT})(-hc\tilde{\nu}) - e^{-hc\nu/kT}(+hc\tilde{\nu})\right] e^{-hc\nu/kT}}{(1-e^{-hc\nu/kT})^2} h\nu\tilde{\nu} \tag{18.4.7}$$

$$= k\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left(1-e^{-\Theta_{\text{vib}}/T}\right)^2} \tag{18.4.8}$$

For large T, the $\bar{C}_V$ becomes:

$$N_A k = R$$

and for small T, $\bar{C}_V$ goes to zero as demonstrated in Figure 18.4.1 .

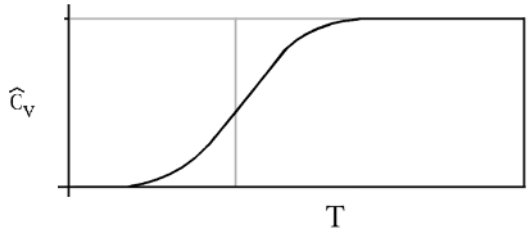


Figure 18.4.1 : Vibrational heat capacity of a diatomic

The vibrational heat capacity is shown as function of the reduced temperature T/Θ to get a general picture valid for all diatomic gases. Compare the parameters on Table 18.4.1 to see on what different absolute scales we have to think for different gases. Clearly the vibrational contribution to the heat capacity *depends on temperature*. For many molecules (especially light ones), the vibrational contribution only kicks in at quite high temperatures.

The value of Θ_{vib} is determined mostly by

1. the strength of a bond (the stronger the higher Θ_{vib})
2. the (effective) mass of the molecule (the lighter the higher Θ_{vib})

Molecules with low Θ_{vib} often dissociate at lower temperatures, although the *harmonic* oscillator model is not sufficient to describe that phenomenon.

Vibrational Populations

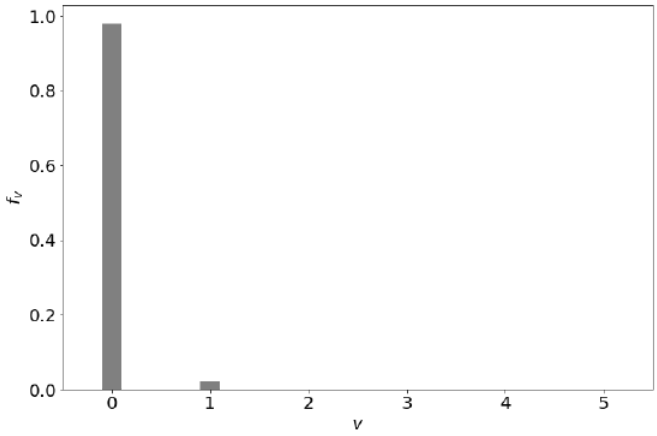
We can calculate the fraction of molecules in each vibrational state. The fraction of molecules in the vth vibrational state is given by:

$$f_v = \frac{e^{-h\nu(v+\frac{1}{2})/kT}}{q_{\text{vib}}}$$

Substituting in Equation 18.4.2, we get:

$$\begin{aligned} f_v &= \left(1-e^{-h\nu/kT}\right) e^{-h\nu v/kT} \\ &= \left(1-e^{-\Theta_{\text{vib}}/T}\right) e^{-\Theta_{\text{vib}} v/T} \end{aligned} \tag{18.4.9}$$

We can plot the fraction molecules in each vibrational state.



The vibrational population of Cl_2 at 300 K. Most of the molecules are in the ground vibrational state, $v = 0$.

From the figure, we can see that most of the Cl_2 molecules are in the ground vibrational state at room temperature (300 K). This is true for most molecules. Only molecules with very weak bonds and low vibrational temperatures will populate a significant fraction of molecules in excited vibrational states.

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

18.4: Most Molecules Are in the Ground Vibrational State at Room Temperature is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.4: Most Molecules are in the Ground Vibrational State** is licensed CC BY-NC-SA 4.0.

18.5: Most Molecules Are in Excited Rotational States at Ordinary Temperatures

The rotational quantum number is J and the energy of the rotations is:

$$E(J) = \tilde{B}J(J+1)$$

Where $\tilde{B}$ is in units of cm^{-1} and is equivalent to:

$$\frac{h}{8\pi^2 Ic}$$

Where c is the speed of light in units of cm^{-1}. However, with the exception of the ground state (i.e., $J = 0$), multiple eigenstates exist for a given value of J. This is a form of **degeneracy**, (g), and the number of levels per energy goes as 1, 3, 5, 7, 9 etc or:

$$g(J) = 2J + 1$$

Therefore, the summation to find the partition function $q_{rot}(T)$ contains an extra factor $g = 2J + 1$. This factor is mathematically very handy, because it is the derivative of:

$$g(J) = J(J+1)$$

This makes it possible to change variables to $X = J(J+1)$ and the integration becomes very easy. Notice that just like in the translation partition function, we approximate the summation with an integral. However, because we are dealing with far fewer levels, this is less justified in the rotational case. How justified it is depends on the gas and the temperature we consider. Roughly speaking we should be at a temperature $T >> \Theta_{rot}$.

? Exercise 18.5.1

Look at table 18.2. When do we need to actually work out the (discrete) summation instead of making a (continuous) integration out of it?

Answer

Only for the lightest gases like $\mathbf{He}$ and $\mathbf{H_2}$ do we need to worry and then only at pretty low cryogenic circumstances. At room temperature, we can take the rotational levels as a continuous set and use an integral. Notice that the vibrational Θ values are much larger! At $T = 300\,\mathrm{K}$, usually only a single level is occupied and we are in the discrete limit. On the surface of the sun that would be a different matter of course.

The rotational constant B is directly linked to the moment of inertia:

$$I = \mu r^2$$

Where μ is the reduced mass of the molecule:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

and r is the bond length. Again we can scale the behavior of different systems to one and the same picture by introducing a characteristic temperature:

$$\Theta_{rot} = \frac{hb}{k} = \frac{\hbar^2}{2Ik_b}$$

As we did for the translations, we can calculate the moment $\langle\epsilon\rangle$. For vibrations we get a relatively complicated function of temperature. However, for rotations, the moment is simply equal to NkT and this means that the rotational contribution to the molar C_v of a diatomic is simply R. As the vibrational and electronic contributions to the heat capacity are typically negligible at room temperature, we get:

- monatomic gas

$$C_v = C_v^{trans} = \frac{3}{2}nR$$

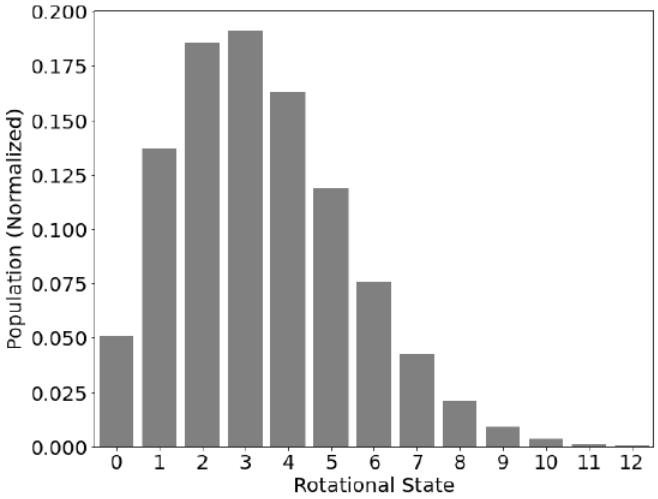
- diatomic

$$C_v = C_v^{trans} + C_v^{rot} \tag{18.5.1}$$

$$= \frac{3}{2}nR + nR \tag{18.5.2}$$

$$= \frac{5}{2}nR \tag{18.5.3}$$

Rotational energies are less than vibrational and electronic energies and, at room temperature, many rotational states will be populated.



The normalized rotational population of HCl at room temperature.

18.5: Most Molecules Are in Excited Rotational States at Ordinary Temperatures is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.5: Most Molecules are Rotationally Excited at Ordinary Temperatures** is licensed CC BY-NC-SA 4.0.

18.6: Rotational Partition Functions Contain a Symmetry Number

The rotational energy levels of a **diatomic molecule** are given by:

$$E_{\text{rot}}(J) = \tilde{B}J(J+1) \tag{18.6.1}$$

where:

$$\tilde{B} = \frac{h}{8\pi^2 Ic}$$

Here, $\tilde{B}$ is the rotational constant expressed in cm^{-1}. The rotational energy levels are given by:

$$E_j = \frac{J(J+1)h^2}{8\pi I}$$

where I is the moment of inertia of the molecule given by μr^2 for a diatomic, and μ is the reduced mass, and r the bond length (assuming rigid rotor approximation). The energies can be also expressed in terms of the rotational temperature, Θ_{rot}, defined as:

$$\Theta_{\text{rot}} = \frac{r^2}{8\pi^2 Ik} \tag{18.6.2}$$

The interpretation of θ_{rot} is as an estimate of the temperature at which thermal energy ($\approx kT$) is comparable to the spacing between rotational energy levels. At about this temperature the population of excited rotational levels becomes important. See Table 1.

Table 1: Select Rotational Temperatures. In each case the value refers to the most common isotopic species.

Molecule	H_2	N_2	O_2	F_2	HF	HCl	CO_2	HBr	CO
Θ_{rot}	87.6	2.88	2.08	1.27	30.2	15.2	0.561	12.2	2.78

In the summation for the expression for rotational partition function (q_{rot}), Equation 18.6.3, we can do an explicit summation:

$$q_{\text{rot}} = \sum_{j=0}(2J+1)e^{-E_J/kT} \tag{18.6.3}$$

if only a finite number of terms contribute. The factor $(2J+1)$ for each term in the expansion accounts for the degeneracy of a rotational state J. For each allowed energy E_J from Equation 18.6.1 there are $(2J+1)$ eigenstates. The Boltzmann factor must be multiplied by $(2J+1)$ to properly account for the degeneracy these states:

$$(2J+1)e^{-E_J/kT}$$

If the rotational energy levels are lying very close to one another, we can integrate similar to what we did for q_{trans} previously to get:

$$q_{\text{rot}} = \int_0^\infty (2J+1)R^{-\tilde{B}J(J+1)/kT}dJ$$

This integration can easily be done by substituting $x = J(J+1)$ and $dx = (2J+1)dJ$:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}} \tag{18.6.4}$$

For a homonuclear diatomic molecule, rotating the molecule by 180° brings the molecule into a configuration which is *indistinguishable* from the original configuration. This leads to an overcounting of the accessible states. To correct for this, we divide the partition function by σ, which is called the **symmetry number** and is equal to the distinct number of ways by which a molecule can be brought into identical configurations by rotations. The rotational partition function becomes:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}\sigma} \tag{18.6.5}$$

or commonly expressed in terms of Θ_{rot}:

$$q_{rot} = \frac{T}{\Theta_{rot}\sigma} \tag{18.6.6}$$

Example 18.6.1

What is the rotational partition function of H_2 at 300 K?

Solution

The value of $\tilde{B}$ for H_2 is 60.864 cm^{-1}. The value of kT in cm^{-1} can be obtained by dividing it by hc, i.e., which is $kT/hc = 209.7\ cm^{-1}$ at 300 K. $\sigma = 2$ for a homonuclear molecule. Therefore from Equation 18.6.5,

$$\begin{aligned} q_{rot} &= \frac{kT}{\tilde{B}\sigma} \\ &= \frac{209.7\ cm^{-1}}{(2)(60.864\ cm^{-1})} \\ &= 1.723 \end{aligned}$$

Since the rotational frequency of H_2 is quite large, only the first few rotational states are accessible at 300 K

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

18.6: Rotational Partition Functions Contain a Symmetry Number is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.6: Rotational Partition Functions of Diatomic Gases Contain a Symmetry Number** is licensed CC BY-NC-SA 4.0.

18.7: The Vibrational Partition Function

As with diatomic molecules, the energies of polyatomic molecules can be approximated by the sum of its individual degrees of freedom. Therefore, we can write the partition function as:

$$Q(N,V,T) = \frac{[q(V,T)]^2}{N!}$$

We can write the polyatomic analog to diatomic molecules:

$$Q(N,V,T) = \frac{(q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}})^N}{N!}$$

When derived for diatomic molecules, we assumed the rigid rotor model for rotations and the harmonic oscillator for vibrations. This allowed us to separate the rotational motion from the vibrational motion of the molecule. Polyatomic molecules are a bit more complicated, but we will still make use of these approximations.

The number of translational states available to any given molecule is far greater than the number of molecules in the system. q_{trans} is given by:

$$q_{\text{trans}} = \left[\frac{2\pi MkT}{h^2}\right]^{3/2} V$$

where M is the mass of the particle. Moving to the electronic partition function:

$$q_{\text{elec}} = \sum_i g_i e^{-E_i/kT}$$

where E_i is the energy of the electronic state i and {g_i} is its degeneracy. Electronic states are typically spaced far apart from each other. The probability of the system being in any state but the ground state is extremely small. We can therefore simplify the electronic partition function to include only the ground electronic state:

$$q_{\text{elec}} = g_{e1}e^{D_e/kT}$$

where $-D_e$ is the energy of the ground electronic state. To complete the polyatomic partition function, we still need q_{vib} and q_{rot}. We will finish this section with q_{vib} and talk about q_{rot} in the next.

The vibrational motion of diatomic molecules can be expressed as a set of independent harmonic oscillators. For polyatomic molecules, the independent vibrational motions are referred to as normal modes of vibration. The vibrational energy is then the sum of the energies for each normal mode:

$$E_{\text{vib}} = \sum_i^{\alpha}\left(v_i + \frac{1}{2}\right)h\nu$$

where ν_i is the vibrational frequency for the ith normal mode and α is the number of vibration degrees of freedom. A linear molecule has $3n-5$ vibrational degrees of freedom and a nonlinear molecule has $3n-6$ vibrational degrees of freedom. Because the normal modes are independent of each other, we can take out results from previous sections:

$$q_{\text{vib}} = \prod_i^{\alpha}\frac{e^{-\theta_{\text{vib},i}/2T}}{1-e^{-\theta_{\text{vib},i}/T}}$$

$$E_{\text{vib}} = Nk\sum_i^{\alpha}\left(\frac{\theta_{\text{vib},i}}{2} + \theta_{\text{vib},i}\frac{e^{-\theta_{\text{vib},i}/T}}{1-e^{-\theta_{\text{vib},i}/T}}\right)$$

$$C_{V,\text{vib}} = Nk\sum_i^{\alpha}\left(\left(\frac{\theta_{\text{vib},i}}{2}\right)^2 + \frac{e^{-\theta_{\text{vib},i}/T}}{(1-e^{-\theta_{\text{vib},i}/T})^2}\right)$$

where $\theta_{\text{vib},i}$ is the characteristic vibrational temperature defined by:

$$\theta_{\text{vib},i} = \frac{h\nu_i}{k}$$

Vibrational Entropy

There is a great deal of utility for thermodynamic functions calculated from the vibrational normal modes of a molecule. The vibrational energy and entropy depend on the shape a multidimensional potential energy surface. If one performs a conformational search of macromolecule it is one obtains energies and structures but little direct information concerning the shape of the potential energy surface for each conformation. The vibrational entropy gives a means determining whether there are significant entropic differences in the structures and therefore whether certain conformations will be favored based on the entropy.

However, it is possible to take appropriate linear combinations of the coordinates so that the cross terms are eliminated and the classical Hamiltonian as well as the operator corresponding to it contains no cross terms and in terms of the new coordinates, the Hamiltonian can be written as,

$$H = \sum_{i=1}^{f} \frac{h^2}{2\mu_i} \frac{\partial}{\partial q_i^2} + \sum_{i=1}^{f} \frac{k_i}{2} q_i^2 \tag{18.7.1}$$

Here, the degrees of freedom f is $3N-5$ for a linear molecule and $3N-6$ for a nonlinear molecule. Here, k_i is the force constant and μ_i is the reduced mass for that particular vibrational mode which is referred to as a **normal mode**.

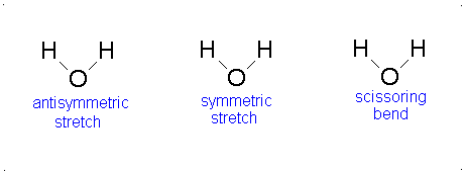


Figure 18.7.1 : The three vibrational modes of water, the symmetric stretch (3656.7 cm^{-1}, 5160 K), the asymmetric stretch (3755.8 cm^{-1} , 5360 K) and the bending mode (1594.8 cm^{-1} ,2290 K) are shown. The vibrational frequencies and the characteristic temperature for each mode are shown in parenthesis. Although not shown in the animation, the oxygen atom also moves with each of these normal modes.

The Equation 18.7.1 represents f linearly independent harmonic oscillators and the total energy for such a system is

$$\epsilon_{vib} = \sum_{i=1}^{f} \left(v_i + \frac{1}{2} \right) h\nu_i$$

The vibrational frequencies are given by

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{k_i}{\mu_i}}$$

The vibrational partition function is given by the product of f vibrational functions for each frequency.

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1 - e^{-\Theta_{vib,i}/T}} \tag{18.7.2}$$

with

$$\Theta_{vib,i} = \frac{h\nu_i}{k_B}$$

As with the previous discussion regarding simple diatomics, $\Theta_{vib,i}$ is called the **characteristic vibrational temperature**. The molar energies and the heat capacities are given by

$$\langle E_{vib} \rangle = Nk \sum_{i=1}^{f} \left[\frac{\Theta_{vib,i}}{2} + \frac{\Theta_{vib,i} e^{-\Theta_{vib,i}/T}}{1 - e^{-\Theta_{vib,i}/T}} \right]$$

and

$$\bar{C}_V = Nk_B \sum_{i=1}^{f} \left(\frac{\Theta_{vib,i}}{T} \right)^2 \frac{e^{-\Theta_{vib,i}/T}}{\left(1 - e^{-\Theta_{vib,i}/T}\right)^2}$$

NO_2 Example

The three characteristic vibrational temperatures for $\mathbf{NO_2}$ are 1900 K, 1980 K and 2330 K. Calculate the vibrational partition function at 300 K.

Solution

The vibrational partition is (Equation 18.7.2)

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1 - e^{-\Theta_{vib,i}/T}}$$

If we calculate q_{vib} by taking the zero point energies as the reference points with respect to which the other energies are measured

$$q_{vib} = \prod_{i=1}^{f} \frac{1}{1 - e^{-\Theta_{vib,i}/T}} = \left(\frac{1}{1 - e^{-1900/300}}\right)\left(\frac{1}{1 - e^{-1980/300}}\right)\left(\frac{1}{1 - e^{-2330/300}}\right)$$
$$= (1.0018)(1.0014)(1.0004) = 1.0035$$

The implication is that very few vibrational states of $\mathbf{NO_2}$ (other than the ground vibrational state) are accessible at 300 K. This is standard of the vibrations of most molecules.

18.7: The Vibrational Partition Function is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.7: Vibrational Partition Functions of Polyatomic Molecules Include the Partition Function for Each Normal Coordinate** is licensed CC BY-NC-SA 4.0.

18.8: The Rotational Partition Function Depends on the Shape of the Molecule

For a polyatomic molecule containing N atoms, the total number of degrees of freedom is $3N$. Out of these, three degrees of freedom are taken up for the translational motion of the molecule as a whole. For nonlinear molecules, there are three rotational degrees of freedom and the $3N–6$ vibrational degrees. For linear molecules, the rotational motion along the molecular axis is quantum mechanically not meaningful as the rotated configuration is indistinguishable from the original configuration. Therefore, linear molecules have two rotational degrees of freedom and $3N–5$ vibrational degrees of freedom.

To investigate the rotational motion, we need to fix the center of mass of the molecule and calculate the three principal moments of inertia I_A, I_B, and I_C of the ellipsoid of inertia. The center of mass is defined as the point for which the following identities hold:

$$\sum_i m_i x_i = \sum_i m_i y_i = \sum_i m_i z_i$$

The inertia products are defined by:

$$I_{xx} = \sum_i m_i \left(y_i^2 + z_i^2\right)$$

$$I_{xy} = \sum_i m_i \left(x_i y_i\right)$$

The other components I_{yy}, I_{xz},.. are defined analogously. To find the direction cosines $\alpha_i, \beta_o, \gamma_i$ of the three principle moments of inertia, we need to solve the following matrix equations:

$$\alpha(I_{xx} - \eta) - \beta I_{xy} - \gamma I_{xz} = 0$$

$$\alpha I_{xy} - \beta(I_{yy} - \eta) - \gamma I_{yz} = 0$$

$$-\alpha I_{xz} - \beta I_{yz} + \gamma(I_{zz} - \eta) = 0$$

If the off diagonal terms I_{xy} are zero in the above equations, then the x, y, z axis will be the principal axis. The energy of a rotor with the three moments of inertia I_A, I_B. and I_C is given by:

$$\epsilon = \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2$$

$$= \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C}$$

Each of the rotational degrees of freedom will have a characteristic rotational temperature in terms of the moment of inertia:

$$\Theta_{rot,i} = \frac{hbar^2}{2I_i k} \qquad i = A, B, C$$

There are many different shapes of molecules and these shapes affect the rotational behavior of the molecules. Molecules are therefore classified according to symmetry into different groups called tops. The three different tops are:

$$\text{Spherical top} \qquad \Theta_{rot,A} = \Theta_{rot,B} = \Theta_{rot,C}$$

$$\text{Symmetric top} \qquad \Theta_{rot,A} = \Theta_{rot,B} \neq \Theta_{rot,C}$$

$$\text{Asymmetric top} \qquad \Theta_{rot,A} \neq \Theta_{rot,B} \neq \Theta_{rot,C}$$

Spherical Tops

The spherical top can be solved exactly to give:

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

$$g_J = (2J + 1^2) \qquad J = 0, 1, 2, \ldots$$

The rotational partition function is:

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)^2 e^{h^2 J(J+1)/2IkT}$$
$$= \sum_{J=0}^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T}$$

For almost all spherical top molecules:

$$\Theta_{\text{rot}} \gg T$$

Therefore, we can convert the sum to an integral:

$$q_{\text{rot}} = \frac{1}{\sigma} \int_0^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T}$$

where we have now included the symmetry term, σ. Solving for this integral, we get:

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{q_{\text{rot}}} \right)^{3/2}$$

Symmetric Tops

Here, ω_A, ω_B, and ω_C are the three angular speeds and L_A, L_B, and L_C are the three angular momenta. For a symmetric top molecule such as ammonia, or chloromethane, two components of the moments of inertia are equal, i.e., $I_B = I_C$. The rotational energy levels of such a molecule are specified by two quantum numbers J and K. The total angular momentum is determined by J and the component of this angular momentum along the unique molecular axis is determined by K. The energy levels are given by:

$$\epsilon_{J,K} = \tilde{B} J(J+1) + (\tilde{A} - \tilde{B}) K^2$$

with rotational constants in units of wavenumbers:

$$\tilde{B} = \frac{h}{8\pi^2 c I_B}$$

and:

$$\tilde{A} = \frac{h}{8\pi^2 c I_A}$$

where

- J takes on values $0, 1, 2, ...\infty$ and
- $K = -J, -J+1, -J+2, ...0, 1, 2, ...J$.

The rotational partition function is given by:

$$q_{rot} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\tilde{B}J(J+1)/kT} \sum_{K=-J}^{J} (2J+1) e^{\tilde{A}-\tilde{B})K^2/kT}$$

This can be converted to an integral and the result is:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi I_B kT}{h^2} \right) \left(\frac{8\pi I_A kT}{h^2} \right)^{1/2}$$

Asymmetric Tops

For asymmetric tops, the expressions for rotational energies are more complex and the conversions to integrations are not easy. One can actually calculate the sum of terms using a computer. An intuitive answer can be obtained by integrating over the angular momenta L_A, L_B and L_C as:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{H(p,q)/kT} \, dL_A \, dL_B \, dL_C = \sqrt{2\pi I_A kT} \sqrt{2\pi I_B kT} \sqrt{2\pi I_C kT}$$

And then multiplying by a factor of $8\pi^2/\sigma h^3$, we get the rotational partition function. The factor of $8\pi^2$ accounts for the angular integration. For any axis chosen in a molecule, a complete rotation contributes a factor of 2π. Integration over all possible orientations of this axis contribute another factor of 4π. The factor of h^3 is for the conversion from the classical phase space to the quantum mechanical phase space.

Symmetry Number

As discussed previously, the **symmetry number** σ corrects for overcounting of rotational configurations. If the molecule has no center of symmetry (e.g. HCN) $\sigma = 1$ whereas if the molecule has a center of symmetry (e.g. CO_2) then $\sigma = 2$.

The final result is:

$$q_{rot} = \frac{\pi^2}{\sigma}\sqrt{\frac{8\pi I_A kT}{h^2}}\sqrt{\frac{8\pi I_B kT}{h^2}}\sqrt{\frac{8\pi I_C kT}{h^2}} \tag{18.8.1}$$

Classical Derivation (Optional)

We can explicitly obtain the classical rotational partition function of an asymmetric top by writing the classical expression for the rotational energy in terms of the Euler angles. The orientation of a rigid rotor can be specified by there Euler angles θ, φ, and ψ with the ranges of angles 0 to π, 0 to 2π and 0 to 2π respectively. The rotational Hamiltonian for the kinetic energy can be written in terms of the angles and their conjugate momenta (p_θ, p_ϕ, p_ψ)

$$H = \frac{\sin^2\psi}{2I_A}\left(p_\theta - \frac{\cos\psi}{\sin\theta\sin\psi}(p_\phi - \cos\theta p_\psi)\right)^2$$

$$+\frac{\cos^2\psi}{2I_B}\left(p_\theta - \frac{\sin\psi}{\cos\theta\cos\psi}(p_\phi - \cos\theta p_\psi)\right)^2 + \frac{1}{2I_C}p_\psi^2$$

The classical rotational partition function is given by

$$q_{rot} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}\frac{1}{h^3}e^{-H(p,q)/kT}\,dp_\theta\,dp_\phi\,dp_\psi\,d\theta\,d\phi\,d\psi$$

The integrations can be simplified by rewriting $H(p,q)/kT$ as

$$\frac{H}{kT} = \frac{1}{2I_A kT}\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)\left(p_\theta + \left(\frac{1}{I_B} - \frac{1}{I_A}\right)\frac{\sin\psi\cos\psi}{\sin\theta\left(\frac{\sin^\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)}(p_\phi - \cos\theta p_\psi)\right)^2$$

$$+\frac{1}{2kTI_AI_B\sin^2\theta}\left(\frac{1}{\sin\theta\left(\frac{\sin^\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)}(p_\phi - \cos\theta p_\psi)\right)^2 + \frac{1}{2KTI_c}p_\psi^2$$

Using the following integral,

$$\int_{-\infty}^{\infty}e^{-a(x+b)^2}dx = \int_{-\infty}^{\infty}e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$$

Integration over p_θ gives using the above expression

$$\sqrt{2\pi kT}\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)^{-1/2} \tag{18.8.2}$$

Integration over p_φ gives the factor,

$$\sqrt{2\pi kTI_AI_B}\sin\theta\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)^{1/2}$$

This cancels partly the second square root in Equation 18.8.2. Integration over p_ψ gives the factor

$$\sqrt{2\pi kTI_c}$$

Integration over θ, φ and ψ gives a factor of $8\pi^2$.

$$\int_0^\pi \sin\theta\, d\theta = 2$$

$$\int_0^{2\pi} d\phi = 2\pi$$

$$\int_0^{2\pi} d\psi = 2\pi$$

Combining all the integrals, we finally get Equation 18.8.1 after reintroduced the symmetry number σ as before with diatomic molecular rotation.

We can simplify calculations by defining **characteristic rotational temperatures** for each axis of rotational:

$$\Theta_A = \frac{h^2}{8\pi^2 I_A k}$$

$$\Theta_B = \frac{h^2}{8\pi^2 I_B k}$$

$$\Theta_C = \frac{h^2}{8\pi^2 I_C k}$$

The polyatomic rotational partition function expressed in Equation 18.8.1 can then be re-expressed as:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}} \tag{18.8.3}$$

or alternatively:

$$\ln q_{rot} = \frac{1}{2}\ln\frac{\pi T}{\Theta_A\Theta_B\Theta_C\sigma^2}$$

Example: Nitrogen Dioxide

The three characteristic rotational temperatures for NO_2 are $111.5\ K$, $0.624\ K$ and $0.590\ K$. Calculate the rotational partition function at 300 K.

Solution

The rotational temperature is given by Equation 18.8.3:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}}$$

The rotational partition function becomes,

$$q_{rot} = \frac{1.772}{2}\sqrt{\frac{300\ K}{(11.5\ K)(0.624\ K)(22.55\ K)}} = 2242.4$$

Thermodynamics Properties

The molar thermodynamic functions can be readily calculated including average rotation energy and molar heat capacity:

$$E_{rot} = \frac{3}{2}RT$$

and:

$$\bar{C}_V = \frac{3}{2}R$$

Improvements over the classical approximation for the rotational partition function derived above have been obtained. One of the improved versions (with no derivation) is:

$$q_{rot} = q^0_{rot}\left[1 + \frac{h^2}{96\pi^2 kT}\left(\frac{2}{I_A} + \frac{2}{I_C} + \frac{2}{I_C} + \frac{I_C}{I_B I_B} - \frac{I_A}{I_B I_C} - \frac{I_B}{I_A I_C}\right)\right]$$

where q^0_{rot} is the classical approximation in Equation 18.8.1.

Comparing this result with the vibrational partition function calculation before ($q_{vib} = 1.0035$), give the implication that while multiple rotational states are accessible at room temperature, very few vibrational states (other than the ground vibrational state) are accessible.

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

18.8: The Rotational Partition Function Depends on the Shape of the Molecule is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **18.8: Rotational Partition Functions of Polyatomic Molecules Depend on the Sphar of the Molecule** is licensed CC BY-NC-SA 4.0.

18.9: Molar Heat Capacities

Learning Objectives

- **Goal**: Specific heat capacity data for a wide range of elements are used to assess the accuracy and limitations of the Dulong-Petit Law.
- **Prerequisites**: An introductory knowledge of statistical thermodynamics including the derivation of the vibrational (harmonic oscillator) contributions to the heat capacity are recommended.
- **Resources you will need**: This exercise should be carried out within a data analysis software environment which is capable of graphing and generating a best-fit line for an x-y data set.

The heat capacity (C) of a substance is a measure of how much heat is required to raise the temperature of that substance by one degree Kelvin. For a simple molecular gas, the molecules can simultaneously store kinetic energy in the translational, vibrational, and rotational motions associated with the individual molecules. In this case, the heat capacity of the substance can be broken down into translational, vibrational, and rotational contributions;

$$C = C_{trans} + C_{vib} + C_{rot} \tag{18.9.1}$$

Monoatomic crystalline solids represent a much simpler case. Einstein proposed a simple model for such substances whereby the atoms only have vibrational energy (each atom can vibrate in three perpendicular directions around its lattice position). Specifically, the 'Einstein Solid Model' assumes that the atoms act like three-dimensional harmonic oscillators (with the vibrational motion of each atom in each perpendicular dimension entirely independent). Statistical mechanics provides a relatively simple expression for the constant volume molar heat capacity ($C_{V,m}$) of a one-dimensional harmonic oscillator

$$C_{V,m}^{1-D} = R\left(\frac{\Theta_v}{T}\right)^2 \left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{18.9.2}$$

where R is the universal gas constant, T is absolute temperature, and Θ_v is called the 'characteristic vibrational temperature' of the oscillator and depends on the vibrational frequency (ν) according to

$$\Theta_v = \frac{h\nu}{k} \tag{18.9.3}$$

with h representing Plank's constant and k representing Boltzmann's constant.

Since the vibrations in each dimension are assumed to be independent, the expression for the constant volume molar heat capacity of a 'three-dimensional' Einstein Solid is obtained by simply multiplying Equation 18.9.2 by three;

$$C_{V,m}^{3-D} = 3R\left(\frac{\Theta_v}{T}\right)^2 \left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{18.9.4}$$

The temperature variation of the heat capacity of most metallic solids is well described by Equation 18.9.4. Furthermore, plots of Equation 18.9.4 as a function of temperature for metals with widely varying vibrational frequencies reveal that the heat capacity always approaches the same asymptotic limit of $3R$ at high temperatures. Stated another way, at high temperatures

$$\lim_{T\to\infty}\left[\left(\frac{\Theta_v}{T}\right)^2 \left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2\right] = 1 \tag{18.9.5}$$

and Equation 18.9.4 reduces to

$$\lim_{T\to\infty}\left[C_{V,m}^{3D}\right] = 3R \tag{18.9.6}$$

(You will be asked to verify this result in the exercise below). According to Equation 18.9.6, the molar heat capacities of metallic solids should approach 24.9 J/(K mol) at high temperatures, regardless of the identity of the metal.

The vibrational frequencies of most metallic solids are usually small enough so that Θ_v lies considerably below room temperature ($\Theta_v \ll 298\ K$). For these substances, the limits implied by Equations 18.9.5 and 18.9.6 are well approximated even at room temperature, leading to the result that $C_{v,m} = 24.9\ J/(K \cdot mol)$ for most metals at room temperature.

In the early 1800s, two French scientists by the names of Pierre Louis Dulong and Alexis Therese Petit empirically discovered the same remarkable result. The Dulong-Petit Law is normally expressed in terms of the specific heat capacity (C_s) and the molar mass (M) of the metal

$$C_s M = C_{V,m} \approx 25 (J\,K^{-1}\,mol^{-1}) \tag{18.9.7}$$

where C_s represents how much heat is required to raise the temperature of 'one gram' of that substance by one degree Kelvin. Dulong and Petit, as well as other scientists of their time, used this famous relationship as a means of establishing more accurate values for the atomic weight of metallic elements (by instead measuring the specific heat capacity of the element and using the Dulong-Petit relationship, which is a relatively simple method of establishing weights in comparison to the more disputable gravimetric methods that were being used at the time to establish the equivalent weights of elements).

In the exercise below, you will look up the specific heat capacities of a number of elements that exist as simple monoatomic solids at room temperature and assess the accuracy of the Dulong-Petit law.

Experimental Data

Consult the CRC Handbook of Chemistry and Physics (CRC Press: Boca Raton, FL) and compile a table of specific heat capacities for a large number of elements that are known to exist as monoatomic solids at room temperature. Also look up and record the molar mass of these elements. The elements that you consider should be restricted to those appearing in groups 1-14 of the periodic table. Make sure you generate a fairly large list which includes a number of elements that are normally considered as metallic in character (such as copper, iron, sodium, lithium, gold, platinum, barium, and aluminum), but also some non-metallic elements that are nonetheless monoatomic isotropic solids (such as carbon-diamond, beryllium, boron, and silicon). Heat capacities that are usually reported in the literature are not actual constant volume heat capacities (C_v), but are instead constant pressure heat capacities (C_p). Fortunately, C_p and C_v are essentially equal for simple solids (within the level of precision that we consider in this exercise), and you can assume that the values from the CRC Handbook represent C_s.

Exercises

1. Enter the element name, the specific heat capacity, and the molar mass of each element in a spreadsheet. Calculate the product of specific heat and molar mass for each element and calculate how much this product differs from the Dulong-Petit prediction (express your result as a percent difference relative to $3R$).
2. Assess the generality of the Dulong-Petit law in an alternate way by generating a plot of specific heat as a function of reciprocal Molar Mass (C_s versus $1/M$), which should be linear with a slope equal to 3R if the data behave according to Equation 18.9.7.
3. Inspect your results from 1 and 2 above and identify any elements that significantly deviate from the Dulong-Petit law. When they occur, do deviations tend to be smaller or larger than 3R? Does the degree of deviation from the Dulong-Petit law seem to correlate with periodic trends in metallic (or covalent) bonding for these elements? Do deviations tend to occur more readily for elements of smaller or higher atomic weight? Explain how the type of bonding and the magnitude of the atomic weight can lead to deviations from the arguments made in Equations 18.9.5-18.9.7 above.
4. Use the plotting method that you employed in step 2 above as a means of determining a value for the universal gas constant (R) - but make sure you throw-out any specific heat data for elements that you suspect do not fall within the limit $\Theta_v \ll 298\,K$. Calculate the percent error in the value of R that you determine.
5. Verify that the limit expressed in Equation 18.9.5 above is true (HINT: expand each of the exponential terms in a power series and note that higher-order terms are negligible in the limit $T \gg \Theta_v$).

18.9: Molar Heat Capacities is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Specific Heat Capacities and the Dulong-Petit Law** by Tandy Grubbs is licensed CC BY-NC-SA 4.0.

18.E: Partition Functions and Ideal Gases (Exercises)

18.E: Partition Functions and Ideal Gases (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

6: The Hydrogen Atom

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

The solution of the Schrödinger equation (wave equation) for the hydrogen atom uses the fact that the Coulomb potential produced by the nucleus is isotropic (it is radially symmetric in space and only depends on the distance to the nucleus). Although the resulting energy eigenfunctions (the orbitals) are not necessarily isotropic themselves, their dependence on the angular coordinates follows completely generally from this isotropy of the underlying potential: the eigenstates of the Hamiltonian (that is, the energy eigenstates) can be chosen as simultaneous eigenstates of the angular momentum operator. This corresponds to the fact that angular momentum is conserved in the orbital motion of the electron around the nucleus. Therefore, the energy eigenstates may be classified by two angular momentum quantum numbers, ℓ and m (both are integers). The angular momentum quantum number ℓ = 0, 1, 2, ... determines the magnitude of the angular momentum. The magnetic quantum number m = $-\ell$, ..., $+\ell$ determines the projection of the angular momentum on the (arbitrarily chosen) z-axis.

6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly

6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics

6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers

6.5: s-orbitals are Spherically Symmetric

6.6: Orbital Angular Momentum and the p-Orbitals

6.7: The Helium Atom Cannot Be Solved Exactly

6.E: The Hydrogen Atom (Exercises)

6: The Hydrogen Atom is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly

The hydrogen atom, consisting of an electron and a proton, is a two-particle system, and the internal motion of two particles around their center of mass is equivalent to the motion of a single particle with a reduced mass. This reduced particle is located at r, where r is the vector specifying the position of the electron relative to the position of the proton. The length of r is the distance between the proton and the electron, and the direction of r and the direction of r is given by the orientation of the vector pointing from the proton to the electron. Since the proton is much more massive than the electron, we will assume throughout this chapter that the reduced mass equals the electron mass and the proton is located at the center of mass.

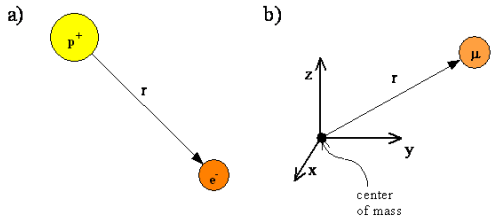


Figure 6.1.1: a) The proton (p^+) and electron (e^-) of the hydrogen atom. b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

Exercise 6.1.1

a. Assuming the Bohr radius gives the distance between the proton and electron, calculate the distance of the proton from the center of mass, and calculate the distance of the electron from the center of mass.
b. Calculate the reduced mass of the electron-proton system.
c. In view of your calculations in (a) and (b), comment on the validity of a model in which the proton is located at the center of mass and the reduced mass equals the electron mass.

Since the internal motion of any two-particle system can be represented by the motion of a single particle with a reduced mass, the description of the hydrogen atom has much in common with the description of a diatomic molecule discussed previously. The Schrödinger Equation for the hydrogen atom

$$\hat{H}(r,\theta,\varphi)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{6.1.1}$$

employs the same kinetic energy operator, $\hat{T}$, written in spherical coordinates. For the hydrogen atom, however, the distance, r, between the two particles can vary, unlike the diatomic molecule where the bond length was fixed, and the rigid rotor model was used. The hydrogen atom Hamiltonian also contains a potential energy term, $\hat{V}$, to describe the attraction between the proton and the electron. This term is the Coulomb potential energy,

$$\hat{V}(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{6.1.2}$$

where r is the distance between the electron and the proton. The Coulomb potential energy depends inversely on the distance between the electron and the nucleus and does not depend on any angles. Such a potential is called a central potential.

The full expression for $\hat{H}$ in spherical coordinates is

$$\hat{H}(r,\theta,\varphi) = -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r} \tag{6.1.3}$$

The contributions from rotational and radial components of the motion become clearer if we write out the complete Schrödinger equation,

$$\left\{-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\right\}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{6.1.4}$$

multiply both sides of Equation 6.1.4 by $2\mu r^2$, and rearrange to obtain

$$\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right) + 2\mu r^2\left[E + \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(r,\theta,\varphi) = \tag{6.1.5}$$

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\varphi) \tag{6.1.6}$$

Manipulating the Schrödinger equation in this way helps us recognize the square of the angular momentum operator in Equation 6.1.6. The square of the angular momentum operator in Equation 6.1.7.

$$\hat{M}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{6.1.7}$$

Substituting Equation 6.1.7 into Equation 6.1.6 produces

$$\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\psi(r,\theta,\varphi)\right) + 2\mu r^2[E - \hat{V}]\psi(r,\theta,\varphi) = \hat{M}^2\psi(r,\theta,\varphi) \tag{6.1.8}$$

Exercise 6.1.2

Show the algebraic steps going from Equation 6.1.4 to 6.1.6 and finally to 6.1.8. Justify the statement that the rotational and radial motion are separated in Equation 6.1.8.

Since the angular momentum operator does not involve the radial variable, r, we can separate variables in Equation 6.1.8 by using a product wavefunction, as we did previously for rigid rotors. We know that the eigenfunctions of the angular momentum operator are the Spherical Harmonic functions (Table M4), $Y(\theta,\varphi)$, so a good choice for a product function is

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi) \tag{6.1.9}$$

> *The Spherical Harmonic functions provide information about where the electron is around the proton, and the radial function $R(r)$ describes how far the electron is away from the proton.*

To separate variables, substitute the product function, Equation 6.1.9 into Equation 6.1.8, evaluate partial derivatives, divide each side by R(r) $Y(\theta,\varphi)$, and set each side of that resulting equation equal to a constant λ.

$$\frac{\hbar^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \frac{2\mu r^2}{R(r)}[E - V]R(r) = \lambda \tag{6.1.10}$$

$$\frac{1}{Y(\theta,\varphi)}\hat{M}^2 Y(\theta,\varphi) = \lambda \tag{6.1.11}$$

Equations 6.1.10 and 6.1.11 represent the radial differential equation and the angular differential equation, respectively. As we describe below, they are solved separately to give the $Y(\theta,\varphi)$ angular functions and the R(r) radial functions.

Exercise 6.1.3

Complete the steps leading from Equations 6.1.8 to 6.1.10 and 6.1.11.

Rearranging Equation 6.1.11 yields

$$\hat{M}^2 Y_l^{m_l}(\theta,\varphi) = \lambda Y_l^{m_l}(\theta,\varphi) \tag{6.1.12}$$

where we have added the indices l and m_l to identify a particular spherical harmonic function. Note that the notation has changed from that used with the Rigid Rotor; it is customary to use J and m_J to represent the angular momentum quantum numbers for rotational states, but for electronic states, it is customary to use l and m_l to represent the same thing. Further, the electronic angular momentum is designated by L and the corresponding operator is called $\hat{L}$. In complete electronic notation, Equation 6.1.12 is

$$\hat{L}^2 Y_l^{m_l}(\theta,\varphi) = \lambda Y_l^{m_l}(\theta,\varphi) \tag{6.1.13}$$

Equation 6.1.13 says that $Y_l^{m_l}(\theta,\varphi)$ must be an eigenfunction of the angular momentum operator $\hat{L}^2$ with eigenvalue λ. We know from the discussion of the Rigid Rotor that the eigenvalue λ is $J(J+1)\hbar^2$, or in electronic notation, $l(l+1)\hbar^2$. Consequently, Equation 6.1.13 becomes

$$\hat{L}^2 Y_l^{m_l}(\theta,\varphi) = l(l+1)\hbar^2 Y_l^{m_l}(\theta,\varphi) \tag{6.1.14}$$

Using this value for λ and rearranging Equation 6.1.10, we obtain

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) - E\right]R(r) = 0 \tag{6.1.15}$$

Exercise 6.1.4

Write the steps leading from Equation 6.1.10 to Equation 6.1.15.

The details for solving Equation 6.1.15 are provided elsewhere, but the procedure and consequences are similar to previously examined cases. As for the harmonic oscillator, an asymptotic solution (valid at large r) is found, and then the complete solutions are written as products of the asymptotic solution and polynomials arising from sequential truncations of a power series expansion.

Contributors

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

6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics

The solutions to the hydrogen atom Schrödinger equation are functions that are products of a spherical harmonic functions and a radial function.

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_l^{m_l}(\theta,\phi) \tag{6.2.1}$$

The wavefunctions for the hydrogen atom depend upon the three variables r, θ, and ϕ and the three quantum numbers n, l, and m_l. The variables give the position of the electron relative to the proton in spherical coordinates. The absolute square of the wavefunction, $|\psi(r,\theta,\phi)|^2$, evaluated at r, θ, and ϕ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r, θ, and ϕ.

Exercise 6.2.1

What is the value of the integral

$$\int_{allspace} |\psi(r,\theta,\phi)|^2 d\tau$$

or in braket notation

$$\langle\psi(r,\theta,\phi)|\psi(r,\theta,\phi)\rangle \ ?$$

The quantum numbers have names:

- n is called the principle quantum number,
- l is called the angular momentum quantum number, and
- m_l is called the magnetic quantum number because (as we will see, the energy in a magnetic field depends upon m_l).

Often l is called the azimuthal quantum number because it is a consequence of the θ-equation, which involves the azimuthal angle Θ, referring to the angle to the zenith. These quantum numbers have specific values that are dictated by the physical constraints or boundary conditions imposed upon the Schrödinger equation: n must be an integer greater than 0, l can have the values 0 to n-1, and m_l can have $2l+1$ values ranging from $-l$ - to $+l$ in unit or integer steps.

The values of the quantum number l usually are coded by a letter: s means 0, p means 1, d means 2, f means 3; the next codes continue alphabetically (e.g., g means $l = 4$). The quantum numbers specify the quantization of physical quantities. The discrete energies of different states of the hydrogen atom are given by n, the magnitude of the angular momentum is given by l, and one component of the angular momentum (usually chosen by chemists to be the z-component) is given by m_l. The total number of orbitals with a particular value of n is n^2.

The Φ function is found to have the quantum number m, where

$$\Phi_m(\phi) = A_m e^{im\phi} \tag{6.2.2}$$

and A_m is the normalization constant and $m = 0, \pm1, \pm2... \pm\infty$. The Θ function was solved and is known as *Legendre polynomials*, which have quantum numbers m and ℓ. When Θ and Φ are multiplied together, the product is known as spherical harmonics with labeling $Y_j^m(\theta,\phi)$.

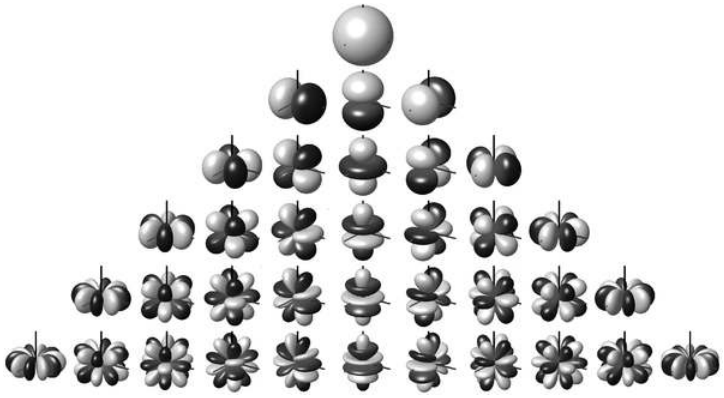


Figure **6.2.1**: Spherical Harmonics as commonly displayed, sorted by increasing energies and aligned for symmetry.

Figure **6.2.1** shows the spherical harmonics Y_J^M, which are solutions of the angular Schrödinger equation of a 3D rigid rotor. These are explicitly written in Table **6.2.1**. Notice that these functions are complex in nature.

Table **6.2.1**: spherical harmonics Y_J^M

m_J	J	$\Theta_J^{m_J}(\theta)$	$\Phi(\varphi)$	$Y_J^{m_J}(\theta,\varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{4\pi}}$
0	1	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi}$
-1	1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$
0	2	$\sqrt{\frac{5}{8}}(3\cos^2\theta-1)$	$\frac{1}{\sqrt{2\pi}}$	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$
1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\varphi}$
-1	2	$\sqrt{\frac{15}{4}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\varphi}$
2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\varphi}$
-2	2	$\sqrt{\frac{15}{16}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{-2i\varphi}$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\varphi}$

Exercise 6.2.2

Consider several values for n, and show that the number of orbitals for each n is n^2.

Exercise 6.2.3

Construct a table summarizing the allowed values for the quantum numbers n, l, and m_l. for energy levels 1 through 7 of hydrogen.

Exercise 6.2.4

The notation 3d specifies the quantum numbers for an electron in the hydrogen atom. What are the values for n and l? What are the values for the energy and angular momentum? What are the possible values for the magnetic quantum number? What are the

possible orientations for the angular momentum vector?

The hydrogen atom wavefunctions, $\psi(r,\theta,\phi)$, are called atomic orbitals. **An atomic orbital is a function that describes one electron in an atom.** The wavefunction with $n = 1$, ℓ = 0\), ($m_e ll = 0$ is called the 1s orbital, and an electron that is described by this function is said to be "in" the ls orbital, i.e. have a 1s orbital state. The constraints on n, ℓ, and m_ℓ that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

Visualizing the variation of an electronic wavefunction with r, θ, and ϕ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron-deficient part of one molecule is attracted to an electron-rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately do not reveal the shape of an orbital very well. The shape can be revealed better in a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$. Do not confuse such plots with polar plots, which look similar. Probability densities also can be represented by contour maps, as shown in Figure **6.2.2**.

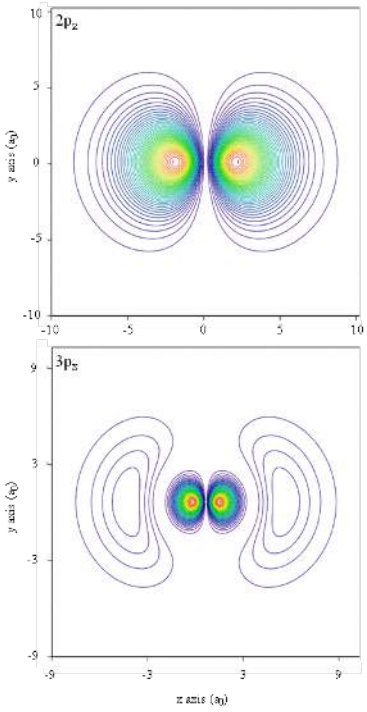


Figure **6.2.2**: Contour plots in the x-y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low $R(r)^2$. The angular function used to create the figure was a linear combination of two Spherical Harmonic functions.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, $R(r)$, for the 1s, 2s, and 2p orbitals plotted in Figure **6.2.3**.

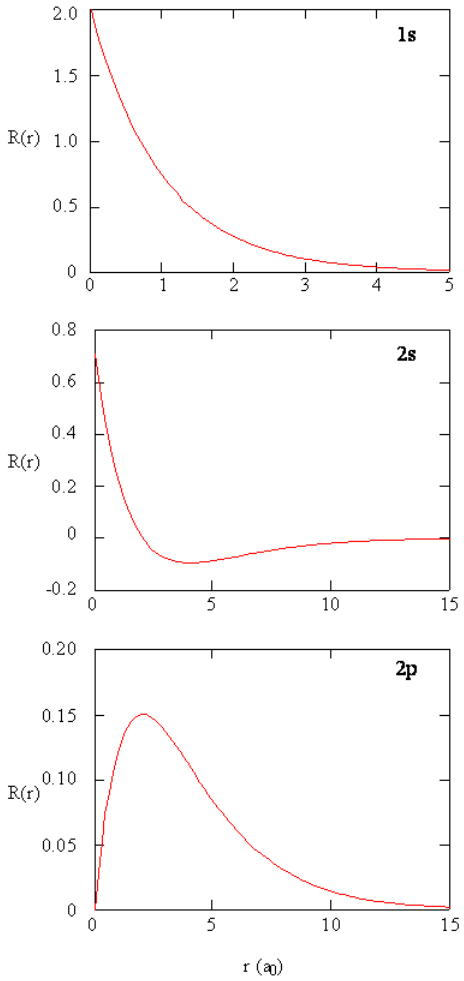


Figure **6.2.3**: Radial function, $R(r)$, for the 1s, 2s, and 2p orbitals.

The 1s function in Figure **6.2.3** starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

Next notice how the radial function for the 2s orbital, Figure **6.2.3**, goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$, but p, d, f and all other functions go to zero at the origin. It is useful to remember that there are $n - 1 - l$ radial nodes in a wavefunction, which means that a 1s orbital has no radial nodes, a 2s has one radial node, and so on.

Exercise 6.2.5

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

Exercise 6.2.6

What mathematical feature of each of the radial functions controls the number of radial nodes?

Answer

The Laguerre polynomial controls the radial nodes with the number of roots for the Laguerre polynomial is the number of radial nodes.

Exercise 6.2.7

At what value of r does the 2s radial node occur?

Answer

A node exists when the radial portion of the wavefunction equals 0. The radial portion of the 2s wavefunction is:

$$\left(\frac{1}{2\sqrt{2}}\right)\left(\frac{Z}{\alpha_0}\right)^{\frac{3}{2}}(2-\rho)e^{\frac{-\rho}{2}} \tag{6.2.3}$$

where

$$\rho = \frac{Zr}{\alpha_0} \tag{6.2.4}$$

*Z=1\(for the hydrogen atom

and $\alpha_0 = \$$ is the Bohr radius

Therefore:

$$\left(\frac{1}{2\sqrt{2}}\right)\left(\frac{1}{\alpha_0}\right)^{\frac{3}{2}}\left(2-\frac{r}{\alpha_0}\right)e^{\frac{-2r}{\alpha_0}} \tag{6.2.5}$$

For this wavefunction,

- $\left(\frac{1}{\alpha_0}\right)^{\frac{3}{2}}$ is a constant and will never equal 0.
- $e^{\frac{-2r}{\alpha_0}}$ is an exponential, and will also never equal 0.

Therefore, our node is when $\left(2-\frac{r}{\alpha_0}\right)=0$ and

$$r = 2\alpha_0 \tag{6.2.6}$$

Exercise 6.2.8

Make a table that provides the energy, number of radial nodes, and the number of angular nodes and total number of nodes for each function with $n=1$, $n=2$, and $n=3$. Identify the relationship between the energy and the number of nodes. Identify the relationship between the number of radial nodes and the number of angular nodes.

Answer

Wavefunction	Energy	Total Nodes	Radial Nodes	Angular Nodes
1s	13.6 eV	0	0	0
2s	3.4 eV	1	1	0
2p	3.4 eV	1	0	1
3s	1.5 eV	2	2	0
3p	1.5 eV	2	1	1
3d	1.5 eV	2	0	2

The energy of the electron in each wavefunction is

$$E = \frac{Z^2 E_h}{2n^2} \tag{6.2.7}$$

The number of total nodes is (N-1\), the number of radial nodes is $N-L-1$ and the number of angular nodes is L.

The quantity $R(r)^*R(r)$ gives the radial probability density; i.e., the probability density for the electron to be at a point located the distance r from the proton. Radial probability densities for three atomic orbitals are plotted in Figure **6.2.4**.

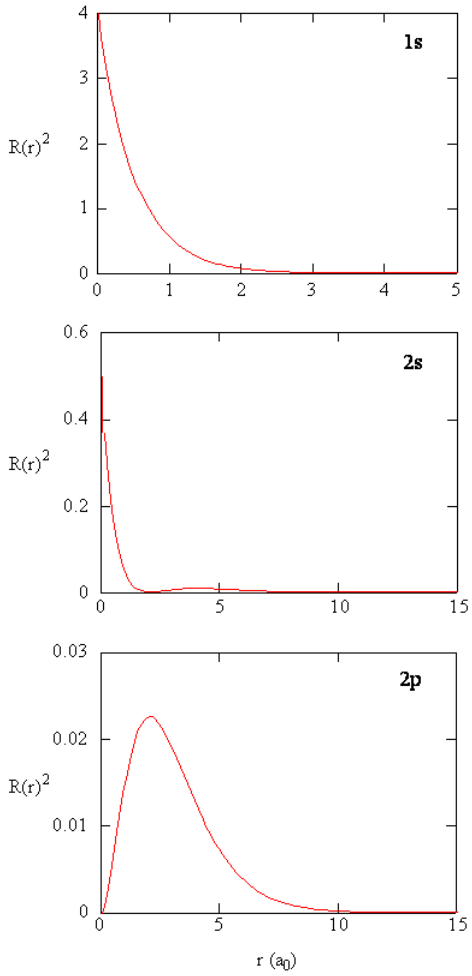


Figure **6.2.4**: Radial probability densities for the 1s, 2s, and 2p orbitals.

When the **radial probability density** for every value of r is multiplied by the area of the spherical surface represented by that particular value of r, we get the radial distribution function. The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the proton. Since the area of a spherical surface is $4\pi r^2$, the radial distribution function is given by

$$\underbrace{4\pi r^2 R(r)^* R(r)}_{radial probability density} \tag{6.2.8}$$

Radial distribution functions are shown in Figure **6.2.5**. At small values of r, the radial distribution function is low because the small surface area for small radii modulates the high value of the radial probability density function near the nucleus. As we increase r, the surface area associated with a given value of r increases, and the r^2 term causes the radial distribution function to increase even though the radial probability density is beginning to decrease. At large values of r, the exponential decay of the radial function outweighs the increase caused by the r^2 term and the radial distribution function decreases.

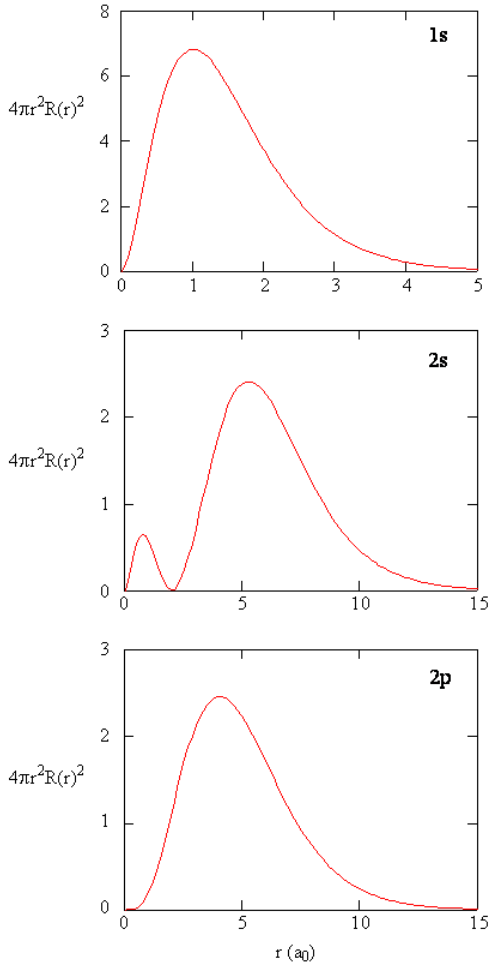


Figure **6.2.5**: The radial distribution function for the 1s, 2s, and 2p orbitals.

Exercise 6.2.9

Write a quality comparison of the radial function and radial distribution function for the 2s orbital. See Figure **6.2.6**.

Answer

$\4piR(r)^2R(r)^2$ gives the radial probability density of the distance of electron at distance r from the nucleus.

The radial probability function is low at small values of r because of a small surface area near nucleus, for example at 2s at a small value of r the radial probability function is low.

At higher values of r the surface area increases while radial probability density decreases, this causes the radial distribution function to increase.

In contrast the radial probability density is high at small surface area and when r is near the nucleus, i.e low values of r.

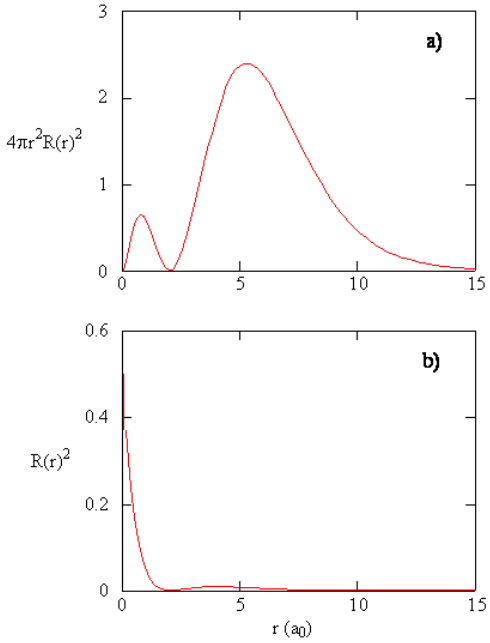


Figure **6.2.6**: Comparison of a) the radial distribution function and b) the radial probability density for the 2s orbital.

Contributors

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

6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics is shared under a not declared 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

Consider a particle described by the Cartesian coordinates $(x, y, z) \equiv \vec{r}$ and their conjugate momenta $(p_x, p_y, p_z) \equiv \vec{p}$. The classical definition of the *orbital angular momentum* of such a particle about the origin is (i.e., via the cross product):

$$\vec{L} = \vec{r} \times \vec{p} \tag{6.3.1}$$

which can be separated into projections into each of the primary axes :

$$L_x = y\,p_z - z\,p_y, \tag{6.3.2}$$
$$L_y = z\,p_x - x\,p_z \tag{6.3.3}$$
$$L_z = x\,p_y - y\,p_x \tag{6.3.4}$$

Extending this discussion to the quantum mechanics, we can us assume that the operators $(\hat{L}_x, \hat{L}_y, \hat{L}_z) \equiv \vec{L}$ which represent the components of orbital angular momentum in quantum mechanics can be defined in an analogous manner to the corresponding components of classical angular momentum. In other words, we are going to assume that the above equations specify the angular momentum operators in terms of the position and linear momentum operators.

In Cartesian coordinates, the three operators for the orbital angular momentum components can be written as

$$\hat{L}_x = -\mathrm{i}\,\hbar\left(y\,\frac{\partial}{\partial z} - z\,\frac{\partial}{\partial y}\right) \tag{6.3.5}$$

$$\hat{L}_y = -\mathrm{i}\,\hbar\left(z\,\frac{\partial}{\partial x} - x\,\frac{\partial}{\partial z}\right) \tag{6.3.6}$$

$$\hat{L}_z = -\mathrm{i}\,\hbar\left(x\,\frac{\partial}{\partial y} - y\,\frac{\partial}{\partial x}\right) \tag{6.3.7}$$

These can be transforming to operators in standard spherical polar coordinates,

$$x = r\,\sin\theta\,\cos\varphi \tag{6.3.8}$$
$$y = r\,\sin\theta\,\sin\varphi \tag{6.3.9}$$
$$z = r\cos\theta \tag{6.3.10}$$

we obtain

Multiple \label

We can introduce a new operator $\hat{L}^2$:

$$\hat{L}^2 = \hat{L}_x^{\,2} + \hat{L}_y^{\,2} + \hat{L}_z^{\,2} \tag{6.3.11}$$
$$= -\hbar^2\left(\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\right) \tag{6.3.12}$$

The eigenvalue problem for $\hat{L}^2$ takes the form

$$\hat{L}^2|\psi\rangle = \lambda\,\hbar^2|\psi\rangle \tag{6.3.13}$$

where $\psi(r, \theta, \varphi)$ is the wavefunction, and λ is a number. Let us write

$$\psi(r, \theta, \varphi) = R(r)\,Y(\theta, \varphi) \tag{6.3.14}$$

By definition,

$$L^2\,Y_l^{m_l} = l\,(l+1)\,\hbar^2\,Y_l^{m_l} \tag{6.3.15}$$

where l is an integer. This is an important conclusion that argues the angular momentum is quantized with the square of the magnitude of the angular momentum only capable of assume one of the discrete set of values (Equation 6.3.15). From this, the **amplitude** of angular momentum can be expressed

$$|\vec{L}| = \sqrt{L^2} = \sqrt{l(l+1)}\hbar \tag{6.3.16}$$

Warning

We often refer to a particle in a state with angular momentum quantum number l as having angular momentum l, rather than saying that it has angular momentum of $\sqrt{l(l+1)}\hbar$ magnitude, primarily since it is awkward to say quickly.

The properties of spherical harmonics that the z-component of the angular momentum (L_z) is also quantized and can only assume a one of a discrete set of values

$$L_z Y_l^{m_l} = m\hbar Y_l^{m_l} \tag{6.3.17}$$

where m_l is an integer lying in the range $-l \leq m_l \leq l$.

- l is sometimes called "azimuthal quantum number" or "orbital quantum number"
- m_l is sometimes called "magnetic quantum number"

Simultaneous Measurements

Note that observables associated with $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ can, in principle, be measured. However, to determine if they can be measured *simultaneously* with infinite precision, the corresponding operators must **commute**. Remember that the fundamental commutation relations satisfied by the position and linear momentum operators are:

Multiple \label

where i and j stand for either x, y, or z. Consider the commutator of the operators $\hat{L}_x$ and $\hat{L}_z$:

Multiple \label

The **cyclic permutations** of the above result yield the fundamental commutation relations satisfied by the components of an orbital angular momentum:

$$[\hat{L}_x, \hat{L}_y] = \mathrm{i}\hbar\hat{L}_z \tag{6.3.18}$$

$$[\hat{L}_y, \hat{L}_z] = \mathrm{i}\hbar\hat{L}_x \tag{6.3.19}$$

$$[\hat{L}_z, \hat{L}_x] = \mathrm{i}\hbar\hat{L}_y \tag{6.3.20}$$

The three commutation relations (Equations 6.3.18 - 6.3.20) are the foundation for the whole theory of angular momentum in quantum mechanics. Whenever we encounter three operators having these commutation relations, we know that the dynamical variables that they represent have identical properties to those of the components of an angular momentum (which we are about to derive). In fact, we shall assume that any three operators that satisfy the commutation relations (Equations 6.3.18 - 6.3.20) represent the components of some sort of angular momentum.

> *In fact, we shall assume that any three operators that satisfy the commutation relations (Equations 6.3.18 - 6.3.20) represent the components of some sort of angular momentum.*

Example 6.3.1: Commutators

Show that the $\hat{L}^2$ and $\hat{L}_x$ operators commute.

