

Quantum Mechanics

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The mathematical content of this course is actually quite simple, though the reader should ensure they are comfortable with the solution of DEs by separation of variables, and also series solutions, as we shall do both with the Schrödinger equation in this course. The concepts form the more difficult part.

There is some crossover with other courses in this part of the tripos, especially Methods; this is useful to bear in mind and might otherwise only become apparent in retrospect.

Course outline

- Some physical background (1+ lectures)
 - Why do we need QM?
- The Schrödinger equation and its solutions (6 lectures)
 - basic equation
 - physical meaning
 - solutions for various potentials in 1D. These are not purely toy examples, as some physical problems have symmetry which reduces them to a problem in 1 dimension.
- Ways in which QM differs from classical mechanics (5 lectures)
 - mathematical representation of physical concepts
 - uncertainty principle
- The Hydrogen atom (5 lectures)
 - a real 3D application of the rest of the course
 - introduction of angular momentum operators

There will be 3 example sheets for this course.

Recommended books

Landshoff, Methnell and Rees' "Essential Quantum Physics" is probably the best text for this course; alternatively Rae's "Quantum Mechanics" is also good. The relevant section of "The Feynman Lectures on Physics" is of course excellent. For more advanced texts Schiff's "Quantum Mechanics" and Gasiorowicz' "Quantum Physics" are both good ways of going beyond this course.

1 Physical background

Much of this appeared in A-level Physics, but it is nevertheless good to know how the theory originated. New theories in general arise because the existing theory is either contradicted experimentally, or has internal problems (in that it is inconsistent or simply incomplete).

1.1 Classical physics

At the end of the 19th Century there were two basic theories of the physical world.

1.1.1 Newtonian mechanics

- This treats matter as made of point particles moving according to Newton's laws e.g. $\vec{F} = m\vec{a}$.
 - Every particle has definite, measurable energy and momentum
- When combined with the law of gravity, this gives a very successful description of electrically neutral macroscopic systems, e.g. the motion of planets

1.1.2 Maxwell's electromagnetic theory

- Maxwell's Equations - the electric and magnetic fields \vec{E} , \vec{B} in empty space satisfy the wave equation, i.e. $\left(\frac{1}{c^2} \frac{d^2}{dt^2} - \vec{\nabla}^2\right) \begin{pmatrix} \vec{E} \\ \vec{B} \end{pmatrix} = \vec{0}$ for some constant c (the speed of light).
 - These fields propagate as waves with speed c
- Clearly separate from the above - EM radiation and matter are distinct

However, at the microscopic level, experiments challenge this neat division between particles and waves.

1.2 Atomic structure

Matter is composed of molecules, on a scale of $10^{-10} - 10^{-8}m$. These are themselves made up of atoms, on the $10^{-10}m$ scale, which are generally electrically neutral. An atom consists of a central positively charged nucleus, on a scale of around $10^{-15}m$, and orbiting electrons. A typical atom will have some number Z of electrons, giving a charge of $-Ze$ (e being standard notation for the charge on an electron) so the nucleus has a charge of $+Ze$. The electrons are held in orbit by their EM attraction to the nucleus; if some are missing we say the atom is ionized

The nucleus itself contains Z protons each with charge $+e$ and also $A - Z$ neutral neutrons, where A is the mass number of this atom. The electrostatic forces between the protons are repulsive, but the nucleus is held together by nuclear forces, which are strong but short ranged so do not affect the electrons. We have $m_p \approx m_n \approx 2000m_e$ for the respective masses of the proton, neutron and electron, so the mass of the atom is approximately the mass of the nucleus. Therefore we can treat the nucleus as fixed with the electrons moving around it when making calculations.

Even before the experiments below challenged the particle-wave division, there was an issue with this model: the electrons are accelerating (as they are orbiting in a circle or ellipse) and charged, so they should radiate energy, losing speed and collapsing into the nucleus, meaning all atoms should be unstable.

1.3 The photoelectric effect

Initially discovered by Hertz in an 1887 experiment to verify the existence of EM wave, there is an effect whereby light shone on certain metals means electrons escape from the metal. Experimentally it was found that the energy of these electrons is \propto the frequency ν of the light, not its intensity; the number of electrons is proportional to the intensity. Also, there is a threshold frequency; with light below this frequency no electrons escape, no matter how intense the light is. This is a problem for classical physics - we would expect the energy of the electrons to depend on the intensity of the light, so there could be a threshold in intensity for electron emission, but intense enough light of any frequency should work.

Einstein's 1904 explanation, which would win him a Nobel prize, was that EM radiation is composed of lumps of energy, "photons", of energy $h\nu$ where h is Planck's constant. If we use the angular frequency $\omega = 2\pi\nu$, the number of radians per second rather than cycles per second, we instead write this as $\hbar\omega$, where $\hbar = \frac{h}{2\pi}$. Experimentally this can be found to be about $1.05 \times 10^{-34} Js$. (h or \hbar are found a lot in QM, and often one can derive the classical result from the quantum one by having $\hbar \rightarrow 0$.)

Each emitted electron is knocked out of place by a single photon. It will have energy $E = h\nu - W$ where W is the energy needed to escape. If this would give $E \leq 0$, no electrons escape. This model gives a threshold frequency, $\nu = \frac{W}{h}$, and also gives that the number of electrons emitted should be \propto the number of

photons hitting the metal, which is of course \propto the intensity of the light.

1.4 Compton Effect

This shows light exhibits particle behaviour when scattering as well as when being absorbed. Compton in 1922 found X-rays scattered off electrons in atoms had their frequency change proportionally to the scattering angle. Classically we would not only expect the radiation to be isotropic (the same in all directions) but we would expect no frequency change at all. The solution is to treat this scattering as a photon-electron collision with these both particles, behaving like “relativistic billiards”. If we perform the conservation of energy and momentum calculation as in the Special Relativity course, taking the electron initially at rest and the photon colliding with it and scattering at angle θ from its original path, we find $\nu_1 - \nu_2 = \frac{h\nu_1\nu_2}{mc^2}(1 - \cos\theta)$, where m is the mass of the electron. In terms of wavelengths we have $\lambda_2 - \lambda_1 = \frac{h}{mc}(1 - \cos\theta)$. $\frac{h}{mc}$ is called the Compton wavelength of the electron.

1.5 Electron Diffraction

Waves diffract as per Young’s slits. In 1927 both Thompson and a collaboration of Davisson and Germer separately found that electrons also display diffraction; even more unexpectedly, we find the same effect with a beam so weak only one electron is in the system at any time. Experimentally we find the wavelength relates to the electron’s momentum in the same way as for a photon, i.e. by $\lambda = \frac{c}{\gamma} = \frac{h}{p}$ where p is the momentum (for a photon this is $\frac{h\nu}{c}$). This shows that particles have a wave aspect.

1.6 Line Spectra and the Bohr Atom

We have already covered instability; another issue with the classical model of the atom is discrete line spectra. Classically we would expect electrons to emit radiation at all wavelengths, but experimentally we find they only do so in discrete lines (which occur in bunches). This observation fits the rule that radiated wavelengths satisfy $\frac{1}{\lambda} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$ for $n > m \in \mathbb{Z}$, where the Rydberg constant R was found experimentally to be around $1.0967758 \times 10^{-7} m^{-1}$, suggesting electrons can only orbit an atom at various fixed radii.

Bohr’s Explanation

From the diffraction experiment we know the electron has some kind of wave associated with it. We postulate that the circumference of the electron orbit must be a whole number of wavelengths so that this wave does not interfere destructively with itself; $2\pi r = n\lambda = n\frac{h}{p}$, so $rp = n\frac{h}{2\pi} = n\hbar$; this is called Bohr’s quantization condition. We then just apply the classical equations of motion and EM force, obtaining $m\frac{v^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}$ or $\frac{v^2}{m} = \frac{e^2}{4\pi\epsilon_0 r}$. Solving these two equations for r , we have $r = \frac{4\pi\epsilon_0 n^2 \hbar^2}{me^2}$; the electron energy is $E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} =$

$\frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}$; substituting from above this is $\frac{-e^2}{8\pi\epsilon_0 r}$, and substituting for r this becomes $\frac{-e^2}{8\pi\epsilon_0} \frac{me^2}{4\pi\epsilon_0 n^2 \hbar^2}$ which we can express (using E_N to denote that this energy depends on n) as $E_n = -\frac{mc^2 \alpha^2}{2n^2}$ where α is the (dimensionless) fine structure constant $\frac{e^2}{4\pi\epsilon_0 \hbar c}$, which experimentally is found to be $\approx \frac{1}{137}$.

The electron is confined to orbits with discrete values of r , and for the atom to radiate it makes a quantum jump to a lower orbit, emitting the energy thereby lost as a photon of frequency ν . Energy is conserved so the electron energy $E = h\nu$ is $\frac{mc^2 \alpha^2}{2} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$, which gives discrete wavelengths satisfying $\frac{1}{\lambda} = \frac{\nu}{c} = \frac{mc\alpha^2}{2h} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$, which agrees with the experimental results, as does $R = \frac{mc\alpha^2}{2h}$.

While this is a successful theory, it fails to address how or why the electron makes these jumps; while it makes accurate predictions, it is not a fundamental theory.

2 Schrödinger eqn

Rather than deriving this equation from a particular experiment we shall justify it - it leads to a consistent theory which makes predictions which agree with a huge variety of experiments.

2.1 de Broglie Wavelength and the SE

In 1923 de Broglie associated waves with particles. A plane wave is generally given by $\Psi = Ae^{i(\vec{k}\cdot\vec{x}-\omega t)}$. The wavelength is $\frac{2\pi}{|\vec{k}|}$; we identify this with $\frac{h}{|\vec{p}|}$; assuming the vectors are parallel this means $\vec{p} = \hbar\vec{k}$. ω is found via the energy-momentum 4-vector - since $\left(\frac{\omega}{c}, \vec{k}\right)$ is a valid 4-vector it makes sense to say $E = \hbar\omega$, especially since this is the same as for a photon. Then the wave satisfies $\vec{p}\cdot\Psi = -i\hbar\nabla\Psi$ and $\vec{E}\cdot\Psi = i\hbar\frac{\partial\Psi}{\partial t}$. This is a simple wave; it corresponds to constant momentum, i.e. a free particle, but we will generalise later to a particle moving in a general potential. In non-relativistic physics the energy of a free particle is its KE so $E = \frac{\vec{p}^2}{2m}$ which combined with the previous two equations suggests Ψ has $i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi$. This is easily generalised; for a potential V the particle's energy is $\frac{\vec{p}^2}{2m} + V$ and we have $i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$; this is the time-dependent SE; it is the central and basic eqn in non-relativistic QM. In principle V can be any time-dependent vector field, but we shall consider the simpler case where V is a function only of position; this is true unless energy is being fed into the system. Note that this is an operator eqn, not algebraic; operators play an important role in QM

2.2 Probability interpretation, probability density and current

For V non-constant the sols are no longer simple plane waves; we shall still call them wavefunctions. There was a lot of discussion over how to interpret these, but it is now generally accepted that $|\Psi(\vec{x}, t)|^2$ (note this is always real even though $\bar{\lambda}$ may be cplx) represents the (relativ) prob density of finding the particle $\vec{\lambda}$ near the point \vec{x} at time t ; the prob of finding the particle in a volume V at time t is $\frac{\int_V |\Psi(\vec{x}, t)|^2 d^3\vec{x}}{\int_{\text{all space}} |\Psi(\vec{x}, t)|^2 d^3\vec{x}}$. We often normalise Ψ (since if Ψ is a sol of the SE so is $\lambda\Psi \forall \lambda \in \mathbb{R}$) so that $\int_{\text{all space}} |\Psi(\vec{x}, t)|^2 d^3\vec{x} = 1$.

