

# Comprehensive Notes

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# 1 Mechanics

## 1.1 Rotations

$$\mathbf{L} = \mathbf{I}\omega$$

Moment's of Inertia:

$$I_{xx} = \int (y^2 + z^2) dm$$

- Thin Rod length  $l$

$$\begin{aligned} I &= \int x^2 dm \quad dm = \rho dv = \rho A dx \\ &= \int_{-\frac{l}{2}}^{\frac{l}{2}} x^2 \rho A dx = \frac{1}{12} ml^2 \end{aligned}$$

- Sphere of uniform density, radius  $R$

$$\begin{aligned} I &= \int \int \int (x^2 + y^2) dm \quad dm = \rho dv = \rho r^2 \sin(\theta) dr d\phi d\theta \\ &= \frac{2}{5} mR^2 \end{aligned}$$

- Disc of radius  $R$

$$\begin{aligned} I &= \int_0^R r^2 dm \quad dm = \rho dv = \rho 2\pi r \\ &= \frac{1}{2} mR^2 \end{aligned}$$

## 1.2 SHO

$$m\ddot{x} = -kx$$

solution is oscillatory with frequency  $\omega^2 = \frac{k}{m}$

$$x = A \sin(\omega t) + B \cos(\omega t)$$

For a damped oscillator

$$m\ddot{x} - \gamma\dot{x} + kx = 0$$

solution of form

$$x(t) = A \exp(pt) + B \exp(-pt)$$

where  $p$  is found by

$$mp^2 - \gamma p + k = 0$$

$$p = \frac{\gamma \pm \sqrt{\gamma^2 - 4mk}}{2m}$$

3 distinct cases,

**Overdamped:**  $\gamma^2 > 4mk$ , The system returns to equilibrium exponentially without oscillating.

**Critically Damped:**  $\gamma^2 = 4mk$ , The system returns to equilibrium exponentially in the shortest possible time, without oscillating.

**Under Damped:**  $\gamma^2 < 4mk$ ,  $p \in \mathbb{C}$ , The system oscillates about equilibrium with exponentially decaying amplitude.

**Q Factor:** Defined as

$$Q = 2\pi \times \frac{\text{Energy Stored}}{\text{Power loss per cycle}}$$

or in the high  $Q$  limit  $Q = \frac{\omega}{\Delta\omega}$ .

### 1.3 Special Relativity

Lorentz Transforms for a boost into a frame  $S'$  with aligned  $x$  axes moving at  $\beta c$  relative to  $S$

$$\begin{aligned} x' &= \gamma(x - \beta ct) \\ ct' &= \gamma(ct - \beta x) \\ y' &= y \\ z' &= z \end{aligned}$$

where  $\gamma = (1 - \beta^2)^{-1/2}$

- Length contraction - an observer in  $S$  will see a moving object whose rest frame is  $S'$  contract to  $l = \frac{l'}{\gamma}$
- Time dilation - an observer in the moving frame  $S'$  will record a time period  $\Delta t$  in the stationary frame  $S$  as  $\Delta t' = \gamma \Delta t$

### Relativistic Kinematics:

$$\begin{aligned} E_{rest} &= mc^2 & E_{total} &= \gamma mc^2 \\ E^2 &= p^2 c^2 + m^2 c^4 & p &= \gamma mv \\ \beta &= \frac{pc}{E} \end{aligned}$$

$v$  transform

$$v' = \frac{dx'}{dt'} = \frac{dx'}{dt} \frac{1}{\frac{dt'}{dt}} = c \frac{(1 - \beta \frac{v}{c})}{(\frac{v}{c} - \beta)}$$

**Kinetic Energy:** In the non-relativistic limit

$$\begin{aligned} E &= \gamma mc^2 \\ \gamma &\sim 1 + \frac{1}{2}\beta^2 \\ E &\sim mc^2 + \underbrace{\frac{1}{2}mv^2}_{KE} \end{aligned}$$

## 2 Waves

### 2.1 Properties

- Travelling waves of the form

$$\cos(kx - \omega t) \quad \sin(kx - \omega t) \quad \exp(i[kx - \omega t])$$

- Standing waves require  $L = \frac{\lambda}{2} \Rightarrow k = \frac{\pi}{L}$ , where  $L$  is the length of the medium in which the wave is set up.

**Superposition:** Different  $\omega \Rightarrow$  beats as  $\sin(\omega_1 t) + \sin(\omega_2 t) = 2 \sin\left(\frac{\omega_1 + \omega_2}{2} t\right) \sin\left(\frac{\omega_1 - \omega_2}{2} t\right)$

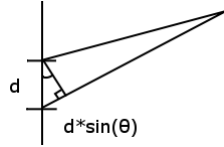
**Velocities:** Phase velocity  $v_p = \frac{\omega}{k}$ , Group velocity  $v_g = \frac{\partial \omega}{\partial k}$  - the group velocity is the flow of physical quantities

**Doppler effect:** Classical waves  $f_{source} = \left(\frac{v+v_o}{v+v_s}\right) f_{observer}$ , where  $v$  is the speed of waves in the medium, and  $v_o, v_s$  are the speeds of the observer and source relative to the medium, respectively.

The relativistic doppler effect is slightly different and arises from time dilation, as  $\Delta t' = \gamma \Delta t$  this leads to  $f_s = \frac{\sqrt{1+\beta}}{\sqrt{1-\beta}} f_o$ .

## 2.2 Diffraction

**Infinitesimal Young's Slits:**



The path difference between the two slits is  $n\lambda = d \sin(\theta)$ . So for  $x \ll$  than the distance to the screen we can also approximate  $\sin(\theta) = \theta$ , this gives us

$$\theta d = m\lambda$$

thus the angular spacing between fringes is

$$\Delta\theta = \frac{\lambda}{d}$$

we can find the vertical distance between fringes as

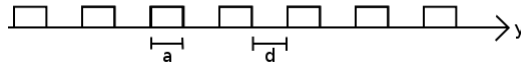
$$\Delta x = R\Delta\theta = R\frac{\lambda}{d}$$

**Grating Equation:** To have constructive interference at a point we must impose  $d \sin(\theta) = m\lambda$ , generalising to  $N$  slits in a grating  $Nd \sin(\theta) = Nm\lambda$ , called the grating equation.

**Infinitesimal Grating:** The transmission function is given by  $T(y) = \text{Rect}(y/a/2) \times \delta(y - nd)$

**Finite Width Grating:** The transmission function for the diffraction grating can be expressed as the product of the grating width and the convolution of each slit with a dirac comb.

$$T(y) = \text{Rect}(y/a/2) \times \{\delta(y - nd) \star \text{Rect}(y/a/2)\}$$



A Dirac comb transforms to another comb where the width is  $\frac{2\pi}{k} \times \frac{1}{d} = \frac{\lambda}{d}$ , the transform of the single slit gives  $A_0 \frac{\sin(\beta)}{\beta}$  and the transform of the width of the grating gives another sinc function, as in reciprocal space small features from real space result in larger features we can see that the sinc generated by the individual slits will be much wider in the diffraction pattern than the sinc generated by the size of the grating. Thus taking the comb and multiplying by the small grating width generated sinc and then we can use the individual slit width generated sinc as an envelope.

## 2.3 Refraction

By Fermat's Principle, Light travels takes the shortest optical path between 2 points, where optical path length is given by  $d = ln$  where  $l$  is the physical distance and  $n$  is the refractive index of the media. From this Snell's law can be derived

$$n_1 \sin(\theta_i) = n_2 \sin(\theta_r)$$

## 3 Quantum Mechanics

**De Broglie Relations:**

$$p = \hbar k \quad E = \hbar \omega$$

### 3.1 Heisenberg Uncertainty Principle

**Position-Momentum:**

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

For a particle travelling through a finite width slit the HUP imposes a position restriction on the particle in the plane of the obstruction, this results in a momentum uncertainty in that plane which gives rise to diffraction.

A confined particle has a finite  $\Delta x$  and thus a finite uncertainty in its momentum.

**Energy-time:**

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

This gives rise to line widths in atomic spectra due to short level lifetimes.

### 3.2 Observables

- Represented by Hermitian operators

$$\int \psi^* \hat{H} \psi dx = \int (\hat{H} \psi)^* \psi dx$$

- Operators have a set of eigenfunctions and eigenvalues
- Hermitian operators non-degenerate eigen-functions are orthogonal and their eigenvalues real
- Energy operator is the hamiltonian  $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x)$

### Representations:

$x$ -rep

$$\hat{x} = x \quad \hat{p} = -i\hbar\nabla$$

$p$ -rep

$$\hat{x} = i\hbar\nabla \quad \hat{p} = p$$

### Schrodinger Equations:

Time Dependant

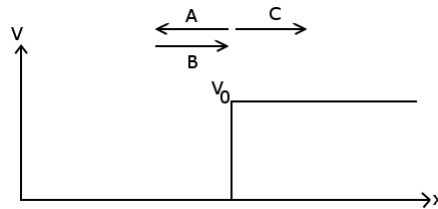
$$-i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

Time Independent

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

### 3.3 Scattering

Particles will scatter off potential steps and barriers. Unlike classically there will be a reflection coefficient for a potential step down.