Solution

We want to confirm that $[\hat{L}^2, \hat{L}_x] = 0$ that from Equation 6.3.11 this can be expanded

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x]$$

from the properties of commutators, this can be expanded

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}_x^2, \hat{L}_x] + [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x]$$

However,

$$[\hat{L}_x^2, \hat{L}_x] = \hat{L}_x^2\hat{L}_x - \hat{L}_x\hat{L}_x^2 = \hat{L}_x\hat{L}_x\hat{L}_x - \hat{L}_x\hat{L}_x\hat{L}_x = 0$$

So

$$\begin{aligned}[\hat{L^2}, \hat{L}_x] &= [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\ &= \hat{L}_y^2\hat{L}_x - \hat{L}_x\hat{L}_y^2 + \hat{L}_z^2\hat{L}_x - \hat{L}_x\hat{L}_z^2 \\ &= \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z\end{aligned}$$

Lets look at some related forms which can be used to simplify the above expression. The first two terms can and final two terms can be rewritten as different commutators

$$\begin{aligned}[\hat{L}_y, \hat{L}_x] &= \hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] \\ &= (\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y)\hat{L}_y + \hat{L}_y(\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y) \\ &= \cancel{\hat{L}_y\hat{L}_x\hat{L}_y} - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_y\hat{L}_y\hat{L}_x - \cancel{\hat{L}_y\hat{L}_x\hat{L}_y}\end{aligned}$$

The first & fourth terms cancel, giving

$$[\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] = \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y$$

Similarly,

$$[Lz, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] = \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z$$

So,

$$\begin{aligned}[\hat{L^2}, \hat{L}_x] &= [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] \\ &= -i\hbar\hat{L}_z\hat{L}_y - i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_z\hat{L}_y \\ &= 0\end{aligned}$$

One can also show similarly that

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

The fact that L_z is known with certainty, but L_x and L_y are **unknown**; therefore every classical vector with the appropriate length and z-component can drawn, forming a cone (Figure **6.3.1**). The expected value of the angular momentum for a given ensemble of systems in the quantum state characterized by l and m_l could be somewhere on this cone while it cannot be defined for a single system (since the components of L do not commute with each other).

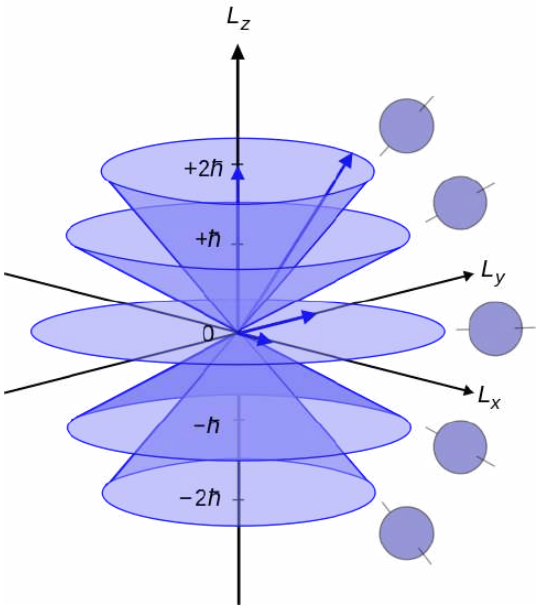


Figure **6.3.1**: Illustration of the vector model of orbital angular momentum. A set of states with quantum numbers $l = 2$, and $m_l = -2, -1, 0, +1, +2$. (Public Domain; Maschen via Wikipedia)

The Physical Meaning of Commutation of Two Operators

The mathematics of commutation relations is relatively straightforward, but what does it physically mean for an observable (Hermitian operator) to commute with another observable (Hermitian operator) in quantum mechanics?

If two operators $\hat{A}$ and $\hat{B}$ commute with each other then

$$\hat{A}\hat{B} - \hat{B}\hat{A} = 0, \tag{6.3.21}$$

which can be rearranged to

$$\hat{A}\hat{B} = \hat{B}\hat{A}. \tag{6.3.22}$$

This is not a trivial statement and many operations do not commute and hence the end-result depends on how you have ordered the operations.

If you recall that operators act on quantum mechanical states and give you a new state in return, then this means that with $\hat{A}$ and $\hat{B}$ commuting, the state you obtain from letting first $\hat{A}$ act and then $\hat{B}$ act on some initial state is the same as if you let first $\hat{B}$ and then $\hat{A}$ act on that state, i.e.,

$$\hat{A}\hat{B}|\psi\rangle = \hat{B}\hat{A}|\psi\rangle. \tag{6.3.23}$$

Recall that when you perform a quantum mechanical measurement, you will always measure an eigenvalue of your operator, and after the measurement your state is left in the corresponding eigenstate. The eigenstates to the operator are precisely those states for which there is **no uncertainty** in the measurement: You will **always** measure the eigenvalue.

Therefore, $\hat{B}|a\rangle$ must be an eigenfunction of $\hat{A}$ with eigenvalue a just like $|a\rangle$ itself is. That is essentially saying that $|a\rangle$ is an eigenfunction of $\hat{B}$.

A key example of this is since $\hat{L}^2$ and $\hat{L}_x$ commute (Example **6.3.1**) then both operators share the same eigenstates. Hence, we do no need to solve two eignevalue problems:

$$\hat{L}^2|\psi\rangle = \lambda|\psi\rangle \tag{6.3.24}$$

and

$$\hat{L}_x|\psi\rangle = \beta|\psi\rangle \tag{6.3.25}$$

If we solve one, we then know the eigenvalues ($|\psi\rangle$) for the other!

What does it mean when some observable $\hat{A}$ commutes with the Hamiltonian $\hat{H}$? First, we get all the result from above: There is a simultaneous eigenbasis of the energy-eigenstates and the eigenstates of $\hat{A}$. This can yield a tremendous simplification of the task of solving Schrödinger equations. For example, the Hamiltonian of the hydrogen atom commutes with $\hat{L}$, the angular momentum operator, and with $\hat{L}_z$, its z-component. This tells you that you can classify the eigenstates by an angular- and magnetic quantum number l and m.

Summary

In the quantum world, angular momentum is quantized. The square of the magnitude of the angular momentum (determined by the eigenvalues of the $\hat{L}^2$ operator) can only assume one of the discrete set of values

$$l(l+1)\hbar^2$$

with $l = 0, 1, 2, ...$

The z-component of the angular momentum (i.e., projection of L onto the z-axis) is also quantized with

$$L_z = m\hbar$$

with

$$m_l = -l, 0-1, ..., 0, ... + l + 1, l$$

for a given value of l. Hence, l and m_l are the *angular momentum quantum number* and the *magnetic quantum number,* respectively.

Contributors

- Richard Fitzpatrick (Professor of Physics, The University of Texas at Austin)

6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers

The solutions to the hydrogen atom Schrödinger equation discussed previously are functions that are products of a **spherical harmonic function** and a **radial function**.

$$\psi_{n,l,m_\ell}(r,\theta,\varphi) = \underbrace{R_{n,\ell}(r)}_{radial}\underbrace{Y_l^{m_\ell}(\theta,\varphi)}_{angular} \tag{6.4.1}$$

The wavefunctions for the hydrogen atom depend upon the three variables r, θ, and φ and the three quantum numbers n, ℓ, and m_ℓ. The variables give the position of the electron relative to the proton in spherical coordinates. The absolute square of the wavefunction, $|\psi(r,\theta,\varphi)|^2$, evaluated at r, θ, and φ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r, θ, and φ.

Exercise 6.4.1

Evaluate the following integrals

a. $\langle\psi(r,\theta,\varphi)|\psi(r,\theta,\varphi)\rangle$
b. $\langle\psi(r,\theta,\varphi)|\psi(r',\theta',\varphi')\rangle$

Answer

a.

This integral is equal to one since $\psi(r,\theta,\varphi)$ are normalized eigenstates.

b.

However, we can explicitly evaluate this integral for any arbitrary pair of eigenstates

$$\begin{aligned}
\langle\psi(r,\theta,\varphi)|\psi(r',\theta',\varphi')\rangle &= \int_{allspace}\psi^*(r,\theta,\varphi)\psi(r',\theta',\varphi')d\tau \\
&= \int_0^\infty dr\int_0^\pi d\theta\int_0^{2\pi} d\varphi(r^2\sin(\theta))\overbrace{\psi*(r,\theta,\varphi)}^{R_{n,l}(r)Y_l^{m_l}(\theta,\varphi)}\overbrace{\psi(r,\theta,\varphi)}^{R_{n',l'}(r)Y_{l'}^{m_l'}(\theta,\varphi)} \\
&= \int_0^\infty dr\int_0^\pi d\theta\int_0^{2\pi} d\varphi(r^2\sin(\theta))[R_{n,l}(r)Y_l^{m_l}(\theta,\varphi)][R_{n',l'}(r)Y_{l'}^{m_l'}(\theta,\varphi)] \\
&= \left[\int_0^\infty r^2[R_{n,l}(r)R_{n',l'}(r)]dr\right]\left[\int_0^{2\pi}\int_0^\pi \sin(\theta)[Y_l^{m_l}(\theta,\varphi)Y_{l'}^{m_l'}(\theta,\varphi)]d\theta d\varphi\right] \\
&= \langle R_{n,l}(r)|R_{n',l'}(r)\rangle\langle Y_l^{m_l}(\theta,\varphi)|Y_{l'}^{m_l'}(\theta,\varphi)\rangle \\
&= (\delta_{nn'}\delta_{ll'})(\delta_{ll'}\delta_{mm'}) = \delta_{nn'}\delta_{ll'}\delta_{mm'}
\end{aligned}$$

While part a demonstrates normality of the eigenstates, part b demonstrates the orthogonality of the eigenstate (and normality too).

The quantum numbers have names:

- n is called the principal quantum number,
- ℓ is called the angular momentum quantum number, and
- m_ℓ is called the magnetic quantum number because the energy in a magnetic field depends upon m_ℓ.

Often ℓ is called the azimuthal quantum number because it is a consequence of the θ-equation, which involves the azimuthal angle Θ, referring to the angle to the zenith.

Radial Part of the Wavefunction

The asymptotic behavior (i.e., far away from the nucleus) to the radial part of the wavefunction is

$$R_{asymptotic}(r) \sim \exp\left(-\frac{r}{n}a_0\right) \tag{6.4.2}$$

where n will turn out to be a quantum number and a_0 is the Bohr radius (~52.9 pm). Note that this function decreases exponentially with distance, in a manner similar to the decaying exponential portion of the harmonic oscillator wavefunctions, but with a different distance dependence, r vs. r^2.

Exercise 6.4.2

What happens to the magnitude of $R_{asymptotic}(r)$ as the distance r from the proton approaches infinity? Sketch a graph of the function, $R_{asymptotic}(r)$. Why might this behavior be expected for an electron in a hydrogen atom?

The polynomials produced by the truncation of the power series are related to the associated Laguerre polynomials, $L_{n,l}(r)$, where the set of c_i are constant coefficients.

$$L_{n,l}(r) = \sum_{r=0}^{n-l-1} c_i r^i \tag{6.4.3}$$

These polynomials are identified by two indices or quantum numbers, n and ℓ. Physically acceptable solutions require that n must be greater than or equal to $l+1$. The smallest value for ℓ is zero, so the smallest value for n is 1. The angular momentum quantum number affects the solution to the radial equation because it appears in the radial differential equation, (Equation 6.4.1).

The $R(r)$ functions that solve the radial differential Equation 6.4.1, are products of the associated Laguerre polynomials and the exponential factor, multiplied by a normalization factor ($N_{n,\ell}$) and $\left(\frac{r}{a_0}\right)^l$.

$$R(r) = N_{n,\ell}\left(\frac{r}{a_0}\right)^l L_{n,\ell}(r) e^{-\frac{r}{na_0}} \tag{6.4.4}$$

The decreasing exponential term overpowers the increasing polynomial term so that the overall wavefunction exhibits the desired approach to zero at large values of r. The first six radial functions are provided in Table 6.4.1. Note that the functions in the table exhibit a dependence on Z, the atomic number of the nucleus. As discussed later in this chapter, other one electron systems have electronic states analogous to those for the hydrogen atom, and inclusion of the charge on the nucleus allows the same wavefunctions to be used for all one-electron systems. For hydrogen, $Z = 1$.

Table 6.4.1: Radial functions for one-electron atoms and ions. Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

n	ℓ	$R_{n,\ell}(\rho)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}$
2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/2}$
3	0	$\frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18\rho+2\rho^2)e^{-\rho/3}$
3	1	$\frac{1}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6\rho+\rho^2)e^{-\rho/3}$
3	2	$\frac{1}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\rho^2 e^{-\rho/3}$

The constraint that n be greater than or equal to $l+1$ also turns out to quantize the energy, producing the same quantized expression for hydrogen atom energy levels that was obtained from the Bohr model of the hydrogen atom.

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2} \tag{6.4.5}$$

Bohr Theory vs. Schrödinger Theory

It is interesting to compare the results obtained by solving the Schrödinger equation with Bohr's model of the hydrogen atom. There are several ways in which the Schrödinger and Bohr models differ.

1. First, and perhaps most strikingly, the Schrödinger model does not produce well-defined orbits for the electron. The wavefunctions only give us the probability for the electron to be at various directions and distances from the proton.
2. Second, the quantization of angular momentum is different from that proposed by Bohr. Bohr proposed that the angular momentum is quantized in integer units of $\hbar$, while the Schrödinger model leads to an angular momentum of $\sqrt{(l(l+1)}\hbar$.
3. Third, the quantum numbers appear naturally during solution of the Schrödinger equation while Bohr had to postulate the existence of quantized energy states. Although more complex, the Schrödinger model leads to a better correspondence between theory and experiment over a range of applications that was not possible for the Bohr model.

Exercise 6.4.3

Explain how the Schrödinger equation leads to the conclusion that the angular momentum of the hydrogen atom can be zero, and explain how the existence of such states with zero angular momentum contradicts Bohr's idea that the electron is orbiting around the proton in the hydrogen atom.

The Three Quantum Numbers

These quantum numbers have specific values that are dictated by the physical constraints or boundary conditions imposed upon the Schrödinger equation: n must be an integer greater than 0, ℓ can have the values 0 to n-1, and m_ℓ can have $2l+1$ values ranging from $-l$ - to $+l$ in unit or integer steps. The values of the quantum number ℓ usually are coded by a letter: s means 0, p means 1, d means 2, f means 3; the next codes continue alphabetically (e.g., g means $l = 4$). The quantum numbers specify the quantization of physical quantities. The discrete energies of different states of the hydrogen atom are given by n, the magnitude of the angular momentum is given by ℓ, and one component of the angular momentum (usually chosen by chemists to be the z-component) is given by m_ℓ. The total number of orbitals with a particular value of n is n^2.

Exercise 6.4.4

Consider several values for n, and show that the number of orbitals for each n is n^2.

Exercise 6.4.5

Construct a table summarizing the allowed values for the quantum numbers n, ℓ , and m_ℓ for energy levels 1 through 7 of hydrogen.

Exercise 6.4.6

The notation 3d specifies the quantum numbers for an electron in the hydrogen atom. What are the values for n and ℓ ? What are the values for the energy and angular momentum? What are the possible values for the magnetic quantum number? What are the possible orientations for the angular momentum vector?

Contributors

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

6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

6.5: s-orbitals are Spherically Symmetric

The hydrogen atom wavefunctions, $\psi(r,\theta,\varphi)$, are called atomic orbitals. An atomic orbital is a function that describes one electron in an atom. The wavefunction with $n = 1$, l = 0 is called the 1s orbital, and an electron that is described by this function is said to be "in" the ls orbital, i.e. have a 1s orbital state. The constraints on n, l, and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

Visualizing the variation of an electronic wavefunction with r, θ, and φ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron deficient part of one molecule is attracted to an electron rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

We can obtain an energy and one or more wavefunctions for every value of n, the principal quantum number, by solving Schrödinger's equation for the hydrogen atom. A knowledge of the wavefunctions, or probability amplitudes ψ_n, allows us to calculate the probability distributions for the electron in any given quantum level. When n = 1, the wave function and the derived probability function are independent of direction and depend only on the distance r between the electron and the nucleus. In Figure **6.5.1**, we plot both ψ_1 and P_1 versus r, showing the variation in these functions as the electron is moved further and further from the nucleus in any one direction. (These and all succeeding graphs are plotted in terms of the atomic unit of length, $a_0 = 0.529 \times 10^{-8}$ cm.)

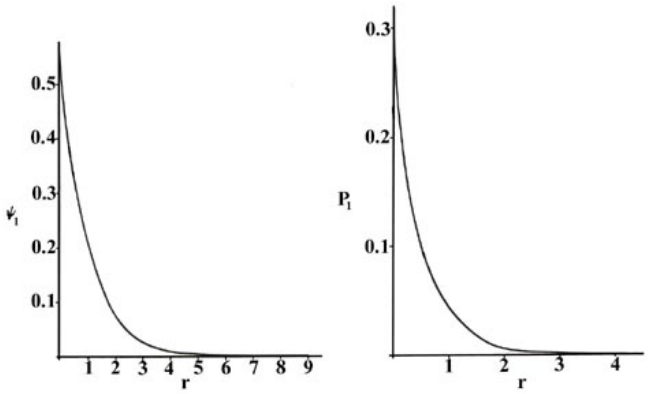


Figure **6.5.1**: The wave function and probability distribution as functions of r for the $n = 1$ level of the H atom. The functions and the radius r are in atomic units in this and succeeding figures.

Two interpretations can again be given to the P_1 curve. An experiment designed to detect the position of the electron with an uncertainty much less than the diameter of the atom itself (using light of short wavelength) will, if repeated a large number of times, result in Figure **6.5.1** for P_1. That is, the electron will be detected close to the nucleus most frequently and the probability of observing it at some distance from the nucleus will decrease rapidly with increasing r. The atom will be ionized in making each of these observations because the energy of the photons with a wavelength much less than 10^{-8} cm will be greater than K, the amount of energy required to ionize the hydrogen atom. If light with a wavelength comparable to the diameter of the atom is employed in the experiment, then the electron will not be excited but our knowledge of its position will be correspondingly less precise. In these experiments, in which the electron's energy is not changed, the electron will appear to be "smeared out" and we may interpret P_1 as giving the fraction of the total electronic charge to be found in every small volume element of space. (Recall that the addition of the value of P_n for every small volume element over all space adds up to unity, i.e., one electron and one electronic charge.)

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately does not reveal the shape of an orbital very well. The shape can be revealed better in

a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$.

We could also represent the distribution of negative charge in the hydrogen atom in the manner used previously for the electron confined to move on a plane (Figure **6.5.2**), by displaying the charge density in a plane by means of a contour map. Imagine a plane through the atom including the nucleus. The density is calculated at every point in this plane. All points having the same value for the electron density in this plane are joined by a contour line (Figure **6.5.2**). Since the electron density depends only on *r*, the distance from the nucleus, and not on the direction in space, the contours will be circular. A contour map is useful as it indicates the "shape" of the density distribution.

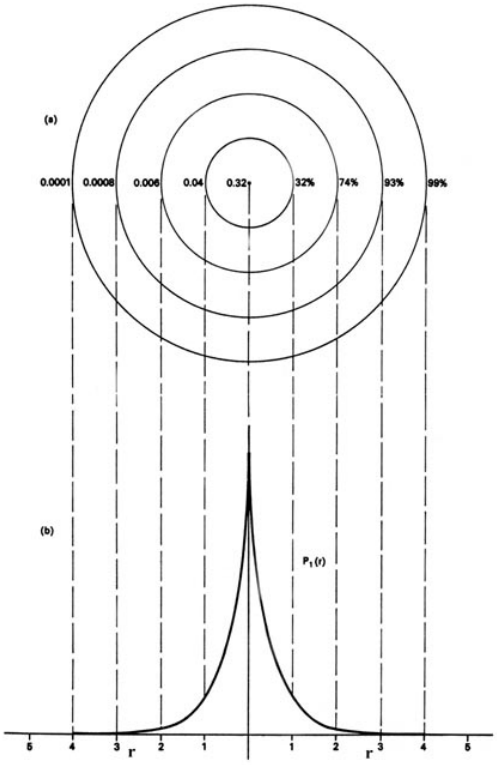


Figure **6.5.2**: (a) A contour map of the electron density distribution in a plane containing the nucleus for the $n = 1$ level of the H atom. The distance between adjacent contours is 1 au. The numbers on the left-hand side on each contour give the electron density in au. The numbers on the right-hand side give the fraction of the total electronic charge which lies within a sphere of that radius. Thus 99% of the single electronic charge of the H atom lies within a sphere of radius 4 au (or diameter = 4.2×10^{-8} *cm*). (b) This is a profile of the contour map along a line through the nucleus. It is, of course, the same as that given previously in Figure **6.5.1** for P_1, but now plotted from the nucleus in both directions.

When the electron is in a definite energy level we shall refer to the P_n distributions as ***electron density distributions***, since they describe the manner in which the total electronic charge is distributed in space. The electron density is expressed in terms of the number of electronic charges per unit volume of space, e^-/V. The volume V is usually expressed in atomic units of length cubed, and one atomic unit of electron density is then e^-/a_0^3. To give an idea of the order of magnitude of an atomic density unit, 1 au of charge density $e^-/a_0^3 = 6.7$ electronic charges per cubic Ångstrom. That is, a cube with a length of 0.52917×10^{-8} *cm*, if uniformly filled with an electronic charge density of 1 au, would contain 6.7 electronic charges.

For every value of the energy E_n, for the hydrogen atom, there is a degeneracy equal to n^2. Therefore, for $n = 1$, there is but one atomic orbital and one electron density distribution. However, for $n = 2$, there are four different atomic orbitals and four different electron density distributions, all of which possess the same value for the energy, E_2. Thus for all values of the principal quantum number n there are n^2 different ways in which the electronic charge may be distributed in three-dimensional space and still possess the same value for the energy. For every value of the principal quantum number, ***one*** of the possible atomic orbitals is independent of direction and gives a spherical electron density distribution which can be represented by circular contours as has been exemplified above for the case of $n = 1$. The other atomic orbitals for a given value of n exhibit a directional dependence and

predict density distributions which are not spherical but are concentrated in planes or along certain axes. The angular dependence of the atomic orbitals for the hydrogen atom and the shapes of the contours of the corresponding electron density distributions are intimately connected with the angular momentum possessed by the electron.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, $R(r)$, for the 1s and 2s orbitals plotted in Figure 6.5.3. The 1s function in Figure 6.5.3; starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

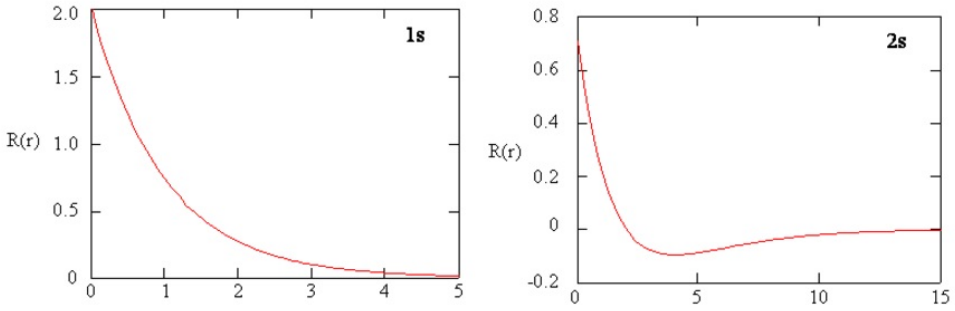


Figure 6.5.3: Radial function, $R(r)$, for the 1s and 2s orbitals. For an interactive graph click here.

Next notice how the radial function for the 2s orbital, Figure 6.5.3;, goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$.

Exercise 6.5.1

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

Exercise 6.5.2

What mathematical feature of each of the radial functions controls the number of radial nodes?

Exercise 6.5.3: Radial Nodes

At what value of r does the 2s radial node occur?

Exercise 6.5.4

Make a table that provides the energy, number of radial nodes, and the number of angular nodes and total number of nodes for each function with $n = 1$, $n = 2$, and $n = 3$. Identify the relationship between the energy and the number of nodes. Identify the relationship between the number of radial nodes and the number of angular nodes.

Radial probability densities for the 1s and 2s atomic orbitals are plotted in Figure 6.5.4.

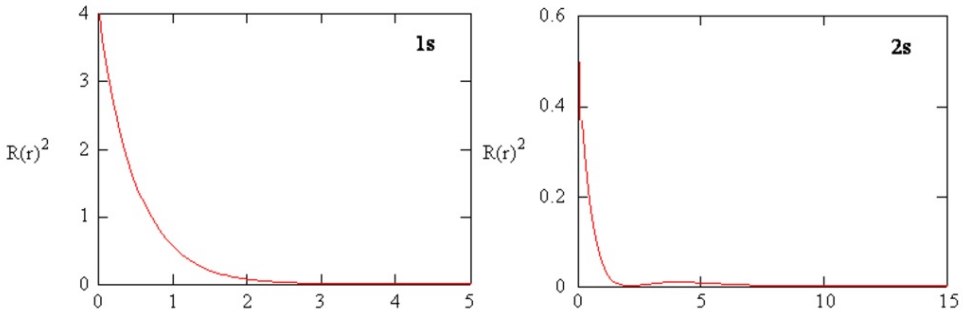


Figure 6.5.4: Radial densities ($R(r)^*R(r)$) for the 1s and 2s orbitals.

Radial Distribution Functions

Rather than considering the amount of electronic charge in one particular small element of space, we may determine the total amount of charge lying within a thin spherical shell of space. Since the distribution is independent of direction, consider adding up all the charge density which lies within a volume of space bounded by an inner sphere of radius r and an outer concentric sphere with a radius only infinitesimally greater, say $r + Dr$. The area of the inner sphere is $4pr^2$ and the thickness of the shell is D*r*. Thus the volume of the shell is $4\pi r^2 \Delta r$ and the product of this volume and the charge density $P_1(r)$, which is the charge or number of electrons per unit volume, is therefore the total amount of electronic charge lying between the spheres of radius r and $r + Dr$. The product $4\pi r^2 P_n$ is given a special name, the **radial distribution function**.

Volume Element for a Shell in Spherical Coordinates

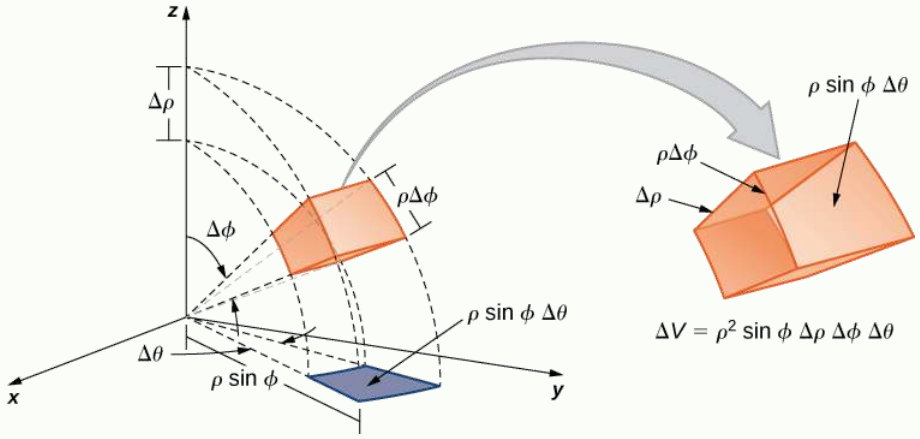
The reader may wonder why the volume of the shell is not taken as:

$$\frac{4}{3}\pi\left[(r+\Delta r)^3 - r^3\right] \tag{6.5.1}$$

the difference in volume between two concentric spheres. When this expression for the volume is expanded, we obtain

$$\frac{4}{3}\pi\left(3r^2\Delta r + 3r\Delta r^2 + \Delta r^3\right) \tag{6.5.2}$$

and for very small values of Δr the $3r\Delta r^2$ and Δr^3 terms are negligible in comparison with $3r^2\Delta r$. Thus for small values of Δr, the two expressions for the volume of the shell approach one another in value and when Δr represents an infinitesimal small increment in r they are identical.



The volume element of a box in spherical coordinates. Image used with permission (CC BY; OpenStax).

The radial distribution function is plotted in Figure 6.5.5 for the ground state of the hydrogen atom.

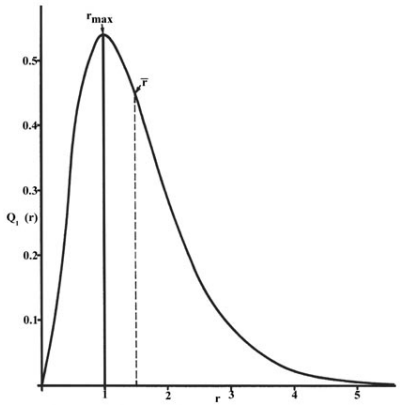


Figure 6.5.5: The radial distribution function for an H atom. The value of this function at some value of r when multiplied by δr gives the number of electronic charges within the thin shell of space lying between spheres of radius r and $r + \delta r$.

The curve passes through zero at $r = 0$ since the surface area of a sphere of zero radius is zero. As the radius of the sphere is increased, the volume of space defined by $4\pi r^2 Dr$ increases. However, as shown in Figure **6.5.4**, the absolute value of the electron density at a given point decreases with r and the resulting curve must pass through a maximum. This maximum occurs at $r_{max} = a_0$. Thus more of the electronic charge is present at a distance a_o, out from the nucleus than at any other value of r. Since the curve is unsymmetrical, the average value of r, denoted by $\bar{r}$, is not equal to r_{max}. The average value of r is indicated on the figure by a dashed line. A "picture" of the electron density distribution for the electron in the $n = 1$ level of the hydrogen atom would be a spherical ball of charge, dense around the nucleus and becoming increasingly diffuse as the value of r is increased.

> *The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the proton. Since the area of a spherical surface is $4\pi r^2$, the radial distribution function is given by $4\pi r^2 R(r)^* R(r)$.*

Radial distribution functions are shown in Figure **6.5.6**. At small values of r, the radial distribution function is low because the small surface area for small radii modulates the high value of the radial probability density function near the nucleus. As we increase r, the surface area associated with a given value of r increases, and the r^2 term causes the radial distribution function to increase even though the radial probability density is beginning to decrease. At large values of r, the exponential decay of the radial function outweighs the increase caused by the r^2 term and the radial distribution function decreases.

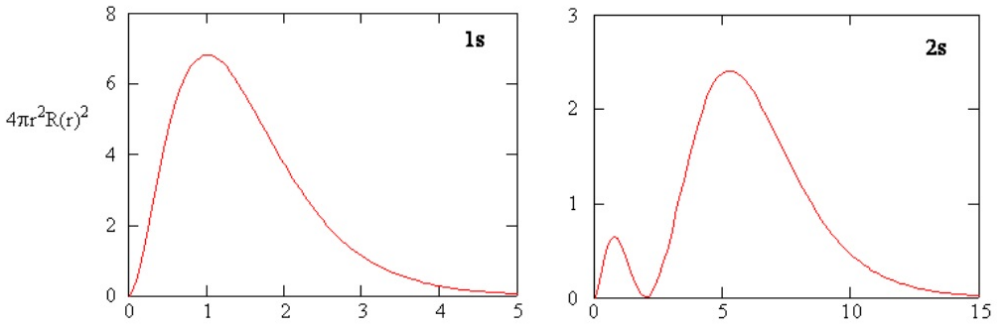


Figure **6.5.6**: The radial distribution function ($4\pi r^2 R(r)^* R(r)$) for the 1s and 2s orbitals. Compare to the radial functions in Figure **6.5.3** or the radial densities in Figure **6.5.4**. For an interactive graph click here.

Example 6.5.1:

Calculate the probability of finding a 1s hydrogen electron being found within distance $2a_o$ from the nucleus.

Solution

Note the wavefunction of hydrogen 1s orbital which is

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\rho}$$

with $\rho = \frac{r}{a_0}$.

The probability of finding the electron within $2a_0$ distance from the nucleus will be:

$$prob = \underbrace{\int_0^{\pi} \sin\theta \, d\theta}_{\text{over } \theta} \overbrace{\frac{1}{\pi a_0^3} \int_0^{2a_0} r^2 e^{-2r/a_0} dr}^{\text{over } r} \underbrace{\int_0^{2\pi} d\phi}_{\text{over } \phi}$$

Since $\int_0^{\pi} \sin\theta d\theta = 2$ and $\int_0^{2\pi} d\phi = 2\pi$, we have

$$prob = 2 \times 2\pi \times \frac{1}{\pi a_0^3} \int_0^2 a_0(-a_0/2) r^2 de^{-2r/a_0}$$

$$= \frac{4}{a_0^3}\left(-\frac{a_0}{2}\right)(r^2 e^{-2r/a_0}|_0^{2a_0} - \int_0^{2a_0} 2re^{-2r/a_0} dr)$$

$$= -\frac{2}{a_0^2}[(2a_0)^2 e^{-4} - 0 - 2\int_0^{2a_0} r\left(-\frac{a_0}{2}\right) de^{-2r/a_0}]$$

$$= -\frac{2}{a_0^2} 4a_0^2 e^{-4} + \frac{4}{a_0^2}(-\frac{a_0}{2})(re^{-2r/a_0}|_0^{2a_0} - \int_0^{2a_0} e^{-2r/a_0} dr)$$

$$= -8e^{-4} - \frac{2}{a_0}\left[2a_0 e^{-4} - 0 - (-\frac{a_0}{2})e^{-2r/a_0}|_0^{2a_0}\right]$$

$$= -8e^{-4} - 4e^{-4} - e^{2r/a_0}|_0^{2a_0}$$

$$= -12e^{-4} - (e^{-4} - 1) = 1 - 13e^{-4} = 0.762$$

There is a 76.2% probability that the electrons will be within $2a_o$ of the nucleus in the 1s eigenstate.

Summary

This completes the description of the most stable state of the hydrogen atom, the state for which $n = 1$. Before proceeding with a discussion of the excited states of the hydrogen atom we must introduce a new term. When the energy of the electron is increased to another of the allowed values, corresponding to a new value for n, y_n and P_n change as well. The wavefunctions y_n for the hydrogen atom are given a special name, ***atomic orbitals***, because they play such an important role in all of our future discussions of the electronic structure of atoms. In general the word orbital is the name given to a wavefunction which determines the motion of a single electron. If the one-electron wave function is for an atomic system, it is called an atomic orbital.

Do not confuse the word orbital with the classical word and notion of an orbit. First, an orbit implies the knowledge of a definite trajectory or path for a particle through space which in itself is not possible for an electron. Secondly, an orbital, like the wave function, has no physical reality but is a mathematical function which when squared gives the physically measurable electron density distribution.

Contributors

- 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")

6.5: s-orbitals are Spherically Symmetric is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

6.6: Orbital Angular Momentum and the p-Orbitals

Classical Angular Momentum

The physical quantity known as angular momentum plays a dominant role in the understanding of the electronic structure of atoms. To gain a physical picture and feeling for the angular momentum it is necessary to consider a model system from the classical point of view. The simplest classical model of the hydrogen atom is one in which the electron moves in a circular orbit with a constant speed or angular velocity (Figure **6.6.1**). Just as the ordinary momentum $m\vec{v}$ plays a dominant role in the analysis of linear motion, so angular momentum plays the central role in the analysis of a system with circular motion as found in the model of the hydrogen atom.

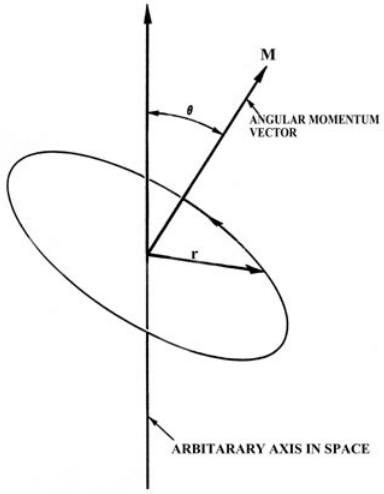


Figure **6.6.1**: The angular momentum vector for a classical model of the atom.

In Figure **6.6.1**, m is the mass of the electron, $\vec{v}$ is the linear velocity (the velocity the electron would possess if it continued moving at a tangent to the orbit as indicated in the figure) and r is the radius of the orbit. The linear velocity $\vec{v}$ is a vector since it possesses at any instant both a magnitude and a direction in space. Obviously, as the electron rotates in the orbit the direction of $\vec{v}$ is constantly changing, and thus the linear momentum $m\vec{v}$ is ***not*** constant for the circular motion. This is so even though the speed of the electron (i.e, the magnitude of $\vec{v}$ which is denoted by $|\vec{v}|$) remains unchanged. According to Newton's second law, a force must be acting on the electron if its momentum changes with time. This is the force which prevents the electron from flying on tangent to its orbit. In an atom the attractive force which contains the electron is the electrostatic force of attraction between the nucleus and the electron, directed along the radius r at right angles to the direction of the electron's motion.

The angular momentum, like the linear momentum, is a vector and is defined as follows:

$$|\vec{L}| = mvr \tag{6.6.1}$$

The angular momentum vector $\vec{L}$ is directed along the axis of rotation. From the definition it is evident that the angular momentum vector will remain constant as long as the speed of the electron in the orbit is constant ($|\vec{v}|$ remains unchanged) and the plane and radius of the orbit remain unchanged. Thus for a given orbit, the angular momentum is constant as long as the angular velocity of the particle in the orbit is constant. In an atom the only force on the electron in the orbit is directed along r; it has no component in the direction of the motion. The force acts in such a way as to change only the linear momentum. Therefore, while the linear momentum is not constant during the circular motion, the angular momentum is. A force exerted on the particle in the direction of the vector $\vec{v}$ would change the angular velocity and the angular momentum. When a force is applied which does change $\vec{L}$, a ***torque*** is said to be acting on the system. Thus angular momentum and torque are related in the same way as are linear momentum and force.

Quantum Angular Momentum

The important point of the above discussion is that both the angular momentum and the energy of an atom remain constant if the atom is left undisturbed. Any physical quantity which is constant in a classical system is both conserved and quantized in a

quantum mechanical system. Thus both the energy and the angular momentum are quantized for an atom.

> *Any physical quantity which is constant in a classical system is both conserved and quantized in a quantum mechanical system.*

There is a quantum number, denoted by l, which governs the magnitude of the angular momentum, just as the quantum number n determines the energy. The ***magnitude*** of the angular momentum may assume only those values given by:

$$|L| = \sqrt{l(l+1)}\hbar \tag{6.6.2}$$

with $l = 0, 1, 2, 3, ...n-1$.

Furthermore, the value of *n* limits the maximum value of the angular momentum as the value of *l* cannot be greater than *n* - 1. For the state *n* = 1 discussed above, l may have the value of zero only. When *n* = 2, *l* may equal 0 or 1, and for *n* = 3, *l* = 0 or 1 or 2, etc. When *l* = 0, it is evident from Equation 6.6.2 that the angular momentum of the electron is zero. The atomic orbitals which describe these states of zero angular momentum are called *s* orbitals. The *s* orbitals are distinguished from one another by stating the value of *n*, the principal quantum number. They are referred to as the 1*s*, 2*s*, 3*s*, etc., atomic orbitals.

The preceding discussion referred to the 1s orbital since for the ground state of the hydrogen atom $n = 1$ and $l = 0$. This orbital, and all s orbitals in general, predict spherical density distributions for the electron as discussed previously.

It is common usage to refer to an electron as being "in" an orbital even though an orbital is, but a mathematical function with no physical reality. To say an electron is in a particular orbital is meant to imply that the electron is in the quantum state which is described by that orbital. For example, when the electron is in the 2*s* orbital the hydrogen atom is in a state for which $n = 2$ and $l = 0$.

Comparing these results with those for the 1*s* orbital in Figure **6.6.2** we see that as n increases the average value of r increases. This agrees with the fact that the energy of the electron also increases as n increases. The increased energy results in the electron being on the average pulled further away from the attractive force of the nucleus. As in the simple example of an electron moving on a line, nodes (values of r for which the electron density is zero) appear in the probability distributions. The number of nodes increases with increasing energy and equals $n-1$.

When the electron possesses angular momentum the density distributions are no longer spherical. In fact for each value of l, the electron density distribution assumes a characteristic shapes in Figure **6.6.2**.

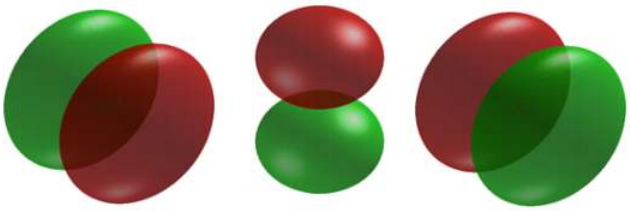


Figure **6.6.2**: The appearance of the three 2p orbitals in three-dimensional space. Image used with permission (CC BY-SA 3.0; I, Sarxos).

When $l = 1$, the orbitals are called *p* orbitals. In this case the orbital and its electron density are concentrated along a line (axis) in space. The 2*p* orbital or wave function is positive in value on one side and negative in value on the other side of a plane which is perpendicular to the axis of the orbital and passes through the nucleus. The orbital has a node in this plane, and consequently an electron in a 2*p* orbital does not place any electronic charge density at the nucleus. The electron density of a 1*s* orbital, on the other hand, is a maximum at the nucleus. The same diagram for the 2*p* density distribution is obtained for any plane which contains this axis. Thus in three dimensions the electron density would appear to be concentrated in two lobes, one on each side of the nucleus, each lobe being circular in cross section Figure **6.6.3**.

> *An electron possesses orbital angular momentum has a density distributions is no longer spherical.*

The m_l Quantum Number and Magnetic Fields

The magnetic quantum number, designated by the letter m_l, is the third quantum numbers which describe the unique quantum state of an electron. The magnetic quantum number distinguishes the orbitals available within a subshell, and is used to calculate the azimuthal component of the orientation of the orbital in space. As with our discussion of rigid rotors, the quantum number m_l refers to the projection of the angular momentum in this arbitrarily chosen direction, conventionally called the z direction or quantization axis. L_z, the magnitude of the angular momentum in the z direction, is given by the formula

$$L_z = m_l \hbar \tag{6.6.3}$$

The quantum number m_l refers, loosely, to the direction of the angular momentum vector. The magnetic quantum number m_l only affects the electron's energy if it is in a magnetic field because in the absence of one, all spherical harmonics corresponding to the different arbitrary values of m_l are equivalent. The magnetic quantum number determines the energy shift of an atomic orbital due to an external magnetic field (this is called the Zeeman effect) - hence the name magnetic quantum number. However, the actual magnetic dipole moment of an electron in an atomic orbital arrives not only from the electron angular momentum, but also from the electron spin, expressed in the spin quantum number, which is the fourth quantum number. m_s and discussed in the next chapter.

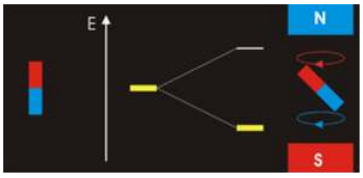


Figure 6.6.3: The orbiting electron with a non-zero l value acts like a magnetic field with is no energetic difference for any particular orientation (only one energy state, on the left),. However, in external magnetic field there is a high-energy state and a low-energy state depending on the relative orientations of the magnet to the external field. Image used with permission (CC SA-BY 3.0; Darekk2).

Which m_l Number Corresponds to Which p-Orbital?

The answer is complicated; while $m_l = 0$ corresponds to the p_z, the orbitals for $m_l = +1$ and $m_l = -1$ lie in the xy-plane (see Spherical Harmonics), but not on the axes. The reason for this outcome is that the wavefunctions are usually formulated in spherical coordinates to make the math easier, but graphs in the Cartesian coordinates make more intuitive sense for humans. The p_x and p_y orbitals are constructed via a linear combination approach from radial and angular wavefunctions and converted into xy (this was discussed previously). Thus, it is not possible to directly correlate the values of $m_l = \pm 1$ with specific orbitals. The notion that we can do so is sometimes presented in introductory courses to make a complex mathematical model just a little bit simpler and more intuitive, but it is incorrect.

The three wavefunctions for $n = 2$ and $l = 1$ are as follows.

$$|\psi_{2,1,0}\rangle = r\cos\theta R(r) \tag{6.6.4}$$

$$|\psi_{2,1,+1}\rangle = -\frac{r}{2}\sin\theta e^{i\phi} R(r) \tag{6.6.5}$$

$$|\psi_{2,1,-1}\rangle = +\frac{r}{2}\sin\theta e^{-i\phi} R(r) \tag{6.6.6}$$

The notation is $|\psi_{n,l,m_l}\rangle$ with $R(r)$ is the radial component of this wavefuction, θ is the angle with respect to the z-axis and ϕ is the angle with respect to the xz-plane.

$$R(r) = \sqrt{\frac{Z^5}{32\pi a_0^5}} e^{-Zr/2a_0} \tag{6.6.7}$$

in which Z is the atomic number (or probably better nuclear charge) and a_0 is the Bohr radius.

In switching from spherical to Cartesian coordinates, we make the substitution $z = r\cos\theta$, so:

$$|\psi_{2,1,0}\rangle = zR(r) \tag{6.6.8}$$

This is ψ_{2p_z} since the value of ψ is dependent on z: when $z = 0$; $\psi = 0$, which is expected since $z = 0$ describes the xy-plane.

The other two wavefunctions are degenerate in the xy-plane. An equivalent statement is that these two orbitals do not lie on the x- and y-axes, but rather bisect them. Thus it is typical to take linear combinations of them to make the equation look prettier. If any set of wavefunctions is a solution to the Schrödinger equation, then any set of linear combinations of these wavefunctions must also be a solution (Section 2.4). We can do this because of the linearity of the Schrödinger equation.

In the equations below, we're going to make use of some trigonometry, notably Euler's formula:

$$e^{i\phi} = \cos\phi + i\sin\phi \tag{6.6.9}$$

$$\sin\phi = \frac{e^{i\phi} - e^{-i\phi}}{2i} \tag{6.6.10}$$

$$\cos\phi = \frac{e^{i\phi} + e^{-i\phi}}{2} \tag{6.6.11}$$

We're also going to use $x = \sin\theta\cos\phi$ and $y = \sin\theta\sin\phi$.

$$\begin{aligned}
\psi_{2p_x} &= \frac{1}{\sqrt{2}}\left(\psi_{2,1,+1} - \psi_{2,1,-1}\right) \\
&= \frac{1}{2}\left(e^{i\phi} + e^{-i\phi}\right) r\sin\theta f(r) \\
&= r\sin\theta\cos\phi f(r) = x f(r) \\
\psi_{2p_y} &= \frac{i}{\sqrt{2}}\left(\psi_{2,1,+1} + \psi_{2,1,-1}\right) \\
&= \frac{1}{2i}\left(e^{i\phi} - e^{-i\phi}\right) r\sin\theta f(r) \\
&= r\sin\theta\sin\phi f(r) = y f(r)
\end{aligned}$$

So, while $m_l = 0$ corresponds to $|p_z\rangle$, $m_l = +1$ and $m_l = -1$ **cannot** be directly assigned to either $|p_x\rangle$ or $|p_y\rangle$, but rather a combination of $|p_x\rangle$ and $|p_y\rangle$. An alternative description is that $m_l = +1$ might correspond to $(|p_x\rangle + |p_y\rangle)$ and $m_l = -1$ might correspond to $(|p_x\rangle - |p_y\rangle)$.

d-Orbitals (even higher angular momenta wavefunctions)

When $l = 2$, the orbitals are called *d* orbitals and Figure **6.6.4** shows the contours in a plane for a 3*d* orbital and its density distribution. Notice that the density is again zero at the nucleus and that there are now two nodes in the orbital and in its density distribution. As the angular momentum of the electron increases, the density distribution becomes increasingly concentrated along an axis or in a plane in space. Only electrons in s orbitals with **zero angular momentum** give spherical density distributions and in addition place charge density at the position of the nucleus.



Figure **6.6.4**: The appearance of the 3d electron density distribution in three-dimensional space. Image used with permission (CC BY-SA 3.0; I, Sarxos)

As with the $p-$ orbitals, the only d-orbital that a specific m_l can be ascribed is the d_{z^2} orbitals with $m_l = 0$. The rest are linear combinations of the hydrogen atom wavefunctions with complex spherical harmonic angular components.

There seems to be neither rhyme nor reason for the naming of the states corresponding to the different values of ℓ (s, *p*, *d*, *f* for *l* = 0, 1, 2, 3). This set of labels had its origin in the early work of experimental atomic spectroscopy. The letter *s* stood for sharp, *p* for principal, *d* for diffuse and *f* for fundamental in characterizing spectral lines. From the letter *f* onwards the naming of the orbitals is alphabetical $l = 4, 5, 6 \rightarrow g, h, i, ...$

We have not as yet accounted for the full degeneracy of the hydrogen atom orbitals which we stated earlier to be n^2 for every value of n. For example, when $n = 2$, there are four distinct atomic orbitals. The remaining degeneracy is again determined by the angular momentum of the system. Since angular momentum like linear momentum is a vector quantity, we may refer to the component of the angular momentum vector which lies along some chosen axis. For reasons we shall investigate, the number of values a particular component can assume for a given value of l is $(2l + 1)$. Thus when $l = 0$, there is no angular momentum and there is but a single orbital, an s orbital. When $l = 1$, there are three possible values for the component (2´ 1 + 1) of the total angular momentum which are physically distinguishable from one another. There are, therefore, three p orbitals. Similarly there are five d orbitals, (2 ´ 2+1), seven f orbitals, (2 ´ 3 +1), etc. All of the orbitals with the same value of n and l, the three $2p$ orbitals for example, are similar but differ in their spatial orientations.

To gain a better understanding of this final element of degeneracy, we must consider in more detail what quantum mechanics predicts concerning the angular momentum of an electron in an atom.

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Dr. Richard F.W. Bader (Professor of Chemistry / McMaster University)
- Stack Exchange (Ben Norris and Loong)

6.6: Orbital Angular Momentum and the p-Orbitals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

6.7: The Helium Atom Cannot Be Solved Exactly

Learning Objectives

- Adding electrons to the quantum hydrogen atom results in analytically unsolvable Schrödinger Equations (they exist, we just do not have analytical forms for them)
- A basic aspect of the corresponding multi-electron Hamiltonians is that they are NOT separable with respect to the spatial coordinate of each electron
- The solutions to multi-electron Schrödinger Equations are called multi-electron wavefunctions and they are often approximated as a product of single-electron wavefunctions (called the orbital approximation).

Multi-electron Hamiltonians

The second element in the periodic table provides our first example of a quantum-mechanical problem which *cannot* be solved exactly. Nevertheless, as we will show, approximation methods applied to helium can give accurate solutions in perfect agreement with experimental results. In this sense, it can be concluded that quantum mechanics is correct for atoms more complicated than hydrogen. By contrast, the Bohr theory failed miserably in attempts to apply it beyond the hydrogen atom.

Figure 6.7.1 shows a schematic representation of a helium atom with two electrons whose coordinates are given by the vectors r_1 and r_2. The electrons are separated by a distance $r_{12} = |r_1 - r_2|$. The origin of the coordinate system is fixed at the nucleus. As with the hydrogen atom, the nuclei for multi-electron atoms are so much heavier than an electron that the nucleus is assumed to be the center of mass. Fixing the origin of the coordinate system at the nucleus allows us to exclude translational motion of the center of mass from our quantum mechanical treatment.

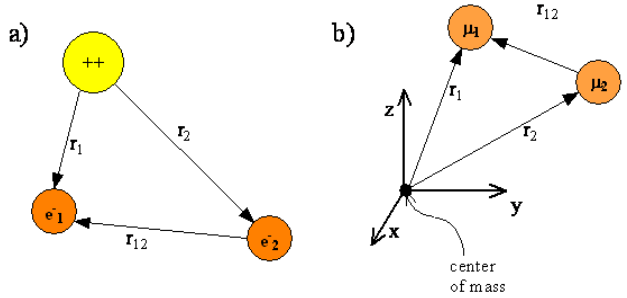


Figure 6.7.1: (a) The nucleus (++) and electrons (e-) of the helium atom. (b) Equivalent reduced particles with the center of mass (approximately located at the nucleus) at the origin of the coordinate system. Note that μ_1 and $\mu_2 \approx m_e$.

The Hamiltonian operator for the hydrogen atom serves as a reference point for writing the Hamiltonian operator for atoms with more than one electron. Start with the same general form we used for the hydrogen atom Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} \tag{6.7.1}$$

Include a kinetic energy term for each electron and a potential energy term for the attraction of each negatively charged electron for the positively charged nucleus and a potential energy term for the mutual repulsion of each pair of negatively charged electrons. The He atom Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V_1(r_1) + V_2(r_2) + V_{12}(r_{12}) \tag{6.7.2}$$

where

$$V_1(r_1) = -\frac{2e^2}{4\pi\epsilon_0 r_1} \tag{6.7.3}$$

$$V_2(r_2) = -\frac{2e^2}{4\pi\epsilon_0 r_2} \tag{6.7.4}$$

$$V_{12}(r_{12}) = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{6.7.5}$$

The two-electron Hamiltonian in Equation 6.7.2 can be extended to any atom or ion by replacing the He nuclear charge of +2 with a general charge Z; e.g.

$$V_1(r_1) = -\frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{6.7.6}$$

and including terms for the additional electrons. The subsequent multi-electron atom with n electron is

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\sum_i^n \nabla_i^2}_{\text{Kinetic Energy}} + \underbrace{\sum_i^n V_i(r_i)}_{\text{Coulombic Attraction}} + \underbrace{\sum_{i\neq j}^{n,n} V_{ij}(r_{ij})}_{\text{electron-electron Repulsion}} \tag{6.7.7}$$

This multi-electron Hamiltonian is qualitatively similar to the 2-electron Hamiltonian (Equation 6.7.1) with each electron having its own kinetic energy and nuclear potential energy terms (Equations 6.7.3 and 6.7.4). The other big difference between single electron systems and multi-electron systems is the presence of the $V_{ij}(r_{ij})$ terms which contain $1/r_{ij}$, where r_{ij} is the distance between electrons i and j. These terms account for the electron-electron repulsion that we expect between like-charged particles.

Exercise 6.7.1: Multi-electron atom Hamiltonians

For the generalized multi-electron atom Hamiltonian (Equation 6.7.7):

a. Explain the origin of each of the three summations.
b. What do these summations over (i.e., what is the origin of the summing index)?
c. Write expressions for $V_i(r_i)$ and $V_{ij}(r_{ij})$.

Exercise 6.7.2: Boron Atom

Boron is the fifth element of the periodic table (Z=5) and is located in Group 13.

a. Write the multi-electron Hamiltonian for a $^{11}\mathbf{B}$ atom.
b. Would it be any different for a $^{11}\mathbf{B}^+$ ion?
c. Would it be any different for a $^{10}\mathbf{B}$ atom?

Answer

a.

$$\hat{H}_{\mathrm{B}}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\vec{r}_5) = -\frac{\hbar^2}{2m_e}\sum_i^5 \nabla_i^2 + \sum_i^5 \frac{-5e^2}{4\pi\epsilon_0 r_i} + \sum_{i\neq j}^{5,5} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

which expands to 20 terms

$$\begin{aligned}\hat{H}_B(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\vec{r}_5) = &-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2m_e}\nabla_3^2 - \frac{\hbar^2}{2m_e}\nabla_4^2 - \frac{\hbar^2}{2m_e}\nabla_5^2 \\ &- \frac{-5e^2}{4\pi\epsilon_0 r_1} - \frac{-5e^2}{4\pi\epsilon_0 r_2} - \frac{-5e^2}{4\pi\epsilon_0 r_3} - \frac{-5e^2}{4\pi\epsilon_0 r_4} - \frac{-5e^2}{4\pi\epsilon_0 r_5} \\ &+ \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{14}} + \frac{e^2}{4\pi\epsilon_0 r_{15}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} + \frac{e^2}{4\pi\epsilon_0 r_{24}} + \frac{e^2}{4\pi\epsilon_0 r_{25}} + \frac{e^2}{4\pi\epsilon_0 r_{34}} + \frac{e^2}{4\pi\epsilon_0 r_{35}} + \frac{e^2}{4\pi\epsilon_0 r_{45}}\end{aligned}$$

b. Yes, $^{11}\mathbf{B}^+$ has one less electron than $^{11}\mathbf{B}$. Its Hamiltonian is

$$\hat{H}_{\mathrm{B}^+}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4) = -\frac{\hbar^2}{2m_e}\sum_i^4 \nabla_i^2 + \sum_i^4 \frac{-5e^2}{4\pi\epsilon_0 r_i} + \sum_{i\neq j}^{4,4} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

or expanded to 14 terms

$$\hat{H}_B(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4) = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2m_e}\nabla_3^2 - \frac{\hbar^2}{2m_e}\nabla_4^2 - \frac{-5e^2}{4\pi\epsilon_0 r_1} - \frac{-5e^2}{4\pi\epsilon_0 r_2} - \frac{-5e^2}{4\pi\epsilon_0 r_3} - \frac{-5e^2}{4\pi\epsilon_0 r_4} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{14}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} + \frac{e^2}{4\pi\epsilon_0 r_{24}} + \frac{e^2}{4\pi\epsilon_0 r_{34}}$$

c. No effect. Changing the number of neutrons in the nucleus does not affect kinetic nor potential energies of the electrons. The Hamilitonian for ^{10}**B** is identical to ^{11}**B**. This is technically correct for this level of discussion, but as we we will see in later, if we expand the Hamiltonian with hyperfine structure the number of neutrons can play a role.

Multi-electron Wavefunctions and the Orbital Approximation

Given what we have learned from the previous quantum mechanical systems we've studied, we predict that exact solutions to the multi-electron Schrödinger equation in Equation 6.7.7 would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their Coulomb repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends *simultaneously* upon the coordinates of all the electrons; i.e., **a multi-electron wavefunction**,

$$\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\cdots\vec{r}_n) \tag{6.7.8}$$

The modulus squared of such a wavefunction would describe the probability of finding the electrons (though not specific ones) at a designated volume (V) in the atom.

$$p(V) = \int_V |\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\cdots\vec{r}_n)|^2 d\tau \tag{6.7.9}$$

All of the electrons are described simultaneously by a multi-electron wavefunction, so the total amount of electron density represented by the wavefunction equals the number of electrons in the atom.

$$\int_{\text{all space}} |\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\cdots\vec{r}_i)|^2 d\tau = n \tag{6.7.10}$$

Unfortunately, the Coulomb repulsion terms (Equation 6.7.5) make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms and molecules even for two electrons atoms. We have to rely on approximations and the *orbital approximation* is central to basic chemistry concepts.

The Orbital Approximation

The most basic approximations to the exact solutions to a multi-electron atom Hamiltonian, $\hat{H}$, (Equation 6.7.7) involve writing a multi-electron wavefunction ($\psi(r_1,r_2,\cdots,r_n)$) as a simple product of single-electron wavefunctions ($\varphi_i(r_i)$):

$$\psi(r_1,r_2,\cdots,r_n) \approx \varphi_1(r_1)\varphi_2(r_2)\cdots\varphi_n(r_n) \tag{6.7.11}$$

or in Dirac notation

$$|\psi(r_1,r_2,\cdots,r_n)\rangle \approx |\varphi_1(r_1)\rangle|\varphi_2(r_2)\rangle\cdots|\varphi_n(r_n)\rangle \tag{6.7.12}$$

The energy of the atom in the state associated with a specific multi-electron wavefunction (E) is obtained from the multi-electron Schrödinger Equation

$$\hat{H}\psi(r_1,r_2,\cdots,r_n) = E\psi(r_1,r_2,\cdots,r_n) \tag{6.7.13}$$

Within the approximation in Equation 6.7.11, E can be expressed sum of the energies of the one-electron components (ϵ_i).

$$E \approx \sum_i \epsilon_i \tag{6.7.14}$$

This is called the orbital approximation.

By writing the multi-electron wavefunction as a product of single-electron functions (Equations 6.7.11 or 6.7.12), we conceptually transform a multi-electron atom into a collection of individual electrons located in individual orbitals whose spatial characteristics and energies can be separately identified. For atoms, these single-electron wavefunctions are called *atomic orbitals* and resemble the wavefunctions for hydrogen-like atoms. For molecules, as we will see in the following chapters, these are called *molecular orbitals*. While a great deal can be learned from such an analysis, it is important to keep in mind that such a discrete, compartmentalized picture of the electrons is an approximation, albeit a powerful one.

Contributors

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

This page titled 6.7: The Helium Atom Cannot Be Solved Exactly is shared under a not declared license and was authored, remixed, and/or curated by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski via source content that was edited to the style and standards of the LibreTexts platform.

6.E: The Hydrogen Atom (Exercises)

Solutions to select questions can be found online.

6.5

$$\int_{-1}^{1} T_n(x)T_m(x)\frac{1}{\sqrt{1-x^2}}dx = \begin{cases} 0, & n \neq m \\ \pi, & n = m = 0 \\ \pi/2, & n = m \neq 0 \end{cases}$$

First 6 Chebyshev Polynomials

$$T_0(x) = 1$$
$$T_1(x) = x$$
$$T_2(x) = 2x^2 - 1$$
$$T_3(x) = 4x^3 - 3x$$
$$T_4(x) = 8x^4 - 8x^2 + 1$$
$$T_5(x) = 16x^5 - 20x^3 + 5x$$

Use the orthogonality of Chebyshev polynomials to determine what the following polynomials are equal to

a. $\int_{-1}^{1} x^2 \frac{dx}{\sqrt{1-x^2}}$
b. $\int_{-1}^{1} 4x^3 - 2x \frac{dx}{\sqrt{1-x^2}}$
c. $\int_{-1}^{1} 1 \frac{dx}{\sqrt{1-x^2}}$
d. $\int_{-1}^{1} 4x^4 - 4x^2 + 1 \frac{dx}{\sqrt{1-x^2}}$

Solution

a. x^2= T_1*T_1; therefore the answer is π /2
b. here the following polynomial is not a product of either Chebyshev polynomials; therefore, answer is doesn't follow orthogonality conditions
c. 1=T_0*T_0; therefore, answer is π
d. x^4-4x^2+1= T_2*T_2; therefore the answer is π/2

6.6

Use Eq. 6.47 to generate the radial functions $R_{nl}(r)$ for $n = 1, 2$.

Solution

$$R_{10}(r) = \left\{\frac{(1-0-1)!}{2(1)[(1+0)!]^3}\right\}^{\frac{1}{2}}\left(\frac{2}{1a_0}\right)^{\frac{0+3}{2}} r^0 e^{-\frac{r}{1a_0}} L_1^1\left(\frac{2r}{1a_0}\right)$$

$$R_{10}(r) = -\left\{\frac{1}{2}\right\}^{\frac{1}{2}}\left(\frac{2}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$$

$$R_{20}(r) = \left\{\frac{(2-0-1)!}{2(2)[(2+0)!]^3}\right\}^{\frac{1}{2}}\left(\frac{2}{2a_0}\right)^{\frac{0+3}{2}} r^0 e^{-\frac{r}{2a_0}} L_2^1\left(\frac{2r}{2a_0}\right)$$

$$R_{20}(r) = \left\{\frac{1}{32}\right\}^{\frac{1}{2}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{2a_0}}\left(-2!\left(2-\frac{r}{a_0}\right)\right)$$

$$R_{20}(r) = -2\left\{\frac{1}{32}\right\}^{\frac{1}{2}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{2a_0}}\left(\left(2-\frac{r}{a_0}\right)\right)$$

$$R_{21}(r) = \left\{\frac{(2-1-1)!}{2(2)[(2+1)!]^3}\right\}^{\frac{1}{2}}\left(\frac{2}{2a_0}\right)^{\frac{1+3}{2}} r^1 e^{-\frac{r}{2a_0}} L_3^3\left(\frac{2r}{2a_0}\right)$$

$$R_{21}(r) = -6\left\{\frac{1}{864}\right\}^{\frac{1}{2}}\left(\frac{1}{a_0}\right)^{2} r^1 e^{-\frac{r}{2a_0}}$$

6.29

Compare ψ_{310} and ψ_{311}.

Hint: What do the subscripts tell you about the wave function? What do they denote?

Solution

The first subscript tells you the quantum number n. The second denotes the angular momentum l. The last denotes the magnetic spin number m_l. These two functions have the same n values, and thus they are degenerate.

6.30

What is the probability density of the 3p orbital by evaluating

$$\left(\sum_{m=-1}^{1}\psi_{31m}^2\right)$$

Solution

$$\sum_{m=-1}^{1}\psi_{31m}^2 = \left(\frac{2}{6561\pi}\right)\left(\frac{z^3}{a_o^3}\right)\sigma^3(6-\sigma)^2\exp^{\frac{-2\sigma}{3}}\left(\cos^2\theta + \sin^2\theta\cos^2\phi + \sin^2\theta\sin^2\phi\right)$$

$$\sum_{m=-1}^{1}\psi_{31m}^2 = \left(\frac{2z^3\sigma^2(6-\sigma)^2\exp^{\frac{-2\sigma}{3}}}{6561\pi a_o^3}\right)\left(\cos^2\theta + \sin^2\theta\left(\cos^2\phi + \sin^2\phi\right)\right)$$

$$\sum_{m=-1}^{1}\psi_{31m}^2 = \left(\frac{2z^3\sigma^2(6-\sigma)^2\exp^{\frac{-2\sigma}{3}}}{6561\pi a_o^3}\right)$$

6.34

Find the energy, and wavefunction for a single electron located in the 2p orbital of the hydrogen atom. Include all possible wavefunctions.

Solution

Identify the quantum numbers for the electron of interest (in our case, $n = 2$; $l = 1$). Energy of the electron can be defined as

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

this leads us to

$$E_2 = \frac{-m_e e^4}{32\epsilon_o^2 h^2}$$

we have two possible wave functions

$$\Psi_{210} = \frac{1}{\sqrt{32}}(\frac{z}{a_o})^{3/2}\sigma/e^{-\sigma/2}\cos\theta$$

and

$$\Psi_{21\pm1} = \frac{1}{\sqrt{32}}(\frac{z}{a_o})^{3/2}\sigma/e^{-\sigma/2}\sin\theta e^{\pm i\theta}$$

6.37

The Hamiltonian is given by $\hat{H} = \frac{-\hbar}{2m}\nabla^2 + V$ is an Hermitian Operator. Using this fact, show that

$$\int \psi^*[\hat{H}, \hat{A}]\psi d\tau = 0$$

where $\hat{A}$ is any operator.

Solution

Through the commutation relation

$$\int \psi^*\hat{H}\hat{A}\psi d\tau - \int \psi^*\hat{A}\hat{H}\psi d\tau = 0$$

because $\hat{H}$ is a *Hermitian* operator, the above goes to

$$\int (\psi\hat{H})^*\hat{A}\psi d\tau - \int \psi^*\hat{A}(\hat{H}\psi)d\tau = 0$$

$$E\int \psi^*\hat{A}\psi d\tau - E\int \psi^*\hat{A}\psi d\tau = 0$$

6.38

Prove that $\langle \hat{K} \rangle = \langle V \rangle = E/2$ for a harmonic oscillator using the virial theorem

Solution

The virial theorem gives us,

$$\left\langle x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z} \right\rangle = 2\langle \hat{K} \rangle$$

For a three-dimensional harmonic oscillator,

$$V(x,y,z) = \frac{k_x x^2}{2} + \frac{k_y y^2}{2} + \frac{k_z z^2}{2}$$

Therefore,

$$x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z} = k_x x^2 + k_y y^2 + k_z z^2 = 2V$$

and substituting into the equation given by the virial theorem gives us $2\langle V \rangle = 2\langle \hat{K} \rangle$. Because $\langle \hat{K} \rangle + \langle V \rangle = E$, we can also write

$$\langle \hat{K} \rangle = \langle V \rangle = \frac{1}{2}E$$

6.41

Find the expected values of $1/r$ and $1/r^2$ for a hydrogenlike atom in the $2p_z$ orbital.