Conservation eqn

We find one of these by assuming the potential is real, i.e $V^* = V$. Let $\rho(\vec{x}, t)$ be the pdf $|\Psi(\vec{x}, t)|^2$; we have $-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}$ so taking the conjugate $-\frac{\hbar^2}{2m}\nabla^2\Psi^* + V\Psi^* = -i\hbar\frac{\partial\Psi^*}{\partial t}$; by taking $\Psi^* \times$ the previous eqn $-\Psi \times$ this we have $-\frac{\hbar^2}{2m}(\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*) = i\hbar\left(\Psi^*\frac{\partial\Psi}{\partial t} + \Psi\frac{\partial\Psi^*}{\partial t}\right) = i\hbar\frac{\partial}{\partial t}(\Psi^*\Psi)$. So $i\hbar\frac{\partial\rho}{\partial t} + \frac{\hbar^2}{2m}\vec{\nabla} \cdot (\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*) = 0$ meaning $\frac{\partial\rho}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0$ (this is the conservation eqn) with a probability current \vec{j} defined by $-\frac{i\hbar}{2m}(\Psi^*\Psi' - \Psi\Psi^*)$.

Proof that total probability remains constant

Consider $\frac{d}{dt} \int_{|\vec{x}| \leq R} |\Psi(\vec{x}, t)|^2 d^3\vec{x} = \frac{d}{dt} \int_{|\vec{x}| \leq R} \rho(\vec{x}, t) d^3\vec{x} = \int_{|\vec{x}| \leq R} \frac{\partial\rho}{\partial t} d^3\vec{x} = \int_{|\vec{x}| \leq R} -\vec{\nabla} \cdot \vec{j} d^3\vec{x}$ from the above, which is $\int_{|\vec{x}|=R} \vec{j} \cdot d\vec{S}$ by the div thm. As $R \rightarrow \infty$ the LHS of this becomes $\frac{d}{dt} \int_{\text{all space}} |\Psi(\vec{x}, t)|^2 d^3\vec{x}$; the RHS $\rightarrow 0$ provided Ψ (and so \vec{j}) $\rightarrow 0$ fast enough as $\vec{x} \rightarrow \infty$, so $\frac{d}{dt} \int_{\text{all space}} |\Psi(\vec{x}, t)|^2 d^3\vec{x} = 0$ and the total probability is constant.

Going back a step, for a given volume V we have $\frac{d}{dt} \int_V \rho(\vec{x}, t) d^3\vec{x} = \int_{\partial V} \vec{j} \cdot d\vec{S}$ - \vec{j} is the rate of flow of probability, $\vec{j} \cdot d\vec{S}$ represents the rate at which probability is flowing into V , equal to the rate of change of the probability of finding the particle represented by Ψ in V .

2.3 Stationary States and the superposition principle

We want to solve the SE to find the energy of a system; one common approach to solving PDEs is by separation of variables, i.e. we look for a sol to the SE of the form $\Psi(\vec{x}, t) = \psi(\vec{x})T(t)$; substituting into the SE and dividing by ψT we have $-\frac{\hbar^2}{2m}\frac{\nabla^2\psi}{\psi} + V(\vec{x}) = \frac{i\hbar}{T}\frac{dT}{dt}$; the LHS is purely a func of \vec{x} and the RHS one of t , so they must both be equal to some constant E . Then we have $i\hbar\frac{dT}{dt} = ET$ so $T(t) = T(0)e^{-\frac{iEt}{\hbar}}$, and $-\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{x})\psi = E\psi$; this last is the time-indep SE. The LHS is the total energy operator $\frac{p^2}{2m} + V$ acting on ψ , so the obvious interpretation of the separation constant E is as total energy; a ψ satisfying this

the spatial wave function of a state with definite energy E and time dependence $e^{-\frac{iEt}{\hbar}}$.

$\Psi(\vec{x}, t) = \psi(\vec{x}) e^{-\frac{iEt}{\hbar}}$; for such a state the prob density is clearly $|\Psi|^2 = |\psi|^2$ indep of t ; states with definite energy are called stationary states.

The time-indep SE in 1D, $\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$ is a Sturm-Liouville eqn so several nice results apply; in particular sols corresponding to different vals of E are orthogonal, $\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = \delta_{mn}$ (assuming the ψ_n are normalised so $\int_{-\infty}^{\infty} |\psi_n|^2 dx = 1$) where ψ_n means a sol ψ for a distinct energy value E_n ; to see this we have $\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} + V(x)\psi_n = E_n\psi_n$ and $\frac{\hbar^2}{2m} \frac{d^2\psi_m}{dx^2} + V(x)\psi_m = E_m\psi_m$; we then have (since $V, E \in \mathbb{R}$) taking the conjugate of the second and multiplying by ψ_m^*, ψ_n respectively that $\frac{\hbar^2}{2m} \psi_m^* \frac{d^2\psi_n}{dx^2} + V(x)\psi_n\psi_m^* = E_n\psi_n\psi_m^*$, $\frac{\hbar^2}{2m} \psi_n \frac{d^2\psi_m^*}{dx^2} + V(x)\psi_n\psi_m^* = E_m\psi_n\psi_m^*$, then subtracting $\frac{\hbar^2}{2m} \left(\psi_m^* \frac{d^2\psi_n}{dx^2} - \psi_n \frac{d^2\psi_m^*}{dx^2} \right) = (E_n - E_m) \psi_n\psi_m^*$ and integrating $\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left(\psi_m^* \frac{d^2\psi_n}{dx^2} - \psi_n \frac{d^2\psi_m^*}{dx^2} \right) dx = (E_n - E_m) \int_{-\infty}^{\infty} \psi_n\psi_m^* dx$; integrating by parts and knowing $\psi_n, \psi_m \rightarrow 0$ as $x \rightarrow \pm\infty$ we have that the LHS is 0, therefore the RHS is also 0 so for $E_n \neq E_m$, $\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0$.

If we have only a discrete spectrum of possible energy variables (which is not the most general situation), furthermore the ψ_n are complete - the most general wave function at $t = 0$ is $\Psi(x, 0) = \sum_n c_n \psi_n(x)$ for constants c_i , which we find for a given $\Psi(x, 0)$ by multiplying both sides by ψ_i^* , integrating and using the orthogonality: $\int_{-\infty}^{\infty} \psi_i^* \Psi(x, 0) dx = \sum_n c_n \int_{-\infty}^{\infty} \psi_i^* \psi_n dx = \sum_n c_n \delta_{in} = c_i$; now we can obtain $\Psi(x, t)$ from this; let $\Psi(x, t) = \sum_n b_n(t) \psi_n(x)$ with $H(\psi_n) = E_n\psi_n$ where $H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V$. Ψ satisfies the time-dep SE $H\Psi = i\hbar \frac{\partial\Psi}{\partial t}$ so $\sum b_n H\psi_n = \sum b_n E_n\psi_n = \sum i\hbar \frac{db_n}{dt} \psi_n$; by orthogonality of ψ_n $E_n b_n = i\hbar \frac{db_n}{dt}$ and $b_n(t) = b_n(0) e^{-\frac{iE_n t}{\hbar}}$, so $\Psi(x, t) = \sum_n b_n(0) e^{-\frac{iE_n t}{\hbar}} \psi_n(x)$; putting $t = 0$ and comparing with the above we have $b_n(0) = c_n$ and $\Psi(x, t) = \sum_n c_n e^{-\frac{iE_n t}{\hbar}} \psi_n(x)$. This is a useful technique for several PDEs; that we can take linear combinations of states with different energies to obtain the general state is called the superposition principle.

The state of a system is therefore in general a linear combination of many different states with definite energies - a superposition. The larger the value of $|c_n|^2$ the more likely the system is to have energy E_n ; in fact for Ψ normalised the reader may verify $\sum |c_n|^2 = 1$ so $|c_n|^2 = \left| \int_{-\infty}^{\infty} \psi_n^*(x) \Psi(x, t) dx \right|^2$ is precisely the probability of the system being in the n th state. We sometimes call this integral an overlay integral.

In the special case $\Psi(x, 0) = \psi_n(x)$ for some n , we have $\Psi(x, t) = \psi_n(x) e^{-\frac{iE_n t}{\hbar}}$; a particular energy eigenstate remains the same state over time. This is another reason we call the states with definite energies stationary states.

3 Sols of the SE in 1D

3.1 The free particle

The wave fn for the free particle satisfies the SE w/ $V = 0$; in 1D, $-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = i\hbar \frac{\partial \Psi}{\partial t}$; we make no assumption of separability due to definite energy. This eqn is the diffusion eqn so can be solved by Fourier anal; taking FTs wrt x we say $\tilde{\Psi}(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-\frac{ipx}{\hbar}} \Psi(x, t) dx$, $\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{ipx}{\hbar}} \tilde{\Psi}(p, t) dp$; note that we have split the constant A and are using $\frac{p}{\hbar}$ in place of k in comparison to the Methods course. Recall that the FT of $\frac{\partial \Psi}{\partial x}$ is $\frac{ip}{\hbar} \tilde{\Psi}$, so the FT of the SE is $-\frac{\hbar^2}{2m} \left(\frac{ip}{\hbar}\right)^2 \tilde{\Psi}(p, t) = i\hbar \frac{\partial \tilde{\Psi}}{\partial t}(p, t)$; $\frac{\partial \tilde{\Psi}}{\partial t} = -\frac{ip^2}{2m\hbar} \tilde{\Psi}$ so $\tilde{\Psi}(p, t) = \tilde{\Psi}(p, 0) e^{-\frac{ip^2 t}{2m\hbar}}$; taking the IFT $\Psi(x, t) = \frac{1}{\sqrt{\hbar}} \int_{-\infty}^{\infty} e^{\frac{ipx}{\hbar}} e^{-\frac{ip^2 t}{2m\hbar}} \tilde{\Psi}(p, 0) dp$ (as $\hbar = 2\pi\hbar$); we can find this for a given $\Psi(x, 0)$ as $\tilde{\Psi}(p, 0) = \frac{1}{\sqrt{\hbar}} \int_{-\infty}^{\infty} e^{-\frac{ipx}{\hbar}} \Psi(x, 0) dt$.

3.2 The Gaussian wave packet

For $\Psi(x, 0) = Ne^{-\frac{x^2}{a^2}}$, assuming this is normalised we must have $1 = \int_{-\infty}^{\infty} |\Psi(x, 0)|^2 dx = |N|^2 \int_{-\infty}^{\infty} e^{-2\frac{x^2}{a^2}} dx = |N|^2 \frac{a}{\sqrt{2}} \sqrt{\pi}$, so $N = a^{-\frac{1}{2}} \left(\frac{\pi}{2}\right)^{-\frac{1}{4}}$. Now we find $\Psi(x, t)$ by the same method as above; $\tilde{\Psi}(p, 0) = \frac{N}{\sqrt{\hbar}} \int_{-\infty}^{\infty} e^{-\frac{ipx}{\hbar}} e^{-\frac{x^2}{a^2}} dx = \frac{N}{\sqrt{\hbar}} \int_{-\infty}^{\infty} e^{-p^2 \left(\frac{a^2}{4\hbar^2} + \frac{it}{2m\hbar}\right) + \frac{ipx}{\hbar}} dx = \left(\frac{2\hbar}{a}\right)^{-\frac{1}{2}} \left(\frac{\pi}{2}\right)^{-\frac{1}{4}} e^{-\frac{p^2 a^2}{4\pi^2}}$. Therefore $\Psi(x, t) = \frac{1}{\sqrt{\hbar}} \int_{-\infty}^{\infty} \frac{a^n}{(2\pi)^{\frac{3}{4}} \hbar} e^{-p^2 \left(\frac{a^2}{4\hbar^2} + \frac{it}{2m\hbar}\right) + \frac{ipx}{\hbar}}$; we let $\frac{\beta^2}{4\hbar^2} = \frac{a^2}{4\hbar^2} + \frac{it}{2m\hbar}$ so $-p^2 \left(\frac{a^2}{4\hbar^2} + \frac{it}{2m\hbar}\right) + \frac{ipx}{\hbar} = -\frac{\beta^2 p^2}{4\hbar^2} + \frac{ipx}{\hbar} = -\left(\frac{\beta p}{2\hbar} - ix\right)^2 - \frac{x^2}{\beta^2}$ [check all of this, I'm zonked] and then this becomes $\frac{a^{\frac{1}{2}}}{(2\pi)^{\frac{3}{4}} \hbar} \sqrt{\pi} \frac{2\hbar}{\beta} e^{-\frac{x^2}{\beta^2}} = \frac{\sqrt{\alpha}}{\beta} \left(\frac{\pi}{2}\right)^{-\frac{1}{4}} e^{-\frac{x^2}{\beta^2}}$; notice that $|\Psi(x, t)|^2 = \left(\frac{\pi}{2}\right)^{-\frac{1}{2}} \frac{a}{|\beta|^2} e^{-2\frac{x^2}{|\beta|^2}}$ which is the expression for $|\Psi(x, 0)|^2$ but with a replaced by $\frac{|\beta|^2}{a}$ (note β is complex) which is $\left(a^2 + \frac{4\hbar^2 t^2}{m^2 a^2}\right)^{\frac{1}{2}}$ so $> a$ for $t > 0$ - the height of the Gaussian is $\frac{1}{a}$ at $t = 0$ and then $\frac{a}{|\beta|^2} < a$ for $t > 0$, while the distance from the centre at which the height is $\frac{1}{2}$ the peak is $a \log \sqrt{2}$ for $t = 0$ but then $\frac{|\beta|^2}{a} \log \sqrt{2}$ [sqrt omitted in lecture] - over time the wave packet spreads out, as we would expect for a free particle.

