BASIC PRINCIPLES OF QUANTUM MECHANICS

1. Planck's Quantum Hypothesis & Black Body Radiation

- **Problem**: Classical physics failed to explain the black-body radiation spectrum (ultraviolet catastrophe).
- **Planck's Hypothesis**: Energy is quantized. Emitted/absorbed in discrete packets (*quanta*).

$$E = nh\nu \quad (n=1,2,3,\dots)$$

where h is Planck's constant, ν is frequency.

- **Blackbody Radiation Formula:**

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} \cdot \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

2. Photoelectric Effect

- Classical View: Intensity increases energy → Incorrect.
- Einstein's Quantum Theory:

$$E_k = h\nu - \phi$$

where ϕ is the work function. Explained threshold frequency & instantaneous emission.

---

3. Bohr's Theory of Hydrogen Atom

- **Postulates:**
  - Electrons orbit nucleus in fixed paths.
  - Angular momentum is quantized: $mvr = nh/2\pi$
  - Energy emitted when jumping between levels.

$$E_n = -13.6/n^2 \text{ eV}$$

- **Limitations:**
  - Only works for hydrogen-like atoms.
  - Cannot explain fine/spectral lines, Zeeman effect.

---

4. Heisenberg's Uncertainty Principle

- It is impossible to know both position and momentum exactly:

$$\Delta x \cdot \Delta p \geq \hbar/2$$

5. Davisson-Germer Experiment

- Proved wave nature of electrons.
- Electrons diffracted by nickel crystal → Confirmed de Broglie hypothesis:

$$\lambda = h/p$$

Quantum Chemistry Postulates

1. State described by a wavefunction ψ
2. Observable quantities correspond to operators.
3. Measurement yields eigenvalues of operators.
4. Evolution of system governed by Schrödinger's equation.
5. Wavefunctions must be normalized and continuous.

Operator Algebra

- Operators: Act on wavefunctions to extract physical quantities.
- Linear Operator: $\hat{A}(a\psi+b\phi) = a\hat{A}\psi + b\hat{A}\phi$
- Hermitian Operators: Real eigenvalues, physical observables.
- Differential Operators: $\hat{p} = -i\hbar(d/dx)$, $\hat{H} = \hat{T}+\hat{V}$
- Angular Momentum Operators: $\hat{L}^2$, $\hat{L}_z$

Eigenvalues and Eigenfunctions

- For operator $\hat{A}$,

$$\hat{A}\psi = a\psi$$

→ ψ: eigenfunction; a: eigenvalue.

🧪 Schrödinger Equation

✅ Time-Dependent:

$$i\hbar(\partial\psi/\partial t) = \hat{H}\psi$$

✅ Time-Independent:

$$\hat{H}\psi = E\psi$$

Quantum Models & Systems

1D Particle-in-a-Box

- Infinite potential walls, length L:

$$E_n = \frac{n^2 h^2}{8mL^2}, \quad \psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

3D Particle-in-a-Box

- Box dimensions L_x, L_y, L_z

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

Rigid Rotator (Model of Rotating Molecule)

- Quantum numbers J, m_J
- Energy:

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

with degeneracy 2J+1

Harmonic Oscillator

- Potential: $V(x) = (½)kx^2$
- Energy levels:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

Hydrogen Atom

- Coulomb potential:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

- Solutions in spherical coordinates.
- Quantum numbers: n,l,m
- Orbitals: s, p, d, f → shapes derived from $\psi_{n,l,m}$

Orbital & Spin Angular Momentum

- Orbital: $L = \sqrt{l(l+1)}\hbar$
- Spin: $S = \sqrt{s(s+1)}\hbar$, where $s = 1/2$

Quantum Tunnelling

- Penetration of particles through a potential barrier.
- Probability decreases with mass & width of barrier.

APPROXIMATION METHODS

---

1. Variational Principle

- Trial function $\psi_t \rightarrow$ estimate ground state energy:

$$E_0 \leq \frac{\langle \psi_t | \hat{H} | \psi_t \rangle}{\langle \psi_t | \psi_t \rangle}$$

- Application: Hydrogen molecule (H_2):
  - Use linear combination of atomic orbitals (LCAO).
  - Estimate bond energy and length.

2. Perturbation Theory

- Used for small corrections to solvable systems.
- First Order Energy:

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$$

- Second Order Energy:

$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle \psi_k^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

- Applications:
  - Stark effect
  - Anharmonic oscillator corrections

Shapes of Orbitals

- s-orbital: Spherical
- p-orbital: Dumbbell along x, y, z
- d-orbitals: Cloverleaf shapes (except d_{z^2})
- Determined from angular part of ψ