

Quantum Chemistry

Introduction

Quantum Chemistry is the theoretical foundation of modern chemistry, providing the rules for how atoms and molecules behave at the electronic level. Spectroscopy is the experimental technique that applies these rules, using the interaction of electromagnetic radiation (light) with matter to determine molecular structure, energy levels, and dynamics. Together, these fields explain the fundamental properties and reactivity of all chemical systems.

This module is structured to first master the quantum mechanical formalism before moving to its spectroscopic applications.

Learning Objectives

By the end of this module, you will be able to:

- Discuss and apply the equations describing the three phenomena that led to the birth of quantum mechanics (black body, photoelectric effect, atomic stability).
- Discuss the postulates of quantum mechanics and relate them to the Schrodinger equation.
- Apply the formalism of quantum mechanics to simple systems (like the particle in a box) and compare the results with the behavior predicted by classical mechanics.
- Construct spectroscopic state (Term Symbols) for elements.
- Construct the wave equation for polyelectronic atoms.
- Describe the quantum mechanical model for diatomic molecules in terms of the Schrodinger equation, wave functions, and energy level diagrams.

Key Concepts and Definitions

Term	Definition
Wave Function (Ψ)	A mathematical description of the quantum state of a particle; the square of its magnitude (Ψ^2) gives the probability density.
Operator	A mathematical instruction that acts on the wave function to extract a physical observable (e.g., energy, momentum).
Hamiltonian Operator (H)	The operator corresponding to the total energy (kinetic plus potential) of the system.
Term Symbol	A concise notation ($2S+1LJ$), representing the electronic quantum state (angular momenta and spin) of an atom or ion.
Born-Oppenheimer Approximation	The assumption that electron motion is so much faster than nuclear motion that the two can be treated separately.
Selection Rules	Rules that specify which transitions between quantum energy levels are allowed.

Detailed Discussion

1. Foundations and The Failure of Classical Mechanics

Quantum mechanics arose from the inability of classical physics to explain three key phenomena:

A. Black-Body Radiation: Classical physics predicted infinite energy at short wavelengths (the "ultraviolet catastrophe"). Planck solved this by postulating that energy is quantized: it can only be absorbed or emitted in discrete packets (quanta).

Planck's Equation :

$$E = h\nu$$

Where: E is energy, h is Planck's constant, and ν is frequency.

B. Photoelectric Effect: The emission of electrons from a metal surface struck by light. Einstein explained that light consists of particles (photons), and the kinetic energy of the emitted electron depends only on the light's frequency, not its intensity.

Photoelectric Effect Equation:

$$E_k = h\nu - \Phi$$

Where: E_k is kinetic energy of the electron, and Φ is the work function of the metal.

C. Atomic Stability (Bohr Model): Classical physics predicted that orbiting electrons should continuously radiate energy and spiral into the nucleus. Bohr solved this by postulating that electrons exist in stable, quantized orbits.

D. Wave-Particle Duality (De Broglie): Particles possess wave-like properties.

De Broglie Wavelength :

$$\lambda = h/p = h/(mv)$$

E. Heisenberg Uncertainty Principle: The limit on simultaneous measurement of conjugate variables. The uncertainty in position (Δx) and momentum (Δp) is inversely related.

Heisenberg Uncertainty Relation :

$$(\Delta x)(\Delta p) \geq h/(4\pi)$$

2. The Schrodinger Equation and Simple Systems

The **Schrodinger Equation** formalizes the postulates of quantum mechanics, describing the evolution and state of a quantum system.

A. Postulates of Quantum Mechanics (Summary):

1. **State:** The state of a system is completely described by its wave function.
2. **Observables:** For every observable property (like energy or position), there is a corresponding mathematical operator (\hat{A}).
3. **Eigenvalues:** Measurement of an observable yields only one of the eigenvalues (a) of its operator: $\hat{A}\Psi = a\Psi$
4. **Expectation Value:** The average value of repeated measurements is the expectation value (l'angle a range).
5. **Evolution:** The wave function evolves in time according to the time-dependent Schrodinger equation.

Time-Independent Schrodinger Equation :

$$H\Psi = E\Psi$$

Where: H is the Hamiltonian operator (kinetic + potential energy), E is the total energy (the eigenvalue), and Psi is the wave function (the eigenfunction).

B. Application: Particle in a One-Dimensional Box (Comparison to Classical): Solving the Schrodinger equation for a particle confined to a box of length L yields quantized energy levels.

Energy of Particle in a Box :

$$E_n = n^2 h^2 / (8mL^2)$$

Comparison:

- **Quantum:** Energy is **quantized** ($n=1, 2, 3\dots$) and proportional to n^2 . The particle cannot have zero energy (E_1 is the non-zero zero-point energy). The probability distribution is not uniform.
- **Classical:** Energy is **continuous** and can be zero. The particle is equally likely to be found anywhere in the box. As n to infinity (large uantum number), the quantum result approaches the classical prediction (the **Correspondence Principle**).