3.3 Motion in 1D potentials, parity

The neatest way to obtain $\Psi(x, t)$ is by expansion in terms of sols ψ of the time-indep SE with definite E ; usually we have $|\psi| \rightarrow 0$ as $|x| \rightarrow \infty$ or alternatively $|\psi| \sim 1$ for wavelike sols; we are not interested in sols which behave badly (i.e. $\rightarrow \infty$) at ∞ . Typically for a given potential $V(x)$ which $\rightarrow V_\infty$ at ∞ there are 3 classes of possible vals of E : for some vals between V_{\min} and V_∞ \exists sols of the SE which $\rightarrow 0$ fairly rapidly at ∞ , while for other E in this range the sols

behave badly at ∞ so are of no interest to us. Finally for any $E > V_\infty \exists$ sols which behave like plane waves at ∞ .

In general the potential will take some minimum value V_0 at, around or near the origin and tend towards its maximum value V_∞ at ∞ . In the range between V_0 and V_∞ there will be a finite or countable number of possible values for E which give class i solutions ($\rightarrow 0$ at ∞); these form the discrete part of the energy spectrum, while the others give class ii solutions (badly behaved at ∞) which we are not interested in. $E > V_\infty$ always has a class iii solution (~ 1 (i.e. behaved like plane waves) at ∞); these form the cnts part of the energy spectrum. We need both classes i and iii to form a complete set of ψ in terms of which we can expand a general $\Psi(\vec{x}, t)$.

Recall that vals of E are the possible results of measuring the energy of the system, and the ψ are the corresponding energy eigenfunctions.

Summary: properties of and requirements on the wf

The WF is a sol of the SE satisfying appropriate BCs; if it is normalizable we have the prob interpretation. For motion in a smooth potential we need only apply the BCs as $|x| \rightarrow \infty$ which are $\psi \rightarrow 0$ for bound states (the discrete part of the spectrim) or $|\psi| \sim 1$ for the cnts part. For a merely piecewise cnts potential we also need BCs at the points of discontinuity; ψ must be a cnts (single-vald) func $\forall x, t$ as otherwise $\frac{\partial^2 \psi}{\partial x^2}$ would blow up, and $\frac{\partial \psi}{\partial x}$ must be cnts everywhere except where there is an infinite jump in V , since this is precisely where $\frac{\partial^2 \psi}{\partial x^2}$ may be infinite to balance the SE.

Parity

WFs are odd or even wrt \vec{x} by the usual definitions; we can write any wf as a sum of even and odd parts as usual.

3.4 The infinite square well

This is a model of a particle confined to a finite region or "box" $0 < x < a$; $V(x) = 0$ for $0 < x < a$, ∞ otherwise. We can assume $\psi(x, t) = 0$ for $x < 0$ or $> a$ as otherwise the $V\psi$ term in the SE is undefined. We look for states with definite energies by solving the time-indep SE: for $0 < x < a$ $-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi$ with $\psi(0) = \psi(a) = 0$; ψ' may be discnts at these points as there is an infinite jump in V . We always assume $V > V_{\min}$, in this case 0. Now to simplify notation we define $k^2 = \frac{2mE}{\hbar^2}$ so the SE becomes $\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0$ so $\psi = A \cos kx + B \sin kx$ for A, B constants. Applying the BCs $A = 0$ and $B \sin ka = 0$; we assume $B \neq 0$ as otherwise the sol is trivial so $k = \frac{n\pi}{a}$ for $n \in \mathbb{Z}$; note this determines E so we have quantized (discrete) energy levels s a direct result of the BCs. We then have $\psi_n = B \sin \frac{n\pi x}{a}$ and normalizing ($\int_{-\infty}^{\infty} |\psi|^2 dx = 1$) we find $B = \frac{\sqrt{2}}{a}$ so $\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ for $n = 1, 2, \dots$ w/ $E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$; we only have the the discrete spectrum since V_∞ is ∞ (we can also take the well being from $-a$ to

+ a in which case we get alternating (as n increases) odd solutions in terms of sin and even ones in terms of cos; the reader may wish to explore this further). The GS will be a lin comb of these energy eigenstates; if $\Psi(x, 0) = \sum_n c_n \psi_n(x)$ then $\Psi(x, t) = \sum_n c_n e^{-\frac{iE_n t}{\hbar}} \psi_n(x)$.

3.5 The (finite) square well

This is somewhat close to a model of the potential produced by the nucleus: $V(x) = -V_0$ for $|x| < a$, 0 otherwise. Since V is symmetric, if $\psi(x)$ is a sol for a given E so is $\psi(-x)$, as the reader may verify by substitution into the SE. Then $\psi_{\pm}(x) = \psi(x) \pm \psi(-x)$ are also sols for this same value of E ; we therefore only need to look for sols of definite parity, as our GS will be a sin comb of these. Note if these two sols are lin dep we have $\psi(-x) = \eta\psi(x)$ so $\eta^2 = 1$ and $\eta = \pm 1$ so ψ has definite parity. We will consider the two types of sol in term.

For bound states (normalizable sols) we need $\psi \rightarrow 0$ as $|x| \rightarrow \infty$ and have $-V_0 < E < 0$. For $|x| > a$ $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$, for $|x| < a$ $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - V_0\psi = E\psi$. We define $\beta^2 = \frac{-2mE}{\hbar^2}$, $k^2 = \frac{2m}{\hbar^2}(E + V_0)$; note β, k real. Then for $|x| > a$, $\psi'' - \beta^2\psi = 0$ with sols $e^{\pm\beta x}$ and for $|x| < a$ $\psi'' + k^2\psi = 0$ w/ sols $\cos kx, \sin kx$ (we use these forms rather than exponentials since we want to consider parity).

Even sols

$\psi = Ae^{-\beta|x|}$ for $|x| > a$, $B \cos kx$ for $|x| < a$. At $x = a$ ψ is cnts so $Ae^{-\beta a} = B \cos ka$ and ψ' is also cnts so $-\beta Ae^{-\beta a} = -kB \sin ka$ (since ψ is even $x = -a$ gives us exactly the same boundary conds); dividing these we have $\beta = k \tan ka$; this is an implicit eqn for E but somewhat horrible when we substitute for β, k and not soluble in closed form. However, we can still ask whether it has sols and what form they take. We have from their defs that $\beta^2 + k^2 = \frac{2mV_0}{\hbar^2}$; let $\xi = \beta a, \eta = ka$. Then $\xi = \eta \tan \eta$, $\xi^2 + \eta^2 = \frac{2mV_0 a^2}{\hbar^2}$. If we plot ξ against η we have stretched tan curves the first eqn ξ and a circle for the second; as V_0 gets larger there are more sols as the circle's radius increases so it intersects the near periodic tanlike curve more times in the first quadrant (we are taking $\beta, k > 0$), but there is always at least one sol where the two curves intersect.

Odd sols

$\psi = Ce^{-\beta x}$ for $x > a$, $D \sin kx$ for $|x| < a$ and $-Ce^{\beta x}$ for $x < -a$; continuity at join (again, we will get the same conds from both joins) gives $Ce^{-\beta a} = D \sin ka$, $-\beta Ce^{-\beta a} = kD \cos ka$ (if we want to find the actual sol we must return to this stage; we can find one constant in terms of the other from these BCs and then use that ψ is normalized to find the final constant); dividing, for ξ, β as before we have $\xi = -\eta \cot \eta$, $\xi^2 + \eta^2 = \frac{2mV_0 a^2}{\hbar^2}$. This time the first graph starts from -1 , curves up through 0 at $\frac{\pi}{2}$, and thereafter behaves as a tanlike curve shifted $\frac{\pi}{2}$ to the right, while the second is of course a circle as before. This

means there are no sols if the radius of the circle is $< \frac{\pi}{2}$, i.e. $\frac{2mV_0a^2}{\hbar^2} < \left(\frac{\pi}{2}\right)^2$ or $V_0 < \frac{\pi^2\hbar^2}{8ma^2}$; again we have more sols as V_0 gets larger, but the results are clearly all discrete and have discrete values of E .

Continuum states

For $E > V_\infty = 0$ define $k^2 = \frac{2mE}{\hbar^2}$, $l^2 = \frac{2m}{\hbar^2}(E + V_0)$, then for $|x| > a$ $\psi'' + k^2\psi = 0$ and for $|x| < a$, $\psi'' + l^2\psi = 0$ so the sols are $A \cos kx + B \sin kx$ for $|x| > a$ (with some changes of sign for $x < 0$ to make ψ odd or even) and $C \cos lx$ for even ψ , $D \sin lx$ for odd ψ , for $|x| < a$; the BCs give no constraints on k, l , we find a sol for general $E > 0$ since both A, B are free to satisfy that ψ, ψ' cnts at $x = \pm a$, so we have a continuum of energy eigenvals. These sols have an interpretation in terms of scattering; see below.

3.6 Scattering from a finite barrier

Consider a potential barrier of height V_0 from $x = 0$ to $x = a$, with $V = 0$ elsewhere; the symmetric version of this reduces to the previous problem when $V_0 < 0$. Classically, if a beam of particles arrives from the left with energy $< V_0$ it will not be able to cross the barrier. For $E > V_0$ we get continuum states as above, so take $0 < E < V_0$:

For $x < 0$ or $x > a$, $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$; for $0 < x < a$, $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V_0\psi = E\psi$. We define $k^2 = \frac{2mE}{\hbar^2}$, $\beta^2 = \frac{2m}{\hbar^2}(V_0 - E)$, then for $x < 0$ or $> a$ $\psi'' + k^2\psi = 0$ and for $0 < x < a$, $\psi'' - \beta^2\psi = 0$. For $x < 0$ or $> a$ we have sols of the form $e^{\pm ikx}$; if we let $\psi = Ae^{ikx}$ $\int |\psi|^2 dx = |A|^2$ per unit length; we interpret this as a beam of particles with density $|A|^2$; they have momentum $\hbar k$ so velocity $\frac{\hbar k}{m}$ and the flux of particles per unit time is $|A|^2 \frac{\hbar k}{m}$. The reader can verify this is exactly the probability current given by $j = -\frac{i\hbar}{2m} \left(\psi^* \frac{d\psi}{dx} - \psi \frac{d\psi^*}{dx} \right)$.

Now let $\psi = Ae^{ikx} + Be^{-ikx}$ and $j = \frac{\hbar k}{m} (|A|^2 - |B|^2)$. We say e^{ikx} is a wave moving to the right as when we consider time dependence this becomes $e^{i(kx - \frac{Et}{\hbar})}$ so a point of certain height moves to the right as t increases, similarly e^{-ikx} moves to the left, so this represents two beams of particles, one moving to the right with density $|A|^2$, the other to the left with density $|B|^2$.

We look for a sol of the SE of the form $\psi = Ae^{ikx} + Be^{-ikx}$ for $x < 0$, $Ce^{\beta x} + De^{-\beta x}$ for $0 < x < a$, and Fe^{ikx} for $x > a$ - there is no wave coming from the right for $x > a$ (though there is a reflected wave moving to the right for $x < 0$) because we are assuming there is no source of particles at $+\infty$.

