0. Introduction

Recommended textbooks: Phillips, A. C. "Introduction to Quantum Mechanics" (Whiley) French, A. P., & Taylor, E. F, "An Introduction to Quantum Physics" (Thomas Nelson)

Other books: Rae, A.I.M. "Quantum Mechanics" (IoP) Gasiorogioz, S. "Quantum Mechanics" (Whiley)

1. Photons, Particles and Waves

1.1 Problems with Waves

Classically, EM radiation was well understood as a wave phenomenon, via Maxwell's theory. Problems arose around 1890 – 1920.

- i) The absence of the aether (Michelson-Morley). How can there be a wave if there's nothing to oscillate?)
- ii) Black body radiation \rightarrow Classical theory predicted intensity rising to infinity as the wavelength went to zero. (Ultraviolet catastrophe). Max Planck hypothesised that EM oscillators (e.g. electrons) with frequency v have energy nhv where n = integer and h = constant.

Average power radiated per unit area for wavelengths from λ to $\lambda + d\lambda$:

$$I(\lambda)d\lambda = \frac{2\pi hc^2}{\lambda^5 \left(e^{\frac{hc}{\lambda kT}} - 1\right)}d\lambda \quad (1)$$

(Planck Radiation Law)

The modern value for h is $h = 6.63 \times 10^{-34} Js$ and $\hbar = \frac{h}{2\pi} = 1.06 \times 10^{-34} Js$

More useful units of energy are eV, KeV, MeV etc.

Also the combination *hc* often crops up. $hc = 1.24 \times 10^{-6} eVm = 1.24 \times 10^{4} eVAngstrom$

1 Angstrom = $10^{-10} m = 0.1 nm$

 $\hbar c = 1.97 \times 10^{-7} eVm = 1980 eVA$

We will tend to use angular frequency ω rather than v. Then $E = hv = \hbar \omega$ (2) is the energy associated with frequency ω .

iii) Photoelectric Effect – the maximum KE of electrons emitted from a metal surface illuminated with radiation of frequency v is:

 $K_{\max} = hv - w - (3)$

where w is the property of the metal (the work function) This was evidence for photons – quanta of EM radiation.

- iv) Atomic structure and Specta Bohr's description used a mixture of classical and quantum ideas (the "old quantum theory"). This was very successful for a hydrogen atom.
- v) Compton effect photons scatter elastically from loosely bound electrons. A real demonstration of photons as particles.



Conservation of momentum and energy

$$P = P' + Pe$$

E = E' + EeFor any particle, including photons:

$$E^2 = p^2 c^2 + m^2 c^4 - (4)$$

For a photon, m=0 so E = pc. i.e. hv = pc So the momentum of a photon:

$$p = \frac{hv}{c} = \frac{h}{\lambda} - (5)$$

The scattered photon has p' < p and $\lambda' > \lambda$.

It turns out that
$$\lambda' - \lambda = \Delta \lambda = \frac{h}{m_e c} (1 - \cos \theta) - (6)$$

The quantity $\lambda_e = \frac{h}{m_e c} = 2.43 \times 10^{-12} m$ is the Compton wavelength of the electron.

1.2 Particles, Waves and Uncertainty

In 1923, de Broglie postulated that matter particles (e.g. electrons) could have wavelength properties. The de Broglie wavelength is:

$$\lambda = \frac{h}{p} - (8)$$

For non-relativistic particles; p = mv

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

Therefore $p = \sqrt{2mE}$ i.e. $\lambda = \frac{h}{\sqrt{2mE}}$ (non-relativistic) (9)

For an electron, $m = 9.1 \times 10^{-31} \text{kg}$. i.e. $\lambda = \sqrt{\frac{1.5}{E}} nm$ with E in electron volts – (10)

Therefore electrons with KE in the eV to keV range (λ in the 0.01 to 1nm range) are diffracted by crystal lattices, since typical atomic sizes and separations are about 0.1nm.

Consider a two slit interference pattern (e.g. Young's slits). Each slit behaves as an independent source of waves in fixed phase relative to each other \rightarrow regions of constructive and destructive interference at a screen. Fringes with a spacing given by

$$s = \frac{D\lambda}{d}$$

where *d* = slit separation and *D* = distance from slits to screen. In a particular electron diffraction experiment *D* = 35cm, *d* = $2x10^{-4}cm$, *K* = 50keV, $\lambda = 0.05A$.

Then $s = 10^{-6} m = 1 \mu m$.

Closing one slit gives the single slit diffraction pattern. With both slits open, any attempt to detect which slit the electron passes though causes the interference fringes to disappear, leaving the diffraction pattern.

At very low intensity, where only one photon or electron is in the apparatus at any one time, the interference pattern persists. Therefore it no longer makes sense to ask which slit an individual electron passes through.

Consider using a single slit to try to locate the y position of a particle.



Momentum at start is all $p_x - p_y = 0$.

After passing through the slit, an particle must have;

$$-\frac{a}{2} < y < +\frac{a}{2}$$

There is equal probability to be anywhere in this range, i.e. $P(y)dy = \frac{1}{a}dy$ so that

$$\int_{-\frac{a}{2}}^{\frac{b}{2}} P(y) dy = 1 \text{ (Normalisation condition)}$$

$$P(y)$$

$$\frac{1}{a}$$

$$-\frac{a}{2}$$

$$\frac{a}{2}$$

The uncertainty on the y position is the standard deviation of the position probability distribution. This can be written as;

$$\left(\Delta \mathbf{y}\right)^2 = \left\langle \mathbf{y}^2 \right\rangle - \left\langle \mathbf{y} \right\rangle^2$$

NB: $\langle \rangle$ denotes the "expectation" or average value.

Now
$$\langle y \rangle = 0$$
 $\left(= \int_{-\frac{a}{2}}^{+\frac{a}{2}} yP(y) dy \right)$
 $\left\langle y^{2} \right\rangle = \int_{-\frac{a}{2}}^{+\frac{a}{2}} y^{2}P(y) dy = \frac{a^{2}}{12}$
 $\Delta y = \frac{a}{\sqrt{12}} = 0.29a$

Diffraction $\rightarrow p_{y}$ of any individual particle will be uncertain after the slit.

The standard deviation of the diffraction pattern

$$\left(\frac{\sin^2\beta}{\beta^2} \text{ where } \beta = \frac{\pi a \sin\theta}{\lambda}\right)$$

Is $\Delta \theta = \frac{\lambda}{a}$ (~ position of first minima)

3

$$\theta \text{ small} \Rightarrow \theta \approx \frac{P_y}{P_x} \Rightarrow \Delta P_y = \frac{h}{\lambda} \theta \frac{\lambda}{a} = \frac{h}{a}$$

We already have $\Delta y = 0.29a$
 $\Delta P_y \Delta y = 0.29h = 1.28\hbar$
 $\left(\hbar = \frac{h}{2\pi}\right)$

1.3 Heisenberg's Uncertainty Principle

It is not possible to know simultaneously the position and momentum of a particle with any more precision than is given by;

$$\Delta P_x \Delta x \ge \frac{\hbar}{2}$$
 - (12)

No experiment can ever do better.

It applies to each pair of $\Delta P_v \Delta y, \Delta P_z \Delta z$

There is also an energy-time version.

$$\Delta E \Delta t \ge \frac{\hbar}{2} - (11)$$

Where ΔE is the uncertainty in energy, and Δt the time over which the particle stays in an energy state.

2. The Schrödinger Equation and the Wave Function

2.1 Schrödinger Equation

Recall that for photons and particles;

$$\lambda = \frac{h}{p} - (7)$$

We postulate that the relation $E = hf = \hbar \omega$ (2) applies to particles as well as photons. If we think of a beam of particles as a free progressive wave of momentum p and energy E (per particle), we should describe the wave using

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} = \frac{p}{\hbar} (14)$$

And $\omega = \frac{2\pi E}{h} = \frac{E}{\hbar} (15)$

For a non-relativistic particle;

$$E = \frac{p^2}{2m} + V (V = \text{potential energy})$$

And $\hbar \omega = \frac{\hbar^2 k^2}{2m} + V$ (16)

(Non-relativistic only)

A classical, progressive wave of wave number k $\left(k = \frac{2\pi}{\lambda}\right)$ and angular frequency ω can

be represented as;

$$y(x,t) = A\sin(kx - \omega t) - (17)$$

You can represent the wave properties of a freely propagating particle similarly by the function;

$$\Psi(\mathbf{x},t) = A\sin(k\mathbf{x}-\omega t)$$

This does not lead to the wave equation satisfying (16) (position differentiated twice, time once), however if we try;

$$\Psi(\mathbf{x},t) = \mathbf{A}\mathbf{e}^{i(k\mathbf{x}-\omega t)}$$

We can find a suitable equation. It turns out that complex solutions are required by quantum mechanics – they are not just a useful tool as before. This is a new and important feature. The wave functions $\Psi(x,t)$ are necessarily complex.

For
$$\Psi(x,t) = Ae^{i(kz-\omega t)}$$
 (18)
 $\frac{\partial \Psi}{\partial x} = ik\Psi$
 $\frac{\partial^2 \Psi}{\partial x^2} = -k^2\Psi$
 $\frac{\partial \Psi}{\partial t} = -i\omega\Psi$
Then;
 $\frac{-\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi = i\hbar\frac{\partial \Psi}{\partial t}$ -(19)

This is the 1 dimensional time-dependant Schrödinger equation. It is the basic equation of non-relativistic quantum mechanics.