Separating the total  $\psi$  into components to the left and right of the step

$$\psi_L = A \exp(-ik_l x) + B \exp(ik_l x)$$

$$\psi_R = C \exp(ik_r x)$$

by  $\frac{p^2}{2m} = E \Rightarrow k_l = \sqrt{2mE/\hbar^2}$ ,  $k_r = \sqrt{2m(E-V_0)/\hbar^2}$ . For a particle with  $E < V_0$  the wavefunction within the step is exponentially decaying, Classically this is a forbidden region. As  $\psi$  and  $\psi'$  must be continuous everywhere except at an infinite discontinuity  $\psi_L = \psi_R$ ,  $\psi'_L = \psi'_R$  at the barrier. This leads to conditions on the amplitudes such that

$$A + B = C$$

$$k_l(B - A) = k_r C$$



The expressions for the transmission and reflection coefficients are given by, where the wavevectors are introduced to keep the flux of particles constant

$$T = \frac{|C|^2 k_r}{|B|^2 k_l} \quad R = \frac{|A|^2 k_l}{|B|^2 k_l}$$

For a finite length barrier the exponentially decay component within the barrier will give rise to another free particle wavefunction at the other side of the barrier. The amplitude of  $\psi_R$  at the other side of the barrier dictates the probability of the particle 'tunnelling' through the classically forbidden barrier.

### 3.4 Potential Wells

**Infinite Well:** A well, half width  $a$ , with infinite potential at  $a, -a$  and no potential within the well. The boundary conditions dictate that any  $\psi$  must be zero at both edges of the well, solving the TISE under these conditions yields the general solution

$$\psi = A \sin(kx) + B \cos(kx)$$

Where  $k = \sqrt{2mE/\hbar^2}$  is the free particle wavevector. From the application of the boundary conditions  $k$  is quantised for 2 cases

$$A = 0 \quad k = \frac{n\pi}{2a} \quad n = 2, 4, 6$$

$$B = 0 \quad k = \frac{n\pi}{2a} \quad n = 1, 2, 3$$

So we arrive at the solution

$$\psi = \begin{cases} \cos(n\pi x/2a) & n \text{ odd} \\ \sin(n\pi x/2a) & n \text{ even} \end{cases}$$

With  $E = \frac{\hbar^2 \pi^2 n^2}{8ma^2}$ .

**Finite Well:** Using a similar argument to the potential step, split up the total  $\psi$  into 3 components wavefunctions  $\psi_L, \psi_C, \psi_R$ . The boundary conditions are now that the wavefunction is continuous over the potential steps these lead to the 2 simultaneous conditions

$$k \tan(ka) = \kappa$$

$$-k \cot(ka) = \kappa$$

where  $k = \sqrt{2mE/\hbar^2}$ ,  $\kappa = \sqrt{2m(E-V_0)/\hbar^2}$ . These can be solved graphically to yield the energy levels allowed.

### 3.5 Harmonic Oscillator

A particle confined to a potential well defined by  $V(x) = \frac{1}{2}Kx^2$ . So the TISE becomes

$$-\frac{\hbar^2}{2m} \frac{\partial^2 u}{\partial x^2} + \frac{1}{2}Kx^2 u = Eu$$

The solution is the set of Hermite polynomials denoted  $H_n(x)$ . The energy levels are given by  $E_n = (n + \frac{1}{2})\hbar\omega$ . note that this system has a minimum energy, called the 'zero-point energy' when  $n = 0$ .

## 4 Electromagnetism

### 4.1 Maxwell's Equations

	Integral form	Differential Form
Gauss' Law for $\mathbf{E}$ —	$\oint_s \mathbf{E} \cdot d\mathbf{s} = \frac{1}{\epsilon_0} \int_\tau \rho d\tau$	$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0}$
Gauss' Law for $\mathbf{B}$ —	$\oint_s \mathbf{B} \cdot d\mathbf{s} = 0$	$\nabla \cdot \mathbf{B} = 0$
Faraday's Law—	$\oint_c \mathbf{E} \cdot d\mathbf{l} = \epsilon = -\frac{d\Phi_B}{dt}$	$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$
Amperian Maxwell Law—	$\oint_c \mathbf{B} \cdot d\mathbf{l} = \mu_0 I + \mu_0 \epsilon_0 \frac{d\Phi_E}{dt}$	$\nabla \times \mathbf{B} = \mu_0 \mathbf{j}_f + \mu_0 \epsilon_0$

**Displacement and Demagnetizing field:**

$$\mathbf{D} = \epsilon \mathbf{E} + \mathbf{P} \quad \mathbf{H} = \frac{\mathbf{B}}{\mu} - \mathbf{M}$$

Where  $\mathbf{P}, \mathbf{M}$  are the polarisation and magnetisation respectively and  $\epsilon = \epsilon_r \epsilon_0$ ,  $\mu = \mu_r \mu_0$ . In an HIL medium

$$\mathbf{D} = \epsilon \mathbf{E} \quad \mathbf{B} = \mu \mathbf{H}$$

These lead to alternate forms of Maxwell's equations containing  $\mathbf{H}$  and  $\mathbf{D}$ .

**Force on a particle:** The force on a charged particle due to Electric and magnetic fields is given by the Lorentz Force

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

In a uniform magnetic field this leads to 'cyclotron' motion, as  $\mathbf{F} \perp \mathbf{v}$ ,  $\mathbf{B}$  the particle exhibits circular motion. Equating the Lorentz force to the required centripetal force the frequency of rotation can be determined as

$$\omega_{cyc} = \frac{qB}{m}$$

## 4.2 Electrostatic Potential

Potential energy of a discrete charge distribution is given by  $U = \frac{q_0}{4\pi\epsilon_0} \sum_i \frac{q_i}{r_i}$  or  $U = \frac{q_0}{4\pi\epsilon_0} \int \frac{dq}{r}$  in the continuous case. The Electrostatic potential is the potential energy per unit charge thus  $V = \frac{U}{q_0}$ . The work done by/against a force is defined as  $W_{a \rightarrow b} = \int_a^b \mathbf{F} \cdot d\mathbf{l}$ , this can be used to work out  $V$  for a given  $\mathbf{E}$

$$V_a - V_b = \int_a^b \mathbf{E} \cdot d\mathbf{l} \rightarrow V = - \int \mathbf{E} \cdot d\mathbf{l}$$

Notice that the value is only dependant on the starting and end points not the path taken. Conversely the Electric field can be calculated by a known potential

$$\mathbf{E} = -\nabla V$$

**Method of Images:** There can be no electric fields within a conductor as free charges will move to counter it. This can be used to find the charge distribution on a conducting surface, there can be no component of  $\mathbf{E}$  tangential to the surface. If another charge is placed near this surface, the charge distribution of the surface will change to obey this condition. By placing 'fake' charges in the conductor such that there is only a component of  $\mathbf{E}$  perpendicular to the surface the charge distribution can be found.

## 4.3 Poynting Vector

**EM Energy:**

- Energy Density in an Electric Field

$$\begin{aligned} - u_E &= \frac{1}{2} \mathbf{E} \cdot \mathbf{D} \\ - \langle u_E \rangle &= \frac{1}{4} \text{Re} \langle \mathbf{E} \cdot \mathbf{D}^* \rangle \end{aligned}$$

- Energy Density in a Magnetic Field

$$\begin{aligned} - u_B &= \frac{1}{2} \mathbf{B} \cdot \mathbf{H} \\ - \langle u_B \rangle &= \frac{1}{4} \text{Re} \langle \mathbf{B} \cdot \mathbf{H}^* \rangle \end{aligned}$$

### Poyntings Theorem:

Poynting Vector

$$\mathbf{N} = \mathbf{E} \times \mathbf{H}$$

Using energy conservation we know the EM energy initially in a volume must either

- Converted by ohmic heating<sup>1</sup>
- Stay Stored in the fields<sup>2</sup>
- Leave the volume<sup>3</sup>

Which leads to the condition that any energy leaving the field must escape the volume or be converted by ohmic heating.

$$\frac{\partial}{\partial t} \int_{\tau} \underbrace{\frac{1}{2} (\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H})}_{2} d\tau + \oint_s \underbrace{\mathbf{N} \cdot d\mathbf{s}}_3 + \underbrace{\int_{\tau} \mathbf{E} \cdot \mathbf{j}_f}_{1} d\tau = 0$$

this can be expressed as a differential

$$\frac{\partial}{\partial t} \frac{1}{2} (\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}) + \nabla \cdot \mathbf{N} + \mathbf{E} \cdot \mathbf{j}_f = 0$$

### Useful Properties of the Poynting Vector:

- Energy Flux

$$- \langle \mathbf{N} \rangle = c \langle u \rangle \hat{\mathbf{k}}$$

- Momentum Density

$$- \langle \rho \rangle = \frac{\langle \mathbf{N} \rangle}{c^2}$$

- Radiation Pressure

$$- \langle Pressure \rangle_{absorb} = \frac{\langle \mathbf{N} \rangle}{c} \hat{\mathbf{k}} = \frac{1}{2} \langle Pressure \rangle_{reflect}$$

## 4.4 Electromagnetic Waves in a Vacuum

### Complex Notation:

Faraday's law

$$\mathbf{H} = \frac{\mathbf{k} \times \mathbf{E}}{\mu\omega}$$

Ampere's law

$$\mathbf{E} = \frac{\mathbf{H} \times \mathbf{k}}{\epsilon\omega}$$

Product Averages

$$\langle AB \rangle = \frac{1}{2} \text{Re} [AB^*]$$

**Wave Equation:** From Maxwell's equations we can derive wave equations for both  $\mathbf{E}, \mathbf{H}$

$$\nabla^2 \mathbf{E} = \mu_0 \varepsilon_0 \frac{\partial^2}{\partial t^2} \mathbf{E}$$

$$\nabla^2 \mathbf{H} = \mu_0 \varepsilon_0 \frac{\partial^2}{\partial t^2} \mathbf{H}$$

Where the speed of propagation is  $c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}}$ , the solution for  $\mathbf{E}$  is given by  $\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$ ,  $\mathbf{H}$  can be found by Faraday's law and it thus always perpendicular to  $\mathbf{E}$ . For fields of this form can use a simple, complex notation to express Maxwell's equations.