Solution

The $2p_z$ orbital:

$$\Psi_{210} = \frac{1}{4\sqrt{2\pi}}(Z/a_0)^{3/2}\rho e^{-\rho}\sin\theta\cos\phi\, d\theta$$

where $\rho = Zr/a_o$

$$\langle 1/r\rangle_{\Psi 210} = \int_0^2 \pi\, d\theta \int_0^{\pi} \sin\theta\cos 2\phi d\theta \int_0^{\infty} (Z^{3/2}/a_o^{3/2}4\sqrt{2\pi}^{2*} r^2 p^* e^{-p*}(1/r)dr$$

$$\int_0^{2\pi} d\theta = 2\pi$$

$$\int_0^{\pi} \sin\theta\cos^2\,\phi\, d\theta = \frac{2}{3}$$

$$\int_0^{\infty} (Z^{3/2}/a_o^{3/2}4\sqrt{2\pi})^2 r^2\phi e - \rho(1/r)dr = (Z^3/a_o^3 32\pi)^*[3!/(Z/ao)^4]$$

$$\langle 1/r\rangle_{\Psi 210} = (Z^3/a_o^3 32\pi)(2\pi)(2/3)[3!/(Z/ao)^4]$$

Simplify to get:

$$\left\langle \frac{1}{r} \right\rangle_{\Psi_{210}} = \frac{Z}{4a_o}$$

For the hydrogen atom $Z = 1$, therefore

$$\langle \frac{1}{r} \rangle_{\Psi_{210}} = \frac{1}{4a_o}$$

For $\langle \frac{1}{r^2} \rangle$

$$\langle \frac{1}{r^2} \rangle_{\Psi_{210}} = \int_0^2 \pi\, d\theta \int_0^{\pi} \sin\theta\cos^2\,\phi\, d\theta \int_0^{\infty} (Z^3/2/a_o^3/24\sqrt{2\pi})^2 r^2 p e^{-p}(1/r^2)dr$$

$$\int_0^{2\pi} d\theta = 2\pi$$

$$\int_0^{\pi} \sin\theta\cos^2\phi d\theta = 2/3$$

$$\int_0^{\infty} (Z^{3/2}/a_o^{3/2}4\sqrt{2\pi})^2 r 2pe^{-p}(1/r^2)dr = (Z^3/a_o^3 32\pi)[2!/(Z/ao)^3]$$

$$\langle 1/r^2\rangle\Psi_{210} = (Z^3/a_o^3 32\pi)(2\pi)(2/3)[2!/(Z/a_o)^3]$$

Simplify to get:

$$\langle \frac{1}{r^2} \rangle_{\Psi_{210}} = \frac{Z^2}{12a_o^2}$$

where $Z = 1$

$$\langle \frac{1}{r^2} \rangle_{\Psi_{210}} = \frac{1}{12a_o^2}$$

6.43

Derive the classical magnetic moment of an electron orbiting a nucleus in terms of charge, mass and angular momentum.

Solution

We can begin by recalling the classical expression for a magnetic moment,

$$\mu = IArea$$

Where I is the current the electron makes by revolving around the nucleus. The definition of current is

$$I = \frac{Q}{time}$$

In this case Q is simply the charge (q_e) of the electron and $time$ is the time it takes the electron to orbit the nucleus once. The area is the of loop that the electron takes when revolving around the nucleus. We also know from classical mechanics that $x = vt$. solving for t and evaluating x to be $2\pi r$ for a circle. We can figure out the time of revolution to be,

$$t = \frac{x}{v} = \frac{2\pi r}{v}$$

Our current equations becomes,

$$I = \frac{q_e v}{2\pi r}$$

To introduce angular momentum $L = m_e v r$ we can multiply the right side of our current equation by $\frac{m_e r}{m_e r}$ to arrive at

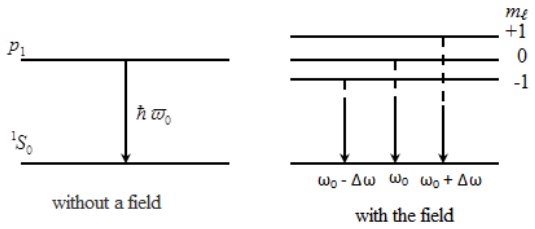
$$I = \frac{q_e m_e v r}{2\pi m_e r^2}$$
$$I = \frac{q_e L}{2\pi m_e r^2}$$

Substituting in the area of a circle (πr^2) we can show that,

$$\boxed{\mu = IArea = \frac{q_e L}{2m_e}}$$

6.46

Find the magnitude of the splitting shown in figure below. The magnetic field in the figure is at 20 T.



Solution

We know from a previous problem that

$$\Delta E = E_2 - E_1 = \beta_e B_z (m_2 - m_1)$$

In the 1\s\ state where m = 0 and in the 2\p\ state where m = 0, \pm\ 1. The condition will cause (m_{2} - m_{1}) become equal to 0, or \pm\ 1 which will affect the magnitude of splitting, calculated below

$$\Delta E = (9.274 * 10^{-24} J * T^{-1})(20T)(1)$$

$$\Delta E = 1.8548 * 10^{-22} J * T^{-1} \text{ or } 0$$

6.47

Consider the transition between the $l = 1$ and the $l = 2$ states for atomic hydrogen. Determine the total number of possible allowed transitions between these two states in an external magnetic field given the following selection rules

a. Light whose electric field vector is parallel to the external magnetic field's direction has a selection rule of $\Delta m = 0$ for allowed transitions.
b. Light whose electric field vector is perpendicular to the external magnetic field's direction has a selection rule of $\Delta m = \pm 1$ for allowed transitions.

Solution

An external magnetic field splits a state with given values n and l into $2l + 1$ levels. So the $l = 1$ state will be split into three states ($m = 0, \pm 1$) and the $l = 2$ state will be split into five states ($m = 0, \pm 1, \pm 2$). This means that the $l = 1 \rightarrow l = 2$ transition will have a possible of 15 transitions (ignoring any selection rules that reduce this number).

Using the selection rule $\Delta m = 0$, then three transitions are possible: $m = 0$, $m = 1$, $m = -1$ Using the selection rule $\Delta m = \pm 1$, then six transitions are possible:

$l = 1$	$\rightarrow$	$l = 2$	Relative Orientation of light Polarization to Magnetic field
m=0		m=1	parallel
m=0		m=-1	parallel
m=1		m=2	perpendicular
m=1		m=0	perpendicular
m=-1		m=-2	perpendicular
m=-1		m=0	perpendicular

6.49

Prove that

$$\hat{L_+}\hat{L_-} - \hat{L_-}\hat{L_+} = 2\hbar\hat{L_z}$$

given that

$$\hat{L_+} = \hat{L_x} + i\hat{L_y}$$

and

$$\hat{L_-} = \hat{L_x} - i\hat{L_y}.$$

Solution

$$\hat{L_+}\hat{L_-} = (\hat{L_x} + i\hat{L_y})(\hat{L_x} - i\hat{L_y}) = \hat{L_x^2} + \hat{L_y^2} - i\hat{L_x^2}\hat{L_y^2} + i\hat{L_y^2}\hat{L_x^2} = \hat{L_x^2} + \hat{L_y^2} + i[\hat{L_y}, \hat{L_x}]$$

$$\hat{L_+}\hat{L_-} = \hat{L^2} - \hat{L_z^2} + \hbar\hat{L_z}$$

and

$$\hat{L_-}\hat{L_+} = (\hat{L_x} - i\hat{L_y})(\hat{L_x} + i\hat{L_y}) = \hat{L_x^2} + \hat{L_y^2} + i\hat{L_x^2}\hat{L_y^2} - i\hat{L_y^2}\hat{L_x^2} = \hat{L_x^2} + \hat{L_y^2} + i[\hat{L_x}, \hat{L_y}]$$

$$\hat{L_-}\hat{L_+} = \hat{L^2} - \hat{L_z^2} - \hbar\hat{L_z}$$

thus

$$\hat{L_+}\hat{L_-} - hatL_-\hat{L_+} = \hat{L^2} - \hat{L_z^2} + \hbar\hat{L_z} - \hat{L^2} + \hat{L_z^2} - \hbar\hat{L_z}$$

$$\hat{L_+}\hat{L_-} - \hat{L_-}\hat{L_+} = 2\hbar\hat{L_z}$$

6.49

Show that the commutative property applies to

$$\hat{L}_-\hat{L}_+$$

Solution

$$\hat{L}_-\hat{L}_+ = \hat{L}_+\hat{L}_-$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y$$

and

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y$$

so

$$\hat{L}_-\hat{L}_+ = [\hat{L}_x - i\hat{L}_y][\hat{L}_x + i\hat{L}_y]$$

$$= \hat{L}_x^2 + i\hat{L}_x\hat{L}_y - i\hat{L}_x\hat{L}_y + \hat{L}_y^2$$

and

$$\hat{L}_+\hat{L}_- = [\hat{L}_x + i\hat{L}_y][\hat{L}_x - i\hat{L}_y]$$

$$= \hat{L}_x^2 - i\hat{L}_y\hat{L}_x + i\hat{L}_x\hat{L}_y + \hat{L}_y^2$$

which shows that

$$\hat{L}_-\hat{L}_+ = \hat{L}_+\hat{L}_-$$

Q7.29

Calculate the ground-state energy for particle in the box model using variational method.

Solution

Variational method equations is:

$$E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

where the wavefunctions are unnormalized

The unnormalized Schrödinger equation for PIB:

$$\phi(x) = A \sin(\frac{xn\pi}{L})$$

$$\langle \phi | \phi \rangle$$

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

and

$$\langle \phi | \hat{H} | \phi \rangle$$

$$= \frac{n^2 h^2}{8mL^2} \cdot \sqrt{\frac{2}{L}}$$

so

$$E_\phi = \frac{\frac{n^2 h^2}{8mL^2} \cdot \sqrt{\frac{2}{L}}}{\sqrt{\frac{2}{L}}}$$

so

$$E_\phi = \frac{n^2 h^2}{8mL^2}$$

where n=1 we get

$$E_\phi = \frac{h^2}{8mL^2}$$

6.50

If two functions commute, they have mutual eigenfunctions, such as $\hat{L}^2$ and $\hat{L}_z$. These mutual eigenfunctions are also known as spherical harmonics, $Y_l^m(\theta, \phi)$, however this information is not pertinent in this case. Let

$\psi_{\alpha\beta}$ be a mutual eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ so that

$$\hat{L}_z \psi_{\alpha\beta} = \beta^2 \backslash_{\alpha\beta}$$

and

$$\hat{L}_z \psi_{\alpha\beta} = \alpha \psi_{\alpha\beta}$$

Now let

$$\psi_{\alpha\beta}{}^{+1} = \hat{L}_+ \psi_{\alpha\beta}$$

Show that

$$\hat{L}_z \psi_{\alpha\beta}{}^{+1} = (\alpha + \hbar) \psi_{\alpha\beta}{}^{+1}$$

and

$$\hat{L}^2 \psi_{\alpha\beta}{}^{+1} = \beta^2 \psi_{\alpha\beta}{}^{+1}$$

This proves that if α is an eigenvalue of $\hat{L}_z$, then $\alpha + \hbar$ also is an eigenvalue.

Solution

Solve this problem as given below:

$\psi_{\alpha\beta}^{+1} = \hat{L}_+\psi_{\alpha\beta}$

$\hat{L}_z\,\psi_{\alpha\beta}^{+1} = \hat{L}_z\,\hat{L}_+\psi_{\alpha\beta}$

$= (\hat{L}_z\,\hat{L}_x + i\hat{L}_z\,\hat{L}_y\,)\psi_{\alpha\beta}$

$z,\,\hat{L}_x] + \hat{L}_x\,\hat{L}_z + i[\hat{L}_z,\,\hat{L}_y] + i\hat{L}_y\,\hat{L}_z)\psi_{\alpha\beta}$

$y + \hat{L}_z\hat{L}_x + i\hbar\hat{L}_x + \hat{L}_y\hat{L}_z)\,\psi_{\alpha\beta}$

$\hat{L}_+\hat{L}_z + \hbar\hat{L}_+)\psi_{\alpha\beta}$

$+(\alpha + \hbar)\psi_{\alpha\beta}$

$\alpha\beta^{+1}$

Therefore proven.

Finally, you can write:

$\hat{L}^2\psi_{\alpha\beta}^{+1} = \hat{L}^2\hat{L}_+\psi_{\alpha\beta}$

$= (\hat{L}^2\hat{L}_x + i\hat{L}^2\hat{L}_y)\psi_{\alpha\beta}$

$=([\hat{L}^2,\hat{L}_x] + \hat{L}_x\hat{L}^2 + i[\hat{L}^2,\hat{L}_y] + i\hat{L}_y\hat{L}^2)\psi_{\alpha\beta}$

$x\hat{L}^2 + i\hat{L}_y\hat{L}^2)\psi_{\alpha\beta}$

$+\beta^2\psi_{\alpha\beta}$

$2\psi_{\alpha\beta}^{+1}$

Therefore proven.

6.E: The Hydrogen Atom (Exercises) is shared under a not declared 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

7: Approximation Methods

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

The Schrödinger equation for realistic systems quickly becomes unwieldy, and analytical solutions are only available for very simple systems - the ones we have described as *fundamental systems* in this module. Numerical approaches can cope with more complex problems, but are still (and will remain for a good while) limited by the available computer power. Approximations are necessary to cope with real systems. Within limits, we can use a pick and mix approach, *i.e.* use *linear combinations* of solutions of the fundamental systems to build up something akin to the real system. There are two mathematical techniques, *perturbation* and *variation* theory, which can provide a good approximation along with an estimate of its accuracy. These two approximation techniques are described in this chapter.

7.1: The Variational Method Approximation

7.2: Linear Variational Method and the Secular Determinant

7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters

7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

7.E: Approximation Methods (Exercises)

7: Approximation Methods is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.1: The Variational Method Approximation

In this section we introduce the powerful and versatile variational method and use it to improve the approximate solutions we found for the helium atom using the independent electron approximation.

The True (i.e., Experimentally Determined) Energy of the Helium Atom

The helium atom has two electrons bound to a nucleus with charge $Z = 2$. The *successive* removal of the two electrons can be considered stepwise:

$$\mathrm{He} \xrightarrow{I_1} \mathrm{He}^+ + e^- \xrightarrow{I_2} \mathrm{He}^{++} + 2e^- \tag{7.1.1}$$

The *first ionization energy* I_1 is the minimum energy required to remove the first electron from helium gas and is experimentally determined:

$$I_1 = -E_{1s}(\mathrm{He}) = 24.59\ eV \tag{7.1.2}$$

The second ionization energy, I_2 can experimentally determined, but also can be calculated exactly from the hydrogen atom solutions since He^+ is a hydrogen-like ion with $Z = 2$. Hence, we have

$$I_2 = -E_{1s}(\mathrm{He}^+) \tag{7.1.3}$$

$$= \frac{Z^2}{2n^2} \tag{7.1.4}$$

$$= 54.42\ \mathrm{eV} \tag{7.1.5}$$

The energy of the three separated particles on the right side of Equation 7.1.1 is zero (by definition). Therefore the ground-state energy of helium atom is given by

$$E_{true} = -(I_1 + I_2) \tag{7.1.6}$$

$$= -79.02\ \mathrm{eV}. \tag{7.1.7}$$

which can be expressed in terms of the ***Rydberg*** constant ($R_H = 13.6\ eV$) that also describes the lowest energy of the hydrogen atom

$$E_{true} = -5.8066\, R \tag{7.1.8}$$

We will attempt to reproduce this **true value**, as close as possible, by different theoretical approaches (all approximations).

The "Ignorance is Bliss" Approximation

The Hamiltonian for the Helium atom is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \cancel{\frac{e^2}{4\pi\epsilon_0 r_{12}}} \tag{7.1.9}$$

If we simply *ignore* the electron-electron repulsion term, then Equation 7.1.9 can be simplified to

$$\hat{H} \approx -\frac{\hbar^2}{2m_e}\nabla^2_{el_1} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla^2_{el_2} - \frac{Ze^2}{4\pi\epsilon_0 r_2} \tag{7.1.10}$$

$$\approx h_1(r_1) + h_2(r_2) \tag{7.1.11}$$

where h_1 and h_2 are one electron Hamiltonians for electron 1 and 2, respectively, and are just the hydrogen-like Hamiltonians. The approximation in Equation 7.1.11 is convenient since electron 1 is *separable* from electron 2, so that the total wavefunction is a product to two one-electron wavefunctions:

$$\Psi_{total} = \psi_{el_1}\psi_{el_2} \tag{7.1.12}$$

or in braket notation

$$|\Psi_{total}\rangle = \hat{H}|\psi_{el_1}\rangle|\psi_{el_2}\rangle \tag{7.1.13}$$

With some operator algebra, something important arises - the one electron energies are **additive**:

$$\hat{H}\Psi_{total} = (\hat{H}_{el_1} + \hat{H}_{el_2})\psi_{n\ el_1}\psi_{n\ el_2} = (E_{n_1} + E_{n_2})\psi_{n\ el_1}\psi_{n\ el_2} \tag{7.1.14}$$

or in bra-ket notation

$$\hat{H}|\Psi_{total}\rangle = \hat{H}|\psi_{el_1}\rangle|\psi_{el_2}\rangle \tag{7.1.15}$$

$$= (E_{n_1} + E_{n_2})|\psi_1\rangle|\psi_2\rangle \tag{7.1.16}$$

The energy for a ground state Helium atom (both electrons in lowest state) is then

$$E_{He_{1s}} = \underbrace{E_{n_1}}_{\text{energy of single electron in helium}} + \underbrace{E_{n_2}}_{\text{energy of single electron in helium}} \tag{7.1.17}$$

$$= -R\left(\frac{Z^2}{1}\right) - R\left(\frac{Z^2}{1}\right) \tag{7.1.18}$$

$$= -8R \tag{7.1.19}$$

This approximation significantly overestimates the true energy of the helium atom $E_{He_{1s}} = -5.8066\ R$. This is a poor approximation and we need to address electron-electron repulsion properly (or better at least).

Shielding and Penetration

One way to take electron-electron repulsion into account is to modify the form of the wavefunction. A logical modification is to change the nuclear charge, Z, in the wavefunctions to an effective nuclear charge (Z_{eff}), from +2 to a smaller value. The rationale for making this modification is that one electron partially shields the nuclear charge from the other electron, as shown in Figure 7.1.1.

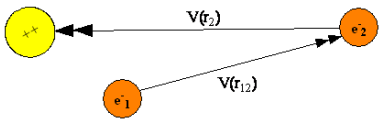


Figure 7.1.1: Electron-electron shielding leading to a reduced effective nuclear charge. The attractive force of the nucleus on electron 2, $V(r_2)$, is partially countered by the repulsive force between electron 1 and electron 2, $V(r_{12})$.

A region of negative charge density between one of the electrons and the +2 nucleus makes the potential energy between them more positive (decreases the attraction between them). We can effect this change mathematically by using $\zeta < 2$ in the wavefunction expression. If the shielding were complete, then Z_{eff} would equal 1. If there is no shielding, then $Z_{eff} = 2$. So a way to take into account the electron-electron interaction is by saying it produces a shielding effect. The shielding is not zero, and it is not complete, so the effective nuclear charge varies between one and two.

In general, a theory should be able to make predictions in advance of knowledge of the experimental result. Consequently, a principle and method for choosing the best value for Z_{eff} or any other adjustable parameter that is to be optimized in a calculation is needed. The Variational Principle provides the required criterion and method and says that the best value for any variable parameter in an approximate wavefunction is the value that gives the **lowest energy for the ground state**; i.e., the value that minimizes the energy. The variational method is the procedure that is used to find the lowest energy and the best values for the variable parameters.

A Better Approximation: The Variational Method

The variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. This allows calculating approximate wavefunctions and is the variational principle. The method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The wavefunction obtained by fixing the parameters to such values is then an approximation to the ground state wavefunction, and the expectation value of the energy in that state is an **upper bound** to the ground state energy.

The variational principle means that the expectation value for the binding energy obtained using an approximate wavefunction and the exact Hamiltonian operator will be higher than or equal to the true energy for the system. This idea is really powerful. When

implemented, it permits us to find the best approximate wavefunction from a given wavefunction that contains one or more adjustable parameters, called a *trial wavefunction*. A mathematical statement of the variational principle is

$$E_{trial} \geq E_{true} \tag{7.1.20}$$

where

$$E_{trial} = \frac{\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{7.1.21}$$

$$= \frac{\int \psi^*_{trial} \hat{H} \psi_{trial} d\tau}{\int \psi^*_{trial} \psi_{trial} d\tau} \tag{7.1.22}$$

Equation 7.1.20 is call the variational theorem and states that for a time-independent Hamiltonian operator, any trial wave function will have an variational energy (i.e., expectation value) that is **greater than or equal** to the true ground state wave function corresponding to the given Hamiltonian (Equation 7.1.20). Because of this, the variational energy is an upper bound to the true ground state energy of a given molecule. The general approach of this method consists in choosing a "trial wavefunction" depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible (Figure **7.1.2**).

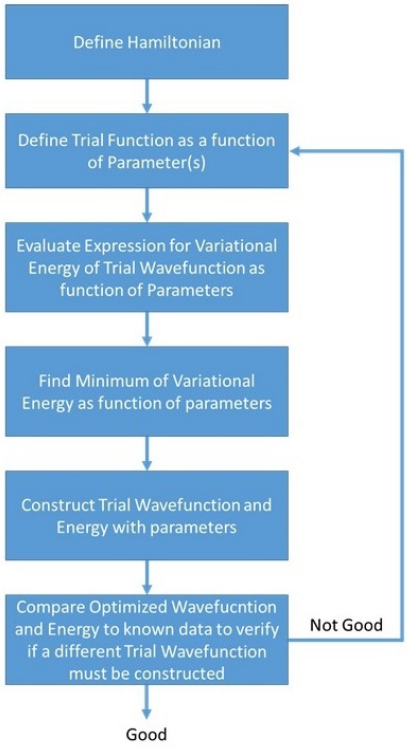


Figure **7.1.2**: Simplified algorithmic flowchart of the Variational Method approximation

> *The variational energy E_{trial} is only equal to the true energy E_{true} when the the corresponding trial wavefunction ψ_{trial} is equal to the true wavefunction ψ_{true}.*

Application to the Helium atom Ground State

Often the expectation values (numerator) and normalization integrals (denominator) in Equation 7.1.22 can be evaluated analytically. For the case of the He atom, let's consider the trial wavefunction as the product wavefunction given by Equation 7.1.23 (this is called the **orbital approximation**),

$$\psi(r_1, r_2) \approx \varphi(r_1)\varphi(r_2) \tag{7.1.23}$$

The adjustable or variable parameter in the trial wavefunction is the effective nuclear charge ζ, and the Hamiltonian is the complete form given below (Note: quantum calculations typically refer to effective nuclear charge as ζ rather than Z_{eff} as we used previously).

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{\zeta e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{7.1.24}$$

the adjustable or variable parameter in the trial wavefunction is the effective nuclear charge ζ (would be equal to $\zeta = 2$ if fully unshielded), and the Hamiltonian is the complete form. When the expectation value for the trial energy (Equation 7.1.22) is evaluated for helium, the result is a variational energy that depends on the adjustable parameter, ζ.

$$E_{trial}(\zeta) = \frac{\mu e^4}{4\epsilon_0^2 h}\left(\zeta^2 - \frac{27}{8}\zeta\right) \tag{7.1.25}$$

This function is plotted in Figure 7.1.1 as a function of ζ. According to the variational principle (Equation 7.1.20), the minimum value of the energy on this graph is the best approximation of the true energy of the system, and the associated value of ζ is the best value for the adjustable parameter.

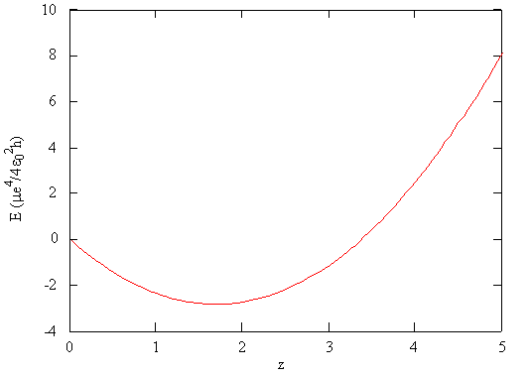


Figure 7.1.2: Graph of trial energies for helium atom as a function of the adjustable parameter ζ in Equation 7.1.25 that represents the effective nuclear charge felt by the electrons.

Using the mathematical function for the energy of a system, the minimum energy with respect to the adjustable parameter can be found by taking the derivative of the energy with respect to that parameter, setting the resulting expression equal to zero, and solving for the parameter, in this case ζ. This is a standard method in calculus for finding maxima and minima.

Exercise 7.1.1

Find the value for ζ that minimizes the helium binding energy for the product trial wavefunction in Equation 7.1.23 with the Hamiltonian in Equation 7.1.24. and compare the binding energy to the experimental value. What is the percent error in the calculated value?

Solution

The variational method requires following the workflow in Figure 7.1.2.

- Step 1: Define the Hamiltonian - This is given by Equation 7.1.24.
- Step 2: Define the trial wavefunction as a function of at least one parameter - This is given by Equation 7.1.23.
- Step 3: Evaluate variational energy (E_{trial} integral (Equation 7.1.22) - This procedure was already above in Equation 7.1.25.
- Step 4: Minimize the variational energy as a function of the parameter(s) - Following the standard approach to find extrema in calculus, evaluate the derivative of E_{trial} with respect to ζ and set to zero:

$$\frac{dE_{trial}}{d\zeta} = \frac{\mu e^4}{4\epsilon_0^2 h}\left(2\zeta - \frac{27}{8}\right) = 0$$

then find solve for the roots of this polynomial

$$2\zeta - \frac{27}{8} = 0$$

or

$$\zeta = \frac{27}{16} \approx 1.6875$$

- Step 5-6: The question does not ask for the optimized wavefunction (Step 5) or to compare the result with the true value to evaluate the quality of the approximation (Step 6). We can skip these steps.

From Exercise **7.1.1**, the $\zeta = 1.6875$ and the approximate energy we calculate using this approximation method, E_{approx} = -77.483 eV. Table **7.1.1** show that a substantial improvement in the accuracy of the computed binding energy is obtained by using shielding to account for the electron-electron interaction. Including the effect of electron shielding in the wavefunction reduces the error in the binding energy to about 2%. This idea is very simple, elegant, and significant.

Table **7.1.1**: Comparison of the results of three approximation methods to experiment.

Method	He binding energy (eV)
"Ignorance is Bliss" Approximation (neglect repulsion between electrons)	-108.8
Variational method with variable effective charge	-77.483
Experimental	-79.0

The improvement we have seen in the total energy calculations using a variable parameter ζ indicates that an important contribution of electron-electron interaction or repulsion to the total binding energy arises from the fact that each electron shields the nuclear charge from the other electron. It is reasonable to assume the electrons are independent; i.e., that they move independently, but the shielding must be taken into account in order to fine-tune the wavefunctions. The inclusion of optimizable parameters in the wavefunction allows us to develop a clear physical image of the consequences of our variation calculation. Calculating energies correctly is important, and it is also important to be able to visualize electron densities for multi-electron systems. In the next two sections, we take a temporary break from our consideration of approximation methods in order to examine multi-electron wavefunctions more closely.

Contributors

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

This page titled 7.1: The Variational Method Approximation is shared under a not declared license and was authored, remixed, and/or curated by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski via source content that was edited to the style and standards of the LibreTexts platform.

7.2: Linear Variational Method and the Secular Determinant

Learning Objectives

- Understand how the variational method can be expanded to include trial wavefunctions that are a linear combination of functions with coefficients that are the parameters to be varied.
- To be able to construct secular equations to solve the minimization procedure intrinsic to the variational method approach.
- To map the secular equations into the secular determinant
- To understand how the Linear Combination of Atomic Orbital (LCAO) approximation is a specific application of the linear variational method.

A special type of variation widely used in the study of molecules is the so-called linear variation function, where the trial wavefunction is a linear combination of N linearly independent functions (often atomic orbitals) that not the eigenvalues of the Hamiltonian (since they are not known). For example

$$|\psi_{trial}\rangle = \sum_{j=1}^{N} a_j |\phi_j\rangle \tag{7.2.1}$$

and

$$\langle\psi_{trial}| = \sum_{j=1}^{N} a_j^* \langle\phi_j| \tag{7.2.2}$$

In these cases, one says that a 'linear variational' calculation is being performed.

Linear Variational Basis Functions

The set of functions $\{\phi_j\}$ are called the 'linear variational' basis functions and are nothing more than members of a set of functions that are convenient to deal with. However, they are typically not arbitrary and are usually selected to address specific properties of the system:

- to obey all of the boundary conditions that the exact state $|\psi_{trial}\rangle$ obeys,
- to be functions of the the same coordinates as $|\psi_{trial}\rangle$,
- to be of the same symmetry as $|\psi_{trial}\rangle$, and
- to be convenient to evaluate Hamiltonian terms elements $\langle\phi_i|H|\phi_j\rangle$.

Beyond these conditions, nothing other than effort can limit the selection and number of such basis functions in the expansions in Equations 7.2.1 and 7.2.2.

As discussed in Section 7.1, the variational energy for a generalized trial wavefunction is

$$E_{trial} = \frac{\langle\psi_{trial}|\hat{H}|\psi_{trial}\rangle}{\langle\psi_{trial}|\psi_{trial}\rangle} \tag{7.2.3}$$

Substituting Equations 7.2.1 and 7.2.2 into Equation 7.2.3 involves addressing the numerator and denominator individually. For the numerator, the integral can be expanded thusly:

$$\langle\psi_{trial}|H|\psi_{trial}\rangle = \sum_{i}^{N}\sum_{j}^{N} a_i^* a_j \langle\phi_i|H|\phi_j\rangle. \tag{7.2.4}$$

$$= \sum_{i,j}^{N,N} a_i^* a_j \langle\phi_i|H|\phi_j\rangle. \tag{7.2.5}$$

We can rewrite the following integral in Equation 7.2.5 as a function of the basis elements (not the trial wavefunction) as

$$H_{ij} = \langle\phi_i|H|\phi_j\rangle \tag{7.2.6}$$

So the numerator of the right side of Equation 7.2.3 becomes

$$\langle \psi_{trial}|H|\psi_{trial}\rangle = \sum_{i,j}^{N,N} a_i^* a_j H_{ij} \tag{7.2.7}$$

Similarly, the denominator of the right side of Equation 7.2.3 can be expanded

$$\langle \psi_{trial}|\psi_{trial}\rangle = \sum_{i,j}^{N,N} a_i^* a_j \langle \phi_i|\phi_j\rangle \tag{7.2.8}$$

We often simplify the integrals on the right side of Equation 7.2.8 as

$$S_{ij} = \langle \phi_i|\phi_j\rangle \tag{7.2.9}$$

where S_{ij} are **overlap integrals** between the different $\{\phi_j\}$ basis functions. Equation 7.2.8 is thus expressed as

$$\langle \psi_{trial}|\psi_{trial}\rangle = \sum_{i,j}^{N,N} a_i^* a_j S_{ij} \tag{7.2.10}$$

Orthonormality

There is no explicit rule that the $\{\phi_j\}$ functions have to be **orthogonal** or **normalized** functions, although they often are selected that way for convenience. Therefore, *a priori*, S_{ij} does not have to be δ_{ij}.

Substituting Equations 7.2.7 and 7.2.10 into the variational energy formula (Equation 7.2.3) results in

$$E_{trial} = \frac{\sum_{i,j}^{N,N} a_i^* a_j H_{ij}}{\sum_{i,j}^{N,N} a_i^* a_j S_{ij}} \tag{7.2.11}$$

For such a trial wavefunction as Equation 7.2.1, the variational energy depends quadratically on the 'linear variational' a_j coefficients. These coefficients can be varied just like the parameters in the trial functions of Section 7.1 to find the optimized trial wavefunction ($|\psi_{trial}\rangle$) that approximates the true wavefunction ($|\psi\rangle$) that we cannot analytically solve for.

Minimizing the Variational Energy

The expression for variational energy (Equation 7.2.11) can be rearranged

$$E_{trial} \sum_{i,j}^{N,N} a_i^* a_j S_{ij} = \sum_{i,j}^{N,N} a_i^* a_j H_{ij} \tag{7.2.12}$$

The optimum coefficients are found by searching for minima in the variational energy landscape spanned by varying the $\{a_i\}$ coefficients (Figure 7.2.1).

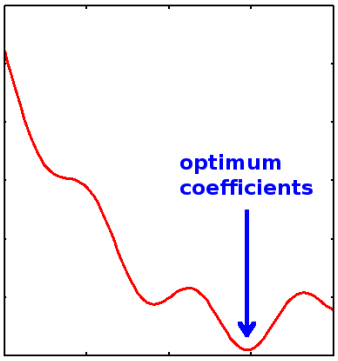


Figure 7.2.1: Linear Variational Principle in action. Two (or more) wavefunctions are mixed by linear combination. The coefficients a_1, a_2 determine the weight each of them is given. The optimum coefficients are found by searching for minima in the potential landscape spanned by a_1 and a_2. (CC BY-SA-NC; Rudolf Winter; Aberystwyth University).

We want to minimize the energy with respect to the linear coefficients $\{a_i\}$, which requires that

$$\frac{\partial E_{trial}}{\partial a_i} = 0 \tag{7.2.13}$$

for all i.

Differentiating both sides of Equation 7.2.12 for the kth coefficient gives,

$$\begin{aligned}\frac{\partial E_{trial}}{\partial a_k} \sum_{i,j}^{N,N} a_i^* a_j S_{ij} + E_{trial} \sum_i \sum_j \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^*\right] S_{ij} \\ = \sum_{i,j}^{N,N} \left[\frac{\partial a_i^*}{\partial a_k} a_j + \frac{\partial a_j}{\partial a_k} a_i^*\right] H_{ij}\end{aligned} \tag{7.2.14}$$

Since the coefficients are independent

$$\frac{\partial a_i^*}{\partial a_k} = \delta_{ik} \tag{7.2.15}$$

and

$$S_{ij} = S_{ji} \tag{7.2.16}$$

and also since the Hamiltonian is a Hermitian Operator (see below)

$$H_{ij} = H_{ji} \tag{7.2.17}$$

then Equation 7.2.14 simplifies to

$$\frac{\partial E_{trial}}{\partial a_k} \sum_i \sum_j a_i^* a_j S_{ij} + 2E_{trial} \sum_i a_i S_{ik} = 2 \sum_i a_i H_{ik} \tag{7.2.18}$$

At the minimum variational energy, when

$$\frac{\partial E_{trial}}{\partial a_k} = 0 \tag{7.2.19}$$

then Equation 7.2.18 gives

$$\sum_i^N a_i (H_{ik} - E_{trial} S_{ik}) = 0 \tag{7.2.20}$$

for all k. The equations in 7.2.20 are call the **Secular Equations**.

Hermitian Operators

Hermitian operators are operators that satisfy the general formula

$$\langle \phi_i | \hat{A} | \phi_j \rangle = \langle \phi_j | \hat{A} | \phi_i \rangle \tag{7.2.21}$$

If that condition is met, then $\hat{A}$ is a Hermitian operator. For any operator that generates a real eigenvalue (e.g., observables), then that operator is Hermitian. The Hamiltonian $\hat{H}$ meets the condition and a Hermitian operator. Equation 7.2.21 can be rewriten as

$$A_{ij} = A_{ji}^* \tag{7.2.22}$$

where

$$A_{ij} = \langle \phi_i | \hat{A} | \phi_j \rangle \tag{7.2.23}$$

and

$$A_{ji} = \langle \phi_j | \hat{A} | \phi_i \rangle \tag{7.2.24}$$

Therefore, when applied to the Hamiltonian operator

$$H_{ij}^* = H_{ji}. \tag{7.2.25}$$

If the functions $\{|\phi_j\rangle\}$ are orthonormal, then the overlap matrix S reduces to the unit matrix (one on the diagonal and zero every where else) and the Secular Equations in Equation 7.2.20 reduces to the more familiar Eigenvalue form:

$$\sum_i^N H_{ij}a_j = E_{trial}a_i. \tag{7.2.26}$$

Hence, the secular equation, in either form, have as many eigenvalues E_i and eigenvectors $\{C_{ij}\}$ as the dimension of the H_{ij} matrix as the functions in $|\psi_{trail}\rangle$ (Example 7.2.1). It can also be shown that between successive pairs of the eigenvalues obtained by solving the secular problem at least one exact eigenvalue must occur (i.e.,$E_{i+1} > E_{exact} > E_i$, for all i). This observation is referred to as '*the bracketing theorem*'.

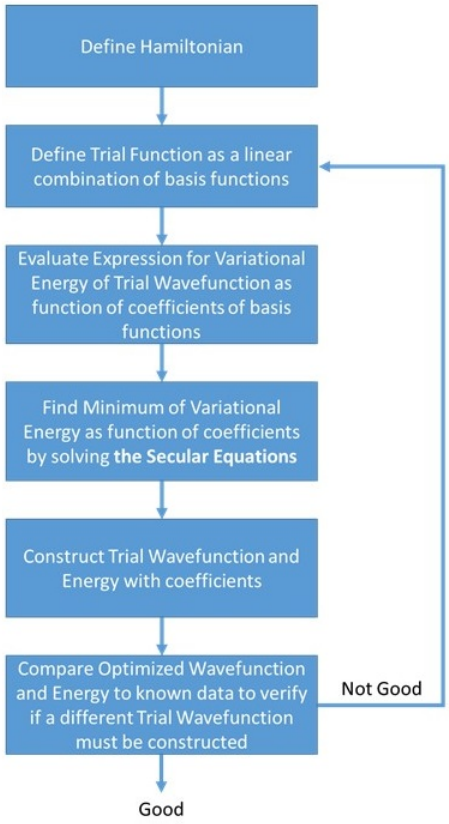


Figure 7.2.2: Simplified algorithmic flowchart of the linear Variational Method approximation. Compared to the similar algorithmic flowchart for the "normal" Variational Method approximation.

Variational methods, in particular the linear variational method, are the most widely used approximation techniques in quantum chemistry. To implement such a method one needs to know the Hamiltonian H whose energy levels are sought and one needs to construct a trial wavefunction in which some 'flexibility' exists (e.g., as in the linear variational method where the a_j coefficients can be varied). This tool will be used to develop several of the most commonly used and powerful molecular orbital methods in chemistry.

The Secular Determinant

From the secular equations with an orthonormal functions (Equation 7.2.26), we have k simultaneous secular equations in k unknowns. These equations can also be written in matrix notation, and for a non-trivial solution (i.e. $c_i \neq 0$ for all i), the determinant of the secular matrix must be equal to zero.

$$|H_{ik}-ES_{ik}| = 0 \tag{7.2.27}$$

Properties of Determinants

- The determinant is a **real** number, it is **not** a matrix.

- The determinant can be a negative number.
- It is **not** associated with absolute value at all except that they both use vertical lines.
- The determinant **only** exists for square matrices (2×2, 3×3, ..., $n \times n$). The determinant of a 1×1 matrix is that single value in the determinant.
- The inverse of a matrix will exist only if the determinant is not zero.

Expanding Determinants

The determinant can be evaluated using an expansion method involving minors and cofactors. Before we can use them, we need to define them. It is the product of the elements on the main diagonal minus the product of the elements off the main diagonal. In the case of a 2×2 matrix, the specific formula for the determinant is

$$|A| = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc. \tag{7.2.28}$$

Similarly, suppose we have a 3×3 matrix A, and we want the specific formula for its determinant $|A|$:

$$\begin{aligned} |A| = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} &= a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \begin{vmatrix} d & e \\ g & h \end{vmatrix} \\ &= aei + bfg + cdh - ceg - bdi - afh. \end{aligned} \tag{7.2.29}$$

To solve Equation 7.2.27, the determinate should be expanded and then set to zero. That generates a polynomial (called a **characteristic equation**) that can be directly solved with linear algebra methods or numerically.

Example 7.2.1: A Simple Two Component Basis Set

If $|\psi_{trial}\rangle$ is a linear combination of two functions. In math terms,

$$|\psi_{trial}\rangle = \sum_{n=1}^{N=2} a_n |f_n\rangle = a_1|\phi_1\rangle + a_2|\phi_2\rangle$$

then the secular determinant (Equation 7.2.27), in matrix formulation would look like this

$$\begin{vmatrix} H_{11} - E_{trial}S_{11} & H_{12} - E_{trial}S_{12} \\ H_{12} - E_{trial}S_{12} & H_{22} - E_{trial}S_{22} \end{vmatrix} = 0$$

Solution

Solving the secular equations is done by finding E_{trial} and putting the value into the expansion of the secular determinant

$$a_1^2 H_{11} + 2a_1 a_2 H_{12} + a_2^2 H_{22} = 0$$

and

$$a_1(H_{12} - E_{trial}S_{12}) + a_2(H_{22} - E_{trial}S_{22}) = 0$$

Equation 7.2.27 can be solved to obtain the energies E. When arranged in order of increasing energy, these provide approximations to the energies of the first k states (each having an energy higher than the true energy of the state by virtue of the variation theorem). To find the energies of a larger number of states we simply use a **greater number** of basis functions $\{\phi_i\}$ in the trial wavefunction (Example 7.2.1). To obtain the approximate wavefunction for a particular state, we substitute the appropriate energy into the secular equations and solve for the coefficients a_i.

Using this method it is possible to find all the coefficients $a_1 \ldots a_k$ in terms of one coefficient; normalizing the wavefunction provides the absolute values for the coefficients.

Example 7.2.2: Linear Combination of Atomic Orbitals (LCAO) Approximation

Trial wavefunctions that consist of linear combinations of simple functions

$$|\psi(r)\rangle = \sum_i a_i |\phi_i(r)\rangle$$

form the basis of the Linear Combination of Atomic Orbitals (LCAO) method introduced by Lennard and Jones and others to compute the energies and wavefunctions of atoms and molecules. The functions $\{|\phi_i\rangle\}$ are selected so that matrix elements can be evaluated analytically. Two basis sets of atomic orbitals functions can be used: Slater type and Gaussian type:

Slater orbitals using Hydrogen-like wavefunctions

$$|\phi_i\rangle = Y_l^m(\theta,\phi)e^{-\alpha r}$$

and Gaussian orbitals of the form

$$|\phi_i\rangle = Y_l^m(\theta,\phi)e^{-\alpha r^2}$$

are the most widely used forms, where $Y_l^m(\theta,\phi)$ are the spherical harmonics that represent the angular part of of the atomic orbitals. Gaussian orbitals form the basis of many quantum chemistry computer codes.

The linear variational method is used extensively in molecular orbitals of molecules and further examples will be postponed until that discussion in Chapters 9.

Contributors

- Claire Vallance (University of Oxford)

This page titled 7.2: Linear Variational Method and the Secular Determinant is shared under a not declared 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.

7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters

An alternative approach to the general problem of introducing variational parameters into wavefunctions is the construction of a wavefunction as a linear combination of other functions each with one or multiple parameters that can be varied

For hydrogen, the radial function decays, or decreases in amplitude, exponentially as the distance from the nucleus increases. For helium and other multi-electron atoms, the radial dependence of the total probability density does not fall off as a simple exponential with increasing distance from the nucleus as it does for hydrogen. More complex single-electron functions therefore are needed in order to model the effects of electron-electron interactions on the total radial distribution function. One way to obtain more appropriate single-electron functions is to use a sum of exponential functions in place of the hydrogenic spin-orbitals.

An example of such a wavefunction created from a sum or linear combination of exponential functions is written as

$$\varphi_{1s}(r_1) = \sum_j c_j e^{-\zeta_j r_j / a_o} \tag{7.3.1}$$

The linear combination permits weighting of the different exponentials through the adjustable coefficients (c_j) for each term in the sum. Each exponential term has a different rate of decay through the zeta-parameter ζ_j. The exponential functions in Equation 7.3.1 are called **basis functions**. Basis functions are the functions used in linear combinations to produce the single-electron orbitals that in turn combine to create the product multi-electron wavefunctions. Originally the most popular basis functions used were the STO's, but today STO's are not used in most quantum chemistry calculations. However, they are often the functions to which more computationally efficient basis functions are fitted.

Physically, the ζ_j parameters account for the effective nuclear charge (often denoted with Z_{eff}). The use of several zeta values in the linear combination essentially allows the effective nuclear charge to vary with the distance of an electron from the nucleus. This variation makes sense physically. When an electron is close to the nucleus, the effective nuclear charge should be close to the actual nuclear charge. When the electron is far from the nucleus, the effective nuclear charge should be much smaller. See Slater's rules for a rule-of-thumb approach to evaluate Z_{eff} values.

A term in Equation 7.3.1 with a small ζ will decay slowly with distance from the nucleus. A term with a large ζ will decay rapidly with distance and not contribute at large distances. The need for such a linear combination of exponentials is a consequence of the electron-electron repulsion and its effect of screening the nucleus for each electron due to the presence of the other electrons.

Exercise 7.3.1

Make plots of φ in Equation 7.3.1 using three equally weighted terms with ζ = 1.0, 2.0, and 5.0. Also plot each term separately.

Computational procedures in which an exponential parameter like ζ is varied are more precisely called the Nonlinear Variational Method because the variational parameter is part of the wavefunction and the change in the function and energy caused by a change in the parameter is not linear. The optimum values for the zeta parameters in any particular calculation are determined by doing a variational calculation for each orbital to minimize the ground-state energy. When this calculation involves a nonlinear variational calculation for the zetas, it requires a large amount of computer time. The use of the variational method to find values for the coefficients, $\{c_j\}$, in the linear combination given by Equation 7.3.1 above is called the Linear Variational Method because the single-electron function whose energy is to be minimized (in this case φ_{1s}) depends linearly on the coefficients. Although the idea is the same, it usually is much easier to implement the linear variational method in practice.

Nonlinear variational calculations are extremely costly in terms of computer time because each time a zeta parameter is changed, all of the integrals need to be recalculated. In the linear variation, where only the coefficients in a linear combination are varied, the basis functions and the integrals do not change. Consequently, an optimum set of zeta parameters were chosen from variational calculations on many small multi-electron systems, and these values, which are given in Table **7.3.1**, generally can be used in the STOs for other and larger systems.

Table **7.3.1**: Orbital Exponents for Slater Orbitals

Atom	ζ_{1s}	$\zeta_{2s,2p}$
H	1.24	
He	1.69	
Li	2.69	0.80
Be	3.68	1.15
B	4.68	1.50
C	5.67	1.72
N	6.67	1.95
O	7.66	2.25
F	8.56	2.55
Ne	9.64	2.88

Exercise 7.3.2

Compare the value ζ_{1s} = 1.24 in Table **7.3.1** for hydrogen with the value you obtained in Exercise **7.3.1**. and comment on possible reasons for any difference. Why are the zeta values larger for 1s than for 2s and 2p orbitals? Why do the ζ_{1s} values increase by essentially one unit for each element from He to Ne while the increase for the $\zeta_{2s,2p}$ values is much smaller?

Answer

ζ values represent the rate of decay in the radial function of an orbital. ζ values are larger for 1s than 2s and 2p orbitals because 1s orbitals have a smaller radial function. As a result, 1s orbitals decrease faster in radial function as you move further from the nucleus, and have a larger ζ value to represent this faster decay. The ζ values for 1s increase essentially by one unit for each element from He to Ne because the 1s orbital is closest to the nucleus, and experiences the greatest effects from change in electronegativity as nuclear density increases from He to Ne. This increase in electronegativity causes the radial function to decay more and more rapidly as atomic number/nucleus density increase. The 2s and 2p orbitals don't experience as great a change in radial function decay rate because they are shielded by the 1s orbital.

The discussion above gives us some new ideas about how to write flexible, useful single-electron wavefunctions that can be used to construct multi-electron wavefunctions for variational calculations. Single-electron functions built from the basis function approach are flexible because they have several adjustable parameters, and useful because the adjustable parameters still have clear physical interpretations. Such functions will be needed in the Hartree-Fock method discussed elsewhere.

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

7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

It is easier to compute the changes in the energy levels and wavefunctions with a scheme of successive corrections to the zero-field values. This method, termed *perturbation theory*, is the single most important method of solving problems in quantum mechanics and is widely used in atomic physics, condensed matter and particle physics. Perturbation theory is another approach to finding approximate solutions to a problem, by starting from the exact solution of a related, simpler problem. A critical feature of the technique is a middle step that breaks the problem into "solvable" and "perturbation" parts. Perturbation theory is applicable if the problem at hand cannot be solved exactly, but can be formulated by adding a "small" term to the mathematical description of the exactly solvable problem.

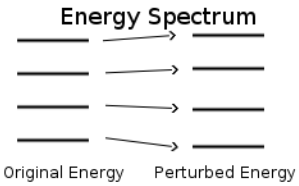


Figure 7.4.1: Perturbed Energy Spectrum. (CC BY-SA 2.0, Frontier).

We begin with a Hamiltonian $\hat{H}^0$ having known eigenkets and eigenenergies:

$$\hat{H}^o|n^o\rangle = E_n^o|n^o\rangle \tag{7.4.1}$$

The task is to find how these eigenstates and eigenenergies change if a small term H^1 (an external field, for example) is added to the Hamiltonian, so:

$$(\hat{H}^0 + \hat{H}^1)|n\rangle = E_n|n\rangle \tag{7.4.2}$$

That is to say, on switching on $\hat{H}^1$ changes the wavefunctions:

$$\underbrace{|n^o\rangle}_{\text{unperturbed}} \Rightarrow \underbrace{|n\rangle}_{\text{Perturbed}} \tag{7.4.3}$$

and energies (Figure 7.4.1):

$$\underbrace{E_n^o}_{\text{unperturbed}} \Rightarrow \underbrace{E_n}_{\text{Perturbed}} \tag{7.4.4}$$

> *The basic assumption in perturbation theory is that H^1 is sufficiently small that the leading corrections are the same order of magnitude as H^1 itself, and the true energies can be better and better approximated by a successive series of corrections, each of order H^1/H^o compared with the previous one.*

The strategy is to **expand** the true wavefunction and corresponding eigenenergy as series in $\hat{H}^1/\hat{H}^o$. These series are then fed into Equation 7.4.2, and terms of the same order of magnitude in $\hat{H}^1/\hat{H}^o$ on the two sides are set equal. The equations thus generated are solved one by one to give progressively more accurate results.

To make it easier to identify terms of the same order in $\hat{H}^1/\hat{H}^o$ on the two sides of the equation, it is convenient to introduce a dimensionless parameter λ which always goes with $\hat{H}^1$, and then expand both eigenstates and eigenenergies as power series in λ,

$$|n\rangle = \sum_i^m \lambda^i |n^i\rangle \tag{7.4.5}$$

$$E_n = \sum_{i=0}^m \lambda^i E_n^i \tag{7.4.6}$$

where m is how many terms in the expansion we are considering. The ket $|n^i\rangle$ is multiplied by λ^i and is therefore of order $(H^1/H^o)^i$.

> *λ is purely a bookkeeping device: we will set it equal to 1 when we are through! It's just there to keep track of the orders of magnitudes of the various terms.*

For example, in first order perturbation theory, Equations 7.4.5 are truncated at $m = 1$ (and setting $\lambda = 1$):

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.7}$$

$$E_n \approx E_n^o + E_n^1 \tag{7.4.8}$$

However, let's consider the general case for now. Adding the full expansions for the eigenstate (Equation 7.4.5) and energies (Equation 7.4.6) into the Schrödinger equation for the perturbation Equation 7.4.2 in

$$(\hat{H}^o + \lambda \hat{H}^1)|n\rangle = E_n|n\rangle \tag{7.4.9}$$

we have

$$(\hat{H}^o + \lambda \hat{H}^1)\left(\sum_{i=0}^{m} \lambda^i |n^i\rangle\right) = \left(\sum_{i=0}^{m} \lambda^i E_n^i\right)\left(\sum_{i=0}^{m} \lambda^i |n^i\rangle\right) \tag{7.4.10}$$

We're now ready to match the two sides term by term in powers of λ. Note that the zeroth-order term, of course, just gives back the unperturbed Schrödinger Equation (Equation 7.4.1).

Let's look at Equation 7.4.10 with the first few terms of the expansion:

$$(\hat{H}^o + \lambda \hat{H}^1)\left(|n^o\rangle + \lambda |n^1\rangle\right) = \left(E_n^0 + \lambda E_n^1\right)\left(|n^o\rangle + \lambda |n^1\rangle\right) \tag{7.4.11}$$

$$\begin{aligned} \hat{H}^o|n^o\rangle + \lambda \hat{H}^1|n^o\rangle + \lambda H^o|n^1\rangle + \lambda^2 \hat{H}^1|n^1\rangle = {} & E_n^0|n^o\rangle + \lambda E_n^1|n^o\rangle \\ & + \lambda E_n^0|n^1\rangle + \lambda^2 E_n^1|n^1\rangle \end{aligned} \tag{7.4.12}$$

Collecting terms in order of λ and coloring to indicate different orders

$$\begin{aligned} & \underset{\text{zero order}}{\hat{H}^o|n^o\rangle} \\ & + \underset{\text{1st order}}{\lambda(\hat{H}^1|n^o\rangle + \hat{H}^o|n^1\rangle)} + \underset{\text{2nd order}}{\lambda^2 \hat{H}^1|n^1\rangle} = \underset{\text{zero order}}{E_n^0|n^o\rangle} + \underset{\text{1st order}}{\lambda(E_n^1|n^o\rangle + E_n^0|n^1\rangle)} + \underset{\text{2nd order}}{\lambda^2 E_n^1|n^1\rangle} \end{aligned} \tag{7.4.13}$$

If we expanded Equation 7.4.10 further we could express the energies and wavefunctions in higher order components.

Zero-Order Terms ($\lambda = 0$)

Collecting the zero order terms in the expansion (black terms in Equation 7.4.10) results in just the Schrödinger Equation for the unperturbed system

$$\hat{H}^o|n^o\rangle = E_n^o|n^o\rangle \tag{7.4.14}$$

First-Order Expression of Energy ($\lambda = 1$)

The summations in Equations 7.4.5, 7.4.6, and 7.4.10 can be truncated at any order of λ. For example, the first order perturbation theory has the truncation at $\lambda = 1$. Matching the terms that linear in λ (red terms in Equation 7.4.13) and setting $\lambda = 1$ on both sides of Equation 7.4.13:

$$\hat{H}^o|n^1\rangle + \hat{H}^1|n^o\rangle = E_n^o|n^1\rangle + E_n^1|n^o\rangle \tag{7.4.15}$$

Equation 7.4.15 is the key to finding the first-order change in energy E_n^1. Taking the **inner product** of both sides with $\langle n^o|$:

$$\langle n^o|\hat{H}^o|n^1\rangle + \langle n^o|\hat{H}^1|n^o\rangle = \langle n^o|E_n^o|n^1\rangle + \langle n^o|E_n^1|n^o\rangle \tag{7.4.16}$$

since operating the zero-order Hamiltonian on the bra wavefunction (this is just the Schrödinger equation; Equation 7.4.14) is

$$\langle n^o|\hat{H}^o = \langle n^o|E_n^o \tag{7.4.17}$$

and via the orthonormality of the unperturbed $|n^o\rangle$ wavefunctions both

$$\langle n^o|n^o\rangle = 1 \tag{7.4.18}$$

and Equation 7.4.8 can be simplified

$$\cancel{E_n^o\langle n^o|n^1\rangle} + \langle n^o|H^1|n^o\rangle = \cancel{E_n^o\langle n^o|n^1\rangle} + E_n^1\cancel{\langle n^o|n^{o\,1}\rangle} \tag{7.4.19}$$

since the unperturbed set of eigenstates are orthogonal (Equation 7.4.18) and we can cancel the other term on each side of the equation, we find that

$$E_n^1 = \langle n^o|\hat{H}^1|n^o\rangle \tag{7.4.20}$$

> *The first-order change in the energy of a state resulting from adding a perturbing term $\hat{H}^1$ to the Hamiltonian is just the **expectation value** of $\hat{H}^1$ in the **unperturbed** wavefunctions.*

That is, the first order energies (Equation 7.4.15) are given by

$$E_n \approx E_n^o + E_n^1 \tag{7.4.21}$$

$$\approx \underbrace{E_n^o + \langle n^o|H^1|n^o\rangle}_{\text{First Order Perturbation}} \tag{7.4.22}$$

Example 7.4.1A: A Perturbed Particle in a Box

Estimate the energy of the ground-state and first excited-state wavefunction within first-order perturbation theory of a system with the following potential energy

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

Solution

The first step in any perturbation problem is to write the Hamiltonian in terms of a unperturbed component that the solutions (both eigenstates and energy) are known and a perturbation component (Equation 7.4.2). For this system, the unperturbed Hamilonian and solutions is the particle in an infiinitely high box and the perturbation is a shift of the potential within the box by V_o.

$$\hat{H}^1 = V_o$$

Using Equation 7.4.20 for the first-order term in the energy of the ground-state

$$E_n^1 = \langle n^o|H^1|n^o\rangle$$

with the wavefunctions known from the particle in the box problem

$$|n^o\rangle = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

At this stage we can do two problems independently (i.e., the ground-state with $|1\rangle$ and the first excited-state $|2\rangle$). However, in this case, the first-order perturbation to any particle-in-the-box state can be easily derived.

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

or better yet, instead of evaluating this integrals we can simplify the expression

$$E_n^1 = \langle n^o|H^1|n^o\rangle = \langle n^o|V_o|n^o\rangle = V_o\langle n^o|n^o\rangle = V_o$$

so via Equation 7.4.22, the energy of each perturbed eigenstate is

$$E_n \approx E_n^o + E_n^1$$

$$\approx \frac{h^2}{8mL^2}n^2 + V_o$$

While this is the first order perturbation to the energy, it is also the exact value.

Example 7.4.1B: An Even More Perturbed Particle in a Box

Estimate the energy of the ground-state wavefunction within first-order perturbation theory of a system with the following potential energy

$$V(x) = \begin{cases} V_o & 0 \le x \le L/2 \\ \infty & x < 0 \; and \; x > L \end{cases}$$

Solution

As with Example 7.4.1, we recognize that unperturbed component of the problem (Equation 7.4.2) is the particle in an infinitely high well. For this system, the unperturbed Hamiltonian and solution is the particle in an infinitely high box and the perturbation is a shift of the potential within half a box by V_o. This is essentially a step function.

Using Equation 7.4.20 for the first-order term in the energy of the any state

$$\begin{aligned} E_n^1 &= \langle n^o | H^1 | n^o \rangle \\ &= \int_0^{L/2} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) V_o \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) dx + \int_{L/2}^{L} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) 0 \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) dx \end{aligned}$$

The second integral is zero and the first integral is simplified to

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

this is evaluated to

$$\begin{aligned} E_n^1 &= \frac{2V_o}{L} \left[\frac{-1}{2\frac{\pi n}{a}} \cos\left(\frac{n\pi}{L}x\right) \sin\left(\frac{n\pi}{L}x\right) + \frac{x}{2} \right]_0^{L/2} \\ &= \frac{2V_o}{\cancel{L}} \frac{\cancel{L}}{4} = \frac{V_o}{2} \end{aligned}$$

The energy of each perturbed eigenstate, via Equation 7.4.22, is

$$\begin{aligned} E_n &\approx E_n^o + \frac{V_o}{2} \\ &\approx \frac{h^2}{8mL^2} n^2 + \frac{V_o}{2} \end{aligned}$$

First-Order Expression of Wavefunction ($\lambda = 1$)

The general expression for the first-order change in the *wavefunction* is found by taking the inner product of the first-order expansion (Equation 7.4.15) with the bra $\langle m^o |$ with $m \neq n$,

$$\langle m^o | H^o | n^1 \rangle + \langle m^o | H^1 | n^o \rangle = \langle m^o | E_n^o | n^1 \rangle + \langle m^o | E_n^1 | n^o \rangle \tag{7.4.23}$$

Last term on right side of Equation 7.4.23

The last integral on the right hand side of Equation 7.4.23 is zero, since $m \neq n$ so

$$\langle m^o | E_n^1 | n^o \rangle = E_n^1 \langle m^o | n^o \rangle \tag{7.4.24}$$

and

$$\langle m^o | n^0 \rangle = 0 \tag{7.4.25}$$

First term on right side of Equation 7.4.23

The first integral is more complicated and can be expanded back into the H^o

$$E_m^o \langle m^o | n^1 \rangle = \langle m^o | E_m^o | n^1 \rangle = \langle m^o | H^o | n^1 \rangle \tag{7.4.26}$$

since

$$\langle m^o|H^o = \langle m^o|E_m^o \tag{7.4.27}$$

so

$$\langle m^o|n^1\rangle = \frac{\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o} \tag{7.4.28}$$

and therefore the wavefunction corrected to first order is:

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.29}$$

$$\approx |n^o\rangle + \underbrace{\sum_{m\neq n} \frac{|m^o\rangle\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o}}_{\text{First Order Perturbation Theory}} \tag{7.4.30}$$

Equation 7.4.30 is essentially is an expansion of the unknown wavefunction correction as a **linear combination** of known unperturbed wavefunctions 7.4.32:

$$|n\rangle \approx |n^o\rangle + |n^1\rangle \tag{7.4.31}$$

$$\approx |n^o\rangle + \sum_{m\neq n} c_{m,n}|m^o\rangle \tag{7.4.32}$$

with the expansion coefficients determined by

$$c_{m,n} = \frac{\langle m^o|H^1|n^o\rangle}{E_n^o - E_m^o} \tag{7.4.33}$$

This is justified since the set of original zero-order wavefunctions forms a **complete basis set** that can describe any function.

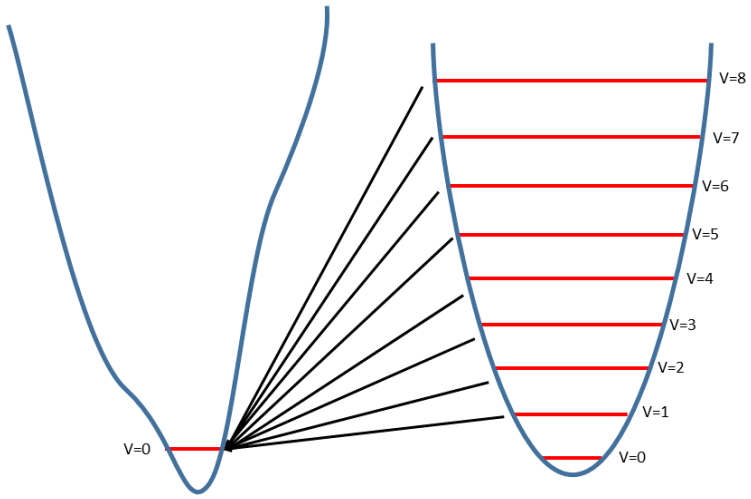


Figure 7.4.2: The first order perturbation of the ground-state wavefunction for a perturbed (left potential) can be expressed as a linear combination of all excited-state wavefunctions of the unperturbed potential (Equation 7.4.32), shown as a harmonic oscillator in this example (right potential). Note that the ground-state harmonic oscillator wavefuncion is not part of this expression and technically all wavefunctions need to be included in the expression, not just the first eight wavefunctions shown here. (CC BY; Delmar Larsen)

Calculating the first order perturbation to the wavefunctions is in general an infinite sum of off diagonal matrix elements of H^1 (Figure 7.4.2).

- However, the denominator argues that terms in this sum will be weighted by states that are of **comparable energy**. That means in principle, these sum can be truncated easily based off of some criterion.
- Another point to consider is that many of these matrix elements will equal zero depending on the symmetry of the $\{|n^o\rangle\}$ basis and H^1 (e.g., some $\langle m^o|H^1|n^o\rangle$ integrals in Equation 7.4.30 could be zero due to the integrand having an odd symmetry; see

Example 7.4.3).

> *The denominators in Equation 7.4.30 argues that terms in this sum will be preferentially dictated by states that are of **comparable energy**. That is, eigenstates that have energies significantly greater or lower than the unperturbed eigenstate will weakly contribute to the perturbed wavefunction.*

Example 7.4.2: A Harmonic Oscillator with a Cubic Perturbation

Estimate the energy of the ground-state wavefunction associated with the Hamiltonian using perturbation theory

$$\hat{H} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \epsilon x^3$$

Solution

The first step in a perturbation theory problem is to identify the reference system with the known eigenstates and energies. For this example, this is clearly the harmonic oscillator model.

Energy

The first steps in flowchart for applying perturbation theory (Figure 7.4.1) is to separate the Hamiltonian of the difficult (or unsolvable) problem into a solvable one with a perturbation. For this case, we can rewrite the Hamiltonian as

$$\hat{H}^o + \hat{H}^1$$

where

- $\hat{H}^o$ is the Hamitonian for the standard Harmonic Oscillator with **known** eigenstates and eigenenergies

$$\hat{H}^{(0)} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

- $\hat{H}^1$ is the pertubtiation

$$\hat{H}^1 = \epsilon x^3$$

The first order perturbation is given by Equation 7.4.20, which for this problem is

$$E_n^1 = \langle n^o | \epsilon x^3 | n^o \rangle$$

Notice that the integrand has an odd symmetry (i.e., $f(x) = -f(-x)$) with the perturbation Hamiltonian being odd and the ground state harmonic oscillator wavefunctions being even. So

$$E_n^1 = 0$$

This means to first order pertubation theory, this cubic terms does not alter the ground state energy (via Equation 7.4.22). However, this is not the case if second-order perturbation theory were used, which is more accurate (not shown).

Wavefunction

Calculating the first order perturbation to the wavefunctions (Equation 7.4.30) is more difficult than energy since multiple integrals must be evaluated (an infinite number if symmetry arguments are not applicable). The harmonic oscillator wavefunctions are often written in terms of Q, the unscaled displacement coordinate:

$$|\Psi_v(x)\rangle = N_v'' H_v(\sqrt{\alpha}Q) e^{-\alpha Q^2/2}$$

with α

$$\alpha = 1/\sqrt{\beta} = \sqrt{\frac{k\mu}{\hbar^2}}$$

and

$$N_v'' = \sqrt{\frac{1}{2^v v!}} \left(\frac{\alpha}{\pi}\right)^{1/4}$$

Let's consider only the first six wavefunctions that use these Hermite polynomials $H_v(x)$:

- $H_0 = 1$
- $H_1 = 2x$
- $H_2 = -2 + 4x^2$
- $H_3 = -12x + 8x^3$
- $H_4 = 12 - 48x^2 + 16x^4$
- $H_5 = 120x - 160x^3 + 32x^5$

The first order perturbation to the ground-state wavefunction (Equation 7.4.30)

$$|0^1\rangle = \sum_{m \neq 0}^{5} \frac{|m^o\rangle \langle m^o|H^1|0^o\rangle}{E_0^o - E_m^o} \tag{7.4.34}$$

given these truncated wavefunctions (we should technically use the infinite sum) and that we are considering only the ground state with $n = 0$:

$$|0^1\rangle = \frac{\langle 1^o|H^1|0^o\rangle}{E_0^o - E_1^o}|1^o\rangle + \frac{\langle 2^o|H^1|0^o\rangle}{E_0^o - E_2^o}|2^o\rangle + \frac{\langle 3^o|H^1|0^o\rangle}{E_0^o - E_3^o}|3^o\rangle + \frac{\langle 4^o|H^1|0^o\rangle}{E_0^o - E_4^o}|4^o\rangle + \frac{\langle 5^o|H^1|0^o\rangle}{E_0^o - E_5^o}|5^o\rangle$$

We can use symmetry of the perturbation and unperturbed wavefunctions to solve the integrals above. We know that the unperturbed harmonic oscillator wavefunctions $\{|n^0\}\rangle$ alternate between even (when v is even) and odd (when v is odd) as shown previously. Since the perturbation is an odd function, only when $m = 2k + 1$ with $k = 1, 2, 3$ would these integrals be non-zero (i.e., for $m = 1, 3, 5, ...$).