If potential V is not a function of time, classically energy is conserved, one has particle states of definite energy (e.g. electrons in stable atoms). These are called stationary states. Then we can separate out the space and time dependence by writing $\Psi(x,t) = \psi(x)T(t)$.

(Separation of variables)

$$\frac{\partial^2 \Psi}{\partial x^2} = T \frac{d^2 \psi}{dx^2}$$
$$\frac{k dT}{\partial t} = \psi \frac{dT}{dt}$$

Putting these into (19) gives;

$$-\frac{\hbar^2}{2m}T\frac{d^2\psi}{dx^2} + V(x)\psi T = i\hbar\psi\frac{dT}{dt}$$

Dividing through by ψT ;

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V(x) = i\hbar\frac{1}{T}\frac{dT}{dt}$$

On the left, we have a function of x only, and on the left a function of t only. This can only be true if both sides are equal to a constant, E.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$
 (20)
$$i\hbar\frac{dT}{dt} = ET - (21)$$

Equation 20 is the 1E time-independent Schrödinger equation.

If we know the form of V(x), we can in general solve (20) to get $\psi(x)$.

Equation 21 is easily solved to give;

$$T(t) = e^{-\frac{i\omega t}{\hbar}} = e^{-i\omega t} (22)$$

if we take E to be the total energy of the system, since $E = \hbar \omega$.

2.2 The Wave Function

The quantity $\Psi(x,t)$ is called the wave function. It is essentially complex, so cannot be

identified with a single physical property of a particle. The wave function contains all the information that the uncertainty principle allows us to know about the state of the particle. According to the Born interpretation (1926) the probability to find the particle in the region of space from x to x + dx at a time t is given by;

$$P(x,t)dx = |\Psi(x,t)|^{2} dx = \Psi^{*}(x,t)\Psi(x,t)dx$$
(23)

Reminders: let $z = a + ib = \operatorname{Re}^{i\theta} = R(\cos\theta + i\sin\theta)$

 $z^* = a - ib = \operatorname{Re}^{-i\theta} = R\left(\cos\theta - i\sin\theta\right)$ Then $|z| = \sqrt{z^* z} = R = \sqrt{a^2 + b^2}$ is the modulus of z. $\theta = \arg(z) = \tan^{-1}\left(\frac{b}{a}\right)$ If z_1 and z_2 are complex, $|z_1 + z_2|^2 = |z_1|^2 + |z_2|^2 + 2\operatorname{Re}(z_1 * z_2)$.

A particle must be found somewhere so there is a normalisation condition;

 $\int_{-\infty}^{\infty} \left| \Psi \left(x, t \right) \right|^2 dx = 1(24)$

Any physically sensible function must satisfy (24).

Equation (20) is linear (it does not contain squares of Ψ) \rightarrow if Ψ_1 is a solution, so also is $A\Psi$ where A is a constant. (e.g. a normalisation constant). Also if Ψ_1 and Ψ_2 are solutions, then $A\Psi_1 + B\Psi_2$ is also a solution.

The phase of A or B is not affected by the normalisation process, so $Ae^{i\alpha}\Psi_1$ must also be a solution, where α is an arbitrary real constant. This does not affect any physical measurable quantities.

Note that the time dependant part $e^{-\frac{iEt}{\hbar}} = e^{-i\omega t}$ of the wave function for a stationary state has no physically significant impact on observables (it disappears when you take the modulus squared).

A suitable wave function must be a solution of the time-independent Schrödinger equation and be normalised and must satisfy boundary conditions;

- a) Must be a continuous single-valued function of x and t (otherwise $|\Psi|^2$ would not be well defined for all positions)
- b) $\int_{-\infty}^{\infty} |\Psi|^2 dx$ must be finite to represent a probability.
- c) $\frac{d\Psi}{dx}$ must be continuous except where there is an infinite discontinuity in potential V(x).

2.3 Observables, Operators and Expectation Values

First rewrite Equation 20 (Time Independent Schrödinger Equation);

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

We can interpret the left hand side as a mathematical "operator" operating on the wave function. The right hand side is the wave function multiplied by some allowed value of the total energy. This has the form;

$$\hat{E}\psi = E\psi$$
 -(25)
Where $\hat{E} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$ -(26)

 \hat{E} is the energy operator.

Solving (25) involves finding particular functions ψ_n which are physically acceptable (they

satisfy all the boundary conditions) and which, when operated on by \hat{E} give allowed values of energy E_n multiplied by ψ_n . This is known as an Eigenvalue question.

i.e.
$$\hat{E}\psi_n = E_n\psi_n$$

 \hat{E} is the operator, ψ_n is the wave function (Eigenfunction), and E_n the Eigenvalue.

Other operators exist;

For the x component of momentum;

$$\hat{P}_x = -i\hbar \frac{\partial}{\partial x} - (27)$$

We can also write;

$$\hat{p}_{x}^{2} = \hat{p}_{x}\hat{p}_{x} = -\hbar^{2}\frac{\partial^{2}}{\partial x^{2}}$$
 (28)

For x position operator it is just the algebraic variable x, i.e. $\hat{x} = x$. Similarly $\hat{x}^2 = \hat{x}\hat{x} = x^2$ (30)

The use of these operators allows us to calculate the expectation values of corresponding dynamical quantities using the "sandwich method".

For an operator \hat{O} the expectation value of the corresponding physical variable, O, is given by;

$$\left< O \right> = \int_{-\infty}^{\infty} \Psi * \hat{O} \Psi dx$$
 (31)

Recall that when we "derived" the Time Independent Schrödinger Equation we separated

out the time dependant part $T(t) = e^{-i\frac{Et}{\hbar}}$ (22).

Thus, the full wave function corresponding to an Eigenfunction of the Time Independent

Schrödinger Equation is $\Psi_n(x,t) = \psi_n(x)e^{-\frac{iE_nt}{\hbar}}$

Example; A particle has a wave function given by;

$$\Psi(x,t) = \sqrt{\frac{2}{a}\cos\frac{\pi x}{a}}e^{-\frac{iEt}{\hbar}} \text{ for } -\frac{a}{2} < x < \frac{a}{2} \text{ (0 outside this region)}$$

The complex conjugate value of P_x^2 is;

$$\left\langle P_{x}^{2} \right\rangle = \int_{-\infty}^{\infty} \sqrt{\frac{2}{a}} \cos \frac{\pi x}{a} e^{\frac{iEt}{\hbar}} \left(-\hbar^{2} \frac{\partial^{2}}{\partial x^{2}} \right) \sqrt{\frac{2}{a}} \cos \frac{\pi x}{a} e^{-\frac{iEt}{\hbar}} dx = \frac{2\hbar^{2}\pi^{2}}{a^{3}} \int_{-\frac{a}{2}}^{\frac{a}{2}} \cos^{2} \frac{\pi x}{a} dx$$
$$\left\langle P_{x}^{2} \right\rangle = \frac{\hbar^{2}\pi^{2}}{a^{3}}$$

Recall that, for any dynamical quantity (e.g. x, p), we defined the uncertainty as;

$$(\Delta x)^{2} = \langle x^{2} \rangle - \langle x \rangle^{2}$$
$$(\Delta p_{x})^{2} = \langle p_{x}^{2} \rangle - \langle p_{x} \rangle^{2}$$
Etc.

2.4 Commutators, Compatible Observables & Uncertainty

Consider two operators \hat{O}_1 and \hat{O}_2 . The commutator is defined as;

$$\left[\hat{O}_{1},\hat{O}_{2}\right] = \hat{O}_{1}\hat{O}_{2} - \hat{O}_{1}\hat{O}_{1}$$
(33)

The operators are said to "commute" if $[\hat{O}_1, \hat{O}_2] = 0$. i.e. $(\hat{O}_1, \hat{O}_2)\Psi = (\hat{O}_2, \hat{O}_1)\Psi$, i.e. it does not matter in which order the operators are applied in.

For example, consider \hat{x} and \hat{P}_x and some wave function Ψ . Then;

$$\begin{bmatrix} \hat{P}_{x}, \hat{x} \end{bmatrix} \Psi = \begin{bmatrix} i\hbar \frac{\partial}{\partial x}, x \end{bmatrix} \Psi$$
$$= -i\hbar \frac{\partial}{\partial x} (x\Psi) - x \left(-i\hbar \frac{d\Psi}{\partial x} \right)$$
$$= -i\hbar \frac{\partial \Psi}{\partial x} - i\hbar \Psi + i\hbar x \frac{\partial \Psi}{\partial x}$$
$$= -i\hbar \Psi$$
i.e.
$$\begin{bmatrix} \hat{p}_{x}, \hat{x} \end{bmatrix} = -i\hbar (34)$$

If the operators do not commute, it is not possible for a quantum state to be an eigenstate simultaneously with both operators \rightarrow uncertainty relation between the two dynamic variables.

For X position and y-momentum;

$$\left[\hat{\rho}_{y},\hat{x}\right] = \left(-i\hbar\frac{\partial}{\partial y}x - x\left(-i\hbar\frac{\partial}{\partial y}\right)\right) = -i\hbar x\frac{\partial}{\partial y} + i\hbar x\frac{\partial}{\partial y} = 0$$

Thus it is a possible for a particle to have exact values of p_{v} and x simultaneously.