**Wave Properties:**

Wave Impedence: From Faraday's law the ratio of  $\mathbf{E}, \mathbf{H}$  is constant, for a wave propagating in the  $\hat{\mathbf{x}}$  direction

$$\frac{|\mathbf{E}|}{|\mathbf{H}|} = \sqrt{\frac{\mu}{\varepsilon}} = z$$

The energy density for the electric and magnetic components are equal thus  $u_E = u_H = \frac{1}{2}u$ , giving the time average energy density of the EM field as

$$\langle u \rangle = \frac{\varepsilon |\mathbf{E}|^2}{2} = \frac{\mu |\mathbf{H}|^2}{2}$$

**Wave Polarisation:** For a wave propagating in the  $\hat{\mathbf{x}}$  direction, linear polarisation is where the direction of the  $\mathbf{E}$  field is at a constant angle to the  $y$  axis. Circular polarisation is where the  $\mathbf{E}$  and  $\mathbf{H}$  fields rotate around the axis of propagation mapping out a circle in the  $y - z$  plane.

## 4.5 Waves in Dielectric

The speed of light in a medium is given by  $c_m = \frac{1}{\sqrt{\varepsilon \mu}} < c$  and thus the refractive index of a material is defined as  $n = \frac{c}{c_m} > 1$ . Maxwell's equations give us conditions for how waves act as they cross a boundary between two dielectric media these result in some familiar laws

- Angle of Incidence = Angle of Reflection

$$- \theta_I = \theta_R$$

- Law of Refraction

$$- k_T = \frac{n_2}{n_1} k_I$$

- Snell's Law

$$- \text{Sin}(\theta_I) = \frac{n_2}{n_1} \text{Sin}(\theta_T)$$

- Brewster Angle

$$- \text{Tan}(\theta_B) = \frac{n_2}{n_1}$$

- At this angle there is no reflected wave, all the energy is transmitted across the boundary.

**Total Internal Reflection:** If  $\left(\frac{n_1}{n_2}\right)^2 \text{Sin}^2(\theta_I) > 1$  then the  $x$  component of  $k_T$  is complex, the  $\theta_I$  that results in  $\left(\frac{n_1}{n_2}\right)^2 \text{Sin}^2(\theta_I) = 1$  is called the critical angle,  $\theta_c$ . This results in an exponential decay envelope in the second medium and the wave does not propagate but is totally reflected. note the above condition can only be satisfied if  $n_1 > n_2$ . Transmitted wave is described as being evanescent, oscillatory with a quickly decaying amplitude.

$$\mathbf{E} = \mathbf{E}_{\text{T0}} e^{i(k_{tz}z - \omega t)} e^{-|k_{tx}|x} \hat{\mathbf{y}}$$

## 4.6 Waves in Conductors

Free charge is given by Ohms law  $\mathbf{j}_f = \sigma \mathbf{E}$  which alters the dispersion relation of the waves to  $k^2 = \omega^2 \mu \epsilon \left(1 + \frac{i\sigma}{\omega \epsilon}\right)$ , as  $k$  is complex the wave within the conductor is evanescent.

**Good Conductors:** In a good conductor Electric Current  $\gg$  Displacement Current  $\Rightarrow \omega \epsilon \ll \sigma$ .  $k$  can be expressed as

$$k = (1 + i) \sqrt{\frac{\sigma \mu \omega}{2}} = k_c (1 + i)$$

This leads to the 'skin depth'  $\delta$  of a good conductor, the depth at which the amplitude of the transmitted wave has fallen by  $e$  as

$$\delta = \frac{1}{k_c} = \sqrt{\frac{2}{\sigma \mu \omega}}$$

## 4.7 EM Waves in a Waveguide

The Transverse Electric Wave, Electric field in waveguide(Width  $a$ , Height  $b$ ) of form. By Maxwell's equations for a conducting waveguide, the electric field tangential to the surface of the conductor and the magnetic field normal to the conductor must be zero. This means we need to quantise the wave such that  $E_t = 0$  at  $z = 0, b$ .

$$\mathbf{E} = E_{0y} \text{Sin} \left( \frac{m\pi}{b} z \right) e^{i(kx - \omega t)} \hat{\mathbf{y}}$$

Wave Equation leads to the dispersion law,

$$\omega^2 = k^2 c^2 + \left( \frac{m\pi}{b} c \right)^2$$

From Faraday's Law the  $\mathbf{H}$  Field can be determined,

$$\mathbf{H} = \left( \frac{E_0}{\mu_0 \omega} \right) \left[ \left( i \frac{m\pi}{b} \right) \text{Cos} \left( \frac{m\pi}{b} z \right) \hat{\mathbf{x}} + k \text{Sin} \left( \frac{m\pi}{b} z \right) \hat{\mathbf{z}} \right] e^{i(kx - \omega t)}$$

For wave to propagate down waveguide  $k^2 > 0$ , if

$$\frac{\omega}{c} < \frac{m\pi}{b}$$

$$\lambda > \frac{2b}{m}$$

wave cannot propagate. Long wavelengths cannot propagate along waveguide.

### Wave Velocities

$$v_p = \frac{c}{\sqrt{1 - \left( \frac{m\pi}{\omega b} c \right)^2}}$$
$$v_g = \frac{c^2}{v_p}$$

## 5 Thermodynamics And Statistical Physics

### 5.1 The Laws

**Zerth Law:** If A is in thermal equilibrium with B and B is in thermal equilibrium with C then A is in thermal equilibrium with C. Can use this to construct isotherms from the ideal gas law.

**First Law:** Conservation of energy states that, The change in internal energy of a system is the sum of total heat energy in less the work performed by the system. For finite changes this is given as  $\Delta U = W + Q$  and for infintesimal changes as

$$dU = dW + dQ$$

**Second Law:** Entropy of a system and its surroundings must increase for any process

$$\Delta S_{AB} \geq \int_A^B \frac{dQ}{T}$$

**Third Law:** The entropy of a system approaches 0 as  $T \rightarrow 0$ .

## 5.2 Equations of State

**Ideal Gas**

$$PV = Nk_B T \quad U = \frac{3}{2} Nk_B T$$

**Van de Waals Gas**

$$\left( P + a \frac{N^2}{V^2} \right) (V - Nb) = Nk_B T \quad U = \frac{3}{2} Nk_B T - a \frac{N^2}{V}$$

where  $a$  characterises the inter-particle attractive force and  $b$  is the volume of a particle.

## 5.3 Reversibility

A process is reversible if once done can be undone without affecting anything outside the system. Any real process is irreversible, this can be explained statistically: for any system consisting of  $N$  particles there are a multitude more ways that they can be configured which differ to the original configuration that it is a statistical impossibility that they will reconfigure unaided.

**Quasi-Static Process:** A Process which evolves 'slowly' so that at each stage the system is in thermodynamic equilibrium.

**Adiabatic Process:** Any process for which  $\Delta Q = 0$  is called an adiabatic process, in this case the first law is  $dU = -PdV$

**Work:** For a system with dissipative forces any process is irreversible thus the work done by an ideal gas is given by

$$W_{rev} = - \int PdV \quad W_{irr} > - \int PdV$$

**Reservoirs:** A system which is in contact with the system under analysis but has many more particles such that its temperature and pressure are effectively fixed.



**Constant Volume:** For a system at constant volume the first law becomes  $dU = dQ$  define the heat capacity at constant volume  $dQ = C_V dT$  thus at constant volume reversible heating can take place.

## 5.4 Engines

**A Heat Engine:** A cyclic process which produces work by using heat flow from a hot reservoir to a cold reservoir. The efficiency of a heat engine is defined as the useful work produced per heat energy used

$$\eta = \frac{W_{out}}{Q_{in}}$$

**A Heat Pump/Fridge:** A cyclic process which heats a hot object/cool a cold object by using work. As the goal of a heat pump and a fridge are different their efficiencies are defined slightly differently

$$\omega_{HP} = \frac{Q_{out}}{W_{in}} \quad \omega_F = \frac{Q_{in}}{W_{in}}$$

**Carnot Cycle:** A cyclic process made of two adiabats and two isotherms. This is a practical cycle that can be used to create efficient heat engines and pumps. Since all heating and cooling done at constant temperature only require one set of heat reservoirs.

**Carnot Theorem:** No engine operating between two heat reservoirs can be more efficient than a Carnot engine. All Carnot engines have the same efficiency given by

$$\eta = 1 - \frac{T_H}{T_C}$$

## 5.5 Entropy

**Clausius' Inequality:** For any cyclic process  $\oint \frac{dQ}{T} \geq 0$  where the equality is for a reversible process and the inequality for an irreversible one.