Energy in this problem is continuous and uninteresting; a more interesting problem is the probabilities of reflection and transmission, which are given by the reflection coefficient $R = \frac{\text{reflected flux}}{\text{incident flux}} = \frac{|j_R|}{|j_I|} = \frac{\frac{\hbar k |B|^2}{m}}{\frac{\hbar k |A|^2}{m}} = \frac{|B|^2}{|A|^2}$ (this formula is true in general) and transmission coefficient $T = \frac{\text{transmitted flux}}{\text{incident flux}} = \frac{|j_T|}{|j_I|} =$

$\frac{\hbar k |F|^2}{\frac{\hbar k |A|^2}{m}} = \frac{|F|^2}{|A|^2}$ (the specifics of this formula depend on the problem); to calculate these we need to relate B, F, A which we do by using the BCs; at $x = 0$ ψ cnts gives $A + B = C + D$ and ψ' cnts implies $ik(A - B) = \beta(C - D)$. Solving these for A, B in terms of C, D we have $A = \frac{1}{2}((1 + \lambda)C + (1 - \lambda)D)$, $B = \frac{1}{2}((1 - \lambda)C + (1 + \lambda)D)$ where $\lambda = \frac{\beta}{ik}$ is simply notation. Then at $x = a$ ψ cnts gives us $F e^{ika} = C e^{\beta a} + D e^{-\beta a}$, ψ' cnts gives $\frac{1}{\lambda} F e^{ika} = C e^{\beta a} - D e^{-\beta a}$ from which we find $C e^{\beta a} = \frac{1}{2}(1 + \frac{1}{\lambda}) F e^{ika}$, $D e^{-\beta a} = \frac{1}{2}(1 - \frac{1}{\lambda}) F e^{ika}$, then substituting into our expressions for A, B we have $A = \frac{1}{2ik\beta}(-(\beta^2 - k^2) \sinh \beta a + 2ik\beta \cosh \beta a) F e^{ika}$, $B = \frac{1}{2ik\beta}(\beta^2 + k^2) \sinh \beta a F e^{ika}$ so $\frac{B}{A} = \frac{(\beta^2 + k^2) \sinh \beta a}{2ik\beta \cosh \beta a - (\beta^2 - k^2) \sinh \beta a}$, $\frac{F}{A} = \frac{2ik\beta e^{-ika}}{2ik\beta \cosh \beta a - (\beta^2 - k^2) \sinh \beta a}$ so the reflection and transmission coeffs are $R = \frac{(\beta^2 + k^2)^2 \sinh^2 \beta a}{4k^2 \beta^2 \cosh^2 \beta a + (\beta^2 - k^2)^2 \sinh^2 \beta a}$, $T = \frac{4k^2 \beta^2}{4k^2 \beta^2 \cosh^2 \beta a + (\beta^2 - k^2)^2 \sinh^2 \beta a}$. $R + T = 1$ as we would expect; the probability is conserved, all particles are either reflected or transmitted.

Note that the trans prob is nonzero - this is the phenomenon of tunnelling. It is especially important for e.g. emission of α particles in radioactive decay - particles can escape the nucleus even with energies $<$ the height of the potential barrier in their way. Note that as $V_0 \rightarrow \infty$ $\beta \rightarrow \infty$, $R \rightarrow 1$ and $T \rightarrow 0$ - all particles are reflected if the barrier is infinitely high.

To study scattering from a well we put $V_0 = -U_0$ but still take $E > 0$; we have $k^2 = \frac{2mE}{\hbar^2}$ as before but $\beta^2 = -\frac{2m}{\hbar^2}(E + U_0) = -\gamma^2$ for γ real so we replace β by $i\gamma$ above and have $R = \frac{(k^2 - \gamma^2)^2 \sin^2 \gamma a}{4k^2 \gamma^2 \cos^2 \gamma a + (k^2 + \gamma^2)^2 \sin^2 \gamma a}$, $T = \frac{4k^2 \gamma^2}{4k^2 \gamma^2 \cos^2 \gamma a + (k^2 + \gamma^2)^2 \sin^2 \gamma a}$; in general (i.e. except for some particular vals of γ and k) R is nonzero, a nonintuitive result; we still have $R + T = 1$. It is in fact the case that only constant potentials have 0 prob of reflection.

3.7 Potential Step

There are various varieties of potential steps. First we consider $V = V_0 > 0$ for $x > 0$, 0 for $x < 0$ with $E > V_0$. For $x < 0$ $-\frac{\hbar^2}{2m}\psi'' = E\psi$, for $x > 0$ $-\frac{\hbar^2}{2m}\psi'' + V_0\psi = E\psi$. We put $k^2 = \frac{2mE}{\hbar^2}$, $l^2 = \frac{2m}{\hbar^2}(E - V_0)$, then for $x < 0$ $\psi = A e^{ikx} + B e^{-ikx}$ and for $x > 0$ $\psi = C e^{ilx}$ (as before we assume there is no source of particles at $+\infty$). Then at $x = 0$ ψ cnts so $A + B = C$, ψ' cnts so $k(A - B) = lC$ so $(k - l)A = (k + l)B$, $2kA = (k + l)C$. Then $R = \frac{(k-l)^2}{(k+l)^2}$ but this time $T = \frac{\hbar l |C|^2}{\frac{\hbar k |A|^2}{m}} = \frac{l|C|^2}{k|A|^2}$; this is different from last time since the potentials are different at $+\infty$ and $-\infty$. If we forget to include the factors of k, l we find $R + T \neq 1$. In this case we have $T = \frac{4kl}{(k+l)^2}$; note that classically all the particles are transmitted.

For the case $0 < E < V_0$ in the same potential we have k^2 as before but put $\beta^2 = \frac{2m}{\hbar^2}(V_0 - E)$; for $x < 0$ $\psi = A e^{ikx} + B e^{-ikx}$ but now for $x > 0$ $\psi = C e^{\beta x} + D e^{-\beta x}$; $C = 0$ as ψ is finite as $x \rightarrow \infty$. Then by continuity at

$x = 0$, $A + B = D$, $ik(A - B) = -\beta D$; we find $(ik + \beta)A = (ik - \beta)B$, $2ikA = (ik - \beta)D$ so $R = 1$, and $T = \frac{|j_T|}{|j_I|} = 0$ as $j_T = 0$, because $j \sim (\psi^*\psi' + \psi\psi'^*)$. So $R + T = 1$ and all particles are reflected, but the probability density for $x > 0$ is $|D|^2 e^{-2\beta x} = \frac{4|A|^2 k^2 e^{-2\beta x}}{k^2 + \beta^2}$ [check]; while this is not 0 it falls off exponentially with distance, so the result makes sense; T measures the probability of being transmitted all the way to $+\infty$.

Finally we consider the case of a potential drop, $V = 0$ for $x < 0$, $-V_0$ for $x > 0$, for $E > 0$. As before we solve the SE; if we put $k^2 = \frac{2mE}{\hbar^2}$, $l^2 = \frac{2m}{\hbar^2}(E + V_0)$ then this reduces to the first case in this section, so we have $R \neq 0, T \neq 0$. This is very surprising; classically no particles would be reflected by a drop in potential.

3.8 The Harmonic Oscillator

This plays a basic role in both classical and quantum physics; even for a forcing f not $\propto x$ we can take the first term of the Taylor series about the point of equilibrium if the oscillations are small.

For the SHO we take $V(x) = \frac{1}{2}m\omega^2 x^2$ (since $F = -\frac{dV}{dx}$ should be $\propto -x$, so $V \propto \frac{x^2}{2}$); we find ω is the freq of the oscillator. $V \rightarrow \infty$ as $|x| \rightarrow \infty$, so we only expect to find discrete sols of the SE, and V is cnts so the only BCs are those at $\pm\infty$. The SE is $-\frac{\hbar^2}{2m}\psi'' + \frac{1}{2}m\omega^2 x^2 \psi = E\psi$; we change vars by $x = \mu y$, $E = \frac{\hbar\omega}{2}\lambda$, where $\mu = \sqrt{\frac{\hbar}{m\omega}}$. Then we have $\psi'' - y^2\psi = -\lambda\psi$ [I probably should have used explicit x and y derivatives for clarity; apologies].

For large y we have $\psi'' - y^2\psi \sim 0$ so $\psi \sim e^{\pm\frac{1}{2}y^2}$ (the reader should check this is the sol; remember to ignore non-dominant terms); we have ψ finite as $y \rightarrow \pm\infty$ so $\psi \sim e^{-\frac{1}{2}y^2}$. We then extract this large y behaviour by $\psi = e^{-\frac{1}{2}y^2}H(y)$ in the hope of obtaining an easier eqn for H ; we find $H'' - 2yH' + (\lambda - 1)H = 0$; then we solve this by series; $y = 0$ is not a singular point so we can simply use $H(y) = \sum_{n=0}^{\infty} a_n y^n$; substituting this in and equating coefficients of y we have $a_{n+2}(n+2)(n+1) - 2a_n n + (\lambda - 1)a_n = 0$ giving $a_{n+2} = \frac{(2n-\lambda+1)}{(n+1)(n+2)}a_n$; so we have a_{2n} in terms of a_0 and a_{2n+1} in terms of a_1 , giving our two lin ind sols, a series of even powers and a series of odd powers. We should at this point be concerned about the BCs; although $e^{-\frac{1}{2}y^2} \rightarrow 0$ as $y \rightarrow \pm\infty$, a sufficiently large H could dominate this meaning $\psi \nrightarrow 0$. The even series is given by $a_{2n+2} = \frac{(4n-\lambda+1)}{(2n+1)(2n+2)}a_{2n}$; for large n $a_{2n+2} \sim \frac{1}{n}a_{2n}$ which is the same behaviour as that of the coeffs in the expansion of $e^{y^2} = \sum_n n!y^{2n}$, so $H \sim e^{y^2}$ and $\psi = He^{-\frac{1}{2}y^2} \sim e^{\frac{1}{2}y^2} \nrightarrow 0$ as $y \rightarrow \infty$; we avoid this problem iff the series terminates, since then $\psi = p(y)e^{-\frac{1}{2}y^2}$ for some poly p . The series terminates if $a_{2n+2} = 0$ for some $n \in \mathbb{N}_0$, meaning $\lambda = 4n + 1$; H will then be a poly of deg $2n$. Sim for odd series $a_{2n+1} = \frac{(4n-\lambda-1)}{2n(2n+1)}a_{2n-1}$ and this must terminate so $\lambda = 4n - 1$ and H is a poly of deg $2n - 1$; combining these two sols for $\lambda = 2N + 1$ we have a sol $H = H_N(y)$ a poly of deg N . These are Hermite polys; for even N they contain only even powers and vv. So the

energy eigenvals are $E_N = \frac{\hbar\omega}{2}\lambda_N = (N + \frac{1}{2})\hbar\omega$ for $N \geq 0$ w/ corresponding efuncs $\psi_N(x) = H_n\left(\sqrt{\frac{N\omega}{\hbar}}x\right)\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$; we have only a discrete spectrum of energy vals as we would expect. The ground state (state w/ lowest energy) is here given by $N = 0$, i.e. $E_0 = \frac{1}{2}\hbar\omega$; this is sometimes called the zero point energy. Classically an energy of 0 would be possible, but in QM a particle of definite location must have some momentum, so some energy, by the uncertainty principle. The corresponding WF is $\psi_0 = H_0 e^{-\frac{1}{2}\frac{m\omega x^2}{\hbar}}$; H_0 is a poly of deg 0 so a constant; normalization gives $1 = \int_{-\infty}^{\infty} |\psi|^2 dx = |H_0|^2 \int_{-\infty}^{\infty} e^{-\frac{1}{\hbar}m\omega x^2} dx = |H_0|^2 \sqrt{\frac{\pi\hbar}{m\omega}}$ so $\psi_0(x) = \sqrt{\frac{m\omega}{\pi\hbar}} e^{-\frac{m\omega x^2}{2\hbar}}$; $H_1 \propto y$, $H_2 \propto 2y^2 - 1$ and so on. We don't need to go through the entire series sol for small N , we can find e.g. H_3 by trying a poly of the right form $(Ay + By^3)$ in the DE for H with $\lambda = 2n + 1$ (7 in this case).