3. One Dimensional Potential Wells

3.1 Infinite Potential Well



Consider a particle confined within an infinite One Dimensional Potential Well $(V(x) = 0 \text{ for } 0 < x < L, V(x) = \infty \text{ elsewhere})$ (The particle in a box)

Classically a particle of energy E would bounce backward and forward within the 1D region 0 < x < L. Outside of the potential well, the wave function must be zero. $\psi = 0$. It is impossible for the particle to be found there – the particle would need infinite energy. i.e. $\psi(0) = \psi(L) = 0$.

We use the Time Independent Schrödinger Equation with V = 0 for 0 < x < L to find $\psi(x)$.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

i.e.
$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

The general solution is;
$$\psi = c_1 e^{ikx} + c_2 e^{-ikx}$$
$$k = \left|\sqrt{\frac{2mE}{\hbar^2}}\right|$$

Where c_1 and c_2 are constants (and possibly complex). Boundary conditions; $\psi(0) = \psi(L) = 0$ $\Rightarrow c_1 + c_2 = 0$ $i.e. \ \psi(x) = c_1(e^{ikx} - e^{-ikx}) = -2ic_1 \sin kx$ $\Rightarrow solution of the form \ \psi = A \sin kx$ where A is a normalisation constant. But $\psi(L) = 0 \Rightarrow \sin kL = 0$ i.e. $kL = n\pi \ (n = 1, 2, 3, ...)$ The values of k are restricted to a discrete set; $k_n = \frac{n\pi}{L}$

 \rightarrow there are an allowable set of energies given by;

$$k_n = \sqrt{\frac{2mE_n}{\hbar^2}} = \frac{n\pi}{L}$$
$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} - (35)$$

Note that E_n is proportional to n^2 and $\frac{1}{m}$ and to $\frac{1}{L^2}$.

The complete set of allowed wave functions (energy eigenfunctions) for the stationary states of a particle in a 1D infinite potential well is therefore;

$$\Psi_n(x,t) = A_n \sin \frac{n\pi x}{L} e^{-\frac{iE_n t}{\hbar}} - (36)$$

For $0 < x < L$, $n = 1, 2, 3, ...,$

If n = 0, $\Psi(x,t) = 0 \rightarrow$ no probability of finding anything in the box \rightarrow no particle.



Normalisation constants A_n can be found using;

$\int_{-\infty}^{+\infty} \left|\Psi\right|^2 dx = 1$

The quantisation of energy levels has arisen from the boundary conditions. Position

probability distributions are obtained, as usual, from $|\Psi|^2$ and generally have points of zero probability, i.e. places where the particle will never be found.

Although a particle in a stationary state has a definite value of energies, it does not have a

definite value of momentum. The uncertainty principle $\left(\Delta \rho_x \Delta x \ge \frac{\hbar}{2}\right) \Rightarrow$ the narrower the

well the larger the uncertainty in momentum. In terms of representing a particle by a wave packet, the narrower the packet the more wavelengths are required to represent it. Fourier analysis is needed as narrow wave packet needs an infinite amount of components to make up the wave.

But a wave packet can have a unique, fixed frequency and also a fixed energy.

3.2 Non-Stationary (Time-Dependant) States

We have Equation (36);

$$\Psi_n(x,t) = A_n \sin \frac{n\pi x}{L} e^{-\frac{iE_n t}{\hbar}}$$

For a set of allowable energy eigenfunctions for stationary (constant energy) state for an infinite potential well.

These functions are orthonormal (orthogonal)

i.e.
$$\int_{-\infty}^{\infty} \Psi_n * \Psi_n dx = \begin{cases} 1 & m = n \\ 0 & otherwise \end{cases}$$
(37)

The Time Independent Schrödinger Equation is linear. Any linear superposition of these Ψ_n 's will also be a solution.

e.g.
$$\Psi = C_1 \Psi_1 + C_2 \Psi_2$$

This will be a solution. Normalised if $C_1^2 + C_2^2 = 1$.

It must be possible for a particle to exist with this new wave function $\Psi = C_1 \Psi_1 + C_2 \Psi_2$.

What does this physically represent? It clearly no longer corresponds to a fixed, definite E.

$$\Psi(x,t) = C_1 \sin \frac{\pi x}{L} e^{-\frac{iE_1 t}{\hbar}} + C_2 \sin \frac{2\pi x}{L} e^{-\frac{iE_2 t}{\hbar}} = f_1 e^{-\frac{iE_1 t}{\hbar}} + f_2 e^{-\frac{iE_1 t}{\hbar}}$$

Where f are the spatial parts of the wave functions. Position probability density is;

$$\left|\Psi\right|^{2} = f_{1}^{2} + f_{2}^{2} + 2\operatorname{Re}\left\{f_{1}f_{2}e^{\frac{iE_{1}t}{\hbar}}e^{-\frac{iE_{2}t}{\hbar}}\right\}$$
$$= f_{1}^{2} + f_{2}^{2} + 2\operatorname{Re}\left\{f_{1}f_{2}e^{\frac{i(E_{1}-E_{2})t}{\hbar}}\right\}$$
$$= f_{1}^{2} + f_{2}^{2} + 2\cos\frac{(E_{2}-E_{1})t}{\hbar}$$

 $(\text{Using }\cos(-\theta) = \cos(\theta))$

Position probability oscillates with frequency depending on $E_2 - E_1$, the energy difference. The particle isn't "moving" in the classical sense, but the probability is changing.

If the particle is an electron, $|\Psi|^2$ also represents the distribution of charge i.e. in this case

the charge oscillates with frequency $\omega = \frac{(E_2 - E_1)}{\hbar}$ i.e. $E_2 - E_1 = \hbar \omega$.

This is the frequency of a photon emitted in a transition from the two energy eigenstates. (From energy eigenstate $E_2 \left[\Psi_2\right]$ to state $E_1 \left[\Psi_1\right]$.

$$\boldsymbol{E}_{2}\boldsymbol{\Psi}_{2}\rightarrow\boldsymbol{C}_{1}\boldsymbol{\Psi}_{1}+\boldsymbol{C}_{2}\boldsymbol{\Psi}_{2}\rightarrow\boldsymbol{E}_{1}\boldsymbol{\Psi}_{1}$$

How can a particle with $\Psi = C_1 \Psi_1 + C_2 \Psi_2$ appear to have more than one energy? We consider the equation in terms of measurement. If we measure the energy we always get either E_1 or E_2 , i.e. one of the allowed eigenvalues E_n . We cannot know beforehand which one is going to happen.

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

The probability of E_1 is C_1^2 .

The probability of E_2 is C_2^2 .

Immediately afterwards the particle will be in the energy eigenstate corresponding to the measured value.

In other words, the measurement has "collapsed" the wave function.

3.3 The Harmonic Oscillator Potential

Classically, this is very important. Force is proportional to small displacement from an equilibrium position, directed toward the equilibrium point.

F(x) = -Cx

Use C to avoid confusion with $k = \frac{2\pi}{\lambda}$.

Potential energy is;

 $V(x) = \frac{1}{2}Cx^2 - (39)$

Thus the potential is time independent. The problem is 1D \rightarrow use the Time Independent Schrödinger Equation in 1D.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}Cx^2\psi = E\psi - (40)$$

We expect (40) to apply to, for example, diatomic molecules.

Classically $\omega_o^2 = \frac{C}{m} \Rightarrow C = m\omega_o^2$ where ω_o = natural frequency of oscillations. So rewrite (40) as:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega_o^2 x^2 \psi = E\psi - (41)$$

Where $\omega_o^2 = \frac{C}{m}$.

We need solutions to (41) such that $\psi \to 0$ as $x \to \pm \infty$ so as to be normalisable. It is found tat for all non-infinite V(x), there is a finite probability to find the particle outside the classically allowed region. This leads to quantum tunnelling and radioactive decay.

It is tedious to solve (41), so we quote the solutions. We define a constant (length) a as;

$$a^{4} = \frac{\hbar^{2}}{mc} = \frac{\hbar^{2}}{m^{2}\omega_{o}^{2}}$$

i.e.
$$a = \sqrt{\frac{\hbar}{m\omega}} - (42)$$

The energy eigenfunctions are;

$$\psi_n(x) = \underbrace{\left(\frac{1}{n!2^n a\sqrt{\pi}}\right)^{\frac{1}{2}}}_{Normalisation factor} \underbrace{H_n\left(\frac{x}{a}\right)}_{Hermite polynomial} \underbrace{e^{-\frac{x^2}{2a^2}}}_{Gaussian exponential function} - (43)$$

Gaussian term determines the behaviour as $\frac{x}{a} \rightarrow \pm \infty$

The Eigenvalues are $E_n = \left(n + \frac{1}{2}\right)\hbar\omega_o$ for n = 0, 1, 2, ... - (44)The first four solutions are;

$$\psi_{0}(x) = \left(\frac{1}{a\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{x^{2}}{a^{2}}} E_{0} = \frac{1}{2}\hbar\omega_{0}$$

$$\psi_{1}(x) = \left(\frac{1}{2a\sqrt{\pi}}\right)^{\frac{1}{2}} 2e^{-\frac{x^{2}}{a^{2}}} E_{0} = \frac{3}{2}\hbar\omega_{0}$$

$$\psi_{2}(x) = \left(\frac{1}{8a\sqrt{\pi}}\right)^{\frac{1}{2}} \left[2 - 4\left(\frac{x}{a}\right)^{2}\right] e^{-\frac{x^{2}}{a^{2}}} E_{0} = \frac{5}{2}\hbar\omega_{0}$$

We verify that one case, $\psi_1(x)$, is an energy eigenfunction with eigenvalue $\frac{3}{2}\hbar\omega_o$.

