1: The Dawn of the Quantum Theory

"With the recognition that there is no logical reason why Newtonian and classical principles should be valid outside the domains in which they have been experimentally verified has come the realization that departures from these principles are indeed necessary. Such departures find their expression through the introduction of new mathematical formalisms, new schemes of axioms and rules of manipulation, into the methods of theoretical physics." - P. A. M. Dirac,

1.1: Blackbody Radiation Cannot Be Explained Classically
1.2: Quantum Hypothesis Used for Blackbody Radiation Law
1.3: Photoelectric Effect Explained with Quantum Hypothesis
1.4: The Hydrogen Atomic Spectrum
1.5: The Rydberg Formula and the Hydrogen Atomic Spectrum
1.6: Matter Has Wavelike Properties
1.7: de Broglie Waves can be Experimentally Observed
1.8: The Bohr Theory of the Hydrogen Atom
1.9: The Heisenberg Uncertainty Principle
1.E: The Dawn of the Quantum Theory (Exercises)

2: The Classical Wave Equation

The aim of this section is to give a fairly brief review of waves in various shaped elastic media—beginning with a taut string, then going on to an elastic sheet, a drumhead, first of rectangular shape then circular, and finally considering elastic waves on a spherical surface, like a balloon.

2.1: The One-Dimensional Wave Equation
2.2: The Method of Separation of Variables
2.3: Oscillatory Solutions to Differential Equations
2.4: The General Solution is a Superposition of Normal Modes
2.5: A Vibrating Membrane
2.E: The Classical Wave Equation (Exercises)

3: The Schrödinger Equation and a Particle in a Box

The particle in a box model provides one of the very few problems in quantum mechanics which can be solved analytically, without approximations. This means that the observable properties of the particle (such as its energy and position) are related to the mass of the particle and the width of the well by simple mathematical expressions. Due to its simplicity, the model allows insight into quantum effects without the need for complicated mathematics.

3.1: The Schrödinger Equation
3.2: Linear Operators in Quantum Mechanics
3.3: The Schrödinger Equation is an Eigenvalue Problem
3.4: Wavefunctions Have a Probabilistic Interpretation
3.5: The Energy of a Particle in a Box is Quantized
3.6: Wavefunctions Must Be Normalized
3.7: The Average Momentum of a Particle in a Box is Zero
3.8: The Uncertainty Principle - Estimating Uncertainties from Wavefunctions
3.9: A Particle in a Three-Dimensional Box
3.E: The Schrödinger Equation and a Particle in a Box (Exercises)

4: Postulates and Principles of Quantum Mechanics
Quantum Mechanics is a framework for the development of physical theories. Quantum mechanics is based on a series of postulates which lead to a very good description of the microphysical realm.

4.1: The Wavefunction Specifies the State of a System
4.2: Quantum Operators Represent Classical Variables
4.3: Observable Quantities Must Be Eigenvalues of Quantum Mechanical Operators
4.4: The Time-Dependent Schrödinger Equation
4.5: Eigenfunctions of Operators are Orthogonal
4.6: Commuting Operators Allow Infinite Precision
4.E: Postulates and Principles of Quantum Mechanics (Exercises)

5: The Harmonic Oscillator and the Rigid Rotor
The harmonic oscillator is common: It appears in many everyday examples. The harmonic oscillator is intuitive: We can picture the forces on systems such as pendulum or a plucked string. This makes it simple to study in the classroom.

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

The solution of the Schrödinger 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 are not necessarily isotropic themselves, their dependence on the angular coordinates follows completely generally from this isotropy of the underlying potential.

6.1: The Schrödinger 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
6.8: The Hydrogen Atom (Exercises)

7: Approximation Methods

The Schrödinger equation for realistic systems quickly becomes unwieldy, and analytical solutions are only available for very simple systems - the ones we have described as fundamental systems in this module. Numerical approaches can cope with more complex problems, but are still (and will remain for a good while) limited by the available computer power. Approximations are necessary to cope with real systems.

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
7.5: Approximation Methods (Exercises)

8: Multielectron Atoms

Electrons with more than one atom, such as Helium (He), and Nitrogen (N), are referred to as multi-electron atoms. Hydrogen is the only atom in the periodic table that has one electron in the orbitals under ground state. We will learn how additional electrons behave and affect a certain atom.