**Entropy:** We define another state variable entropy, such that an infinitesimal change in entropy is given by  $dS = \frac{dQ}{T}$ . For any irreversible path between two points in state space we can also define a reversible path, since these are variables of state this becomes a cyclic process and from Clausius' inequality we arrive at the Entropy form of the second law

$$\Delta S_{AB} \geq \int_A^B \frac{dQ}{T}$$

**Changes in Entropy:** The entropy change over any process can be split up into two reversible paths, one isobar and one isochor such that  $\Delta S_{AB} = \Delta S_{AA'} + \Delta S_{A'B} = \int_A^{A'} C_P \frac{dT}{T} + \int_{A'}^B C_V \frac{dT}{T}$ . Which for an ideal gas leads to

$$\Delta S_{ideal\ gas} = C_V \ln \left( \frac{T}{T_0} \right) + Nk_B \ln \left( \frac{V}{V_0} \right)$$

## 5.6 Functions of State Variables

**Fundamental Equation of Thermodynamics:** Using the equalities for infinitesimal changes in  $W$  and  $Q$  we can rewrite the first law as

$$dU = TdS - PdV$$

Since this is a link between infinitesimal changes in state variables for any irreversible process we can build a reversible process that starts and ends at the same points in state variable space. Thus we can calculate entropy changes over any process using  $dS = \frac{dU + PdV}{T}$ . Interpreting the FETD as the perfect differential of  $U(S, V)$  we see

$$\left( \frac{\partial U}{\partial V} \right)_S = -P \quad \left( \frac{\partial U}{\partial S} \right)_V = T$$

**Free Energy:** For a system in contact with a heat reservoir at  $T = T_0$  the first law becomes  $\Delta(U - T_0S) \leq W$ , define  $F \equiv U - TS$  as the free energy. Thus the work produced by a system is less than its drop in free energy, for a irreversible process or equal to the drop, in a reversible process.

**Gibb's Function:** The gibb's function has it's application in determining if a phase change is energetically viable. For a given set of state variables the phase with the smallest value for the Gibb's function will be the stable state. The gibb's function is given by  $G = U + PV - TS$ .

**Enthalpy:** The enthalpy is related to the heat exchange during a thermodynamic process and is given by  $H = U + PV$ .

**Maxwell Relations:** By examining infinitesimal changes in  $F$ ,  $G$  and  $H$  and by use of the FETD differential relations between state variables can be derived. As an example for  $F$  we first notice that expressing  $F$  as a total differential,

$$dF = dU - TdS - SdT \xrightarrow{FETD} dF = -PdV - SdT$$

thus  $S = -\left(\frac{\partial F}{\partial T}\right)_V$  and  $P = -\left(\frac{\partial F}{\partial V}\right)_T$ . As mixed, second partial derivatives are equal we arrive at

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$$

Similar relations can be derived for  $G$  and  $H$ .

## 5.7 Classical Statistical Physics

**Microstate:** The state of all the individual particles corresponding to a system

**Macrostate:** The state as described by state variables, there are many microstates that correspond to the same macrostate.

**Statistical Definition of Entropy:** The Boltzmann definition of entropy is given by

$$S = k_B \ln(\Omega)$$

where  $\Omega$  is the multiplicity of the system, the multiplicity for choosing  $M$  distinguishable objects from  $N$  is given by  $\Omega(M) = \frac{N!}{M!(N-M)!}$ .

**Microcanonical Ensemble:** All macrostates, denoted by  $\alpha$ , are equiprobable  $\therefore$  the microcanonical ensemble is defined by  $p_\alpha = \frac{1}{\Omega}$ . The system is constrained from losing particles or energy to its surroundings thus  $M = \sum_i^N r_i$ , where  $M = U/\epsilon_0$  and the energy of each particle is  $\epsilon = \epsilon_0 r$  for  $N$  distinguishable particles.

**Canonical Ensemble:** The system is now allowed to exchange energy with its surroundings but the total particle number is still constrained. The probability distribution for this ensemble is found to relate to the energy of the microstate in questions and to have the form of the Boltzmann distribution

$$p_\alpha = \frac{1}{Z} \exp(-\epsilon_\alpha/k_B T)$$

Where  $Z$  is the canonical partition function and is naively introduced so that the distribution is normalised and is thus given by  $Z = \sum_\alpha p_\alpha$ . The partition function can be used as a link to the macroscopic thermodynamic state variables. The internal energy of a system is given by

$$U = -\frac{\partial [\ln Z]}{\partial \beta} = k_B T^2 \frac{\partial [\ln Z]}{\partial T}$$

The statistical physics equivalent to the free energy is given by  $F = U - TS = -k_B T \ln(Z)$  where the usual thermodynamic relations can be used to find other state variables.

**Generalised Entropy:** The statistical physics generalised form of  $S$  is given by  $S = -k_B \sum_\alpha \ln(p_\alpha)$ .

**Density of states:** Examining momentum states in  $3D$  we see that each state in each dimension is spaced by  $\Delta p = \frac{h}{2L}$ , where  $L$  is the confinement in a given dimension. For the partition function, the summation over all momentum states becomes

$$Z_{tr} = \frac{1}{(\Delta p)^3} \sum_{n_x}^{\infty} \Delta p \sum_{n_y}^{\infty} \Delta p \sum_{n_z}^{\infty} \Delta p \exp[-\beta \epsilon(p)]$$

which can be taken to integrals and integrated in polar coordinates to yield

$$Z_{tr} = \frac{L^3}{h^3} 4\pi \int_0^{\infty} p^2 \exp[-\beta \epsilon(p)] dp$$

this integral depends on if the particles in question are non-relativistic,  $\epsilon(p) = \frac{p^2}{2m}$ , or ultra-relativistic,  $\epsilon = pc$ . The full partition function also contains a degeneracy factor  $g$  which relates to the non-internal degrees of freedom.

**Grand Canonical Ensemble:** The system is allowed to exchange both energy and particles with the surroundings, the probability of a given microstate is given by

$$p_{\alpha} = \frac{1}{\mathcal{Z}} \exp[-\beta(\epsilon_{\alpha} - \mu N_{\alpha})]$$

where  $\mu = -T \left( \frac{\partial S}{\partial N} \right)_V$ . Similarly to the Canonical ensemble we can draw a link to thermodynamics, this time by the Grand Potential Function

$$\Phi = -k_B T \ln(\mathcal{Z}) = U - TS - \mu N$$

## 5.8 Bose-Einstein and Fermi-Dirac Statistics

The Grand Partition Function is most simply expressed as a sum over all possible values of all occupation numbers

$$\mathcal{Z} = \left( \sum_{n_0} \sum_{n_1} \dots \right) \exp \left[ -\beta \sum_r n_r (\epsilon_r - \mu) \right]$$

this factorises out as a product of the individual state occupation sums  $\mathcal{Z} = \prod_r (\sum_{n_r} \exp[-\beta n_r (\epsilon_r - \mu)])$  where we express this as a product of individual single particle state partition functions  $\mathcal{Z} = \prod_r \mathcal{Z}_r$ . As possible occupancy numbers depend on what type of particles the system is made up of there are two separate distributions for occupancy. For bosons the occupancy sum runs from  $0 \rightarrow \infty$ , and for fermions, by the PEP, it runs from  $0 \rightarrow 1$ . The average occupancy can then be determined from these partition functions by  $\bar{n}_r = \sum_{n_r} n_r p_{r,n_r} = -\frac{1}{\beta} \frac{\partial \ln(\mathcal{Z}_r)}{\partial \epsilon_r}$  resulting in,

$$\bar{n}_{BE/FD} = \frac{1}{\exp[\beta(\epsilon_r - \mu)] \pm 1}$$

From these distributions we can see that if  $\beta(\epsilon_r - \mu) \gg 1$  the  $\pm 1$  in the denominator of the distributions becomes insignificant and thus these distributions both converge on the classical boltzmann distribution  $\bar{n}_B = \exp[-\beta(\epsilon_r - \mu)]$ . In this limit  $\bar{n}_r \ll 1$  therefore we expect the different properties of bosons and fermions to be less evident.  $\bar{n}_{BE}$  diverges for  $\epsilon \rightarrow \mu$  so we must impose

$$\mu < \epsilon_{min}$$

## 5.9 Black Body Radiation

Modelling the system as a photon gas, photons are spin 1 and are thus bosons, massless and thus always ultrarelativistic. They have a degeneracy of  $g = 2$  due to two orthogonal polarisation states. The chemical potential of a photon gas is  $\mu = 0$  as particles are not conserved. The occupancy distribution becomes

$$\bar{n}_{BE} \rightarrow \bar{n} = \frac{1}{\exp[\beta\epsilon_r] - 1}$$

We can find the internal energy of this system by  $U = \sum_r \bar{n}_r \epsilon_r$ , it is more insightful to change the integration variable to find the spectral energy density want in the form  $u = \frac{U}{V} = \int u_s(\omega) d\omega$  by evaluating the integral we see the energy density of the photon gas is given by

$$u = \frac{\pi^2 k_B^4}{15 \hbar^3 c^3} T^4$$

## 6 Atomic Physics

### 6.1 Spectral Lines

When electrons make transitions between energy states the energy deficit must be absorbed or emitted, usually as EM radiation. A transition between 2 levels with energy  $E_1$  and  $E_2$  emits or absorbs a photon of frequency  $\nu = \frac{E_2 - E_1}{h}$  any given atoms has a myriad of energy levels and allowed transitions. These emission 'spectra' from atoms are used to classify atoms by their unique fingerprint of available transitions. The emitted photons aren't at a single frequency but rather the emission 'lines' are broadened by various effects.

