

Most equations needed will be given in an examination, but it is important to understand the meaning of the variables in all the major formulae encountered. Also, it would not hurt, at a minimum, to memorize the following formulae.

$$\begin{aligned} E &= h\nu & \Delta E &= hcR \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ \lambda &= \frac{h}{p} & \hat{\mathcal{H}}\psi_n &= E_n\psi_n \\ \hat{\mathcal{H}} &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) & &= \hat{T} + \hat{V} \\ E_\phi &= \frac{\int \phi^* \hat{\mathcal{H}} \phi d\tau}{\int \phi^* \psi d\tau} & E^{(1)} &= \int \psi^{(0)*} \hat{\mathcal{H}}^{(1)} \psi^{(0)} d\tau \end{aligned}$$

Topic list:

- **History** (*Ch. 1*):

Blackbody radiation – what is BBR? Meaning of the Wien displacement law and the Rayleigh-Jeans law. The ultraviolet catastrophe. Planck and the quantum.

Photoelectric effect – What does the energy of the electron depend on? What does it not depend on? What does this mean?

Wave-particle duality – Electron diffraction and the De Broglie equation.

H atom spectrum – Relation of series of lines in spectrum to arrangement of fixed energy levels. The Rydberg equation and the Bohr model.

- **The Classical Wave Equation** (*Ch. 2*):

Solving simple differential equations. The role of separation of (space and time) variables in solving the wave equation. Characteristics of the solutions (normal modes).

- **The Schrödinger Equation** (*Ch. 3, 4*):

Form of the time-independent SE and meaning of $\hat{\mathcal{H}}$, ψ , and E . Eigenvalues, eigenfunctions, and operators. Requisites for a QM operator. Orthogonality and normalization. Relationship between ψ^2 and probability.

Average (expectation) value of an operator.

The Heisenberg Uncertainty Principle – Relationship between the HUP and the commutation properties of operators; relationship between the HUP and simultaneous measurement of physical quantities.

- **Application: The particle in a box** (*Ch. 3*):

The effect of boundary conditions on the solutions of the SE. Differences between the PIAB and the free particle in terms of momentum and energy quantization.

Energy levels (zero-point energy) and eigenfunctions (nodes).

The n -dimensional PIAB and *degeneracy*.

- **Application: The simple harmonic oscillator** (*Ch. 5*):

The classical SHO – force and energy relationships (Hooke's law). The SHO represents a pendulum or spring. The QM SHO can represent vibrations of a chemical bond.

Basis of SHO model of chemical bond on expansion of a potential around its minimum.

Concept of *anharmonicity*. Other non-harmonic models of the chemical bond (Morse potential).

Eigenvalues (equally spaced; existence of a ZPE); eigenvectors (Hermite polynomials); selection rule (calculated using Hermite polynomial recursion properties): $\Delta v = \pm 1$.

- **Application: The rigid rotator** (*Ch. 5*):

Model for rotations of a diatomic molecule (approximate – centrifugal force stretches bond when molecule rotates). Eigenvalues; eigenfunctions are spherical harmonics.

- **The Hydrogen Atom** (*Ch. 6*):

Separability of radial and angular parts of the Hamiltonian leads to angular solutions which are spherical harmonics and radial solutions which are exponentials multiplied by (associated Laguerre) polynomials.

Conditions for solutions to be real lead to three quantum numbers: n , l , and m_l . Relationship between these solutions and quantum numbers and the H atom orbitals and their labels.

Dependence of energy and radius on Z and μ .

For a one-electron atom, orbitals of a given n are degenerate; for a multielectron atom, due to “penetration” and “shielding” effects, energies lie in the order $s < p < d < \dots$ for a given n .

SE not separable for two-electron atom; necessity of approximate methods.

- **Approximate methods** (*Ch. 7*):

The variational method – A method for finding an *upper bound* for the GS energy. Rayleigh ratio. Rayleigh-Ritz method (LCAO). Variational method for H with an exponential trial function gives the exact GS solution; with other functions (for example gaussian functions) it gives an approximation.

Perturbation theory – finding an approximate solution to an unknown problem *via* the exact solution to a known problem that resembles it. Form of the first-order energy expression.

Rudiments of the self-consistent field method.

- **Multi-electron atoms** (*Ch. 8*):

The Stern-Gerlach experiment and electron spin. Angular momentum conservation and selection rules. Antisymmetry and the Pauli principle. Determinantal wavefunctions. Angular momentum coupling, term symbols, and selection rules for many-electron atoms.

- **Molecular structure and bonding** (*Ch. 9, 10*):

The Born-Oppenheimer approximation. Molecular orbital treatment of H_2^+ – bonding and antibonding orbitals. The Hückel method for π -electron systems.

- **Spectroscopy** (*Ch. 13*):

EM radiation and spectroscopy – typical λ values for electronic/vibrational/rotational transitions; vibrational structure in electronic spectra (I_2 lab); anharmonicity effects in vibrational spectra (HCl lab).