Some useful constants:

- $h$ (Planck's constant) $= 6.626 \times 10^{-34}$ J-s

- $c$ (Speed of light) $= 2.998 \times 10^8 \approx 3 \times 10^8$ m/s

- $m_e$ (Mass of electron) $= 9.1 \times 10^{-31}$ kg

- $e$ (Charge on an electron) $= 1.6 \times 10^{-19}$ C

- $\hbar$ (Reduced Planck's constant) $= 1.055 \times 10^{-34}$ J-s

# 1 Photoelectric effect

- Let the frequency of the incident light on the metal surface be $\nu$, and the work function of the metal be $\phi$. The energy of the ejected photon is given by:

$$E = h\nu - \phi$$

Which can be rewritten in terms of the wavelength ($\lambda$) and the speed of light ($c$) as:

$$E = \frac{hc}{\lambda} - \phi$$

In the case where

$$\phi = h\nu_0 = \frac{hc}{\lambda_0}$$

$\nu_0$ and $\lambda_0$ are called the **threshold frequency and wavelength** respectively.

- For a particle of mass $m$ travelling with a velocity $v$, its (De Broglie) wavelength takes the form:

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

Where $p$ is the linear momentum of the particle in question.

- When an electron of charge $-e$ is accelerated across a potential difference $V$, it acquires the kinetic energy $E = eV$. From this, it follows that the *De Broglie wavelength* of the particle is:

$$\lambda = \frac{h}{\sqrt{2m_e eV}}$$

$m_e$ being the mass of the electron.

# 2 Schrödinger equation

- The **time independent Schrödinger equation** for a particle having the wavefunction $\psi$ (in a single dimension) is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

The left hand side of the above equation is abbreviated to a *single operator* known as the **Hamiltonian**, which represents the **total energy of a particular system**. We now have a compact version of the S.E: $\boxed{\hat{H}\psi = E\psi}$

- A wavefunction $\psi$ is said to be **normalised** if its probability density over the entire space is 1. More formally, the following relation must hold

$$\int_{-\infty}^{\infty} \psi^*\psi dx = 1$$

Where $\psi^*$ is the **complex conjugate** of $\psi$. Note that *psi* is normalized only for a 1 dimensional case above.

- Suppose that $\Delta x$ and $\Delta p$ denotes the uncertainty in the measurement of position and momentum respectively. Heisenberg's uncertainty principle states

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

# 3  Particle In a Box

1. **1D case**:
   We consider a box of length $L$, quantum number $n$, particle mass $m$ and wavelength of the particle $\lambda$

   - Acceptable values of linear momentum $p = \frac{nh}{2L}$
   - Solution to the Schrödinger equation for the $n^{\text{th}}$ excited state:

   $$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

   - Permitted energy values:

   $$E_n = \frac{n^2 h^2}{8mL^2}$$

   The energy of the lowest state $(n = 1)$ is called the **zero-point energy**

2. **2D case**:
   A box of dimensions $L_x$ and $L_y$ along the $x$ and $y$ directions is considered, with the quantum numbers $n_x$ and $n_y$

   - Solution to the Schrödinger equation:

   $$\psi_{n_x n_y}(x, y) = \sqrt{\left(\frac{4}{L_x L_y}\right)} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right)$$

   - Permissible energy values:

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

# 4  Rigid Rotor

1. **2D case**:
   We consider here a particle of mass $m$ rotating in a circle of radius $r$. The moment of inertia of the system is taken to be $I = mr^2$

   - Angular momentum $J_z = m_l \hbar$ where $m_l = 0, \pm 1, \pm 2 \ldots$
   - Permissible energy values $E_n = \frac{n^2 \hbar^2}{2I} = \frac{m_l^2 \hbar^2}{2I}$ where $m_l$ and $n = 0, \pm 1, \pm 2 \ldots$

2. **3D case**:
   In addition to the previously defined quantities, we introduce $l$: the **orbital angular momentum quantum number**.

   - Permissible energy values $E_l = l(l+1)\frac{\hbar^2}{2mr^2}$
     Here, $l = 0, 1, 2 \ldots$ and $m_l = -l, (-l+1) \ldots (l-1), l$
   - Angular momentum is **quantized** and given by the values $J = \sqrt{l(l+1)}\hbar$

# 5  Simple Harmonic Oscillator

Here, we are concerned only with the permissible energy values:

$$E_v = \left(v + \frac{1}{2}\right) h\nu$$

Where $\nu$ is the **vibrational frequency** given by $\frac{1}{2\pi}\sqrt{\frac{k}{m}}$. The values of $\nu$ include the set of all non-negative integers.

# 6  Spectra of Complex Atoms

- **Total orbital angular momentum**: $L = l_1 + l_2, \ldots, |l_1 - l_2|$

- **Total spin angular momentum**: $S = s_1 + s_2, \ldots, |s_1 - s_2|$

- **Total angular momentum**: $J = L + S, \ldots, |L - S|$

- **Term symbol**: $^{2S+1}L_J$
  Here, $L$ takes integral values starting from 0, corresponding to the sub-shell, that is $0(s)$, $1(p)$, ... etc.

