We want to solve the Schroedinger equation - the full, time dependent Schroedinger equation - for the wavefunction $\Psi(x,t)$. If the potential is constant in time then the wavefunction is separable in space and time. we find the spatial bit by solving the time independent Schroedinger equation - and in general there are multiple solutions, $H\psi_n = E_n\psi_n$. Then a particular solution is $\Psi_n(x,t) = \psi_n(x)e^{-iE_n t/\hbar}$ and the general solution is $\Psi(x,t) = \sum_n c_n\psi_n(x)e^{-iE_n t/\hbar}$.

A single particular solution (energy eigenfunction) is a stationary state - all expectatino values are constant in time. A general solution which is made of multiple particular solutions is NOT. we saw the probability distribution $|\Psi(x,t)|^2$ was time dependent! so all expectation values are as well!

e.g. for 2 terms in the infinite square well the probability density included a term $\cos\omega t$ where $\omega = (E_2 - E_1)/\hbar$

Consider an electron in the ground state of an atom. This is a single eigenfunction, so $<x>$ is not dependent on time as its a standing wave. since an electron is charged, then this is saying that the charge distribution is constant also, so there is no radiation. so QM provides a way to resolve the paradox you get by thinking of electrons as particles which orbit around atoms. in this picture the electron is accelerating (circular motion) so should radiate and hence the orbit should decay. But in QM the probability is stationary so the charge is not 'moving' so it doesn't radiate.

But atoms in their excited states do eventually make a transition down to the ground state. So if we have an atom in state $n = 2$ then it has some probability of being in state 1 as well - of decaying down. If its a mix of two states then its probability density and hence charge distribution oscillate in time with frequency $\hbar\omega = E_2 - E_1$ which is precisely the frequency of photon which is emitted to carry away the energy difference. This can't happen for the ground state as there is no lower state for this to mix with.

Schroedingerwrote 'It is hardly necessary to point out how much more gratifying it would be to concieve of a quantum transition as an energy change from one vibrational mode to another, than to regard it as a jumping of an electron'

Wavefunctions which are mixtures of eigenstates give expectation values which depend on time! pure eigenstates do not.

3.7 How to find the c_n for any function

Going from the particular solution to the general solution we are making the assumption that the energy eigenfunctions span the entire space, that they are good basis functions. then any arbitrary function can be expanded out as a sum of these basis functions.

we have $f(x) = \sum_n c_n \psi_n$ so multiply by ψ_m^* and integrate

$$\int \psi_m^* f(x) dx = \int \psi_m^* \sum_n c_n \psi_n = \sum_n c_n \int \psi_m^* \psi_n dx = \sum_n c_n \delta_{mn} = c_m$$

so for any functional form $f(x)$ we can decompose it into a weighted sum of energy eigenfunction $c_n \psi_n$, calculating each $c_n = \int \psi_n^* f(x) dx$

e.g. $\psi(x, t = 0) = A$ $0x < L/2$ and 0 for $L/2x < L$ in an infinite square well potential $0 < x < L$. normalise to get $A = \sqrt{2/L}$. Then we can decompose it into the sum of energy eigenfunctions for this potential $\psi_n(x) = \sqrt{2/L} \sin n\pi x/L = N \sin n\pi x/L$

$$c_n = AN \int_0^{L/2} \sin n\pi x/L dx = AN[-\frac{cosn\pi x/L}{(n\pi/L)}]_0^{L/2}$$

$$= -\frac{ANL}{n\pi}[cosn\pi/2 - cos0] = -\frac{2}{n\pi}(cos(n\pi/2) - 1)$$

this is different for even and odd n. For odd n $cos(n\pi/2) = 0$ while for even $cos(n\pi/2) = \mp 1$ e.g. $c_1 = 2/\pi$, $c_2 = -1/(2\pi)(cos\pi - 1) = 1/\pi$ etc... (sorry, got this wrong in the lecture)

4 Central 1 D potentials

4.1 infinite square well

$\Psi_n(x, t) = \psi_n(x) e^{-iE_n t/\hbar}$ where the energy eigenfunctions $\psi_n(x) = \sqrt{\frac{2}{L}} \sin(n\pi x/L)$ corresponding to energy $E_n = n^2 E_1$ and $E_1 = \pi^2 \hbar^2/(2mL^2)$. This is for $V = 0$ for $0 < x < L$, and $v = \infty$ elsewhere.