Now,
$$\psi_1 = \left(\frac{2}{a^3\sqrt{\pi}}\right)^{\frac{1}{2}} x e^{-\frac{x^2}{2a^2}} = Ax e^{-\frac{x^2}{2a^2}}$$
 where $A = \left(\frac{2}{a^3\sqrt{\pi}}\right)^{\frac{1}{2}} = const$.

$$\frac{d\psi_1}{dx} = \frac{\psi_1}{x} - \frac{x}{a^2}\psi_1$$

$$\frac{d^2\psi_1}{dx^2} = \frac{1}{x}\frac{d\psi_1}{dx} - \frac{\psi_1}{x^2} - \frac{\psi_1}{a^2} - \frac{x}{a^2}\frac{d\psi_1}{dx}$$

$$= \frac{\psi_1}{x^2} - \frac{\psi_1}{a^2} - \frac{\psi_1}{x^2} - \frac{\psi_1}{a^2} - \frac{\psi_1}{a^2} + \frac{x^2}{a^4}\psi_1$$

$$= -\frac{3\psi_1}{a^2} + \frac{x^2\psi_1}{a^4}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} = \frac{3\hbar^2\psi_1}{2ma^2} - \frac{\hbar^2x^2\psi_1}{2ma^4}$$
And $V(x)\psi_1 = \frac{1}{2}m\omega_o^2x^2\psi_1 = \frac{\hbar^2}{2ma^4}x^2\psi_1$ since $a^4 = \frac{\hbar^2}{m^2\omega_o^2}$

Therefore
$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} + V(x)\psi_1 = \frac{3\hbar^2\psi_1}{2ma^2} = \frac{3}{2}\hbar\omega_o\psi_1$$

i.e.
$$E_1 = \frac{3}{2}\hbar\omega_o$$
 QED.

We note that the allowed eigenfunctions are either even ($\psi(-x) = \psi(x) \Rightarrow$ even parity) or odd ($\psi(-x) = -\psi(x) \Rightarrow$ odd parity). For any symmetric potential, V(x), this has to be true. For any continuous odd function, $\psi = 0$.

For any continuous even function, $\frac{d\psi}{dx} = 0$ at x = 0.

For any sensible ψ w $\psi \rightarrow 0$ for $x \rightarrow \pm \infty$

This allows one to sketch possible wave functions, especially if the order of polynomial is known.

The energy levels for stationary states of a SHO are equally spaced by $\hbar\omega_{\rm o}$. The ground

state has (zero point) energy $\frac{1}{2}\hbar\omega_{o}$.

Non-stationary states can be constructed (as for infinite square wall)

e.g.
$$\Psi = \frac{1}{\sqrt{2}} \psi_o e^{-\frac{iE_o t}{\hbar}} + \frac{1}{\sqrt{2}} \psi_1 e^{-\frac{iE_t t}{\hbar}}.$$

3.4 Diatomic Molecules

To a good approximation, the force between atoms of a diatomic molecule (e.g. O_2 , N_2 , CO, HCI etc) can be described by SHO for small displacements about the equilibrium position.

The total energy is $E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{1}{2}Cx^2$.

In the centre of the mass frame of the two particles;

$$\underline{p}_1 = -\underline{p}_2$$

i.e. equal and opposite. Then;

$$E = \frac{p^2}{2m_1} + \frac{p^2}{2m_2} + \frac{1}{2}Cx^2 \text{ where } p = |p_1| + |p_2|$$

i.e. $E = \frac{p^2}{2} \left(\frac{1}{m_1} + \frac{1}{m_2}\right) + Cx^2$

With reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ - (45)

Then
$$E = \frac{p^2}{2\mu} + \frac{1}{2}Cx^2$$
 - (46)

Formally this is equivalent to a single particle of mass μ in a 1D potential $V(x) = \frac{1}{2}Cx^2 \rightarrow$ solutions (43) will apply for vibrational states of diatomic molecules.

Example; observed frequency of EM radiation from transitions between adjacent vibrational levels in *CO* (Carbon Monoxide) is 6.43×10^{13} Hz. Estimate the force constant *C*. Level spacing is $\Delta E = \hbar \omega_0 = hv = 4.26 \times 10^{-20} J = 0.266 eV$ (Infrared)

Now
$$\omega_o = \sqrt{\frac{C}{\mu}} \Rightarrow C = \mu \omega_o^2$$

For Carbon Monoxide $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{12x16}{12 + 16} = 1.14x10^{-26} kg$

Therefore spring constant $C = \mu \omega_o^2 = 1680 Nm^{-1}$

In practice, such molecules also have rotational energy. It is difficult to deduce the vibrational energy levels from observing the spectra of the radiation.

4. Quantum Mechanics in Two or Three Dimensions

Think of a parabola rotated around to form a bowl or dish.

4.1 2D Simple Harmonic Oscillator

Suppose a bound particle can move in the xy plane in a 2D parabolic potential.

$$V(x,y) = \frac{1}{2}C(x^{2} + y^{2}) - (47)$$

i.e.
$$V(x,y) = \frac{1}{2}m\omega_o^2(x^2 + y^2)$$

An example may be an atom in a plane in a crystalline structure. The kinetic energy is now;

$$E_{k}=\frac{p_{x}^{2}}{2m}+\frac{p_{y}^{2}}{2m}$$

The 1D Time Independent Schrödinger Equation can naturally be extended;

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)+\frac{1}{2}m\omega_o^2\left(x^2+y^2\right)\psi=E\psi-(48)$$

Now $\psi = \psi(x, y)$ and $|\psi|^2 dxdy =$ probability to find a particle within an elemental area dxdy around (x, y).

We look for solutions that are products of solutions to the 1D equations for the X and Y components of the motion. i.e. $\psi(x,y) = f(x)g(y)$ where f and g are solutions to (41). Then

$$\frac{\partial^2 \psi}{\partial x^2} = g(y) \frac{d^2 f}{dx^2}$$
$$\frac{\partial^2 \psi}{\partial x^2} = f(x) \frac{d^2 g}{dy^2}$$

Since g is constant with respect to x, and f to y. Then (48) becomes;

$$g(y)\left[-\frac{\hbar^2}{2m}\frac{d^2f}{dx^2} + \frac{1}{2}m\omega_o^2 x^2 f(x)\right] + f(x)\left[-\frac{\hbar^2}{2m}\frac{d^2g}{dy^2} + \frac{1}{2}m\omega_o^2 y^2 g(y)\right] = ef(x)g(y)$$

i.e. $g(y)E_{nx}f(x) + f(x)E_{ny}g(y) = Ef(x)g(y)$ since $f(x)$ and $g(y)$ are any eigenfunctions of the 1D problem. i.e. $(E_{nx} + E_{ny})f(x)g(y) = Ef(x)g(y)$.

So $E = E_{nx} + E_{ny}$ is an energy eigenvalue of the 2D oscillator, corresponding to

eigenfunction f(x)g(y).

Total energy

$$E = E_{nx} + E_{ny} = \left(n_x + \frac{1}{2}\right)\hbar\omega_o + \left(n_y + \frac{1}{2}\right)\hbar\omega_o = \left(n_x + n_y + 1\right)\hbar\omega_o$$

for $n_x = 0, 1, 2, \dots$ $n_y = 0, 1, 2, \dots$

The 2D wave functions are;

$$\psi_{n_x n_y}\left(x, y\right) = H_{n_x}\left(\frac{x}{a}\right) H_{n_y}\left(\frac{y}{a}\right) e^{-\frac{\left(x^2 + y^2\right)}{2a^2}} - (49)$$

Now we can have more than one state with the same energy. E.g. $\psi_{1,0}(x, y)$ as the same

energy $(2\hbar\omega_{o})$ as $\psi_{0,1}(x,y)$. This is known as "degeneracy".

In the 2D case the energy of the stationary state is no longer enough to specify the eigenstate; we need two quantum numbers. These could be n_x and n_y , but could also be

energy (i.e. $n_x + n_y$), and some other equation number.

In practice, n_x and n_y have little physical significance.

4.2 The Z-Component of Angular Momentum

We take a cue from classical physics, experiment (e.g. fine structure in atomic spectra), and symmetry.

A particle moving in the xy-plane has angular momentum about the z-axis (i.e. \underline{L} is in the $\pm z$ direction). Charged particles with orbital or spin angular momentum give rise to magnetic moments – experiments show that these are quantised.

Classically, angular momentum of a particle with momentum p and position \underline{r} is;

$$\underline{L} = \underline{r} x \underline{\rho} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ \rho_x & \rho_y & \rho_z \end{vmatrix} (50, 51)$$

For motion in a plane r = (x, y, 0) $p = (p_x, p_y, 0)$ and L points along the z axis with magnitude

 $L_z = xp_y - yp_x(52)$

We postulate that the Quantum Mechanics operator for L_z is just;

$$\hat{L}_{z} = \hat{x}\hat{\rho}_{y} - \hat{y}\hat{\rho}_{x} = x\left(-i\hbar\frac{\partial}{\partial x}\right) - y\left(-i\hbar\frac{\partial}{\partial y}\right) = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial y}\right)$$
(53)

We will use plane polar coordinates (r, ϕ) where

$$x = r\cos\phi$$

 $y = r \sin \phi$

The chain rule of implicit differentiation says;

$$\frac{\partial}{\partial \phi} = \frac{\partial x}{\partial \phi} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi} \frac{\partial}{\partial y} = -r \sin \phi \frac{\partial}{\partial x} + r \cos \phi \frac{\partial}{\partial y} = x \frac{\partial}{\partial y} + y \frac{\partial}{\partial x}$$

i.e. $\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$ (54)

We write wave function as $\phi(r, \phi)$.