**Radiative Transitions:** A transition between 2 levels happens at a rate/probability given by Fermi's Golden Rule which states that the transition rate is proportional to the matrix element of the interaction with the initial and final states.

$$\frac{1}{\tau_{if}} \propto |\langle f | H' | i \rangle|^2$$

For an incident, oscillating electric field on an electric dipole the perturbation is given by  $H' = -\mathbf{P}_d \cdot \mathbf{E}$  which to first order gives the Electric Dipole

approximation  $H' \simeq e\mathbf{E}_0 \cdot \mathbf{r}$ . The rate is given by the product of the radial and angular integrals

$$e^2 |E_0|^2 \int_0^\infty R_{n_f l_f}^* r R_{n_i l_i} r^2 dr \int_0^{2\pi} \int_0^\pi Y_{n_f l_f}^* \hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_{\text{rad}} Y_{n_i l_i} \sin(\theta) d\theta d\varphi$$

The angular integral evaluates to 0 unless selection rules are obeyed. Since the parity of  $Y_{nl}$  is given by  $(-1)^l$  the angular integral must have a parity change between the states this gives the selection rule that  $\Delta L = \pm 1$ .

**Intrinsic Broadening:** Electrons in excited states have a finite lifetime governed by the Einstein coefficients such that  $\tau = \frac{1}{A_{21}}$ , where  $A_{21}$  is the coefficient for spontaneous decay of an energy level with no incident EM field. By the HUP anything with a finite confinement in time must also have a finite uncertainty in energy given by  $\Delta t \Delta E \sim \hbar$  thus  $\Delta \nu = \frac{A_{21}}{2\pi}$ . Thus transitions with shorter lifetimes are broader than comparatively long lived levels. The actual intensity profile is given by

$$I(\nu) = I_0 \frac{\left(\frac{\Delta \nu}{2}\right)^2}{(\nu - \nu_0)^2 + \left(\frac{\Delta \nu}{2}\right)^2}$$

In a real atom there are many levels and both the higher and lower levels are broadend, so the total broadening of the spectral line is given by

$$\Delta \nu_{21} = \frac{1}{2\pi\tau_2} + \frac{1}{2\pi\tau_1}$$

**Doppler Width:** This has a greater broadening effect than the quantum mechanical effect of the HUP. An effect due to the thermal velocity of the emitting particles, an emitter approaching an observer with velocity  $v_x$  sees a shifted wavelength of  $\frac{\Delta \lambda}{\lambda_0} = \frac{\Delta \nu}{\nu_0} = \beta_x$ . Using the Boltzman distribution to find the number of atoms at a given velocity,  $P_v(\nu)$ , the velocity distribution describes a gaussian about the thermal velocity, and thus the doppler broadening given by the FWHM of the  $P_v(\nu)$  can be shown to be

$$\frac{\Delta \nu_D}{\nu_0} = \frac{2}{c} \sqrt{\frac{2KT \ln(2)}{m}}$$

which can easily be linked to a change in  $\lambda$  by  $\frac{d\nu}{\nu_0} = -\frac{d\lambda}{\lambda_0}$

## 6.2 Hydrogen Atoms

The hydrogenic wavefunctions are valid for hydrogen and, with certain perturbations, for other 1 electron system. They can be split up into radial and angular parts as  $\psi_{tot} = R_{nl}(r) Y_m^l(\theta, \varphi)$ . The 3D radial distribution is given by  $\int_0^\infty 4\pi |\chi_{nl}|^2 dr$  where  $\chi_{nl} = r R_{nl}$ . For a hydrogen atom the principle quantum

number  $n$  determines the energy of the unperturbed state. The angular momentum  $l$  is under the constraint that  $n > l$ . The spectroscopic notation for a state of  $l = 0, 1, 2, 3, 4, \dots$  is given by  $s, p, d, f, g, \dots$  continuing alphabetically as  $l$  gets larger. The projection of  $l$  onto the  $z$  axis is given by the quantum number  $m_l$  which can take values under the constraint  $|m_l| < l$ . For the unperturbed hydrogenic wavefunction the energy is uniquely determined by  $n$  and thus there is a  $\sum_{i < n} g_s [2i + 1]$  degeneracy, where  $g_s = 2$  for the spin degeneracy. Various perturbations lift this degeneracy, Spin-orbit interactions to a  $2j + 1$  degeneracy in  $m_j$  where  $j$  is the total angular momentum  $j = l + s$  and the Zeeman effect somewhat lifts this  $m_j$  degeneracy.

### 6.3 Perturbation Theory

If a small change in the hamiltonian results in a small change in the observed energies and  $\psi$ 's perturbation theory can be used. For  $H_{total} = H_0 + H'$ , where  $H'$  is a small 'perturbation' to the unperturbed hamiltonian  $H_0$  the first order change in energy is given by

$$E_i^{(1)} = \int u_i^{*(0)} H' u_i^{(0)} d\tau$$

where  $u_i^{(0)}$  is the unperturbed eigenfunction of state  $i$  and  $E_i^{total} = E_i^{(0)} + E_i^{(1)}$ . The first order perturbation to the wavefunction is given by

$$u_i^{(1)} = \sum_{k \neq i} \frac{\int u_k^{(0)} H' u_i^{(0)} d\tau}{E_i^{(0)} - E_k^{(0)}} u_k^{(0)}$$

where  $u_i^{total} = u_i^{(0)} + u_i^{(1)}$ .

**Relativistic Mass Variation:** As the electrons gain momentum their motion becomes relativistic and the non-relativistic approximation of  $KE = \frac{p^2}{2m}$  becomes invalid. The first order correction is given by

$$H'_{mv} = -\frac{1}{8} \frac{P^4}{m_e^3 c^2}$$

**Spin Orbit Interaction:** The interaction between the magnetic moment generated by the electron's intrinsic spin and its motion about the nucleus. The energy change is given by  $H'_{SO} = -\boldsymbol{\mu} \cdot \mathbf{B}$ , when calculating for an electron under the influence of a nuclear potential becomes

$$H'_{SO} = \frac{1}{m_e^2 c^2} \frac{1}{r^3} \frac{Ze^2}{4\pi\epsilon_0} [\mathbf{L} \cdot \mathbf{S}]$$

Where  $\mathbf{l} \cdot \mathbf{s}$  is found by introducing  $j$  as a new quantum number,  $j = |l + s|, l + s - 1, \dots, |l - s|$ . Since  $\mathbf{J}$  is an angular momentum generator we know that  $\mathbf{J}^2 \Psi = j(j + 1) \Psi$  so  $\mathbf{J}^2 = [\mathbf{L} + \mathbf{S}]^2$  thus  $\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} [\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2]$ . The selection rule between levels is given as  $\Delta J = 0, \pm 1$  but not  $J = 0 \rightarrow 0$ .

**Stark Effect:** In an external electric field,  $\varepsilon$ , the electron orbitals about an atom will be distorted, this effect can be described by the perturbation  $H'_\varepsilon = -\mathbf{d} \cdot \varepsilon$ , so for an electric field in the  $\hat{z}$  direction the perturbation is given by

$$H'_\varepsilon = -e\varepsilon_z z$$

## 6.4 Zeeman Effect

The Zeeman effect is the observed splitting of electronic levels, lifting the degeneracy on the magnetic quantum number, in the presence of an external magnetic field. The perturbation is given by the magnetic interaction between a magnetic moment and the applied  $\mathbf{B}$  field. Considering spin the perturbation becomes  $H'_{mag} = -\boldsymbol{\mu} \cdot \mathbf{B} = 2\frac{\mu_B}{\hbar} \mathbf{S} \cdot \mathbf{B}$ . For a magnetic field only in the  $\hat{z}$  direction we have

$$\Delta E = 2m_s \mu_B B_z$$

as a result the degeneracy in  $m_{S_z}$  is lifted. The electron's orbit also produces a magnetic moment where the perturbation is given by  $H'_{mag} = \frac{\mu_B}{\hbar} \mathbf{L} \cdot \mathbf{B}$ . Again considering a field in the  $\hat{z}$  direction

$$\Delta E = m_l \mu_B B_z$$

as a result  $m_{l_z}$  is no longer a degenerate quantum number. The total magnetic interactions for an electron is thus the addition of these two effects and the Spin-Orbit interaction. There are two distinct regimes depending on the strength of the external field.

**Strong External Field:** We ignore  $H_{SO}$ , thus  $j$  is not a good quantum number, as the  $\mathbf{L}$  and  $\mathbf{S}$  do not interact, and the Zeeman effect affects the intrinsic and orbital magnetic moments individually. For a  $2p$   $e^-$  which has  $l = 1, s = \frac{1}{2}$ , there are 6 states for all possible combinations of  $m_l = \pm 1, 0$  and  $m_s = \pm \frac{1}{2}$ .

**Weak External Field:**  $j$  is still a good quantum number as  $\Delta E_{SO} \gg \Delta E_{zeeman}$ , thus can use  $m_j$  to give the Zeeman shift as  $\Delta E = g_J \mu_B m_j B_z$ .