So of the original five unperturbed wavefunctions, only $|m = 1\rangle$, $|m = 3\rangle$, and $|m = 5\rangle$ mix to make the first-order perturbed ground-state wavefunction so

$$|0^1\rangle = \frac{\langle 1^o|H^1|0^o\rangle}{E_0^o - E_1^o}|1^o\rangle + \frac{\langle 3^o|H^1|0^o\rangle}{E_0^o - E_3^o}|3^o\rangle + \frac{\langle 5^o|H^1|0^o\rangle}{E_0^o - E_5^o}|5^o\rangle$$

At this stage, the integrals have to be manually calculated using the defined wavefuctions above, which is left as an exercise. Notice that each unperturbed wavefunction that can "mix" to generate the perturbed wavefunction will have a reciprocally decreasing contribution (w.r.t. energy) due to the growing denominator in Equation 7.4.34.

Exercise 7.4.3: Harmonic Oscillator with a Quartic Perturbation

Use perturbation theory to estimate the energy of the ground-state wavefunction associated with this Hamiltonian

$$\hat{H} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \gamma x^4.$$

Answer

The model that we are using is the harmonic oscillator model which has a Hamiltonian

$$H^0 = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

Making the perturbed Hamiltonian

$$H^1 = \gamma x^4$$

To find the perturbed energy we approximate it using Equation 7.4.22

$$E^1 = \langle n^0 \left| H^1 \right| n^0 \rangle$$

where is the wavefunction of the ground state harmonic oscillator

$$n^0 = \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}}$$

When we substitute in the Hamiltonian and the wavefunction we get

$$E^1 = \left\langle \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}} \middle| \gamma x^4 \middle| \left(\frac{a}{\pi}\right)^{\left(\frac{1}{4}\right)} e^{-\frac{ax^2}{2}} \right\rangle$$

Changing this into integral form, and combining the wavefunctions,

$$E^1 = \int_{-\infty}^{\infty} \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} e^{\frac{-ax^2}{2}} \gamma x^4 dx$$
$$= \gamma \left(\frac{a}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} x^4 e^{-ax^2} dx$$

Now we use the integral table value

$$\int_0^{\infty} x^{2\pi} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \ldots (2n-1)}{2^{m+1} a^n} \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

Where we plug in $\mathbf{n = 2}$ and $\mathbf{a = \alpha}$ for our integral

$$E^1 = 2\gamma \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} \int_0^{\infty} x^4 e^{-ax^2} dx$$
$$E^1 = 2\gamma \left(\frac{a}{\pi}\right)^{\left(\frac{1}{2}\right)} \frac{1 \cdot 3}{2^3 a^2} \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

This is our perturbed energy

Now we have to find our ground state energy using the formula for the energy of a harmonic oscillator that we already know,

$$E_r^0 = \left(v + \frac{1}{2}\right) hv$$

Where in the ground state $v = 0$ so the energy for the ground state of the quantum harmonic oscillator is

$$E_r^0 = \frac{1}{2} hv$$

Putting both of our energy terms together gives us the ground state energy of the wavefunction of the given Hamiltonian,

$$E = E^0 + E^1$$
$$E = \tfrac{1}{2} hv + \gamma \tfrac{3}{4a^2}$$

Second-Order Terms ($\lambda = 2$)

There are higher energy terms in the expansion of Equation 7.4.5 (e.g., the blue terms in Equation 7.4.13), but are not discussed further here other than noting the whole perturbation process is an infinite series of corrections that ideally converge to the correct answer. It is truncating this series as a finite number of steps that is the approximation. The general approach to perturbation theory applications is giving in the flowchart in Figure **7.4.1**.

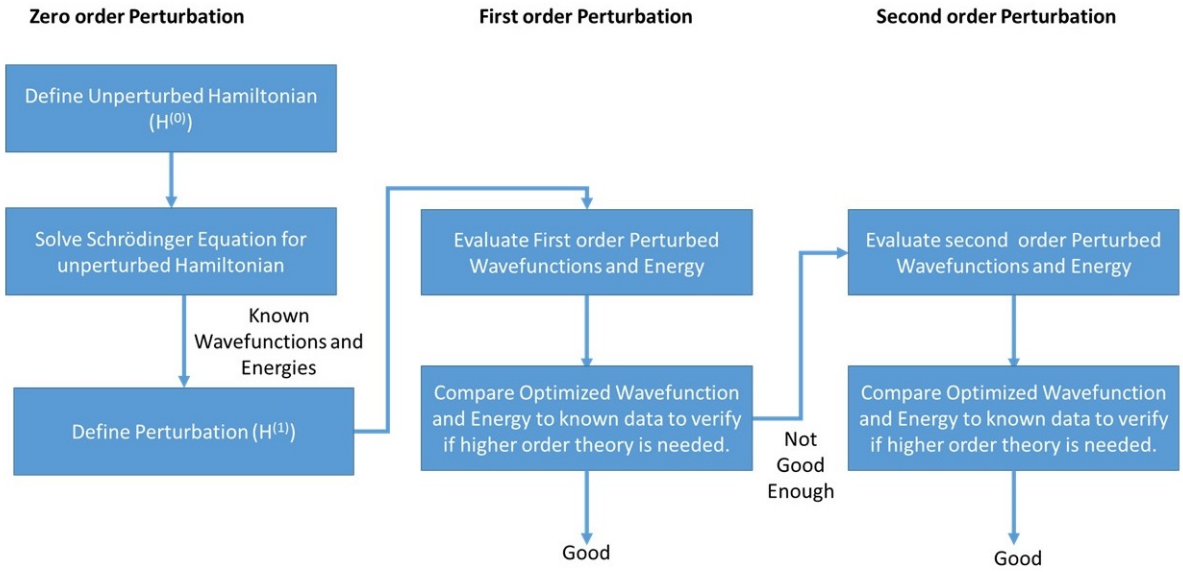


Figure **7.4.1**: Simplified algorithmic flowchart of the Perturbation Theory approximation showing the first two perturbation orders. The process can be continued to third and higher orders. (CC BY; Delmar Larsen)

Perturbation Theory Does not always Work

It should be noted that there *are* problems that cannot be solved using perturbation theory, even when the perturbation is very weak, although such problems are the exception rather than the rule. One such case is the one-dimensional problem of free particles perturbed by a localized potential of strength λ. Switching on an arbitrarily weak attractive potential causes the $k = 0$ free particle wavefunction to drop below the continuum of plane wave energies and become a localized bound state with binding energy of order λ^2. However, changing the sign of λ to give a repulsive potential there is no bound state, the lowest energy plane wave state stays at energy zero. Therefore the energy shift on switching on the perturbation **cannot** be represented as a power series in λ, the strength of the perturbation.

Contributors

- Michael Fowler (Beams Professor, Department of Physics, University of Virginia)

7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

7.E: Approximation Methods (Exercises)

Solutions to select questions can be found online.

7.3

Calculate the ground state energy of Harmonic Oscillator using variation method with the following trial wavefunction

$$\phi(x) = |\phi(x)\rangle = \frac{1}{(1+\beta x^2)^2}$$

You may require these definite integrals:

$$\int_{-\infty}^{\infty} \frac{dx}{(1+\beta x^2)^n} = \frac{(2n-3)(2n-5)(2n-7)\ldots(1)}{(2n-2)(2n-4)(2n-6)\ldots(2)\cdot\pi/\beta^{1/2}}$$

$$\int_{-\infty}^{\infty} \frac{dx}{(1-\beta x^2)^n} = \frac{(2n-5)(2n-7)\ldots(1)}{(2n-2)(2n-4)\ldots(2)\cdot\pi/\beta^{3/2}}$$

Solution

First, we must know the Hamiltonian operator for the harmonic oscillator, which is

$$\hat{H} = \frac{-\hbar}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

From this point on, the determination of E_ϕ can be found using the trail function

$$|\phi(x)\rangle = \frac{1}{(1+\beta x^2)^2}$$

which once substitute get the following equation for the numerator portion:

$$\int_{-\infty}^{-\infty} \frac{1}{(1+\betax^2)^2[\hbar^2/\mu * 2\beta/(1+\betax^2)^3 - \hbar^2/\mu * 12\beta^2x^2/(1+\betax^2)^4 + \frac{kx^2}{2}(1+\betax^2)^2]}$$

$$= 2\beta\hbar^2/\mu * (7*5*3*1*\pi/8*6*4*2*\beta 1/2) - 12\beta^2\hbar^2/\mu * (7*5*3*1*\pi/10*8*6*4*2*\beta 1/2) + k/2 * (3*1*\pi/6*4*2*\beta^{3/2})$$

$$= \frac{7\pi\beta^{1/2}\hbar}{32\mu + k\pi/32\beta^{3/2}}$$

Now solving the denominator:

$$\int_{\infty}^{\infty} \phi^*\phi\, dx = \int_{\infty}^{\infty} \frac{1}{(1+\beta x^2)^4} = \frac{5*3*1*\pi}{6*4*2*\beta^{1/2}} = \frac{5\pi}{/16\beta^{1/2}}$$

After this we will find

$$E_\phi = \frac{7\pi\beta^{1/2}\hbar^2}{32\mu * (16\beta^{1/2}/5\pi)} + \frac{k\pi}{32\beta^{3/2} * (16\beta^{1/2}/5\pi)} = \frac{7/10 * \beta\hbar 2}{\mu} + \frac{1}{10}\frac{k}{\beta}$$

Then find minimum value

\[\dfrac{dE_\phi}{d \beta}= \dfrac{7 \hbar^2}{10μ} -\dfrac{ k}{10 \beta^2_{min} = 0\nonumber \]

therefore

$$\beta_{min} = \sqrt{\frac{\mu k}{7\hbar^2}}$$

\[E_{min}= \dfrac{7^{1/2} \hbar }{5 * (k/μ)^{1/2}} + \dfrac{7^{1/2} \hbar }{5 (k/μ)^{1/2} }= 71/2 \hbar /5 (k/μ)^{1/2} = 0.53 \hbar *(k/μ)^{1/2\nonumber \]

Therefore overall get

$$E_{exact} = 0.500\hbar\sqrt{(k/\mu)}$$

⇒ this value differs by 6%.

7.8

What is the variational (trial) energy of the trial function

$$|\phi\rangle = e^{-ax^2}$$

for the ground-state of a harmonic oscillator? Just set up the integral, but do not evaluate. Use

$$\hat{H} = \frac{\hbar^2}{2m}\nabla n^2 + \frac{kx^2}{2}$$

Solution

The variational energy:

$$E_{trial}(a) = \frac{\langle \phi(a) \left| \hat{H} \right| \phi(a) \rangle}{\langle \phi(a) | \phi(a) \rangle} \geq E_{true}$$

numerator:

$$\langle \phi | \phi \rangle = \int_{-\infty}^{\infty} e^{-2ax^2} dx$$

All combined together to extract the trial energy as a function of a:

$$E_{trial}(a) = \frac{\int_{-\infty}^{\infty} e^{-ax^2} \left[\frac{\hbar^2}{2m} \frac{d^2(e^{-ax^2})}{dx^2} + \frac{kx^2}{2} \right] e^{-ax^2} dx}{\int_{-\infty}^{\infty} e^{-2ax^2} dx}$$

Use the components of $\hat{H}$ to operate on ϕ

$$\langle \phi \left| \hat{H} \right| \phi \rangle = \int_{-\infty}^{\infty} e^{-ax^2} \left[\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right] e^{-ax^2} dx$$

denominator:

$$\langle \phi | \phi \rangle = \int_{-\infty}^{\infty} e^{-ax^2} e^{-ax^2} dx$$

7.9

Use the trial function

$$|\exp^{\frac{-ax^2}{2}}\rangle$$

to set up the integrals to find the ground state energy of a anharmonic oscillator whose potential is $V(x) = cx^5$, but do not evaluate.

Solution

$$E = \frac{\int_{-\infty}^{\infty} \phi^* \hat{H} \phi d\tau}{\int_{-\infty}^{\infty} \phi^* \phi d\tau}$$

$$\int_{-\infty}^{\infty} \phi^* \phi d\tau = \int_{-\infty}^{\infty} \exp^{-\alpha x^2} dx$$

$$\int_{-\infty}^{\infty} \phi^* \hat{H} \phi d\tau = \int_{-\infty}^{\infty} (\frac{\hbar^2}{2m}\nabla^2 + \frac{kx^2}{2} + cx^5) \exp^{-\alpha x^2} dx$$

$$E = \frac{\int_{-\infty}^{\infty} (\frac{\hbar^2}{2m}\nabla^2 + \frac{kx^2}{2} + cx^5) \exp^{-\alpha x^2} dx}{\int_{-\infty}^{\infty} \exp^{-\alpha x^2} dx}$$

7.12

Consider a particle of mass m in a box from $x = -a$ to $x = a$ with $V(x) = -V_0$ for $|x| \geq a$. Assume a trial function of the form

$$|\phi(x)\rangle = l^2 - x^2$$

for $-l < x < l$ and $\psi(x) = 0$ otherwise. l is the parameter. Does the trial function satisfy the requirements of a particle in a box wavefunction?

The result of the variational method was

$$E_\phi(s) = \frac{5}{16}\frac{\hbar^2}{ma^2}\left[\frac{4}{s^2} + \frac{4}{5}\left(8 - \frac{15}{s} + \frac{10}{s^3} - \frac{3}{s^5}\right)\right]$$

Where $s = \frac{l}{a}$ is a new variational parameter for convenience of expression. Derive a polynomial expression for s that can be solved to obtain the value of s that yields the ground state energy, but do not attempt to solve for this value of s .

Solution

Yes, it is finite over all x values, it's first and second derivatives are continuous, and it meets the boundary conditions $\psi(-a) = \psi(a) = 0$, and it is normalizable for a choice of l.

Taking the derivative of E with respect to s,

$$\frac{\partial E}{\partial s} = 0 = -\frac{8}{s^3} + \frac{4}{5}\left(\frac{15}{s^2} - \frac{30}{s^4} + \frac{15}{s^6}\right)$$

With some algebra, this becomes,

$$3s^4 - 2s^3 - 6s^2 + 3 = 0$$

With a calculator or other root finding procedure, s can be solved for.

7.13

Given a trial wavefunction equal to $\sin\lambda(x)$, explain in words a stepwise procedure on how you would go about solving for the energy of this trial wavefunction as well as how to minimize the error.

Solution

1. Denote $\sin(\lambda(x)) = \phi_n$
2. Solve the integral $\langle\phi_n^*|\phi_n\rangle$
3. Solve the integral $\langle\phi_n^*|\hat{H}|\phi_n\rangle$
4. Now that you solved for steps 2 and 3, plug into the equation

$$E_n = \frac{\langle\phi_n^*|\hat{H}|\phi_n\rangle}{\langle\phi_n^*|\phi_n\rangle}$$

5. Take the derivative of E_n with respect to λ and set equal to 0.

$$\frac{dE_n}{d\lambda}$$

6. Solve for λ and plug back into equation in step 4.

7.16

Using the variational method approximation, find the ground state energy of a particle in a box using this trial function:

$$|\phi\rangle = N\cos\left(\frac{\pi x}{L}\right)$$

How does is it compare to the true ground state energy?

Solution

The problem asks that we apply variational methods approximation to our trial wavefunction.

$$E_\phi = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} \geq E_o$$

$$\langle\phi|\phi\rangle = 1 = \int_0^L N^2\cos^2\left(\frac{\pi x}{L}\right)$$

Performing this integral and solving for N yields

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

The Hamiltonian for a particle in a one dimensional box is $\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$

$$\begin{aligned}\langle\phi|\hat{H}|\phi\rangle &= \langle N\cos\left(\frac{\pi x}{L}\right)\Big|\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\Big|N\cos\left(\frac{\pi x}{L}\right)\rangle \\ &= \int_0^L N\cos\left(\frac{\pi x}{L}\right)\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}N\cos\left(\frac{\pi x}{L}\right)dx \\ &= \frac{N^2\pi^2\hbar^2}{2mL^2}\int_0^L\cos^2\left(\frac{\pi x}{L}\right)dx\end{aligned}$$

where $N = \sqrt{\frac{2}{L}}$. The above equation after the integral becomes

$$\frac{\pi^2\hbar^2}{mL^3}\left(\frac{L}{2}\right)$$

$$E_\phi = \frac{\pi^2\hbar^2}{2mL^2}$$

This is equal to the ground state energy of the particle in a box that we calculated from the Schrodinger equation using

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

7.17

For the three-electron detrimental wavefunction

$$\psi = \begin{vmatrix} \phi_A(1) & \phi_A(2) & \phi_A(3) \\ \phi_B(1) & \phi_B(2) & \phi_B(3) \\ \phi_C(1) & \phi_C(2) & \phi_C(3) \end{vmatrix}.$$

confirm that:

a. the interchange of two columns changes the sign of the wavefunction,
b. the interchange of two rows changes the sign of the wavefunction, and
c. the three electrons cannot have the same spin orbital.

Solution

First find the determinant

$$\psi = \phi_A(1) \begin{vmatrix} \phi_B(2) & \phi_B(3) \\ \phi_C(2) & \phi_C(3) \end{vmatrix} - \phi_A(2) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(1) & \phi_B(2) \\ \phi_C(1) & \phi_C(2) \end{vmatrix}$$

$$= \phi_A(1)\left(\phi_B(2)\phi_C(3) - \phi_C(2)\phi_B(3)\right) - \phi_A(2)\left(\phi_B(1)\phi_C(3) - \phi_C(1)\phi_B(3)\right) + \phi_A(3)\left(\phi_B(1)\phi_C(2) - \phi_C(1)\phi_B(2)\right)$$

$$\psi = \phi_A(1)\phi_B(2)\phi_C(3) - \phi_A(1)\phi_C(2)\phi_B(3) - \phi_A(2)\phi_B(1)\phi_C(3) + \phi_A(2)\phi_C(1)\phi_B(3) + \phi_A(3)\phi_B(1)\phi_C(2) - \phi_A(3)\phi_C(1)\phi_B(2)$$

a) Switch column **1** with column **2**

$$\psi_{(a)} = \begin{vmatrix} \phi_A(2) & \phi_A(1) & \phi_A(3) \\ \phi_B(2) & \phi_B(1) & \phi_B(3) \\ \phi_C(2) & \phi_C(1) & \phi_C(3) \end{vmatrix}$$

Now find the determinant

$$\phi_{(a)} = \phi_A(2) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} - \phi_A(1) \begin{vmatrix} \phi_B(2) & \phi_B(3) \\ \phi_C(2) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(2) & \phi_B(1) \\ \phi_C(2) & \phi_C(1) \end{vmatrix}$$

$$\phi_{(a)} = \phi_A(2)\phi_B(1)\phi_C(3) - \phi_A(2)\phi_C(1)\phi_B(3) - \phi_A(1)\phi_B(2)\phi_C(3) + \phi_A(1)\phi_C(2)\phi_B(3) + \phi_A(3)\phi_B(2)\phi_C(1) - \phi_A(3)\phi_C(2)\phi_B(1)$$

Comparing equation (5) with equation (6) we see that $\phi = -\phi_{(a)}$

b) Switch row **2** with row **3**

$$\phi_{(b)} = \begin{vmatrix} \phi_A(1) & \phi_A(2) & \phi_A(3) \\ \phi_C(1) & \phi_C(2) & \phi_C(3) \\ \phi_B(1) & \phi_B(2) & \phi_B(3) \end{vmatrix}.$$

Now find the determinant

$$\phi_{(b)} = \phi_A(1) \begin{vmatrix} \phi_C(2) & \phi_C(3) \\ \phi_B(2) & \phi_B(3) \end{vmatrix} - \phi_A(2) \begin{vmatrix} \phi_C(1) & \phi_C(3) \\ \phi_B(1) & \phi_B(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_C(1) & \phi_C(2) \\ \phi_B(1) & \phi_B(2) \end{vmatrix}$$

$$\phi_{(b)} = \phi_A(1)\phi_C(2)\phi_B(3) - \phi_A(1)\phi_B(2)\phi_C(3) - \phi_A(2)\phi_C(1)\phi_B(3) + \phi_A(2)\phi_B(1)\phi_C(3) + \phi_A(3)\phi_C(1)\phi_B(2) - \phi_A(3)\phi_B(1)\phi_C(2)$$

Comparing equation (5) with equation (7) we see that $\phi = -\phi_{(b)}$

c) Replace column **2** with column **1**

$$\phi_{(c)} = \begin{vmatrix} \phi_A(1) & \phi_A(1) & \phi_A(3) \\ \phi_B(1) & \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(1) & \phi_C(3) \end{vmatrix}$$

Now find the determinant

$$\phi_{(c)} = \phi_A(1) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} - \phi_A(1) \begin{vmatrix} \phi_B(1) & \phi_B(3) \\ \phi_C(1) & \phi_C(3) \end{vmatrix} + \phi_A(3) \begin{vmatrix} \phi_B(1) & \phi_B(1) \\ \phi_C(1) & \phi_C(1) \end{vmatrix}$$

The first two terms are identical but opposite so they cancel one another. The third has a determinant of zero.

$$\phi_{(c)} = 0 + \phi_A(3) \cdot (0) = 0$$

7.20

a. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for an oscillator that has a potential of

$$V(x) = (1/2)kx^2 + x^3 + x^4 + x^5?$$

b. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for a particle in a box that has a potential of $V(x) = 0$ between 0<x<L?

c. What is $\hat{H}^{(0)}$, $\hat{H}^{(1)}$, $\Psi^{(0)}$, and $E^{(0)}$ for a hydrogenlike atom that has a potential of

$$V(x) = \frac{-e^2}{4\pi\epsilon_o r} + \frac{1}{2}\epsilon r\cos\theta?$$

Solution

For an oscillator:

$$\hat{H} = \frac{-\hbar 2}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}kx^2 + x^3 + x^4 + x^6$$

$\hat{H}^{(0)}$ is the Hamiltonian for a simple harmonic oscillator, therefore

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}kx^2$$

$\hat{H}^{(1)}$ is what is added to the Hamiltonian for a simple harmonic oscillator. therefore

$$\hat{H}^{(1)} = x^3 + x^4 + x^5$$

$\Psi^{(0)}$ is the wave function for a simple harmonic oscillator, therefore

$$\Psi^{(0)} = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

$E^{(0)}$ is the energy for a simple harmonic oscillator, therefore

$$E^{(0)} = h\nu\left(v + \frac{1}{2}\right)$$

where v= 0,1, 2... ∞

Particle in a box

Using this as an example, we find that for a particle in a box with potential V(x) = 0 between 0<x<L

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$\hat{H}^{(0)} = -\frac{\hbar 2}{2m}\frac{\partial^2}{\partial x^2}$$

\[\hat{H}^{(1)} = 0\nonumber \]

$\Psi^{(0)}$ =B*sin(nπx/L)

$E^{(0)} = n^2h^2 / 8mL^2$ where n= 1, 2, 3 ... ∞

Hydrogen like Atom

For a hydrogen like atom that has a potential of

$$V(x) = -\frac{e^2}{4\pi\epsilon_o r} + (1/2)\epsilon r\cos\theta$$

\[\hat{H} = - ħ ^2/2μ ∂2 /∂x2 ∇^2 -e^2/(4πϵ_o r) + (1/2)ϵrcosθ\nonumber \]

\[\hat{H}^{(0)} = - ħ ^2/2μ ∂2 /∂x2 ∇^2 -e^2/(4πϵ_o r)\nonumber \]

\[\hat{H}^{(1)} =(1/2)ϵrcosθ\nonumber \]

$\Psi^{(0)} = \Psi_{n,l,m}(r,\theta,\phi)$

$E^{(0)} = \mu e^4 / 8\epsilon_o^2 h^2 n^2$

7.21

Using a harmonic oscillator as the unperturbed problem, calculate the first-order correction to the energy of the $v = 0$ level for the system described as

$$V(x) = \frac{k}{2}x^2 + \frac{m}{6}x^3 + \frac{b}{24}x^4$$

7.22

Using the first order perturbation theory for particle in a box, calculate the ground-state energy for the system

$$V(x) = ax^3 \qquad 0 < x < b$$

Solution

$$\psi_1 = \sqrt{\frac{2}{b}}\sin(\frac{\pi x}{b})$$

$$\widehat{H} = \widehat{H}^0 + \widehat{H}^1$$

$$\widehat{H}^1 = ax^3$$

$$E_1 = E_1^0 + E_1^1$$

$$E_1^0 = \frac{h^2}{8mb^2}$$

$$E_1^1 = \langle \psi^1 \left| \widehat{H}^1 \right| \psi^1 \rangle$$

$$= \int_0^b \frac{2a}{b}x^3 \sin^2(\frac{\pi x}{b})\mathrm{dx}$$

$$= \frac{2a}{b}\frac{(\pi^2 - 3)b^4}{8\pi^2}$$

$$= \frac{(\pi^2 - 3)ab^3}{4\pi^2}$$

$$E_1 = \frac{h^2}{8mb^2} + \frac{(\pi^2 - 3)ab^3}{4\pi^2}$$

7.23

In your chemistry lab you were able to manipulate an external electric field to have the strength κ. You're supervisor wants you to figure out what the first-order correction to the ground state energy of a hydrogen like atom of charge N in this electric field.

Solution

You should remember, or look up the ground state wavefunction for a hydrogen atom and find that

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{Z_\circ}\right)^{\frac{3}{2}} e^{-r/a_\circ}$$

Our change in energy equation has a familiar form

$$\Delta E = \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)} d\tau$$

For this problem you construct a Hamiltonian for a Hydrogen atom in an electron field with strength κ.

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ne^2}{4r\pi\kappa_\circ} + er\kappa\cos\theta$$

Luckily you have previously calculated $\hat{H}^{(1)}$ for this system in a previous experiment, simply allowing you to substitute your variables into your expressions to find that

$$\Delta E = \frac{Ne\kappa}{\pi}\left(\frac{1}{Z_\circ}\right)^3 \int_0^\infty r^3 e^{\frac{-r}{a_\circ}} dr \int_0^{2\pi} d\phi \int_0^\pi \sin\theta\cos\theta d\theta$$

Notice that the problem gets simplified by the fact that

$$\int_0^\pi \sin\theta\cos\theta d\theta = 0$$

So your answer is a trivial solution.

$$\boxed{\Delta E = 0}$$

7.25A

Use first-order perturbation theory to calculate ground-state energy of a harmonic oscillator with a cx^7 added to the end of the potential.

Solution

The Hamiltonian to the system can be formulated as

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^7$$

we then solve

$$E^1 = \langle\psi_0|cx^7|\psi_0\rangle$$

We know that the integral is of an odd function over a symmetric boundary is 0, so by symmetry we can conclude that the energy is 0.

7.25B

In order to calculate the first-order correction to the ground-state energy of the quartic oscillator, use first-order perturbation theory. The potential energy is $V(x) = cx^4$. For this potential use the harmonic oscillator as the unperturbed system. Solve for the perturbing potential as well.

Solution

The Hamiltonian operator is given below:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + cx^4$$

To use a harmonic oscillator as the reference system, add and subtract $\frac{1}{2}kx^2$ from $\hat{H}$.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d}{dx^2} + \frac{1}{2}kx^2 \; + cx^4 - \frac{1}{2}kx^2$$

Hence we get :

$$\hat{H}^{(0)} = cx^4 - \frac{1}{2}kx^2$$

Now we have:

$$\Delta E = \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}\, d\tau \ldots .$$

By putting the values in the equation above, we get:

$$\Delta E = \left(\frac{\alpha}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} dx e^{-x^2\alpha}\left(cx^4 - \frac{1}{2}kx^2\right)$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} 2\left[\frac{3c}{8\alpha^2}\left(\frac{\pi}{\alpha}\right)^{1/2} - \frac{k}{8\alpha}\left(\frac{\pi}{\alpha}\right)^{1/2}\right]$$

$$= \frac{3c}{4\alpha^2} - \frac{k}{4\alpha}$$

7.26

Solve the following integrals using this trial wavefunction

$$|\phi\rangle = c_1 x(a-x) + c_2 x^2(a-x)^2$$

For simplicity purposes, we can assume that a = 1.

$$H_{11} = \frac{\hbar^2}{6m} \; S = \frac{1}{30}$$
$$H_{12} = H_{22} = \frac{\hbar^2}{30m} \; S_{12} = S_{21} = \frac{1}{140}$$
$$H_{22} = \frac{\hbar^2}{105m} \; S_{22} = \frac{1}{630}$$

Solution

We know that for a particle in a box

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

We also know the two components of the trial function that was given are

$$\phi_1 = x(a-x)$$

and

$$\phi_2 = x^2(a-x)^2$$

Using this we will have

$$\hat{H}\phi_1 = \frac{\hbar^2}{2m}$$

and

$$\hat{H}\phi_2 = \frac{\hbar^2}{m}(a^2 - 6ax + 6x^2)$$

Using this we can solve for H_{ii} and S_{ij} using this integral

$$\int_0^1 x^m(1-x)^n dx = \frac{m!n!}{(m+n+1)!}$$

Letting $a = 1$, we can now solve for

$$H_{11} = \frac{\hbar^2}{m}$$

$$\int_0^1 x(1-x)dx = \frac{\hbar^2}{6m}$$

$$H_{12} = \frac{\hbar^2}{m}$$

$$\int_0^1 x(1-x)(1-6x+6x^2)dx = \frac{\hbar^2}{30m}$$

$$H_{21} = \frac{\hbar^2}{m}$$

$$\int_0^1 x^2(1-x)^2 dx = \frac{\hbar^2}{30m}$$

$$H_{22} = \frac{\hbar^2}{105m}$$

$$S_{11} = \int_0^1 x^2(1-x)^2 dx = \frac{4}{5!} = \frac{1}{30}$$

$$S_{12} = S_{21} = \int_0^1 x^3(1-x)^3 dx = \frac{36}{7!} = \frac{1}{140}$$

$$S_{22} = \int_0^1 x^4(1-x)^4 dx = \frac{576}{9!} = \frac{1}{630}$$

7.27

Use Perturbation Theory to add cubic and quartic perturbations to the SHO and find the first three SHO energy levels. Do this by expanding the Morse potential:

$$V(x) = D(1 - e^{-Bx})^2$$

into polynomials (i.e., a Taylor expansion). Show that the Hamiltonian can be written as

$$\frac{-h^2\nabla^2}{8\pi^2 m} + ax^2 + bx^3 + cx^4$$

Note which terms can be associated with H^0 and which are the H^1 perturbation. What are the relationships between a, b, c, and D, B? How do the new energy levels compare to the old ones?

Solution

The e^{-Bx} function can be expanded noting that

$$e^x \approx 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + ... + Ox^n$$

So e^{-Bx} will expand similarly, replacing x in the above expansion with -Bx, so

\[e^{-Bx] = 1 - Bx + B^2x^2/2 - B^3x^3/6 + ... + Ox^n\nonumber \]

The Morse Potential therefore is

$$D(1 - (1 - Bx + B^2\frac{x^2}{2} - B^3\frac{x^3}{6})^2$$

The expansion is shortened to 4 terms only.

$$= D(Bx - B^2x^2/2 + B^3x^3/6)^2$$

$$=D (B^6x^6/36 - B^5x^5/6 + 7B^4x^4/12 - B^3x^3 + B^2x^2)$$

$$= DB^6x^6/36 - DB^5x^5/6 + 7DB^4x^4/12 - DB^3x^3 + DB^2x^2$$

$$= 7DB^4x^4/12 - DB^3x^3 + DB^2x^2$$

(We have truncated above the quartic term)

Here, it is seen that DB^2x^2 corresponds to the H^0 potential, and $7DB^4x^4/12 - DB^3x^3$ is H^1

We can also see that $a = DB^2$, $b = - DB^3$, $c = 7DB^4/12$ in in the Hamiltonian potential: $ax^2 + bx^3 + cx^4$

Perturbation theory states that

$$E_n = E_n^0 + E_n^1 = E_n^0 + \int \Psi_n^0 H^1 \Psi_n^0 \, d\tau$$

Therefore, with $E^0_0 = hv/2$ and $\Psi^0_0 = (\alpha/\pi)^{1/4}e^{-\alpha(x^2)/2}$

$E^0_1 = 3hv/2$ and $\Psi^0_1 = (4\alpha^3/\pi)^{1/4}xe^{-\alpha(x^2)/2}$

$E^0_2 = 5\ hv/2$ and $\Psi^0_2 = (\alpha/4\pi)^{1/4}(2\alpha x^2 - 1)e^{-\alpha(x^2)/2}$

$H^1 = bx^2 + cx^2$

the first three energy levels are:

$E_0 = hv/2 + \int (\alpha/\pi)^{1/4}e^{-\alpha(x^2)/2}(bx^3 + cx^4)(\alpha/\pi)^{1/4}e^{-\alpha(x^2)/2}dx$

$= hv/2 + (\alpha/\pi)^{1/2} \int e^{-\alpha(x^2)}(bx^3 + cx^4)dx$

$= hv/2 + (\alpha/\pi)^{1/2} [\int e^{-\alpha(x^2)}bx^3dx + \int e^{-\alpha(x^2)}cx^4dx]$ (The cubic integral is odd so evaluates to 0)

$= hv/2 + (\alpha/\pi)^{1/2} \int e^{-\alpha(x^2)}cx^4dx$

We can use $\int x^{2n}e^{-\alpha x^2}dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= hv/2 + 2 * c(\alpha/\pi)^{1/2} * 3/(2^3\alpha^2) * (\pi/\alpha)^{1/2}$

$= hv/2 + 3c/(4\alpha^2)$

$E_1 = 3h\nu/2 + \int (4\alpha^3/\pi)^{1/4} x e^{-\alpha(x^2)/2} (\, bx^3 + cx^4)(4\alpha^3/\pi)^{1/4} x e^{-\alpha(x^2)/2} dx$

$= 3h\nu/2 + (4\alpha^3/\pi)^{1/2} \int x^2 e^{-\alpha(x^2)} (\, bx^3 + cx^4) dx$

$= 3h\nu/2 + (4\alpha^3/\pi)^{1/2} [\int x^2 e^{-\alpha(x^2)}\, bx^3 dx + \int x^2 e^{-\alpha(x^2)}\, cx^4 dx\ ]$ (First integral evaulates to 0)

$= 3h\nu/2 + c(4\alpha^3/\pi)^{1/2} \int x^6 e^{-\alpha(x^2)}\, dx$

We can use $\int x^{2n} e^{-\alpha x^2} dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= 3h\nu/2 + 2^* c(4\alpha^3/\pi)^{1/2} {}^* 15/(2^4\alpha^3) * (\pi/\alpha)^{1/2}$

$= 3h\nu/2 + 15c/(4\alpha^2)$

$E_{2o} = 5h\nu/2 + \int (\alpha/4\pi)^{1/4} (2\alpha x^2 - 1) e^{-\alpha(x^2)/2} (\, bx^3 + cx^4)\, (\alpha/4\pi)^{1/4} (2\alpha x^2 - 1) e^{-\alpha(x^2)/2} dx$

$= 5h\nu/2 + (\alpha/4\pi)^{1/2} \int (\, bx^3 + cx^4)(2\alpha x^2 - 1)^2 e^{-\alpha(x^2)} dx$

$= 5h\nu/2 + (\alpha/4\pi)^{1/2} [\int bx^3 (2\alpha x^2 - 1)^2 e^{-\alpha(x^2)} dx + \int cx^4 e^{-\alpha(x^2)} (2\alpha x^2 - 1)^2 dx$

$= 5h\nu/2 + (\alpha/4\pi)^{1/2} \int cx^4 e^{-\alpha(x^2)} (2\alpha x^2 - 1)^2 dx$ (First integral evaluates to 0)

$= 5h\nu/2 + (\alpha/4\pi)^{1/2} \int 4c\alpha^2 x^8 e^{-\alpha(x^2)} - 4\alpha c x^6 e^{-\alpha(x^2)} + cx^4 e^{-\alpha(x^2)} dx$

We can use $\int x^{2n} e^{-\alpha x^2} dx = n!/(2\alpha^{n+1})$ (This is true from 0 to infinity, so we must double it)

$= 5h\nu/2 + (\alpha/4\pi)^{1/2} [4c\alpha^2 {}^* 2 {}^* (105/(32\alpha^4)) {}^* (\pi/\alpha)^{1/2} - \alpha c {}^* 2 {}^* 15/(2^4\alpha^3) * (\pi/\alpha)^{1/2} + c {}^* 2 {}^* 3/(2^3\alpha^2) * (\pi/\alpha)^{1/2}]$

$= 5h\nu/2 + 39c/4\alpha^2$

It is evident that as the energy levels increase, the perturbation to the energy increases as well, making the Hooke potential increasingly bad as an approximation of intramolecular potential.

7.27

Use the perturbation theory to calculate the first - order corrections to the ground state energy of

a. A harmonic oscillator that arises from a cubic and quartic term.
b. A quartic oscillator that arises from only using a quartic term cx^4

and compare the results.

Solution

A) The Hamiltonian for this problem is

$$\hat{H} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2 + bx^3 + cx^4$$

We use the harmonic oscillator Hamiltonian for $\hat{H}^{(0)}$

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2$$

$$\hat{H}^{(1)} = bx^3 + cx^4$$

$$\psi^{(0)} = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

$$E^{(0)} = h\mu(v + \frac{1}{2})$$

$$E_0 = E_0^{(0)} + \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}\, d\tau$$

$$E_0 = \frac{\hbar\mu}{2} + b(\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx x^3 e^{-x^2\alpha} + c(\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx x^4 e^{-x^2\alpha}$$

$$E_0 = \frac{\hbar\mu}{2} + 0 + 2c\frac{\alpha}{\pi}^{1/2}\int_{0}^{\infty} dx x^4 e^{-x^2\alpha}$$

$$E_0 = \frac{\hbar\mu}{2} + \frac{3c}{4\alpha^2}$$

B) The Hamiltonian for this problem is

$$\hat{H} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + cx^4$$

We use the harmonic oscillator Hamiltonian for $\hat{H}^{(0)}$

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + ax^2$$

$$\hat{H}^{(1)} = cx^4 - \frac{kx^2}{2}$$

$$E = \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}\, d\tau$$

$$E = (\frac{\alpha}{\pi})^{1/2}\int_{-\infty}^{\infty} dx e^{-x^2\alpha}(cx^4 - \frac{kx^2}{2})$$

$$E = (\frac{\alpha}{\pi})^{1/2}2(\frac{3c}{8\alpha^2}(\frac{\alpha}{\pi})^{1/2} - \frac{k}{8\alpha}(\frac{\alpha}{\pi})^{1/2})$$

$$E = \frac{3c}{4\alpha^2} + \frac{k}{4\alpha}$$

7.E: Approximation Methods (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

8: Multielectron Atoms

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

Electrons with more than one atom, such as Helium (He), and Nitrogen (N), are referred to as multi-electron atoms. Hydrogen is the only atom in the periodic table that has one electron in the orbitals under ground state. We will learn how additional electrons behave and affect a certain atom.

8.1: Atomic and Molecular Calculations are Expressed in Atomic Units
8.2: Perturbation Theory and the Variational Method for Helium
8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method
8.4: An Electron Has an Intrinsic Spin Angular Momentum
8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants
8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data
8.8: Term Symbols Gives a Detailed Description of an Electron Configuration
8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number
8.E: Multielectron Atoms (Exercises)
8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States
8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

8: Multielectron Atoms is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.1: Atomic and Molecular Calculations are Expressed in Atomic Units

Atomic units (au or a.u.) form a system of natural units which is especially convenient for atomic physics calculations. Atomic units, like SI units, have a unit of mass, a unit of length, and so on. However, the use and notation is somewhat different from SI. Suppose a particle with a mass of m has 3.4 times the mass of electron. The value of mass m can be written in three ways:

- $m = 3.4\ m_e$: This is the clearest notation (but least common), where the atomic unit is included explicitly as a symbol.
- $m = 3.4\ a.u.$: This notation is ambiguous, but is common. Here, it means that the mass m is 3.4 times the atomic unit of mass. If considering a length L of 3.4 times the atomic unit of length, the equation would look the same, $L = 3.4\ a.u.$ The dimension needs to be inferred from context, which is sloppy.
- $m = 3.4$: This notation is similar to the previous one, and has the same dimensional ambiguity. It comes from formally setting the atomic units to 1 (Table 8.1.1).

This article deals with "Hartree type" of atomic units, where the numerical values of the following four fundamental physical constants are all unity by definition:

Table 8.1.1: Fundamental atomic units

Dimension	Name	Symbol/Definition	Value in SI units	Value in Atomic Units
mass	electron rest mass	m_e	9.109×10^{-31} kg	1
charge	elementary charge	e	1.602×10^{-19} C	1
action	reduced Planck's constant	$\hbar = \frac{h}{2\pi}$	1.054×10^{-34} J·s	1
electric constant^{-1}	Coulomb force constant	$k_e = \frac{1}{4\pi\epsilon_o}$	8.987 x 10^9 kg·m^3·s^{-2}·C^{-2}	1

Example 8.1.1: Simplifying the Hamiltonian

Use the atomic units definitions in Table 8.1.1 to contrast the Hamiltonian for a Helium atom in Si units and in atomic units.

Solution

In SI units, the Hamiltonian for a Helium atom is

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

In atomic units, the same Hamiltonian

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

All the units that make the SI version of the Hamiltonian disappear to emphasize the key aspects of the operator.

Atomic units are derived from certain fundamental properties of the physical world, and are free of anthropocentric considerations. It should be kept in mind that atomic unites were designed for atomic-scale calculations in the present-day universe, with units normalize the reduced Planck constant and also mass and charge of the electron are set to 1, and, as a result, the speed of light in atomic units is a large value, $1/\alpha \approx 137$. For example, the orbital velocity of an electron around a small atom is of the order of 1 in atomic units. Table 8.1.2 give a few derived units. Some of them have proper names and symbols assigned, as indicated in the table.

Table 8.1.2: Derived atomic units

Dimension	Name	Symbol	Expression	Value in SI units
length	bohr	a_o	$4\pi\epsilon_0\hbar^2/(m_e e^2) = \hbar/(m_e c\alpha)$	$0.529\,177\,210\,67(12) \times 10^{-10}$ m
energy	hartree	E_h	$m_e e^4/(4\pi\epsilon_0\hbar)^2 = \alpha^2 m_e c^2$	$4.359\,744\,722\,2071(85) \times 10^{-18}$ J

			$\mathrm{mol^{-1}}$
time		$\hbar/E_\mathrm{h}$	$2.418 \times 10^{-17}\ \mathrm{s}$
velocity		$a_0 E_\mathrm{h}/\hbar = \alpha c$	$2.187 \times 10^{6}\ \mathrm{m\,s^{-1}}$

Contributors

- Wikipedia

8.1: Atomic and Molecular Calculations are Expressed in Atomic Units is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.2: Perturbation Theory and the Variational Method for Helium

Both perturbation theory and variation method (especially the linear variational method) provide good results in approximating the energy and wavefunctions of multi-electron atoms. Below we address both approximations with respect to the helium atom.

Perturbation Theory of the Helium Atom

We use perturbation theory to approach the analytically unsolvable helium atom Schrödinger equation by focusing on the Coulomb repulsion term that makes it different from the simplified Schrödinger equation that we have just solved analytically. The electron-electron repulsion term is conceptualized as a correction, or perturbation, to the Hamiltonian that can be solved exactly, which is called a zero-order Hamiltonian. The perturbation term corrects the previous Hamiltonian to make it fit the new problem. In this way the Hamiltonian is built as a sum of terms, and each term is given a name. For example, we call the simplified or starting Hamiltonian, $\hat{H}^0$, the zero order term, and the correction term $\hat{H}^1$.

$$\hat{H} = \hat{H}^0 + \hat{H}^1 \tag{8.2.1}$$

The Hamilonian for the helium atom (in atomic units) is:

$$\hat{H}^0 = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}}_{\text{H atom Hamiltonian}} - \underbrace{\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}}_{\text{H atom Hamiltonian}} \tag{8.2.2}$$

$$\hat{H}^1 = \frac{1}{r_{12}} = \frac{1}{|r_1 - r_2|} \tag{8.2.3}$$

The expression for the first-order correction to the energy is

$$\begin{aligned} E^1 &= \langle \psi^0 | \hat{H}^1 | \psi^0 \rangle \\ &= \int \psi^{0*} \hat{H}^1 \psi^0 \, d\tau \end{aligned}$$

Equation ??? is a general expression for the first-order perturbation energy, which provides an improvement or correction to the zero-order energy we already obtained. Hence, E^1 is the average interaction energy of the two electrons calculated using wavefunctions that assume there is no interaction.

The solution to $\hat{H}^0$ (Equation 8.2.2) is the product of two single-electron hydrogen wavefunctions (scaled by the increased nuclear charge) since $\hat{H}^0$ can be separated into independent functions of each electron (i.e., Separation of Variables).

$$|\psi^0\rangle = |\varphi_{1s}(r_1)\varphi_{1s}(r_2)\rangle \tag{8.2.4}$$

So the integral in Equation ??? is

$$E^1 = \iint \varphi_{1s}(r_1)\varphi_{1s}(r_2)\frac{1}{r_{12}}\varphi_{1s}(r_1)\varphi_{1s}(r_2)\, d\tau_1 d\tau_2 \tag{8.2.5}$$

where the double integration symbol represents integration over all the spherical polar coordinates of both electrons $r_1, \theta_1, \varphi_1, r_2, \theta_2, \varphi_2$. The evaluation of these six integrals is lengthy. When the integrals are done, the result is E^1 = +34.0 eV so that the total energy calculated using our second approximation method, first-order perturbation theory, is

$$E_{approx2} = E^0 + E^1 = -74.8eV \tag{8.2.6}$$

The new approximate value for the binding energy represents a substantial (~30%) improvement over the zero-order energy:

$$E^0 = \frac{2}{n^2} + \frac{2}{n^2} = 4 \underbrace{E_h}_{hartrees} = 108.8\, eV \tag{8.2.7}$$

so the interaction of the two electrons is an important part of the total energy of the helium atom. We can continue with perturbation theory and find the additional corrections, E^2, E^3, etc. For example,

$$E^0 + E^1 + E^2 = -79.2\, eV. \tag{8.2.8}$$

So with two corrections to the energy, the calculated result is within 0.3% of the experimental value of -79.01 eV. It takes thirteenth-order perturbation theory (adding E^1 through E^{13} to E^0) to compute an energy for helium that agrees with experiment to within the experimental uncertainty. Interestingly, while we have improved the calculated energy so that it is much closer to the experimental value, we learn nothing new about the helium atom wavefunction by applying the first-order perturbation theory to the energy above. He need to expand the wavefunctions to first order perturbation theory, which requires more effort. Below, we will employ the variational method approximation to modify zero-order wavefunctions to address one of the ways that electrons are expected to interact with each other.

The hartree unit of energy

The hartree is the atomic unit of energy (named after the British physicist Douglas Hartree) and is defined as

$$E_h = 2R_H hc$$

where R_H is the Rydberg constant, h is the Planck constant and c is the speed of light.

$$\begin{aligned} E_h &= 4.359 \times 10^{-18}\, J \\ &= 27.21\, eV. \end{aligned}$$

The hartree is usually used as a unit of energy in atomic physics and computational chemistry. As discussed before for hydrogen emission, IR, and microwave spectroscopies, experimental measurements prefer the electronvolt (eV) or the wavenumber (cm^{-1}).

Variational Method Applied to the Helium Method

As discussed in Section 6.7, because of the electron-electron interactions, the Schrödinger's Equation cannot be solved exactly for the helium atom or more complicated atomic or ionic species. However, the ground-state energy of the helium atom can be estimated using approximate methods. One of these is the variational method which requires the minimizing of the following variational integral.

$$E_{trial} = \frac{\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \tag{8.2.9}$$

$$= \frac{\int_0^\infty \psi^*_{trial} \hat{H} \psi_{trial} d\tau}{\int_0^\infty \psi^2_{trial}\, d\tau} \tag{8.2.10}$$

The five trial wavefunctions discussions below are equally "valid" trial wavefunctions that describe the probability of finding each electron (technically the wavefunction squared). What separates the "poor" approximations from the "good" approximation is whether the trial wavefunction predicts experimental results. Consequently, for all the approximations used for the rest of this TextMap, it is important to compare the theoretical results to the "true" (i.e., experimental) results. No matter how complicated an approximation is, it is only as good as the accuracy of its predicted values to experimental values.

Trial Wavefunction #1: Simple Orbital Approximation with One Parameter

As is clear from Equation 8.2.9, the variational method approximation requires that a trial wavefunction with one or more adjustable parameters be chosen. A logical first choice for such a multi-electron wavefunction would be to assume that the electrons in the helium atom occupy two identical, but scaled, hydrogen 1s orbitals.

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{8.2.11}$$

$$= \exp\left[-\alpha(r_1 + r_2)\right] \tag{8.2.12}$$

The variational energy obtained after minimizing Equation 8.2.10 after substituting the trial wavefunction (Equation 8.2.12) by varying α is

$$E_{trial} = -2.84766\ E_h \tag{8.2.13}$$

and the experimentally determined ground-state energy for the helium atom is the sum of first and second ionization energies

$$E_{exp} = I_1 + I_2 = -2.90372\ E_h \tag{8.2.14}$$

The deviation of energy for the optimized trial wavefunction from the experimental value is

$$\left|\frac{E_{trial}(\alpha) - E_{exp}}{E_{exp}}\right| = \left|\frac{-2.84766\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.15}$$

$$= 1.93\% \tag{8.2.16}$$

The value of -2.8477 hartrees is within 2% of the known ground-state energy of the helium atom. The error in the calculation is attributed to the fact that the wavefunction is based on the orbital approximation and, therefore, does not adequately take electron-electron interactions into account. In other words, this wavefunction gives the electrons too much independence, given that they have like charges and tend to avoid one another.

Trial Wavefunction #2: Orbital Approximation with Two Parameters

Some electron-electron interactions can be built into the multi-electron wavefunction by assuming that each electron is in an orbital which is a linear combination of two different and scaled hydrogen 1s orbitals.

$$\phi(r_1) = \exp(-\alpha r_1) + \exp(-\beta r_1) \tag{8.2.17}$$

Under the orbital approximation this assumption gives a trial wavefunction of the form

$$|\psi(1,2)\rangle_{trial} = \phi(1)\phi(2) \tag{8.2.18}$$

$$\begin{aligned} &= \exp(-\alpha r_1)\exp(-\alpha r_2) + \exp(-\alpha r_1)\exp(-\beta r_2) \\ &\quad + \exp(-\beta r_1)\exp(-\alpha r_2) + \exp(-\beta r_1)\exp(-\beta r_2) \end{aligned} \tag{8.2.19}$$

Inspection of this trial wavefunction indicates that 50% of the time the electrons are in different orbitals, while for the first trial wavefunction the electrons were in the same orbital 100% of the time. Notice the enormous increase in the complexity of the variational expression for the energy for this trial wavefunction (Equation 8.2.10). However, the calculation is very similar to that using the previous trial wavefunction. The differences are that in this case the expression for the energy is more complex and that it is being minimized simultaneously with respect to two parameters (α and β) rather than just one (α).

The variational energy obtained after minimizing Equation 8.2.10 after substituting the trial wavefunction (Equation 8.2.19) by varying α and β is

$$E_{trial} = -2.86035\ E_h \tag{8.2.20}$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.14) is

$$\left|\frac{E_{trial}(\alpha,\beta) - E_{exp}}{E_{exp}}\right| = \left|\frac{-2.86035\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.21}$$

$$= 1.49\% \tag{8.2.22}$$

Clearly introducing some electron-electron interactions into the trial wavefunction has improved the agreement between theory and experiment (Equation 8.2.16 vs. 8.2.22).

Trial Wavefunction #3: Orbital Approximation with Two Parameters

The extent of electron-electron interactions can be increased further by eliminating the first and last term in the second trial wavefunction (Equation 8.2.19). This yields a multi-electron wavefunction of the form,

$$|\psi(1,2)\rangle_{trial} = \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) \tag{8.2.23}$$

This trial wavefunction places the electrons in different scaled hydrogen 1s orbitals 100% of the time this adds further improvement in the agreement with the literature value of the ground-state energy is obtained. The variational energy obtained after minimizing Equation 8.2.10 after substituting the trial wavefunction (Equation 8.2.23) by varying α and β is

$$E_{trial} = -2.87566\ E_h \tag{8.2.24}$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.14) is

$$\left|\frac{E_{trial}(\alpha,\beta)-E_{\exp}}{E_{\exp}}\right| = \left|\frac{-2.87566\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.25}$$

$$= 0.97\% \tag{8.2.26}$$

This result is within 1% of the actual ground-state energy of the helium atom.

Trial Wavefunction #4: Approximation with Two Parameters

The third trial wavefunction, however, still rests on the orbital approximation and, therefore, does not treat electron-electron interactions adequately. Hylleraas took the calculation a step further by introducing electron-electron interactions directly into the first trial wavefunction by adding a term, r_{12}, involving the inter-electron separation.

$$|\psi_{trial}(1,2)\rangle = (\exp[-\alpha(r_1+r_2)])\,(1+\beta r_{12}) \tag{8.2.27}$$

In the trial multi-electron wavefunction of Equation 8.2.27, if the electrons are far apart, then r_{12} is large and the magnitude of the wave function increases to favor that configuration. The variational energy obtained after minimizing Equation 8.2.10 after substituting the trial wavefunction (Equation 8.2.27) by varying α and β is

$$E_{trial} = -2.89112\ E_h \tag{8.2.28}$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.14) is

$$\left|\frac{E_{trial}(\alpha,\beta)-E_{\exp}}{E_{\exp}}\right| = \left|\frac{-2.89112\ E_h + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.29}$$

$$= 0.43\% \tag{8.2.30}$$

This modification of the trial wavefunction has further improved the agreement between theory and experiment to within 0.5%.

Fifth Trial Wavefunction #5: Approximation with Three Parameters

Chandrasakar brought about further improvement by adding Hylleraas's r_{12} term to the third trial wave function (Equation 8.2.23) as shown here.

$$|\psi(1,2)\rangle_{trial} = [\exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2)]\,[1+\gamma r_{12}] \tag{8.2.31}$$

Chandrasakar's three parameter wavefunction gives rise to a fairly complicated variational expression for ground-state energy. The variational energy obtained after minimizing Equation 8.2.10 after substituting the trial wavefunction (Equation 8.2.31) by varying α, β and γ is

$$E_{trial} = -2.90143\ E_h \tag{8.2.32}$$

The deviation of energy for the optimized trial wavefunction from the experimental value (Equation 8.2.14) is

$$\left|\frac{E_{trial}(\alpha,\beta,\gamma)-E_{\exp}}{E_{\exp}}\right| = \left|\frac{-2.90143 + 2.90372\ E_h}{-2.90372\ E_h}\right| \tag{8.2.33}$$

$$= 0.0789\% \tag{8.2.34}$$

Chandrasakar's wavefunction gives a result for helium that is within 0.07% of the experimental value for the ground-state energy.

Summary

The purpose of this Module is to examine five trial wavefunctions for the helium atom used within the Perturbation Theory and Variational method approximation. For the Variational method approximation, the calculations begin with an uncorrelated wavefunction in which both electrons are placed in a hydrogenic orbital with scale factor α. The next four trial functions use several methods to increase the amount of electron-electron interactions in the wave function. As the summary of results that is appended shows this gives increasingly more favorable agreement with the experimentally determined value for the ground-state energy of the species under study. The detailed calculations show that the reason for this improved agreement with experiment is due to a reduction in electron-electron repulsion.

Five variational method calculations that have been outlined above for the helium atom ($Z = 2$) can be repeated for two-electron atoms (e.g., H^-, Li^+, Be^{2+}, etc). The hydride anion is a particularly interesting case because the first two trial wavefunctions do not

predict a stable ion (i.e., they are poor approximations). This indicates that electron-electron interactions is an especially important issue for atoms and ions with small nuclear charge.

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Prof. Emeritus Frank Rioux (St. John's University and College of St. Benedict)

8.2: Perturbation Theory and the Variational Method for Helium is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method

The Hartree method is used to approximate the wavefunction and the energy of a quantum multi-electron system in a stationary state. This approximation assumes that the exact N-body wavefunction of the system can be approximated by a product of single-electron wavefucntions. By invoking the variational method, one can derive a set of N-coupled equations for the N spin orbitals. A solution of these equations yields the Hartree wavefunction and energy of the system. It is one step better than the "Ignorance is Bliss" approach, discussed previously, but still far from a good approximation.

The Unsolvable System

The generic multielectron atom including terms for the additional electrons with a general charge Z; e.g.

$$V_{\text{nuclear-electron}}(r_1) = -\frac{Z}{|\mathbf{r}-\mathbf{R}|} \tag{8.3.1}$$

in atomic units with $|\mathbf{r}-\mathbf{R}|$ is the distance between the electron and the nucleus, The Hamiltonian must also have terms for electron-electron repulsion (also in atomic units)

$$V_{\text{electron-electron}}(r_{12}) = \frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{8.3.2}$$

with $|\mathbf{r}-\mathbf{r}'|$ is the distance between electron 1 and electron 2. So the proper multi-electron Hamiltonian can be constructed

$$\hat{H}(r_1, r_2, ...r_n) = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V_{\text{nuclear-electron}}(r_i) + \sum_{i\neq j} V_{\text{electron-electron}}(r_{ij}) \tag{8.3.3}$$

Given what we have learned from the previous quantum mechanical systems we've studied, we predict that exact solutions to the multi-electron Schrödinger equation would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue. These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.

The fact that electrons interact through their electron-electron repulsion (final term in Equation 8.3.3) means that an exact wavefunction for a multi-electron system would be a single function that depends **simultaneously** upon the coordinates of all the electrons; i.e., a multi-electron wavefunction:

$$|\psi(r_1, r_2, \cdots r_i)\rangle \tag{8.3.4}$$

Unfortunately, the electron-electron repulsion terms make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms.

The Hartree Approximation

The method for finding best possible one-electron wavefunctions that was published by Douglas Hartree in 1948 and improved two years later by Vladimir Fock. For the Schrödinger equation to be analytically solvable, the variables must be separable - the variables are the coordinates of the electrons. To separate the variables in a way that retains information about electron-electron interactions, the electron-electron term (Equation 8.3.1) must be approximated so it depends only on the coordinates of one electron. Such an approximate Hamiltonian can account for the interaction of the electrons in **an average way**. The exact one-electron eigenfunctions of this approximate Hamiltonian then can be found by solving the Schrödinger equation. These functions are the best possible **one-electron functions**.

The Hartree approximation starts by invoking an initial *ansatz* that the multi-electron wavefunction in Equation 8.3.4 can be expanded as a product of single-electron wavefunctions (i.e., orbitals)

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)\rangle \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_N(\mathbf{r}_N) \tag{8.3.5}$$

from which it follows that the electrons are *independent*, and interact only via the mean-field Coulomb potential. This yields one-electron Schrödinger equations of the form

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \tag{8.3.6}$$

or

$$H_e(r)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \tag{8.3.7}$$

where $V(r)$ is the potential in which the electron moves; this includes both the nuclear-electron interaction

$$V_{nucleus}(\mathbf{r}) = -Ze^2\sum_R \frac{1}{|\mathbf{r}-\mathbf{R}|} \tag{8.3.8}$$

and the mean field arising from the $N-1$ other electrons. We smear the other electrons out into a smooth negative charge density $\rho(\mathbf{r}')$ leading to a potential of the form

$$V_{electron}(\mathbf{r}) = -e\int d\mathbf{r}'\rho(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{8.3.9}$$

where

$$\rho(\mathbf{r}) = \sum_i^{\text{occupied}} |\psi(\mathbf{r})|^2. \tag{8.3.10}$$

The sum over runs over all occupied states; i.e., only the states of electrons that exist in the atom. The wavefunctions that from this approach with the Hamiltonian $H_e(r)$ involve possess three kinds of energies discussed below.

Three Energies within the Hartree Approximation

- **Kinetic Energy:** The Kinetic energy of the electron has an average value is computed by taking the expectation value of the kinetic energy operator

  $$\frac{-\hbar^2}{2m}\nabla^2 \tag{8.3.11}$$

  with respect to any particular solution $\phi_j(r)$ to the Schrödinger equation:

  $$KE = \langle\phi_j|\frac{-\hbar^2}{2m}\nabla^2|\phi_j\rangle \tag{8.3.12}$$

- **Nuclear-Electron Coulombic Attraction Energy:** Coulombic attraction energy with the nucleus of charge Z:

  $$\langle\phi_j|\frac{-Ze^2}{|\mathbf{r}-\mathbf{R}|}|\phi_j\rangle \tag{8.3.13}$$

- **Electron-Electron Coulombic Repulsion Energy:** Coulomb repulsion energies with all of the $N-1$ other electrons, which are assumed to occupy other atomic orbitals denoted ϕ_K, with this energy computed as

  $$\sum_{j\neq k}\langle\phi_j(r)\phi_k(r')|\frac{e^2}{|r-r'|}|\phi_j(r)\phi_k(r')\rangle. \tag{8.3.14}$$

  The Dirac notation $\langle\phi_j(r)\phi_k(r')|\frac{e^2}{|r-r'|}|\phi_j(r)\phi_k(r')\rangle$ is used to represent the two-electron (six-dimensional) Coulomb integral

  $$J_{j,k} = \int |\phi_j(r)|^2|\phi_k(r')|^2\frac{e^2}{r-r'}drdr' \tag{8.3.15}$$

  that describes the Coulomb repulsion between the charge density $|\phi_j(r)|^2$ for the electron in ϕ_j and the charge density $|\phi_k(r')|^2$ for the electron in ϕ_k. Of course, the sum over k must be limited to exclude $k=j$ to avoid counting a "self-interaction" of the electron in orbital ϕ_j with itself.

The total energy ϵ_j of the orbital ϕ_j, is the sum of the above three contributions:

$$\epsilon_J = \langle\phi_j|\frac{-\hbar^2}{2m}\nabla^2|\phi_j\rangle + \langle\phi_j|\frac{-Ze^2}{|\mathbf{r}-\mathbf{R}|}|\phi_j\rangle + \sum_{j\neq k}\langle\phi_j(r)\phi_k(r')|\frac{e^2}{|r-r'|}|\phi_j(r)\phi_k(r')\rangle. \tag{8.3.16}$$

This treatment of the electrons and their orbitals is referred to as the Hartree-level of theory.

When screened hydrogenic atomic orbitals are used to approximate the ϕ_j and ϕ_K orbitals, the resultant ϵ_J values do **not** produce accurate predictions. For example, the negative of ϵ_J should approximate the ionization energy for removal of an electron from the orbitals ϕ_j. Such ionization potentials (IP s) can be measured, and the measured values do not agree well with the theoretical values when a crude screening approximation is made for the atomic orbitals.

The Self-Consistant Field (SCF) Approach to the Variational Method

The Hartree Equations are nonlinear and must be solved iteratively. This is because if particles interact, that interaction must be in the Hamiltonian. So until we know where the particles are, we cannot write down the Hamiltonian, but until we know the Hamiltonian, we cannot tell where the particles are.

The idea is to solve the Schrödinger equation for an electron moving in the potential of the nucleus and all the other electrons. We start with a guess for the trial electron charge density, solve N/2 one-particle Schrödinger equations (initially identical) to obtain N electron wavefunctions. Then we construct the potential for each wavefunction from that of the nucleus and that of all the other electrons, symmetrize it, and solve the N/2 Schrödinger equations again. This method is ideal for a computer, because it is easily written as an algorithm Figure **8.3.1**.

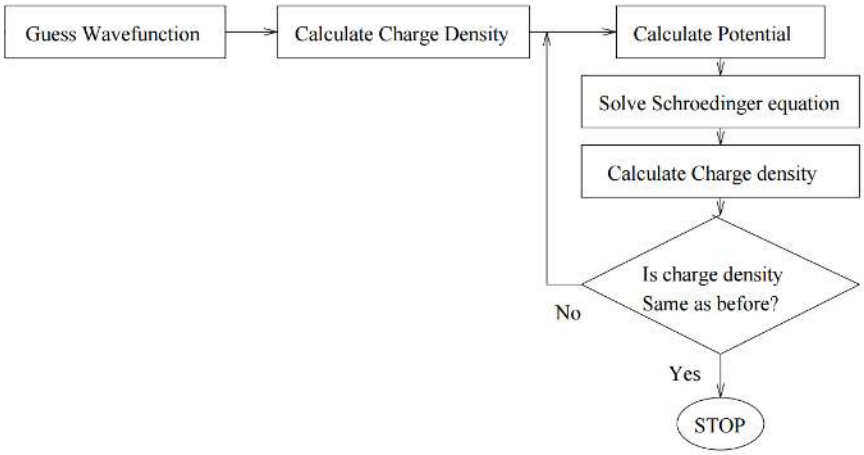


Figure **8.3.1**: Algorithm for Self-consistent field theory.

Although we are concerned here with atoms, the same methodology is used for molecules or even solids (with appropriate potential symmetries and boundary conditions). This is a variational method, so wherever we refer to wavefunctions, we assume that they are expanded in some appropriate basis set.

> *Fock improved on Hartree's method by using proper "antisymmetrized wavefunctions" (called the Hartree-Fock method) instead of simple one-electron wavefunctions.*

Shielding and Effective Charges from the HF method are Good, but not Good Enough

For an atom, one can approximate the orbitals by using the solutions of the hydrogenic Schrödinger equation. These orbitals are labeled by n, l, and m quantum numbers for the bound states and by l and m quantum numbers and the energy E for the continuum states. These hydrogen-like orbitals provide qualitative descriptions of orbitals of atoms with more than a single electron. By introducing the concept of screening as a way to represent the repulsive interactions among the electrons of an atom, an effective nuclear charge Z_{eff} can be used in place of Z in the hydrogenic $\psi_{n,l,m}$ and $E_{n,l}$ formulas to generate approximate atomic orbitals to be filled by electrons in a many-electron atom. For example, in the crudest approximation of a carbon atom, the two $1s$ electrons experience the full nuclear attraction so $Z_{\text{eff}} = 6$ for them, whereas the $2s$ and $2p$ electrons are screened by the two $1s$ electrons, so $Z_{\text{eff}} = 4$ for them. Within this approximation, one then occupies two $1s$ orbitals with $Z = 6$, two $2s$ orbitals with $Z = 4$ and two $2p$ orbitals with $Z = 4$ in forming the full six-electron product wavefunction of the lowest-energy state of carbon

$$|\psi(1,2,\ldots,6)\rangle = |\psi_{1s}(1)\psi_{1s}(2)\psi_{2s}(3)\ldots\psi_{1p}(6)\rangle. \tag{8.3.17}$$

However, such approximate orbitals are not sufficiently accurate to be of use in quantitative simulations of atomic and molecular structure. In particular, their energies do not properly follow the trends in atomic orbital (AO) energies that are taught in introductory chemistry classes (Figure 8.3.2).