The 2D Simple Harmonic Oscillator potential depends only or r (where $r^2 = x^2 + y^2$) and not ϕ . Therefore we assume solutions of the form;

$$\psi(r,\phi) = R(r)\Phi(\phi)$$
(55)

Consider applying the \hat{L}_{z} operator.

$$\hat{L}_z \psi = -i\hbar \frac{\partial \psi}{\partial \phi}$$

Eigenfunction of \hat{L}_{z} would satisfy;

$$-i\hbar \frac{\partial}{\partial \phi} \left(R(r) \Phi(\phi) \right) = \hat{L}_z \left(R(r) \Phi(\phi) \right)$$

i.e.
$$-i\hbar R \frac{\partial \Phi}{\partial \phi} = \hat{L}_z R \Phi$$
$$-i\hbar \frac{\partial \Phi}{\partial \phi} = \hat{L}_z \Phi - (56)$$

(Similar to (21))

i.e.
$$\frac{\partial \Phi}{\partial \phi} - \frac{i\hat{L}_z}{\hbar} \Phi = 0$$

The solutions $\Phi = e^{\frac{i\hat{L}_{z\phi}}{\hbar}} - (57)$

Compare this with $T(t) = e^{-\frac{iEt}{\hbar}}$ for the Time-Dependent part of stationary state wave functions.

The boundary conditions are that $\Phi^*\Phi$ and $\frac{\partial \Phi}{\partial \phi}$ have to be single-valued at every point

For example $\Phi(\phi + 2\pi) = \Phi(\phi)$

$$e^{j\frac{\hat{L}_{z}(\phi+2\pi)}{\hbar}} = e^{j\frac{\hat{L}_{z}\phi}{\hbar}}$$
$$e^{j\frac{\hat{L}_{z}2\pi}{\hbar}} = 1$$
i.e. $\frac{2\pi L_{z}}{\hbar} = m2\pi$ for $m = 0, \pm 1, \pm 2, \pm 3, ...$ $L_{z} = m\hbar$ for $m = 0, \pm 1, \pm 2, \pm 3, ...$

Then $\psi(r,\phi) = R(r)e^{im\phi}$ (58) could be a solution.

This striking result is borne out by experiment – every measurement of one component of orbital angular momentum (conventionally the z component) always yields an integer multiple of \hbar . i.e. \hbar is the fundamental quantum of orbital angular momentum.

4.3 Angular Momentum Eigenfunctions for 2D Simple Harmonic Oscillator

Can we find linear combinations of the degenerate energy eigenfunctions of the type (49) such that the results are of the type (58)?

We take wave functions labelled by n_{y} and n_{y} with the same energy eigenvalues and

combine to produce new wave functions labelled by $n = n_x + n_y$ (i.e. total energy) and m

(giving L_z).

Combined states will have the same time-dependent factor $e^{-\frac{iEt}{\hbar}}$ so combined states will still be solutions of the time-dependent Schrödinger equation. Recall (49);

$$\psi_{n_{x}n_{y}}(x,y) = H_{n_{x}}\left(\frac{x}{a}\right)H_{n_{y}}\left(\frac{y}{a}\right)e^{-\frac{(x^{2}+y^{2})^{2}}{2a^{2}}}$$

And (58)

$$\begin{split} \psi(r,\phi) &= R(r)e^{im\phi} \\ \text{Clearly } e^{-\frac{(x^2+y^2)}{2\sigma^2}} = e^{-\frac{r^2}{2\sigma^2}} \text{ and so this is part of } R(r) \, . \\ \text{For simplicity, we take the case } n_x + n_y = 1 \, . \\ \text{Two possibilities; } (n_x,n_y) &= (1,0) \text{ or } (0,1) \, . \\ \text{i.e. (from (43) et seq.)} \\ \psi_{1,0} &= Cxe^{-\frac{r^2}{2\sigma^2}} \\ \psi_{0,1} &= Cye^{-\frac{r^2}{2\sigma^2}} \\ \text{Where C is an overall constant.} \\ \psi_{1,0} &= Cr\cos(\phi)e^{-\frac{r^2}{2\sigma^2}} \\ \text{Where C is an overall constant.} \\ \psi_{1,0} &= Cr\sin(\phi)e^{-\frac{r^2}{2\sigma^2}} \\ \text{Note by inspection that;} \\ \psi_{1,0} &+ i\psi_{0,1} = Cr(\cos\phi + i\sin\phi)e^{-\frac{r^2}{2\sigma^2}} = Cre^{-\frac{r^2}{2\sigma^2}}e^{i\phi} \end{split}$$

And
$$\psi_{1,0} - i\psi_{0,1} = Cre^{-\frac{r^2}{2a^2}}e^{-i\phi}$$

Thus, we have two functions of the form $R(r)e^{im\phi}$ where $R(r) = Cre^{-\frac{r^2}{2a^2}}$ and $m = \pm 1$. These are clearly eigenstates of total energy $E = (n+1)\hbar\omega_o$ and z component of angular momentum, with $L_z = \pm \hbar$.

4.4 Angular Momentum in 3D

Recall classically;

$$\underline{L} = \underline{r} x \underline{p} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$
(Equations 50, 51)
$$\underline{L} = \left(y p_z - z p_y, z p_x - x p_z, x p_y - y p_x \right)$$
In terms of operators;
$$\hat{L}_x = \hat{y} \hat{P}_z - \hat{z} \hat{P}_y = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$
(59)
$$\hat{L}_y = \hat{z} \hat{P}_x - \hat{x} \hat{P}_z = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$
(60)
$$\hat{L}_z = \hat{x} \hat{P}_y - \hat{y} \hat{P}_x = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$
(61)

Can a particle be simultaneously in an eigenvalue state of any two of these operators? Consider e.g. \hat{L}_z , \hat{L}_x . Look at the commutator $\begin{bmatrix} \hat{L}_z, \hat{L}_x \end{bmatrix}$ acting on some wave function ψ . Then;

$$\begin{split} \left[\hat{L}_{z},\hat{L}_{x}\right]\psi &= \left(L_{z}L_{x}-L_{x}L_{z}\right)\psi \\ &= -\hbar^{2}\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right) + \hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right) \\ &= -\hbar\left(x\frac{\partial\psi}{\partial z}-z\frac{\partial\psi}{\partial x}\right) \\ &= \hbar\left(z\frac{\partial\psi}{\partial x}-x\frac{\partial\psi}{\partial z}\right) = i\hbar\hat{L}_{y}\psi \\ \text{i.e.}\left[\hat{L}_{z},\hat{L}_{x}\right] &= i\hbar\hat{L}_{y}. \end{split}$$

The same applies to the other directions, i.e.;

$$\begin{bmatrix} \hat{L}_{z}, \hat{L}_{x} \end{bmatrix} = i\hbar \hat{L}_{y}$$
$$\begin{bmatrix} \hat{L}_{x}, \hat{L}_{y} \end{bmatrix} = i\hbar \hat{L}_{z}$$
$$\begin{bmatrix} \hat{L}_{y}, \hat{L}_{z} \end{bmatrix} = i\hbar \hat{L}_{x}$$
$$(62)$$

Commutators are non-zero; no states for which any pair of angular momentum components have simultaneous eigenvalues.

Thus it is only possible to know one component precisely. (Conventionally taken as L_z) i.e.

so we can't know the "direction of vector \underline{L} ". But can we know $|\underline{L}|$?

We look at operator for square of total angular momentum.

$$\widehat{L^{2}} = \widehat{L_{x}^{2}} + \widehat{L_{y}^{2}} + \widehat{L_{z}^{2}} = \widehat{L_{x}^{2}}\widehat{L_{x}^{2}} + \widehat{L_{y}^{2}}\widehat{L_{y}^{2}} + \widehat{L_{z}^{2}}\widehat{L_{z}^{2}}$$
(63)
i.e.
$$\widehat{L^{2}} = -\hbar^{2} \left(\left(y \frac{d}{dz} - z \frac{d}{dy} \right) \left(y \frac{d}{dz} - z \frac{d}{dy} \right) + \left(z \frac{d}{dx} - x \frac{d}{dz} \right) \left(z \frac{d}{dx} - x \frac{d}{dz} \right) + \left(x \frac{d}{dy} - y \frac{d}{dx} \right) \right) \right)$$

We will treat mainly spherically symmetric problems, we use symmetrical polars:-



<u>4.5 Eigenfunctions and Eigenvalues of</u> $\widehat{L^2}$ We shall be looking for wave functions $\psi(r, \theta, \phi)$ which are simultaneously eigenfunctions of $\widehat{L^2}$ and $\widehat{L_z}$. Note that the $\widehat{L^2}$ operator does not depend on $r \rightarrow try$ separating out the r dependence.

i.e.
$$\psi(r,\theta,\phi) = R(r)F(\theta,\phi)$$

The eigenvalue equation will be;

$$\begin{aligned} \widehat{L^2}\psi &= L^2\psi\\ \text{i.e.;}\\ \widehat{L^2}\left(R(r)F(\theta,\phi)\right) &= L^2R(r)F(\theta,\phi)\\ R(r)\widehat{L^2}\left(F(\theta,\phi)\right) &= R(r)L^2F(\theta,\phi) \end{aligned}$$