- For a given value of $J$, there are $(2J + 1)$ degenerate states and for a term, $(2L + 1)(2S + 1)$ states exist.

- Note that all atomic transitions must take place in compliance to the **selection rules**:

  1. $\Delta L = 0, \pm 1$
  2. $\Delta S = 0$
  3. $\Delta J = 0, \pm 1$ (an exception being the forbidden transition between two levels where $J = 0$)

To determine the ground state of an atom, we use the following procedure:

1. Compute the highest value of $S$ using the above definition

2. Similarly, compute the highest value of $L$

3. Using these values, calculate the maximum and minimum values of $J$. From here, 2 cases arise:

   (a) Less than $\frac{1}{2}$ filled sub-shell $\implies J_{\max}$
   (b) Greater than $\frac{1}{2}$ filled sub-shell $\implies J_{\min}$

# 7  Spectroscopy

Nomenclature of some frequently used symbols:

1. $I_0 \to$ Intensity of incident radiation

2. $I \to$ Intensity of transmitted radiation

3. $[C] \to$ Concentration

4. $L \to$ Path length of radiation through the sample

5. $\epsilon \to$ Molar absorption coefficient $\left( = \frac{1}{[C][L]} \right)$

- **Absorbance** $= A = \log\left(\frac{I_0}{I}\right)$ and **transmittance** $T = \left(\frac{I}{I_0}\right)$. From this, it can be inferred that $A = -\log T$.
  An alternate for of absorbance is $A = \epsilon[C]L$

- The total absorbance of a mixture at a given wavelength $\lambda$ is

$$A = A_A + A_B$$
$$= \epsilon_A[A]I + \epsilon_B[B]I$$

- The individual absorbance for a mixture of 2 light absorbing species (albeit at two separate wavelengths: $\lambda_1$ and $\lambda_2$) is obtained by solving a system of 2 simultaneous equations (similar to the one above)

$$[A] = \frac{\epsilon_{B2}A_1 - \epsilon_{B1}A_2}{L(\epsilon_{A1}\epsilon_{B2} - \epsilon_{A2}\epsilon_{B1})}$$
$$[B] = \frac{\epsilon_{A1}A_2 - \epsilon_{A2}A_1}{L(\epsilon_{A1}\epsilon_{B2} - \epsilon_{A2}\epsilon_{B1})}$$

### 7.0.1 Rotational Spectroscopy

- **Rotational constant** $B = \frac{\hbar^2}{4\pi I}$

- **Energy levels** $E_j = hBJ(J+1) = J(J+1)\frac{\hbar^2}{2I}$
  In this case $J = 0, 1, 2, \ldots$ denotes the **rotational quantum number**, $B$ denotes the rotational constant and $I = \sum m_i r_i^2$, the **moment of inertia**.

- In the absence of an electric/magnetic field, all rotational levels are $(2J+1)$ fold degenerate.

- Population of molecules follows the **Boltzmann distribution**, ie:

$$\frac{N_2}{N_1} = e^{-(E_2 - E_1)/kT}$$

Here, $E_j$ indicates the energy level of the $j^{\text{th}}$ state.
In the state of thermal equilibrium, the population of any level $P_j$ is given by the relation

$$\frac{P_j}{P_0} = (2J+1)e^{-(hBJ(J+1)/kT)}$$

### 7.0.2 Vibrational Spectroscopy

- Depth of potential well = **Strength of bond** (in terms of the force constant $k$)

- The energy levels are **equally spaced** by a gap of $h\nu$ and the **zero point energy** is given by $\frac{h\nu}{2}$

- Vibrational energy levels become **less widely spaced** due to **anharmonicity**.

- In a molecule having $N$ atoms, the position (degrees of freedom) of all atoms is $3N$.

  1. Translational: 3
  2. Rotational: 2 (linear) or 3 (non-linear)
  3. Vibrational: $3N - 5$ (linear) or $3N - 6$ (non-linear)

### 7.0.3 IR Spectroscopy

- Below 1500cm$^{-1}$: **fingerprint region**

- When IR radiation is absorbed, the intensity of transmitted radiation **decreases** and hence a **dip** in the spectrum

Some important peaks in the IR spectrum:

| IR spectrum | |
|---|---|
| Functional group | Typical absorption (cm$^{-1}$) |
| =C-H stretch | 3000-3100 |
| N-H stretch | 3300-3500 |
| O-H stretch | 3550-3200 |
| C=C stretch | 1680-1620 |
| C=C bending | 1500-1700 |
| C=O stretch | $\approx 1700$ |

It must be noted that the O-H stretching frequency **decreases** due to **H-bonding** (ie - the spectral graph *broadens* due to this)