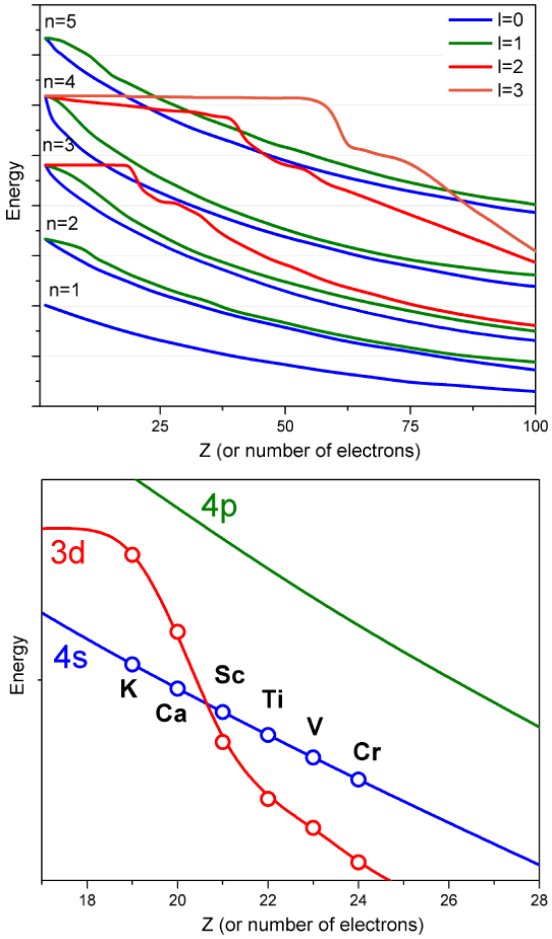


Figure 8.3.2: Energies of Atomic Orbitals as Functions of the number of electrons in Neutral Atoms. Image used with permission (CC BY; Delmar Larsen).

For example, the relative energies of the $3d$ and $4s$ orbitals are not adequately described in a model that treats electron repulsion effects in terms of a simple screening factor. So, now it is time to examine how we can move beyond the screening model and take the electron repulsion effects, which cause the inter-electronic couplings that render the Schrödinger equation insolvable, into account in a more reliable manner.

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Jack Simons (Henry Eyring Scientist and Professor of Chemistry, U. Utah) Telluride Schools on Theoretical Chemistry
- Graeme Ackland (University of Edinburgh)

8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.4: An Electron Has an Intrinsic Spin Angular Momentum

Imagine doing a hypothetical experiment that would lead to the discovery of electron spin. Your laboratory has just purchased a microwave spectrometer with variable magnetic field capacity. We try the new instrument with hydrogen atoms using a magnetic field of 10^4 Gauss and look for the absorption of microwave radiation as we scan the frequency of our microwave generator (Figure 8.4.1).

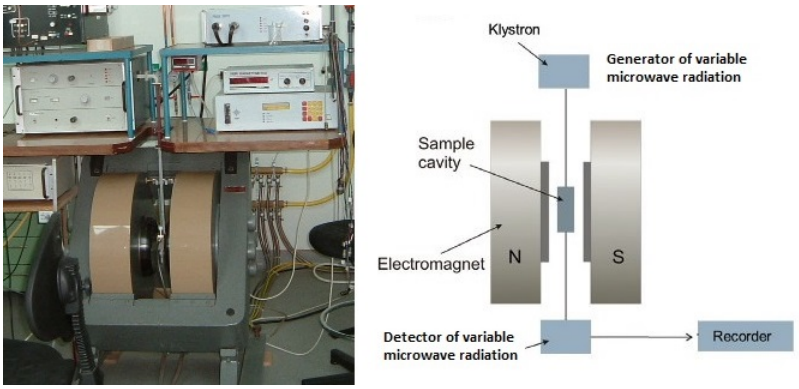


Figure 8.4.1: Schematic diagram of a microwave spectrometer transmission Electron Spin Resonance (ESR) spectrometer with the sample in a magnetic field. (left) ESR spectrometer Faculty of Biochemistry, Biophysics and Biotechnology Jagiellonian University. (right) Schematic of the ESR instrument. The strength of the magnetic field is set, and the sample's absorption of microwave photons is measured for a range of microwave photon energies (or frequencies). (CC BY 3.0)

Finally we see absorption at a microwave photon frequency of $28 \times 10^9\ Hz$ (28 gigahertz). This result is really surprising from several perspectives. Each hydrogen atom is in its ground state, with the electron in a 1s orbital. The lowest energy electronic transition that we predict based on existing theory (the electronic transition from the ground state (ψ_{100} to ψ_{21m}) requires an energy that lies in the vacuum ultraviolet (the lower Lyman line at 121 nm), not the microwave, region of the spectrum. Furthermore, when we vary the magnetic field we note that the frequency at which the absorption occurs varies in proportion to the magnetic field.

The Zeeman Effect: Breaking Degeneracy

Magnetism results from the circular motion of charged particles. This property is demonstrated on a macroscopic scale by making an electromagnet from a coil of wire and a battery. Electrons moving through the coil produce a magnetic field, which can be thought of as originating from a magnetic dipole or a bar magnet. Electrons in atoms also are moving charges with angular momentum so they too produce a magnetic dipole, which is why some materials are magnetic. A *magnetic dipole* interacts with a magnetic field, and the energy of this interaction is given by the scalar product of the magnetic dipole moment, and the magnetic field, $\vec{B}$.

$$E_B = -\vec{\mu}_m \cdot \vec{B} \tag{8.4.1}$$

Pieter Zeeman was one of the first to observe the splittings of spectral lines in a magnetic field caused by this interaction. Consequently such splittings are known as the Zeeman effect. (Figure 8.4.2). The m_l quantum number degeneracy of the hydrogen atom is removed by the externally applied magnetic field. For example, the three hydrogen atom eigenstates $|\psi_{211}\rangle$, $|\psi_{21-1}\rangle$, and $|\psi_{210}\rangle$ are degenerate in zero magnetic field, but have different energies in an externally applied magnetic field (Figure 8.4.2).

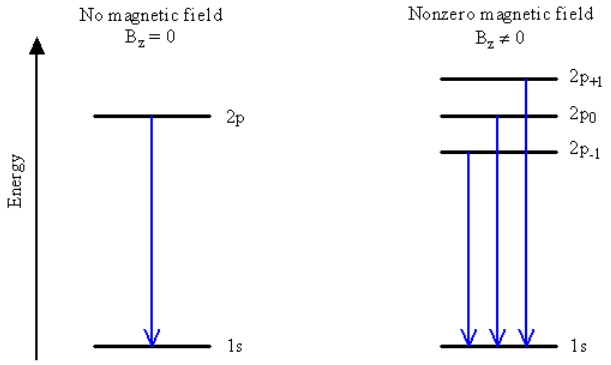


Figure **8.4.2**: The Zeeman effect for the $2s \rightarrow 1s$ transition. Emission when an electron switches from a 2p orbital to a 1s orbital occurs at only one energy in the absence of a magnetic field, but can occur at three different energies in the presence of a magnetic field.

The $m_l = 0$ state, for which the component of angular momentum and hence also the magnetic moment in the external field direction is zero, experiences no interaction with the magnetic field. The $m_l = +1$ state, for which the angular momentum in the z-direction is +ħ and the magnetic moment is in the opposite direction, against the field, experiences a raising of energy in the presence of a field. Maintaining the magnetic dipole against the external field direction is like holding a small bar magnet with its poles aligned exactly opposite to the poles of a large magnet. It is a higher energy situation than when the magnetic moments are aligned with each other.

Electron Spin and the Stern-Gerlach Experiment

To discover new things, experimentalists sometimes must explore new areas in spite of contrary theoretical predictions. Our theory of the hydrogen atom at this point gives no reason to look for absorption in the microwave region of the spectrum. By doing the crazy experiment outlines above, we discovered that when an electron is in the $|1s\rangle$ orbital of the hydrogen atom, there are two different states that have the same energy. When a magnetic field is applied, this degeneracy is removed, and microwave radiation can cause transitions between the two states. In the rest of this section, we see what can be deduced from this experimental observation. This experiment actually could be done with electron spin resonance spectrometers available today (Figure **8.4.1**).

To explain our observations, a new model for the hydrogen atom. Our original model for the hydrogen atom accounted for the motion of the electron and proton in our three-dimensional world; the new model needs something else that can give rise to an additional Zeeman-like effect. We need a charged particle with angular momentum to produce a magnetic moment, just like that obtained by the orbital motion of the electron. We can postulate that our observation results from a motion of the electron that was not considered in the last section - electron spin. We have a charged particle spinning on its axis. We then have charge moving in a circle, angular momentum, and a magnetic moment, which interacts with the magnetic field and gives us the Zeeman-like effect that we observed (Figure **8.4.3**).

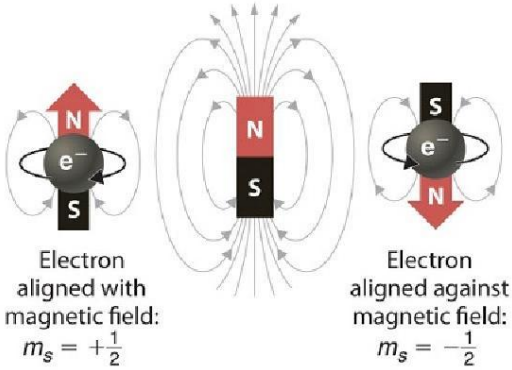


Figure **8.4.3**: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden. (CC BY-SA-NC; Anonymous by request).

In 1920, Otto Stern and Walter Gerlach designed an experiment, which unintentionally led to the discovery that electrons have their own individual, continuous spin even as they move along their orbital of an atom. Today, this electron spin is indicated by the fourth quantum number, also known as the **Electron Spin Quantum Number** and denoted by m_s. In 1925, Samuel Goudsmit and George Uhlenbeck made the claim that features of the hydrogen spectrum that were unexamined might by explained by assuming electrons act as if it has a spin, which can be denoted by an arrow pointing up, which is +1/2, or an arrow pointing down, which is -1/2. The Stern and Gerlach experiment which demonstrated this was done with a beam of vaporized silver atoms that split into two beams after passing through a magnetic field (Figure 8.4.4).

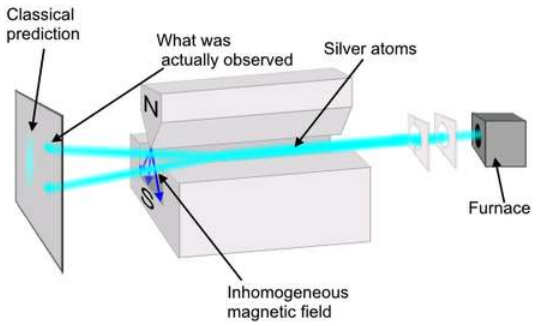


Figure 8.4.4: Stern–Gerlach experiment: silver atoms travel through an inhomogeneous magnetic field and are deflected up or down depending on their spin. (CC BY-SA 3.0 unported; Theresa Knott).

An explanation of this is that an electron has a magnetic field due to its spin. When electrons that have opposite spins are put together, there is no net magnetic field because the positive and negative spins cancel each other out. The silver atom used in the experiment has a total of 47 electrons, 23 of one spin type, and 24 of the opposite. Because electrons of the same spin cancel each other out, the *one unpaired electron* in the atom will determine the spin.

Electron "spin" does not Originate Actual Spinning

Electron's hypothetical surface would have to be moving *faster* than the speed of light for it to rotate quickly enough to produce the observed angular momentum. Hence, an electron is not simply a spinning ball or ring and electron spin appears to be an *intrinsic angular moment* of the particle rather than a consequence of the rotation of a charge particle like Figure 8.4.3 suggests. Despite this, the term "electron spin" persists in quantum vernacular.

Spin Eigenstates and Eigenvalues

To describe electron spin from a quantum mechanical perspective, we must have spin wavefunctions and spin operators. The properties of the spin states are deduced from experimental observations and by analogy with our treatment of the states arising from the orbital angular momentum of the electron. The important feature of the spinning electron is the spin angular momentum vector, which we label $\boldsymbol{S}$ 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

$$\hat{L}^2|Y_l^{m_l}\rangle = l(l+1)\hbar^2|Y_l^{m_l}\rangle \tag{8.4.2}$$

so by analogy for the spin states, we must have

$$\hat{S}^2|\sigma_s^{m_s}\rangle = s(s+1)\hbar^2|\sigma_s^{m_s}\rangle \tag{8.4.3}$$

where σ is a spin wavefunction with quantum numbers s and m_s that obey the same rules as the quantum numbers l and m_l associated with the spherical harmonic wavefunction Y. We also found the project of the orbital angular momentum on the z-axis is

$$\hat{L}_z|Y_l^{m_l}\rangle = m_l\hbar|Y_l^{m_l}\rangle \tag{8.4.4}$$

so by analogy, we must have a similar projection for the spin angular momentum:

$$\hat{S}_z|\sigma_s^{m_s}\rangle = m_s\hbar|\sigma_s^{m_s}\rangle \tag{8.4.5}$$

Since m_l ranges in integer steps from $-l$ to $+l$, also by analogy m_s ranges in integer steps from $-s$ to $+s$. In our hypothetical experiment, we observed one absorption transition, which means there are two spin states. Consequently, the two values of m_s must be $+s$ and $-s$, and the difference in m_s for the two states, labeled f and i below, must be the smallest integer step, i.e., 1. The result of this logic is that

$$\begin{aligned} m_{s,f} - m_{s,i} &= 1 \\ (+s) - (-s) &= 1 \\ 2s &= 1 \\ s &= \frac{1}{2} \end{aligned} \tag{8.4.6}$$

Therefore our conclusion is that the magnitude of the spin quantum number is 1/2 and the values for m_s are +1/2 and -1/2. The two spin states correspond to spinning clockwise and counter-clockwise with positive and negative projections of the spin angular momentum onto the z-axis. The state with a positive projection, m_s = +1/2, is called α; the other is called β. These spin states are arbitrarily labeled α and β, and the associated spin wavefunctions also are designated by $|\alpha\rangle$ and $|\beta\rangle$.

From Equation 8.4.5, the magnitude of the z-component of spin angular momentum, S_z, is given by

$$S_z = m_s \hbar \tag{8.4.7}$$

so the value of S_z is $+\hbar/2$ for spin state α and $-\hbar/2$ for spin state β. Hence, we conclude that the α spin state, where the magnetic moment is aligned against the external field direction, has a **greater energy** than the β spin state.

Even though we do not know their functional forms, the spin wavefunctions are taken to be normalized and orthogonal to each other.

$$\int \alpha^* \alpha \, d\tau_s = \int \beta^* \beta \, d\tau_s = 1 \tag{8.4.8}$$

or in braket notation

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \tag{8.4.9}$$

and

$$\int \alpha^* \beta \, d\tau_s = \int \beta^* \alpha \, d\tau_s = 0 \tag{8.4.10}$$

or in braket notation

$$\langle \alpha | \beta \rangle = \langle \alpha | \beta \rangle = 0 \tag{8.4.11}$$

where the integral is over the spin variable τ_s.

Contributors

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

This page titled 8.4: An Electron Has an Intrinsic Spin Angular Momentum is shared under a not declared license and was authored, remixed, and/or curated by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski via source content that was edited to the style and standards of the LibreTexts platform.

8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

Quantum mechanics allows us to predict the results of experiments. If we conduct an experiment with indistinguishable particles a correct quantum description cannot allow anything which distinguishes between them. For example, if the wavefunctions of two particles overlap, and we detect a particle, which one is it? The answer to this is not only that we do not know, but that we cannot know. Quantum mechanics can only tell us the probability of finding a particle in a given region. The wavefunction must therefore describe both particles.

The Schrödinger equation for the helium atom is then:

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_1^2)-V(\mathbf{r}_1)-V(\mathbf{r}_2)+V_{12}(\mathbf{r}_1,\mathbf{r}_2)\right]\psi(\mathbf{r}_1,\mathbf{r}_2)=E\psi(\mathbf{r}_1,\mathbf{r}_2) \tag{8.5.1}$$

where the subscripts label each particle, and there are six coordinates, three for each particle. While $|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle$ is a six dimensional wavefunction (three for each electron) and contains all the information we can measure (a Postulate of Quantum Mechanics), it only provide the probability of finding the electron at a specific volume element, and does **not** tell us which particle is which (e.g., is it electon 1 or electron 2?).

What basis states would be appropriate for $|\psi\rangle$? If we consider the orbital approximation that uses a product wavefunction

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle=|\varphi_a(\mathbf{r}_1)\rangle|\varphi_b(\mathbf{r}_2)\rangle \tag{8.5.2}$$

where $|\varphi_a(\mathbf{r}_1)\rangle$ and $|\varphi_b(\mathbf{r}_2)\rangle$ are one-particle spin-orbitals (with both spin and spatial components) of atoms 1 and 2. This approximation allows us to separate the two particle equation into two one-electron equations:

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2+V(\mathbf{r}_1)\right]|\varphi_a(\mathbf{r}_1)\rangle=E|\varphi_a(\mathbf{r}_1)\rangle \tag{8.5.3}$$

$$\left[-\frac{\hbar^2}{2m}\nabla_2^2+V(\mathbf{r}_2)\right]|\varphi_b(\mathbf{r}_2)\rangle=E|\varphi_a(\mathbf{r}_2)\rangle \tag{8.5.4}$$

provided that the particles do not interact (e.g., ∇_1^2 does not act on $|\varphi_b(\mathbf{r}_2)\rangle$ and $V_{12}=0$).

Unfortunately, by doing this we have introduced unphysical *labels* to the indistinguishable particles. And this is wrong: the effect of it is that the particles do not interfere with each other because they are in different dimensions (six dimensional space - remember?). When we construct a two particle wavefunction out of two one-particle wavefunctions we must be ensure that the probability density (the measurable quantity $|\psi|^2$) is independent of the **artificial** labels.

The Exchange Operator

We can deepen our understanding of the quantum mechanical description of multi-electron atoms by examining the concepts of electron indistinguishability and the Pauli Exclusion Principle in detail. We will use the following statement as a guide to keep our explorations focused on the development of a clear picture of the multi-electron atom: “When a multi-electron wavefunction is built as a product of single-electron wavefunctions, the corresponding concept is that exactly one electron’s worth of charge density is described by each atomic spin-orbital.”

A subtle, but important part of the conceptual picture, is that the electrons in a multi-electron system are not distinguishable from one another by any experimental means. Since the electrons are indistinguishable, the probability density we calculate by squaring the modulus of our multi-electron wavefunction also cannot change when the electrons are interchanged (permuted) between different orbitals. In general, if we interchange two identical particles, the world does not change. As we will see below, this requirement leads to the idea that the world can be divided into two types of particles based on their behavior with respect to permutation or interchange.

In order for the probability density to remain unchanged when two particles are permuted, the wavefunction itself can change only by a factor of $e^{i\varphi}$, which represents a complex number, when the particles described by that wavefunction are permuted. As we will show below, the $e^{i\varphi}$ factor is possible because the probability density depends on the absolute square of the function and all expectation values involve $\psi\psi^*$. Consequently $e^{i\varphi}$ disappears in any calculation that relates to the real world because $e^{i\varphi}e^{-i\varphi}=1$.

We could symbolically write an approximate two-particle wavefunction as $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 ($\mathbf{r}_1$) for the coordinates of particle 2 ($\mathbf{r}_2$) and vice versa, to get the new wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This new wavefunction must have the property that

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = \psi(\mathbf{r}_2, \mathbf{r}_1)^* \psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2)^* \psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.5}$$

since the probability density of the electrons in the atom does **not** change upon permutation of the electrons.

Exercise 8.5.1

Permute the electrons the product function for He wavefunction:

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = |\varphi_{1s}(\mathbf{r}_1)\rangle |\varphi_{1s}(\mathbf{r}_2)\rangle$$

Equation 8.5.5 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{i\varphi} \psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.6}$$

so that

$$\left(e^{-i\varphi} \psi(\mathbf{r}_1, \mathbf{r}_2)^*\right) \left(e^{i\varphi} \psi(\mathbf{r}_1, \mathbf{r}_2)^*\right) = \psi(\mathbf{r}_1, \mathbf{r}_2)^* \psi(\mathbf{r}_1, \mathbf{r}_2) \tag{8.5.7}$$

If we exchange or permute two identical particles twice, we are (by definition) back to the original situation. If each permutation changes the wavefunction by $e^{i\varphi}$, the double permutation must change the wavefunction by $e^{i\varphi} e^{i\varphi}$. Since we then are back to the original state, the effect of the double permutation must equal 1; i.e.,

$$e^{i\varphi} e^{i\varphi} = e^{i2\varphi} = 1 \tag{8.5.8}$$

which is true only if $\varphi = 0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature.

Exercise 8.5.2

Use Euler's Equality

$$e^{i\pi} + 1 = 0$$

to show that $e^{i2\varphi} = 1$ when $\varphi = 0$ or $n\pi$ and consequently $e^{i\varphi} = \pm 1$.

We can introduce the *exchange operator* $\hat{P}_{12}$: an operator which permutes the labels of the particles in a multi-particle wavefucntion. This is a rather strange operator, because it only changes the *unphysical* labels which we have attached to the one-particle wavefunctions in order to make the maths more easy. For a meaningful solution we must have a wavefunction which has a probability amplitude unchanged by $\hat{P}_{12}$: it must be either symmetric or antisymmetric with respect to exchange:

$$\hat{P}_{12} |\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \pm |\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle \tag{8.5.9}$$

Bosons and femions

Physical solutions must be eigenfunctions of $\hat{P}_{12}$ (i.e., $\hat{H}$ and $\hat{P}_{12}$ commute). Moveover, Equation 8.5.9 argues that the eigenvalues of the Exchange Operator are either +1 (bosons) or −1 (fermions).

Bosons

Wavefunctions for which $e^{i\varphi} = +1$ are defined as symmetric with respect to permutation, because the wavefunction is identical before and after a single permutation. Wavefunctions that are symmetric with respect to interchange of the particles obey the following mathematical relationship,

$$\hat{P}_{12} |\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = + |\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle \tag{8.5.10}$$

The behavior of some particles requires that the wavefunction be symmetric with respect to permutation. These particles are called bosons and have integer spin such as deuterium nuclei, photons, and gluons.

Fermions

The behavior of other particles requires that the wavefunction be antisymmetric with respect to permutation ($e^{i\varphi} = -1$). A wavefunction that is antisymmetric with respect to electron interchange is one whose output changes sign when the electron coordinates are interchanged, as shown below.

$$\hat{P}_{12}|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = -|\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle \tag{8.5.11}$$

These particles are called fermions and have half-integer spin and include electrons, protons, and neutrinos. Since electrons are fermion, any wavefunction used to describe multiple electrons **must** be antisymmetric with respect to permutation of the electrons. The requirement that the wavefunction be antisymmetric applies to all multi-electron functions $\psi(\mathbf{r}_1, \mathbf{r}_2, \cdots r_i)$, including those approximated as products of single electron functions

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \cdots r_i)\rangle \approx \varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\cdots\varphi_i(r_i) \tag{8.5.12}$$

Exercise 8.5.4

What is meant by the term permutation symmetry?

Exercise 8.5.5

Explain why the product function $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ could describe two bosons (deuterium nuclei), but can not describe two fermions (e.g. electrons).

The Pauli's Exclusion Principle

Any physically meaningful Hamiltonian must commute with $\hat{P}_{12}$, otherwise $\hat{H}$ and $\hat{P}_{12}$ could not have common eigenfunctions and the system could not remain in an eigenstate of exchange. A simple product wavefunction like that in Equation 8.5.12 does **not** satisfy this (unless $\varphi_a = \varphi_b$). A **linear combination of all permutations** is required to satisfy indistinguishability constraints.

For a two particle system (e.g., Helium) there is the asymmetric combination

$$|\psi^-\rangle = \frac{1}{\sqrt{2}}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.13}$$

and symmetric combination

$$|\psi^+\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle + C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle + C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.14}$$

where the C_{ab} terms are expansion and normalization parameters.

> *Note that the antisymmetric combination (Equation 8.5.13) **cannot** include terms where both particles are in the same state (spin-orbital), but there are three possibilities for the symmetric state (Equation 8.5.14).*

Although any linear combinations of C_{ab}, C_{bb}, and C_{aa} in Equation 8.5.14 is possible, there are three limiting expressions for possible symmetric combinations:

$$|\psi_1^{+i}\rangle = C_{ab}|\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.15}$$

$$|\psi_2^{+i}\rangle = C_{aa}|\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\rangle \tag{8.5.16}$$

$$|\psi_3^{+i}\rangle = C_{bb}|\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\rangle \tag{8.5.17}$$

If $\varphi_a(\mathbf{r}_1) = \varphi_a(\mathbf{r}_2)$, then $|\varphi^{-i}\rangle = 0$. Thus there is no possible antisymmetric combination involving electrons in the same state (spin-orbit). This is the Pauli exclusion principle.

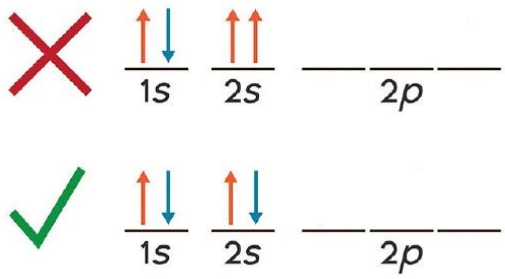


Figure 8.5.1: The 1s and 2s subshells for beryllium atoms can hold only two electrons and when filled, since each electrons is described by a specific spin-orbital and each orbital (spatial) can hold either an α or a β electron (i.e., they must have opposite spins). Otherwise they will have the same four quantum numbers, in violation of the Pauli Exclusion Principle.

The Pauli Exclusion Principle argues that two electrons **could not** be described by the same spin-orbital. To see the relationship between this statement and the requirement that the wavefunction be antisymmetric for electrons, try to construct an anti-symmetric wavefunction for two electrons that are described by the same spin-orbital

$$|\varphi_b(\mathbf{r}_1)\rangle = \varphi_a(\mathbf{r}_2)\rangle \tag{8.5.18}$$

For example, if this were the case for the anti-symmetric combination for helium (Equation 8.5.13), then the wavefunction collapses to zero. We can only constructs wavefunctions that are antisymmetric with respect to permutation symmetry only if each electron is described by a different function.

> *The Pauli Exclusion Principle is simply the requirement that the wavefunction be antisymmetric for electrons, since they are fermions.*

Contributors

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

8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants

Let's try to construct an antisymmetric function that describes the two electrons in the ground state of helium. Blindly following the first statement of the Pauli Exclusion Principle, then each electron in a multi-electron atom **must** be described by a different spin-orbital. For the ground-state helium atom, this gives a $1s^2 2s^0 2p^0$ configuration (Figure **8.6.1**).

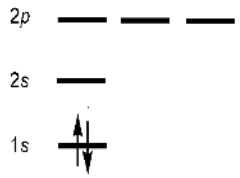


Figure **8.6.1**: Electron configuration for ground state of the helium atom.

We try constructing a simple product wavefunction for helium using two different spin-orbitals. Both have the 1s spatial component, but one has spin function α and the other has spin function β so the product wavefunction matches the form of the ground state electron configuration for He, $1s^2$.

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) \tag{8.6.1}$$

After permutation of the electrons, this becomes

$$|\psi(\mathbf{r}_2, \mathbf{r}_1)\rangle = \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1) \tag{8.6.2}$$

which is different from the starting function since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are different spin-orbital functions. Hence, the simple product wavefunction in Equation 8.6.1 does not satisfy the indistinguishability requirement since an antisymmetric function must produce the same function multiplied by (–1) after permutation of two electrons, and that is not the case here. We must try something else. To avoid getting a totally different function when we permute the electrons, we can make **a linear combination of functions**. A very simple way of taking a linear combination involves making a new function by simply adding or subtracting functions. The function that is created by subtracting the right-hand side of Equation 8.6.2 from the right-hand side of Equation 8.6.1 has the desired antisymmetric behavior. The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}[\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2)\varphi_{1s\beta}(\mathbf{r}_1)] \tag{8.6.3}$$

We can introduce a shorthand notation for the arbitrary *spin-orbital*

$$\varphi_{i\alpha}(\mathbf{r}_j) = \varphi_i\alpha(j) \tag{8.6.4}$$

or

$$\varphi_{i\beta}(\mathbf{r}_j) = \varphi_i\beta(j) \tag{8.6.5}$$

as determined by the m_s quantum number. This wavefunction in Equation 8.6.3 can be decomposed into spatial and spin components:

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{1s}(2)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.6}$$

Exercise 8.6.1

Show that the linear combination in Equation 8.6.3 is antisymmetric with respect to permutation of the two electrons. (Hint: replace the minus sign with a plus sign (i.e. take the positive linear combination of the same two functions) and show that the resultant linear combination is symmetric).

Answer

$|\Psi(r1,r2)>= 1/\sqrt{2}[\varphi 1s\alpha(r))\varphi 1s\beta(r2) - \varphi 1s\beta(r2) - \varphi 1s\alpha(r2)\varphi 1s\beta(r1)](8.6.3) \rightarrow$show this is antisymmetric

Change the minus sign to plus sign show this is symmetric

(1) $|\Psi(r1,r2)>= 1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2) - \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]$
(2) $|\Psi(r1,r2)>= 1/\sqrt{2}[\varphi 1\,sa(r1)\varphi 1s\beta(r2) + \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]$

To see if symmetric $|\Psi_{(r1,r2)}>=|\Psi(r2,r1)> |\Psi(r1,r2)>= 1/\sqrt{2}[\varphi 1sa(r1)\varphi 1s\beta(r2) + \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]=$

$|\Psi(r2,r1)>= 1/\sqrt{2}[\varphi 1s\alpha(r2)\varphi 1s\beta(r1) + \varphi 1s\alpha(r1)\varphi 1s\beta(r2)]$

Can rearrange and $|\Psi(r1,r2)>= 1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2) + \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]=$

$|\Psi(r1,r2)>= 1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2) + \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]$

So $|\Psi(r1,r2)>= 1/\sqrt{2}[\varphi 1\,sa(r1)\varphi 1s\beta(r2) + \varphi 1s\alpha(r2)\varphi 1s\beta(r1)]$ is symmetric

Now for antisymmetric $|\Psi(r1,r2)>=-|\Psi(r2,r1)>$ $|\Psi(r1,r2)>=1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2)-\varphi 1s\alpha(r2)\varphi 1s\beta(r1)]=$ $|\Psi(r2,r1)>=-1/\sqrt{2}[\varphi 1s\alpha(r2)\varphi 1s\beta(r1)-\varphi 1s\alpha(r1)\varphi 1s\beta(r2)]$

Simplify equation above and $1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2)-\varphi 1s\alpha(r2)\varphi 1s\beta(r1)]=1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2)-\varphi 1s\alpha(r2)\varphi 1s\beta(r1)]$

$$|\Psi(r1,r2)> \quad -|\Psi(r2,r1)> \tag{8.6.7}$$

$|\Psi_{(r1,r2)}\rangle=1/\sqrt{2}[\varphi 1s\alpha(r1)\varphi 1s\beta(r2)-\varphi 1s\alpha(r2)\varphi 1s\beta(r1)]\rightarrow$ is antisymmetric

The first excited state of He is $1s^1 2s^1 2p^0$ and we can envision four microstates for this configuration (Figure 8.6.2) that also must satisfy indistinguishability requirement just like the ground state.

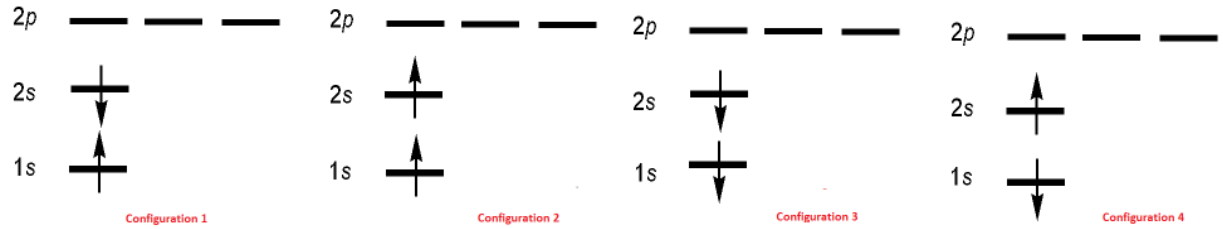


Figure 8.6.2: Electron configurations for first-excited state of the helium atom.

These electron configurations are used to construct four possible excited-state two-electron wavefunctions (but not necessarily in a one-to-on correspondence):

$$|\psi_1(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)+\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)-\alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.8}$$

$$|\psi_2(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\alpha(2)]}_{\text{spin component}} \tag{8.6.9}$$

$$|\psi_3(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\alpha(1)\beta(2)+\alpha(2)\beta(1)]}_{\text{spin component}} \tag{8.6.10}$$

$$|\psi_4(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{2}\underbrace{[\varphi_{1s}(1)\varphi_{2s}(2)-\varphi_{1s}(2)\varphi_{2s}(1)]}_{\text{spatial component}}\underbrace{[\beta(1)\beta(2)]}_{\text{spin component}} \tag{8.6.11}$$

All four wavefunctions are antisymmetric as required for fermionic wavefunctions (which is left to an exercise). Wavefunctions $|\psi_1\rangle$ and $|\psi_4\rangle$ correspond to the two electrons both having spin up or both having spin down (Configurations 2 and 3 in Figure 8.6.2, respectively). Wavefunctions $|\psi_1\rangle$ and $|\psi_3\rangle$ are more complicated and are antisymmetric (Configuration 1 - Configuration 4) and symmetric combinations (Configuration 1 + 4). That is, a single electron configuration does not describe the wavefunction. For many electrons, this ad hoc construction procedure would obviously become unwieldy. However, there is an elegant way to construct an antisymmetric wavefunction for a system of N identical particles.

Determinantal Wavefunctions

A linear combination that describes an appropriately antisymmetrized multi-electron wavefunction for any desired orbital configuration is easy to construct for a two-electron system. However, interesting chemical systems usually contain more than two electrons. For these multi-electron systems a relatively simple scheme for constructing an antisymmetric wavefunction from a product of one-electron functions is to write the wavefunction in the form of a determinant. John Slater introduced this idea so the determinant is called a Slater determinant.

John C. Slater introduced the determinants in 1929 as a means of ensuring the antisymmetry of a wavefunction, however the determinantal wavefunction first appeared three years earlier independently in Heisenberg's and Dirac's papers.

The Slater determinant for the two-electron ground-state wavefunction of helium is

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1)\\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2)\end{vmatrix} \tag{8.6.12}$$

A shorthand notation for the determinant in Equation 8.6.12 is then

$$|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle = 2^{-\frac{1}{2}}Det|\varphi_{1s\alpha}(\mathbf{r}_1)\varphi_{1s\beta}(\mathbf{r}_2)| \tag{8.6.13}$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is $(N!)^{-\frac{1}{2}}$ for N electrons.

The generalized Slater determinant for a multi-electrom atom with N electrons is then

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \varphi_2(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_1) \\ \varphi_1(\mathbf{r}_2) & \varphi_2(\mathbf{r}_2) & \cdots & \varphi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(\mathbf{r}_N) & \varphi_2(\mathbf{r}_N) & \cdots & \varphi_N(\mathbf{r}_N) \end{vmatrix} \tag{8.6.14}$$

Now that we have seen how acceptable multi-electron wavefunctions can be constructed, it is time to revisit the "guide" statement of conceptual understanding with which we began our deeper consideration of electron indistinguishability and the Pauli Exclusion Principle. What does a multi-electron wavefunction constructed by taking specific linear combinations of product wavefunctions mean for our physical picture of the electrons in multi-electron atoms? Overall, the antisymmetrized product function describes the configuration (the orbitals, regions of electron density) for the multi-electron atom. Because of the requirement that electrons be indistinguishable, we cannot visualize specific electrons assigned to specific spin-orbitals. Instead, we construct functions that allow each electron's probability distribution to be dispersed across each spin-orbital. The total charge density described by any one spin-orbital cannot exceed one electron's worth of charge, and each electron in the system is contributing a portion of that charge density.

The four configurations in Figure **8.6.2** for first-excited state of the helium atom can be expressed as the following Slater Determinants

$$|\phi_a(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} \tag{8.6.15}$$

$$|\phi_b(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \tag{8.6.16}$$

$$|\phi_c(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \tag{8.6.17}$$

$$|\phi_d(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} \tag{8.6.18}$$

Slater determinants are constructed by arranging spinorbitals in columns and electron labels in rows and are normalized by dividing by $\sqrt{N!}$, where N is the number of occupied spinorbitals. As you can imagine, the algebra required to compute integrals involving Slater determinants is extremely difficult. It is therefore most important that you realize several things about these states so that you can avoid unnecessary algebra:

- A Slater determinant corresponds to a single electron configuration diagram (Figure **8.6.2**). Furthermore, recall that for the excited states of helium we had a problem writing certain stick diagrams as a (space)x(spin) product and had to make linear combinations of certain states to force things to separate (Equation 8.6.9 and 8.6.11). Because of the direct correspondence of configuration diagrams and Slater determinants, the same pitfall arises here: Slater determinants sometimes may not be representable as a (space)x(spin) product, in which case a linear combination of Slater determinants must be used instead. This generally only happens for systems with unpaired electrons (like several of the Helium excited-states).
- A Slater determinant is anti-symmetric upon exchange of any two electrons. We recall that if we take a matrix and interchange two its rows, the determinant changes sign.

The wavefunctions in 8.6.8-8.6.11 can be expressed in term of the four determinants in Equations 8.6.15-8.6.18.

$$\begin{aligned} |\psi_2\rangle &= |\phi_b\rangle \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \\ |\psi_4\rangle &= |\phi_d\rangle \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} \end{aligned}$$

but the wavefunctions that represent combinations of spinorbitals and hence combinations of electron configurations (e.g., igure **8.6.2**) are combinations of Slater determinants (Equation 8.6.15-8.6.17)

$$\begin{aligned} |\psi_1\rangle &= |\phi_a\rangle - |\phi_c\rangle \\ &= \frac{1}{2}\left(\begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} - \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \right) \\ |\psi_3\rangle &= |\phi_a\rangle + |\phi_c\rangle \\ &= \frac{1}{2}\left(\begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) \end{vmatrix} + \begin{vmatrix} \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) \\ \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) \end{vmatrix} \right) \end{aligned}$$

Note the expected change in the normalization constants.

Exercise 8.6.3

Show that the determinant wavefunction in Equation 8.6.12 is the same as the form for the helium wavefunction that is given in Equation 8.6.3.

Exercise 8.6.4

Expand the Slater determinant in Equation 8.6.12 for the He atom.

Answer

To expand the Slater determinant of the Helium atom, the wavefunction of Helium in the form of a two-electron system:

$$|\psi(\mathrm{r}_1,\mathrm{r}_2)| = 1/\sqrt{(2)}\,|\Psi_{1s}(1)\mathrm{a}(1) \quad \psi_{1s}(1)\beta(1)| \tag{8.6.19}$$

$$|\psi_{1s}(2)a(2)\Psi_{1s}(2)\beta(2)| \tag{8.6.20}$$

Apply the definition of determinant of a regular 2×2 matrix to this wavefunction. The determinant of a 2×2 matrix is:

$$W = |ab| \rightarrow \det(w) = ad - bc \tag{8.6.21}$$

$$|cd| \tag{8.6.22}$$

Using this definition, expand the Slater determinant of Helium in a similar fashion.

$$\det\left(|\Psi(\mathrm{r}_1,\mathrm{r}_2)|\right) = 1/\sqrt{(2)}\left[\Psi_{1s}(1)\mathrm{a}(1)\Psi_{1s}(2)\right]\beta(2) - \Psi_{1s}(1)\beta(1)\Psi_{1s}(2)\mathrm{a}(2)\Big] \tag{8.6.23}$$

Exercise 8.6.5

Write and expand the Slater determinant for the ground-state Li atom.

Answer

Slater determinant for Li atom:

$$\psi(1,2,3) = \frac{1}{\sqrt{6}}\det\begin{pmatrix} 1S\alpha(1) & 1S\beta(1) & 2S\alpha(1) \\ 1S\alpha(2) & 1S\beta(2) & 2S\alpha(2) \\ 1S\alpha(3) & 1S\beta(3) & 2S\alpha(3) \end{pmatrix} \tag{8.6.24}$$

Expansion of Slater determinant (Laplace):

$$\psi(1,2,3) = \frac{1}{\sqrt{6}}[1S\alpha(1)1S\beta(2)2S\alpha(3) - 1S\alpha(1)1S\beta(3)2S\alpha(2) + 1S\alpha(3)1S\beta(1)2S\alpha(2) - 1S\alpha(3)1S\beta(2)2S\alpha(1) + 1S\alpha(2)1S\beta(3)2S\alpha(3) \tag{8.6.25}$$

Exercise 8.6.6

Write the Slater determinant for the ground-state carbon atom. If you expanded this determinant, how many terms would be in the linear combination of functions?

Solution

Carbon has 6 electrons which occupy the 1s 2s and 2p orbitals. Each row in the determinant represents a different electron and each column a unique spin-obital where the electron could be found. There are 6 rows, 1 for each electron, and 6 columns, with the two possible p orbitals both alpha (spin up), in the determinate. There are two columns for each s orbital to account for the alpha and beta spin possibilities. There are two different p orbitals because the electrons in their ground state will be in the different p orbitals and both spin up. N=6 so the normalization constant out front is 1 divided by the square-root of 6!

$$\psi(1,2,3,4,5,6)$$

$$= \frac{1}{6!^{1/2}}\begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) & \varphi_{2s}(1)\alpha(1) & \varphi_{2s}(1)\beta(1) & \varphi_{2px}(1)\alpha(1) & \varphi_{2py}(1)\alpha(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) & \varphi_{2s}(2)\alpha(2) & \varphi_{2s}(2)\beta(2) & \varphi_{2px}(2)\alpha(2) & \varphi_{2py}(2)\alpha(2) \\ \varphi_{1s}(3)\alpha(3) & \varphi_{1s}(3)\beta(3) & \varphi_{2s}(3)\alpha(3) & \varphi_{2s}(3)\beta(3) & \varphi_{2px}(3)\alpha(3) & \varphi_{2py}(3)\alpha(3) \\ \varphi_{1s}(4)\alpha(4) & \varphi_{1s}(4)\beta(4) & \varphi_{2s}(4)\alpha(4) & \varphi_{2s}(4)\beta(4) & \varphi_{2px}(4)\alpha(4) & \varphi_{2py}(4)\alpha(4) \\ \varphi_{1s}(5)\alpha(5) & \varphi_{1s}(5)\beta(5) & \varphi_{2s}(5)\alpha(5) & \varphi_{2s}(5)\beta(5) & \varphi_{2px}(5)\alpha(5) & \varphi_{2py}(5)\alpha(5) \\ \varphi_{1s}(6)\alpha(6) & \varphi_{1s}(6)\beta(6) & \varphi_{2s}(6)\alpha(6) & \varphi_{2s}(6)\beta(6) & \varphi_{2px}(6)\alpha(6) & \varphi_{2py}(6)\alpha(6) \end{vmatrix}$$

Expanding this determinant would result in a linear combination of functions containing 720 terms. An expanded determinant will contain N! factorial terms, where N is the dimension of the matrix.

Exercise 8.6.7

Write the Slater determinant for the $1s^1 2s^1$ excited state orbital configuration of the helium atom.

Answer

Since there are 2 electrons in question, the Slater determinant should have 2 rows and 2 columns exactly. Additionally, this means the normalization constant is $1/\sqrt{2}$.

Each element of the determinant is a different combination of the spatial component and the spin component of the $1s^1 2s^1$ atomic orbitals

$$\frac{1}{\sqrt{2}} \begin{bmatrix} \varphi 1_s(1)\alpha(1) & \varphi 2_s(1)\beta(1) \\ \varphi 1_s(2)\alpha(2) & \varphi 2_s(2)\beta(2) \end{bmatrix} \tag{8.6.26}$$

Exercise 8.6.8

Critique the energy level diagram and shorthand electron configuration notation from the perspective of the indistinguishability criterion. Can you imagine a way to represent the wavefunction expressed as a Slater determinant in a schematic or shorthand notation that more accurately represents the electrons? (This is not a solved problem!)

Contributors

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

8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

The Hartree method discussed previously is useful as an introduction to the solution of many-particle system and to the concepts of self-consistency and of the self-consistent- eld, but its importance is con ned to the history of physics. In fact the Hartree method is not just approximate: it is wrong, by construction, since its wavefunction is not antisymmetric to electron permutation! The Hartree-Fock approach discussed below is a better approach, which correctly takes into account the antisymmetric character of the trial wavefunctions.

Although these *Hartree equations* are numerically tractable via the self-consistent field method, it is not surprising that such a crude approximation fails to capture elements of the essential physics. The Pauli exclusion principle demands that the many-body wavefunction be antisymmetric with respect to interchange of any two electron coordinates, e.g.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) \tag{8.7.1}$$

which clearly cannot be satisfied by the multi-electron wavefunctions of the form used in the Hartree Approximation (Equation 8.7.2).

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_N(\mathbf{r}_N) \tag{8.7.2}$$

This indistinguishability condition can be satisfied by forming a Slater determinant of single-particle orbitals

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N}} |\psi(\mathbf{r}_1)\psi(\mathbf{r}_2)\dots\psi(\mathbf{r}_N)| \tag{8.7.3}$$

This decouples the electrons resulting in single-particle **Hartree-Fock** equations:

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r}) + V_{electron}(\mathbf{r})\psi_i(\mathbf{r}) \\ -\sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = \epsilon_i\psi_i(\mathbf{r}). \end{aligned} \tag{8.7.4}$$

As with the *Hartree* equations, the first term is the kinetic energy of the ith electron

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) \tag{8.7.5}$$

and the second term is the electron-nuclear potential between the ith electron and nucleus

$$V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r}) \tag{8.7.6}$$

The third term (sometimes called the “Hartree” term) is the electrostatic potential between the ith electron and the **average** charge distribution of the other N-1 electrons.

$$V_{electron}(\mathbf{r})\psi_i(\mathbf{r}) = J_{j,k} = \int |\phi_j(r)|^2 |\phi_k(r')|^2 \frac{e^2}{r-r'} dr dr' \tag{8.7.7}$$

These three terms are identical to Hartree Equations with the product wavefunction ansatz (i.e., orbital approximation). The fourth term of Equation 8.7.4 is not in the Hartree Equations:

$$\sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \tag{8.7.8}$$

and is the *exchange* term. This term resembles the direct Coulomb term, but for the exchanged indices. It is a manifestation of the Pauli exclusion principle, and acts so as to separate electrons of the same spin. This “exchange” term acts only on electrons with the same spin and comes from the Slater determinant form of the wavefunction. Physically, the effect of exchange is for like-spin electrons to avoid each other. The exchange term adds considerably to the complexity of these equations.

The Hartree-Fock Equations in Equation 8.7.4 can be recast as series of Schrödinger-like equations:

$$\hat{F}|\varphi_i\rangle = \epsilon_i|\varphi_i\rangle \tag{8.7.9}$$

where $\hat{F}$ is called the **Fock operator** and $\{|\varphi_i\rangle\}$ are the Hatree-Fock orbitals with corresponding energies ϵ_i.

The Fock operator is a one-electron operator and solving a Hartree-Fock equation gives the energy and Hartree-Fock orbital for one electron. For a system with 2N electrons, the variable i will range from 1 to N; i.e there will be one equation for each orbital. The reason for this is that only the spatial wavefunctions are used in Equation 8.7.9. Since the spatial portion of an orbital can be used to describe two electrons, each of the energies and wavefunctions found by solving Equation 8.7.9 will be used to describe two electrons.

The nature of the Fock operator reveals how the Hartree-Fock (HF) or Self-Consistent Field (SCF) Method accounts for the electron-electron interaction in atoms and molecules while preserving the idea of **independent atomic orbitals**. The wavefunction written as a Slater determinant of spin-orbitals is necessary to derive the form of the Fock operator, which is

$$\hat{F} = \hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) \tag{8.7.10}$$

As shown by the expanded version on the far right, the first term in this equation, $\hat{H}^0$, is the familiar hydrogen-like operator that accounts for the kinetic energy of an electron and the potential energy of this electron interacting with the nucleus. The next term accounts for the potential energy of one electron in an average field created by all the other electrons in the system. The $\hat{J}$ and $\hat{K}$ operators result from the electron-electron repulsion terms in the full Hamiltonian for a multi-electron system. These operators involve the one-electron orbitals as well as the electron-electron interaction energy.

The Fock operator (Equation 8.7.10 depends on **all occupied** orbitals (because of the exchange and Coulomb operators). Therefore, a specific orbital can only be determined if all the others are known. One must use iterative methods to solve the HF equations like the Self-consistent field method discussed previously for the Hartree Approximation.

Exchange Energy

The exchange interaction is a quantum mechanical effect that only occurs between identical particles. Despite sometimes being called an exchange force in analogy to classical force, **it is not a true force**, as it lacks a force carrier. The effect is due to the wavefunction of indistinguishable particles being subject to exchange symmetry, that is, either remaining unchanged (symmetric) or changing its sign (antisymmetric) when two particles are exchanged. Both bosons and fermions can experience the exchange interaction. For fermions, it is sometimes called Pauli repulsion and related to the Pauli exclusion principle. For bosons, the exchange interaction takes the form of an effective attraction that causes identical particles to be found closer together, as in Bose–Einstein condensation.

Example 8.7.1: Hartree-Fock Energy of Helium

For example, the electron 1 in helium (with $Z = 2$, then

$$\hat{H}^0(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} \tag{8.7.11}$$

The Fock operator is couched in terms of the coordinates of the one electron whose perspective we are taking (which we will call electron 1 throughout the following discussion), and the **average field created by all the other electrons** in the system is built in terms of the coordinates of a generic “other electron” (which we’ll call electron 2) that is considered to occupy each orbital in turn during the summation over the N spatial orbitals.

> *As with the Hartree Equations, solving the Hartree-Fock Equations is mathematically equivalent to assuming each electron interacts only with the average charge cloud of the other electrons. This is how the electron-electron repulsion is handled. This also why this approach is also called the Self-Consistant Field (SCF) approach.*

The best possible one-electron wavefunctions, by definition, will give the **lowest possible total energy** for a multi-electron system used with the complete multielectron Hamiltonian to calculate the expectation value for the total energy of the system. These wavefunctions are called the **Hartree-Fock wavefunctions** and the calculated total energy is the Hartree-Fock energy of the system.

Hartree-Fock Energy

The Hartree-Fock equations $h_e\phi_i = \epsilon_i\phi_i$ imply that the orbital energies ϵ_i can be written as:

$$\epsilon_i = \langle\phi_i|h_e|\phi_i\rangle \tag{8.7.12}$$

$$= \langle\phi_i|T+V|\phi_i\rangle + \sum_{j(\text{occupied})} \langle\phi_i|J_j - K_j|\phi_i\rangle \tag{8.7.13}$$

$$= \langle\phi_i|T+V|\phi_i\rangle + \sum_{j(\text{occupied})} [J_{i,j} - K_{i,j}], \tag{8.7.14}$$

where $T+V$ represents the kinetic (T) and nuclear attraction (V) energies, respectively. Thus, ϵ_i is the average value of the kinetic energy plus Coulombic attraction to the nuclei for an electron in ϕ_i plus the sum over all of the spin-orbitals occupied in ψ of Coulomb minus Exchange interactions of these electrons with the electron in ϕ_i.

If ϕ_i is an occupied spin-orbital, the $j = i$ term $[J_{i,i} - K_{i,i}]$ disappears in the above sum and the remaining terms in the sum represent the Coulomb minus exchange interaction of ϕ_i with all of the $N-1$ other occupied spin-orbitals. If ϕ_i is a virtual spin-orbital, this cancelation does not occur because the sum over j does not include $j = i$. So, one obtains the Coulomb minus exchange interaction of ϕ_i with all N of the occupied spin-orbitals in ψ. Hence the energies of occupied orbitals pertain to interactions appropriate to a total of N electrons, while the energies of virtual orbitals pertain to a system with $N+1$ electrons. This difference is very important to understand and to keep in mind.

To give an idea of how well HF theory can predict the ground state energies of several atoms, consider Table 8.7.1 below:

Table 8.7.1: Hartree-Fock Calculations of Ground Energies of Select Atoms (all energies are in R_H)

Atom	Hartree-Fock Energy	Experiment
He	−5.72	−5.80
Li	−14.86	−14.96
Ne	−257.10	−257.88
Ar	−1053.64	−1055.20

Koopmans' Theorem

Koopmans' theorem states that the first ionization energy is equal to the negative of the orbital energy of the highest occupied molecular orbital. Hence, the ionization energy required to generated a cation and detached electron is represented by the removal of an electron from an orbital without changing the wavefunctions of the other electrons. This is called the "frozen orbital approximation." Let us consider the following model of the detachment or attachment of an electron in an N-electron system.

1. In this model, both the parent molecule and the species generated by adding or removing an electron are treated at the single-determinant level.
2. The Hartree-Fock orbitals of the parent molecule are used to describe both species. It is said that such a model neglects orbital relaxation (i.e., the re-optimization of the spin-orbitals to allow them to become appropriate to the daughter species).

Within this model, the energy difference between the daughter and the parent can be written as follows (ϕ_k represents the particular spin-orbital that is added or removed:

- for electron detachment (vertical ionization energies)

$$E_{N-1} - E_N = -\epsilon_k \tag{8.7.15}$$

- and for electron attachment (electron affinities)

$$E_N - E_{N+1} = -\epsilon_k. \tag{8.7.16}$$

Example 8.7.2: Electron Affinity

Let's derive this result for the case in which an electron is added to the $N+1^{st}$ spin-orbital. The energy of the N-electron determinant with spin-orbitals ϕ_1 through f_N occupied is

$$E_N = \sum_{i=1}^{N} \langle \phi_i | T + V | \phi_i \rangle + \sum_{i=1}^{N} [J_{i,j} - K_{i,j}]$$

which can also be written as

$$E_N = \sum_{i=1}^{N} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N} [J_{i,j} - K_{i,j}].$$

Likewise, the energy of the $N+1$-electron determinant wavefunction is

$$E_{N+1} = \sum_{i=1}^{N+1} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N+1} [J_{i,j} - K_{i,j}].$$

The difference between these two energies is given by

$$\begin{aligned} E_N - E_{N+1} &= -\langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \frac{1}{2} \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ &\quad - \frac{1}{2} \sum_{j=1}^{N+1} [J_{N+1,j} - K_{N+1,j}] \\ &= -\langle \phi_{N+1} | T + V | \phi_{N+1} \rangle - \sum_{i=1}^{N+1} [J_{i,N+1} - K_{i,N+1}] \\ &= -\epsilon_{N+1}. \end{aligned}$$

That is, the energy difference is equal to minus the expression for the energy of the $N+1^{st}$ spin-orbital, which was given earlier.

> *The Hartree-Fock equations deal with exchange exactly; however, the equations neglect more detailed correlations due to many-body interactions. The effects of electronic correlations are not negligible; indeed the failure of Hartree-Fock theory to successfully incorporate correlation leads to one of its most celebrated failures.*

Advanced: Electron Correlation and the "Exchange Hole"

In the Copenhagen Interpretation, the squared modulus of the wavefunction gives the probability of finding a particle in a given place. The many-body wavefunction gives the N-particle distribution function, i.e. $|\Phi(r_1, ..., r_N)|^2$ is the probability density that particle 1 is at r_1, ..., and particle N is at r_N. However, when trying to work out the interaction between electrons, what we want to know is the probability of finding an electron at r, given the positions of all the other electrons $\{r_i\}$. This implies that the electron behaves quantum mechanically when we evaluate its wavefunction, but as a classical point particle when it contributes to the potential seen by the other electrons.

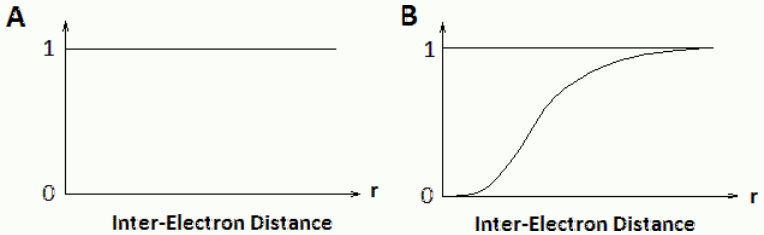


Figure 8.7.2: Normalized Conditional Probability for from electron-electron interactions (excluding coulomb effects) in (A) the Hartree approximation and (B) the Hartree-Fock approximation.

The contributions of electron-electron interactions in N-electron systems within the Hartree and Hartree-Fock methods are shown in Figure 8.7.2. The conditional electron probability distributions $n(r)$ of $N-1$ electrons around an electron with given

spin situated at $r = 0$. Within the Hartree approximation, all electrons are treated as independent, therefore $n(r)$ is structureless. However, within the Hartree-Fock approximation, the N-electron wavefunction reflects the Pauli exclusion principle and near the electron at $r = 0$ the exchange hole can be seen where the the density of spins equal to that of the central electron is reduced. Electrons with opposite spins are **unaffected** (not shown).

Summary

So, within the limitations of the HF, frozen-orbital model, the ionization potentials (IPs) and electron affinities (EAs) are given as the negative of the occupied and virtual spin-orbital energies, respectively. This statement is referred to as Koopmans' theorem; it is used extensively in quantum chemical calculations as a means of estimating ionization potentials (Equation 8.7.15) and Electron Affinities (Equation 8.7.16) and often yields results that are qualitatively correct (i.e., ± 0.5 eV). In general Hartree-Fock theory gives a great first order solution (99%) to describing multi-electron systems, but that last 1% is still too great for quantitatively describing many aspects of chemistry and more sophisticated approaches are necessary. These are discussed elsewhere.

Contributors

- Template:ContribAukland
- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Jack Simons (Henry Eyring Scientist and Professor of Chemistry, U. Utah) Telluride Schools on Theoretical Chemistry

8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.8: Term Symbols Gives a Detailed Description of an Electron Configuration

Conveniently for chemists, an atom's electronic state depends entirely on its unfilled sub shells. Because electrons distribute themselves in a symmetric manner, the inner shell electrons end up canceling out each other's momenta. For an atom in the configuration $1s^2 2s^2 p^2$, only the two p-electrons matter. For an atom in the configuration $1s^2 2s^1 2p^1$, we have to examine the 2s and 2p electrons. Atoms have quantum numbers that are directly analogous to the electronic quantum numbers.

The Total Orbital Angular Momentum Quantum Number: L

One might naively think that you could get the total angular momentum of an atom by simply adding up the l values of the individual electrons. The problem with this idea is that the angular momenta of the various electrons are not necessarily pointing in the same direction. If two electrons are revolving in the same direction as each other, you would add their l values.

$$L = \sum_{i}^{n} l_i \tag{8.8.1}$$

If they were revolving opposite to each other, you would subtract them. If they are revolving at some off - angle relative to each other, you would partially subtract them. To figure out all of the possible combinations of l for a pair of electrons, simply add them together to get the co-aligned case, subtract them to get the opposing case, and then fill in all the numbers in between to get the off-angle cases. If you prefer to have a formula, you can use this:

$$L = |l_1 + l_2|, |l_1 + l_2\text{-}1|, \ldots, |l_1\text{-}l_2| \tag{8.8.2}$$

Example 8.8.1: Carbon

What are the possible L values for the electrons in the $1s^2 2s^2 2p^2$ configuration of carbon?

Solution

Both open-shell electrons (i.e., the 2p electrons) are $l = 1$. The possible combinations are 2, 1, 0.

Example 8.8.2

What are the possible L values for the electrons in the $[Xe]6s^2 4f^1 5d^1$?

Solution

We have an $l = 3$ and an $l = 2$ electron.

$$3 + 2 = 5 \tag{8.8.3}$$

and

$$3\text{-}2 = 1 \tag{8.8.4}$$

The possible combinations are 5, 4, 3, 2, 1

The Total Magnetic Quantum Number: M_l

M_l is the total z-component of all of the relevant electrons' orbital momentum. Where L told you how much angular momentum there was, M_l tells you which direction it is pointing. Like L, a given configuration can have several possible values of M_l, depending on the electrons' relative orientation. Unlike L, M_l is allowed to have negative values. To list the possible M_l values for a two electron system, take the case where both m_l are positive, then take the case where they are both negative, and then fill in the numbers in between.

$$M_l = m_{l1} + m_{l2}, m_{l1} + m_{l2}\text{-}1, \ldots, \text{-}m_{l1}\text{-}m_{l2} \tag{8.8.5}$$

Example 8.8.3: Zirconium ground state

What are the possible values M_l of a zirconium atom with the $[Kr]5s^2 4d^2$ electron configuration?

Solution

Both open-shell electrons (i.e., the 4d electrons) are $l = 2$, so the values are 4, 3, 2, 1, 0, -1, -2, -3, -4.

The Total Spin Magnetic Quantum Number: M_s

M_s is the sum total of the z-components of the electrons' inherent spin. Do not confuse it with M_l, which is the sum total of the z-component of the **orbital angular momentum**. It is easily computed by finding all of the possible combinations of m_s. Since m_s for each individual electron can only be +1/2 or - 1/2, this isn't too complicated.

$$M_s = m_{s1} + m_{s2}, m_{s1} + m_{s2}\text{-}1, ..., m_{s1}\text{-}m_{s2} \tag{8.8.6}$$

Example 8.8.4: Carbon Ground State

What are the M s values for $1s^2 2s^2 2p^2$?

Solution

$M_s = 1, 0, \text{-}1$

The Total Intrinsic Spin Quantum Number: S

The sum total of the spin vectors of all of the electrons is called S. The difference between S and M_s is subtle, but vital for understanding multiplicity. M_s measures the total z-component of the electrons' spins, while S measures the entire resultant vector. The values of S are computing in a manner very similar to M_s. Because S measures the magnitude of a vector, it cannot ever be negative.

$$S = |s_1 + s_2|, |s_1 + s_2\text{-}1|, ..., |s_1\text{-}s_2| \tag{8.8.7}$$

Example 8.8.5: The Hydrogen Ground State

Find S for $1s^1$.

Solution

S clearly has to be ½ since that's the spin of a single electron and there's only one electron to worry about.

Example 8.8.6: The Beryllium Excited State

Find S for $1s^2 2s^1 2p^1$.

Solution

$S = 1, 0$

Example 8.8.7: The Carbon Ground State

Find S for carbon atoms with the $1s^2 2s^2 2p^2$ electron configuration.

Solution

$S = 1, 0$ This is the same as the previous problem. Notice that S is not affected by which orbitals the electrons are in. S only cares about how many **open-shell electrons** (i.e., unpaired electrons) there are, not about where they are. This is because S measures an inherent property of the electrons themselves

Example 8.8.8

Find S for nitrogen atoms with the $1s^2 2s^2 2p^3$ electron configuration.

Solution

We have not done a three electron case yet, but they are not hard. Find all the combinations for a single pair first, and then factor in the third electron. For two electrons, we already know that the two possible S values are S=1,0. A third electron can either add or subtract ½ from these values, so the final S can be $S = 3/2, 1, 1/2$.

The Total Angular Momentum Quantum Number J

The total orbital angular momentum of an atom (measured in terms of L), and the total spin angular momentum of an atom (measure in S) combine to form total angular momentum, a number that is quantized by the number J. L and do not necessarily have to be pointing in the same direction (Figure 8.8.1), so J can range from $L + S$ to $|L–S|$.

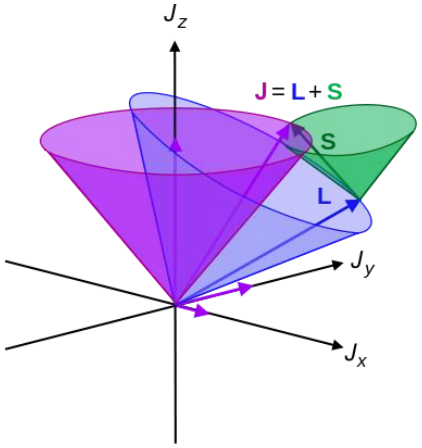


Figure 8.8.1: Illustration of L-S coupling. Total angular momentum J is purple, orbital L is blue, and spin S is green.

Table 8.8.1: Quantum Numbers and associated ranges

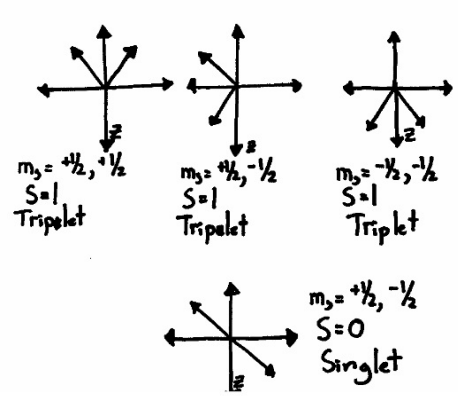
Symbol	Name	Allowed Range
L	Total orbital angular momentum	$\|l_1 + l_2\|, ..., \|l_1\text{-}l_2\|$
M_l	Magnet Quantum number	$[m_{l1} + m_{l2}, ..., \text{-}m_{l1}\text{-}m_{l2}]$
M_s	Spin Magnetic Quantum Number	$\|m_{s1} + m_{s2}\|, ..., \|m_{s1}\text{-}m_{s2}\|$
S	Inherent Spin Number	$\|s_1 + s_2\|, ..., \|s_1\text{-}s_2\|$
M	Multiplicity	2S+1
J	Total Angular Momentum	$L + S, ..., \|L - S\|$

Multiplicity

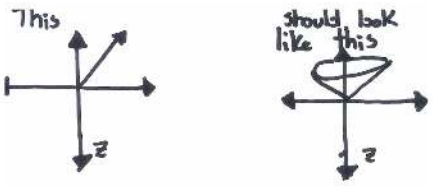
Multiplicity is a simple - sounding concept that defies simple explanations. You know from your first - year education that a singlet is when the net spin (S) is equal to zero (e.g. all the electrons are spin paired), and a triplet happens when the net spin is equal to 1 (e.g. two electrons are pointing in the same direction). They are called “singlet” and “triplet” because there are 3 ways to combine a pair of electron spins to get S=1, but only one way to get $S = 0$. If you draw a picture of the possible ways that two electrons can arrange their spins, you get something like this:



Figure 8.8.1). When we call an electron spin “up,” what we really mean is that it has a positive z-component (e.g. $m_s = +½$).



While this picture is an improvement over the simple up-down model, it is still misleading. The three spin axes of an electron share a Heisenberg Uncertainty Principle. The more you know about S_x, the less you can know about either S_y or S_z. The same is true for all other combinations of x, y and z. Since we have defined S_z as a known and fixed value, the values of S_x and S_y must be **completely unknown**. This causes the x and y orientations of the electrons to become smeared out across all possible values:



Constructing Term Symbols

Atomic term symbols contain two pieces of information. They tell you the total orbital angular momentum of the atom (L), and they tell you the multiplicity (M). L is denoted by a simple code, similar to the code used to delineate the types of atomic orbitals:

- $L = 0 \rightarrow S$
- $L = 1 \rightarrow P$
- $L = 2 \rightarrow D$
- $L = 3 \rightarrow F$

Note that while the notation is similar, L does NOT say anything about what types of orbitals the electrons are in. A state that has the term symbol P does NOT necessarily have an open p-shell. The multiplicity is indicated by appending a number to the upper left of the symbol. A $L = 2$, $M = 3$ state would be represented by ${}^3D$. The secret to writing the term symbols for an atom is to discover what combinations of L and M are possible for that atom with that specific electronic configuration. An atom that only has closed shells will always be $1S$.

