

# Quantum Mechanics in Chemistry

by

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## **Words to the reader about how to use this textbook**

### I. What This Book Does and Does Not Contain

This is a text dealing with the basics of quantum mechanics and electronic structure theory. It provides an introduction to molecular spectroscopy (although most classes on this subject will require additional material) and to the subject of molecular dynamics (whose classes again will require additional material).

### II. How to Use This Book

Other sources of information may be needed to build background in the areas of mathematics and physics. These additional subjects are treated briefly in the associated Appendices whose readings are recommended at selected places within the text in the following format: [Suggested Extra Reading- Appendix A: Mathematics Review].

### III. QMIC Computer Programs

Included with this text are a set of Quantum Mechanics in Chemistry (QMIC) computer programs. They appear on the floppy disk on the inside of the back cover. To learn more about what they contain and how to use them, read the (Microsoft Word) "README" and "writeme" files on this disk.

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## Section 1 The Basic Tools of Quantum Mechanics

### Chapter 1

Quantum mechanics describes matter in terms of wavefunctions and energy levels. physical measurements are described in terms of operators acting on wavefunctions

#### I. Operators, Wavefunctions, and the Schrödinger Equation

##### A. Operators

##### B. Wavefunctions

##### C. The Schrödinger Equation

##### 1. The Time-Dependent Equation

##### 2. The Time-Independent Equation

#### II. Examples of Solving the Schrödinger Equation

##### A. Free-Particle Motion in Two Dimensions

##### 1. The Schrödinger Equation

##### 2. Boundary Conditions

##### 3. Energies and Wavefunctions for Bound States

##### 4. Quantized Action Can Also be Used to Derive Energy Levels

##### B. Other Model Problems

##### 1. Particles in Boxes

##### 2. One Electron Moving About a Nucleus

[Suggested Extra Reading- Appendix B: The Hydrogen Atom Orbitals]

##### 3. Rotational Motion for a Rigid Diatomic Molecule

##### 4. Harmonic Vibrational Motion

#### III. The Physical Relevance of Wavefunctions, Operators and Eigenvalues

##### A. The Basic Rules and Relation to Experimental Measurement

##### B. An Example Illustrating Several of the Fundamental Rules

[Suggested Extra Reading- Appendix C: Quantum Mechanical Operators and Commutation]

## Chapter 2

Approximation methods can be used when exact solutions to the Schrödinger equation can not be found

### I. The Variational Method

### II. Perturbation Theory

[Suggested Extra Reading- Appendix D: Time Independent Perturbation Theory]

### III. Example Applications of Variational and Perturbation Methods

## Chapter 3

The application of the Schrödinger equation to the motions of electrons and nuclei in a molecule lead to the chemists' picture of electronic energy surfaces on which vibration and rotation occurs and among which transitions take place.

### I. The Born-Oppenheimer Separation of Electronic and Nuclear Motions

#### A. Time Scale Separation

#### B. Vibration/Rotation States for Each Electronic Surface

### II. Rotation and Vibration of Diatomic Molecules

#### A. Separation of Vibration and Rotation

#### B. The Rigid Rotor and Harmonic Oscillator

#### C. The Morse Oscillator

### III. Rotation of Polyatomic Molecules

#### A. Linear Molecules

#### B. Non-Linear Molecules

### IV. Summary

Summary

**Section 1 Exercises and Problems and Solutions**

## Section 2 Simple Molecular Orbital Theory

### Chapter 4

Valence atomic orbitals on neighboring atoms combine to form bonding, non-bonding and antibonding molecular orbitals

#### I. Atomic Orbitals

- A. Shapes
- B. Directions
- C. Sizes and Energies

#### II. Molecular Orbitals

- A. Core Orbitals
- B. Valence Orbitals
- C. Rydberg Orbitals
- D. Multicenter Orbitals
- E. Hybrid Orbitals

### Chapter 5

Molecular orbitals possess specific topology, symmetry, and energy-level patterns

#### I. Orbital Interaction Topology

#### II. Orbital Symmetry

[Suggested Extra Reading- Appendix E: Point Group Symmetry]