## 6.5 Molecules

For single electron molecules can use LCAO (Linear Combination of Atomic Orbitals) to create single electron molecular wavefunctions. By using the hydrogen wavefunctions can construct two superpositional states for the molecular wavefunctions



$$\Psi_g(\mathbf{r}, R) = \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_a) + \psi(\mathbf{r}_b)] \quad \text{gerade} \equiv \text{even}$$

$$\Psi_u(\mathbf{r}, R) = \frac{1}{\sqrt{2}} [\psi_{1s}(\mathbf{r}_a) - \psi(\mathbf{r}_b)] \quad \text{ungerade} \equiv \text{odd}$$

where  $\mathbf{r}_a, \mathbf{r}_b$  are the distances of the electrons from nucleus  $A, B$  respectively. Where  $\Psi_g$  corresponds to a bonding state where the electron has a finite probability of being between the two nuclei,  $\Psi_u$  corresponds to an anti-bonding state where the electron has a low probability of being between the nuclei and a zero probability directly at the mid-point between the two. In molecules  $\lambda = |m_l|$  is an important quantum number where states with  $\lambda = 0, 1, 2, 3$  are labelled  $\sigma, \pi, \delta, \phi$  states respectively.

**Vibrational Modes:** The form of the potential for intermolecular bonds can be approximated by the morse potential  $V(x) = D_{eq}(1 - \exp[-ax])^2$ . Expanding the exponential to first order gives a SHO potentials. Modelling vibrations as SHO the energy is given by  $E_v = \hbar\omega_0(v + \frac{1}{2})$ , where  $v$  is the vibrational quantum number  $\Delta\varepsilon_v = \frac{\Delta E_v}{hc} = \bar{\omega}_{osc}$  where  $\bar{\omega}_{osc} = \frac{\omega_0}{2\pi c}$ . This is a valid approximation for heteronuclear molecules.

For a more accurate model the morse potential gives energies of  $\varepsilon_v = \bar{\omega}_e(v + \frac{1}{2}) - x_e\bar{\omega}_e(v + \frac{1}{2})^2$ . This can be expressed in a similar form to SHO but with a  $v$  dependant frequency,

$$\varepsilon_v = \bar{\omega}_e \left[ 1 - x_e \left( v + \frac{1}{2} \right) \right] \left( v + \frac{1}{2} \right)$$

The selection rules state  $\Delta v = \pm 1, \pm 2, \pm 3 \dots$  where  $\pm 1$  is called the fundamental transition, and higher are called the  $n^{th}$  overtones. The fundamental transition is by far the most important. At room temperature heteronuclear molecules undergo IR vibrational transitions, homonuclear molecules do not absorb.

**Rotational States:** Classically rotational energy is given by  $E = \frac{L^2}{2I}$ , where  $I = \mu R_0^2$ . The quantum mechanical operator is thus given by  $H_{rot} = \frac{L^2}{2I}$ , calling the rotational quantum number  $J$  we see  $\langle H_{rot} \rangle = \frac{\hbar^2 J(J+1)}{2I}$ .

$$\varepsilon_J = BJ(J+1)$$

Where  $B = \frac{\hbar^2}{2hcI}$ , can use  $B$  to find  $I$  and thus  $R_0$ . The selection rule for these transitions is given by  $\Delta J = \pm 1$ . Pure rotational spectra are not seen in homonuclear molecules.

**Rotation Coupled Spectra:** For a fundamental vibrational transition  $V = 0 \rightarrow 1$ ,  $\Delta\varepsilon = \Delta\varepsilon_v - [B^u J^u (J^u + 1) - B^l J^l (J^l + 1)]$ .  $\Delta J = J^u - J^l$  splits the total transition into two branches, the  $P - \Delta J = -1$  and the  $R - \Delta J = +1$  branch.

Rotational transitions also couple to electronic transitions where the selection rules become  $\Delta J = 0, \pm 1$  but not  $J = 0 \rightarrow 0$ .

## 7 Electrons in Solids/Solid State Physics

### 7.1 Free Electron Model

**Density of States:** The FEA gives a  $k$  quantisation condition  $k_n = \frac{n\pi}{L}$  so the size of a  $k$  state in  $d$  dimensional space is  $\Delta k = \left(\frac{\pi}{L}\right)^d$ . Find the number of  $e^-$  states which can fit between  $k \rightarrow k + dk$  this gives  $D(k) dk$  which can be changed into the density of states at a given energy by a change of variables  $D(k) dk = \underbrace{D(E)}_{D(E)} \frac{dk}{dE} dE$ . This method yields to following results for 1,2,3 dimensional Density of States

$$D_{1d}(E) = \sqrt{\frac{8mL^2}{h^2}} \frac{1}{\sqrt{E}}$$

$$D_{2d}(E) = \frac{4\pi mL^2}{h^2}$$

$$D_{3d}(E) = \frac{\pi}{2} \left(\frac{8mL^2}{h^2}\right)^{3/2} \sqrt{E}$$

Can use these to determine the  $\varepsilon_f$ , The Fermi Energy - the energy of the highest occupied state/lowest unoccupied state at  $0K$ , and the internal energy at  $0K$ ,  $U_0$  by

$$N = \int_0^{\varepsilon_f} D(E) dE \quad U_0 = \int_0^{\varepsilon_f} ED(E) dE$$

**Fermi Wavevector:** The wavevector of an free electron with Energy equal to the Fermi Energy  $k_f = \frac{\sqrt{2m\varepsilon_f}}{\hbar}$

**Bloch Theorem:** The energy states of a  $1e^-$  in a periodic potential can be chosen to have the form of a plane wave modulated by a function with the periodicity of the lattice.

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})$$

where  $u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{R}) \Rightarrow |\psi_k(\mathbf{r})|^2 = |\psi(\mathbf{r} + \mathbf{R})|^2$ . The probability of the particle particles position is equally distributed in any cell.

### Formation of Bands:

- The Kronig-Penny model yields a band structure by enforcing boundary conditions on Bloch electrons in a periodic potential defined by cells of no potential with delta potentials bounding each cell.
- by the LCAO(Linear Combination of Atomic Orbitals) we see that bringing two atoms close to each other results in energy states being split into two the so called 'Bonding' and 'Anti-Bonding' states, extending this to  $N$  atoms in a solid we can qualitatively see a bands of states forming.

What type of solid depends on the location of the Fermi level relative to this band structure.

- Metal -  $\epsilon_f$  is in a band - conduction states just above valence states.
- S/C -  $\epsilon_f$  lies in a gap between bands but  $\epsilon_{gap}$  is small
- Insulator - same as an S/C but  $\epsilon_{gap}$  is large

**Laue Condition:** This is equivalent to the Bragg condition but in  $\mathbf{k}$  space

$$\mathbf{G} = \mathbf{k}' - \mathbf{k}$$

where  $\mathbf{k}, \mathbf{k}'$  are the incident and scattered  $\mathbf{k}$ 's respectively.  $\Rightarrow \Delta P = -\hbar\mathbf{G}$  momentum transfered to the lattice.

**Brillouin Zones:** The locus of all points which obey the Laue condition and thus can be scattered by the crystal. The  $n^{th}$  BZ is the locus of all points which can 'reach' the origin by crossing  $(n - 1)$  Bragg Planes/BZ surfaces. At BZ surfaces electrons scatter - cannot travel through the crystal.

### Observations of K-P Dispersion:

1.  $E(k)$  is discontinuous at  $ka = n\pi$
2. Near  $k = 0$ ,  $E = 0$  is not allowed
3. At zone boundaries  $E(k)$  has zero slope

## 7.2 Carriers

**Electrons and Holes:** When electrons are excited across a band gap they leave behind an empty state, it is valid to model this empty state as a particle in itself called a hole. A is a 'not electron' and thus has  $m_h = -m_e$ ,  $q_h = +e$ . Particles which exhibit the Bloch wavefunction can be modelled as travelling through the solid as a free particle but with a modified and  $k$  dependant mass, called the effective mass. From the group velocity

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk}$$

$$F = m^* \frac{dv_g}{dt} = \hbar^2 \underbrace{\left( \frac{d^2 E}{dk^2} \right)^{-1}}_{m^*} \frac{dv_g}{dt}$$

At BZ zone boundaries as  $E(k)$  has zero slope  $m^* = \infty$ , carriers cannot travel through the crystal with these values of  $k$  and are thus scattered into free states.

**Carrier Density:** The effective Density of States near the band edges is given by

$$N_{C/V} = 2 \left( \frac{m_{n/p}^* k_B T}{2\pi\hbar^2} \right)^{3/2}$$

And the carrier density at the band edges is given by

$$n/p = N_{C/V} \exp \left( \frac{\mp [\epsilon_{C/V} - \epsilon_f]}{k_B T} \right) \quad (1)$$

the product  $np$  is found to be constant for a given  $\epsilon_f$

$$np = N_C N_V \exp \left( \frac{-\epsilon_g}{k_B T} \right)$$

**Intrinsic S/C:**  $n_i = p_i, \quad np = n_i^2 = p_i^2$

**Extrinsic S/C:** In General the bulk S/C is neutral so  $n_i + N_A = p_i + N_d$ . Therefore for an n-type  $n = p + N_d, \quad n \gg p$  and vice versa for p-type. In an n-type  $\epsilon_f$  is closer to  $\epsilon_c$  and vice versa for p-type.