Each term symbol represents a discrete energy level. We can place these levels in the correct order by using these simple rules:

- 1: High multiplicity values mean low energy
- 2: If there is a tie, high L values mean low energy
- 3a: If there is still a tie and the shell is less than half full, then low J means low energy
- 3b: If the shell is more than half full, then high J means low energy

These rules reliably predict the ground state. They have only erratic agreement with experiment when ordering the other levels.

Example 8.8.9: Hydrogen Ground State

What are the term symbols for the microstates possible for $1s^1$ electronic configuration of hydrogen?

Solution

Since there is only one electron, this is a simple problem. $L = 0$ and $M = 1$, so the only possible term symbol is ${}^2S$. With only one electron, $S = ½$, so $J = 0 + ½ = ½$. Only one microstate exists for this configuration and it has a term symbol of ${}^2S_{½}$.

Example 8.8.10: Boron

What are the term symbols for the microstates possible for $1s^2 2s^2 2p^1$ electronic configuration of boron?

Solution

There still only one open shell electron, so $L = 1$, $M = 1$ and $S = ½$. We get a term symbol of the type ^2P, which gets split into separate symbols because $J = 3/2$ and $1/2$. Two possible microstates exist for this system with term symbols of $^2P_{3/2}$ and $^2P_{1/2}$.

Example 8.8.11: Beryllium Excited State

What are the term symbols for the microstates possible for the $1s^2 2s^1 2p^1$ excited-state electronic configuration of Beryllium?

Solution

Now we have two electrons to worry about. Since $l_1 = 0$ and $l_2 = 1$, the only possible combination is $L = 1$. The possible combinations of S are: $S = 1, 0$. This means that $M = 3$ or $M = 1$. The term symbols will be of the form ^1P and ^3P. For the ^1P state, $L = 1$ and $S = 0$, so $J = 1$. For the second state, $L = 1$ and $S = 1$, so $J = 2, 1, 0$. There are four microstates for this configuration with term symbols of $^1P_1$ and $^3P_2$, $^3P_1$, and $^3P_0$.

Example 8.8.12: Zirconium

What are the term symbols for the microstates possible for the $[Kr]5s^2 4d^2$ ground-state electronic configuration of zirconium?

Solution

This is a much harder problem. We will need to use a special technique to disentangle all of the possible combinations of L and M. Let's start be listing the relevant quantum numbers for the two open-shell electrons:

$l_1 = 2$	$l_2 = 2$
$m_{l1} = 2, 1, 0, -1, -2$	$m_{l2} = 2, 1, 0, -1, -2$
$m_{s1} = ½, -½$	$m_{s1} = ½, -½$

Let's combine these numbers to generate the atomic quantum numbers:

$$L = 4, 3, 2, 1, 0 \tag{8.8.8}$$

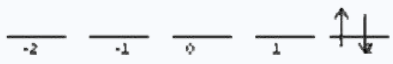
$$M_l = 4, 3, 2, 1, 0, -1, -2, -3, -4 \tag{8.8.9}$$

$$M_s = 1, 0 \tag{8.8.10}$$

We know that there will at least one each of S, P, D, F and G. It isn't immediately clear which of these will be singlets and which will be triplets. To figure this out, we need to systematically examine the possible microstates. It turns out that there are **45** possible ways to put distribute two electrons between 5 d orbitals. That's a lot! The easiest way to list the states is to organize them into a chart:

$M_s = -1$	$M_s = 0$	$M_s = +1$

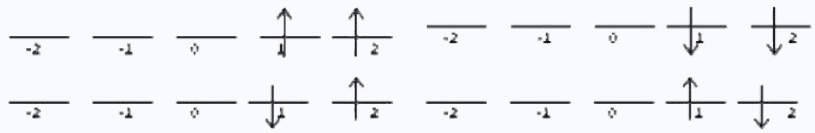
Attacking the chart one row at a time. Ask yourself, how many ways can I arrange the two electrons to give me $M_l = 4$? It turns out there is only one possible combination that does this:



This state is has $M_s = 0$. This means that there is only 1 microstate that corresponds to $M_l = 4$ and $M_s = 0$, and none that correspond to $M_l = 4$ and $M_s = \pm$-1. We add this microstate to the chart like this:

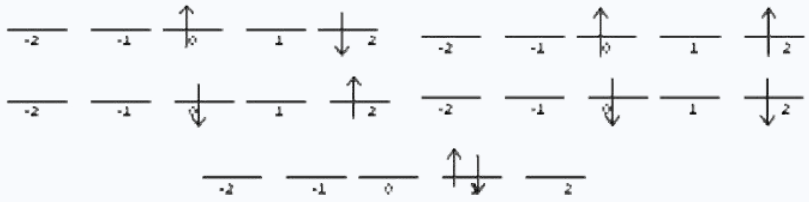
M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0

Now, how many ways are there to get $M_l = 3$?



M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1

For $M_l = 2$, we find the following states:



M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1

You should be able to draw the microstates on your own by now. You should find 8 states, four of which are singlet and four of which are triplets.

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1
1	2	4	2

There are only nine possible ways to arrange the electrons to get $M_l = 0$

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	**1**	0
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2

The rest of the chart will be symmetric to the first half, so we do not need to do any more work:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
-4	0	1	0

Now that we have a listing of all of the microstates, we need to figure out how to divide them up between the term symbols. It turns out that each term symbol can have, at most, one microstate from each box on the chart. The term symbols always end up claiming a "box" of microstates, centered on the middle of the chart. This is easier shown than said.

Attacking the chart from the top, we can see that the $M_l = 4$ $M_s = 0$ state clearly belongs to a ^1G symbol. The $M_l = -4$ $M_s = 0$ box also clearly belongs to this symbol. If I connect these states with a "box," I get this:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
~~4~~	~~0~~	~~1~~	~~0~~
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
~~-4~~	~~0~~	~~1~~	~~0~~

The strickthough configurations all belong to the ^1G state. Let's subtract them from the chart to indicate that they are not available for other term symbols.

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1

The next row indicates a $L = 3$ state. Because there are three M_s values available, this is a **triplet**. The term symbol will be ^3F, which reduces the chart down to

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	2	4	2
0	2	5	2
-1	2	4	2

The next state will be ^1D. Leaving us with

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	1	1	1
0	1	2	1
-1	1	1	1

Next is a ^3P state. The chart is getting pretty small now wtih

M_l	$M_s = 0$
	0

The last remaining microstate comprises the ^1S term symbol.

The total listing is

$$^1G,\ ^3F,\ ^1D,\ ^3P,\ ^1S.$$

Assigning J values, we get

$$^1G_4,\ ^3F_4,\ ^3F_3,\ ^3F_2,\ ^1D_2,\ ^3P_2,\ ^3P_1,\ ^3P_0,\ ^1S_0$$

If you can do this problem, you can do almost any atomic term symbol.

Note

The secret to writing the term symbols for an atom is to discover what combinations of L and M are possible for that atom with that specific electronic configuration.

Shortcuts

There is a deep symmetry that connects different electronic configurations. It turns out that a p^1 configuration has the same term symbols as a p^5. Similarly, $p^2 = p^4$. A similar relationship can be used to figure out high electron number term symbols for the d and f orbitals.

Contributors

- Mattanjah de Vries (Chemistry, University of California, Santa Barbara)

8.8: Term Symbols Gives a Detailed Description of an Electron Configuration is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number

We need to be able to identify the electronic states that result from a given electron configuration and determine their relative energies. An electronic state of an atom is characterized by a specific energy, wavefunction (including spin), electron configuration, total angular momentum, and the way the orbital and spin angular momenta of the different electrons are coupled together. There are two descriptions for the coupling of angular momentum. One is called **j-j coupling**, and the other is called **L-S coupling**. The j-j coupling scheme is used for heavy elements (z > 40) and the L-S coupling scheme is used for the lighter elements. Only L-S coupling is discussed below.

L-S Coupling of Angular Momenta

L-S coupling also is called R-S or Russell-Saunders coupling. In L-S coupling, the orbital and spin angular momenta of all the electrons are combined separately

$$L = \sum_i l_i \tag{8.9.1}$$

$$S = \sum_i s_i \tag{8.9.2}$$

The total angular momentum vector then is the sum of the total orbital angular momentum vector and the total spin angular momentum vector.

$$J = L + S \tag{8.9.3}$$

The total angular momentum quantum number parameterizes the total angular momentum of a given particle, by combining its orbital angular momentum and its intrinsic angular momentum (i.e., its spin). Due to the spin-orbit interaction in the atom, the orbital angular momentum no longer commutes with the Hamiltonian, nor does the spin.

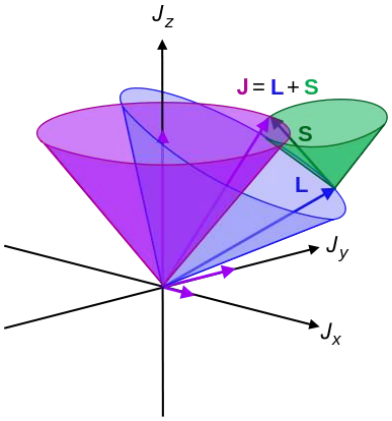


Figure 8.9.1: "Vector cones" of total angular momentum $\boldsymbol{J}$ (purple), orbital $\boldsymbol{L}$ (blue), and spin $\boldsymbol{S}$ (green). The cones arise due to quantum uncertainty between measuring angular momentum components (see vector model of the atom). (Public Domain; Maschen).

However the total angular momentum $\boldsymbol{J}$ does commute with the Hamiltonian and so is a constant of motion (does not change in time). The relevant definitions of the angular momenta are:

Orbital Angular Momentum

$$|\vec{L}| = \hbar\sqrt{\ell(\ell+1)} \tag{8.9.4}$$

with its projection on the z-axis

$$L_z = m_\ell \hbar \tag{8.9.5}$$

Spin Angular Momentum

$$|\vec{S}| = \hbar\sqrt{s(s+1)} \tag{8.9.6}$$

with its projection on the z-axis

$$S_z = m_s \hbar \tag{8.9.7}$$

Total Angular Momentum

$$|\vec{J}| = \hbar\sqrt{j(j+1)} \tag{8.9.8}$$

with its projection on the z-axis

$$J_z = m_j \hbar \tag{8.9.9}$$

where

- l is the azimuthal quantum number of a single electron,
- s is the spin quantum number intrinsic to the electron,
- j is the total angular momentum quantum number of the electron,

The quantum numbers take the values:

$$m_\ell \in \{-\ell, -(\ell-1) \cdots \ell-1, \ell\}, \quad \ell \in \{0, 1 \cdots n-1\} \tag{8.9.10}$$
$$m_s \in \{-s, -(s-1) \cdots s-1, s\}, \tag{8.9.11}$$
$$m_j \in \{-j, -(j-1) \cdots j-1, j\}, \tag{8.9.12}$$
$$m_j = m_\ell + m_s, \quad j = |\ell + s| \tag{8.9.13}$$

and the magnitudes are:

$$|\mathbf{J}| = \hbar\sqrt{j(j+1)} \tag{8.9.14}$$
$$|\mathbf{J_1}| = \hbar\sqrt{j_1(j_1+1)} \tag{8.9.15}$$
$$|\mathbf{J_2}| = \hbar\sqrt{j_2(j_2+1)} \tag{8.9.16}$$

in which

$$j \in \{|j_1 - j_2|, |j_1 - j_2| - 1 \cdots j_1 + j_2 - 1, j_1 + j_2\} \tag{8.9.17}$$

This process may be repeated for a third electron, then the fourth etc. until the total angular momentum has been found.

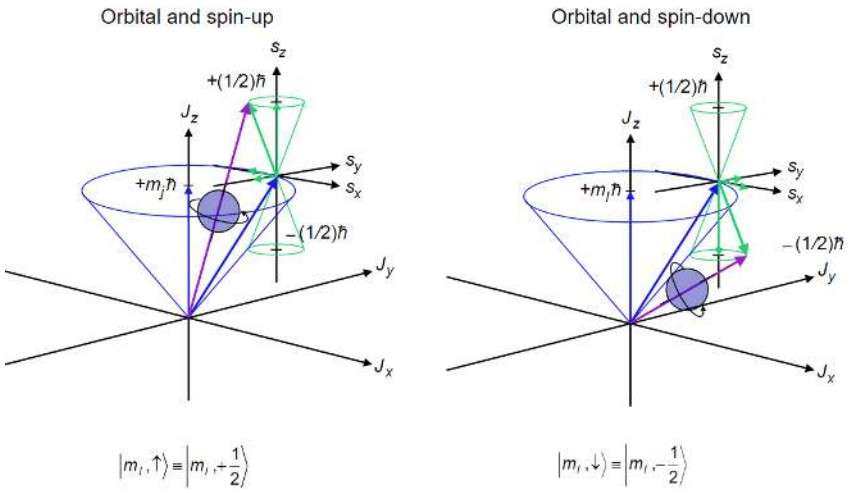


Figure 8.9.2: Vector model of total angular momentum: spin and orbital coupling (spin-1/2 particles). (Public Domain; Maschen).

The result of these vector sums is specified in a code that is called a Russell-Saunders term symbol, and each term symbol identifies an energy level of the atom. Consequently, the energy levels also are called terms. A term symbol has the form $^{2s+1}L_J$ where the code letter that is used for the total orbital angular momentum quantum number L = 0, 1, 2, 3, 4, 5 is S, P, D, F, G, H, respectively. Note how this code matches that used for the atomic orbitals. The superscript $2S+1$ gives the spin multiplicity of the state, where S is the total spin angular momentum quantum number. The spin multiplicity is the number of spin states associated

with a given electronic state. In order not to confuse the code letter S for the orbital angular momentum with the spin quantum number S, you must examine the context in which it is used carefully. In the term symbol, the subscript J gives the total angular momentum quantum number. Because of spin-orbit coupling, only J and M_j are valid quantum numbers, but because the spin-orbit coupling is weak L, M_l, S, and m_s still serve to identify and characterize the states for the lighter elements.

For example, the ground state, i.e. the lowest energy state, of the hydrogen atom corresponds to the electron configuration in which the electron occupies the 1s spatial orbital and can have either spin α or spin β. The term symbol for the ground state is $^2S_{1/2}$, which is read as “doublet S 1/2”. The spin quantum number is 1/2 so the superscript 2S+1 = 2, which gives the spin multiplicity of the state, i.e. the number of spin states equals 2 corresponding to α and β. The S in the term symbol indicates that the total orbital angular momentum quantum number is 0 (For the ground state of hydrogen, there is only one electron and it is in an s-orbital with $l = 0$). The subscript ½ refers to the total angular momentum quantum number. The total angular momentum is the sum of the spin and orbital angular momenta for the electrons in an atom. In this case, the total angular momentum quantum number is just the spin angular momentum quantum number, ½, since the orbital angular momentum is zero. The ground state has a degeneracy of two because the total angular momentum can have a z-axis projection of $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$, corresponding to m_J = +1/2 or -1/2 resulting from the two electron spin states α and β. We also can say, equivalently, that the ground state term or energy level is two-fold degenerate.

Exercise 8.9.1

Write the term symbol for a state that has 0 for both the spin and orbital angular momentum quantum numbers.

Exercise 8.9.2

Write the term symbol for a state that has 0 for the spin and 1 for the orbital angular momentum quantum numbers

Contributors

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

8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.E: Multielectron Atoms (Exercises)

Solutions to select questions can be found online.

8.4

Prove the speed of electron in first Bohr orbit is $e^2/4\pi\epsilon_0\hbar = 2.188 \times 10^6 m \bullet s^{-1}$. The speed is in atomic units.

Solution

Use following formula in order to make the calculations

$$v = \frac{\hbar}{m_e a_0}$$

$$v = \frac{\hbar}{m_e}\left(\frac{m_e e^2}{4\pi\epsilon_0\hbar^2}\right)$$

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

Substituting values get the following:

$$v = \frac{(1.6022 \times 10^{-19}\ C)^2}{(1.1127 \times 10^{-10} C^2 \cdot J^{-1} \cdot m^{-1})(1.0546 \times 10^{-34}\ J \cdot s)}$$

$$v = 2.1877 \times 10^6\ m \cdot s^{-1}$$

This is the speed in atomic units. Are either of the two separate terms in the two term helium Hartree-Fock Orbital acceptable wavefunctions by themselves?

$$\psi(r) = 0.81839e^{-1.44608r} + 0.52072e^{-2.86222r}$$

8.15

Explain why:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1dr_2d\sigma_1d\sigma_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1dr_2d\sigma_1d\sigma_2}$$

can be rewritten as:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1dr_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1dr_2}$$

Solution

The Hamiltonian does not depend on spin, so the spin integral can be factored out.

8.16

Why must you distinguish the two electrons in separated hydrogen atoms?

Solution

They must be distinguished from one another because they each belong to a separate nucleus, not to an individual one.

8.17

In both the Hartree-Fock approximation and hydrogen atomic wavefunction, why is the angular dependence the same?

Solution

Since the Hamiltonian used in the approximation only depends on r, the angular dependence is not affected in the Hartree-Fock approximation. So both the Hartree-Fock approximation and hydrogen atom will have the same angular dependence.

8.20

Given the two electron determinate wavefunction below, determine if the spin component of the system is symmetric, anti-symmetric, or neither.

$$\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\alpha(2) \end{vmatrix}$$

Solution

We have to solve the determinate.

$$1s1\alpha(2)1s2\beta(2) - 1s1\beta(2)1s1\alpha(2)$$

Now we have to factor out the spatial part from the spin part.

$$1s11s2[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

We are focused on the spin part and by observation, we can tell that the spin component is anti-symmetric.

8.23

Given $\hat{S}_z\alpha = \frac{\hbar}{2}\alpha$ and $\hat{S}_z\alpha = \frac{-\hbar}{2}\beta$, show that Ψ_{200} is an eigenfunction of $S_{z,total} = \hat{S}_{za} + \hat{S}_{zB}$.

Solution

Start with $\Psi_{200} = C(\psi_{2sa} + \psi_{2sB})$.

$$\hat{S}_{z.total}\Psi = C(\hat{S}_{za} + \hat{S}_{zB})[\psi_{2sa} + \psi_{2sB}]$$

$$= C\left(\frac{\hbar}{2} - \frac{\hbar}{2}\right)[\psi_{2sa} + \psi_{2sB}]$$

$$= 0$$

8.24

For the wavefunction:

$$\psi = \begin{vmatrix} \psi_A(1) & \psi_A(2) \\ \psi_B(1) & \psi_B(2) \end{vmatrix}$$

discuss the effect on the wavefunction of (a) swapping rows of the matrix and (b) swapping columns of the matrix.

Solution

Let's expand the determinant to inspect the complete multi-electron wavefunction:

$$\psi = \psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1)$$

If we swap rows:

$$\psi_{RowSwap} = \psi_A(2)\psi_B(1) - \psi_A(1)\psi_B(2) = -\psi$$

If we swap columns:

$$\psi_{ColumnSwap} = \psi_A(2)\psi_B(1) - \psi_A(1)\psi_B(2) = -\psi$$

Conclusion: swapping the either two rows or two columns of a Slater determinant changes the sign of the wavefunction.

8.27

What are the term symbols for carbon and oxygen atoms in the ground state?

Solution

Carbon: The electron configuration for carbon at ground state (lowest energy) is $1s^2 2s^2 2p^2$

Since the 1s and 2s orbitals are completely filled, they can be neglected when calculating for S. For the lowest energy, you need to use the highest values of S and L, therefore we find that S= 1/2 +1/2=1 and L=1 which corresponds to the letter P. Since the 2p orbital is less than half-way filled, we use J=|L-S|=|1-1|=0.

The term symbol is $^{2S+1}L_J$ which is $^3P_0$ for the ground-state of carbon atoms.

Oxygen: The electron configuration for oxygen at ground state (lowest energy) is $1s^2 2s^2 2p^4$

Again, the 1s and 2s orbitals may be neglected when calculating for S.

$$S = 1/2 + 1/2 + 1/2 - 1/2 = 1$$

The last electron has a spin down due to the Pauli Exclusion Principle.

L=1 which corresponds to the letter P.

Since the 2p orbital for oxygen is more than half-filled,

$$J = L + S = 2$$

The term symbol for the ground-state oxygen atom is $^3P_2$

8.28

Show that the number of sets of magnetic quantum number (m_l) and spin quantum number (m_s) associated with any term symbol is equal to $(2L + 1)(2S + 1)$. Apply this result to the np^2 case and show that symbol ^1S, ^3P and ^1D account for all the possible sets of magnetic quantum numbers and spin quantum numbers

8.29

Calculate all possible numbers of term symbol for an np^1 electron configuration.

Solution

$$N = \frac{G!}{e!(G-e)!}$$

where G is the highest number of electrons that an orbital can hold and e is the highest number of electrons that a subshell can hold

$$N = \frac{6!}{2!(6-2)!} = 15$$

8.30

Determine the ground state term symbol for the electron configuration of the Halogens.

Solution

Halogens have the electron configuration np^5 we can determine the term symbols for this configuration by mapping out all possible configurations the electrons can fit into the six spin orbitals. To quickly determine how many possible combinations there are we can use a statistical method of $N_{Comb.} = \binom{spinorbitals}{electrons}$

$$N_{comb} = \binom{6}{5} = \frac{6!}{5!(6!-5!)} = 6$$

Now we know that there are 6 different configurations that we can map out to determine the term symbols. Since we are working with the p orbital we know $l = 1$ and $m_s = -1,\ 0,\ 1$. I will denote spin using α as spin up $+\frac{1}{2}$ and β as spin down $-\frac{1}{2}$. M_L is the sum of the m_s values corresponding to the number of electrons in that energy level. For example if you have $\alpha\beta$ in $m_s = +1$ only, you then have 2 electrons in $m_s = +1$ resulting in $M_L = +1 + 1 = 2$. M_s is the sum of the spin up and spin down values.

+1	0	-1	M_L	M_s
$\alpha\beta$	$\alpha\beta$	α	+1	$+\frac{1}{2}$
$\alpha\beta$	α	$\alpha\beta$	0	$+\frac{1}{2}$
α	$\alpha\beta$	$\alpha\beta$	-1	$+\frac{1}{2}$
$\alpha\beta$	$\alpha\beta$	β	+1	$-\frac{1}{2}$
$\alpha\beta$	β	$\alpha\beta$	0	$-\frac{1}{2}$
β	$\alpha\beta$	$\alpha\beta$	-1	$-\frac{1}{2}$

Now we need to determine the maximum value of M_L and M_s. Looking at the table we see that

$$max\ M_L = 1$$
$$max\ M_s = \frac{1}{2}$$

From this we know our maximum value of L and S

$$L_{max} = 1$$
$$S_{max} = \frac{1}{2}$$

Our possible values for L and S are

$$L = 1,\ 0$$
$$S = \frac{1}{2}$$

Since S is only $\frac{1}{2}$ we know we can only have doublet term symbols since $2\left(\frac{1}{2}\right) + 1 = 2$. L ranges from 1 to 0 so our possible corresponding symbols will be P and S. This leaves us with the possibility of having

$$^2P,\ ^2S$$

To figure out what is there we start with the term symbol that has the largest L value, with is the P. We see that for P, $L = 1$ and $S = \frac{1}{2}$. For a value of $L = 1$ our m_l can be $+1,\ 0,\ -1$ and for an $S = \frac{1}{2}$ our $m_s = +\frac{1}{2},\ -\frac{1}{2}$. In the table above all rows that contain these possible

combination include every row. Therefore all of the configurations are contained in this doublet P term symbol. Including values of J we know that $L+S \geq J \geq |L-S|$. Since $L=1$ and $S=\frac{1}{2}$ our final term symbols are

$$^2P_{\frac{3}{2}},\ ^2P_{\frac{1}{2}}$$

Hund's rules say that when L and S are the same with a subshell more than half filled, you look to the largest J value to be the most stable. Therefore our final answer and the ground state term symbol for halogens is

$$\boxed{^2P_{\frac{3}{2}}}$$

8.33

^2P, ^2D, and ^4S are the term symbols for an atom with the np^3 electron configuration. Using the term symbols for the np^3 electron configuration, calculate the J values associated with each of the term symbol. Then find out which term symbol represent the ground state.

Solution

To calculate J we use this equation

$$J = L + S$$

This equation can be further expanded to be

$$J = L+S, L+S-1, L+S-2, \ldots |L-S|$$

Term Symbol	L	S	J	Full Term Symbol
^2P	1	$\frac{1}{2}$	$\frac{3}{2}, \frac{1}{2}$	$^2P_{3/2}$ and $^2P_{1/2}$
^2D	2	$\frac{1}{2}$	$\frac{5}{2}\ \frac{3}{2}$	$^4D_{5/2}$ and $^4D_{3/2}$
^4S	0	$\frac{3}{2}$	$\frac{3}{2}$	$^4S_{3/2}$

8.34

What are the ground state electron configuration and term symbol for Calcium?

Solution

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

or

$$[Ar]4s^2$$

For the term symbol:

Spin Multiplicity: S = 0 (all electrons paired)

$$J = S + L = 0$$

There is only one valid value of J, so the term symbol for this configuration is

$$^{2S+1}L_J = {}^1S0$$

$$2S + 1 = 1$$

Orbital Angular Multiplicity: L = 0 because we consider an s orbital. This corresponds to S.

8.34

Find the ground state term symbol for Ca.

Solution

ns^2 electron configurations have the term symbol $^1S_0$, so the term symbol for Ca in the ground state is $^1S_0$.

8.36

Write the electron configuration for vanadium and use this information to find the ground-state term symbol for V.

Solution

The electron configuration for vanadium is $[Ar]3d^3 4s^3$

Spin Multiplicity: The electron configuration predicts three unpaired electrons, so

$$S = 1/2 + 1/2 + 1/2 = 3/2$$

and the multiplicity of $2S + 1$ predicts that this will be a quartet. Orbital Angular Momentum: The electron configuration predicts three electrons with $l = 2$ and the rest so not contribute, so $L = 1 + 1 + 1 = 3$, which is an F state

The ground-state term symbol for vanadium is $^4F_{3/2}$ since vanadium has a half-filled 3d subshell.

- Total Angular Momentum: The shell is half full

8.36

What is the ground-state term symbol for Ne.

Solution

The term symbol is $^{2S+1}L_J$

where

S is the total electron spin L is the total orbital angular momentum

so $2S+1 = 2 \cdot 0 + 1 = 1$ and $J = 0 + 0 = 0$. So the term symbol for Ne is $^1S_0$.

and

$$J = L + S$$

The electron configuration for:Ne is $1s^2 2s^2 2p^6$ since Ne has spherical symmetry, we get:

$$L = 0 + 0 = S$$

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} = 0$$

8.37

Looking at the $1s2p$ electron configuration for He. Solve for the term symbols (states) of the Helium configuration and the degeneracies. If electron spin orbit coupling is included, what effect will this have?

Solution

There are two possible sets of m_l and m_s for the ns electron and six possible sets of m_l and m_s for the np electron, so there are 2 × 6 = 12 possible sets of m_l and m_s for the system. We can denote values for the electron in the ns orbital as m_{1j} and those for the electron in the np orbital as m_{2j}. The allowed values are given below:

Microstate	$m_l(1)$	$m_s(1)$	$m_l(2)$	$m_s(2)$	M_L	M_S	M_J
	Electron 1 in $1s$ *orbital*		*Electron 2 in* $2p$ *orbital*		*Combined Angular Momenta of both Electrons*		
1	0	+ 1/2	1	+ 1/2	1	1	2
2	0	- 1/2	1	+ 1/2	1	0	0
3	0	+ 1/2	1	- 1/2	1	0	0
4	0	- 1/2	1	- 1/2	1	-1	1
5	0	+ 1/2	0	+ 1/2	0	1	0
6	0	- 1/2	0	+ 1/2	0	0	1
7	0	+ 1/2	0	- 1/2	0	0	0
8	0	- 1/2	0	- 1/2	0	-1	0
9	0	+ 1/2	-1	+ 1/2	-1	1	0
10	0	- 1/2	-1	+ 1/2	-1	0	-1
11	0	+ 1/2	-1	- 1/2	-1	0	-2
12	0	- 1/2	-1	- 1/2	-1	-1	-2

Entries 1, 2, 4, 5, 6, 8, 9, 10, and 12 correspond to L = 1 and S = 1, or ^{3}P term symbol, and entries 3, 7, and 11 correspond to L = 1 and S = 0, which is a ^{1}P term symbol. The values of J can be derived from the table or by using

$$J = (L + S), (L + S - 1), (L + S - 2), \ldots\ldots\ldots, (|L + S|),$$

The final results given the term symbols below:

$^3P_2$ $^3P_1$ $^3P_0$ $^1P_1$

($\boldsymbol{L}$ + $\boldsymbol{S}$) ($\boldsymbol{L}$ + $\boldsymbol{S}$ - 1) (|$\boldsymbol{L}$ - $\boldsymbol{S}$|) (|$\boldsymbol{L}$ + $\boldsymbol{S}$|)

The states corresponding to this electron configuration and their degeneracies are:

Term symbol: $^3P_2$ $^3P_1$ $^3P_0$ $^1P_1$

Degeneracy: 5 3 1 3

According to Hund's rule, the ground state $^3P_0$. Including the effect of spin-orbit coupling removes the degeneracy of the electronic states, and no spin orbit coupling splits the lines in an atomic spectra.

8.E: Multielectron Atoms (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States

The Aufbau section discussed how that electrons fill the lowest energy orbitals first, and then move up to higher energy orbitals only after the lower energy orbitals are full. However, there a problem with this rule. Certainly, 1s orbitals should be filled before 2s orbitals, because the 1s orbitals have a lower value of n, and thus a lower energy. What about the three different 2p orbitals? In what order should they be filled? The answer to this question involves Hund's rule, which make a lot more sense in the context of generated term symbols that are used to combine the various L and S values represent vector additions of possible microstates.

Hund's Rules

1. State with the largest value of S is most stable and stability decreases with decreasing S.
2. For states with same values of S, the state with the largest value of L is the most stable.
3. If states have same values of L and S then, for a subshell that is less than half filled, state with smallest J is most stable; for subshells that are more than half filled, state with largest value of J is most stable.

Example 8.10.1

Rank these terms associated with an electronic configuration of an atom based on energy (via Hund's rules):

$$^3D,\ ^3P,\ ^3S,\ ^1D,\ ^1P,\ ^1S$$

Hund's First Rule (Maximize Spin Multiplicity)

According to the first rule, electrons always enter an empty orbital before they pair up. Electrons are negatively charged and, as a result, they repel each other. Electrons tend to minimize repulsion by occupying their own orbitals, rather than sharing an orbital with another electron. Furthermore, quantum-mechanical calculations have shown that the electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus.

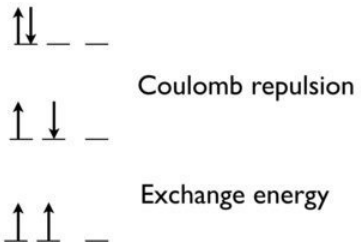


Figure 8.10.1: Origin of Hund's First Rule. Hund's first rule is that for a given electron configuration, a state in which the spins are unpaired has lower total energy than one in which the spins are paired.

There's a Coulomb repulsion between two electrons to put them in the same orbital (a spin pairing energy often discussed in Crystal Field Theory). However, there's also a quantum mechanical effect. The *exchange energy* (which is favorable) increases with the number of possible exchanges between electrons with the same spin and energy. In transitioning from the top state to the middle state of Figure 8.10.1, we remove the Coulomb repulsion between electrons in the same orbital. Moreover, In transitioning from the middle state to the bottom state (most stable state predicted by Hund's first rule), we *gain* the *exchange energy*, because these two electrons are indistinguishable.

Hund's Second Rule (Maximize Orbital Angular Multiplicity)

What matters is the total (scalar) angular momentum, not the direction. The negative and positive signs refer only to the direction of the angular momentum, not the magnitude. The direction is furthermore arbitrary (except in, say, a magnetic or electric field). So is the spin direction, incidentally. By convention we usually draw the first electron in each orbital as "up" (positive spin). However we could just as easily draw it "down". It makes no difference - in the absence of an external EM field, the energy is the same, if only because molecules/atoms are rotating with respect to the lab frame anyway. "Up" and "down", in other words, is artificial. What matters is the *relative* momentum vectors of the various electrons in the system, and hence their sum total.

Hund's Third Rule (Minimize less than half filled or maximize greater than half filled shells)

A long time ago someone offering a reasonably simple explanation related to the fact that when the shell is more than half full, it's easier to visualize the system as an interaction between the spin and orbital momenta of holes rather than electrons, in which case

the energetic stabilization term is reversed in sign. This would be because the spin angular momentum of a single hole would be opposite in sign compared to the spin angular momentum of a single electron. Taking as an example - the three p-orbitals. A situation with 1 electron and 5 electrons are functionally similar, except that one has a single electron and one has a single hole. All things being equal, the total spin angular momentum of the 1 electron system would be opposite in sign to whatever the total spin angular momentum of the 5 electron system is. So the expectations for Hund's rules would be switched. You can kind of see this if you draw out all the microstates of the 1-electron and 5-electron configurations: the everything is pretty much changed in sign in the latter case.

Example 8.10.2

What terms and levels can arise from an atom with the ground-state configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^1 3d^1$? Which is the most stable (lowest in energy) state?

Solution

Possible states include:

$$^1F_3,\ ^1D_2,\ ^1P_1,\ ^3F_4,\ ^3F_3,\ ^3F_2,\ ^3D_3,\ ^3D_2,\ ^3D_1,\ ^3P_2,\ ^3P_1,\ ^3P_0.$$

There are two unpaired electrons in this system from the electron configuration.

- Rule 1 predicts that the ground state will be a triplet with $S = 1$ so $2S + 1 = 3$. So the ground state is from this more narrowed list: $^3F_4,\ ^3F_3,\ ^3F_2,\ ^3D_3,\ ^3D_2,\ ^3D_1,\ ^3P_2,\ ^3P_1,\ ^3P_0$.
- Rule 2 predicts a F state since that is the highest multiplicity with $L = 3$: So the ground state is from this more narrowed list: $^3F_4,\ ^3F_3,\ ^3F_2$
- Rule 3 predicts the lowest J term since the d shell is less than half full. That is the $J = 2$ state.

Therefore for this system, the atom will have a ground-state structure of

$$^3F_2$$

Example 8.10.3: Titanium cation

The ground configuration of a Ti^{2+} ion is $[Ar]3d^2$. What is the term of lowest energy state?

Solution

- Rule 1: two unpaired electrons ⇒ highest S = 1 ⇒ 2S + 1 = 3
- Rule 2: two in d in parallel spin ⇒ highest L = 1 + 2 = 3 ⇒ 3F
- Rule 3:.L = 3, S = 1 ⇒ J = 4, 3, 2; less than half-filled ⇒ $^3F_2$

Exercise 8.10.3

What is the term of lowest energy state for the following atoms and ions.

- C: $[He]2s^2 2p^2$
- N: $[He]2s^2 2p^3$
- O: $[He]2s^2 2p^4$
- Cr^{3+}: $[Ar]3d^3$
- Mn^{3+}: $[Ar]3d^4$
- Fe^{3+}: $[Ar]3d^5$

Answer

$^3P_0$, $^4S_{3/2}$, $^3P_2$, $^4F_{3/2}$, $^5D_0$, and $^6S_{5/2}$, respectively.

8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

Around 1930, several spectroscopists using high resolution instruments found that lines in the hydrogen atom spectrum actually are not single lines but they are multiplets as shown for an isotopic mixture of hydrogen,(H_α^1) and deuterium, (H_α^2), in Figure **8.11.1**. A multiplet consists of two or more closely spaced lines. Two lines together form a doublet, three a triplet, etc. Multiplets also are called fine structure. The term fine structure means the lines are spaced close together, i.e. finely spaced. Such fine structure also was found in spectra of one-electron ions such as $\mathbf{He^+}$.

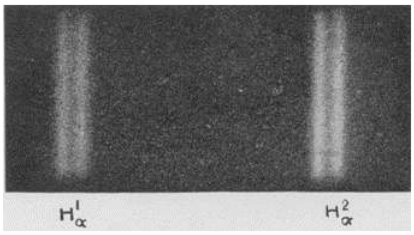


Figure **8.11.1**: Photograph of the first line in the Balmer series for atomic hydrogen and deuterium. These lines are identified as H_α^1 (hydrogen) and H_α^2 (deuterium), respectively. From H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) p. 132 and G.N. Lewis and F.H. Spedding, Phys. Rev. 43, 964 (1933). The doublet splitting for H_α^1 at 656.279 nm was measured to be 0.326 cm^{-1}.

You should recall that the H_α^1 line in the Balmer series at 656.279 nm was understood as resulting from a single transition of an electron from the n = 3 energy level to the n = 2 level. The observation of fine structure revealed that an orbital energy level diagram does not completely describe the energy levels of atoms. This fine structure also provided key evidence at the time for the existence of electron spin, which was used not only to give a qualitative explanation for the multiplets but also to furnish highly accurate calculations of the multiplet splittings.

Spin-Orbit Couping

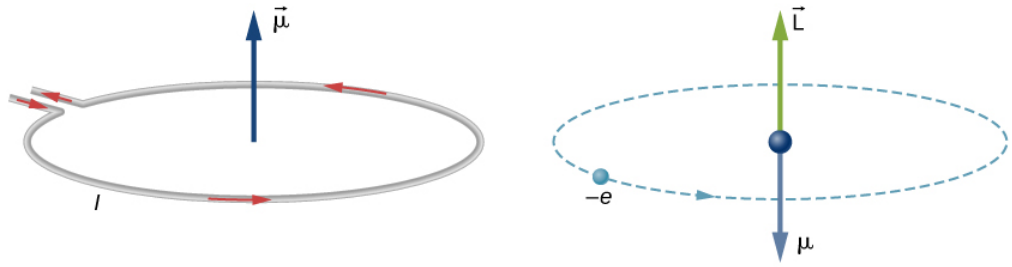
Specifying the orbital configuration of an atom does not uniquely identify the electronic state of the atom because the orbital angular momentum, the spin angular momentum, and the total angular momentum are not precisely specified. For example in the hydrogen $2p^1$ configuration, the electron can be in any of the three p-orbitals, m_l = +1, 0, and –1, and have spins with m_s = +1/2 or –1/2. Thus, there are 3 times 2 different possibilities or states. Also, the orbital and spin angular momentum of the electrons combine in multiple ways to produce angular momentum vectors that are characteristic of the entire atom not just individual electrons, and these different combinations can have different energies. This coupling of orbital and spin angular momentum occurs because both the electron spin and orbital motion produce magnetic dipole moments. As we have seen previously, the relationship between the angular momentum and the magnetic moment is given by the gyromagnetic ratio. These magnetic dipoles interact just like two tiny bar magnets attracting and repelling each other. This interaction is called spin-orbit interaction. The interaction energy is proportional to the scalar product of the magnetic dipole moments, which are proportional to the angular momentum vectors.

$$E_{s-o} \propto S \cdot L \tag{8.11.1}$$

with the following terms added to the Hamiltonian

$$\hat{H}_{s-o} \propto \hat{S} \cdot \hat{L} \tag{8.11.2}$$

where the constant of proportionality is called the spin-orbit coupling constant. The spin-orbit interaction couples the spin motion and orbital motion of all the electrons together. This coupling means that exact wavefunctions are not eigenfunctions of the spin and orbital angular momentum operators separately. Rather the total angular momentum $J = L + S$, the vector sum of the spin and orbital angular momentum, is required to be coupled for a completely accurate description of the system. Trying to describe the coupled system in terms of spin and orbital angular momentum separately is analogous to trying to describe the positions of two coupled bar magnets independently. It cannot be done; their interaction must be taken into account (Figure **8.11.1**).



(a) Current-carrying loop (b) Hydrogen atom

Figure 8.11.1: An electron that orbits the nucleus induces a "current" and a magnetic field. Similarly, the rotating electron (really intrinsic spin) of the electron induces a different magnet. Both a magnetic (dipole) moments will interact with each other via spin-orbit coupling to generate fine structure atomic spectra.Image used with permission (CC-SA OpenStax).

Atomic Spectroscopy

Higher energy or excited orbital configurations also exist. The hydrogen atom can absorb energy, and the electron can be promoted to a higher energy orbital. The electronic states that result from these excited orbital configurations also are characterized or labeled by term symbols. The details of how to determine the term symbols for multi-electron atoms and for cases where both the orbital and spin angular momentum differ from zero are given elsewhere, along with rules for determining the relative energies of the terms.

We have found that the selection rules for promoting a single electron moving from one atomic orbital to another via the absorption or emission of light are

$$\Delta l = \pm 1 \tag{8.11.3}$$

$$\Delta m_l = 0, \pm 1 \tag{8.11.4}$$

These selection rules arise from the conservation fo angular momentum during a spectroscopic transition and the fact that a photon has a spin 1. Within the limits of L-S coupling, these rules can be expressed in terms of atomic term symbols resulting in the resulting Russell-Saunders selection rules:

$$\Delta S = 0 \tag{8.11.5}$$

$$\Delta L = 0, \pm 1 \tag{8.11.6}$$

$$\Delta J = 0, \pm 1, \tag{8.11.7}$$

but the $J = 0$ to $J = 0$ transition is forbidden

$$\Delta m_J = 0, \pm 1 \tag{8.11.8}$$

but the $m_J = 0$ to $m_J = 0$ transition is forbidden if $\Delta J = 0$.

These selection rules result from the general properties of angular momentum such as the conservation of angular momentum and commutation relations. The $\Delta L = 0$ option in Equation 8.11.6 does not violate the conservation of angular momentum discussed previously, since $\Delta l = \pm 1$ is still required. The orbital angular momentum of an electron must change upon absorption, but this does not necessarily affect the overall momentum of the state given by Equation 8.11.6.

The selection rules apply only to atoms that can be described with Russell-Saunders (LS) coupling. These rules fail as the atomic number increases because the S and L quantum numbers become "bad" quantum numbers; this occurs when the jj-coupling coupling approach is more applicable. For example, the transition between single ($S = 1/2$ and triplet $S = 1$ states (volition of selection rule in Equation 8.11.5) are allowed and experimentally observed, in heavy atoms.

Example 8.11.1: Sodium Atoms

An example of this fine structure is the emission of sodium atoms.

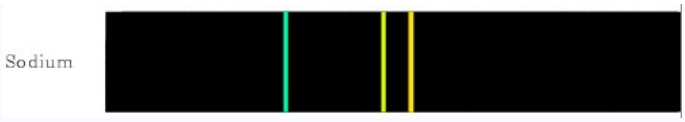


Figure above does not show this splitting).

616.07 nm	615.42 nm	589.00 nm	589.59 nm	568.82 nm	568.26 nm

How can these transitions be described in terms of transitions between microstates

Solution

We need to discussed states in terms of not only electron configurations, but in terms of microstates (i.e., term symbols) and the principal quantum number of the valence electron, n:

- The ground state has a $(Ne]ns^1$ configuration, which has only one microstate $^2S_{1/2}$
- The excited state with the valence electron in the p-orbitals has an electron configuration of $[Ne]np^1$, which has two microstates: $^2P_{3/2}$ and $^2P_{1/2}$
- The excited state with the valence electron in the p-orbitals has an electron configuration of $[Ne]nd^1$, which has two microstates of $^2D_{5/2}$ and $^2D_{3/2}$

Observed lines can be explained:

- $5S \rightarrow 3P$ gives two lines since the initial configuration has two microstates: 616.07, 615.42 nm
- $3P \rightarrow 3S$ gives two lines since the terminal configuration has two microstates: 589.00, 589.59 nm
- $4D \rightarrow 3P$ gives two lines since the terminal configuration has two microstates: 568.82, 568.26 nm

Splitting of the Sodium D Line

One notable atomic spectral line of sodium vapor is the so-called D-line, which may be observed directly as the sodium flame-test line and also the major light output of low -pressure sodium lamps (these produce pressure sodium lamps (these produce an unnatural yellow). The D-line is one of the classified Fraunhofer lines in Sodium vapor in the upper layers of lines. Sodium vapor in the upper layers of the sun creates a dark line in the emitted spectrum of electromagnetic radiation by absorbing visible light in a band of wavelengths around 589.5 nm. This wavelength corresponds to transitions in atomic sodium in which the valence-electron transitions from a 3s to 3p electronic state.

Closer examination of the visible spectrum of atomic sodium reveals that the D-line actually consists of two lines called the D_1 and D_2 lines at 589 6 nm and 589.0 nm, respectively. The splitting between these lines arises because of spin-orbit coupling. Na has one unpaired electron ($S = ½$). If we consider the $S \rightarrow P$ transition, then for the excited state, P, we have $L = 1$. Thus, $J = 3/2$ or $J = 1/2$.

Now we want to apply these ideas to understand why multiplet structure is found in the luminescence spectrum of hydrogen and single electron ions. As we have said, the H_α line in the Balmer series at 656.279 nm can be understood via a transition of an electron in a n = 3 atomic orbital to a n = 2 atomic orbital. When this spectral line was examined using high-resolution instruments, it was found actually to be a doublet, i.e. two lines separated by 0.326 cm^{-1}.

There are 9 degenerate orbitals associated with the n = 3 level, and 4 associated with the n = 2 level. Since an electron can be in any orbital with any one of two spins, we expect the total number of states to be twice the number of orbitals. The number of orbitals is given by n^2 so there should be 8 states associated with n = 2 and 18 states associated with n = 3. Using the ideas of vector addition of angular momentum, the terms that result from having an electron in any one of these orbitals are given in Table **8.11.1**.

Table **8.11.1**: H Atom Terms Originating from n = 1, 2, and 3

Orbital Configuration	Term Symbols	Degeneracy
$1s^1$	$^2S_{1/2}$	2
$2s^1$	$^2S_{1/2}$	2
$2p^1$	$^2P_{1/2}$, $^2P_{3/2}$	2, 4
$3s^1$	$^2S_{1/2}$	2
$3p^1$	$^2P_{1/2}$, $^2P_{3/2}$	2, 4
$3d^1$	$^2D_{3/2}$, $^2D_{5/2}$	4, 6

Table **8.11.1** shows that there are three terms associated with n = 2, and 5 terms associated with n = 3. In principle, each term can have a different energy. The degeneracy of each term is determined by the number of projections that the total angular momentum vector has on the z-axis. These projections depend on the m_J quantum number, which ranges from $+J$ to $-J$ in integer steps. J is the total angular momentum quantum number, which is given by the subscript in the term symbol. This relationship between m_J and J (m_J varies from $+J$ to $-J$ in integer steps) is true for any angular momentum vector.

Exercise 8.11.3

Confirm that the nine term symbols in Table **8.11.1** are correct.

Exercise 8.11.4

Confirm that the values for the degeneracy in Table **8.11.1** are correct and that the total number of states add up to 8 for n = 2 and 18 for n = 3.

The energies of the terms depend upon spin-orbit coupling and relativistic corrections that need to be included in the Hamiltonian operator in order to provide a more complete description of the hydrogen atom. As a consequence of these effects, all terms with the same n and (J\) quantum numbers have the **same energy,** while terms with different values for n or J have different energies. The theoretical term splittings as given by H.E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934) pp. 132-137 and are shown in Figure **8.11.2**.

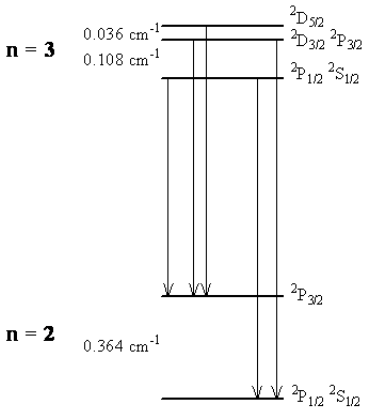


Figure **8.11.2**: Energy level diagram for the electronic states of hydrogen corresponding to an electron with the principal quantum number n = 3 and n = 2. While the relative energies of the terms are drawn to scale, the energy of n = 3 relative to n = 2 is not. Transitions to the $2P_{3/2}$ and ($2P_{1/2}$ and $2S_{1/2}$) levels correspond to the two lines in the H_α^1 band, which have a measured separation of 0.326 cm^{-1}.

Figure **8.11.2** shows 5 allowed transitions for the electron in the states associated with n = 3 to the states associated with n = 2. Of these five, two are most intense and are responsible for the doublet structure. These two transitions are indicated by the wide black lines at the bottom of the figure to correspond to the lines observed in the photographic spectrum shown in Figure **8.11.2**. The other transitions contribute to the width of these lines or are not observed. The theoretical value for the doublet splitting is 0.328 cm^{-1},

which is in excellent agreement with the measured value of 0.326 cm^{-1}. The value of 0.328 cm^{-1} is obtained by taking the difference, 0.364 – 0.036 cm^{-1},in the term splittings.

As we have just seen, the electronic states, as identified by the term symbols, are essential in understanding the spectra and energy level structure of atoms, but it also is important to associate the term symbols and states with the orbital electron configurations. The orbital configurations help us understand many of the general or coarse features of spectra and are necessary to produce a physical picture of how the electron density changes because of a spectroscopic transition.

Exercise 8.11.5

Use the Russell-Saunders selection rules to determine which transitions contribute to the H_α line in the hydrogen spectrum.

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Stefan Franzen (North Carolina State University)

8.11: Using Atomic Term Symbols to Interpret Atomic Spectra is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

9: Chemical Bonding in Diatomic Molecules

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

Our basis for understanding chemical bonding and the structures of molecules is the electron orbital description of the structure and valence of atoms, as provided by quantum mechanics. We assume an understanding of the periodicity of the elements based on the nuclear structure of the atom and our deductions concerning valence based on electron orbitals.

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

9: Chemical Bonding in Diatomic Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules

Using quantum mechanics to predict the chemical bonding patterns, optimal geometries, and physical and chemical properties of molecules is a large and active field of research known as *molecular quantum mechanics* or more commonly as *quantum chemistry*. The density functional theory referred to in the previous lecture, for which the chemistry Nobel prize was given in 1998, has had a tremendous impact in quantum chemistry, with some of the papers in this subject having acquired some 10,000 citations each since their publication. In fact, the 1998 chemistry Nobel prize was shared between Walter Kohn, one of the inventors of density functional theory and John Pople, the developer of a commonly used quantum chemistry software package.

Quantum chemistry calculations allow the geometries of molecules to be computed as well as a wide range of properties. Quantum chemistry can also be used in a novel way, in which the electrons are treated using quantum mechanics but the nuclei are treated as classical particles. We use quantum mechanics to calculate the internuclear forces but then use these forces in Newton's Second Law to study the motion of the nuclei during chemical reactions. This gives us a microscopic window into the specific motions, the complex dance, executed by the nuclei during a simple or complex chemical process.

The methods of quantum chemistry have become very sophisticated, and there are various software packages that can be downloaded for carrying out the calculations of quantum chemistry. It should be noted that these packages use a series of approximations to solve the Schrödinger equation because for all but the simplest of molecules, exact solutions are not available. We will discuss some of these methods, but first we need to introduce some of the underlying theory.

The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is one of the basic concepts underlying the description of the quantum states of molecules. This approximation makes it possible to separate the motion of the nuclei and the motion of the electrons. This is not a new idea for us. We already made use of this approximation in the particle-in-a-box model when we explained the electronic absorption spectra of cyanine dyes without considering the motion of the nuclei. Then we discussed the translational, rotational and vibrational motion of the nuclei without including the motion of the electrons. In this chapter we will examine more closely the significance and consequences of this important approximation. Note, in this discussion nuclear refers to the atomic nuclei as parts of molecules not to the internal structure of the nucleus.

The Born-Oppenheimer approximation neglects the motion of the atomic nuclei when describing the electrons in a molecule. The physical basis for the Born-Oppenheimer approximation is the fact that the mass of an atomic nucleus in a molecule is much larger than the mass of an electron (more than 1000 times). Because of this difference, the nuclei move much more slowly than the electrons. In addition, due to their opposite charges, there is a mutual attractive force of Ze^2/r^2 acting on an atomic nucleus and an electron. This force causes both particles to be accelerated. Since the magnitude of the acceleration is inversely proportional to the mass, a = F/m, the acceleration of the electrons is large and the acceleration of the atomic nuclei is small; the difference is a factor of more than 2000. Consequently, the electrons are moving and responding to forces very quickly, and the nuclei are not. You can imagine running a 100-yard dash against someone whose acceleration is a 2000 times greater than yours. That person could literally run circles around you.

Example 9.1.1: Coupled Oscillators with Dissimilar Masses

If two particles interact in some way, and one is much heavier than the other, the light particle will move essentially as a "slave" of the heavy particle. That is, it will simply follow the heavy particle wherever it goes, *and*, it will move rapidly in response to the heavy particle motion. As an illustration of this phenomenon, consider the simple mechanical system pictured below:

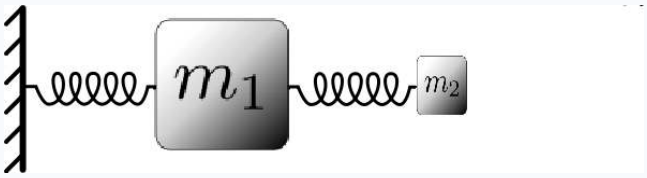


Image used with permission (CC BY-SA 3.0 Unported; Jim.belk via Wikipedia).

Considering this as a classical system, we expect that the motion will be dominated by the large heavy particle (m_1), which is attached to a fixed wall by a spring. The small, light particle (m_2, which is attached to the heavy particle by a spring will simply follow the heavy particle and execute rapid oscillations around it.

So a good approximation is to describe the electronic states of a molecule by thinking that the nuclei are not moving, i.e. that they are stationary. The nuclei, however, can be stationary at different positions so the electronic wavefunction can depend on the positions of the nuclei even though their motion is neglected.

Now we look at the mathematics to see what is done in solving the Schrödinger equation after making the Born-Oppenheimer approximation. For a diatomic molecule as an example, the Hamiltonian operator is grouped into three terms

$$\hat{H}(r,R) = \hat{T}_{nuc}(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} + \hat{H}_{elec}(r,R) \tag{9.1.1}$$

where

$$\hat{T}_{nuc}(R) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 \tag{9.1.2}$$

and

$$\hat{H}_{elec}(\vec{r},\vec{R}) = \frac{-\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left(-\sum_i \frac{Z_A}{r_{Ai}} - \sum_i \frac{Z_B}{r_{Bi}} + \frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{r_{ij}}\right) \tag{9.1.3}$$

In Equation 9.1.1, the first term represents the kinetic energy of the nuclei, the second term represents the Coulomb repulsion of the two nuclei, and the third term represents the contribution to the energy from the electrons, which consists of their kinetic energy, mutual repulsion for each other, and attraction for the nuclei. $\vec{r}$ and $\vec{R}$ are vectors specifying the positions of all the electrons and all the nuclei, respectively.

Exercise 9.1.1

Define all the symbols in Equations 9.1.1 through 9.1.3.

Answer

$$\hat{H}(r,R) = \underbrace{\hat{T}_{nuc}(R)}_{\text{Kinetic Energy Term for nuclei}} + \underbrace{\frac{e^2}{4\pi\epsilon_o}\frac{Z_A Z_B}{R}}_{\text{Repulsion Term for nuclei}} + \underbrace{\hat{H}_{elec}(r,R)}_{\text{Hamiltonian for electrons}}$$

$$\hat{T}_{nuc}(R) = \underbrace{\frac{\hbar^2}{2m_A}\nabla_A^2}_{\text{Kinetic Energy Term for nuclei A}} - \underbrace{\frac{\hbar^2}{2m_b}\nabla_B^2}_{\text{Kinetic Energy Term for nuclei B}}$$

$$\hat{H}_{elec}(\vec{r},\vec{R}) = \underbrace{\frac{-\hbar^2}{2m}\sum_i \nabla_i^2}_{\text{Kinetic Energy Term for electrons}} + \frac{e^2}{4\pi\epsilon_o}\left(\underbrace{-\sum_i \frac{Z_A}{r_{Ai}}}_{\text{Attraction Term between nuclei A and electron i}} \underbrace{-\sum_i \frac{Z_B}{R_{Bi}}}_{\text{Attraction Term between nuclei B and electron i}} + \underbrace{\frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{r_{ij}}}_{\text{Repulsion Term between electrons}}\right)$$

where, Z_x is the charge of particle x, m_x is the mass of particle x and r_{xz} is the distance between particle x and z.

Exercise 9.1.2

Explain why the factor of 1/2 appears in the last term in Equation 9.1.3.

Answer

The 1/2 term is there to make sure we do not double count the potential energies via the two summations. Otherwise, we would independently add the potential energy of electron 1 with electron 2 and the potential energy of electron 2 with electron 1. These are the same and hence one has to be removed.

The Born-Oppenheimer approximation says that the nuclear kinetic energy terms in the complete Hamiltonian, Equation 9.1.1, can be neglected in solving for the electronic wavefunctions and energies. Consequently, the electronic wavefunction $\varphi_e(r,R)$ is found as a solution to the electronic Schrödinger equation

$$\hat{H}_{elec}(r,R)\varphi_e(r,R) = E_e(R)\varphi_e(r,R) \tag{9.1.4}$$

Even though the nuclear kinetic energy terms are neglected, the Born-Oppenheimer approximation still takes into account the variation in the positions of the nuclei in determining the electronic energy and the resulting electronic wavefunction depends upon the nuclear positions, R. As a result of the Born-Oppenheimer approximation, the molecular wavefunction can be written as a product

$$\psi_{ne}(r,R) = X_{ne}(R)\varphi_e(r,R) \tag{9.1.5}$$

This product wavefunction is called the Born-Oppenheimer wavefunction. The function $X_{ne}(R)$ is the vibrational wavefunction, which is a function of the nuclear coordinates R and depends upon both the vibrational and electronic quantum numbers or states, n and e, respectively. The electronic function, $\varphi_e(r,R)$, is a function of both the nuclear and electronic coordinates, but only depends upon the electronic quantum number or electronic state, e. Translational and rotational motion is not included here. The translational and rotational wavefunctions simply multiply the vibrational and electronic functions in Equation 9.1.5 to give the complete molecular wavefunction when the translational and rotational motions are not coupled to the vibrational and electronic motion.

In the *Crude Born-Oppenheimer Approximation*, R is set equal to R_o, the equilibrium separation of the nuclei, and the electronic wavefunctions are taken to be the same for all positions of the nuclei (i.e., the nuclei never move). The electronic energy, $E_e(R)$, in Equation 9.1.4 combines with the

repulsive Coulomb energy of the two nuclei, to form the potential energy function that controls the nuclear motion as shown in Figure **9.1.1**.

$$V_e(R) = E_e(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} \tag{9.1.6}$$

Consequently the Schrödinger equation for the vibrational motion is

$$(\hat{T}_{nuc}(R) + V(R))X_{ne}(R) = E_{ne}X_{ne}(R) \tag{9.1.7}$$

Potential Energy Curves and Surfaces

Previously, the potential energy was approximated as a harmonic potential or Morse potential depending on the displacement, R, of the nuclei from their equilibrium positions.

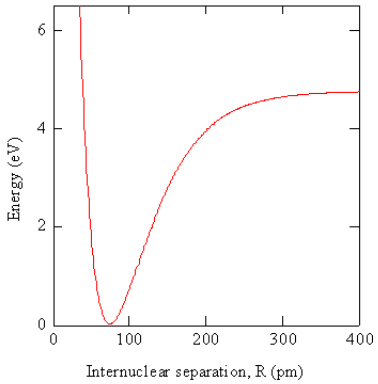


Figure **9.1.1**: The potential energy function for a diatomic molecule.

In practice the electronic Schrödinger equation is solved using approximations at particular values of R to obtain the wavefunctions $\varphi_e(r, R)$ and potential energies $V_e(R)$. The potential energies can be graphed as illustrated in Figure **9.1.1**.

The graph in Figure **9.1.1** is the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When R is very large there are two atoms that are weakly interacting. As R becomes smaller, the interaction becomes stronger, the energy becomes a large negative value, and we say a bond is formed between the atoms. At very small values of R, the internuclear repulsion is very large so the energy is large and positive. This energy function controls the motion of the nuclei. Previously, we approximated this function by a harmonic potential to obtain the description of vibrational motion in terms of the harmonic oscillator model. Other approximate functional forms could be used as well, e.g. the Morse potential. The equilibrium position of the nuclei is where this function is a minimum, i.e. at $R = R_0$. If we obtain the wavefunction at $R = R_0$ and use this function for all values of R, we have employed the *Crude Born-Oppenheimer* approximation.

Exercise 9.1.3

Relate Equation 9.1.7 to the one previously used in our description of molecular vibrations in terms of the harmonic oscillator model.

While the potential energy function, $V_e(R)$, for a diatomic molecule is a 1-D curve (Figure **9.1.1**), molecules with more than two atoms will have multi-dimensional **potential energy surfaces** with 3N-6 (or 3N-5 for linear molecule) dimensions for the number of internal degrees of freedom.

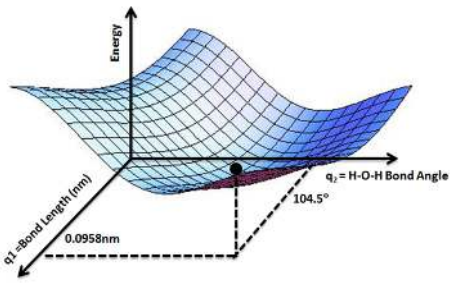


Figure **9.1.2**: The potential energy surface for a water molecule: Shows the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958 nm and H-O-H bond angle of 104.5°. Image used with permission from Wikipeda (AimNature)

The potential energy surface concept can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction. Qualitatively the reaction coordinate diagrams (one-dimensional slices through the potential energy surfaces) have numerous applications. Chemists use reaction coordinate diagrams as both an analytical and pedagogical aid for rationalizing and illustrating kinetic and thermodynamic events. The purpose of energy profiles and surfaces is to provide a qualitative representation of how potential energy varies with molecular motion for a given reaction or process.

Exercise 9.1.4

Explain the difference between the Born-Oppenheimer approximation and the Crude Born-Oppenheimer approximation.

Summary

In this section we started with the Schrödinger equation for a diatomic molecule and separated it into two equations, an electronic Schrödinger equation and a nuclear Schrödinger equation. In order to make the separation, we had to make an approximation. We had to neglect the effect of the nuclear kinetic energy on the electrons. The fact that this assumption works can be traced to the fact that the nuclear masses are much larger than the electron mass. We then used the solution of the electronic Schrödinger equation to provide the potential energy function for the nuclear motion. The solution to the nuclear Schrödinger equation provides the vibrational wavefunctions and energies.

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

9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.2: The H_2^+ Prototypical Species

Molecular orbital theory is a conceptual extension of the orbital model, which was so successfully applied to atomic structure. As was once playfully remarked, "a molecule is nothing more than an atom with more nuclei." This may be overly simplistic, but we do attempt, as far as possible, to exploit analogies with atomic structure. Our understanding of atomic orbitals began with the exact solutions of a prototype problem – the hydrogen atom. We will begin our study of homonuclear diatomic molecules beginning with another exactly solvable prototype, the hydrogen molecule-ion H_2^+.

The Hydrogen Molecular Ion

The simplest conceivable molecule would be made of two protons and one electron, namely H_2^+. This species actually has a transient existence in electrical discharges through hydrogen gas and has been detected by mass spectrometry and it also has been detected in outer space. The Schrödinger equation for H_2^+ can be solved exactly within the Born-Oppenheimer approximation (i.e., fixed nuclei). This ion consists of two protons held together by the electrostatic force of a single electron. Clearly the two protons, two positive charges, repeal each other. The protons must be held together by an attractive Coulomb force that opposes the repulsive Coulomb force. A negative charge density between the two protons would produce the required counter-acting Coulomb force needed to pull the protons together. So intuitively, to create a chemical bond between two protons or two positively charged nuclei, a high density of negative charge between them is needed. We expect the molecular orbitals that we find to reflect this intuitive notion.

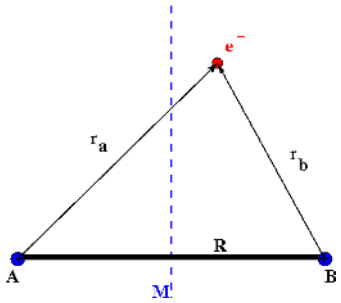


Figure 9.2.1: Hydrogen molecular ion H_2^+ with fixed nuclei A and B, internuclear distance R.

The electronic Hamiltonian for H_2^+ is

$$\hat{H}_{elec}(r,R) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \tag{9.2.1}$$

where

- r_A and r_B are the distances electron from the A and B hydrogen nuclei, respectively and
- R is the distance between the two protons.

Although the Schrödinger equation for H_2^+ can be solved exactly (albeit within the Born-Oppenheimer approximation where the nuclei are fixed) because there is only one electron, we will develop approximate solutions in a manner applicable to other diatomic molecules that have more than one electron.

Linear Combination of Atomic Orbitals

For the case where the protons in H_2^+ are infinitely far apart, we have a hydrogen atom and an isolated proton when the electron is near one proton or the other. The electronic wavefunction would just be $1s_A(r)$ or $1s_B(r)$ depending upon which proton, labeled A or B, the electron is near. Here $1s_A$ denotes a 1s hydrogen atomic orbital with proton A serving as the origin of the spherical polar coordinate system in which the position $\mathbf{r}$ of the electron is specified. Similarly $1s_B$ has proton B as the origin. A useful approximation for the molecular orbital when the protons are close together therefore is a linear combination of the two atomic orbitals. The general method of using

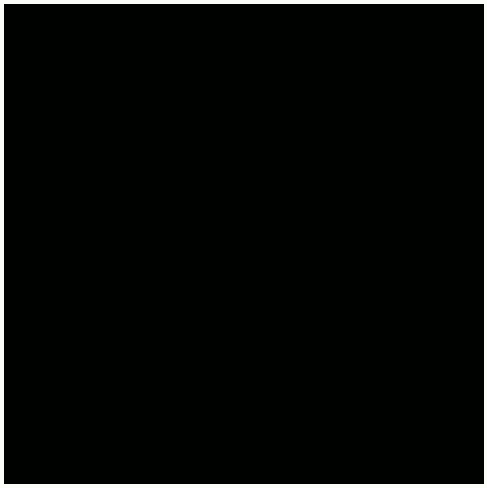
$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \tag{9.2.2}$$

i.e. of finding molecular orbitals as linear combinations of atomic orbitals is called the *Linear Combination of Atomic Orbitals - Molecular Orbital (LCAO-MO) Method*. In this case we have two basis functions in our basis set, the hydrogenic atomic orbitals $1s_A$ and $1s_B$.

The Linear Combination of Atomic Orbitals (LCAO) Approximation and Interference

The LCAO approximation is an example of the linear variational method discussed previously with the true molecular orbital wavefunction approximated as an expansion of a basis set of atomic orbitals on each atom of the molecule with variable coefficients that can be optimized (e.g., via the secular equations). As discussed previously, the number of wavefunctions (solutions) extracted from solving the secular determinant is equal the number of elements in the expansion. So for the expansion in Equation 9.2.2 with two atomic orbitals contributing result in two molecule orbitals.

This method yields a approximate picture of the molecular orbitals in a molecules. The figure below shows two atoms approaching along the axis of one of their **2*p*** states. In the top row, the two lobes facing one another have the same sign; in the bottom row they have opposite sign. These are two different linear combinations of the same two atomic states, on different atoms and with difference phases (i.e., signs of C_A vs. C_B in the expansion). In the first example, the electron density increases between the nuclei and in the second example, a very steep-sided node between the two nuclei causes all the probability density to face away from the atom opposite.