- A. Non-linear Polyatomic Molecules
- B. Linear Molecules
- C. Atoms

### Chapter 6

Along "reaction paths", orbitals can be connected one-to-one according to their symmetries and energies. This is the origin of the Woodward-Hoffmann rules

I. Reduction in Symmetry Along Reaction Paths

II. Orbital Correlation Diagrams- Origins of the Woodward-Hoffmann Rules

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The most elementary molecular orbital models contain symmetry, nodal pattern, and approximate energy information

I. The LCAO-MO Expansion and the Orbital-Level Schrödinger Equation

II. Determining the Effective Potential  $V$

A. The Hückel Parameterization of  $V$

B. The Extended Hückel Method

[Suggested Extra Reading- Appendix F; Qualitative Orbital Picture and Semi-Empirical Methods]

**Section 2 Exercises and Problems and Solutions**

## **Section 3 Electronic Configurations, Term Symbols, and States**

### Chapter 8

Electrons are placed into orbitals to form configurations, each of which can be labeled by its symmetry. The configurations may "interact" strongly if they have similar energies.

I. Orbitals Do Not Provide the Complete Picture; Their Occupancy by the N Electrons Must be Specified

II. Even N-Electron Configurations are Not Mother Nature's True Energy States

III. Mean-Field Models

The mean-field model, which forms the basis of chemists' pictures of electronic structure of molecules, is not very accurate

IV. Configuration Interaction (CI) Describes the Correct Electronic States

V. Summary

### Chapter 9

Electronic wavefunctions must be constructed to have permutational antisymmetry because the N electrons are indistinguishable Fermions

I. Electronic Configurations

II. Antisymmetric Wavefunctions

A. General Concepts

B. Physical Consequences of Antisymmetry

## Chapter 10

Electronic wavefunctions must also possess proper symmetry. These include angular momentum and point group symmetries

### I. Angular Momentum Symmetry and Strategies for Angular Momentum Coupling

[Suggested Extra Reading- Appendix G; Angular Momentum Operator Identities]

- A. Electron Spin Angular Momentum
- B. Vector Coupling of Angular Momenta
- C. Scalar Coupling of Angular Momenta
- D. Direct Products for Non-Linear Molecules

### II. Atomic Term Symbols and Wavefunctions

- A. Non-Equivalent Orbital Term Symbols
- B. Equivalent Orbital Term Symbols
- C. Atomic Configuration Wavefunctions
- D. Inversion Symmetry
- E. Review of Atomic Cases

### III. Linear Molecule Term Symbols and Wavefunctions

- A. Non-Equivalent Orbital Term Symbols
- B. Equivalent-Orbital Term Symbols
- C. Linear-Molecule Configuration Wavefunctions
- D. Inversion Symmetry and  $\sigma_v$  Symmetry for  $\Sigma$  States
- E. Review of Linear Molecule Cases

### IV. Non-Linear Molecule Term Symbols and Wavefunctions

- A. Term Symbols for Non-Degenerate Point Group Symmetries
- B. Wavefunctions for Non-Degenerate Non-Linear Point Molecules
- C. Extension to Degenerate Representations for Non-Linear Molecules

Summary

## Chapter 11

One must be able to evaluate the matrix elements among properly symmetry adapted N-electron configuration functions for any operator, the electronic Hamiltonian in particular. The Slater-Condon rules provide this capability

I. CSFs Are Used to Express the Full N-Electron Wavefunction

II. The Slater-Condon Rules Give Expressions for the Operator Matrix Elements Among the CSFs

III. Examples of Applying the Slater-Condon Rules

IV. Summary

## Chapter 12

Along "reaction paths", configurations can be connected one-to-one according to their symmetries and energies. This is another part of the Woodward-Hoffmann rules

I. Concepts of Configuration and State Energies

A. Plots of CSF Energies Give Configuration Correlation Diagrams

B. CSFs Interact and Couple to Produce States and State Correlation Diagrams

C. CSFs that Differ by Two Spin-Orbitals Interact Less Strongly than CSFs that Differ by One Spin-Orbital

D. State Correlation Diagrams

II. Mixing of Covalent and Ionic Configurations

A. The H<sub>2</sub> Case in Which Homolytic Bond Cleavage is Favored

B. Cases in Which Heterolytic Bond Cleavage is Favored

C. Analysis of Two-Electron, Two-Orbital, Single-Bond Formation

III. Various Types of Configuration Mixing

A. Essential CI

B. Dynamical CI



## Section 3 Exercises and Problems and Solutions

## Section 4 Molecular Rotation and Vibration

### Chapter 13

Treating the full internal nuclear-motion dynamics of a polyatomic molecule is complicated. It is conventional to examine the rotational movement of a hypothetical "rigid" molecule as well as the vibrational motion of a non-rotating molecule, and to then treat the rotation-vibration couplings using perturbation theory.