Interpretation of wave functions

As stated before, $|\psi(x)|^2$ represents the prob of finding the particle represented by ψ between x and $x + dx$. In the infinite sqare well example, $|\psi_n(x)|^2 = \frac{2}{a} \sin^2 \frac{n\pi x}{a}$; for $n = 1$ this is a central bump, for $n = 2$ there are two bumps and the probability is in fact 0 at the origin; for all n it is 0 at the boundary of the well; contrast this with classical mechanics where the prob density would be $\frac{1}{a}$ for the whole of the well. For the finite sqare well we have similar oscillations within the well but we have exponential decay outside the well rather than zero probability; the particle may be outside the well. For a potential step upwards from 0 to V_0 with $0 < E < V_0$ we have sinusodal oscillations approaching from $-\infty$ with a maximum at 0, then exponential decay; there is a nonzero prob of crossing the step but the probability of reaching $+\infty$ decays exponentially; $j_T = 0$. For SHO we have a gaussian or similar for $n = 0$, a similar wave but with two bumps for $n = 1$, and for n large many oscillations in the middle but again exponential decay at both ends.

4 Observables and expectation values

We need to set up our basic postulates to put the theory on a firm conceptual basis; we also want to relate the theory to experiment so we consider the process of measurement, observables and so forth.

4.1 Basic postulates of QM

Postulate I: The wave function

At any given time the states of a physical system correspond to nonzero cplx-vald funcs (wavefuncs) ψ of the position coordinates \vec{x} with $\psi(\vec{x})$ and $\lambda\psi(x)$ for $\lambda \neq 0 \in \mathbb{C}$ corresponding to the same state; furthermore the wavefunc of a physical state is square integrable so we may def $\|\psi\| = \int |\psi(\vec{x})|^2 d\vec{x}$ [LHS

squared in lecture]; to give meaning to this for a plane wave sol we consider it as being confined to a large but finite region.

Def a complex inner (scalar) product in the space of wavefunctions by $(\phi, \psi) = \int_{\text{all space}} \phi^*(\vec{x}) \psi(\vec{x}) d^3\vec{x}$ (we could equally well use $\phi\psi^*$ but must take one or the other). Note:

1. Since $\frac{\psi(x)}{\|\psi\|}$ represents the same physical state as $\psi(x)$ we can usually take $\|\psi\| = 1$; in this case we say the wf is normalized.
2. For two particles at \vec{x}_1, \vec{x}_2 we have a wf $\psi(\vec{x}_1, \vec{x}_2)$, and similarly for n particles
3. We have the usual cplx scalar prod props: $(\phi, \psi) = (\psi, \phi)^*$, $(\phi, \lambda_1\psi_1 + \lambda_2\psi_2) = \lambda_1(\phi, \psi_1) + \lambda_2(\phi, \psi_2)$, $(\lambda_1\phi_1 + \lambda_2\phi_2, \psi) = \lambda_1^*(\phi_1, \psi) + \lambda_2^*(\phi_2, \psi)$

Postulate II: Observables and operators

The observables (measurable dynamical variables) such as position, momentum and energy correspond to Hermitian (i.e. self-adjoint) linear (possibly differential) operators Q on the sp of wfs; since these are lin we may form lin combs of wfs; again this is the superposition prinzip. The evals are the possible results of measuring the corresponding observable; the expectation value of Q , the average result of measuring Q in a normalized state ψ , is $\langle Q \rangle = \frac{(\psi, Q\psi)}{(\psi, \psi)} = (\psi, Q\psi) = \int \psi^* Q\psi d^3\vec{x}$. Note the hermitian conj Q^\dagger of Q is defd by $(\phi, Q\psi) = (Q^\dagger\phi, \psi)$; since Q is Hermitian we have $(\phi, Q\psi) = (Q\phi, \psi)$ which implies that the evals of Q are real; suppose $Q\psi_i = q_i\psi_i$, then $(\psi_i, Q\psi_i) = (Q\psi_i, \psi_i) \therefore (\psi_i, q_i\psi_i) = (q_i\psi_i, \psi_i)$ so $q_i(\psi_i, \psi_i) = q_i^*(\psi_i, \psi_i)$; $\|\psi_i\|^2 \neq 0$ since ψ_i is an estate so $q_i = q_i^*$ meaning $q_i \in \mathbb{R}$. Also $(\psi_i, Q\psi_j) = (Q\psi_i, \psi_j)$ so $(q_j - q_i)(\psi_i, \psi_j) = 0$; $(\psi_i, \psi_j) = 0$ for $q_i \neq q_j$ and the estates are orthog. Finally $\frac{(\psi, Q\psi)}{(\psi, \psi)}$ is invariant under $\psi \mapsto \lambda\psi$, supporting the claim that $\psi, \lambda\psi$ represent the same physical state.

Postulate III: Dynamics

If $\Psi(\vec{x}, t)$ is the wf of the system at time t then $i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$ determines $\Psi(\vec{x}, t)$ in terms of $\Psi(\vec{x}, 0)$ where H is the Hamiltonian of the system, in general the energy operator $-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x})$, so this eqn is simply the normal SE. Note that H is Hermitian, since we shall later show $-i\hbar \frac{\partial}{\partial x}$ is Hermitian so $-\hbar \frac{\partial^2}{\partial x^2}$ is, and so forth.

4.2 Position and momentum operators

Position is represented by the Hermitian operator \vec{x} or \hat{x} (the $\hat{}$ indicating this is an operator); this is Hermitian since $(\phi, \vec{x}\psi) = \int \phi^* \vec{x}\psi d\vec{x} = \int \vec{x}\phi^* \psi d\vec{x} = (\vec{x}\phi, \psi)$ since \vec{x} is real. The expectation of this is $\langle \vec{x} \rangle = (\psi, \vec{x}\psi) = \int \vec{x} |\psi|^2 d^3\vec{x}$ (if

$\|\psi\| = 1$); this agrees with our interpretation of $|\psi|^2$ as the p.d.f. of finding the particle near \vec{x} .

The operator corresponding to momentum p is $-i\hbar\nabla$, as was assumed in 2.1. We shall only show it is Hermitian in 1D, but the generalisation to 3D is straightforward: $p = -i\hbar\frac{\partial}{\partial x}$ and then $(\phi, p\psi) = -i\hbar\int_{-\infty}^{\infty}\phi^*\frac{\partial\psi}{\partial x}dx$ which integrating by parts is $-i\hbar[\phi^*\psi]_{-\infty}^{\infty} + i\hbar\int_{-\infty}^{\infty}\frac{\partial\psi^*}{\partial x}\psi dx$; the first term is 0 for the class of functions we are considering ($\psi, \phi \rightarrow 0$ as $|x| \rightarrow \infty$) so this is $\int_{-\infty}^{\infty}\left(-i\hbar\frac{\partial\phi}{\partial x}\right)^*\psi dx$ and done.

The expectation of \vec{p} at any time is $\langle\vec{p}\rangle = (\psi, \vec{p}\psi) = -i\hbar\int\psi^*\nabla\psi d^3\vec{x}$ (where we normalize so $\|\psi\| = 1$ as always).

For example, consider the following generalisation of the Gaussian wave packet (sol for free particle) at $t = 0$: $\Psi(x, 0) = \sqrt{\frac{2}{\pi a^2}}e^{-\frac{x^2}{a^2} + i\frac{p_0 x}{\hbar}}$; the reader may verify this is normalized; want to find $\langle x \rangle, \langle p \rangle$.

$\langle x \rangle = \int_{-\infty}^{\infty}\Psi^*x\Psi = \sqrt{\frac{2}{a^2\pi}}\int_{-\infty}^{\infty}xe^{-2\frac{x^2}{a^2}}dx = 0$ since the integrand is odd, as we would expect since $|\psi|^2$ is symmetric.

$\langle p \rangle = \int_{-\infty}^{\infty}\Psi^*p\Psi = -i\hbar\sqrt{\frac{2}{a^2\pi}}\int_{-\infty}^{\infty}e^{-\frac{x^2}{a^2} - i\frac{p_0 x}{\hbar}}\frac{d}{dx}\left(e^{-\frac{x^2}{a^2} + i\frac{p_0 x}{\hbar}}\right)dx = -i\hbar\sqrt{\frac{2}{a^2\pi}}\int_{-\infty}^{\infty}e^{-\frac{x^2}{a^2} - i\frac{p_0 x}{\hbar}}\frac{d}{dx}\left(e^{-\frac{x^2}{a^2} + i\frac{p_0 x}{\hbar}}\right)dx = -i\hbar\sqrt{\frac{2}{a^2\pi}}\int_{-\infty}^{\infty}\left(-\frac{2x}{a^2} + i\frac{p_0}{\hbar}\right)e^{-2\frac{x^2}{a^2}}dx$ which is $-i\hbar i\frac{p_0}{\hbar} = p_0$; this gives a physical interpretation of p_0 in our original wave packet.

We want to find the variance as well as the mean, so we calculate $\langle x^2 \rangle = \sqrt{\frac{2}{a^2\pi}}\int_{-\infty}^{\infty}x^2e^{-2\frac{x^2}{a^2}}dx$ which integrating by parts we find is $\frac{a^2}{4}$ and $\langle p^2 \rangle = -\hbar^2\sqrt{\frac{2}{a^2\pi}}\int_{-\infty}^{\infty}e^{-\frac{x^2}{a^2} - i\frac{p_0 x}{\hbar}}\frac{d^2}{dx^2}\left(e^{-\frac{x^2}{a^2} + i\frac{p_0 x}{\hbar}}\right)dx = \hbar^2\sqrt{\frac{2}{a^2\pi}}\int_{-\infty}^{\infty}\left(\frac{4x^2}{a^2} - \frac{4ip_0 x}{a^2\hbar} - \frac{p_0^2}{\hbar^2} - \frac{2}{a^2}\right)e^{-2\frac{x^2}{a^2}}dx = -\hbar^2\left(\frac{4}{a^4}\frac{a^2}{4} - \frac{p_0^2}{\hbar^2} - \frac{2}{a^2}\right) = p_0^2 + \frac{\hbar^2}{a^2}$. We then define spread or variance in the usual

way as $(\delta x)^2 = \langle (x - \langle x \rangle)^2 \rangle$ and similar; as in probability this is $\langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle = \langle x^2 \rangle - 2\langle x \rangle\langle x \rangle + \langle x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2$ and sim for δp ; here we find $(\delta x)^2 = \frac{a^2}{4}$, $(\delta p)^2 = \frac{\hbar^2}{a^2}$, so $(\delta x)(\delta p) = \frac{\hbar}{2}$. δx measures the "spread" of the wave packet or wf in position, δp the spread in momentum, so this means the particle cannot be completely localised in both position and momentum at the same time; if we know the position very accurately δx is small so $\delta p = \frac{\hbar}{2\delta x}$ must be large and vv. This is an example of the famous uncertainty principle; in general it states $(\delta p)(\delta x) \geq \frac{\hbar}{2}$, so this is the best case in that we have the minimum possible uncertainty.

4.3 Ehrenfest's T, correspondence prinz (not directly examinable, but useful in exams)

A good new physical theory should reproduce the results of that it repstacklaces where these were accurate; QM is important in microscopic problems where \hbar is not small compared with the other quantities (of same dimensions, those of action) involved, but classical mechanics is accurate and successful in macroscopic

problems where \hbar is small, so we should recover its results by letting $\hbar \rightarrow 0$.

Ehrenfest's Thm

Certain expectations satisfy the classical eqns of motion (without taking $\hbar \rightarrow 0$) and give these classical eqns when we let $\hbar \rightarrow 0$.

We shall obtain the eqns of motion for $\langle x \rangle, \langle p \rangle$ in 1D; again the generalisation to 3D is straightforward. We consider the time derivs (and assume x, t indep variables); $\frac{d}{dt} \langle x \rangle = \frac{d}{dt} (\Psi, x\Psi) = (\frac{\partial \Psi}{\partial t}, x\Psi) + (\Psi, x \frac{\partial \Psi}{\partial x})$ which using the SE $i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$ becomes $(-\frac{i}{\hbar} H\Psi, x\Psi) + (\Psi, -\frac{i}{\hbar} xH\Psi) = \frac{1}{\hbar} ((H\Psi, x\Psi) - (\Psi, xH\Psi))$ (remember we take the conj of the first term as we are taking a cplx scalar prod); the first of the inner terms is $(\Psi, Hx\Psi)$ since H Hermitian so this is $\frac{i}{\hbar} (\Psi, (Hx - xH)\Psi)$ and this much is true for any Hermitian operator in place of x , we have not yet used any special properties of x : $i\hbar \frac{d}{dt} \langle Q \rangle = (\psi, [H, Q]\psi) = \langle [H, Q] \rangle$ where $[H, Q]$ is the commutator $HQ - QH$.