For H_2^+, the simplest molecule, the starting function is given by Equation 9.2.2. We must determine the values for the coefficients, C_A and C_B. We could use the variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition $|C_A|^2 = |C_B|^2$; namely, $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\psi_+ = C_+(1s_A + 1s_B) \tag{9.2.3}$$

$$\psi_- = C_-(1s_A - 1s_B) \tag{9.2.4}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for ψ_+ is enhanced (Figure **9.2.2** (bottom) between the two protons, whereas it is diminished for ψ_- as shown in Figures **9.2.2** (top). ψ_- has a node in the middle while ψ_+ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons.

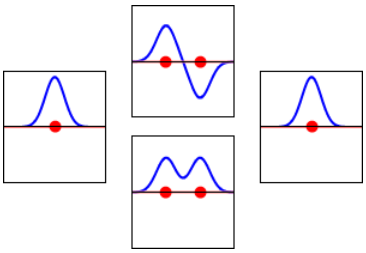


Figure 9.2.2: Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H_2^+ ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red dots mark the locations of the nuclei. The electron wavefunction oscillates according to the Schrödinger wave equation, and orbitals are its standing waves. The standing wave frequency is proportional to the orbital's kinetic energy. (This plot is a one-dimensional slice through the three-dimensional .)

So ψ_+ is called a *bonding molecular orbital*. If the electron were described by ψ_-, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so ψ_- is called an *antibonding molecular orbital*.

Contributors

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

9.2: The H_2^+ Prototypical Species is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.3: The Overlap Integral

For H_2^+, the simplest molecule, we must determine the values for the coefficients, C_A and C_B for the LCAO approximation for the molecular orbital as a linear combination of the two atomic orbitals

$$|\psi(r)\rangle = C_A 1s_A(r) + C_B 1s_B(r) \tag{9.3.1}$$

We could use the linear variational method to find a value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition

$$|C_A|^2 = |C_B|^2 \tag{9.3.2}$$

so $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\underbrace{|\psi_+\rangle = C_+(1s_A + 1s_B)}_{\text{bonding molecular orbital}} \tag{9.3.3}$$

and

$$\underbrace{|\psi_-\rangle = C_-(1s_A - 1s_B)}_{\text{antibonding molecular orbital}} \tag{9.3.4}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for $|\psi_+\rangle$ is enhanced between the two protons, whereas it is diminished for $|\psi_-\rangle$ as shown in Figures **9.3.1**. ψ_- has a node in the middle while $|\psi_+\rangle$ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons. So $|\psi_+\rangle$ is called a *bonding molecular orbital*. If the electron were described by $|\psi_-\rangle$, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so $|\psi_-\rangle$ is called an *antibonding molecular orbital*.

Now we want to evaluate C_+ and C_- and then calculate the energy. The bonding and antibonding character of ψ_+ and ψ_- also should be reflected in the energy. If $|\psi_+\rangle$ indeed describes a bonding orbital, then the energy of this state should be less than that of a proton and hydrogen atom that are separated. The calculation of the energy will tell us whether this simple theory predicts H_2^+ to be stable or not and also how much energy is required to dissociate this molecule.

The constants C_+ and C_- are evaluated from the standard normalization condition:

$$\int \psi_\pm^* \psi_\pm d\tau = \langle \psi_\pm | \psi_\pm \rangle = 1 \tag{9.3.5}$$

$$\langle C_\pm(1s_A \pm 1s_B) | C_\pm(1s_A \pm 1s_B) \rangle = 1 \tag{9.3.6}$$

$$|C_\pm|^2[\underbrace{\langle 1s_A|1s_A\rangle}_{1} + \underbrace{\langle 1s_B|1s_B\rangle}_{1} \pm \underbrace{\langle 1s_B|1s_A\rangle}_{S} \pm \underbrace{\langle 1s_A|1s_B\rangle}_{S^*}] = 1 \tag{9.3.7}$$

Since the atomic orbitals are normalized, the first two integrals are just 1. The last two integrals are called *overlap integrals* and are symbolized by S and S^*, respectively, since one is the complex conjugate of the other.

The overlap integrals are telling us to take the value of $1s_B$ at a point multiply by the value of $1s_A$ at that point and sum (integrate) such a product over all of space (Figure **9.3.1**). If the functions do not overlap, i.e. if one is zero when the other one is not and vice versa, these integrals then will be zero. It also is possible in general for such integrals to be zero even if the functions overlap because of the cancelation of positive and negative contributions.

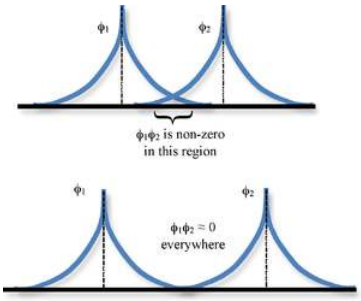


Figure 9.3.1: The wavefunctions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case both S is close to zero.

If the overlap integral is zero, for whatever reason, the functions are said to be *orthogonal*. Notice that the overlap integral ranges from 0 to 1 as the separation between the protons varies from $R = \infty$ to $R = 0$. Clearly when the protons are infinite distance apart, there is no overlap, and when $R = 0$ both functions are centered on one nucleus and $\langle 1s_A | 1s_B \rangle$ becomes identical to $\langle 1s_B | 1s_A \rangle$, which is normalized to 1, because $1s_A = 1s_B$.

With these considerations and using the fact that $1s$ wavefunctions are real so

$$\langle 1s_A | 1s_B \rangle = \langle 1s_B | 1s_A \rangle = S \tag{9.3.8}$$

Equation 9.3.7 becomes

$$|C_{\pm}|^2 (2 \pm 2S) = 1 \tag{9.3.9}$$

The solution to Equation 9.3.9 is given by

$$C_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} \tag{9.3.10}$$

Hence, the normalized molecular orbitals in Equations 9.3.3 and 9.3.3 are

$$|\psi_+\rangle = \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B) \tag{9.3.11}$$

and

$$|\psi_-\rangle = \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B) \tag{9.3.12}$$

The energies associated with these wavefunctions requires a bit more effort to calculate though as demonstrated in the following section.

For the overlap integral of two 1s orbitals from the hydrogen dimer discussed above is difficult to evaluate analytically and is explained here. The final answer is:

$$S(R) = \langle 1s_A | 1s_B \rangle \tag{9.3.13}$$

$$= e^{-R/a_o} \left(1 + \frac{R}{a_o} + \frac{R^2}{3a_o^2} \right) \tag{9.3.14}$$

The overlap integral for two 1s atomic orbitals of hydrogen is graphically displayed below

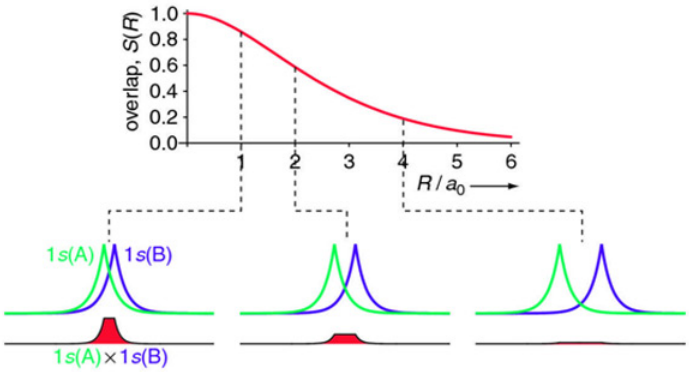


Figure 9.3.2: The overlap integral at different proton separations.

Example 9.3.1

Calculate the difference in the electronic charge density (C/pm^3) at a point halfway between the two nuclei for H_2^+ for an electron in the bonding molecular orbital compared to one in the antibonding molecular orbital.

Solution

The electronic charge density is calculated with the formula $|e\psi^2|$ where $e = 1.602 \times 10^{-19} C$

a: Bonding Molecular Orbital

First, squaring the bonding molecular orbital (Equation 9.3.11) gives us:

$$\begin{aligned}\psi_+^2 &= \frac{1}{2(1+S)}(1s_A + 1s_B)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3}\left(e^{-r_A/a_0} + e^{-r_B/a_0}\right)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3} \\ &= (0.561)^2 \times \left(\frac{1}{\pi \times (52.9\ \text{pm})^3}\right) = 6.7672 \times 10^{-7}\ \text{pm}^{-3}\end{aligned}$$

(Note: The value of C^2 is obtained from equation 9.3.12 and the value of S is from Equation 9.3.14)

To find the density at halfway between A and B for the bonding orbital evalulate at 1/2 R,

$$r_A = \frac{1}{2}R \text{ and } r_B = \frac{1}{2}R$$

$$\psi_+^2 = 3.7 \times 10^{-7}\ \text{pm}^{-3} \tag{9.3.15}$$

Now multiply this answer by e to generate the electronic charge density,

$$P = \left(3.7 \times 10^{-7}\ \text{pm}^{-3}\right) \times \left(1.602 \times 10^{-19}\right)\ \text{C} = 5.93 \times 10^{-26} C/pm^3 \tag{9.3.16}$$

b: Antibonding Molecular Orbital

To find the halfway between A and B for the anti-bonding orbital at $r_A = \frac{1}{2}R$ and $r_B = \frac{1}{2}R$. However, simple inspection of Equation 9.3.12 or Figure 9.3.1 shows this will be zero.

$$e\psi_-^2 = 0 \tag{9.3.17}$$

Obviously, when multiplied by e, the answer is still zero. This makes logical sense as there would be no charge density between the two atoms as there lies a node with no probability of finding an electron.

Exercise 9.3.1

Show that for two arbitrary functions $\langle\varphi_B|\varphi_A\rangle$ is the complex conjugate of $\langle\varphi_A|\varphi_B\rangle$ and that these two integrals are equal if the

functions are real.

Contributors

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

9.3: The Overlap Integral is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.4: Chemical Bond Stability

As shown previously, we can construct two molecular orbitals for the H_2^+ system using the LCAO approximation with a basis set of two 1s atomic orbitals (i.e., the $1s$ orbitals on hydrogen A ($1s_A$) and hydrogen B ($1s_B$):

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}}(1s_A \pm 1s_B) \tag{9.4.1}$$

The energy of these two molecular orbitals can be calculated from the expectation value integral of the Hamiltonian,

$$E_{\pm} = \left\langle \psi_{\pm} | \hat{H}_{elec} | \psi_{\pm} \right\rangle \tag{9.4.2}$$

which can be expanded using the expanded molecular orbital wavefunctions in Equations 9.4.1 to give

$$E_{\pm} = \frac{1}{2(1 \pm S)} \tag{9.4.3}$$
$$\left[\underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{BA}} \right]$$

where S is the overlap integral between the two atomic orbitals of the basis. The four integrals in Equation 9.4.3 can be represented by H_{AA}, H_{BB}, H_{AB}, and H_{BA}, respectively.

$$E_{\pm} = \frac{1}{2(1 \pm S)} \left[H_{AA} + H_{BB} \pm H_{AB} \pm H_{BA} \right] \tag{9.4.4}$$

Exercise 9.4.1

Show that Equation 9.4.2 expands to give Equation 9.4.3 within the LCAO approximation that uses a basis set of only two 1s atomic orbitals.

Answer:

Here we have the wavefunction within the LCAO approximation that uses a basis set of only two 1s atomic orbitals (Equation 9.4.1).

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}} (1_{Sa} \pm 1_{Sb})$$

And our LCAO approximation is equivalent to this if we plug in the wavefunction directly.

$$E_{\pm} = \langle \psi_{\pm} | \hat{H} | \psi_{\pm} \rangle = N^2 \langle (1_{Sa} \pm 1_{Sb}) | \hat{H} | (1_{Sa} - 1_{Sb}) \rangle$$

We can see form above that the normalization constant squared results in:

$$N^2 = \frac{1}{2(1 \pm S)}$$

We now FOIL the mulitple (i.e., expaned term by term):

$$\langle 1_{Sa} | \hat{H} | 1_{Sa} \rangle + \langle 1_{Sb} | \hat{H} | 1_{Sb} \rangle \pm \langle 1_{Sa} | \hat{H} | 1_{Sb} \rangle \pm \langle 1_{Sb} | \hat{H} | 1_{Sa} \rangle$$

Now we can see this is now equivalent to Equation 9.4.3 if the equation above is inserted (and adding a subscript to emphasize this only applies to the electronic wavefunction):

$$E_{\pm} = \frac{1}{2(1 \pm S)} \left[\underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{AA}} + \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{BB}} \pm \underbrace{\left\langle 1s_A | \hat{H}_{elec} | 1s_B \right\rangle}_{H_{AB}} \pm \underbrace{\left\langle 1s_B | \hat{H}_{elec} | 1s_A \right\rangle}_{H_{BA}} \right]$$

Notice that A and B appear equivalently in the Hamiltonian operator. This equivalence means that integrals involving $1s_A$ must be the same as corresponding integrals involving $1s_B$, i.e.

$$H_{AA} = H_{BB} \tag{9.4.5}$$

and since the wavefunctions are real

$$|A\rangle = \langle A| \tag{9.4.6}$$

so

$$H_{AB} = H_{BA} \tag{9.4.7}$$

These two equalities simplify Equation 9.4.4:

$$E_{\pm} = \frac{1}{1 \pm S}(H_{AA} \pm H_{AB}) \tag{9.4.8}$$

Now examine the details of H_{AA} after inserting the Hamiltonian operator for H_2^+ (Equation 9.2.1):

$$H_{AA} = \underbrace{\left\langle 1s_A \left| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} \right| 1s_A \right\rangle}_{E_H} + \frac{e^2}{4\pi\epsilon_0 R}\cancelto{1}{\langle 1s_A | 1s_A \rangle} \underbrace{- \left\langle 1s_A \left| \frac{e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle}_{J_{AB}} \tag{9.4.9}$$

- The first term is just the integral for the energy of the hydrogen atom of the 1s orbital, E_H.
- The second integral is equal to 1 by normalization; the prefactor is just the Coulomb repulsion of the two protons.
- The last integral, *including the minus sign*, is represented by J and is called the **Coulomb integral**.

Physically J_{AB} is the potential energy of interaction of the electron located around proton A with proton B. It is negative because it is an attractive interaction. It is the average interaction energy of an electron described by the $1s_A$ function with proton B.

The Coulomb Integral (J)

The *Coulomb Integral* is the potential energy of electrostatic repulsion between the electron with the electron density in $1S_A$ and the the electron with the electron density function $1S_B$

Now consider H_{AB}.

$$\begin{aligned} H_{AB} &= \underbrace{\left\langle 1s_A \left| -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_B} \right| 1s_B \right\rangle}_{E_H S} + \frac{e^2}{4\pi\epsilon_0 R}\cancelto{S}{\langle 1s_A | 1s_B \rangle} \underbrace{- \left\langle 1s_A \left| \frac{e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle}_{K_{AB}} \end{aligned} \tag{9.4.10}$$

- In the first integral we have the hydrogen atom Hamiltonian and the H atom function $1s_B$. The function $1s_B$ is an eigenfunction of the operator with eigenvalue E_H. Since E_H is a constant it factors out of the integral, which then becomes the overlap integral, S. The first integral therefore reduces to $E_H S$.
- The second term is just the Coulombic energy of the two protons times the overlap integral.
- The third term, *including the minus sign*, is given the symbol K and is called the *exchange integral* because the electron is described by the $1s_A$ orbital on one side and by the $1s_B$ orbital on the other side of the operator. The electron changes or exchanges position in the molecule.

The Exchange Integral (K)

In a *Coulomb integral*, the electron always is in the same orbital; whereas, in an *Exchange Integral*, the electron is in one orbital on one side of the operator and in a different orbital on the other side.

Using the expressions for H_{AA} (Equation 9.4.9) and H_{AB} (Equation 9.4.10) and substituting into Equation 9.4.8 produces:

$$E_{\pm} = \frac{1}{1 \pm S}\left[\left(E_H + \frac{e^2}{4\pi\epsilon_0 R}\right)(1 \pm S) + J \pm K\right] \tag{9.4.11}$$

$$= E_H + \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{9.4.12}$$

Equation 9.4.12 tells us that the energy of the H_2^+ molecule is the energy of a hydrogen atom plus the repulsive energy of two protons plus some additional electrostatic interactions of the electron with the protons. These additional interactions are given by the last term

$$\frac{J \pm K}{1 \pm S}.$$

If the protons are infinitely far apart then only E_H is nonzero, which we can set to zero by subtracting off:

$$\Delta E_{\pm} = E_{\pm} - E_H \tag{9.4.13}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{9.4.14}$$

To get a chemical bond and a stable H_2^+ molecule $\Delta E_{\pm}$ must be less than zero and have a minimum, i.e. $\frac{J \pm K}{1 \pm S}$ must be sufficiently negative to overcome the positive repulsive energy of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ for some value of R. For large R, these terms are zero, and for small R, the **Coulomb repulsion of the protons rises to infinity.**

Exercise 9.4.2

Show that Equation 9.2.1 follows from Equation 9.4.8

The Coulomb and Exchange Integrals

We will examine more closely how the Coulomb repulsion term and the integrals J, K, and S depend on the separation of the protons, but first we want to discuss the physical significance of J, the Coulomb integral, and K, the exchange integral. J and K have been defined as

$$J_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_A}(r)\frac{e^2}{4\pi\epsilon_0 r_B}d\tau \tag{9.4.15}$$

$$K_{AB} = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle = -\int \varphi^*_{1s_A}(r)\varphi_{1s_B}(r)\frac{e^2}{4\pi\epsilon_0 r_A}d\tau \tag{9.4.16}$$

Figure 9.4.2 shows graphs of the four terms contributing to the energy of H_2^+ (Equation 9.4.14). In this figure you can see that as the internuclear distance R approaches zero,

- the Coulomb repulsion of the two protons goes from near zero to a large positive number,
- the overlap integral goes for zero to one, and
- J and K become increasingly negative.

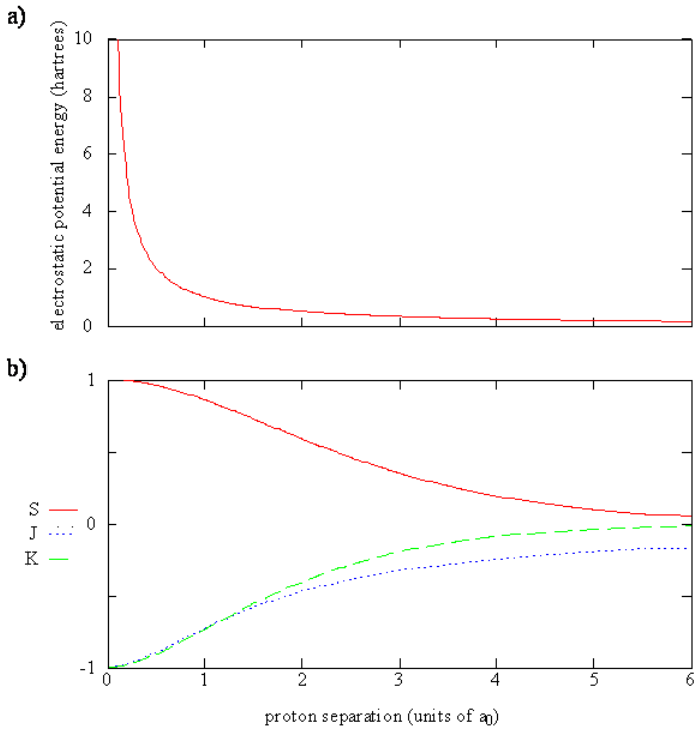


Figure **9.4.2**: (a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance R in units of the Bohr radius (52.92 pm). (b) The overlap (S), Coulomb (J), and exchange (K) integrals at different proton separations. The units for J and K are hartrees; S has no units.

Note that both J and K integrals are **negative** since all quantities in the integrands of Equation 9.4.15 and 9.4.16 are positive. In the Coulomb integral, $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the charge density of the electron around proton A, since **r** represents the coordinates of the electron relative to proton A. Since r_B is the distance of this electron to proton B, the Coulomb integral gives the potential energy of the charge density around proton A interacting with proton B. J can be interpreted as an average potential energy of this interaction because $e\varphi^*_{1s_A}(r)\varphi_{1a_A}(r)$ is the probability density for the electron at point r, and $\frac{e^2}{4\pi\epsilon_0 r_B}$ is the potential energy of the electron at that point due to the interaction with proton B. Essentially, J accounts for the attraction of proton B to the electron density of hydrogen atom A. As the two protons get further apart, this integral goes to zero because all values for r_B become very large and all values for $1/r_B$ become very small.

In the exchange integral, K, the product of the two functions is nonzero **only** in the regions of space where the two functions overlap. If one function is zero or very small at some point then the product will be zero or small. The exchange integral also approaches zero as internuclear distances increase because the both the overlap and the 1/r values become zero. The product $e\varphi^*_{1s_A}(r)\varphi_{1a_B}(r)$ is called the *overlap charge density*. Since the overlap charge density is significant in the region of space between the two nuclei, it makes an important contribution to the chemical bond. The exchange integral, K, is the potential energy due to the interaction of the overlap charge density with one of the protons. While J accounts for the attraction of proton B to the electron density of hydrogen atom A, K accounts for the added attraction of the proton due the build-up of electron charge density between the two protons.

Exercise 9.4.3

Write a paragraph describing in your own words the physical significance of the Coulomb and exchange integrals for $\mathbf{H_2^+}$.

Figure **9.4.3** shows the energy of H_2^+ relative to the energy of a separated hydrogen atom and a proton as given by Equation 9.4.12. For the electron in the ψ_- orbital, the energy of the molecule, $E_{el}(R)$, **always** is greater than the energy of the separated atom and proton.

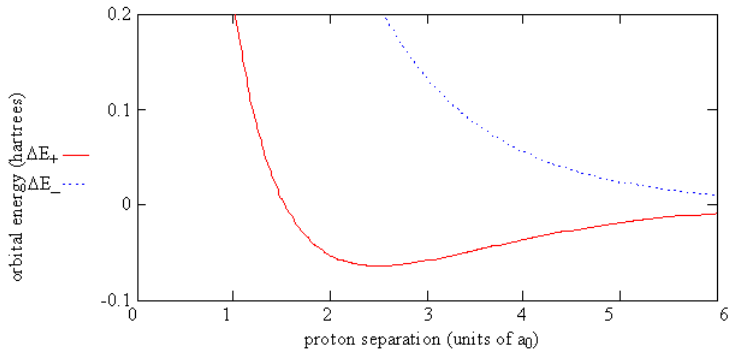


Figure **9.4.3** : Energy of the H2+ bonding molecular orbital ΔE_+ and the molecular orbital ΔE_-, relative to the energy of a separated hydrogen atom and proton.

For the electron in the ψ_+ orbital, you can see that the big effect for the energy of the bonding orbital, $E_+(R)$, is the balance between the repulsion of the two protons $\frac{e^2}{4\pi\epsilon_0 R}$ and J and K, which are both negative. J and K manage to compensate for the repulsion of the two protons until their separation is less than 100 pm (i.e the energy is negative up until this point), and a minimum in the energy is produced at 134 pm. This minimum represents the formation of a chemical bond. The effect of S is small. It only causes the denominator in Equation 9.4.12 to increase from 1 to 2 as R approaches 0.

For the antibonding orbital, -K is a positive quantity and essentially cancels J so there is not sufficient compensation for the Coulomb repulsion of the protons. The effect of the -K in the expression, Equation 9.4.12, for E_- is to account for the absence of overlap charge density and the enhanced repulsion because the charge density between the protons for ψ_- is even lower than that given by the atomic orbitals.

Contributors

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

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

9.5: Bonding and Antibonding Orbitals

The two molecular orbitals created via the linear combinations of atomic orbitals (LCAOs) approximation were created from the sum and the difference of two atomic orbitals. Within this approximation, the jth molecular orbital can be expressed as a linear combination of many atomic orbitals $\{\phi_i\}$:

$$|\psi_J\rangle = \sum_i^N c_{J,i}|\phi_i\rangle \tag{9.5.1}$$

A molecule will have as many molecular orbitals as there are atomic orbitals used in the basis set (N in Equation 9.5.1). Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1s orbitals is called a σ_{1s} combination (parts (a) and (b) of Figure 9.5.1).

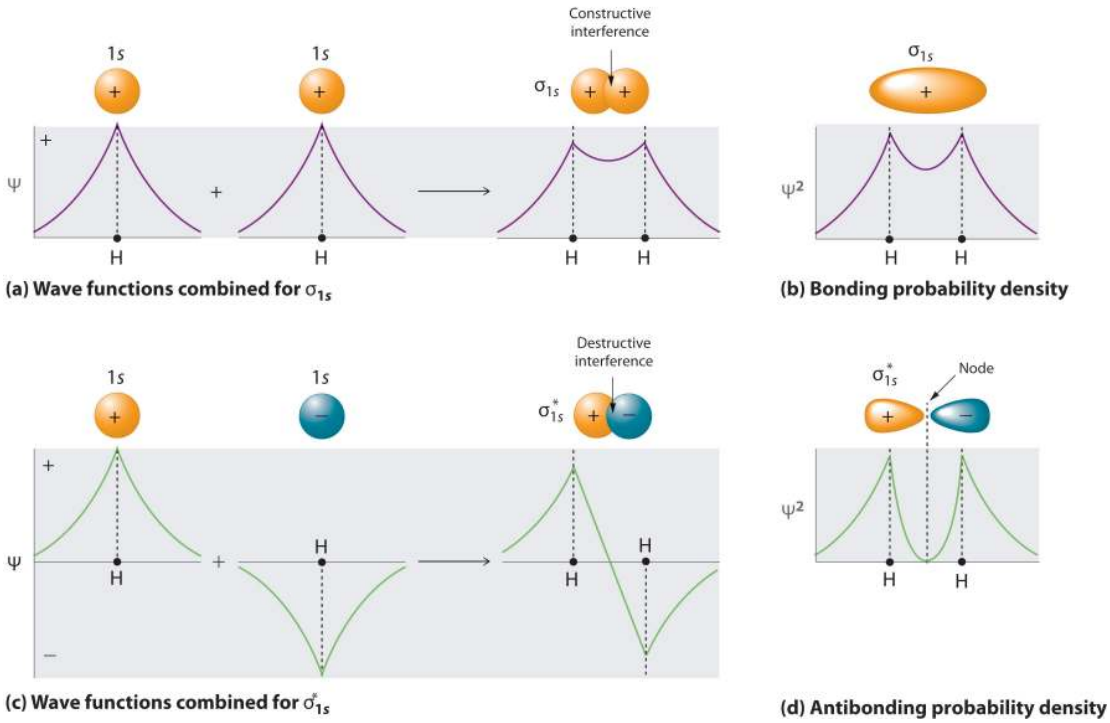


Figure 9.5.1: Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ1s molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the atomic orbital wavefunctions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function (Ψ2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei. Image used with permission (CC BY-SA-NC; anonymous by request).

In the sigma (σ) orbital, the electron density along the internuclear axis and between the nuclei has *cylindrical symmetry*; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1s denotes the atomic orbitals from which the molecular orbital was derived.

$$|\sigma_{1s}\rangle = \frac{1}{\sqrt{2(1+S)}}\left(|1s_A\rangle + |1s_B\rangle\right) \tag{9.5.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 9.5.1). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} and has a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$|\sigma_{1s}^{*}\rangle = \frac{1}{\sqrt{2(1-S)}}\left(|1s_A\rangle - |1s_B\rangle\right) \tag{9.5.3}$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the σ_{1s}^{*} orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ_{1s}^{*} orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the σ_{1s}^{*} orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the σ_{1s}^{*} molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the σ_{1s}^{*} (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure **9.5.2**

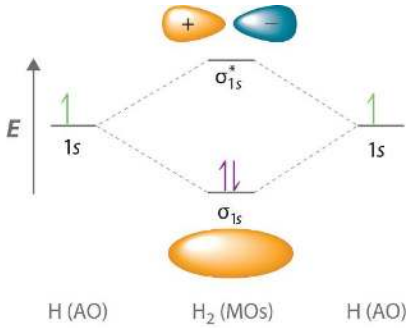


Figure **9.5.2**: Molecular Orbital Energy-Level Diagram for H2. The two available electrons (one from each H atom) in this diagram fill the bonding σ1s molecular orbital. Because the energy of the σ1s molecular orbital is lower than that of the two H 1s atomic orbitals, the H2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> *A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).*

Expanding Beyond the 1s Orbital Basis Set

This picture of bonding in H_2^+ in the previous section is very simple, but gives reasonable results when compared to an exact calculation. The equilibrium bond distance is 134 pm compared to 106 pm (exact), and a dissociation energy is 1.8 eV compared to 2.8 eV (exact). To better describe chemical bonding we need to account for the increase in electron density between the two nuclei. The 1s orbitals alone are not particularly good for this purpose because they are spherically symmetric and show no preference for the space between the atomic nuclei. The use of additional atomic orbitals can correct this situation and provide additional parameters, which can be optimized by the linear variational method, to give a better function with a lower energy and more accurate description of the charge density.

The energy of the non-normalized molecular orbital can be calculated from the expectation value integral of the Hamiltonian,

$$E_J = \frac{\left\langle \psi_J | \hat{H}_{elec} | \psi_J \right\rangle}{\langle \psi_J | \psi_J \rangle} \tag{9.5.4}$$

This is the variational energy using $|\psi_J\rangle$ as the trail wavefunction. After substituting the LCAO expansion for $|\psi_J\rangle$ (Equation 9.5.1) into the energy expression of Equation 9.5.4 results in:

$$E_J = \frac{\left\langle \sum_i c_{J,i}^* \phi_i | \hat{H}_{elec} | \sum_j c_{J,i} \phi_j \right\rangle}{\left\langle \sum_i c_{J,i}^* \phi_j | \sum_j c_{J,j} \phi_j \right\rangle} \tag{9.5.5}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} \left\langle \phi_i | \hat{H}_{elec} | \phi_j \right\rangle}{\sum_{i,j} c_{J,i}^* c_{J,j} \langle \phi_i | \phi_j \rangle} \tag{9.5.6}$$

$$= \frac{\sum_{i,j} c_{J,i}^* c_{J,j} H_{ij}}{\sum_{i,j} c_{J,i}^* c_{J,j} S_{ij}} \tag{9.5.7}$$

where H_{ij} is the Hamiltonian matrix element.

$$H_{ij} = \langle \phi_i | \hat{H}_{elec} | \phi_j \rangle \tag{9.5.8}$$

Following the variational theorem, to determine the coefficients of the LCAO expansion c_i, we need to minimize E_J

$$\frac{\partial E_J}{\partial c_k} = 0 \tag{9.5.9}$$

for all k. This requires solving N linear equations to hold true (where N is the number of atomic orbitals in the basis)

$$\sum_{i=1}^{N} c_i (H_{ki} - E S_{ki}) = 0 \tag{9.5.10}$$

These equations are the **secular equations** and were discussed previously in the context of the linear variational method approximation. For the two basis set expansion (N) in Figure 9.5.1, these are

$$\begin{aligned} c_1(H_{11} - E S_{11}) + c_2(H_{12} - E S_{12}) &= 0 \\ c_1(H_{12} - E S_{12}) + c_2(H_{22} - E S_{22}) &= 0 \end{aligned} \tag{9.5.11}$$

where c_1 and c_2 are the coefficients in the linear combination of the atomic orbitals used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

$$\begin{pmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} \\ H_{12} - E S_{12} & H_{22} - E S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{9.5.12}$$

Solving these secular equations with N different atomic orbitals in the expansion (Equation 9.5.1) requires finding the N roots of an N order polynomial.

$$\begin{vmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} & \ldots \\ H_{12} - E S_{12} & H_{22} - E S_{22} & \ldots \\ \ldots & \ldots & \ldots \end{vmatrix} = 0 \tag{9.5.13}$$

Each molecular orbital ($|\psi_J\rangle$) from this treatment has an energy E_J that is given by a different set of coefficients, $\{c_{ij}\}$ where i runs over all N functions in the basis (i.e., number of the atomic orbitals in the LCAO approximation of Equation 9.5.1), and J runs over molecular orbitals. Solve the set of linear equations using that specific E_J to determine c_{ij} values.

Steps in a Solving the Secular Equations

1. Select a set of N basis functions
2. Determine all N(N –1)/2 values of both H_{ij} and S_{ij}
3. Form the secular determinant; determine N roots E_j of secular equation
4. For each E_J solve the set of linear equations to determine the basis set coefficients \(c_{ij\}) for the j-th molecular orbital

For more information on solving the Secular equations check here.

The greater the number of atomic orbitals N that combine to genera the molecular orbitals (Equation 9.5.1), the more accurate the LCAO approximation is. This is expected based on our discussions of the variational method examples. Hence, the ψ_+ and ψ_- molecular orbitals for H_2^+ are better expressed with higher energy hydrogenic wavefunctions

$$|\psi_J\rangle = c_{J,1}1s_A + c_{J,2}1s_B + c_{J,3}2s_A + c_{J,4}2s_B + c_{J,5}2p_{z,A} + c_{J,6}2p_{z,B} \tag{9.5.14}$$

The reasons that only the p_z atomic orbitals are included in this expansion are discussed later.

Contributors

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

9.5: Bonding and Antibonding Orbitals is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, ψ_i, as a linear combination of other functions, φ_j, which are called basis functions because they provide the basis for representing the molecular orbital.

$$|\psi_i\rangle = \sum_j c_{ij}\varphi_j \tag{9.6.1}$$

where

- j is the index for the jth basis function (e.g., atomic orbital)
- i is the ith molecular orbitals and
- c_{ij} is the expansion coefficient of the jth basis function for the ith molecular orbital.

The variational method is used to find values for parameters in the basis functions and for the constant coefficients in the linear combination that optimize these functions, i.e. make them as good as possible. The criterion for quality in the variational method is making the ground state energy of the molecule as low as possible. Here and in the rest of this chapter, the following notation is used: σ is a general spin function (can be either α or β), φ is the basis function (this usually represents an atomic orbital), ψ is a molecular orbital, and Ψ is the electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. Just as for atoms, each electron in a molecule can be described by a product of spin-orbitals. Since electrons are fermions, the electronic wavefunction must be **antisymmetric** with respect to the permutation of any two electrons. A Slater determinant containing the molecular spin orbitals produces the antisymmetric wavefunction. For example for two electrons,

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_A(r_1)\alpha(1) & \psi_B(r_1)\beta(1)\\ \psi_A(r_2)\alpha(2) & \psi_B(r_2)\beta(2)\end{vmatrix} \tag{9.6.2}$$

Solving the Schrödinger equation in the orbital approximation will produce a set of spatial molecular orbitals, each with a specific energy, ϵ. Following the Aufbau Principle, two electrons with different spins (α and β, consistent with the Pauli Exclusion Principle discussed for muliti-electron atoms) are assigned to each spatial molecular orbital in order of increasing energy. For the ground state of the 2n electron molecule, the n lowest energy spatial orbitals will be occupied, and the electron configuration will be given as $\psi_1^2\psi_2^2\psi_3^2 \ldots \psi_n^2$. The electron configuration also can be specified by an orbital energy level diagram as shown in Figure **9.6.1**. Higher energy configurations exist as well, and these configurations produce excited states of molecules. Some examples are shown in Figure **9.6.1**.

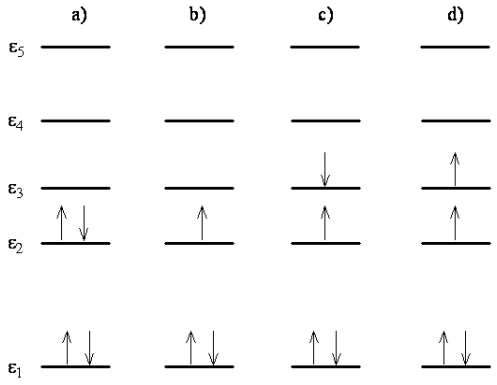


Figure **9.6.1**: a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration.

Symmetry

Molecular orbitals usually are identified by their symmetry or angular momentum properties. For example, a typical symbol used to represent an orbital in an electronic configuration of a diatomic molecule is $2\sigma_g^2$. The superscript in symbol means that this orbital is occupied by two electrons; the prefix means that it is the second sigma orbital with *gerade* symmetry.

Diatomic molecules retain a component of angular momentum along the internuclear axis. The molecular orbitals of diatomic molecule therefore can be identified in terms of this angular momentum. A Greek letter, e.g. σ or π, encodes this information, as well as information about the symmetry of the orbital. A σ means the component of angular momentum is 0, and there is no node in any plane containing the internuclear axis, so the orbital must be symmetric with respect to reflection in such a plane. A π means there is a node and the wavefunction is antisymmetric with respect to reflection in a plane containing the internuclear axis. For homonuclear diatomic molecules, a *g* or a *u* is added as a subscript to designate whether the orbital is symmetric or antisymmetric with respect to the center of inversion of the molecule.

A homonuclear diatomic molecule has a center of inversion in the middle of the bond. This center of inversion means that $\psi(x,y,z) = \pm\psi(-x,-y,-z)$ with the origin at the inversion center. Inversion takes you from (x,y,z) to $(-x,-y,-z)$. For a heteronuclear diatomic molecule, there is no center of inversion so the symbols g and u are not used. A prefix 1, 2, 3, etc. simply means the first, second, third, etc. orbital of that type. We can specify an electronic configuration of a diatomic molecule by these symbols by using a superscript to denote the number of electrons in that orbital, e.g. the lowest energy configuration of N_2 is

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 \tag{9.6.3}$$

Contrasting LCAO with other Quantum Chemistry Methods

As we have already seen, the LCAO approach is very approximate, yielding only qualitative results. It should be noted that the Hartree-Fock method discussed earlier for atoms can also be used for molecules. For example, the molecule He_2^+ has three electrons, and the Li atom also has three electrons. As usual with Hartree-Fock, the idea is to optimize the shapes of the single-electron orbitals $\psi_1(r)$, $\psi_2(r)$ and $\psi_3(r)$ by minimizing the guess to the ground state energy E_g. Of course, we will not get the same answer as for Li because there is a different V_{en} energy for He_2^+ due to the presence of two positively charge nuclei ($charge = +2e$) separated by a distance R in contrast to the single $+3e$ charged nucleus for Li. When the shapes of the orbitals are optimized, we also obtain three energy ε_1, ε_2 and ε_3. Not unexpectedly, we find that two of the HF orbitals resemble $1\sigma_g$ while the third resembles $1\sigma_u^*$ and the first two energies ε_1 and ε_2 will be nearly equal, while the third ε_3 will be noticeably higher. To contrast with the LCAO approach, in LCAO, we do not optimize the shapes of the orbitals (these are assumed *a priori* to be $1s$ shaped). All we do is choose the mixing coefficients so as to minimize the guess to the ground-state energy E_g.

We note, finally, that the density functional theory alluded to earlier can also be used for molecules. It is often the case that density functional theory yields a more accurate description than Hartree-Fock, but this depends on the molecule. In any case, both are more accurate than LCAO. There is also a hierarchy of methods called *post Hartree-Fock* methods, all of which are based on the wave function rather than the electron density, that can be used to improve upon the HF approximation systematically. The greater the accuracy that is desired for the calculation, the more costly computationally the post HF methods become, so quantum chemistry is often a trade-off between accuracy and efficiency, an issue that becomes more critical to take into account when calculations on large molecules must be carried out!

Contributors

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

9.6: A Simple Molecular-Orbital Treatment of H₂ Places Both Electrons in a Bonding Orbital is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.7: Molecular Orbitals Can Be Ordered According to Their Energies

The LCAO-MO method that we used for H_2^+ can be applied qualitatively to homonuclear diatomic molecules to provide additional insight into chemical bonding. A more quantitative approach also is helpful, especially for more complicated situations, like heteronuclear diatomic molecules and polyatomic molecules. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they are often ignored in constructing molecular orbitals. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

Molecular Orbitals Formed from *ns* Orbitals

The molecular orbitals diagrams formatted for the dihydrogen species are similar to the diagrams to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure **9.7.1**, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

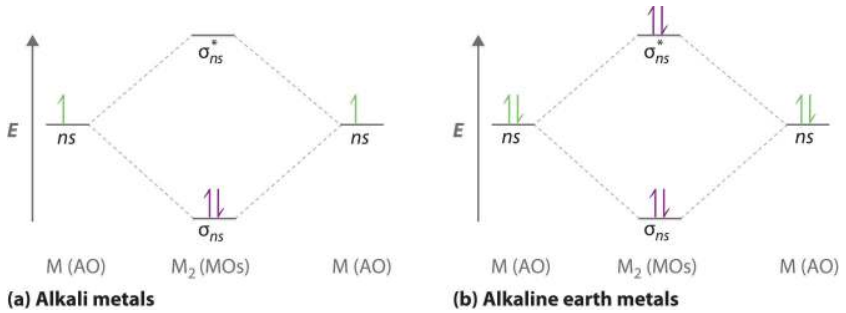


Figure **9.7.1**: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σns (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ^*_{ns} (nonbonding) levels, leading to a predicted bond order of 0. (CC BY-SA-NC; anonymous by request).

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule. As shown in Figure **9.7.1***b*, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

Example 9.7.1: Sodium Dimer Ion

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

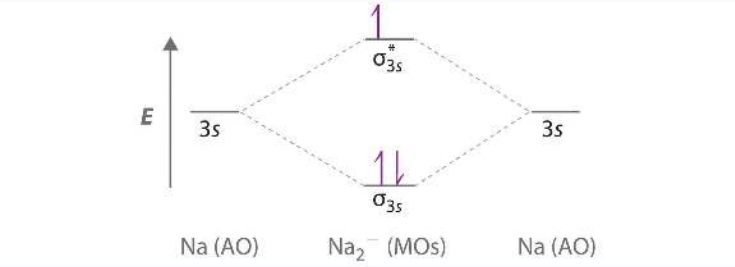
Strategy

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals.

B The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $(\sigma_{3s})^2(\sigma^*_{3s})^1$ electron configuration.



(CC BY-SA-NC; anonymous by request).

C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

Exercise 9.7.1: Calcium Dimer Cation

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer

Ca_2^+ has a $(\sigma_{4s})^2(\sigma^*_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

Molecular Orbitals Formed from n*p* Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{9.7.1}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure **9.7.2**, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{9.7.2}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{9.7.3}$$

In this combination, shown in part (b) in Figure **9.7.2**, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

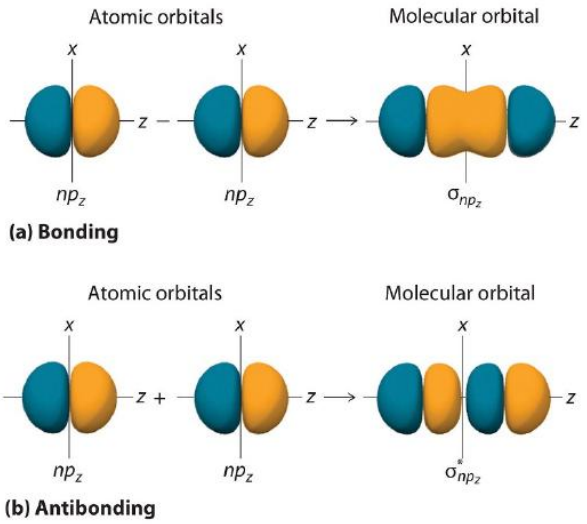


Figure **9.7.2**: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous by request).

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure **9.7.3**, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_z} = np_x\,(A) + np_x\,(B) \tag{9.7.4}$$

$$\pi^*_{np_z} = np_x\,(A) - np_x\,(B) \tag{9.7.5}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^*_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_z} and π_{np_y}molecular orbitals are a degenerate pair, as are the $\pi^*_{np_z}$ and $\pi^*_{np_y}$ molecular orbitals.

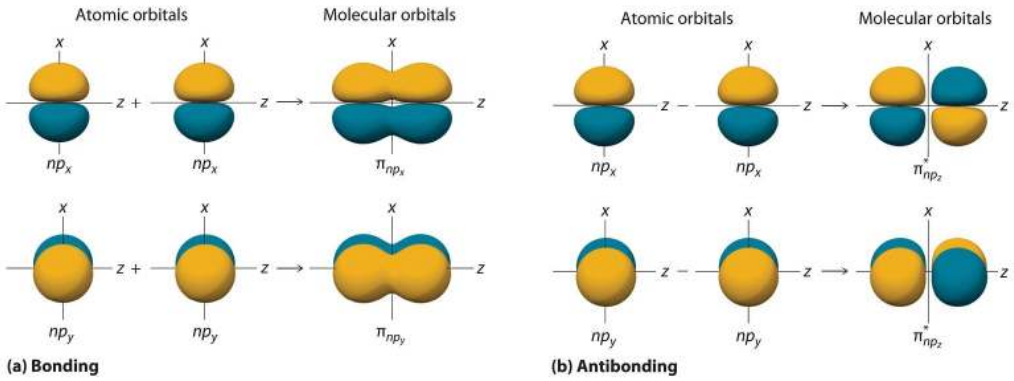


Figure **9.7.3**: Formation of π Molecular Orbitals from npx and npy Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the npx and the npy atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous by request).

Energies for Homonuclear Diatomic Molecules

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

Figure **9.7.4** is an energy-level diagram that can be applied to two *identical* interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

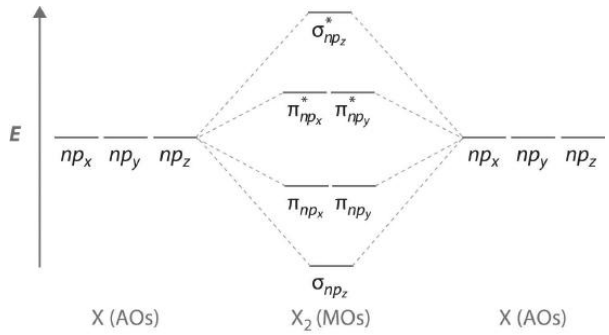


Figure **9.7.4**: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals. (CC BY-SA-NC; anonymous by request).

> *The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.*

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in Figure **9.7.5***a*; the $n = 1$ orbitals (σ_{1s} and σ_{1s}*) are located well below those of the $n = 2$ level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^*_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rules. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π* orbitals, for a total of 14 electrons.

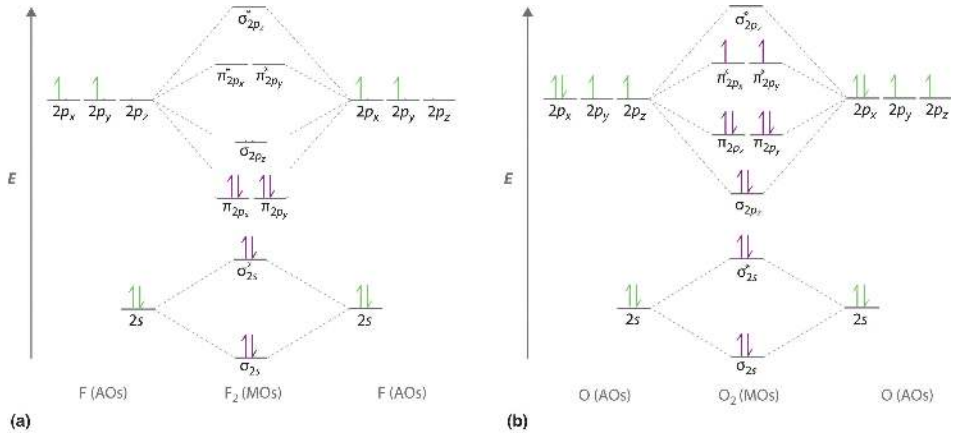


Figure **9.7.5**: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For C_2, with 8 valence electrons (4 from each F atom). This diagram shows 6 electrons in bonding orbitals and 2 in antibonding orbitals, resulting in a bond order of 2. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{np_x}, \pi^*_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. (CC BY-SA-NC; anonymous by request).

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^*_{np_x}$ and $\pi^*_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the $2p_z$ orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure **9.7.6**. Experimentally, the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure **9.7.6**). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

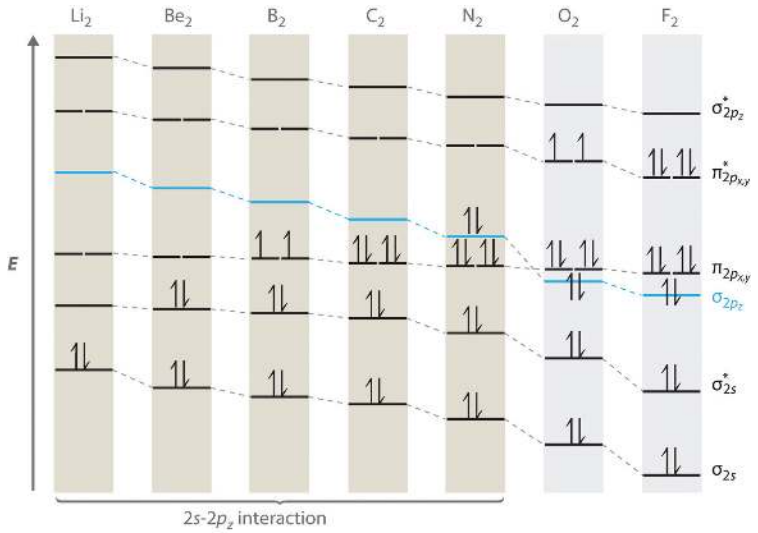


Figure **9.7.6**: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is *lower* in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2*s* and 2*p* atomic orbitals as the nuclear charge increases across the row. (CC BY-SA-NC; anonymous by request).

Example 9.7.2: Diatomic Sulfur

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

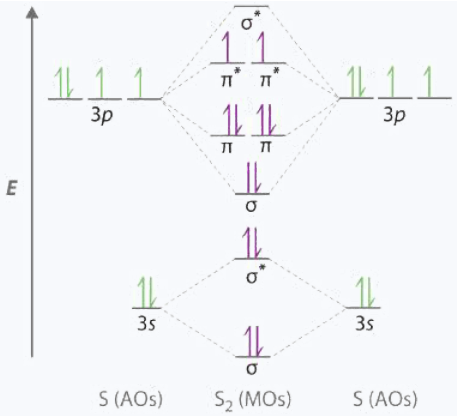
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^23p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figures **9.7.6** and **9.7.7**, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases, the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



(CC BY-SA-NC; anonymous by request).

Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_z} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^*_{3p_z}$ and $\pi^*_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^*_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi^*_{3p_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise 9.7.2

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_{x,y}})^4(\pi^*_{2p_{x,y}})^4$ bond order of 1; no unpaired electrons

Molecular Orbitals Formed from *ns* with n*p* Orbitals

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure **9.7.7**, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

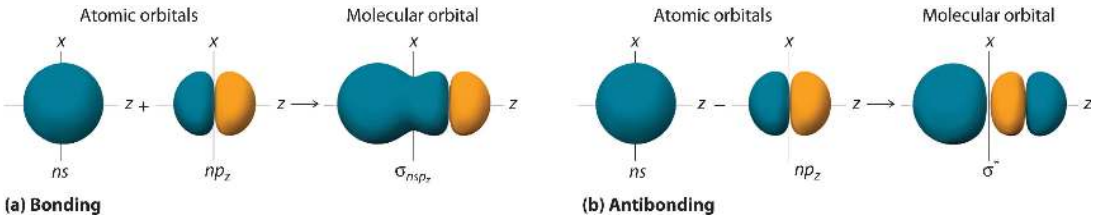


Figure **9.7.7**: Formation of Molecular Orbitals from an *ns* Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous by request).

9.7: Molecular Orbitals Can Be Ordered According to Their Energies is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

Bond Order

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. Within the molecular orbital approach, *bond order* is defined as one-half the *net* number of bonding electrons:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \tag{9.8.1}$$

To calculate the bond order of H_2, we know that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ^*_{1s} (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\text{bond order} = \frac{2-0}{2} = 1 \tag{9.8.2}$$

This result corresponds to the single covalent bond; double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams to describe the bonding in other pairs of atoms and ions where n = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's Rules.

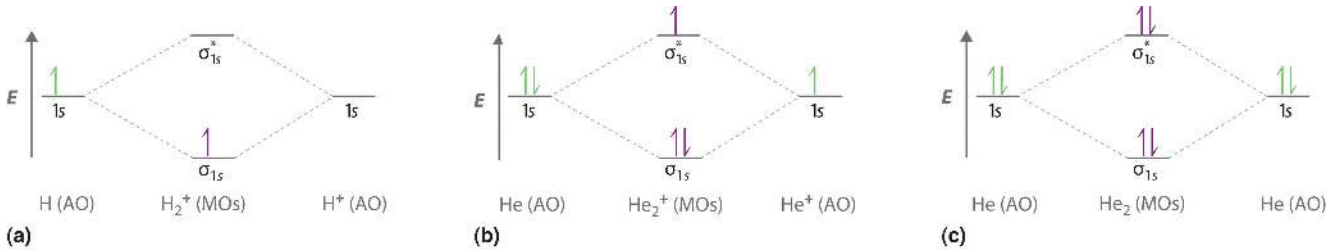


Figure 9.8.1: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here. Image used with permission (CC BY-SA-NC; anonymous by request).

Figure 9.8.1*a* shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (via Equation 9.8.1)

$$\text{bond order} = \frac{1-0}{2} = 1/2 \tag{9.8.3}$$

Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 9.8.1, these predictions agree with the experimental data.

Table 9.8.1: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Species	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	5,500	4.6×10^{-5}

Figure 9.8.1*b* is the molecular orbital energy-level diagram for He_2^{2+}. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the σ_{1s}^* antibonding orbital, giving a $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ electron configuration. This electron configuration gives a bond order (via Equation 9.8.1) of

$$\text{bond order} = \frac{2-1}{2} = 1/2 \tag{9.8.4}$$

As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 9.8.1).

Example 9.8.1: The He_2^{2+} ion

Use a molecular orbital energy-level diagrams to predict the bond order and stability of the He_2^{2+} ion.

Given: chemical species

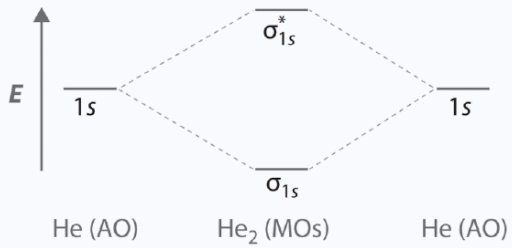
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

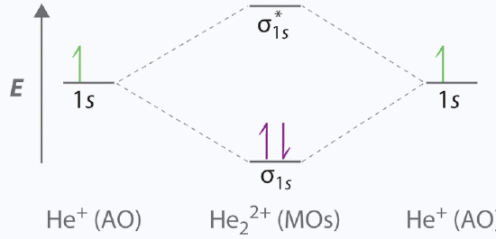
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ_{1s}^* antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired.

C So the bond order is (via Equation 9.8.1)

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise 9.8.1: The H_2^{2-} Ion

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ with a bond order of 0. It is therefore predicted to be unstable.

The Helium Dimer

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure **9.8.1c** is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and σ_{1s}^* antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ electron configuration, with a predicted bond order (via Equation 9.8.1) of

$$\text{bond order}=\frac{2-2}{2}=0 \tag{9.8.5}$$

which indicates that the He_2 molecule has no net covalent bond and is not a stable species.

The ability to track bond order to bond strength is due to the fact that the energy difference between the anti-bonding σ_{1s}^* molecular orbital and the original $1s$ atomic orbital is *larger* than the energy difference between the bonding σ_{1s} molecular orbital and the $1s$ atomic orbitals. This was derived previously where the stabilization energy (ΔE_+) of the σ_{1s} molecular orbital is less than the destabilization energy (ΔE_-) of the anti-bonding σ_{1s}^* molecular orbital:

$$\Delta E_\pm = E_\pm - E_H \tag{9.8.6}$$

$$= \frac{e^2}{4\pi\epsilon_0 R}+\frac{J\pm K}{1\pm S} \tag{9.8.7}$$

Hence, the anti-bonding σ_{1s}^* molecular orbital is more destabilized relative to the atomic orbitals than the bonding σ_{1s} molecular orbital is stabilized relative to the $1s$ atomic orbitals (E_H.

The fact that the anti-bonding MO energy difference is larger than the bonding σ_{1s} molecular orbital energy difference is the true reason that helium dimer is not predicted to exist with a covalent bond. Of the four valence electrons in helium dimer, two will fill the bonding σ_{1s} molecular orbital, and the other two will fill the anti-bonding σ_{1s}^* molecular orbital. The two electrons in the bonding σ_{1s} molecular orbital will achieve some stabilization relative to the $1s$ atomic orbitals, but the two electrons in the anti-bonding σ_{1s}^* molecular orbital will achieve *greater* de-stabilization relative to their position in the atomic orbitals. The net result is a less stable molecule than if the electrons remained in their respective $1s$ atomic orbitals.

> *The electrons in antibonding orbitals cancel (and exceed) the stabilization resulting from electrons in bonding orbitals. Consequently, any system that has equal numbers of*

bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature (at least as a covalent bonding).

However, Van der Waals Helium Dimers do exist

Based on molecular orbital theory discussed above, the He_2 molecule should not exist since no covalent bond formed between the helium atoms (Equation 9.8.5). However, the molecular orbital description above neglects the van der Waals force that exists between the atoms as demonstrated by the existence of liquid helium (at 4 K). So a "molecule" composed of two helium atoms bound by the van der Waals force may exist by this attractive force instead - and it does.

A helium dimer molecule bound by Van der Waals forces was first proposed by John Clarke Slater in 1928 and observed in 1993 by Gentry and coworkers. Interestingly, He_2 is the largest known molecule of two atoms when in its ground state with an extremely long bond length with a separation of about 5,200 pm. The binding energy is only $4.6 \times 10^{-5}\ kJ/mol$, so the **He—He** bond is 5,000 times weaker than the covalent bond in the hydrogen molecule (Table 9.8.1).

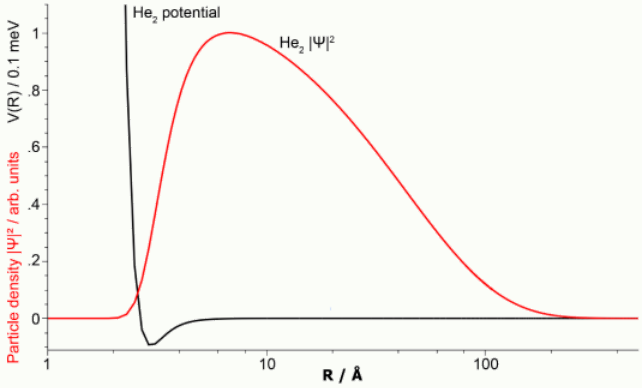


Figure 9.8.2: The weak helium-helium Van der Waals potential decrease leads to the particle probability density distribution leaking more into the classically forbidden region (i..e, tunneling). This effect allows the wavefunction to extend to sizes of fullerenes, the diameter of DNA and even small viruses (He_2 potential and wavefunction taken from Przybytek 2010), while the classical turning point is located at 13.6 Å, the overall wavefunction extends to more than 200 Å. Image used with permission (Inspire; http://inspirehep.net/record/1415151/plots)

Conclusion

The decrease in energy caused by the bonding orbital (constructive interference of the atomic orbitals) is canceled by the increase in energy caused by the antibonding orbital (destructive interference of the atomic orbitals), so it is not energetically favorable for the helium atoms to be in such proximity, so if that situation arises, they'll separate quickly since there's no force keeping them there.

9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle

The Pauli exclusion principle plays as important a role in the understanding of the electronic structure of molecules as it does in the case of atoms. The end result of the Pauli principle is to limit the amount of electronic charge density that can be placed at any one point in space. For example, the Pauli principle prevents the 1s orbital in an atom from containing more than two electrons. Since the 1s orbital places most of its charge density in regions close to the nucleus, the Pauli principle, by limiting the occupation of the 1s orbital, limits the amount of density close to the nucleus. Any remaining electrons must be placed in orbitals which concentrate their charge density further from the nucleus.

In an earlier discussion we pointed out that the reason the electron doesn't fall onto the nucleus is because it must possess kinetic energy if Heisenberg's uncertainty principle is not to be violated. This is one reason why matter doesn't collapse. The Pauli principle is equally important in this regard. The electron density of the outer electrons in an atom cannot collapse and move closer to the nucleus since it can do so only if the electrons occupy an orbital with a lower n value. If, however, the inner orbital contains two electrons, then the Pauli principle states that the collapse cannot occur. We must be careful in our interpretation of this aspect of the Pauli principle. The density from a 2s orbital has a small but finite probability of being found well within the density of the 1s orbital. Do not interpret the Pauli principle as implying that the density from an occupied orbital has a clearly defined and distinct region in real space all to its own. This is not the case. The operation of the Pauli principle is more subtle than this. In some simple cases, such as the ones we wish to discuss below, the limiting effect of the Pauli principle on the density distribution can, however, be calculated and pictured in a very direct manner.

The Pauli principle demands that when two electrons are placed in the same orbital their spins must be paired. What restriction is placed on the spins of the electrons during the formation of a molecule, when two orbitals, each on a different atom, overlap one another? For example, consider the approach of two hydrogen atoms to form a hydrogen molecule. Consider atom A to have the configuration $1s^1\alpha$ and atom B the configuration $1s^1\beta$. Even when the atoms approach very close to one another the Pauli principle would be satisfied as the spins of the two electrons are opposed. This is the situation we have tacitly assumed in our previous discussion of the hydrogen molecule. However, what would occur if two hydrogen atoms approached one another and both had the same configuration and spin, say $1s^1\alpha$? When two atoms are relatively close together the electrons become **indistinguishable**. It is no longer possible to say which electron is associated with which atom as both electrons move in the vicinity of both nuclei. Indeed this is the effect which gives rise to the chemical bond. In so far as we can still regard the region around each atom to be governed by its own atomic orbital, distorted as it may be, two electrons with the same spin will not be able to concentrate their density in the binding region. This region is common to the orbitals on both atoms, and since the electrons possess the same spin they cannot both be there simultaneously. In the region of greatest overlap of the orbitals, the binding region, the presence of one electron will tend to exclude the presence of the other if their spins are parallel. Instead of density accumulating in the binding region as two atoms approach, electron density is removed from this region and placed in the antibonding region behind each nucleus where the overlap of the orbitals is much smaller. Thus the approach of two hydrogen atoms with parallel spins does not result in the formation of a stable molecule. This repulsive state of the hydrogen molecule, in which both electrons have the same spin and atomic orbital quantum numbers, can be detected spectroscopically.

> *We can now give the general requirements for the formation of a chemical bond. Electron density must be accumulated in the region between the nuclei to an extent greater than that obtained by allowing the original atomic density distributions to overlap. In general, the increase in charge density necessary to balance the nuclear force of repulsion requires the presence of two electrons.*

We are now in a position to build up and determine the electronic configurations of the homonuclear diatomic molecules by adding electrons two at a time to the molecular orbitals with the spins of the electrons paired, always filling the orbitals of lowest energy first. We shall, at the same time, discuss the effectiveness of each orbital in binding the nuclei and make qualitative predictions regarding the stability of each molecular configuration.

The Pauli Exclusion Principle in Hydrogen Dimer

The two electrons in the hydrogen molecule may both be accommodated in the $1s_g$ orbital if their spins are paired and the molecular orbital configuration for H_2 is $1s_g^2$. Since the $1s_g$ orbital is the only occupied orbital in the ground state of H_2, the density distribution shown previously in Figure **9.9.2** for H_2 is also the density distribution for the $1s_g$ orbital when occupied by two electrons. The remarks made previously regarding the binding of the nuclei in H_2 by the molecular charge distribution apply directly to the properties of the $1s_g$ charge density.

The Pauli Exclusion Principle in Helium Dimer

The electronic configuration of He_2 is $1s_g^2\ 1s_u^2$. A s_u orbital, unlike a s_g orbital, possesses a node in the plane midway between the nuclei and perpendicular to the bond axis. The $1s_u$ orbital and all s_u orbitals in general, because of this nodal property, cannot concentrate charge density in the binding region. It is instead concentrated in the antibinding region behind each nucleus (Figure **9.9.3**).

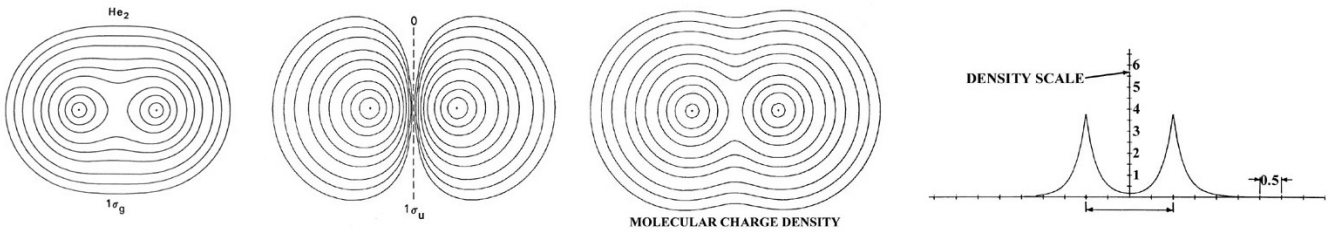


Figure **9.9.3**: Contour maps of the doubly-occupied $1\sigma_g$ and $1\sigma_u$ molecular orbital charge densities and of the total molecular charge distribution of He_2 at R = 2.0 au. A profile of the total charge distribution along the internuclear axis is also shown.

The s_u orbitals are therefore classified as ***antibonding***. It is evident from the form of density distribution for the $1s_u$ orbital that the charge density in this orbital pulls the nuclei apart rather than drawing them together. Generally, the occupation of an equal number of s_g and s_u orbitals results in an unstable molecule. The attractive force exerted on the nuclei by the charge density in the s_g orbitals is not sufficient to balance both the nuclear force of repulsion and the antibinding force exerted by the density in the s_u orbitals. Thus molecular orbital theory ascribes the instability of He_2 to the equal occupation of bonding and antibonding orbitals. Notice that the Pauli exclusion principle is still the basic cause of the instability. If it were not for the Pauli principle, all four electrons could occupy a s_g-type orbital and concentrate their charge density in the region of low potential energy between the nuclei. It is the Pauli principle, and not a question of energetics, which forces the occupation of the $1s_u$ antibonding orbital.

The total molecular charge distribution is obtained by summing the individual molecular orbital densities for single or double occupation numbers as determined by the electronic configuration of the molecule. Thus the total charge distribution for He_2 (Figure **9.9.3**) is given by the sum of the $1s_g$ and $1s_u$ orbital densities for double occupation of both orbitals. The adverse effect which the nodal property of the $1s_u$ orbital has on the stability of He_2 is very evident in the total charge distribution. Very little charge density is accumulated in the central portion of the binding region. The value of the charge density at the mid-point of the bond in He_2 is only 0.164 au compared to a value of 0.268 au for H_2.

We should reconsider in the light of molecular orbital theory the stability of He_2^+ and the instability of the hydrogen molecule with parallel spins. He_2^+ will have the configuration $1s_g^2\ 1s_u^1$. Since the $1s_u$ orbital is only singly occupied in He_2^+, less charge density is accumulated in the antibinding regions than is accumulated in these same regions in the neutral molecule. Thus the binding forces of the doubly-occupied $1s_g$ density predominate and He_2^+ is stable. The electron configuration of (triplet) H_2 is $1s_g^1(\alpha)1s_u^1(\alpha\text{-})$ when the electronic spins are parallel. The electrons **must** occupy separate orbitals because of the Pauli exclusion principle. With equal occupation of bonding and antibonding orbitals, the triplet H_2 species is predicted to be unstable.