8.1: Atomic and Molecular Calculations are Expressed in Atomic Units
8.2: Perturbation Theory and the Variational Method for Helium
8.3: Hartree-Fock Equations are Solved by the Self-Consistent Field Method
8.4: An Electron Has an Intrinsic Spin Angular Momentum
8.5: Wavefunctions must be Antisymmetric to Interchange of any Two Electrons
9: Chemical Bonding in Diatomic Molecules

Our basis for understanding chemical bonding and the structures of molecules is the electron orbital description of the structure and valence of atoms, as provided by quantum mechanics. We assume an understanding of the periodicity of the elements based on the nuclear structure of the atom and our deductions concerning valence based on electron orbitals.

- 9.1: The Born-Oppenheimer Approximation Simplifies the Schrödinger Equation for Molecules
- 9.2: The H₂⁺ 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 H₂ 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

10: Bonding in Polyatomic Molecules

The concept of a molecular orbital is readily extended to provide a description of the electronic structure of a polyatomic molecule. In general a molecular orbital in a polyatomic system extends over all the nuclei in a molecule and it is essential, if we are to understand and predict the spatial properties of the orbitals, that we make use of the symmetry properties possessed by the nuclear framework.

- 10.1: Hybrid Orbitals Account for Molecular Shape
11: Computational Quantum Chemistry

Quantum chemistry addresses the equations and approximations derived from the postulates of quantum mechanics; specifically involving solving the Schrödinger equation for molecular systems and is typically separated into ab initio, which uses methods that do not include any empirical parameters or experimental data and semi-empirical that do.

- 11.1: Overview of Quantum Calculations
- 11.2: Gaussian Basis Sets
- 11.3: Extended Basis Sets
- 11.4: Orbital Polarization Terms in Basis Sets
- 11.5: The Ground-State Energy of H₂
- 11.6: Quantum Calculations
- 11.E: Computational Quantum Chemistry (Exercises)

12: Group Theory - The Exploitation of Symmetry

One important application, the theory of symmetry groups, is a powerful tool for the prediction of physical properties of molecules and crystals. It is for example possible to determine whether a molecule can have a dipole moment. Many important predictions of spectroscopic experiments (optical, IR or Raman) can be made purely by group theoretical considerations.

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

Spectroscopy generally is defined as the area of science concerned with the absorption, emission, and scattering of electromagnetic radiation by atoms and molecules. Visible electromagnetic radiation is called light, although the terms light, radiation, and electromagnetic radiation can be used interchangeably. Spectroscopy played a key role in the development of quantum mechanics and is essential to understanding molecular properties and the results of spectroscopic experiments.

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

14: Nuclear Magnetic Resonance Spectroscopy

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

15: Lasers, Laser Spectroscopy, and Photochemistry

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

16: The Properties of Gases
16.1: All Dilute Gases Behave Ideally
16.2: van der Waals and Redlich-Kwong Equations of State
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
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.

17.1: The Boltzmann Factor
17.2: The Thermal Boltzman Distribution
17.3: The Average Ensemble Energy
17.4: Heat Capacity at Constant Volume
17.5: Pressure in Terms of Partition Functions
17.6: Partition Functions of Distinguishable Molecules
17.7: Partition Functions of Indistinguishable Molecules
17.8: Partition Functions can be Decomposed
17.E: Boltzmann Factor and Partition Functions (Exercises)

18: Partition Functions and Ideal Gases
18.1: Translational Partition Functions of Monotonic Gases
18.2: Most Atoms are in the Ground Electronic State
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
18.5: Most Molecules are Rotationally Excited at Ordinary Temperatures
18.6: Rotational Partition Functions of Diatomic Gases
18.7: Vibrational Partition Functions of Polyatomic Molecules
18.8: Rotational Partition Functions of Polyatomic Molecules
18.9: Molar Heat Capacities
18.E: Partition Functions and Ideal Gases (Exercises)
18.10: Ortho and Para Hydrogen
18.11: The Equipartition Principle

19: The First Law of Thermodynamics
19.1: Overview of Classical Thermodynamics
19.2: Pressure-Volume Work
19.3: Work and Heat are not State Functions, but Energy is a State Function
19.4: Energy is a State Function
19.5: An Adiabatic Process is a Process in which No Energy as Heat is Transferred
19.6: The Temperature of a Gas Decreases in a Reversible Adiabatic Expansion
19.7: Work and Heat Have a Simple Molecular Interpretation
19.8: Pressure-Volume Work
19.9: Heat Capacity is a Path Function
19.E: The First Law of Thermodynamics (Exercises)
19.10: Relative Enthalpies Can Be Determined from Heat Capacity Data and Heats of Transition
19.11: Enthalpy Changes for Chemical Equations are Additive
19.12: Heats of Reactions Can Be Calculated from Tabulated Heats of Formation
19.13: The Temperature Dependence of ΔH