Now we evaluate $(Hx - xH)\Psi$; we assume $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V$ as in the SE and have $\frac{\partial^2}{\partial x^2} (x\Psi) = 2\frac{\partial \Psi}{\partial x} + x\frac{\partial^2 \Psi}{\partial x^2}$ and the reader may verify $(Hx - xH)\Psi = -\frac{\hbar^2}{2m} \frac{\partial \Psi}{\partial x}$.

So $\frac{d}{dt} \langle x \rangle = \frac{i}{\hbar} \times -\frac{\hbar^2}{m} (\Psi, \frac{\partial \Psi}{\partial x}) = \frac{1}{m} (\Psi, -i\hbar \frac{\partial \Psi}{\partial x}) = \frac{1}{m} (\Psi, p\Psi) = \frac{1}{m} \langle p \rangle$ as we would expect since classically we have $\frac{dx}{dt} = \frac{1}{m} p$.

Similarly we have $\frac{d}{dt} \langle p \rangle = -i\hbar \frac{d}{dt} (\Psi, \frac{\partial \Psi}{\partial x}) = (i\hbar \frac{\partial \Psi}{\partial t}, \frac{\partial \Psi}{\partial x}) + (\Psi, -i\hbar \frac{\partial}{\partial x} (\frac{\partial \Psi}{\partial t}))$ (again assuming $[x, t]$ independent so) we can exchange the order of differentiation which is $(H\Psi, \frac{\partial \Psi}{\partial x}) + (\Psi, -\frac{\partial}{\partial x} (H\Psi))$; now $\frac{\partial}{\partial x} (H\Psi) = \frac{\partial}{\partial x} \left(\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right) \Psi \right) = (H \frac{\partial}{\partial x} + \frac{\partial V}{\partial x}) \Psi$ [unchecked] so $\frac{d}{dt} \langle p \rangle = -(\Psi, \frac{\partial V}{\partial x} \Psi) = -\langle \frac{\partial V}{\partial x} \rangle$; this is the analogue of $\frac{dp}{dt} = F = -\frac{dV}{dx}$.

As $\hbar \rightarrow 0$, Ψ centres on $\langle x \rangle$, the spread of x and $p \rightarrow 0$ and their mean points (which become their only points) move according to the classical eqns of motion.

4.4 The process of measurement

Suppose Q an observable and $\{\psi_i\}$ a basis of evecs of Q $Q\psi_i = q_i\psi_i$; if $q_i \neq q_j$ $(\psi_i, \psi_j) = 0$ and in fact we can arrange that $(\psi_i, \psi_j) = \delta_{ij}$ even when $q_i = q_j$ by taking linear combinations where necessary (this is the Gram-Schmidt Process; see Lin Al)

Consider measuring Q in some normalized state ψ ; write $\psi = \sum c_i \psi_i$; we can find the c_i by (ψ_i, ψ) (reader may verify - substitute expansion of ψ and use linearity and orthogonality); note the ψ_i are not generally energy eigenstates.

$\|\psi\|^2 = 1$ [the lecturer appears to use $\|\|$ and $\|\|$ interchangeably] means $1 = (\psi, \psi) = (\sum c_j \psi_j, \sum c_i \psi_i) = \sum c_j^* c_i \delta_{ij} = \sum |c_i|^2$. Then $\langle Q \rangle = (\psi, Q\psi) = (\sum c_j \psi_j, \sum c_i q_i \psi_i) = \sum q_i |c_i|^2$; the prob of getting the result q_i when we measure Q on ψ is $|c_i|^2$, assuming for now the q_i are all distinct, in which case we say the eigenstates are nondegenerate.

Now say we measure Q at $t = 0$ when the wf is $\psi(x)$; then the prob of getting q_i is $|c_i|^2 = |(\psi_i, \psi)|^2$; we evaluate the “overlap integral” $[\int \psi_i^* \psi]$. Suppose we then measure Q again just after $t = 0$; were the wf still ψ (or cntsly near it) prob of getting q_i again would be $\approx |c_i|^2$, but experimentally we find the second measurement almost always gives the same result as the first; this forces us to conclude that ψ changes discntly at the time of measurement into ψ_i so q_i co the certain result of the next measurement; as long as no measurement is made a quantum system evolves according to the SE ($i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$) but when a measurement is made the system jumps w/ prob $|c_i|^2$ into the state ψ_i w/ q_i being the result of the measurement; after this it again evolves according to the SE. This phenomenon is called the collapse of the wf and its interpretation remains somewhat controversial.

For example, suppose an observable represented by Q has just two estates (forming a complete basis) ϕ_1, ϕ_2 w/ respective evals q_1, q_2 ; for $t < 0$ the system is in a lin comb of ϕ_1, ϕ_2 ; then at $t = 0$ Q is measured w/ result q_1 , so $\Psi(x, 0) = \phi_1(x)$; we want the prob of obtaining q_2 when we measure Q at time $t > 0$. For this we need to calculate $\Psi(x, t)$ so need to express $\Psi(x, 0)$ in terms of energy estates; suppose the system has only two energy estates ψ_1, ψ_2 w/ respective evals E_1, E_2 (so $H\psi_1 = E_1\psi_1$ etc); write $\Psi(x, 0) = \phi_1 = c_1\psi_1 + c_2\psi_2$ with $c_i = (\psi_i, \phi_1)$. Then $\Psi(x, t) = c_1\psi_1 e^{-i\frac{E_1 t}{\hbar}} + c_2\psi_2 e^{-i\frac{E_2 t}{\hbar}}$, as normal; the prob of obtaining q_2 at time t (i.e. of being in state ϕ_2 at t) is $|(\phi_2, \Psi(x, t))|^2 = \left| c_1 (\phi_2, \psi_1) e^{-i\frac{E_1 t}{\hbar}} + c_2 (\phi_2, \psi_2) e^{-i\frac{E_2 t}{\hbar}} \right|^2$.

4.5 Pairs of observables

Let α, β observables; if we measure α , then β , then α again the final result for α will not in general be the same as the initial one even if we perform the measurements in very quick succession [measuring β forces ψ to jump into an eigenstate for β , which will not in general be the same as the eigenstate of α we jump into after measuring that]. The cond for the measurement of β not to change the result of α , i.e. for α, β to be simultaneously measurable, is that α, β commute; α, β are simultaneously measurable iff $[\alpha, \beta] = \alpha\beta - \beta\alpha = 0$; this follows from our assumptions abot measurement and reflects the following:

Thm

If two Herm ops α, β commute, \exists a basis of simultaneous estates (i.e. evecs of both α and β); the proof is in the Lin Al course. This makes sense since for a simultaneous estate $|a, b\rangle$ (where its evals are a wrt α , b wrt β) $\alpha\beta|a, b\rangle = \alpha b|a, b\rangle = b\alpha|a, b\rangle = ba|a, b\rangle = ab|a, b\rangle = \dots = \beta\alpha|a, b\rangle$.

As an example consider the position and momentum operators x and $p = -i\hbar \frac{\partial}{\partial x}$ in 1D; $[x, p] = -i\hbar [x, \frac{\partial}{\partial x}] = -i\hbar (x \frac{\partial}{\partial x} - \frac{\partial}{\partial x} x)$; recall this is an operator acting on wfs so this is $-i\hbar (x \frac{\partial}{\partial x} - 1 - x \frac{\partial}{\partial x}) = i\hbar$; this is the canonical commutation relation for x and p ; it is nonzero so we cannot measure position and momentum simultaneously. This makes sense from the physics - if we try and

measure the position of a particle by firing photons at it then on the microscopic scale these will disturb the particle and change its momentum.

In 3D the canonical CRs are $[x_i, x_j] = 0$, $[p_i, p_j] = 0$, $[x_i, p_j] = i\hbar\delta_{ij}$.

4.6 The Uncertainty Principle

Another way of considering the relation between simultaneous measurability and the commutator $[\alpha, \beta]$ of two observables is to consider the variance (or “spread”) of measurements of α and β in the same state ψ : $((\alpha + i\lambda\beta)\psi, (\alpha + i\lambda\beta)\psi) = \|(\alpha + i\lambda\beta)\psi\|^2 \geq 0$ but this is $(\psi, (\alpha + i\lambda\beta)^\dagger (\alpha + i\lambda\beta)\psi)$ which since α, β are observables so Hermitian is $(\psi, (\alpha - i\lambda\beta)(\alpha + i\lambda\beta)\psi) = (\psi, (\alpha^2 + i\lambda\alpha\beta - i\lambda\beta\alpha + \lambda^2\beta^2)(\alpha - i\lambda\beta)\psi) = (\psi, \alpha^2\psi) + (\psi, i\lambda[\alpha, \beta]\psi) + (\psi, \lambda^2\beta^2\psi) = \langle\alpha^2\rangle + \lambda i\langle[\alpha, \beta]\rangle + \lambda^2\langle\beta^2\rangle$; considering this as a quadratic in λ since it is always ≥ 0 its discriminant must be ≤ 0 i.e. $4\langle\alpha^2\rangle\langle\beta^2\rangle \geq |i\langle[\alpha, \beta]\rangle|^2$. Now if we replace α by $\alpha - \langle\alpha\rangle$ and sim. for β we have $(\delta\alpha)^2(\delta\beta)^2 \geq \frac{1}{4}|\langle[\alpha, \beta]\rangle|^2$; since all the quantities here are *ve* we can take the square root $(\delta\alpha)(\delta\beta) \geq \frac{1}{2}|\langle[\alpha, \beta]\rangle|$; if α, β commute we may simultaneously reduce their spreads to arbitrarily small i.e. we may simultaneously measure α, β , but if not this gives a limit on how accurately we can measure the two quantities simultaneously - the uncertainty principle. The classic example of this is of course to take $\alpha = x, \beta = p = -i\hbar\frac{\partial}{\partial x}$ and then we have $[x, p] = i\hbar$ so $(\delta x)(\delta p) \geq \frac{\hbar}{2}$.

5 3D problems w/ spherical symmetry

5.1 Sep of vars

We solved the 1D SHO and particle in a box; the corresponding probs in 3D are easily solved by sep of vars in Cartesian coords; see Exs3. Now we consider other potentials $V(\vec{r})$ where this fails; the time-indep SE in 3D is $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x}) + V(\vec{r})\psi(\vec{x}) = E\psi(\vec{x})$ (of course $\vec{r} = \vec{x}$). We take the special case where $V(\vec{r}) = V(r)$, a function purely of the radius $r = |\vec{r}|$. Although the potential is spherically symmetric, the solutions will not necessarily all be; we use spherical polars and separate variables; $\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$; we are looking for sols of the form $\psi(\vec{r}) = R(r)\Theta(\theta)\Phi(\phi)$ so the SE becomes (multiplying by $\frac{2M}{\hbar^2}$) $-\frac{1}{r^2R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2M}{\hbar^2}V(r) - \frac{1}{r^2\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{1}{r^2\Phi\sin^2\theta}\frac{d^2\Phi}{d\phi^2} = \frac{2ME}{\hbar^2}$ (we use M for the mass of the particle since we shall later want to use m for another number), so we have $-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = \frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + r^2\sin^2\theta\frac{2M}{\hbar^2}(E - V) + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$ and these must = some separation constant m^2 , then $\frac{m^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = \frac{2M}{\hbar^2}r^2(E - V) + \frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)$ which = another separation constant which we take to be $l(l+1)$. So we have equations for our three functions $\Phi'' + m^2\Phi = 0$, $\frac{1}{\sin\theta}(\sin\theta\Theta')' + (l(l+1) - \frac{m^2}{\sin^2\theta})\Theta =$

$0, -\frac{\hbar^2}{2m} \frac{1}{r^2} (r^2 R')' + \left(V + \frac{\hbar^2}{2Mr^2} l(l+1) \right) R = ER$; this is the radial SE in 3D.