**Temperature Dependence:**

- Intrinsic region - high  $T$  - intrinsic carriers dominate
- Saturation region - dopants are fully ionised - device operating temperature
- Freeze-out region - extrinsic carriers frozen back to dopant atoms.

### 7.3 Semiconductor Transitions

- Phonons - Horizontal  $\sim 50$  phonons to a vertical transition of  $\epsilon_g$
- Photons - Vertical  $\sim 1000$  Photons to a horizontal transition of a BZ width

### Direct Gap Semiconductors:

- Vertical transitions possible between  $CB_{min}$  and  $VB_{max}$  at 300K
- emit light
- rapid rise in absorption at  $\epsilon_g$

### Indirect Gap Semiconductors:

- Vertical transitions not possible between  $CB_{min}$  and  $VB_{max}$
- transitions require both photons and phonons to be emitted, so have a much lower probability
- don't emit light
- slow rise in absorption at  $\epsilon_g$

## 7.4 pn Junctions

When p-type and n-type are brought together, an equilibrium state is found by competition between majority carrier diffusion across the junction and an opposing  $\mathbf{E}$  which is set up as diffusion exposes the charged dopant atoms. At equilibrium junction has a built in potential  $V_0$ ,  $\epsilon_f$  must also be the same everywhere at equilibrium.

**Depletion Region:** Region depleted of carriers around the junction, width  $W = x_{n0} + x_{p0}$  which are the respective depleted regions on the  $n$  and  $p$  sides. Charge due to exposed dopant atoms on each side given by  $\rho_{n/p} = \pm qN_{d/a}$ . This charge creates an electric field

$$\frac{dE(x)}{dx} = \frac{\rho(x)}{\epsilon} \Rightarrow E_{n/p} = \pm \frac{e}{\epsilon} N_d x + E_0$$

$E = 0$  at the edge of the depletion region  $\Rightarrow E_0 = -\frac{e}{\epsilon} N_d x_{n0} = -\frac{e}{\epsilon} N_a x_{p0}$ .  
Can use the field to find the potential by  $V(x) = \int \mathbf{E} \cdot dx$ .

### Junction Under Bias:

- Forward bias  $V$ ,  $\epsilon_f$  split between n and p side by  $eV$ , barrier height reduced to  $e(V_0 - V)$
- If a forward bias of  $V = V_0 \rightarrow$  called flat band
- Reverse bias  $V = -V_r$ ,  $\epsilon_f$  split by  $-eV_r$ , barrier height increased to  $e(V + V_r)$ .  $W$  increased.

### Shockley Ideal Diode Equation:

$$I = I_0 \left[ \exp \left( \frac{eV}{nk_B T} \right) - 1 \right]$$

where  $n$  is the ideality factor which varies between 1 & 2. Diode follows this equation between  $V = 0$  and  $V = V_0$  in forward bias, and in reverse bias. For  $V > V_0$  the equation is no longer valid, and the diode is said to be in the breakdown region.

## 8 Particle And Nuclear Physics

### 8.1 Matter

**Generations:** In the standard model there are 3 generations of matter particles, which leads to 6 quarks and 6 leptons. Particles in different generations have the same charge but greater masses for the higher generations, in all other ways they are identical. All matter particles have  $S = \frac{1}{2}$  and are thus fermions.

**Antimatter:** for every matter particle there is also an antimatter particle which is identical but has opposite charge. The antimatter particle is denoted with a  $\bar{q}$ . So the 'anti-electron' or positron has  $+e$  charge, it can be denoted  $\bar{e}$  but is often given the symbol  $e^+$ .

**Quarks:** The two sets are  $u, c, t$  which have  $+\frac{2}{3}e$  charge and  $d, s, b$  which have  $-\frac{1}{3}e$ . Quarks cannot exist alone, they can form into two distinct types of composite particles collectively called hadrons. Mesons consist of a  $q\bar{q}$  pair and baryons a  $qqq$  or  $\bar{q}\bar{q}\bar{q}$  triplet.

### 8.2 Nuclear Stability

**Liquid Drop Model:** Combination of a repulsive part to keep nucleons at a distance from each other and an attractive force which has a short range. For nuclear stability we want the highest binding energy. The nucleons on the edge of the nucleus have less bonds, and thus reduce the binding energy relative to a deeper within the nucleus.

$$BE = a_v A - a_s A^{2/3}$$

Where  $A$  is the nucleon number, and  $a_v, a_s$  are determined experimentally.

**Semi Empirical Mass Formula:** The liquid drop reproduces the gross features of  $BE$  but it has no  $N, Z$  dependence and doesn't take QM effects into account. There are 3 extra terms to include.

The Coulomb term is the electric potential energy which would be required to bring the nucleus together from the point of view of 1 proton -  $\Delta BE = -a_c \frac{z(z-1)}{A^{1/3}}$ .

The  $p$ 's and  $n$ 's must fit into quantum energy levels, each has it's own set of energy levels, by the PEP they must fill up to higher energies. If there are more neutrons than protons, for the same  $A$  the nucleus would have a higher binding energy if some of those neutrons were protons thus the asymmetry is given by  $\Delta BE = -a_a \frac{(A-2Z)^2}{A}$ , note  $(A - 2Z) = (N - Z)$ .

Again treating the  $p$ 's and  $n$ 's separately, the total binding energy will be more if there's an even number of particles. By the PEP they pair up in the same spatial states but with opposing spin states, this results in a large  $\psi$  overlap and thus a larger binding energy. The correction is given by  $\Delta BE = \frac{a_p}{A^{1/2}}$  where  $a_p > 0$  if both  $N, Z$  are even,  $a_p = 0$  if one is even and the other odd, and  $a_p < 0$  if both are odd.

The total SEMF is given by

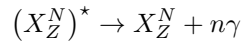
$$BE = a_v A - a_s A^{2/3} - a_c \frac{z(z-1)}{A^{1/3}} - a_a \frac{(A-2Z)^2}{A} + a_p \frac{1}{A^{1/2}}$$

**Shell Model:** The SEMF is good for smooth trends in  $BE$  but some values of  $N, Z$  are found to have particularly high  $BE$ , these are called the magic numbers. For  $N$  or  $Z$  or both = 2, 8, 20, 28, 50, 82, 126... it is observed that these nuclei are particularly stable. These magic numbers correspond to a filled energy level, analogous to the inert properties of the noble gases. The form of  $V(r)$  required to solve the TISE to find what number corresponds to a filled level is complicated.

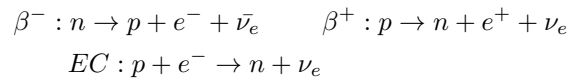
Spin orbit coupling splits the  $2j + 1$  degeneracy in  $j = l \pm \frac{1}{2}$  states giving  $2l + 2$  states for  $j = l + \frac{1}{2}$  and  $2l$  for  $j = l - \frac{1}{2}$ . These have different energies as  $\Delta BE \propto \mathbf{l} \cdot \mathbf{s}$ , so for  $j = l + \frac{1}{2}$ ,  $\Delta BE \propto l$ , and for  $j = l - \frac{1}{2}$   $\Delta BE = -(l + 1)$ . This predicts the experimentally determined magic numbers.

### 8.3 Decays

**Gamma Decay:** Due to EM forces and thus cannot change quark flavor, only for energy level decay from nuclear excited state to ground state.



**Beta Decay:** As this is due to the weak force quark flavor can be changed and thus there are more possible decays. There are 3 process' by which beta decay can make a nucleus more stable.



For odd  $A$  there is a single value with the minimum mass (maximum  $BE$ ), a given unstable nucleus will decay towards this with  $\beta^-$ ,  $\beta^+$  and  $EC$ . If the change in mass is too small then there are some decays which lower  $Z$  which can only be achieved by  $EC$  and not by  $\beta^+$ . For even  $A$  then a loss of a  $p/n$  and thus a gain of a  $n/p$  will swap between  $N, Z$  being odd and even for each decay thus there are two curves one for even  $Z$  and one for odd  $Z$ . The lowest mass isotope on the odd  $Z$  curve can have multiple decay paths available to it by having more than 1 isotope with less mass than it on the even  $Z$  curve.  $N, Z$  changes for the decays are

$$\begin{aligned}\beta^- : X_Z^N &\rightarrow X_{Z+1}^{N-1} + e^- + \bar{\nu}_e \\ \beta^+ : X_Z^N &\rightarrow X_{Z-1}^{N+1} + e^+ + \nu_e \\ EC : X_Z^N + e^- &\rightarrow X_{Z-1}^{N+1} + \nu_e\end{aligned}$$

**Alpha Decay:** The emission of an alpha particle from the nucleus to increase stability. To be possible  $\Delta m_{nuc} > \Delta m_\alpha$  this is at about  $A \sim 150$ , for a decent  $\Delta m$  require  $A > 200$ . As  $\Delta A = 4$  likely to be a decay chain until stability, as  $A$  decreases ratio of  $\frac{N}{Z} \rightarrow 1$  for stability so decay chains often also include  $\beta^-$  emission. Consider the alpha particle as a separate entity within the nucleus and form a potential out of the coulomb repulsion and the 'Saxon-Woods' residual strong force attraction. The particle has to tunnel through this potential to escape the nucleus, we can derive a formula which gives good agreement with data as to decay times.  $N, Z$  changes for the decay are

$$X_Z^N \rightarrow X_{Z-2}^{N-2} + \alpha$$

## 8.4 Nuclear Reactions

**Fission:** For a fission reaction to be possible it is required that  $Q = BE_{products} - BE_{reactant} > 0$ .  $Q$  can be calculated from the SEMF. From the SEMF we see that for fission to be possible  $\frac{Z^2}{A} > 0.7 \frac{a_s}{a_c} \sim 18$ . During a fission reaction the nucleus will deform to eject the products, this deformation changes the  $BE$  so for a nucleus to undergo spontaneous fission the deformation must increase the  $BE$ . Changing from a sphere to an ellipsoid decreases the binding energy associated with the surface 'tension' and increases the Coulomb term. It can be derived that for a nucleus to undergo spontaneous fission  $\frac{Z^2}{A} > \frac{2a_s}{a_c} \sim 51$ . Nuclei for which this is true are very unstable and decay with the speed of a strong force interaction, nuclei with  $51 > \frac{Z^2}{A} > 18$ , fission is possible but the nucleus must be given energy. This can be given by  $\gamma$ 's but the cross section for these reactions is very small, it can also be done by injecting extra nucleons. Neutrons are the most suited as there is no Coulomb barrier for them to overcome.