Therefore $\widehat{L^2}F(\theta,\phi) = L^2F(\theta,\phi)$ since R is constant with respect to $\widehat{L^2}$. Using equation 65 gives;

$$-\hbar^{2}\left(\frac{\partial^{2}}{\partial\theta^{2}} + \cot\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^{2}\theta} \frac{\partial^{2}}{\partial\phi^{2}}\right)F = L^{2}F - (67)$$

We know that the ϕ dependence of F must include the term $e^{im\phi}$ since F is assumed to be an eigenfunction of $\widehat{L_z}$. We try to find $F(\theta,\phi) = P(\theta)e^{im\phi}$. We can then substitute for F, and divide by $e^{im\phi}$, to get;

$$-\hbar^2 \left(\frac{d^2}{d\theta^2} + \cot\theta \frac{d}{d\theta} + \frac{m^2}{\sin^2\theta} \right) P = L^2 P$$

Now L^2 is the square of an angular momentum so we write it as $\lambda \hbar^2$ where λ is some constant (This could in principle be a fraction, not a real number.) So we have;

$$\frac{d^{2}P}{d\theta^{2}} + \frac{\cos\theta}{\sin\theta}\frac{dP}{d\theta} + \left(\lambda - \frac{m^{2}}{\sin^{2}\theta}\right)P = 0 \ (68)$$

Solving to (68) will be functions P(0) that are consistent with the eigenvalue equation (67),

such that $L^2 = \lambda \hbar^2$ and $L_z = m\hbar$. Let's try various possible solutions for (68).

a) *P* = *const*. This works if;

$$\lambda - \frac{m^2}{\sin^2 \theta} = 0$$

This has to be true for all $\theta \rightarrow \lambda = m = 0$. ($\forall \theta \rightarrow \text{all values of } \theta$)

b) $P(\theta) = \sin \theta$. $\frac{dP}{d\theta} = \cos \theta$ and $\frac{d^2P}{d\theta^2} = -\sin \theta$ This gives; $\sin \theta + \frac{\cos^2 \theta}{\partial \theta} + 2\sin \theta = \frac{m^2}{2} = 0$

$$-\sin\theta + \frac{\sin\theta}{\sin\theta} + \lambda\sin\theta - \frac{\sin\theta}{\sin\theta} = 0$$
$$-\sin\theta + \frac{1 - \sin^2\theta}{\sin\theta} + \lambda\sin\theta - \frac{m^2}{\sin\theta} = 0$$
$$-2\sin\theta + \lambda\sin\theta + \frac{1}{\sin\theta} - \frac{m^2}{\sin\theta} = 0$$

This works if $\lambda = 2$ and $m^2 = 1$ $(m = \pm 1)$

c) $P(\theta) = \cos \theta$. This gives; $-2\cos\theta + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\cos\theta = 0$ This works for $\lambda = 2, m = 0$.

 $\frac{1}{1} = \frac{1}{2}$

d) $P(\theta) = \sin^2 \theta$

This works for $\lambda = 6$, $m^2 = 4$ i.e. $m = \pm 2$

Etc... Systematic exploration shows that solutions to (68) exist for a series $\lambda = 0, 2, 6, 12, 20, ...$

These are the solutions for λ of the form $\lambda = \ell(\ell + 1)$ where $\ell = 0, 1, 2, 3, ...$

For each value of L there are $(2\ell + 1)$ solutions corresponding to $m = -\ell, ..., 0, ..., +\ell$.

L is the orbital angular momentum quantum number.

The simultaneous quantisation of L^2 and L_z has lead to;

$$L^{2} = \ell \left(\ell + 1 \right) \quad \ell = 0, 1, 2, \dots \\ L_{z} = m\hbar \qquad \left| m \right| \le \ell$$
 (69)

Figure 11.3 of French and Taylor gives a semi-classical pictorial representation.



The eigenfunctions satisfying (68) are called associated legendre function $P_{_{\ell m}}(heta)$.

The combination $F(\theta,\phi) = P_{\ell,m}(\theta)e^{im\phi}$ is called a spherical harmonic, usually

written $\mathsf{Y}_{\ell,m}ig(heta,\phiig)$ (See tables in textbooks)

The complete eigenfunctions would be; $\psi(r,\theta,\phi) = R(r)Y_{\ell,m}(\theta,\phi)$ - (70)

4.6 Rotational States of Molecules

We can treat molecules as rigid bodies (e.g. neglecting vibrations which have very small amplitude relative to the equilibrium separations). For a rigid body, E_k of the rotation is;

$$E_{rot} = \frac{1}{2}I\omega^2$$

Where I is the moment of inertia about the axis through the centre of mass.

 ω = angular frequency of rotation. But *L* = $I\omega$

Therefore
$$E_{rot} = \frac{1}{2}I\frac{L^2}{I^2} = \frac{L^2}{2I}$$
 (71)

But L^2 is quantised with $L^2 = \ell (\ell + 1)\hbar^2$ for $\ell = 0, 1, 2, ...$ and we expect rotational energy levels

$$\boldsymbol{E}_{\ell} = \frac{\ell \left(\ell + 1\right) \hbar^2}{2I} (72)$$

For a diatomic molecule with atoms of mass m_1, m_2 separated by r_0 , reduced mass is;

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

And $I = \mu r_o^2$
Then;
 $E_\ell = \frac{\ell (\ell + 1) \hbar^2}{2\mu r_o^2}$ (73)

Example; hydrogen chloride HCI

о

$$r_{_o} \approx 1A$$
, $\mu \approx 1.67 \, x 10^{-27 \, kg}$ (Note that since $m_{_{C/}} >> m_{_{H}}$, $\mu \approx m_{_{H}}$)

Then
$$E_{\ell} - E_{\ell-1} = \frac{\hbar^2}{2\mu r_o^2} \left(\ell^2 + \ell - \left(\ell^2 - \ell \right) \right) = \frac{\ell \hbar^2}{\mu r_o^2}$$

The vibrational energy level spacings increase with ℓ in contrast to the even spacings in the vibrational spectra. E.g. for *HCl*;



5. Central Force Problems and the Hydrogen Atom

5.1 The Schrödinger Equation in 3D

We simply extend from 1D and 2D to write;

$$-\frac{\hbar^{2}}{2m}\left(\frac{\partial^{2}}{\partial x^{2}}+\frac{\partial^{2}}{\partial y^{2}}+\frac{\partial^{2}}{\partial z^{2}}\right)\Psi}{E_{\mu} \text{ term}}+\underbrace{V\left(x,y,z\right)\Psi}_{E_{\mu} \text{ term}}=i\hbar\frac{\partial\Psi}{\partial t}$$

Where $\Psi = \Psi(x, y, z, t)$. The last part of the equation is the time evolution of the wave function.

The time independent version of this can be written in terms of Laplacian and $\underline{r} = (x, y, z)$

and for $V = V(\underline{r})$ (time-independent potential) as;

$$-\frac{\hbar^{2}}{2m}\nabla^{2}\psi(\underline{r})+V(\underline{r})\psi(\underline{r})=E\psi(\underline{r})$$
(74)

Where $\Psi(\underline{r},t) = \psi(\underline{r})e^{-\frac{\hbar t}{\hbar}}$

In polar coordinates;

-

$$\nabla^{2} = \left(\frac{\partial^{2}}{\partial r^{2}} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{r^{2}}\left(\frac{\partial}{\partial \theta^{2}} + \cot\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{r^{2}\sin^{2}\theta}\frac{\partial^{2}}{\partial \phi^{2}} - (75)$$

Note alternative form for first term of ∇^2 ;

$$\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - (76)$$

For 2D problems, no θ dependence. sin² θ = 1.

$$\Rightarrow \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi} = \frac{1}{r^2} \left(\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\partial^2}{\partial \phi^2} \right)$$

5.2 Motion under a Central force



Classically, we can resolve the velocity vector into radial, v_r , and transverse, v_t , components.

Total energy is; $E = \frac{1}{2}mv_r^2 + \frac{1}{2}mv_t^2 + V(r) - (77)$

since V is a function of radial distance from the origin.

The angular momentum $L = mvr_t$. Classically *L* is conserved for central force motion. This gives;

$$v_t = \frac{L}{mr}$$

We write radial component of linear momentum as $P_r = mv_r$

Then (77) becomes;

$$E = \frac{p^2}{2m} + \frac{L^2}{2mr^2} + V(r) - (78)$$

Moving from classical to quantum;

$$P_r^2 \to \widehat{p_r^2} = -\hbar^2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) (\text{From (75)})$$
$$L^2 \to \widehat{L^2} = -\hbar \left(\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) (\text{From (65)})$$

So the Time Independent Schrödinger Equation would be;

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\psi - \frac{\hbar^2}{2mr}\left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right)\psi + V(r)\psi = E\psi$$
(79)

It turns out to be useful to write (79) in terms of $r\psi$ rather that just ψ . First we note that;

$$\frac{\partial^2}{\partial r^2}(r\psi) = \frac{\partial}{\partial r}\left(\psi + r\frac{\partial\psi}{\partial r}\right) = 2\frac{\partial\psi}{\partial r} + r\frac{\partial^2\psi}{\partial r^2} = r\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\psi$$

Multiplying (79) by r gives;

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}(r\psi) - \frac{L^2}{2mr}(r\psi) + V(r)(r\psi) = Er\psi$$
(80)

This is the 3D Time Independent Schrödinger Equation for a central force. We will be looking for solutions to (80) of the form;

$$\psi(r,\theta,\phi) = R(r)Y_{\ell,m}(\theta,\phi)$$

since we already know that $Y_{\ell,m}(\theta,\phi)$ are eigenfunctions of $\widehat{L^2}$ and $\widehat{L_z}$. Thus we write the function R(r) as;

$$R(r) = \frac{u(r)}{r} (81)$$

so that $r\psi = u(r)Y_{\ell,m}(\theta,\phi) = rR(r)Y_{\ell,m}(\theta,\phi)$

Note that since ψ must remain finite as $r \to 0$ then we must have $u(r) \to 0$ as $r \to 0$. We will also use the result; $\widehat{L^{2}}(r\psi) = \ell(\ell+1)\hbar^{2}(r\psi)$

so there is no longer any $(heta,\phi)$ dependence in the equation, and we can cancel through the

$$Y_{\ell,m}(\theta,\phi) \text{ to get;} \\ \left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} - \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r)\right]u = Eu - (82)$$

We have reduced the problem to a 1D equation in the radial coordinate r.