20: Entropy and The Second Law of Thermodynamics
20.1: Energy Does not Determine Spontaneity
20.2: Nonequilibrium Isolated Systems Evolve in a Direction That Increases Their Probability
20.3: Unlike heat, Entropy Is a State Function
20.4: The Second Law of Thermodynamics
20.5: The Famous Equation of Statistical Thermodynamics
20.6: We Must Always Devise a Reversible Process to Calculate Entropy Changes
20.7: Thermodynamics Provides Insight into the Conversion of Heat into Work
• 20.8: Entropy Can Be Expressed in Terms of a Partition Function
• 20.9: The Molecular Formula $S = k_B$ in $W$ is Analogous to the Thermodynamic Formula $dS = \delta q_{rev}$
• 20.E: Entropy and The Second Law of Thermodynamics (Exercises)

• 22: Helmholtz and Gibbs Energies
  • 22.1: Helmholtz Energy
  • 22.2: Gibbs Energy
  • 22.3: The Maxwell Relations
  • 22.4: The Enthalpy of an Ideal Gas
  • 22.5: Thermodynamic Functions have Natural Variables
  • 22.6: The Standard State for a Gas is Ideal Gas
  • 22.7: The Gibbs-Helmholtz Equation
  • 22.8: Fugacity Measures Nonideality of a Gas
  • 22.E: Helmholtz and Gibbs Energies (Exercises)

• 23: Phase Equilibria
  • 23.1: A Phase Diagram Summarizes the Solid-Liquid-Gas Behavior of a Substance
  • 23.2: Gibbs Energies and Phase Diagrams
  • 23.3: The Chemical Potentials of a Pure Substance in Two Phases in Equilibrium
  • 23.4: The Clausius-Clapeyron Equation
  • 23.5: Chemical Potential Can be Evaluated From a Partition Function
  • 23.E: Phase Equilibria (Exercises)

• 24: Solutions I- Liquid-Liquid Solutions
  • 24.1: Partial Molar Quantities in Solutions
  • 24.2: The Gibbs-Duhem Equation
  • 24.3: Chemical Potential of Each Component Has the Same Value in Each Phase in Which the Component Appears
  • 24.4: Ideal Solutions obey Raoult’s Law
  • 24.5: Most Solutions are Not Ideal
  • 24.6: Vapor Pressures of Volatile Binary Solutions
  • 24.7: Activities of Nonideal Solutions
  • 24.8: Activities are Calculated with Respect to Standard States
  • 24.9: Gibbs Energy of Mixing of Binary Solutions in Terms of the Activity Coefficient
  • 24.E: Solutions I- Liquid-Liquid Solutions (Exercises)
25: 25. Solutions II - Solid-Liquid Solutions

- 25.1: Raoult's and Henry's Laws Define Standard States
- 25.2: The Activities of Nonvolatile Solutes
- 25.3: Colligative Properties Depend only on Number Density
- 25.4: Osmotic Pressure can Determine Molecular Masses
- 25.5: Electrolytes Solutions are Nonideal at Low Concentrations
- 25.6: The Debye-Hückel Theory
- 25.7: Extending Debye-Hückel Theory to Higher Concentrations
- 25.8: Homework Problems

26: Chemical Equilibrium

The natural tendency of chemical systems is to seek a state of minimum Gibbs function. Once the minimum is achieved, movement in any chemical direction will not be spontaneous. It is at this point that the system achieves a state of equilibrium.

- 26.1: Equilibrium Results when Gibbs Energy is Minimized
- 26.2: An Equilibrium Constant is a Function of Temperature Only
- 26.3: Standard Gibbs Energies of Formation Can Be Used to Calculate Equilibrium Constants
- 26.4: A Plot of the Gibbs Energy of a Reaction Mixture Against the Extent of Reaction Is a Minimum at Equilibrium
- 26.5: Reaction Quotient and Equilibrium Constant Ratio Determines Reaction Direction
- 26.6: The Sign of $\Delta G$ and not $\Delta G^*$ Determines the Direction of Reaction Spontaneity
- 26.7: The Van't Hoff Equation
- 26.8: Equilibrium Constants in Terms of Partition Functions
- 26.9: Molecular Partition Functions and Related Thermodynamic Data Are Extensively Tabulated
- 26.10: Real Gases Are Expressed in Terms of Partial Fugacities
- 26.11: Thermodynamic Equilibrium Constants Are Expressed in Terms of Activities
- 26.12: Activities are Important for Ionic Species
- 26.13: Homework Problems

27: The Kinetic Theory of Gases

The Maxwell-Boltzmann distribution is used to determine how many molecules are moving between velocities.