Contributors

- Dr. Richard F.W. Bader (Professor of Chemistry / McMaster University)

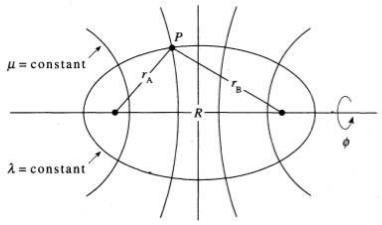
9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.E: Chemical Bond in Diatomic Molecules (Exercises)

Solutions to select questions can be found online.

9.3

The overlap integral and other integrals that arise in two-center systems like that of H_2 which is called a **two-center integral**. The two center integrals are much easier being evaluated by simply using the coordinate system, elliptic coordinates. In the coordinate system, where there are simply two fixed points which are separated by distance R.



A point P is given by three coordinates which are

- $\lambda = r_A + r_B/R$
- $\mu = r_A + r_B/R$

the angle ø is the angle that (r_A, r_B, R) triangle makes the interfocal axis. The differential volume element (elliptic coordinates) $\Leftrightarrow dr = R^3/8(\lambda^2 - \mu^2)d\lambda\, d\mu\, d\phi$

Given definitions λ, μ, ϕ → prove that

- $1 \leq \lambda < \infty$
- $-1 \leq \mu \leq 1$
- $0 \leq \phi \leq 2\pi$

Use elliptic coordinates to evaluate the overlap integral.

Use Equation:

$$S = \int dr\, 1s_A 1s_B = \frac{Z^3}{\pi} \int dr\, e^{-Zr_A} e^{-Zr_B}$$

Solution

From simple inspection of the figure:

- Have $r_A + r_B$ is never less than that of R. Therefore, $1 \leq \lambda < \infty$.
- $r_A - r_B$ can never have a of magnitude greater that that of R, therefore have $-1 \leq \mu \leq 1$.
- The variable ϕ can undergo 1 complete revolution therefore have/get $0 \leq \phi \leq 2\pi$.

Knowing all of this information, we can now solve for this equation:

$$\begin{aligned}
S &= \frac{Z^3}{\pi} \int dr e^{-Zr_A} e^{-Zr)B} \\
&= \frac{Z^3}{\pi} \int_0^{2\pi} d\phi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu R^3/8(\lambda^2 - \mu^2) e^{-Z(r_A + r_B)} \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu (\lambda^2 - \mu^2) e^{-ZR\lambda} \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda e^{-ZR\lambda} \int_{-1}^{1} d\mu (\lambda^2 - \mu^2) \\
&= \frac{R^3 Z^3}{4} \int_1^{\infty} d\lambda e^{-ZR\lambda} (2\lambda^2 - 2/3) \\
&= \frac{R^3 Z^3}{2} \left[(1/ZR + 2/Z^2R^2 + 2/Z^3R^3) e^{-ZR} - 1/3ZRe^{-ZR} \right] \\
&= e^{-ZR}(1 + ZR + Z^2R^2/3)
\end{aligned}$$

9.4

Repeat the calculation in 9.3 for $\psi_- = 1s_A - 1s_B$

Solution

$$E_- = \frac{\int dr \psi^*_- H \psi_-}{\int dr \psi^*_- \psi_-}$$

The denominator is

$$\int dr \psi^*_- \psi_- = 2(1 - S)$$

The numerator can be evaluated using equations 9.18, 9.19, 9.20, 9.21 with a simple exchange of a minus sign in equations 9.18 and 9.21,

$$\int dr \psi^*_- H \psi_- = 2E_{1s}(1 + S) + 2J - 2K$$

So

$$E_- = \frac{2E_{1s}(1 + S) + 2J - 2K}{2(1 - S)}$$

9.9

Show that the $2p_x$ and the $2p_y$ orbitals do not overlap. Use $2p_x \equiv C \cos\theta$ and $2p_y \equiv C \sin\theta \cos\theta$ and $f(r)$ as the radial component.

Solution

If $\int \Psi_1 \Psi_2 dr \neq 0$ then the orbitals overlap.

Substituting in:

$$\int C \cos^2\theta \sin\theta f(r)$$

$$C \int_0^{\pi} cos^2\theta \sin\theta \int_0^{\infty} f(r) \neq 0$$

This orbitals do not overlap.

9.10

what does the overlap integral represent?

Solution

The overlap integral represents the amount of overlap there is between the orbitals of 2 or more different nuclei. It is only significant for orbitals that have a large overlap. It is a component of the energy integral of the nuclei.

9.14

Which of the three species is the is the least stable due to bond order: O_2, O_2^+, O_2^{2-}. Hint it may be helpful to draw molecular orbitals for each species although it is not required.

Solution

We have to use the bond order formula for each of the situations.

$$\text{Bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of anti-bonding electrons})}{2}$$

For O_2: We have 12 valence electrons. Therefore

$$\text{Bond order} = \frac{10-8}{2} = 1$$

From the bond orders, we can see that O_2^{2-} is the least stable.

$$\text{Bond order} = \frac{10-5}{2} = \frac{5}{2}$$

For O_2^{2-}: We have 14 valence electrons. Therefore

$$\text{Bond order} = \frac{10-6}{2} = 2$$

For O_2^+: We have 11 valence electrons. Therefore

9.17

Write the electron configuration and bond order of carbon monoxide.

Solution

The electron configuration for carbon monoxide

$$CO : KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma 2_{p_z})^2$$

The bond order of CO is three.

9.17

Determine the bond order diphosphorus P_2.

Solution

Each phosphorus atom will contribute 5 valence electrons, so there will be a total of 10 valence electrons. We use these ten valence electrons to fill up atomic orbitals and we learn that the ground state electron configuration has 8 electron in bonding orbitals and 2 electrons in antibonding orbitals. To find bond order we take bonding electrons(8 electrons) minus antibonding (2 electrons) and divide by 2 to find the bond order of 3.

9.18

Determine the bond order for the bond in nitrogen oxide cation, NO^+.

Solution

The equation for bond order is

Misplaced '#'

There are 10 electrons total in the $2p$ level that have to fill the $\sigma_1, \sigma_1^*, \pi, \sigma_2, \pi^*\sigma_2^*$ in order of increasing energy, respectively. If one fills out the MO diagram, they will find that the number of bonding electrons is 8 and the number of antibonding electrons is 2.

Thus, the bond order is

$$\frac{1}{2}[8-2] = 3$$

This indicates that there is triple bond for NO^+

9.18

What is the electron configuration and bond order of nitric oxide ion?

Solution

The electron configuration of NO^+ is

$$NO^+ : KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^1$$

The bond order of NO^+ is $2\frac{1}{2}$

9.21

Determine the bond order for the NO molecule.

Solution

Bond Order = [(# of binding electrons) - (# of anitbonding electrons)] /2

From drawing the Molecular Orbital Diagram, we find that there are 6 binding electrons and 1 antibonding electron, therefore,

Bond Order = (6-1)/2 =5/2

9.22

How is the energy-level diagram for diatomic OH radical differ from that of NH? What is the highest occupied molecular orbital of OH?

9.23

If a light source generates a light at 73.4 nm while a photoelectron spectrometer is measuring the kinetic energy of the electrons ionized when the molecule absorbs this light, what is the largest electron binding energy that can be measured? Also, is it possible to determine the energy of the occupied molecular orbitals of a molecule using the kinetic energy of the ionized electrons measured? If yes, explain. *Hint* : Recall the photoelectron effect discussed in lecture 2.

Solution

The energy of the source light is

$$E = \frac{hc}{\lambda} = 2.71 \times 10^{-18}\ J$$

So 2.71 x 10^{-18} J is the largest electron binding energy that can be measured using this radiation source.

Using Einstein's explanation of the photoelectric effect, we know that

$$\varphi + KE = h\nu$$

Hence, if we know the kinetic energy of the ionized electrons, as well as the energy absorbed by the electron ν, we can find φ, which is the energy of the molecular orbital occupied by the electron being ionized.

9.24

Why would the ionization energy of a $3p$ electron from HCl molecule be lower than a $3p$ electron from a chlorine atom?

Solution

The electrons that are shared between the two atoms in HCl are pulled closer to the Chlorine atom because it has a greater electronegativity than hydrogen. This creates a dipole moment and the bonding electrons become localized in such a way that they shield the nonbonding $3p$ electrons on the chlorine atom more than the inner shells of just a chlorine atom. Since shielding is greater for HCl the electrons require less energy to be pulled away from the molecule. Less shielded valence electrons will experience a greater attractive force decreasing the radius and increasing ionization energy.

9.27

Photoelectron spectroscopy involves the measurement of kinetic energy of photoelectrons to determine the binding energy, intensity and angular distributions of these electrons and use the information obtained to examine the electronic structure of molecules. It differs from the conventional methods of spectroscopy in that it detects electrons rather than photons to study electronic structures of a material. The O_2 photoelectron spectrum emits two bands of 52.3898 MJ* mol^{-1} and 52.311 MJ*mol^{-1}. This emission corresponds to the 1\(\s) ionization of the oxygen electron. In your own words explain the observation.

Solution

The two bands that oxygen is emitted corresponds to the spin $(+\frac{1}{2},-\frac{1}{2})$ ionization in the $1s$ electron. The marginal difference in energy is due to the spin-orbit coupling, which is also known as spin-pairing. Spin-orbit coupling describes the weak magnetic interaction between the orbital motion and the particle spin in a particle

9.28

Would the ionization energies of non-bonding 1s electrons be different for HCl and Cl_2?

Solution

The shielding effects for the 1s electrons are different for these two systems. In HCl, the bonding electron is localized on the more electronegative Cl, while in Cl_2 the bonding electrons are right in between the two atoms. This means that the 1s electrons are more shielded in HCl than in Cl_2 , and so the electron is easier to rip off in HCl. So the ionization energy for 1s electrons in HCl is smaller than in Cl_2.

9.28

First write out the ground-state electron configuration for the homonuclear diatomic molecule F_2. Then given the experimental ionization energies for a 1s fluorine electron for HF and F_2 as 66.981 and 67.217 $MJ \cdot mol^{-1}$, explain why even though the 1s electrons of fluorine are not involved in the chemical bonds their ionization energies are different.

Solution

The ground state configuration is

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g)^2(1\pi_g)^2$$

The ionization energies are different because the 1s electrons affect the attraction of those electrons to the nucleus, even though they are not involved in the actual bond. The F_2 bonding electrons are equally distributed between two atoms, whereas the HF bonding electrons are localized on the fluorine atom. Therefore there is increased shielding of the 1s orbital on HF which causes a smaller ionization energy.

9.30

Try to solve for the ground-state term symbols for the diatomic molecules H_2^+ and H_2, given that the ground-state electron configuration for H_2^+ is $(\sigma_g 1s)^1$ and for H_2 is $(\sigma_g 1s)^2$.

Solution

$(1\sigma_g)^1$ corresponds to M_L=0 and M_s=1/2, meaning that there is an unpaired electron in the symmetric molecular orbitals of g and there is change in the $1\sigma_g$ wavefunction. The ground-state term symbol for H_2^+ will then be

$$^2\Sigma_g^+ \qquad (9.E.1)$$

$(1\sigma_g)^2$ corresponds to M_L=0 and M_s=0, meaning that there is an unpaired electron in the molecular orbitals of g and there is change in the $1\sigma_g$ wavefunction. The ground-state term symbol for H_2 will then be

$$^1\Sigma_g^+ \qquad (9.E.2)$$

9.30

Find the ground-state term symbols for B_2.

Solution

The ground state electron configuration is

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^1(1\pi_u)^1$$

We do not care about the filled orbitals because their

$$M_L = M_S = 0$$

The two unfilled orbitals are

$$(1\pi_u)^1(1\pi_u)^1$$

all possible combinations of

$$m_{l1}, m_{s1}, m_{l2}, m_{s2}$$

for B_2 are:

$$M_S, M_L :$$

$$(0,2) : 1^+, 1^-$$

$$(0,0) : 1^-, -1^+$$

$$(0,-2) : -1^+, -1^-$$

With these possible combinations we find the following to be possible ground state term symbols:

$$^1\Delta, ^3\Sigma, ^1\Sigma$$

Following Hund's Rule we detect $^3\Sigma$ to be our ground-state term symbol because the largest spin multiplicity will be the ground state of B_2. Now we take the two unoccupied orbitals and take the product to get the symmetry of the molecular orbital.

$$u \cdot u = g$$

So the ground-state term symbol for

$$B_2$$

is: $^3\Sigma_g^-$

9.31

Solve for the ground-state molecular term symbols for O_2, N_2, N_2^+, and O_2^+.

Solution

The ground state molecular term symbols are given below:

O_2

The molecular term symbol of O_2 without the ± designation is $^3\Sigma_g$. The electron configuration is (filled orbital) $(1\pi_g 2p_x)^1(1\pi_g 2p_y)^1$, so the symmetry with respect to a reflection through the x-z plane is (+) (-) = (-); therefore, the complete molecular term symbol of O_2 is $^3\Sigma_g^-$.

N_2

$(1\sigma_g)^2\ (1\sigma u)^2\ (2\sigma_g)^2(2\sigma u)^2(1\pi u)^2(1\pi u)^2(3\sigma_g)^2$ Corresponds to $|M_L| = 0$ and $|M_S| = 0$ of a $^1\Sigma$ term symbol. The symmetry of the molecule is g. The complete ground state term symbol of N_2 is $^1\Sigma_g^+$ because the molecular wave function does not change when reflected through a plane containing the two nuclei.

N_2^+

$(1\sigma_g)^2\ (1\sigma u)^2\ (2\sigma_g)^2(2\sigma u)^2(1\pi u)^2(1\pi u)^2(3\sigma_g)^1$ Corresponds to $|M_L| = 0$ and $|M_S| = 0.5$ of a $^2\Sigma$ term symbol. The symmetry of the molecule is g. The complete ground state term symbol of N_2^+ is $^2\Sigma_g^+$ because the molecular wave function does not change when reflected through a plane containing the two nuclei.

O_2^+

$(1\sigma_g)^2$ $(1\sigma u)^2$ $(2\sigma_g)^2(2\sigma u)^2(3\sigma_g)^2(1\pi u)^2(1\pi u)^2(1\pi g)^1$ Corresponds to | M_L | = 1 and | M_S | = 0.5 of a $^2\Pi$ term symbol. The symmetry of the molecule is g, since the only unfilled molecular orbital has symmetry g, so the complete ground state term symbol of O_2^+ is $^2\Pi_g$.

9.E: Chemical Bond in Diatomic Molecules (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic

In general chemistry courses, students learn that covalent bonds can come as either single, double or triple bonds, which are identifies by their bond order. Both bond length and bond energy changes as the bond order increases and as the number of electrons shared between two atoms in a molecule increases, the bond order of a bond increases, the strength of the bond increases and the distance between nuclei decreases (Table **9.10.1**).

Table **9.10.1**: General Correlation between Bond Strength, length and order in Covalent bonds

Bond	Bond Order	Bond Enthalpy (kJ/mol)	Bond Length (Å)
C–C	1	348	1.54
C=C	2	614	1.34
C≡C	3	839	1.20
N–N	1	163	1.47
N=N	2	418	1.24
N≡N	3	941	1.10

The above trend can be observed in the first row diatomics in Figure **9.10.1**. The bond order can be determined directly form the molecular orbital electron configurations.

$$\text{bond order} = \frac{\text{number of electrons in bonding MOs} - \text{number of electrons in antbonding MOs}}{2} \tag{9.10.1}$$

For diatomics, the occupations can correlate to bond length, bond energies (Figure **9.10.1**) and behavior in applied magnetic fields.

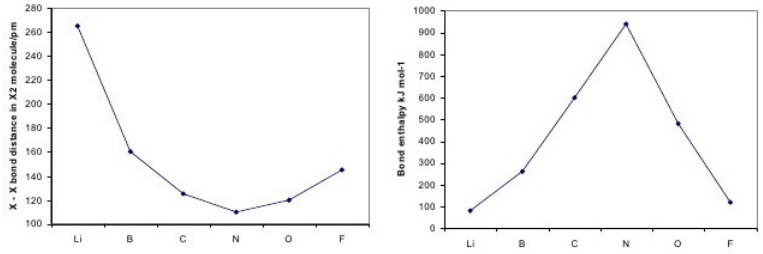


Figure **9.10.1**: Plot of bond length (left) and bond energy (right) for first row diatomics.

Example 9.10.1: Molecular Oxygen

Arrange the following four molecular oxygen species in order of increasing bond length: O_2^+, O_2, O_2^-, and O_2^{2-}.

Solution

The bond length in the oxygen species can be explained by the positions of the electrons in molecular orbital theory. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in Figure **9.10.1**. We again fill the orbitals according to Hund's rules and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, two more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. According to Hund's first rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving a multiplicity of 3 (a triplet state) with two unpaired electrons. This leads to a predicted bond order of

$$\frac{8-4}{2} = 2$$

which corresponds to a double bond, in agreement with experimental data: the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

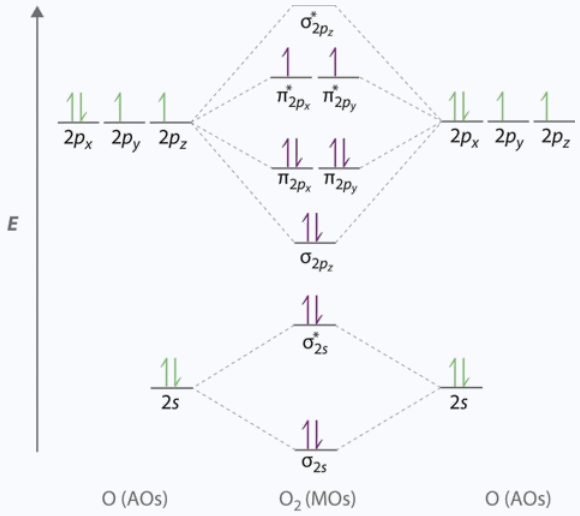


Figure 9.10.1: Molecular Orbital Energy-Level Diagrams for O_2. With 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $(\pi^*_{np_z}, \pi^*_{np_y})$ pair of orbitals. Hund's first rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. Image used with permission (CC BY-SA-NC; Anonymous by request).

The bond order is determined from the the electron configurations via Equation 9.10.1. The electron configurations for the four species are contrasted below.

- O_2:

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^1\pi_{2p_y}^{*\,1}$$

  From Equation 9.10.1, the bond order for O_2 is 2 (i.e., a double bond).

- O_2^+:

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^1\pi_{2p_y}^{*\,0}$$

  From Equation 9.10.1, the bond order for O_2^+ is 2.5. An alternative and equally valid configuration is

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^0\pi_{2p_y}^{*\,1}$$

- O_2^-:

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^2\pi_{2p_y}^{*\,1}$$

  From Equation 9.10.1, the bond order for O_2^- is 1.5. An alternative and equally valid configuration is

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^1\pi_{2p_y}^{*\,2}$$

- O_2^{2-}:

$$\sigma_{1s}^2\sigma_{1s}^{*\,2}\sigma_{2s}^2\sigma_{2s}^{*\,2}\sigma_{2p}^2\pi_{2p_y}^2\pi_{2p_y}^{*\,2}\pi_{2p_z}^2\pi_{2p_y}^{*\,2}$$

  From Equation 9.10.1, the bond order for O_2^{2-} is 1.

The bond order decreases and the bond length increases in the order. The predicted order of increasing bondlength then is O_2^+ < O_2 < O_2^- < O_2^{2-}. This trend is confirmed experimentally with O_2^+ (112.2 pm), O_2 (121 pm), O_2^- (128 pm) and O_2^{2-} (149 pm).

Molecular Oxygen is Paramagnetic

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. None of the other bonding models (e.g., Valence Bond theory or Lewis bonding) can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure **9.10.2**, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches.



Figure **9.10.2**: Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

Advanced: Spin Barriers

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*.

9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{9.11.1}$$

You can see from Equation 9.11.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 9.11.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals 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.

9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{9.12.1}$$

You can see from Equation 9.12.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 9.12.1

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.

9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules 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.

9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{9.13.1}$$

You can see from Equation 9.13.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 9.13.1

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.

9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently 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.

9.14: Molecular Term Symbols Describe Electronic States of Molecules

Molecular term symbols specify molecular electronic energy levels. Term symbols for diatomic molecules are based on irreducible representations in linear symmetry groups, derived from spectroscopic notations. They usually consist of four parts: spin multiplicity, azimuthal angular momentum, total angular momentum and symmetry. All molecular term symbols discussed here are based on Russel-Saunders coupling.

Introduction

Molecular term symbols mark different electronic energy levels of a diatomic molecule. These symbols are similar to atomic term symbols, since both follow the Russell-Saunders coupling scheme. Molecular term symbols employ symmetry labels from group theory. The possibility of an electronic transition can be deducted from molecular term symbols following selection rules. For multi-atomic molecules, symmetry labels play most of term symbols' roles.

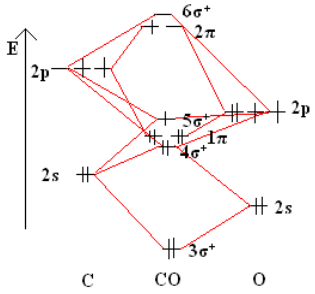
For homonuclear diatomics, the term symbol has the following form:

$$^{2S+1}\Lambda^{(+/-)}_{\Omega,(g/u)} \tag{9.14.1}$$

whereas Λ is the projection of the orbital angular momentum along the internuclear axis: Ω is the projection of the total angular momentum along the internuclear axis; *g*/*u* is the parity; and +/− is the reflection symmetry along an arbitrary plane containing the internuclear axis. Λ may be one of the greek letters in the sequence: Σ Π Δ Φ... when Λ = 0, 1, 2, 3..., respectively. For heteronuclear diatomics, the term symbol does not include the *g*/*u* part, for there is not inversion center in the molecule.

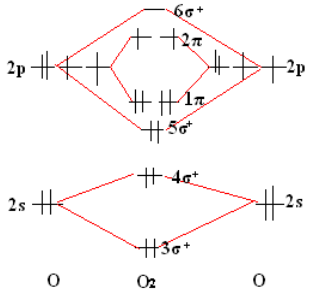
Determining term symbols of diatomics

Let's start with CO again. As we have seen before, the molecule has a close-shell configuration. Its ground state is a totally symmetric singlet, $^1\Sigma^+$, since the only possible values of (*S*, Λ) are (0, 0). If one of the HOMO electrons on the $5\sigma^+$ orbital has jumped to the LUMO, this molecule will be in an excited state as follows.



Suppose a CO molecule is in the excited state shown above. In order to know the term symbol of this state, a direct product of the labels is required for the two MO's with unpaired electrons. The multiplication is such as $\Pi \times \Sigma^+ = \Pi$. According to Pauli's exclusion rule, these two unpaired electrons can never share the same set of quantum numbers, therefore the spin degeneracy *S* can reach its maximum 3. The resulting term symbols are $^1\Pi$ and $^3\Pi$.

Now if we look at O_2, it does not have a close-shell configuration at its ground state. There are two unpaired electrons each occupying one of the two degenerate 2π orbitals, which can be seen in the diagram below.



The term symbol for oxygen molecule at its ground state is therefore derived such as Π x Π = Σ^+ + Σ^- + [Δ], as the symbol in brackets does not allow the oxygen atoms to commute.

Transition between electronic states of diatomics

We'll focus on selection rules. Like atomic electronic states, different selection rules apply when differently incurred transitions occur. Usually for electric dipole field induced transitions, the selection rules are the same as for atoms.

1. $\Delta\Lambda = 0, \pm1$ except $\Lambda = 0 \ddagger \Lambda' = 0$
2. $\Delta S = 0$
3. $\Delta\Omega = 0; \pm1$ except $\Omega = 0 \ddagger \Omega' = 0$

References

1. Harris, Daniel C. (republished in 1989). *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy.* Dover Publications. pp. 421-478. ISBN 0-486-66144-X
2. D. J. Willock (2009). *Molecular Symmetry*. John Wiley & Sons Ltd. ISBN 0-470-85348-4

https://www1.udel.edu/pchem/C444/spL...s/05152008.pdf

Excitations between molecular electronic states provide information about properties of molecules. Molecular electronic transitions are induced by UV/VIS radiation, and so these transitions involve much more energy compared to the vibrational-rotational spectroscopies that require microwave and infrared frequencies. However, much as in the case of IR spectroscopy, electronic spectroscopy of molecules includes a ”fine structure” arising from vibrational-rotational transitions associated with changes in electronic states.

Before discussing electronic spectroscopy, we will investigate the description of molecular electronic states in terms of molecular term symbols as in the case of atomic electronic transitions. This should highlight the fact that multiple states are possible given a particular molecular electronic configuration based on the angular momentum and spin.

Molecular Term Symbols: Diatomic Molecules

As with atoms, ML and MS are the ”good” quantum numbers (L and S commute with Hamiltonian for diatomic molecules • Only unfilled subshells contribute to the term orbital and spin angular momentum • For first and second row diatomics, MO’s are either of σ or π type. 1 • ML and MS are generated as follow: – ML = P i mli – MS = P i msi • For MO’s with σ symmetry, ml = 0 • For MO’s with π symmetry, ml = ±1 – Note that there is no ml = 0 for π MO’s since the Pz atomic orbital is associated with the σ MO • As in the atomic case, −L ≤ ML ≤ L and −S ≤ MS ≤ S. • We need to determine the maximum values of ML and MS and generate term symbols • The values of ML corresponding to the various total angular momentum values possible are labelled with Λ. • The possible values of Λ can be 0, 1, 2, 3, ... – As with the atomic case, each numerical value of Λ corresponds to a letter, in the molecular case being Greek letters. • The term symbols are of the form: 2S+1Λ

9.14: Molecular Term Symbols Describe Electronic States of Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **Molecular Term Symbols** by Anda Zheng, Sudarson S Sinha is licensed CC BY 4.0.

9.15: Molecular Term Symbols Designate Symmetry

The quantum numbers for diatomic molecules are similar from the atomic quantum numbers. Be cautious, because the rules for finding the possible combinations are different. The total orbital angular momentum quantum number For the molecular case, this number is called Λ instead of L. It follows the same naming convention as L, except that instead of using capital English letters, it uses capital Greek letters:

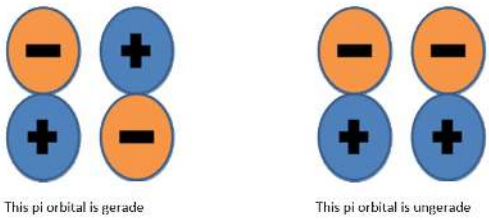
- $\Lambda = 0 \rightarrow \Sigma$
- $\Lambda = 1 \rightarrow \Pi$
- $\Lambda = 2 \rightarrow \Delta$
- $\Lambda = 3 \rightarrow \Phi$

Unlike L, there is not a general formula for finding the possible combinations of Λ. You have to examine the individual microstates. This is easier than it sounds.

- **The total magnetic quantum number M_L**: M_L works like M_l with atoms, except that there is no formula for finding the combinations.
- **The total spin magnetic quantum number M_S**: M_S works exactly like M_s. Electrons can either point with or against the z - axis, and being in a molecular orbital versus an atomic orbital doesn't change this. M_S can range from $m_{s1} + m_{s2}$ to m_{s1}-m_{s2}.

Two new components: parity and reflection

Molecular orbitals are more complex than atomic ones and require more modifiers to completely define. **Parity** (sometimes called "inversion") tells you if the orbital is *symmetric* or *anti-symmetric* when an inversion operation is performed. The symmetry notation **u** and **g** are sometimes used when describing molecular orbitals. This refers to the operation of inversion, which requires starting at an arbitrary point in the orbital, traveling straight through the center, and then continuing outwards an equal distance from the center. The orbital is designated **g** (for gerade, even) if the phase is the same, and **u** (for ungerade, uneven) if the phase changes sign.



To determine whether or not a given state is g or u, find the parity of each individual open-shell electron and uses these simple (Laporte rules):

- $g + g \rightarrow g$
- $g + u \rightarrow u$
- $u + u \rightarrow g$

Example 9.15.1: Closed Shell Configuration

What is the parity of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

Solution

Since both open shell electrons are ungerade, the overall parity is g. Helpful hint: bonding sigma orbitals and anti - bonding pi orbitals are always gerade. Anti - bonding sigmas and bonding pis are always ungerade. Draw them and see for yourself.

Reflection determines if a given orbital is symmetric or anti-symmetric upon reflection through a plane that contains both nuclei. The choice of symmetry planes is arbitrary. As long as you pick a plane and stick with it, you will always get the right answer. When an orbital is symmetric, it is labeled +. When an orbital is anti - symmetric, it is labeled - . To find the overall reflection of a state, use these rules:

- (+)(+) \rightarrow +

- (+)(-) \rightarrow -
- (-)(-) \rightarrow +

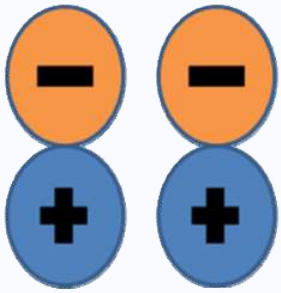
Reflection only applies to Σ states! For Λ > 0, there are no reflection labels! If you experiment with the rules, you will quickly realize why this is the case.

Example 9.15.2

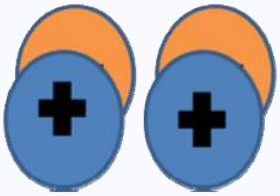
What is the reflection of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

Solution

You need to know what the orbitals look like. Draw a picture and then pick a plane. For this example, the plane of the page is selcted, but the orthogonal plane would have worked just as well.



The “vertical” orbital is +



The “horizontal” orbital is -

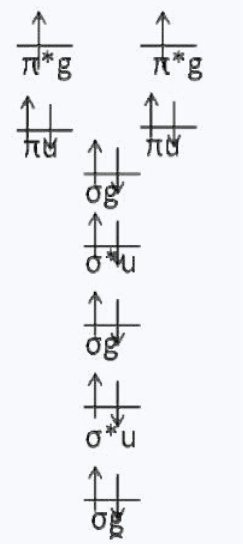
The “vertical” orbital is + The “horizontal” orbital is - Since one is + and one is - , the overall reflection is - . Try using the orthogonal plane and convince yourself that you still get the same answer.

Example 9.15.3: Oxygen

What are the term symbols for O_2 ?

Solution

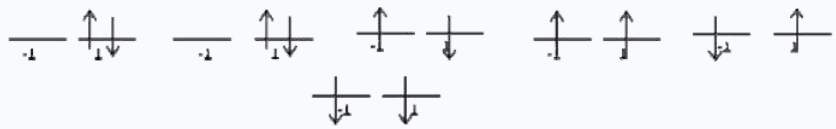
The molecular orbital diagram for O_2 is



Where I chose arbitrary configurations for the last two electrons.

There are two open - shell electrons occupying the anti-bonding π_g orbitals. These are the only electrons that matter. It is easiest to simply draw all of the permutations and figure out the bounds on Λ and M_L by inspection. If we do this, it is easy to see that Λ

$= 2, 0$ and that $M_L = 2, 0, -2$



$M_s = -1$	$M_s = 0$	$M_s = 2$
0	**1**	0
1	2	1
0	1	0

The top row is a $\Lambda = 2$ $M_S = 0$ state, so it is $^1\Delta$. Both electrons are in the rightmost orbital. This orbital is gerade, and (g)(g) = g, so the parity label is g. We do not assign reflection labels to non Σ states, so the term symbol is $^1\Delta_g$. After removing the used up microstates, the chart becomes

$M_s = -1$	$M_s = 0$	$M_s = 2$
1	**1**	0

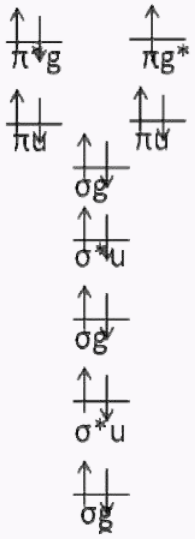
This is a Λ =0 state with three possible spin configurations, so it is $^3\Sigma$. We know that the electrons are in different sub-orbitals (if you cannot see this, try drawing all of the possible combinations that give $\Lambda = 0$). Both of the orbitals are gerade, so the overall parity is gerade. One of the orbitals will be +, the other will be - . The final answer is $^1\Delta_g \backslash (^3\Sigma_g^+$

Exercise 9.15.1

Write the term symbols for O_2^-

Solution

First draw the electron configuration diagram.



There are only two possible configurations. It should be easy to see that the term symbol is $^2\Pi_g$.

Contributors

- Mattanjah de Vries (Chemistry, University of California, Santa Barbara)

9.15: Molecular Term Symbols Designate Symmetry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

9.16: Most Molecules Have Excited Electronic States

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{9.16.1}$$

You can see from Equation 9.16.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 9.16.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

9.16: Most Molecules Have Excited Electronic States 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

Back Matter

Index

Glossary

Detailed Licensing

Index

A

Anharmonicity
- 13.5: Vibrational Overtones

antibonding molecular orbital
- 9.5: Bonding and Antibonding Orbitals

atomic term symbols
- 8.8: Term Symbols Gives a Detailed Description of an Electron Configuration
- 8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

Atomic units
- 8.1: Atomic and Molecular Calculations are Expressed in Atomic Units

B

Boltzmann factor
- 17: Boltzmann Factor and Partition Functions

bond order
- 9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

bonding molecular orbital
- 9.5: Bonding and Antibonding Orbitals

bosons
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

bracketing theorem
- 7.2: Linear Variational Method and the Secular Determinant

C

centrifugal force
- 13.4: The Pure Rotational Spectrum has Unequal Spacings

Chandrasakar wavefunction
- 8.2: Perturbation Theory and the Variational Method for Helium

CONDON APPROXIMATION
- 13.7: The Franck-Condon Principle

Coulomb integral
- 10.5: The \(\pi\)-Electron Approximation of Conjugation

cyclic permutations (angular momenta)
- 6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

D

delocalization energy
- 10.6: Butadiene is Stabilized by a Delocalization Energy

E

Exchange Operator
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

extended basis sets
- 11.2: Extended Basis Sets

F

fermions
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

fine structure
- 8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

G

Gaussian Type Orbitals
- 11.1: Gaussian Basis Sets

H

Hückel theory
- 10.5: The \(\pi\)-Electron Approximation of Conjugation

hartree (unit)
- 8.2: Perturbation Theory and the Variational Method for Helium

Hartree equations
- 8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

Hermitian operators
- 7.2: Linear Variational Method and the Secular Determinant

Hund's Rules
- 8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States

hybridization (water)
- 10.2: Different Hybrid Orbitals Used for Bonding in Water

Hylleraas Wavefunction
- 8.2: Perturbation Theory and the Variational Method for Helium

I

intrinsic spin
- 8.4: An Electron Has an Intrinsic Spin Angular Momentum

K

Koopmans' Theorem
- 10.4: Photoelectron Spectroscopy

L

LCAO
- 9.4: Chemical Bond Stability
- 9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently

M

molecular term symbols
- 9.14: Molecular Term Symbols Describe Electronic States of Molecules
- 9.15: Molecular Term Symbols Designate Symmetry

O

orbital angular momentum
- 6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

orbital approximation
- 6.7: The Helium Atom Cannot Be Solved Exactly

overlap
- 9.3: The Overlap Integral

Overlap integral
- 9.3: The Overlap Integral

overtones
- 13.5: Vibrational Overtones

P

partition functions
- 17: Boltzmann Factor and Partition Functions

Pauli’s exclusion principle
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

penetration
- 7.1: The Variational Method Approximation

permutation operator
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

Pertubation Theory for Helium
- 8.2: Perturbation Theory and the Variational Method for Helium

perturbation theory
- 7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

physical
- 13.1: The Electromagnetic Spectrum
- 13.2: Rotational Transitions Accompany Vibrational Transitions
- 13.3: The Vibration-Rotation Spectrum
- 13.5: Vibrational Overtones

Polarization Terms
- 11.3: Orbital Polarization Terms

R

resonance integral
- 10.5: The \(\pi\)-Electron Approximation of Conjugation

S

Secular Determinant
- 7.2: Linear Variational Method and the Secular Determinant

secular equations
- 7.2: Linear Variational Method and the Secular Determinant
- 9.5: Bonding and Antibonding Orbitals

shielding
- 7.1: The Variational Method Approximation

Slater determinant wavefunction
- 8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants

Slater Type Orbitals
- 11.1: Gaussian Basis Sets

Spherical harmonics

6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics

STO

7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters

symmetry number

18.6: Rotational Partition Functions Contain a Symmetry Number

T

total angular momentum

8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number

Total Angular Momentum Quantum Number (J)

8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number

trial wavefunction

7.2: Linear Variational Method and the Secular Determinant

V

Variational Method

7.1: The Variational Method Approximation
7.2: Linear Variational Method and the Secular Determinant

Variational Method for Helium

8.2: Perturbation Theory and the Variational Method for Helium

W

Walsh diagrams

10.3: Why is BeH_2 Linear and H_2O Bent?

Z

Zeeman effect

8.4: An Electron Has an Intrinsic Spin Angular Momentum

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: BCU: CH 332 Physical Chemistry II

Webpages: 188

All licenses found:

- Undeclared: 99.5% (187 pages)
- CC BY-SA 4.0: 0.5% (1 page)

By Page

- BCU: CH 332 Physical Chemistry II - *Undeclared*
  - 00: Front Matter - *Undeclared*
    - Table of Contents - *Undeclared*
  - AGENDA - *Undeclared*
    - Rethinking Hybridization - *Undeclared*
  - Homework - *Undeclared*
    - Homework 1 - *Undeclared*
    - Solutions 1 - *Undeclared*
    - Homework 2 - *Undeclared*
    - Solutions 2 - *Undeclared*
    - Homework 3 - *Undeclared*
    - Solutions 3 - *Undeclared*
    - Homework 4 - *Undeclared*
    - Solutions 4 - *Undeclared*
    - Homework 5 - *Undeclared*
    - Solutions 5 - *Undeclared*
    - Homework 6 - *Undeclared*
    - Solutions 6 - *Undeclared*
    - Homework 7 - *Undeclared*
    - Solutions 7 - *Undeclared*
    - Homework 8 - *Undeclared*
    - Solutions 8 - *Undeclared*
    - Homework 9 - *Undeclared*
    - Solutions 9 - *Undeclared*
    - Homework 10 - *Undeclared*
    - Solutions 10 - *Undeclared*
    - Homework 11 - *Undeclared*
    - Solutions 11 - *Undeclared*
    - Homework 12 - *Undeclared*
    - Solutions 12 - *Undeclared*
    - Homework 13 - *Undeclared*
    - Solutions 13 - *Undeclared*
    - Homework 14 - *Undeclared*
    - Solutions 14 - *Undeclared*
    - Homework 15 - *Undeclared*
    - Solutions 15 - *Undeclared*
  - Text - *Undeclared*
    - Front Matter - *Undeclared*
      - TitlePage - *Undeclared*
      - InfoPage - *Undeclared*
      - Table of Contents - *Undeclared*
      - Licensing - *Undeclared*
    - 6: The Hydrogen Atom - *Undeclared*
      - 6.E: The Hydrogen Atom (Exercises) - *Undeclared*
      - 6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly - *Undeclared*
      - 6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics - *Undeclared*
      - 6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision - *Undeclared*
      - 6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers - *Undeclared*
      - 6.5: s-orbitals are Spherically Symmetric - *Undeclared*
      - 6.6: Orbital Angular Momentum and the p-Orbitals - *Undeclared*
      - 6.7: The Helium Atom Cannot Be Solved Exactly - *Undeclared*
    - 7: Approximation Methods - *Undeclared*
      - 7.E: Approximation Methods (Exercises) - *Undeclared*
      - 7.1: The Variational Method Approximation - *Undeclared*
      - 7.2: Linear Variational Method and the Secular Determinant - *Undeclared*
      - 7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters - *Undeclared*
      - 7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems - *Undeclared*

- 8: Multielectron Atoms - *Undeclared*
  - 8.E: Multielectron Atoms (Exercises) - *Undeclared*
  - 8.1: Atomic and Molecular Calculations are Expressed in Atomic Units - *Undeclared*
  - 8.2: Perturbation Theory and the Variational Method for Helium - *Undeclared*
  - 8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method - *Undeclared*
  - 8.4: An Electron Has an Intrinsic Spin Angular Momentum - *Undeclared*
  - 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons - *Undeclared*
  - 8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants - *Undeclared*
  - 8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data - *Undeclared*
  - 8.8: Term Symbols Gives a Detailed Description of an Electron Configuration - *Undeclared*
  - 8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number - *Undeclared*
  - 8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States - *Undeclared*
  - 8.11: Using Atomic Term Symbols to Interpret Atomic Spectra - *Undeclared*
- 9: Chemical Bonding in Diatomic Molecules - *Undeclared*
  - 9.E: Chemical Bond in Diatomic Molecules (Exercises) - *Undeclared*
  - 9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules - *Undeclared*
  - 9.2: The H_2^+ Prototypical Species - *Undeclared*
  - 9.3: The Overlap Integral - *Undeclared*
  - 9.4: Chemical Bond Stability - *Undeclared*
  - 9.5: Bonding and Antibonding Orbitals - *Undeclared*
  - 9.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital - *Undeclared*
  - 9.7: Molecular Orbitals Can Be Ordered According to Their Energies - *Undeclared*
  - 9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule - *Undeclared*
  - 9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle - *Undeclared*
  - 9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic - *Undeclared*
  - 9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals - *Undeclared*
  - 9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules - *Undeclared*
  - 9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently - *Undeclared*
  - 9.14: Molecular Term Symbols Describe Electronic States of Molecules - *Undeclared*
  - 9.15: Molecular Term Symbols Designate Symmetry - *Undeclared*
  - 9.16: Most Molecules Have Excited Electronic States - *Undeclared*
- 10: Bonding in Polyatomic Molecules - *Undeclared*
  - 10.1: Hybrid Orbitals Account for Molecular Shape - *Undeclared*
  - 10.2: Different Hybrid Orbitals Used for Bonding in Water - *Undeclared*
  - 10.3: Why is BeH_2 Linear and H_2O Bent? - *Undeclared*
  - 10.4: Photoelectron Spectroscopy - *Undeclared*
  - 10.5: The \(\pi\)-Electron Approximation of Conjugation - *Undeclared*
  - 10.6: Butadiene is Stabilized by a Delocalization Energy - *Undeclared*
- 11: Computational Quantum Chemistry - *Undeclared*
  - 11.0: Overview of Quantum Calculations - *Undeclared*
  - 11.1: Gaussian Basis Sets - *Undeclared*
  - 11.2: Extended Basis Sets - *Undeclared*
  - 11.3: Orbital Polarization Terms - *Undeclared*
  - 11.4: The Ground-State Energy of H_2 - *Undeclared*
  - 11.5: Quantum Calculations - *Undeclared*
- 12: Group Theory - Exploiting Symmetry - *Undeclared*
  - 12.1: Using Symmetry to Simplify Calculations - *Undeclared*
  - 12.2: The Symmetry of Molecules - *Undeclared*
  - 12.3: Symmetry Operations Define Groups - *Undeclared*
  - 12.4: Symmetry Operations can be Represented by Matrices - *Undeclared*
  - 12.5: The \(C_3V\) Point Group Has a 2-D Irreducible Representation - *Undeclared*
  - 12.6: Character Tables - *Undeclared*
  - 12.7: Relations involving Characters - *Undeclared*

- 12.8: Using Symmetry to Predict Zero in a Secular Determinant - *Undeclared*
- 12.9: Generating Operators for Irreducible Representations - *Undeclared*

- 13: Molecular Spectroscopy - *Undeclared*
  - 13.1: The Electromagnetic Spectrum - *Undeclared*
  - 13.2: Rotational Transitions Accompany Vibrational Transitions - *Undeclared*
  - 13.3: The Vibration-Rotation Spectrum - *Undeclared*
  - 13.4: The Pure Rotational Spectrum has Unequal Spacings - *Undeclared*
  - 13.5: Vibrational Overtones - *Undeclared*
  - 13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information - *Undeclared*
  - 13.7: The Franck-Condon Principle - *Undeclared*
  - 13.8: Rotational Spectra of Polyatomic Molecules - *Undeclared*
  - 13.9: Normal Modes in Polyatomic Molecules - *Undeclared*
  - 13.10: Irreducible Representation of Point Groups - *Undeclared*
  - 13.11: Time-Dependent Perturbation Theory - *CC BY-SA 4.0*
  - 13.12: The Selection Rule for the Rigid Rotator - *Undeclared*
  - 13.13: The Harmonic Oscillator Selection Rule - *Undeclared*
  - 13.14: Group Theory Determines Infrared Activity - *Undeclared*
  - 13.E: Molecular Spectroscopy (Exercises) - *Undeclared*
- 14: Nuclear Magnetic Resonance Spectroscopy - *Undeclared*
  - 14.1: Nuclei Have Intrinsic Spin Angular Momenta - *Undeclared*
  - 14.2: Magnetic Moments Interact with Magnetic Fields - *Undeclared*
  - 14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz - *Undeclared*
  - 14.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded - *Undeclared*
  - 14.5: Chemical Shifts is Sensitive to Chemical Environment of the Nucleus - *Undeclared*
  - 14.6: Spin-Spin Coupling Results in Multiplets in NMR Spectra - *Undeclared*
  - 14.7: Spin-Spin Coupling Between Chemically Equivalent Protons Is Not Observed - *Undeclared*
  - 14.8: The n+1 Rule Applies Only to First-Order Spectra - *Undeclared*
  - 14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method - *Undeclared*
- 15: Lasers, Laser Spectroscopy, and Photochemistry - *Undeclared*
  - 15.1: Electronically Excited Molecules - *Undeclared*
  - 15.2: Transitions Modeled as Kinetics - *Undeclared*
  - 15.3: Two-Level Systems Cannot Form Population Inversions - *Undeclared*
  - 15.4: Population Inversion via Three-Level Systems - *Undeclared*
  - 15.5: Laser Fundamentals - *Undeclared*
  - 15.6: The Helium-Neon Laser - *Undeclared*
  - 15.7: High-Resolution Laser Spectroscopy - *Undeclared*
  - 15.8: Photochemical Dynamics - *Undeclared*
- 16: The Properties of Gases - *Undeclared*
  - 16.1: All Dilute Gases Behave Ideally - *Undeclared*
  - 16.2: van der Waals and Redlich-Kwong Equations - *Undeclared*
  - 16.3: A Cubic Equation of State - *Undeclared*
  - 16.4: The Law of Corresponding States - *Undeclared*
  - 16.5: The Second Virial Coefficient - *Undeclared*
  - 16.6: The Repulsive Term in the Lennard-Jones Potential - *Undeclared*
  - 16.7: Van der Waals Constants in Terms of Molecular Parameters - *Undeclared*
  - 16.E: The Properties of Gases (Exercises) - *Undeclared*
- 17: Boltzmann Factor and Partition Functions - *Undeclared*
  - 17.1: The Boltzmann Factor Is One of the Most Important Quantities in the Physical Sciences - *Undeclared*
  - 17.2: The Thermal Boltzman Distribution - *Undeclared*
  - 17.3: We Postulate That the Average Ensemble Energy Is Equal to the Observed Energy of a System - *Undeclared*
  - 17.4: The Heat Capacity at Constant Volume - *Undeclared*

- 17.5: Express the Pressure in Terms of a Partition Function - *Undeclared*
- 17.6: Partition Functions of Systems of Distinguishable Molecules are Products of Molecular Partition Functions - *Undeclared*
- 17.7: Partition Function of Indistinguishable Components - *Undeclared*
- 17.8: A Molecular Partition Function Can Be Decomposed into Partition Functions for Each Degree of Freedom - *Undeclared*
- 17.E: Exercises - *Undeclared*

- 18: Partition Functions and Ideal Gases - *Undeclared*
  - 18.1: The Translational Partition Function of a Monatomic Ideal Gas - *Undeclared*
  - 18.2: Most Atoms Are in the Ground Electronic State at Room Temperature - *Undeclared*
  - 18.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms - *Undeclared*
  - 18.4: Most Molecules Are in the Ground Vibrational State at Room Temperature - *Undeclared*
  - 18.5: Most Molecules Are in Excited Rotational States at Ordinary Temperatures - *Undeclared*
  - 18.6: Rotational Partition Functions Contain a Symmetry Number - *Undeclared*
  - 18.7: The Vibrational Partition Function - *Undeclared*
  - 18.8: The Rotational Partition Function Depends on the Shape of the Molecule - *Undeclared*
  - 18.9: Molar Heat Capacities - *Undeclared*
  - 18.E: Partition Functions and Ideal Gases (Exercises) - *Undeclared*
- Back Matter - *Undeclared*
  - Index - *Undeclared*
  - Glossary - *Undeclared*
  - Detailed Licensing - *Undeclared*

- Workgroup Activities - *Undeclared*
  - Workgroup 1: Valence Bond Orbitals for Hydrogen - *Undeclared*
  - Workgroup 2: Symmetry and Assigning Point Groups - *Undeclared*
  - Workgroup 3: Using Symmetry to Solve Integrals - *Undeclared*
  - Workgroup 4: Deriving Selection Rules with Symmetry - *Undeclared*
  - Workgroup 5: Translation Partition Function - *Undeclared*
  - Workgroup 6: Rotational Partition Functions - *Undeclared*

Index

A

Anharmonicity
- 13.5: Vibrational Overtones

antibonding molecular orbital
- 9.5: Bonding and Antibonding Orbitals

atomic term symbols
- 8.8: Term Symbols Gives a Detailed Description of an Electron Configuration
- 8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

Atomic units
- 8.1: Atomic and Molecular Calculations are Expressed in Atomic Units

B

Boltzmann factor
- 17: Boltzmann Factor and Partition Functions

bond order
- 9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

bonding molecular orbital
- 9.5: Bonding and Antibonding Orbitals

bosons
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

bracketing theorem
- 7.2: Linear Variational Method and the Secular Determinant

C

centrifugal force
- 13.4: The Pure Rotational Spectrum has Unequal Spacings

Chandrasakar wavefunction
- 8.2: Perturbation Theory and the Variational Method for Helium

CONDON APPROXIMATION
- 13.7: The Franck-Condon Principle

Coulomb integral
- 10.5: The \(\pi\)-Electron Approximation of Conjugation

cyclic permutations (angular momenta)
- 6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

D

delocalization energy
- 10.6: Butadiene is Stabilized by a Delocalization Energy

E

Exchange Operator
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

extended basis sets
- 11.2: Extended Basis Sets

F

fermions
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

fine structure
- 8.11: Using Atomic Term Symbols to Interpret Atomic Spectra

G

Gaussian Type Orbitals
- 11.1: Gaussian Basis Sets

H

Hückel theory
- 10.5: The \(\pi\)-Electron Approximation of Conjugation

hartree (unit)
- 8.2: Perturbation Theory and the Variational Method for Helium

Hartree equations
- 8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data

Hermitian operators
- 7.2: Linear Variational Method and the Secular Determinant

Hund's Rules
- 8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States

hybridization (water)
- 10.2: Different Hybrid Orbitals Used for Bonding in Water

Hylleraas Wavefunction
- 8.2: Perturbation Theory and the Variational Method for Helium

I

intrinsic spin
- 8.4: An Electron Has an Intrinsic Spin Angular Momentum

K

Koopmans' Theorem
- 10.4: Photoelectron Spectroscopy

L

LCAO
- 9.4: Chemical Bond Stability
- 9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently

M

molecular term symbols
- 9.14: Molecular Term Symbols Describe Electronic States of Molecules
- 9.15: Molecular Term Symbols Designate Symmetry

O

orbital angular momentum
- 6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision

orbital approximation
- 6.7: The Helium Atom Cannot Be Solved Exactly

overlap
- 9.3: The Overlap Integral

Overlap integral
- 9.3: The Overlap Integral

overtones
- 13.5: Vibrational Overtones

P

partition functions
- 17: Boltzmann Factor and Partition Functions

Pauli’s exclusion principle
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

penetration
- 7.1: The Variational Method Approximation

permutation operator
- 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons

Pertubation Theory for Helium
- 8.2: Perturbation Theory and the Variational Method for Helium

perturbation theory
- 7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems

physical
- 13.1: The Electromagnetic Spectrum
- 13.2: Rotational Transitions Accompany Vibrational Transitions
- 13.3: The Vibration-Rotation Spectrum
- 13.5: Vibrational Overtones

Polarization Terms
- 11.3: Orbital Polarization Terms

R

resonance integral
- 10.5: The \(\pi\)-Electron Approximation of Conjugation

S

Secular Determinant
- 7.2: Linear Variational Method and the Secular Determinant

secular equations
- 7.2: Linear Variational Method and the Secular Determinant
- 9.5: Bonding and Antibonding Orbitals

shielding
- 7.1: The Variational Method Approximation

Slater determinant wavefunction
- 8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants

Slater Type Orbitals
- 11.1: Gaussian Basis Sets

Spherical harmonics

6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics

STO

7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters

symmetry number

18.6: Rotational Partition Functions Contain a Symmetry Number

T

total angular momentum

8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number

Total Angular Momentum Quantum Number (J)

8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number

trial wavefunction

7.2: Linear Variational Method and the Secular Determinant

V

Variational Method

7.1: The Variational Method Approximation
7.2: Linear Variational Method and the Secular Determinant

Variational Method for Helium

8.2: Perturbation Theory and the Variational Method for Helium

W

Walsh diagrams

10.3: Why is BeH_2 Linear and H_2O Bent?

Z

Zeeman effect

8.4: An Electron Has an Intrinsic Spin Angular Momentum

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: BCU: CH 332 Physical Chemistry II

Webpages: 188

All licenses found:

- Undeclared: 99.5% (187 pages)
- CC BY-SA 4.0: 0.5% (1 page)

By Page

- BCU: CH 332 Physical Chemistry II - *Undeclared*
  - 00: Front Matter - *Undeclared*
    - Table of Contents - *Undeclared*
  - AGENDA - *Undeclared*
    - Rethinking Hybridization - *Undeclared*
  - Homework - *Undeclared*
    - Homework 1 - *Undeclared*
    - Solutions 1 - *Undeclared*
    - Homework 2 - *Undeclared*
    - Solutions 2 - *Undeclared*
    - Homework 3 - *Undeclared*
    - Solutions 3 - *Undeclared*
    - Homework 4 - *Undeclared*
    - Solutions 4 - *Undeclared*
    - Homework 5 - *Undeclared*
    - Solutions 5 - *Undeclared*
    - Homework 6 - *Undeclared*
    - Solutions 6 - *Undeclared*
    - Homework 7 - *Undeclared*
    - Solutions 7 - *Undeclared*
    - Homework 8 - *Undeclared*
    - Solutions 8 - *Undeclared*
    - Homework 9 - *Undeclared*
    - Solutions 9 - *Undeclared*
    - Homework 10 - *Undeclared*
    - Solutions 10 - *Undeclared*
    - Homework 11 - *Undeclared*
    - Solutions 11 - *Undeclared*
    - Homework 12 - *Undeclared*
    - Solutions 12 - *Undeclared*
    - Homework 13 - *Undeclared*
    - Solutions 13 - *Undeclared*
    - Homework 14 - *Undeclared*
    - Solutions 14 - *Undeclared*
    - Homework 15 - *Undeclared*
    - Solutions 15 - *Undeclared*
  - Text - *Undeclared*
    - Front Matter - *Undeclared*
      - TitlePage - *Undeclared*
      - InfoPage - *Undeclared*
      - Table of Contents - *Undeclared*
      - Licensing - *Undeclared*
    - 6: The Hydrogen Atom - *Undeclared*
      - 6.E: The Hydrogen Atom (Exercises) - *Undeclared*
      - 6.1: The Schrodinger Equation for the Hydrogen Atom Can Be Solved Exactly - *Undeclared*
      - 6.2: The Wavefunctions of a Rigid Rotator are Called Spherical Harmonics - *Undeclared*
      - 6.3: The Three Components of Angular Momentum Cannot be Measured Simultaneously with Arbitrary Precision - *Undeclared*
      - 6.4: Hydrogen Atomic Orbitals Depend upon Three Quantum Numbers - *Undeclared*
      - 6.5: s-orbitals are Spherically Symmetric - *Undeclared*
      - 6.6: Orbital Angular Momentum and the p-Orbitals - *Undeclared*
      - 6.7: The Helium Atom Cannot Be Solved Exactly - *Undeclared*
    - 7: Approximation Methods - *Undeclared*
      - 7.E: Approximation Methods (Exercises) - *Undeclared*
      - 7.1: The Variational Method Approximation - *Undeclared*
      - 7.2: Linear Variational Method and the Secular Determinant - *Undeclared*
      - 7.3: Trial Functions Can Be Linear Combinations of Functions That Also Contain Variational Parameters - *Undeclared*
      - 7.4: Perturbation Theory Expresses the Solutions in Terms of Solved Problems - *Undeclared*

- 8: Multielectron Atoms - *Undeclared*
  - 8.E: Multielectron Atoms (Exercises) - *Undeclared*
  - 8.1: Atomic and Molecular Calculations are Expressed in Atomic Units - *Undeclared*
  - 8.2: Perturbation Theory and the Variational Method for Helium - *Undeclared*
  - 8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method - *Undeclared*
  - 8.4: An Electron Has an Intrinsic Spin Angular Momentum - *Undeclared*
  - 8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons - *Undeclared*
  - 8.6: Antisymmetric Wavefunctions can be Represented by Slater Determinants - *Undeclared*
  - 8.7: Hartree-Fock Calculations Give Good Agreement with Experimental Data - *Undeclared*
  - 8.8: Term Symbols Gives a Detailed Description of an Electron Configuration - *Undeclared*
  - 8.9: The Allowed Values of J - the Total Angular Momentum Quantum Number - *Undeclared*
  - 8.10: Hund's Rules Determine the Term Symbols of the Ground Electronic States - *Undeclared*
  - 8.11: Using Atomic Term Symbols to Interpret Atomic Spectra - *Undeclared*
- 9: Chemical Bonding in Diatomic Molecules - *Undeclared*
  - 9.E: Chemical Bond in Diatomic Molecules (Exercises) - *Undeclared*
  - 9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules - *Undeclared*
  - 9.2: The H_2^+ Prototypical Species - *Undeclared*
  - 9.3: The Overlap Integral - *Undeclared*
  - 9.4: Chemical Bond Stability - *Undeclared*
  - 9.5: Bonding and Antibonding Orbitals - *Undeclared*
  - 9.6: A Simple Molecular-Orbital Treatment of H_2 Places Both Electrons in a Bonding Orbital - *Undeclared*
  - 9.7: Molecular Orbitals Can Be Ordered According to Their Energies - *Undeclared*
  - 9.8: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule - *Undeclared*
  - 9.9: Electrons Populate Molecular Orbitals According to the Pauli Exclusion Principle - *Undeclared*
  - 9.10: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic - *Undeclared*
  - 9.11: Photoelectron Spectra Support the Existence of Molecular Orbitals - *Undeclared*
  - 9.12: Molecular-Orbital Theory Also Applies to Heteronuclear Diatomic Molecules - *Undeclared*
  - 9.13: An SCF-LCAO-MO Wave Function Is a Molecular Orbital Formed from a Linear Combination of Atomic Orbitals and Whose Coefficients Are Determined Self-Consistently - *Undeclared*
  - 9.14: Molecular Term Symbols Describe Electronic States of Molecules - *Undeclared*
  - 9.15: Molecular Term Symbols Designate Symmetry - *Undeclared*
  - 9.16: Most Molecules Have Excited Electronic States - *Undeclared*
- 10: Bonding in Polyatomic Molecules - *Undeclared*
  - 10.1: Hybrid Orbitals Account for Molecular Shape - *Undeclared*
  - 10.2: Different Hybrid Orbitals Used for Bonding in Water - *Undeclared*
  - 10.3: Why is BeH_2 Linear and H_2O Bent? - *Undeclared*
  - 10.4: Photoelectron Spectroscopy - *Undeclared*
  - 10.5: The \(\pi\)-Electron Approximation of Conjugation - *Undeclared*
  - 10.6: Butadiene is Stabilized by a Delocalization Energy - *Undeclared*
- 11: Computational Quantum Chemistry - *Undeclared*
  - 11.0: Overview of Quantum Calculations - *Undeclared*
  - 11.1: Gaussian Basis Sets - *Undeclared*
  - 11.2: Extended Basis Sets - *Undeclared*
  - 11.3: Orbital Polarization Terms - *Undeclared*
  - 11.4: The Ground-State Energy of H_2 - *Undeclared*
  - 11.5: Quantum Calculations - *Undeclared*
- 12: Group Theory - Exploiting Symmetry - *Undeclared*
  - 12.1: Using Symmetry to Simplify Calculations - *Undeclared*
  - 12.2: The Symmetry of Molecules - *Undeclared*
  - 12.3: Symmetry Operations Define Groups - *Undeclared*
  - 12.4: Symmetry Operations can be Represented by Matrices - *Undeclared*
  - 12.5: The \(C_3V\) Point Group Has a 2-D Irreducible Representation - *Undeclared*
  - 12.6: Character Tables - *Undeclared*
  - 12.7: Relations involving Characters - *Undeclared*

- 12.8: Using Symmetry to Predict Zero in a Secular Determinant - *Undeclared*
- 12.9: Generating Operators for Irreducible Representations - *Undeclared*

- 13: Molecular Spectroscopy - *Undeclared*
  - 13.1: The Electromagnetic Spectrum - *Undeclared*
  - 13.2: Rotational Transitions Accompany Vibrational Transitions - *Undeclared*
  - 13.3: The Vibration-Rotation Spectrum - *Undeclared*
  - 13.4: The Pure Rotational Spectrum has Unequal Spacings - *Undeclared*
  - 13.5: Vibrational Overtones - *Undeclared*
  - 13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information - *Undeclared*
  - 13.7: The Franck-Condon Principle - *Undeclared*
  - 13.8: Rotational Spectra of Polyatomic Molecules - *Undeclared*
  - 13.9: Normal Modes in Polyatomic Molecules - *Undeclared*
  - 13.10: Irreducible Representation of Point Groups - *Undeclared*
  - 13.11: Time-Dependent Perturbation Theory - *CC BY-SA 4.0*
  - 13.12: The Selection Rule for the Rigid Rotator - *Undeclared*
  - 13.13: The Harmonic Oscillator Selection Rule - *Undeclared*
  - 13.14: Group Theory Determines Infrared Activity - *Undeclared*
  - 13.E: Molecular Spectroscopy (Exercises) - *Undeclared*
- 14: Nuclear Magnetic Resonance Spectroscopy - *Undeclared*
  - 14.1: Nuclei Have Intrinsic Spin Angular Momenta - *Undeclared*
  - 14.2: Magnetic Moments Interact with Magnetic Fields - *Undeclared*
  - 14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz - *Undeclared*
  - 14.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded - *Undeclared*
  - 14.5: Chemical Shifts is Sensitive to Chemical Environment of the Nucleus - *Undeclared*
  - 14.6: Spin-Spin Coupling Results in Multiplets in NMR Spectra - *Undeclared*
  - 14.7: Spin-Spin Coupling Between Chemically Equivalent Protons Is Not Observed - *Undeclared*
  - 14.8: The n+1 Rule Applies Only to First-Order Spectra - *Undeclared*
  - 14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method - *Undeclared*
- 15: Lasers, Laser Spectroscopy, and Photochemistry - *Undeclared*
  - 15.1: Electronically Excited Molecules - *Undeclared*
  - 15.2: Transitions Modeled as Kinetics - *Undeclared*
  - 15.3: Two-Level Systems Cannot Form Population Inversions - *Undeclared*
  - 15.4: Population Inversion via Three-Level Systems - *Undeclared*
  - 15.5: Laser Fundamentals - *Undeclared*
  - 15.6: The Helium-Neon Laser - *Undeclared*
  - 15.7: High-Resolution Laser Spectroscopy - *Undeclared*
  - 15.8: Photochemical Dynamics - *Undeclared*
- 16: The Properties of Gases - *Undeclared*
  - 16.1: All Dilute Gases Behave Ideally - *Undeclared*
  - 16.2: van der Waals and Redlich-Kwong Equations - *Undeclared*
  - 16.3: A Cubic Equation of State - *Undeclared*
  - 16.4: The Law of Corresponding States - *Undeclared*
  - 16.5: The Second Virial Coefficient - *Undeclared*
  - 16.6: The Repulsive Term in the Lennard-Jones Potential - *Undeclared*
  - 16.7: Van der Waals Constants in Terms of Molecular Parameters - *Undeclared*
  - 16.E: The Properties of Gases (Exercises) - *Undeclared*
- 17: Boltzmann Factor and Partition Functions - *Undeclared*
  - 17.1: The Boltzmann Factor Is One of the Most Important Quantities in the Physical Sciences - *Undeclared*
  - 17.2: The Thermal Boltzman Distribution - *Undeclared*
  - 17.3: We Postulate That the Average Ensemble Energy Is Equal to the Observed Energy of a System - *Undeclared*
  - 17.4: The Heat Capacity at Constant Volume - *Undeclared*

- 17.5: Express the Pressure in Terms of a Partition Function - *Undeclared*
- 17.6: Partition Functions of Systems of Distinguishable Molecules are Products of Molecular Partition Functions - *Undeclared*
- 17.7: Partition Function of Indistinguishable Components - *Undeclared*
- 17.8: A Molecular Partition Function Can Be Decomposed into Partition Functions for Each Degree of Freedom - *Undeclared*
- 17.E: Exercises - *Undeclared*

- 18: Partition Functions and Ideal Gases - *Undeclared*
  - 18.1: The Translational Partition Function of a Monatomic Ideal Gas - *Undeclared*
  - 18.2: Most Atoms Are in the Ground Electronic State at Room Temperature - *Undeclared*
  - 18.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms - *Undeclared*
  - 18.4: Most Molecules Are in the Ground Vibrational State at Room Temperature - *Undeclared*
  - 18.5: Most Molecules Are in Excited Rotational States at Ordinary Temperatures - *Undeclared*
  - 18.6: Rotational Partition Functions Contain a Symmetry Number - *Undeclared*
  - 18.7: The Vibrational Partition Function - *Undeclared*
  - 18.8: The Rotational Partition Function Depends on the Shape of the Molecule - *Undeclared*
  - 18.9: Molar Heat Capacities - *Undeclared*
  - 18.E: Partition Functions and Ideal Gases (Exercises) - *Undeclared*
- Back Matter - *Undeclared*
  - Index - *Undeclared*
  - Glossary - *Undeclared*
  - Detailed Licensing - *Undeclared*

- Workgroup Activities - *Undeclared*
  - Workgroup 1: Valence Bond Orbitals for Hydrogen - *Undeclared*
  - Workgroup 2: Symmetry and Assigning Point Groups - *Undeclared*
  - Workgroup 3: Using Symmetry to Solve Integrals - *Undeclared*
  - Workgroup 4: Deriving Selection Rules with Symmetry - *Undeclared*
  - Workgroup 5: Translation Partition Function - *Undeclared*
  - Workgroup 6: Rotational Partition Functions - *Undeclared*