5.3 The Coulomb Potential and the Hydrogen Atom

Coulomb Potential $V(r) = -\frac{e^2}{4\pi\varepsilon_o r}$ for an electron in a z = 1 atom (e.g. hydrogen). We will be looking for solutions to (80) of the form; $\Psi(r,\theta,\phi) = R(r)Y_{\ell,m}(\theta,\phi)$

since we already know $Y_{\ell,m}(\theta,\phi)$ are eigenfunctions of $\widehat{L^2}$ and $\widehat{L_z}$. We use the Bohr Radius;

$$\boldsymbol{a}_{o} = \left(\frac{4\pi\varepsilon_{o}}{\mathbf{e}^{2}}\right)\frac{\hbar^{2}}{m_{e}} = 0.53 \overset{o}{A}$$

and rewrite $r = a_o \rho$ (i.e. $\rho = \frac{r}{a_o}$)

and use the Rydberg energy
$$E_{R} = \frac{e^{2}}{2(4\pi\varepsilon_{o})a_{o}}$$
 13.6eV

and rewrite
$$E = \varepsilon_o E_R$$
 (i.e. $\varepsilon = \frac{E}{E_R}$)

Equation 82;

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}-\frac{\ell(\ell+1)\hbar^2}{2mr^2}-\frac{e^2}{4\pi\varepsilon_o r}\right]u=Eu$$

(V(r) has been replaced with the electrostatic potential)

$$\Rightarrow -\frac{d^2u}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2}u - \frac{2}{\rho}u = \varepsilon u - (83)$$

i.e. $-\frac{d^2u}{d\rho^2} + V_{eff}u = \varepsilon u - (84)$

where the "effective potential" defined in terms of dimensionless quantity ρ is;

$$v_{eff}(\rho) = \frac{\ell(\ell+1)}{\rho^2} - \frac{2}{\rho} - (85)$$

Or in terms of r;

$$v_{eff}(r) = \frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\varepsilon_o r} - (86)$$

("Centrifugal potential" - Coulomb Potential)

5.4 Radial Wave Functions for Hydrogen

We first look at the behaviour of (83) for some limiting cases.

For very large distances, $\rho \rightarrow \infty$

Then we have
$$\frac{d^2u}{d\rho} \approx -\varepsilon u \ (\rho \to \infty)$$

Bound states correspond to negative total energy (i.e. need to put in energy to free electrons) i.e. $-\varepsilon$ is positive.

We set $b^2 = -\varepsilon$ (b is real and positive)

Then, $u \sim e^{-b\rho}$ and $u \sim e^{-b\rho}$ would be possible solutions, but $e^{+b\rho}$ is not acceptable because the wave function would not be normalisable.

For small distances, $\rho \rightarrow 0$

The leading order terms are $-\frac{d^2u}{d\rho^2} + \frac{\ell(\ell+1)u}{\rho^2} = \varepsilon u$

(Because the third $(\frac{1}{\varepsilon})$ term becomes much smaller than $\frac{1}{\rho^2}$ term as $\rho \to 0$). The equation has two forms of solutions; $u(\rho) \sim \rho^{\ell+1}$ and $u(\rho) \sim \rho^{-\ell}$.

(But $R(r) = \frac{u(r)}{r} \Rightarrow u(r) \rightarrow 0$ as $r \rightarrow 0$ to keep R(r) finite) However $\rho^{-\ell}$ does not go to zero as $\rho \rightarrow 0$ (see equation 81)

Thus, we assume $u(\rho) \sim \rho^{\ell+1}$ for the range $\rho \to 0$.

Therefore we write solutions to (83) as; $u(\rho) = \rho^{\ell+1} e^{b\rho} f(\rho)$ (87)

where $f(\rho)$ is a function that does not involve the required small and large ρ behaviour. We can substitute (87) into (83) and obtain (after much algebra and calculus [exercise]);

$$\rho \frac{d^2 f}{d\rho^2} + 2\left[\left(\ell + 1\right) - b\rho\right] \frac{df}{d\rho} + 2\left[1 - b\left(\rho + 1\right)\right]f = 0 - (88)$$

Solutions exist only for certain values of energy parameter b (recall $b^2 = -\varepsilon = \frac{E}{E_R}$)

Simplest solution is $f = cons \tan t - (89)$ which works for $1 - b(\ell + 1) = 0$

i.e. $b = \frac{1}{\ell + 1}$

This solution corresponds to energy

$$\boldsymbol{E} = -\boldsymbol{b}^2 \boldsymbol{E}_R = -\frac{\boldsymbol{E}_R}{\left(\ell + 1\right)^2}$$

since l + 1 is an integer, E is quantised.

We know that, in the Bohr modes, energy levels are given by $E_n = -\frac{E_R}{n^2} n = 1, 2, 3, ...$

So w can identify this solution as belonging to a principle quantum number n such that $n = \ell + 1$ or $\ell = n - 1$.

We go on to look for solutions to (88) where $f(\rho) =$ polynomial.

The simplest such solution is;

$$u(\rho) = (c_o - c_1 \rho) \rho^{\ell + 1} e^{-b\rho} - (90)$$

This works (exercise) if;

$$b = \frac{1}{\ell + 2}$$

i.e. $E = -\frac{E_R}{\left(\ell + 2\right)^2}$

This corresponds to $n = \ell + 2$, or $\ell = n - 2$.

We can classify states in terms of a particular value of ℓ so states corresponding to (89) and (90) correspond to different energies. Alternatively, we could take states as belonging to the same value of n and so they have the same energy, but different ℓ . ($\ell = n - 1$ and l = n - 2).

Systematic analysis of possible of possible solutions shows that polynomials f(
ho) exist for

all values of
$$\ell$$
 with $\frac{1}{b}(=n) = \ell + 1, \ell + 2,...$

Alternatively, for a given value of $n\left(=\frac{1}{b}\right)$, solutions can be found for integer values of ℓ

such that $\ell \leq n-1$.

It is usually more convenient to classify states first with *n*, the principle quantum number.

The general form of the full solutions is;

$$u_{n,\ell}(\rho) = \rho^{\ell+1} e^{-\frac{\rho}{n}} \sum_{i=0}^{n-\ell-1} (-1)^i c_i \rho^i - (91)$$

Notes:

Solutions are indexed by n and ℓ .

We have set $b = \frac{1}{n}$.

The coefficients, c_i , are positive, and $(-1)^i$ factors ensure alternating signs.

 $\ell = 1$

The number of nodes in $f(\rho)$ is given by $n_r = n - \ell - 1$ (not counting the nodes at 0 and ∞). n_r is called the radial quantum number.

 $\ell = 2$

From (81), the complete radial Coulomb wave functions are;

$$R_{n,\ell}(\rho) = \rho^{\ell} e^{-\frac{\rho}{n}} \sum_{i=0}^{n_{\ell}} (-1)^{i} c_{i} \rho^{i}$$
(92)

where $n_r = n - \ell - 1$ and $\rho = \frac{r}{a_o}$.

 $\ell = 0$

Some functions $R_{n,\ell}(r)$;

$$1 \qquad e^{-\frac{r}{a_{o}}} \qquad - \qquad -$$

$$2 \qquad \left(1 - \frac{r}{2a}\right)e^{-\frac{r}{2a_{o}}} \qquad \frac{r}{a_{o}}e^{-\frac{r}{2a_{o}}} \qquad -$$

$$3 \qquad \left(1 - \frac{2r}{3a_{o}} + \frac{2r^{2}}{27a_{o}}\right)e^{-\frac{r}{3a_{o}}} \qquad \left(\frac{r}{a_{o}}\left(1 - \frac{r}{6a_{o}}\right)\right)e^{-\frac{r}{3a_{o}}} \qquad \left(\frac{r}{a_{o}}\right)^{2}e^{-\frac{r}{3a_{o}}}$$

5.5 Complete Wave Functions for Hydrogen

From equations (70) and (92), the complete stationary state wave function for an electron in a coulomb potential:

$$\psi_{n,\ell,m}(r,\theta,\phi) = R_{n,\ell}(r)Y_{\ell,m}(\theta,\phi)$$
$$= R_{n,\ell}(r)P_{\ell}(\theta)e^{im\phi} - (93)$$

where $P_{\ell,m}(\theta,\phi)$ are associated Legendre functions.

$$R_{n,\ell}(r) = \left(\frac{r}{a_o}\right)^{\ell} e^{-\frac{r}{na_o}} \sum_{i=0}^{-\ell-1} \left(-1\right)^{\ell} c_i\left(\frac{r}{a_o}\right)$$

The eigenfunctions are characterised by three quantum numbers;

n - the principle quantum number. (n = 1, 2, 3...) $E = -\frac{E_R}{n^2}$

 ℓ - the orbital angular momentum quantum number. $(\ell = 0, ..., n-1) L^2 = \ell (\ell + 1) \hbar^2$

m = azimuthal (or magnetic) quantum number. $(m = -\ell, ..., \ell) L_z = m\hbar$.