**Chain Reactions:** Fission reactions often produce extra  $n$ 's, these can be absorbed by other nuclei to speed up their fission reactions. the parameter  $m$



is used to characterise a possible chain reaction,  $m$  is the average number of neutrons produced per reactions taking into account unwanted reactions and neutrons escaping the reactive material without interacting. for  $m > 1$  the total reaction rate will increase - super-critical,  $m = 1$  the reaction rate will stay constant - critical,  $m < 1$  the reaction rate will decrease - sub-critical.

**Fusion:** Similar to  $\alpha$  decay 'in reverse', for reactions bar addition of a neutron, reactants both have a net positive charge and thus there is a Coulomb barrier to overcome. This barrier can be overcome either by tunnelling or by the reactants having enough  $KE$  to overcome the potential. The product is a single nucleus in an excited state, this decays to the product we see from a fusion reaction. The energy release associated with the change in binding energy is carried away by the products or  $\gamma$ 's.

## 9 Probability And Statistics

### 9.1 Properties of distributions

**Normalisation:** A distribution is normalised if  $\sum_i P_i = 1$  for discrete  $P_i$  or  $\int p(x) dx = 1$  for continuous  $p(x)$ .

**Expectation Value:** For a function on  $x$ ,  $f(x)$  the expectation value of that function under a distribution  $P_i$  is given by  $\langle f(x) \rangle = \sum_i f(x_i) P_i$  for the discrete case and  $\langle f(x) \rangle = \int f(x) p(x) dx$ . Thus the mean  $\langle x \rangle = \sum_i x_i P_i$  or  $\int xp(x) dx$ .

**Variance:**  $\text{var } x = \langle (x - \mu)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$ , the standard deviation  $\sigma = \sqrt{\text{var } x}$

**Central Limit Theorem:** For a large  $N$ , the sum  $X = \sum_{j=1}^N x_j$  is normally distributed with  $\langle X \rangle = N \langle x \rangle$  and  $\text{var } X = N \text{var } x$ .

### 9.2 Binomial Distribution

$$P(r|N, P) = \frac{N!}{r!(N-r)!} P^r (1-P)^{N-r}$$

**Expectation Value**

$$\begin{aligned} E(x) &= \sum_{x=0}^n x P(x) = \sum_{x=1}^n x \frac{n!}{x!(n-x)!} P^x (1-P)^{n-x} \\ &= nP \sum_{x=1}^n x \frac{(n-1)!}{(x-1)![(n-1)-(x-1)!]} P^{x-1} (1-P)^{(n-1)-(x-1)} \end{aligned}$$

By the normalisation of the binomial distribution

$$=nP \sum_{x=0}^n \frac{n!}{x!(n-x)!} P^x (1-P)^{n-x}$$

$$E(x) = nP$$

### Variance

$$\sigma^2 = E(x^2) - E(x)^2 = E(x(x-1) + x) - E(x)^2$$

By effectively carrying out the process above twice we arrive at

$$=nP \sum_{x=0}^n \frac{n!}{x!(n-x)!} P^x (1-P)^{n-x}$$

$$E(x) = nP$$

$$E(x(x-1)) = \sum_{x=0}^n x(x-1) P(n) = n(n-1)$$

$$\sigma^2 = n(n-1)P^2 + nP - (nP)^2$$

$$\sigma^2 = nP(1-P)$$

### 9.3 Poisson Distribution

$$P(n) = \frac{(\lambda t)^n}{n!} e^{-\lambda t}$$

#### Expectation Value

$$x \frac{d}{dx} e^x = x e^x = \sum_k k \frac{x^k}{k!}$$

$$E(n) = \sum_{n=0}^{\infty} n \frac{\lambda^n}{n!} e^{-\lambda} = \lambda e^{-\lambda} e^{\lambda}$$

$$E(n) = \lambda$$

#### Variance

$$\begin{aligned}
x^2 \frac{d}{dx} e^x &= x^2 e^x = \sum_k k(k-1) \frac{x^k}{k!} \\
\sum_k k^2 \frac{x^k}{k!} &= x^2 e^x + x e^x \\
E(n^2) &= \sum_{n=0}^{\infty} n^2 \frac{\lambda^n}{n!} e^{-\lambda} = \lambda^2 + \lambda \\
\sigma^2 &= \lambda
\end{aligned}$$

## 9.4 Gaussian Distribution

$$G(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[ -\frac{1}{2} \left( \frac{x - \bar{x}}{\sigma} \right)^2 \right]$$

**Expectation Value**  
Standard Integral

$$\begin{aligned}
E(G(x)) &= \int_{-\infty}^{\infty} x e^{-a(x-b)^2} dx = b \sqrt{\frac{\pi}{a}} \\
&= \int_{-\infty}^{\infty} x \frac{1}{\sqrt{2\pi}\sigma} \exp \left[ -\frac{1}{2} \left( \frac{x - \bar{x}}{\sigma} \right)^2 \right] dx = \frac{1}{\sqrt{2\pi}\sigma} \bar{x} \sqrt{2\pi}\sigma^2 = \bar{x}
\end{aligned}$$

**Variance**

$$Var(G(x)) = \sigma^2$$

**Multiplication of Gaussian**

$$\begin{aligned}
G^*(x) &= \prod_{i=1}^N G(x) = \prod_{i=1}^N \frac{1}{\sqrt{2\pi}\sigma} \exp \left[ -\frac{1}{2} \frac{(x - \hat{x}_i)^2}{\sigma^2} \right] \\
&= G_0 \exp \left[ -\frac{1}{2} \sum_{i=0}^N \frac{(x - \hat{x}_i)^2}{\sigma^2} \right] = G_0 \exp \left[ -\frac{1}{2\sigma^2} \left( Nx^2 - 2 \sum_{i=0}^N x \hat{x}_i + \sum_{i=0}^N \hat{x}_i^2 \right) \right] \\
&= G_0 \exp \left[ -\frac{N}{2\sigma^2} \left( x^2 - 2x\bar{x} + \frac{1}{N} \sum_{i=0}^N \hat{x}_i^2 \right) \right]
\end{aligned}$$

Taking  $\sum \hat{x} = N\bar{x}$  as the mean of the separate gaussian parameters and absorbing everything not x dependent into the constant

$$G^*(x) = G_0 \exp \left[ -\frac{1}{2} \frac{(x - \bar{x})^2}{\sigma^2/N} \right]$$

The standard deviation of this new Gaussian is  $\Sigma = \frac{\sigma}{\sqrt{N}}$ .

## 9.5 Propagation of Errors

If we have a function,  $y(x)$ , where we know  $x = \bar{x} + \sigma_x$ , what is error on  $y$ ? By Taylor expanding,

$$E(y) = E \left[ y(\bar{x}) + \left. \frac{\partial y}{\partial x} \right|_{x=\bar{x}} (x - \bar{x}) \right] = y(\bar{x}) + \left. \frac{\partial y}{\partial x} \right|_{x=\bar{x}} E(x - \bar{x}) = y(\bar{x})$$

$$Var(y) = E \left( [y(x) - E(y(x))]^2 \right) = E \left( \left[ \left. \frac{\partial y}{\partial x} \right|_{x=\bar{x}} (x - \bar{x}) \right]^2 \right)$$

$$\sigma_y^2 \simeq \left[ \left. \frac{\partial y}{\partial x} \right|_{x=\bar{x}} \right]^2 E \left( [x - \bar{x}]^2 \right) = \left[ \left. \frac{\partial y}{\partial x} \right|_{x=\bar{x}} \right]^2 \sigma_x^2$$

In general

$$\underline{x} = \{x_1, x_2, \dots, x_n\}, y(\underline{x})$$

$$\sigma_y^2 = \sum_i \sigma_{x_i}^2 \left[ \left. \frac{\partial y}{\partial x_i} \right|_{x=\bar{x}} \right]^2$$

### Linear

$$y = ax_1 + bx_2$$

$$\sigma_y = \sqrt{\sigma_{x_1}^2 + \sigma_{x_2}^2}$$

### Product, Ratio

$$y = x_1 \cdot x_2$$

$$y = \frac{x_1}{x_2}$$

$$\frac{\sigma_y}{y} = \sqrt{\frac{\sigma_{x_1}^2}{x_1^2} + \frac{\sigma_{x_2}^2}{x_2^2}}$$