#### I. Rotational Motions of Rigid Molecules

##### A. Linear Molecules

1. The Rotational Kinetic Energy Operator
2. The Eigenfunctions and Eigenvalues

##### B. Non-Linear Molecules

1. The Rotational Kinetic Energy Operator
2. The Eigenfunctions and Eigenvalues for Special Cases
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  - b. Symmetric Tops
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#### II. Vibrational Motion Within the Harmonic Approximation

##### A. The Newton Equations of Motion for Vibration

1. The Kinetic and Potential Energy Matrices
2. The Harmonic Vibrational Energies and Normal Mode Eigenvectors

##### B. The Use of Symmetry

1. Point Group Symmetry of the Harmonic Potential
2. Symmetry Adapted Modes

#### III. Anharmonicity

##### A. The Expansion of $E(v)$ in Powers of $(v+1/2)$

##### B. The Birge-Sponer Extrapolation to Compute $D_e$

## Section 5 Time Dependent Processes

### Chapter 14

The interaction of a molecular species with electromagnetic fields can cause transitions to occur among the available molecular energy levels (electronic, vibrational, rotational, and nuclear spin). Collisions among molecular species likewise can cause transitions to occur. Time-dependent perturbation theory and the methods of molecular dynamics can be employed to treat such transitions.

#### I. The Perturbation Describing Interactions With Electromagnetic Radiation

- A. The Time-Dependent Vector  $A(\mathbf{r}, t)$  and Scalar  $\phi(\mathbf{r}, t)$  Potentials
- B. The Associated Electric  $E(\mathbf{r}, t)$  and Magnetic  $H(\mathbf{r}, t)$  Fields
- C. The Resulting Hamiltonian

#### II. Time-Dependent Perturbation Theory

- A. The Time-Dependent Schrödinger Equation
- B. Perturbative Solution
- C. Application to Electromagnetic Perturbations
  - 1. First-Order Fermi-Wentzel "Golden Rule"
  - 2. Higher Order Results
- D. The "Long-Wavelength" Approximation
  - 1. Electric Dipole Transitions
  - 2. Magnetic Dipole and Electric Quadrupole Transitions

#### III. The Kinetics of Photon Absorption and Emission

- A. The Phenomenological Rate Laws
- B. Spontaneous and Stimulated Emission
- C. Saturated Transitions and Transparency
- D. Equilibrium and Relations Between A and B Coefficients
- E. Summary

## Chapter 15

The tools of time-dependent perturbation theory can be applied to transitions among electronic, vibrational, and rotational states of molecules.

### I. Rotational Transitions

### II. Vibration-Rotation Transitions

#### A. The Dipole Moment Derivatives

#### B. Selection Rules on $v$ in the Harmonic Approximation

#### C. Rotational Selection Rules

### III. Electronic-Vibration-Rotation Transitions

#### A. The Electronic Transition Dipole and Use of Point Group Symmetry

#### B. The Franck-Condon Factors

#### C. Vibronic Effects

#### D. Rotational Selection Rules for Electronic Transitions

### IV. Time Correlation Function Expressions for Transition Rates

#### A. State-to-State Rate of Energy Absorption or Emission

#### B. Averaging Over Equilibrium Boltzmann Population of Initial States

#### C. Photon Emission and Absorption

#### D. The Line Shape and Time Correlation Functions

#### E. Rotational, Translational, and Vibrational Contributions to the Correlation Function

#### F. Line Broadening Mechanisms

##### 1. Doppler Broadening

##### 2. Pressure Broadening

##### 3. Rotational Diffusion Broadening

##### 4. Lifetime or Heisenberg Homogeneous Broadening

##### 5. Site Inhomogeneous Broadening

## Chapter 16

Collisions among molecules can also be viewed as a problem in time-dependent quantum mechanics. The perturbation is the "interaction potential", and the time dependence arises from the movement of the nuclear positions.