How to deduce n, ℓ, m by inspecting the wave function, and to check if it is a possible wave function.

$$\psi \sim \left(\frac{r}{a_o}\right)^{\ell} e^{-\frac{1}{n}\left(\frac{r}{a_o}\right)} (polynomial) P_{\ell,m}(\theta) e^{im\phi}$$

 ℓ is the power in the leading $\left(\frac{r}{a_o}\right)$ term = the sum of the $sin\theta$ and $\cos\theta$ terms in $P_{\ell,m}$.

e.g.; $\sin\theta\cos\theta \Rightarrow \ell = 2$

$$3\cos^2\theta - 1 \Rightarrow \ell = 2$$

n is the divisor of $-\frac{r}{a_o}$ term in the exponential.

 $n_r = n - \ell - 1 =$ number of nodes in the polynomial = order of polynomial.

m = integer factor in the $e^{im\phi}$ term. The usual normalisation condition is;

 $\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} \left| \psi_{n,\ell,m}(r,\theta,\phi) \right|^2 r^2 dr \sin\theta d\theta d\phi$

where $dV = r^2 dr \sin\theta d\theta d\phi$ = infinitesimal volume element.

Note that taking θ from $0 \rightarrow \pi$ while taking ϕ from $0 \rightarrow 2\pi$ sweeps out all of angular space.

No ϕ dependence in $|\psi|^2$ because $|e^{im\phi}|^2 = 1 \rightarrow$ probability is uniform in azimuthal angle ϕ . The radial probability density for position (and so also charge) is got by integrating over θ and ϕ :

 $P(r)dr = 4\pi r^2 \left[R(r)\right]^2 dr$

which is the probability to find an electron within a spherical shell between r and r + dr. Increasing n gives a tendency for the electron to be further form the nucleus. There is a maximum probability at $r = n^2 a_0$ for $\ell = n - 1$.

For $\ell = 0$, the electron can be found in the vicinity of the nucleus. This leads to electron capture (by a proton), thus radioactive decay.

States with $n_r = n - \ell - 1 = 0$ are the most Bohr-like, i.e. no nodes in radial probability distribution (no positions of zero probability).

(www.quantumatomica.co.uk)

We look also at the θ dependent modulation of the probability distributions. We use polar diagrams;

Distance from origin $\propto [P(\theta)]^2$ For $\ell = 0$, no θ dependence. For $\ell = 0, m = 0 \cdot |Y_{\ell,m}|^2 \sim \cos^2 \theta$. $m = 0 \Rightarrow L_z = 0$

This agrees with the semi-classical picture of electron close to z-axis.

For
$$\ell = 1, m = \pm 1, |Y_{\ell,m}|^2 \sim \sin^2 \theta$$

 $m = \pm 1 \Longrightarrow L_z = \pm \hbar$

Particle is more likely to be in the xy plane.

 $He^+(z=2)$, $Li^{++}(z=3)$. Nuclear charge becomes $+z_{a}$.

5.6 Other single-electron atoms

We extend the analysis of hydrogen (z = 1) atom, to similar one-electron atoms, e.g.

Potential is
$$V = -\frac{Ze^2}{4\pi\varepsilon_o r}$$
, and the Bohr radius becomes $a_o' = \frac{a_o}{z}$. The energies become $E_n = -\frac{z^2 E_R}{n^2}$.

Thus for He^+ , energy levels are times 4 compared with Hydrogen and the electron "orbits" a factor of 2 closer to the nucleus.

For Li^{++} , factors are x9 and x3.

We have assumed that the mass of the electron will be negligible compared with the nuclear mass. Strictly, we should used reduced mass, which will give small shifts in energy levels, and differences between H, He^+ and Li^{++} .

6. Multi-Electron Atoms

6.1 Electron Spin

The Stern-Gerlach experiment (1921) showed that electrons have intrinsic (spin) angular momentum which gives rise to magnetic moment.

The total spin angular momentum is given by $S^2 = s(s+1)\hbar^2$ - (94)

in analogy with L^2 , where s = spin angular momentum quantum number. In fact, s can take only one value $s = \frac{1}{2}$. Therefore $S^2 = \frac{3}{4}\hbar^2$ for an electron (and proton and neutron). There is 2s + 1 = 2 possible values for the z component of spin, labelled by the quantum number m_s . (Sometimes m for orbital angular momentum components is labelled m_s .)

$$m_s = +\frac{1}{2} \rightarrow$$
 "spin up"
 $m_s = -\frac{1}{2} \rightarrow$ "cpin down"

 $m_s = -\frac{1}{2} \Rightarrow$ "spin down" Therefore to completely specify quantum states of an electron in an atom \rightarrow 4 quantum numbers: n, ℓ , m, m_s . Then for each value of n, n-1 values of ℓ , $2\ell + 1$ values of m, 2

values of m_s.

Thus degeneracy is $2n^2$, since (to first order) energy depends only on n.

6.3 Combined states of two identical particles

Consider two non-interacting electrons in the same potential (e.g. He atoms). For simplicity, consider a 1D case.

It can be shown that the wave function can be written as a product:

$$\Psi(x_1, x_2, t) = \psi_A(x_1)\psi_B(x_2)e^{-\frac{i\pi t}{h}} - (97)$$

where;

 $\psi_{A}(x_{1})$ = wave function for electron A at x_{1}

 $\psi_{B}(x_{2})$ = wave function for electron B at x_{2}

 $E = E_A + E_B (E_A, E_B)$ are the energy eigenvalues)

The position probability density is probability to find electron A near x_1 at the same time as electron B near x_2 is;

$$P(x_{1}, x_{2}) dx_{1} dx_{2} = |\psi_{A}(x_{1})|^{2} dx_{1} |\psi_{B}(x_{2})|^{2} dx_{2}$$

The electrons are indistinguishable \rightarrow we never know whether we are observing A or B. Probability must be the same if interchangeable labels i.e. $P(x_1, x_2) dx_1 dx_2 = P(x_2, x_1) dx_2 dx_1$

i.e. $|\psi_{A}(x_{1})|^{2} |\psi_{B}(x_{2})|^{2} = |\psi_{A}(x_{2})|^{2} |\psi_{B}(x_{1})|^{2}$

 ψ_{A} and ψ_{B} are, in general, different functions and this condition will not be satisfied. We can construct functions that do satisfy the "interchange of labels" requirement:

$$\psi_{S}(x_{1},x_{2}) = \frac{1}{\sqrt{2}} \left[\psi_{A}(x_{1}) \psi_{B}(x_{2}) + \psi_{A}(x_{2}) \psi_{B}(x_{1}) \right] - (98)$$

is the symmetric combination, since $\psi_{s}(x_{1}, x_{2}) = \psi_{s}(x_{2}, x_{1})$.

$$\psi_{a}(x_{1},x_{2}) = \frac{1}{\sqrt{2}} \left[\psi_{A}(x_{1}) \psi_{B}(x_{2}) - \psi_{A}(x_{2}) \psi_{B}(x_{1}) \right] - (99)$$

Now $\psi_a(x_1, x_2) = -\psi_a(x_2, x_1)$

This is the antisymmetric combination.

A full analysis would include the spin part of the wave functions.

6.4 Pauli Exclusion Principle

It turns out that nature always chooses antisymmetric wave functions for combinations of two or more spin- $\frac{1}{2}$ particles (known as fermions).

Particles with integer spin occur in the symmetric combinations. These are called Bosons. Since, for 2 electrons, the overall function must be of type (99), $\psi_A \neq \psi_B$ or ψ_a would be

zero. Therefore each electron must have a different wave function (i.e. different set of quantum numbers in an atom) \rightarrow Pauli's Exclusion Principle.

"No two electrons in the same atom can have all quantum numbers the same." - (100)

6.5 Multi-Electron atoms

The energy of a level in a multi-electron atom depends on overall charge distribution of the nucleus and other electrons.

Inner electrons partially shield outer ones from nuclear charge, reducing z to z^* or z_{eff} (effective).

Atoms of alkali metals (Li, K, Na, Cs) are particularly "hydrogen-like". Most loosely bound

electron is in $\ell = 0$ state well shielded from the nucleus.

Conventional spectroscopic notation is to label the angular momentum states;

 $\ell = \ 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ \dots$

spd fgh

and precede with values of n. Some ground state configurations are;

He:
$$(1s)^2$$
 (2 electrons, $m_s = \pm \frac{1}{2}$ in 1s level.

Li:
$$(1s)^{2}(2s)^{1}$$

ΚL

Na: $(1s)^{2}(2s)^{2}(2p)^{6}(3s)$

K:
$$(1s)^{2}(2s)^{2}(2p)^{6}(3s)^{2}(3p)^{6}(4s)$$

M N ← Shells

In *k*, the 4s electron "penetrates" closer to nucleus than 3d and so "sees" a larger z_{aff} and so has lower (more negative) energy i.e. more tightly bound.