- 27.1: The Average Translational Kinetic Energy of a Gas
- 27.2: The Distribution of the Components of Molecular Speeds are Described by a Gaussian Distribution
- 27.3: The Distribution of Molecular Speeds is Given by the Maxwell-Boltzmann Distribution
- 27.4: The Frequency of Collisions
- 27.5: The Maxwell-Boltzmann Distribution Has Been Verified Experimentally
28: Chemical Kinetics I - Rate Laws

In general, increases in temperature increase the rates of chemical reactions. It is easy to see why, since most chemical reactions depend on molecular collisions. Since the frequency with which molecules collide increases with increased temperature. But also, the kinetic energy of the molecules increases, which should increase the probability that a collision event will lead to a reaction. An empirical model was proposed by Arrhenius to account for this phenomenon.

29: Chemical Kinetics II- Reaction Mechanisms

In this chapter, we will expand on the concepts of chemical reaction rates by exploring what the rate law implies about the mechanistic pathways that reactions actually follow to proceed from reactants to products. Typically, one determines a rate law that describes a chemical reaction, and then suggests a mechanism that can be (or might not be!) consistent with the observed kinetics.
30: Gas-Phase Reaction Dynamics

- 30.1: The Rate of Bimolecular Gas-Phase Reaction Can Be Calculated Using Hard-Sphere Collision Theory and an Energy-Dependent Reaction Cross Section
- 30.2: A Reaction Cross Section Depends Upon the Impact Parameter
- 30.3: The Rate Constant for a Gas-Phase Chemical Reaction May Depend on the Orientations of the Colliding Molecules
- 30.4: The Internal Energy of the Reactants Can Affect the Cross Section of a Reaction
- 30.5: A Reactive Collision Can Be Described in a Center-of-Mass Coordinate System
- 30.6: Reactive Collisions Can be Studied Using Crossed Molecular Beam Machines
- 30.7: Reactions Can Produce Vibrationally Excited Molecules
- 30.8: The Velocity and Angular Distribution of the Products of a Reactive Collision Provide a Molecular Picture of the Chemical Reaction
- 30.9: Not All Gas-Phase Chemical Reactions Are Rebound Reactions
- 30.E: Gas-Phase Reaction Dynamics (Exercises)
- 30.10: The Potential-Energy Surface Can Be Calculated Using Quantum Mechanics

31: Solids and Surface Chemistry

- 31.1: The Unit Cell Is the Fundamental Building Block of a Crystal
- 31.2: The Orientation of a Lattice Plane Is Described by its Miller Indices
- 31.3: The Spacing Between Lattice Planes Can Be Determined from X-Ray Diffraction Measurements
- 31.4: The Total Scattering Intensity Is Related to the Periodic Structure of the Electron Density in the Crystal
- 31.5: The Structure Factor and the Electron Density Are Related by a Fourier Transform
- 31.6: A Gas Molecule can Physisorb or Chemisorb to a Solid Surface
- 31.7: Isotherms are Plots of Surface Coverage as a Function of Gas Pressure at Constant Temperature
- 31.8: The Langmuir Isotherm Can Be Used to Derive Rate Laws for Surface-Catalyzed Gas-Phase Reactions
- 31.9: The Structure of a Surface is Different from that of a Bulk Solid
- 31.E: Homework Problems
- 31.10: The Reaction Between H2(g) and N 2(g) to Make NH3 (g) Can Be Surface Catalyzed

32: Math Chapters

- 32.1: Complex Numbers
- 32.2: Probability and Statistics
- 32.3: Vectors
- 32.4: Spherical Coordinates
- 32.5: Determinants
- 32.6: Matrices
• 32.7: Numerical Methods
• 32.8: Partial Differentiation
• 32.9: Series and Limits
• 32.10: The Binomial Distribution and Stirling's Approximation
• 32.11: Fourier Analysis
  ▪ 32.11.1: Fourier Analysis in Matlab
  ▪ 32.11.2: Fourier Synthesis of Periodic Waveforms