The sols for Φ are $\Phi = e^{\pm im\phi}$ with $\Phi(\phi + 2\pi) = \Phi(\phi)$ i.e. we must have $m \in \mathbb{Z}$; we take wlog $e^{im\phi}$ since we allow $m < 0$ so would otherwise have duplicate solutions. Since we want a sol for Θ well behaved at $\theta = 0, \pi$ we must have $l \in \mathbb{Z}$ and $l \geq |m|$ [$|l| \geq m$ in lectures but I think this must be wrong], then $\Theta(\theta) = P_l^m(\cos\theta)$ for some polys P_l^m ; we can write the entire angular dependence as $Y_{lm}(\theta, \phi) = N_{lm} P_l^m(\cos\theta) e^{im\phi}$ for some normalization constants N_{lm} . There are $2l + 1$ spherical harmonics for each l , i.e. $m = -l, -l + 1, \dots, 0, \dots, l$. For example the first few are $Y_{00} = \frac{1}{\sqrt{4\pi}}, Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta, Y_{1\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}$. The energy levels E_{ln} for $n \geq l + 1$ are the evals of the radial SE; they have degeneracy $2l + 1$ since they each correspond to this many possible values of m . We shall see later that $l(l+1)\hbar^2$ can be interpreted as the square of the orbital angular momentum and $m\hbar$ as the z cpt thereof. The sols for $l = 0, 1, 2, 3, \dots$ are called S,P,D,F,... wave sols.

5.2 The Spherical Well

$V(r) = -V_0$ for $|r| < a, 0$ for $|r| > a$ - this is the generalization of the 1D square well. We have a constant $-ve$ potential within some square and zero potential elsewhere.

We shall only look at the spherically symmetric sols for now, though in fact not all sols of this are. Put $\psi(\vec{r}) = R(r) \Phi_{lm}(\theta, \phi)$, then put $l = m = 0$ for a spherically symmetric sol and we only need to solve the radial eqn $-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} (r^2 \frac{dR}{dr}) + V(r) R = ER$; we have $\frac{1}{r^2} \frac{d}{dr} (r^2 \frac{dR}{dr}) = \frac{1}{r} \frac{d^2}{dr^2} (rR)$ so putting $\chi = rR$ we obtain $-\frac{\hbar^2}{2M} \frac{d^2\chi}{dr^2} - V_0\chi = E\chi$ for $0 < r < a, -\frac{\hbar^2}{2M} \frac{d^2\chi}{dr^2} = E\chi$ for $r > a$. We look for bound state sols $-V_0 < E < 0$ so def $k^2 = \frac{2M}{\hbar^2} (E + V_0), \beta^2 = -\frac{2ME}{\hbar^2}$, then for $0 < r < a$ $\chi'' + k^2\chi = 0 \Rightarrow \chi = A \cos kr + B \sin kr \Rightarrow \psi = \frac{A \cos kr}{r} + \frac{B \sin kr}{r}$ and for $r > a$ $\chi'' - \beta^2\chi = 0 \Rightarrow \chi = C e^{\beta r} + D e^{-\beta r} \Rightarrow \psi = \frac{C e^{\beta r}}{r} + \frac{D e^{-\beta r}}{r}$; there is no question of odd or even sols since $r > 0$ covers the whole domain, but we can apply BCs: ψ finite at $r = 0 \Rightarrow A = 0, \psi \rightarrow 0$ as $r \rightarrow \infty \Rightarrow C = 0$, and since ψ, ψ' are cnts at $r = a$ so are χ, χ' so $B \sin ka = D e^{-\beta a}, kB \cos ka = -\beta D e^{-\beta a}$; dividing these $k \cot ka = -\beta$ and from the def of k, β we have $k^2 + \beta^2 = \frac{2mV_0}{\hbar^2}$; these are the same as the eqns for odd parity bound states in the 1D potential well, so as then we have that if $\frac{2mV_0 a^2}{\hbar^2} < \frac{\pi^2}{4}$ there are no bound states, if $\frac{\pi^2}{4} < \frac{2mV_0 a^2}{\hbar^2} < \frac{9\pi^2}{4}$ there is one bound state etc.

5.3 The Hydrogen Atom

We will look at the simplest case rather than giving a complete treatment at this stage; we have 1 proton w/ charge $+e$, 1 electron w/ charge $-e$ held together by Coulomb attraction; to a good approximation we can treat the nucleus as fixed at the origin since $m_p \approx 1836m_e$, and consider the motion of the electron in a

potential $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$; were we being completely accurate we would separate vars and calculate centre of mass motion and relative motion w/ reduced mass [and this is necessary to accurately consider muonic hydrogen]; we look at the simplest sol, i.e. the spherically symmetric sol $l = m = 0$. We only need to solve the radial eqn w/ $l = 0$: $-\frac{\hbar^2}{2M} \frac{1}{r^2} (r^2 R')' - \frac{e^2}{4\pi\epsilon_0 r} R = ER$; the form of the sol is non-obvious so we might solve this by series (and will do later when considering the general problem), but for now try $R = e^{-\frac{r}{a}}$ for some a , then $\frac{1}{r^2} (r^2 R')' = \frac{1}{r^2} \left(\frac{r^2}{a} e^{-\frac{r}{a}} \right)' = -\frac{1}{ar^2} \left(2r e^{-\frac{r}{a}} - \frac{r^2}{a} e^{-\frac{r}{a}} \right) = \left(\frac{1}{a^2} - \frac{2}{ar} \right) e^{-\frac{r}{a}}$; substituting this into the SE we have $-\frac{\hbar^2}{2M} \left(\frac{1}{a^2} - \frac{2}{ar} \right) e^{-\frac{r}{a}} - \frac{e^2}{4\pi\epsilon_0 r} e^{-\frac{r}{a}} = E e^{-\frac{r}{a}}$; dividing out $e^{-\frac{r}{a}}$ and equating coeffs of powers of r we have $-\frac{\hbar^2}{2M} \left(-\frac{2}{a} \right) - \frac{e^2}{4\pi\epsilon_0} = 0$ so $a = \frac{4\pi\epsilon_0 \hbar^2}{Me^2}$ from the r^{-1} terms and $-\frac{\hbar^2}{2M} \frac{1}{a^2} = E$ so $E = -\frac{\hbar^2}{2M} \left(\frac{Me^2}{4\pi\epsilon_0 \hbar^2} \right)^2 = -\frac{Mc^2}{2} \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 = -\frac{Mc^2 \alpha^2}{2}$ from the r^0 terms, which is exactly the same energy as the lowest energy state ($n = 1$) of the Bohr atom; $\psi \propto e^{-\frac{r}{a}}$ in fact does correspond to the ground state (state with lowest energy) since any angular momentum ($l \neq 0$ states) will only increase energy. To find the normalised ground state wf we put $P = Ne^{-\frac{r}{a}}$ and use $1 = \int_{\text{all space}} |R|^2 dV = |N|^2 \int_0^\infty e^{-2\frac{r}{a}} 4\pi r^2 dr$ (since in 3D w/ spherical symmetry $dV = 4\pi r^2 dr$) $= 4\pi |N|^2 \int_0^\infty e^{-2\frac{r}{a}} r^2 dr$; integrating by parts we find $\int_0^\infty r^2 e^{-\beta r} dr = \frac{2}{\beta^3}$ so $1 = 4\pi |N|^2 2 \frac{a^3}{8}$; taking N real $N = \frac{1}{\sqrt{\pi a^3}}$ and $\psi(\vec{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{r}{a}}$; for a hydrogen-like atom w/ Z protons and just one electron the potential is $-\frac{Ze^2}{4\pi\epsilon_0 r^2}$ so we just replace e^2 by Ze^2 in the sol.

6 Angular momentum operators and general sol for the hydrogen atom

We want to interpret the $l(l+1)$ which appears in the radial SE when separating vars in spherical polars.

6.1 Def of angular momentum and CRs

Classically angular momentum is $\vec{L} = \vec{x} \times \vec{p}$; $L_i = \epsilon_{ijk} x_j p_k$. In QM we use the same def, but \vec{x}, \vec{p} are now operators satisfying the canonical CRs $[x_i, p_j] = i\hbar \delta_{ij}$; from this we can find the CRs for cpts of L . $[L_1, L_2] = [x_2 p_3 - x_3 p_2, x_3 p_1 - x_1 p_3] = [x_2 p_3, x_3 p_1] - [x_2 p_3, x_1 p_3] - [x_3 p_2, x_3 p_1] + [x_3 p_2, x_1 p_3]$; the second and third terms are 0 [since x_1, x_2, p_3 all commute, likewise p_1, p_2, x_3] and this is $x_2 p_1 [p_3, x_3] + p_2 x_1 [x_3, p_3] = x_1 p_2 i\hbar - x_2 p_1 i\hbar = i\hbar L_3$. By symmetry we have that the general relation is $[L_i, L_j] = i\hbar \epsilon_{ijk} L_k$.

Now consider $[L_3, \vec{L}^2] = [L_3, L_1^2 + L_2^2 + L_3^2] = [L_3, L_1^2] + [L_3, L_2^2] + [L_3, L_3^2]$. We have some useful formulae: $[A, BC] = [A, B]C + B[A, C]$ since RHS = $(AB - BA)C + B(AC - CA) = ABC - BCA =$ LHS, and $[AB, C] = [A, C]B + A[B, C]$ by a similar proof left as an exercise. So $[L_3, L_1^2] = [L_3, L_1]L_1 +$

$L_1 [L_3, L_1] = i\hbar (L_2 L_1 + L_1 L_2)$, $[L_3, L_2^2] = [L_3, L_2] L_2 + L_2 [L_3, L_2] = i\hbar (-L_1 L_2 - L_2 L_1)$
 $([L_3, L_3^2] = 0)$ so $[L_3, \vec{L}^2] = 0$ and by symmetry $[L_i, \vec{L}^2] = 0$; the cpts of \vec{L} do
not commute w/ each other, but each commutes w/ \vec{L}^2 so we can measure one
and \vec{L}^2 simultaneously; we usually take this one to be L_3 and have simultaneous
estates of L_3 and \vec{L}^2 .

6.2 Relation between \vec{L}^2 and the Laplacian

We express \vec{L}^2 in spherical polars and relate it to the Laplacian, allowing us
to interpret the separation constants $l(l+1), m$. There are several ways to do
this all of which are in some way hard.

Method 1

Use $L_i = -i\hbar \epsilon_{ijk} x_j \nabla_k$ [my notation: $\nabla_k = \frac{\partial}{\partial x_k}$] (using that $p_k = -i\hbar \nabla_k$; we
could have used this to find the CR for $[L_i, L_j]$ but the method we used was eas-
ier), then \vec{L}^2 [using summation convention] $= L_i L_i = -\hbar^2 \epsilon_{ijk} x_j \nabla_k \epsilon_{irs} x_r \nabla_s =$
 $-\hbar^2 (\delta_{jr} \delta_{ks} - \delta_{js} \delta_{kr}) x_j \nabla_k x_r \nabla_s = -\hbar^2 (x_j \nabla_k x_j \nabla_k - x_j \nabla_k x_k \nabla_j)$ and using the
product rule this $= -\hbar^2 (x_j \delta_{jk} \nabla_k + x_j x_j \nabla_k \nabla_k - x_j \delta_{kk} \nabla_j - x_j x_k \nabla_k \nabla_j) = -\hbar^2 (x_j \nabla_j + r^2 \nabla^2 - 3x_j \nabla_j -$
Now $x_j \nabla_j = r \frac{\partial}{\partial r}$ since $x_j \nabla_j = x_j \frac{\partial r}{\partial x_j} \frac{\partial}{\partial r}$ by chain rule, and $\frac{\partial r}{\partial x_j} = \frac{\partial}{\partial x_j} (x_k x_k)^{\frac{1}{2}} =$
 $\frac{1}{2r} 2x_k \delta_{jk} = \frac{x_j}{r}$ so $x_j \frac{\partial}{\partial x_j} = x_j \frac{x_j}{r} \frac{\partial}{\partial r} = r \frac{\partial}{\partial r}$. So $\vec{L}^2 = -\hbar^2 (r^2 \nabla^2 - r \frac{\partial}{\partial r} - r \frac{\partial}{\partial r} r \frac{\partial}{\partial r}) =$
 $-\hbar^2 (r^2 \nabla^2 - \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r})$; rearranging $-\hbar^2 \nabla^2 = -\frac{\hbar^2}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\vec{L}^2}{r^2}$. We have as per
5.1 $-\hbar^2 \nabla^2 = -\frac{\hbar^2}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}) - \frac{\hbar^2}{r^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$ so $\vec{L}^2 = -\frac{\hbar^2}{r^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$.