### I. One Dimensional Scattering

- A. Bound States
- B. Scattering States
- C. Shape Resonance States

### II. Multichannel Problems

- A. The Coupled Channel Equations
- B. Perturbative Treatment
- C. Chemical Relevance

### III. Classical Treatment of Nuclear Motion

- A. Classical Trajectories
- B. Initial Conditions
- C. Analyzing Final Conditions

### IV. Wavepackets

## **Section 6 More Quantitative Aspects of Electronic Structure Calculations**

### **Chapter 17**

Electrons interact via pairwise Coulomb forces; within the "orbital picture" these interactions are modelled by less difficult to treat "averaged" potentials. The difference between the true Coulombic interactions and the averaged potential is not small, so to achieve reasonable (ca. 1 kcal/mol) chemical accuracy, high-order corrections to the orbital picture are needed.

I. Orbitals, Configurations, and the Mean-Field Potential

II. Electron Correlation Requires Moving Beyond a Mean-Field Model

III. Moving from Qualitative to Quantitative Models

IV. Atomic Units

### **Chapter 18**

The single Slater determinant wavefunction (properly spin and symmetry adapted) is the starting point of the most common mean field potential. It is also the origin of the molecular orbital concept.

I. Optimization of the Energy for a Multiconfiguration Wavefunction

A. The Energy Expression

B. Application of the Variational Method

C. The Fock and Secular Equations

D. One- and Two- Electron Density Matrices

II. The Single Determinant Wavefunction

III. The Unrestricted Hartree-Fock Spin Impurity Problem

IV. The LCAO-MO Expansion

## V. Atomic Orbital Basis Sets

- A. STOs and GTOs
- B. Basis Set Libraries
- C. The Fundamental Core and Valence Bases
- D. Polarization Functions
- E. Diffuse Functions

## VI. The Roothaan Matrix SCF Process

## VII. Observations on Orbitals and Orbital Energies

- A. The Meaning of Orbital Energies
- B. Koopmans' Theorem
- C. Orbital Energies and the Total Energy
- D. The Brillouin Theorem

## Chapter 19

Corrections to the mean-field model are needed to describe the instantaneous Coulombic interactions among the electrons. This is achieved by including more than one Slater determinant in the wavefunction.

### I. Different Methods

- A. Integral Transformations
- B. Configuration List Choices

### II. Strengths and Weaknesses of Various Methods

- A. Variational Methods Such as MCSCF, SCF, and CI Produce Energies that are Upper Bounds, but These Energies are not Size-Extensive
- B. Non-Variational Methods Such as MPPT/MBPT and CC do not Produce Upper Bounds, but Yield Size-Extensive Energies
- C. Which Method is Best?

### III. Further Details on Implementing Multiconfigurational Methods

- A. The MCSCF Method
- B. The Configuration Interaction Method

- C. The MPPT/MBPT Method
- D. The Coupled-Cluster Method
- E. Density Functional or X-alpha (X ) Methods

## Chapter 20

Many physical properties of a molecule can be calculated as expectation values of a corresponding quantum mechanical operator. The evaluation of other properties can be formulated in terms of the "response" (i.e., derivative) of the electronic energy with respect to the application of an external field perturbation.

### I. Calculations of Properties Other Than the Energy

#### A. Formulation of Property Calculations as Responses

#### B. The MCSCF Response Case

##### 1. The Dipole Moment

##### 2. The Geometrical Force

#### C. Responses for Other Types of Wavefunctions

#### D. The Use of Geometrical Energy Derivatives

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##### 2. Transition State Rate Coefficients

##### 3. Harmonic Vibrational Frequencies

##### 4. Reaction Path Following

### II. Ab Initio, Semi-Empirical and Empirical Force Fields

#### A. Ab Initio Methods

#### B. Semi-Empirical and Fully Empirical Methods

#### C. Strengths and Weaknesses

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**Point Group Symmetry E**

**Qualitative Orbital Picture and Semi-Empirical Methods F**

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