3. Polyelectronic Atoms and Term Symbols

A. Wave Equation for Polyelectronic Atoms:

For an atom with N electrons, the exact Hamiltonian operator includes the kinetic energy of all N electrons, the nucleus-electron attraction, and most importantly, the **electron-electron repulsion** terms.

The full wave equation for a polyelectronic atom cannot be solved exactly due to these electron repulsion terms. Therefore, approximations are necessary.

Hartree-Fock (HF) Approximation: This is the most famous approximation. It replaces the complex electron-electron interaction with a simpler term: the average repulsive potential experienced by one electron due to the combined presence of all other electrons. This simplifies the N -electron equation into N single-electron equations, which are solved iteratively.

B. Spectroscopic State and Term Symbols: The electronic state of an atom or ion is described by a **Term Symbol**, which summarizes the coupling of the orbital and spin angular momenta of all electrons. This is done via **Russell-Saunders (L-S) Coupling**.

1. **Total Spin Angular Momentum Quantum Number (S):** Calculated by summing the spin magnetic quantum numbers (m_s) of all unpaired electrons.
2. **Spin Multiplicity ($2S+1$):** Indicates the number of possible spin states (e.g., singlet, doublet, triplet).
3. **Total Orbital Angular Momentum Quantum Number (L):** Calculated by summing the individual m_l values. The resulting L value is converted to a letter (S, P, D, F...).
4. **Total Angular Momentum Quantum Number (J):** Calculated by combining L and S : $J = |L-S|$ to $|L+S|$.

Term Symbol Format :

$\text{Multiplicity } L_J$

4. Quantum Models for Diatomic Molecules

The Born-Oppenheimer approximation allows the treatment of electronic motion separately from the nuclear motion (vibrations and rotations). The nuclear motion of a diatomic molecule can be modeled by two simple quantum systems: the Rigid Rotor and the Harmonic Oscillator.

A. The Rigid Rotor (Rotational Model): This model treats the two atoms as point masses connected by a rigid, non-stretching bond.

Energy of Rigid Rotor

$$E_J = BJ(J + 1)$$

Where: J is the rotational quantum number (J = 0, 1, 2, ...) and B is the rotational constant, related to the moment of inertia and bond length.

- **Wave Functions:** Describe the spatial orientation of the molecule.
- **Energy Level Diagram:** Levels are not equally spaced; the spacing increases linearly with J.

B. The Harmonic Oscillator (Vibrational Model): This model treats the bond between the two atoms as a perfect spring.

Energy of Harmonic Oscillator :

$$E_v = h\nu(v + 1/2)$$

- **Wave Functions:** Define the probability of finding the atoms at a specific displacement.
- **Energy Level Diagram:** Levels are **equally spaced**. Crucially, the minimum energy is not zero; $E_0 = 1/2 h\nu$ (the zero-point energy).

Detailed Discussion: Molecular Spectroscopy

This section covers the experimental application of the quantum mechanical models described above.

5. Molecular Spectroscopy Types and Requirements

Spectroscopy probes the transitions between molecular energy levels (rotational, vibrational, electronic) induced by the absorption or emission of photons. The selection rules define which transitions are allowed.

A. Rotational Spectroscopy (Microwave Region):

- **Origin:** Transitions between rotational energy levels.
- **Molecular Requirement:** The molecule **must possess a permanent dipole moment** (e.g., HCl, CO, but not CO₂ or H₂).
- **Selection Rule:** $\Delta J = \pm 1$

B. Vibrational Spectroscopy (Infrared and Raman):

- **Origin:** Transitions between vibrational energy levels .
- **Infrared (IR) Requirement:** The vibration **must cause a change in the molecular dipole moment**.
- **Selection Rule (Harmonic Oscillator):** $\Delta v = \pm 1$

C. Electronic Spectroscopy (UV-Vis):

- **Origin:** Transitions of an electron between molecular orbitals (e.g., HOMO to LUMO).

- **Chromophores:** The part of the molecule responsible for light absorption (often unsaturated groups like $C=C$).

6. Quantification: Beer-Lambert Law

The concentration of an absorbing species in solution is determined using the **Beer-Lambert Law** in Electronic Spectroscopy.

Beer-Lambert Law :

$$A = \epsilon cl$$

Where:

- A : Absorbance (unitless).
- ϵ : Molar absorptivity (a constant for the specific molecule and wavelength).
- c : Concentration (in {mol/L}).
- l : Path length of the light through the sample (in {cm}).

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