Method 2

This makes calculation of \vec{L}^2 very difficult but is useful for finding L_3 : put
 $x_1 = r \sin \theta \cos \phi$, $x_2 = r \cos \theta \cos \phi$, $x_3 = r \sin \theta$ and use the chain rule to express
 L_i in terms of $\frac{\partial}{\partial \theta}, \frac{\partial}{\partial \phi}$; we find $L_3 = -i\hbar \left(x_1 \frac{\partial}{\partial x_2} - x_2 \frac{\partial}{\partial x_1} \right) = -i\hbar \frac{\partial}{\partial \phi}$ since $\frac{\partial}{\partial \phi} =$
 $\frac{\partial x_1}{\partial \phi} \frac{\partial}{\partial x_1} + \frac{\partial x_2}{\partial \phi} \frac{\partial}{\partial x_2} + \frac{\partial x_3}{\partial \phi} \frac{\partial}{\partial x_3}$; $\frac{\partial x_1}{\partial \phi} = -r \sin \theta \sin \phi = -x_2$, $\frac{\partial x_2}{\partial \phi} = x_1$
 $(\frac{\partial x_3}{\partial \phi} = 0)$ so this is $-x_2 \frac{\partial}{\partial x_1} + x_1 \frac{\partial}{\partial x_2}$ as required.

Now we consider \vec{L}^2, L_3 acting on $\psi(\vec{r}) = R(r) Y_{lm}(\theta, \phi)$, where $Y_{lm} =$
 $N_{lm} P_l^m(\cos \theta) e^{im\phi}$ (where N_{lm} are normalization constants); $\vec{L}^2 R = 0$ since \vec{L}^2
contains only θ and ϕ derivatives, $\vec{L}^2 Y_{lm}(\theta, \phi) = -\hbar^2 N_{lm} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) P_l^m(\cos \theta) e^{im\phi} =$
 $\hbar^2 N_{lm} \left(\frac{m^2}{\sin^2 \theta} - \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) P_l^m(\cos \theta) e^{im\phi}$. Recall $\Theta = P_l^m(\cos \theta)$ satisfies
 $\frac{1}{\sin \theta} (\sin \theta \Theta')' + \left(l(l+1) - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0$, so this is simply $l(l+1) \hbar^2 N_{lm} P_l^m(\cos \theta) e^{im\phi} =$
 $l(l+1) \hbar^2 Y_{lm}(\theta, \phi)$. $[L_3 R \text{ of course} = 0]$ $L_3 Y_{lm}(\theta, \phi) = -i\hbar \frac{\partial}{\partial \phi} (N_{lm} P_l^m(\cos \theta) e^{im\phi}) =$
 $m\hbar Y_{lm}(\theta, \phi)$. So the evals of the square of total angular momentum \vec{L}^2 are

$l(l+1)\hbar^2$ for $l = 0, 1, 2, \dots$ and the corresponding evals for L_3 are $m\hbar$ with $m \in \mathbb{Z}, |m| \leq l$ i.e. $m = -l, -l+1, \dots, l$.

Returning to the radial eqn $-\frac{\hbar^2}{2M} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(V(r) + \frac{\hbar^2}{2Mr^2} l(l+1) \right) R = ER$. In practice we use that the first term is $-\frac{\hbar^2}{2M} \frac{1}{r} \frac{d^2}{dr^2} (rR)$; substituting $\chi = rR$ as in the spherical well we obtain $-\frac{\hbar^2}{2M} \frac{d^2\chi}{dr^2} + \left(V(r) + \frac{\hbar^2}{2Mr^2} l(l+1) \right) \chi = E\chi$, which reduces to the usual 1D SE when $l = 0$. The effect of angular momentum or angular motion is to add a term to the potential in this 1D eqn; since $l \geq 0$ this term is always *+*ve so its effect is to increase the energy, which makes sense. Note that R finite at $r = 0 \Rightarrow \chi(0) = 0$ and $\int |\psi|^2 d^3\vec{r}$ converges $\Rightarrow \int_0^\infty |\chi|^2 dr$ [guessing limits] must converge.

6.3 GS of the hydrogen atom

We look for bound states of the H atom; these satisfy the 3D time-indep SE $-\frac{\hbar^2}{2M} \nabla^2 \psi - \frac{e^2}{4\pi\epsilon_0 r} \psi = E\psi$; $V_\infty = 0$ so since we want bound states we take $E < 0$; $E > 0$ gives a continuum of scattering states. We separate vars by $\psi(\vec{r}) = R(r) Y_{lm}(\theta, \phi)$ where $R(r)$ is a sol of the radial SE $-\frac{\hbar^2}{2M} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{e^2}{4\pi\epsilon_0 r} R + \frac{l(l+1)\hbar^2 R}{2Mr^2} = ER$; putting $\chi = rR$ this becomes $-\frac{\hbar^2}{2M} \frac{d^2\chi}{dr^2} - \frac{e^2}{4\pi\epsilon_0 r} \chi + \frac{l(l+1)\hbar^2 \chi}{2Mr^2} = E\chi$; define $\beta^2 = -\frac{8ME}{\hbar^2}$, $\rho = \beta r$, then $\frac{d}{dr} = \frac{d\rho}{dr} \frac{d}{d\rho} = \beta \frac{d}{d\rho}$ and similarly and the eqn becomes $-\frac{\hbar^2}{2M} \beta^2 \frac{d^2\chi}{d\rho^2} - \frac{e^2}{4\pi\epsilon_0 \rho} \beta \chi + \frac{l(l+1)\hbar^2}{2M\rho^2} \beta^2 \chi = -\frac{\hbar^2 \beta^2 \chi}{8M}$ or $\frac{d^2\chi}{d\rho^2} - \frac{l(l+1)}{\rho^2} \chi - \frac{1}{4} \chi + \frac{\lambda}{\rho} \chi = 0$ where $\lambda = \frac{2Me^2}{4\pi\epsilon_0 \hbar^2 \beta} = \frac{2Me^2 \hbar}{4\pi\epsilon_0 \hbar^2 \sqrt{-8ME}} = \frac{e^2}{4\pi\epsilon_0 \hbar} \sqrt{-\frac{M}{2E}}$ i.e. $E = -\frac{Mc^2}{2\lambda^2} \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 = -\frac{Mc^2 \alpha^2}{2\lambda^2}$; we want to compare this with the previous formula for the energy levels of the H atom, but first we must determine the values of λ . We proceed as we did for the SHO: for large ρ $\frac{d^2\chi}{d\rho^2} \approx \frac{\chi}{4}$ i.e. $\chi \sim e^{\pm \frac{\rho}{2}}$ as $\rho \rightarrow \infty$; we want R bounded as $r \rightarrow \infty$ so $\chi \sim e^{-\frac{1}{2}\rho}$. Then for general ρ we put $\chi = e^{-\frac{1}{2}\rho} f(\rho)$ and have $\frac{d\chi}{d\rho} = \left(-\frac{1}{2}f + f'\right) e^{-\frac{1}{2}\rho}$, $\frac{d^2\chi}{d\rho^2} = \left(\frac{1}{4}f - f' + f''\right) e^{-\frac{1}{2}\rho}$; substituting this into the DE and dividing by $e^{-\frac{1}{2}\rho}$ we have $f'' - f' + \frac{1}{4}f - \frac{l(l+1)f}{\rho^2} - \frac{1}{4}f + \frac{\lambda}{\rho}f = 0$ or multiplying by ρ^2 , $\rho^2 f'' - \rho^2 f' + (\lambda\rho - l(l+1))f = 0$; we solve this by series; $\rho = 0$ is a regular singular point so we look for a sol of the form $f(\rho) = \sum_{k=0}^\infty a_k \rho^{k+\sigma}$ w/ $a_0 \neq 0$; substituting into the DE $\sum_{k=0}^\infty a_k (k+\sigma)(k+\sigma-1)\rho^{k+\sigma} - \sum_{k=0}^\infty a_k (k+\sigma)\rho^{k+\sigma+1} + \lambda \sum_{k=0}^\infty a_k \rho^{k+\sigma+1} - l(l+1) \sum_{k=0}^\infty a_k \rho^{k+\sigma}$; equating coeffs of $\rho^{k+\sigma}$ $a_k (k+\sigma)(k+\sigma-1) - a_{k-1}(k+\sigma-1) + \lambda a_{k-1} - l(l+1)a_k = 0$ i.e. $a_k = \frac{k+\sigma-1-\lambda}{(k+\sigma)(k+\sigma-1)-l(l+1)} a_{k-1}$ for $k > 0$; the coeffs of ρ^σ give $a_0 \sigma(\sigma-1) - a_0 l(l+1) = 0$; since $a_0 \neq 0$ we must have $\sigma = -l$ or $l+1$. We want ρ to be bounded at $r = 0$ so we must have $\sigma = l+1$. Now unless $a_k = 0$ for some k then $\frac{a_k}{a_{k+1}} \sim \frac{1}{k}$ for large k so $a_k \sim \frac{1}{k!}$ and $f \sim e^\rho$ so $\chi \sim e^{-\frac{1}{2}\rho} e^\rho = e^{\frac{1}{2}\rho} \rightarrow \infty$ as $\rho \rightarrow \infty$, so the series must terminate; $a_{k+1} = 0$ for some $k \in \mathbb{N}_0$ so f is a poly of deg k , i.e. $k+1+\sigma-1-\lambda = 0$; $\lambda = k+\sigma = l+k+1$, $k \in \mathbb{N}_0$ so $\lambda \in \mathbb{N}$; $\lambda = n > l \geq 0$. Recall $E = -\frac{Mc^2 \alpha^2}{2\lambda^2}$ so

for a given l we have $E_n = -\frac{Mc^2\alpha^2}{2n^2}$ for $n = l + 1, l + 2, \dots$. The corresponding energy efuncs are $\psi_{nlm}(r, \theta, \phi) = \frac{\chi}{r} Y_{lm}(\theta, \phi) = \rho^l e^{-\frac{1}{2}\rho} L_{n+l}^{2l+1}(\rho) Y_{lm}(\theta, \phi)$ where $\rho = \beta_n r, \beta_n = \frac{-8ME_n}{\hbar^2}$ and L_{n+l}^{2l+1} is a poly of degree $n - l - 1, \sum_{k=0}^{n-l-1} a_k \rho^k$ ($n = l + k + 1 \Rightarrow k = n - l - 1$).

Notation

Because of these results for $V(r) \propto \frac{1}{r}$ it is traditional to label the energy levels for any $V(r)$ as E_{nl} for $n > l$; for Hydrogen E_{nl} is independent of l . How many states correspond to E_n for the hydrogen atom? For a given n the possible values of l are $0, 1, \dots, n - 1$; for each l there are $2l + 1$ possible values of m , namely $-l, -l + 1, \dots, l$, so the total degeneracy (no. of states with that value of E) is $\sum_{l=0}^{n-1} (2l + 1) = \frac{2(n-1)n}{2} + n = n^2$; the degeneracy for E_n seems to be n^2 at this stage (but see below).

Jargon

n is called the principal quantum number; as we have seen it labels the energy levels. l is the angular momentum quantum number. m is the magnetic quantum number, since if a uniform magnetic field is applied in the z direction states with different m acquire different energy shifts, breaking the degeneracy.

The ground state is non-degenerate; it is called the $1s$ state. The first excited state is called either $2s$ for $l = 0$ or $2p$ for $l = 1$, so there are 4 possible states (since there are 3 possible values of m for $l = 1$); the second excited state is $3s$ for $l = 0$, $3p$ for $l = 1$ and $3d$ for $l = 2$, giving 9 states. We label the states in general by nq where q [is a letter] indicating the value of l .

The Pauli exclusion principle states that only one electron can occupy each state, but there are actually 2 electron states corresponding to each of those listed; electrons with the same n, l, m may have spin up or spin down giving distinct states, so the degeneracies of the energy levels are really $2n^2$.

Since electrons can move to lower states by emitting photons, the lowest energy levels are filled first; atoms with levels filled exactly are inert while those with just one electron missing from a level or one in a new level are the most reactive.