BUT!! this is actually a bit inconvienient - we are wanting to do Hydrogen - we will want potentials which are symmetric about 0 rather than $L/2$. so we could simply change the variable to $x' = x - L/2$ and we are in a centrally

symmetric potential. Energy doesn't change, this is just a shift in axis - so instead of sines we get a bunch of sine and cosine functions depending on whether n is even or odd....

$$\psi_n(x') = \sqrt{\frac{2}{L}} \sin(n\pi(x' + L/2)/L)$$

$$= \sqrt{\frac{2}{L}} \sin(n\pi x'/L + n\pi/2) = \sqrt{\frac{2}{L}}(\sin(n\pi x'/L)\cos(n\pi/2) + \cos(n\pi x'/L)\sin(n\pi/2))$$

but this depends on n. n=1, then $\sin\pi/2 = 1$ and $\cos\pi/2 = 0$

$$\psi_1(x') = \sqrt{\frac{2}{L}} \cos(\pi x'/L)$$

similarly for $n = 2$ then $\sin\pi = 0$ and $\cos(\pi) = -1$ so

$$\psi_2(x') = -\sqrt{\frac{2}{L}} \sin(2\pi x'/L)$$

$$\psi_3(x') = -\sqrt{\frac{2}{L}} \cos(3\pi x'/L)$$

$$\psi_4(x') = \sqrt{\frac{2}{L}} \sin(4\pi x'/L)$$

4.2 The finite well

now lets bring the infinite potential step down to a finite step. so now we have three regions. The bit in the middle with $-L/2 < x < L/2$ is a solution of the Schroedinger equation with $V = 0$ i.e.

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

$$\frac{d^2\psi}{dx^2} = \frac{-2mE}{\hbar^2}\psi = -k^2\psi$$

where bound solutions have $0 < E < V_0$ so $k^2 = 2mE/\hbar^2$ This has a general solution $\psi = A\cos(kx) + B\sin(kx)$

4.2.1   odd n, peaking at zero

We can see from symmetry that for odd n this will peak at zero i.e. to be cosines only so $\psi = A\cos kx$. When it does, then the bit to the left and right are equal (for even n, the bit to the left and right are equal and opposite). so lets do the bit to the right at x is +ve so its easier!

$$\frac{-\hbar^2}{2m}\frac{\partial \psi^2}{\partial x^2} = \frac{2m}{\hbar^2}(V_0 - E)\psi = \rho^2\psi$$

we are looking for bound solutions so $V_0 > E$. this has a general solution $\psi = Ce^{\rho x} + De^{-\rho x}$ boundary condition at $x \to \infty$ is $C = 0$ so $\psi = De^{-\rho x}$. need to match wavefunction at $x = L/2$ where $A\cos kL/2 = De^{-\rho L/2}$. we also need to match derivatives at $L/2$ $-Ak\sin kL/2 = -\rho De^{-\rho L/2}$ divide and get $k\tan ka = \rho$. let $ka = z$ and then $\rho a = z\tan z$.

$$\rho^2 = 2m(V_0 - E)/\hbar^2 = 2mV_0/\hbar^2 - 2mE/\hbar^2 = 2mV_0/\hbar^2 - z^2/a^2$$

$$\rho^2 a^2 = z_0^2 - z^2$$

where $z_0^2 = (2mV_0/\hbar^2 a^2)$ i.e. $V_0 = z_0^2\hbar^2 a^2/(2m)$. Then we get $\sqrt{z_0^2 - z^2} = z\tan z$ or $\sqrt{(z_0/z)^2 - 1} = \tan z$

This is a trancendental equation!! bad news. but we can solve it with if we know z_0 i.e. V_0 e.g. suppose $z_0 = 4$. Then type:
Solve Sqrt[(4/z)^ 2-1] = Tan[z]
into wolfram mathematica and get that this has two +ve solutions at $z_1 = 1.25..$ and $z_2 = 3.59..$ (the -ve one doesn't correspond to a physical solution). So there are two bound states. we can find the energies by substituting these back into $z_n = k^2 a^2 = 2mE_n a^2/\hbar^2$ so $E_n = \hbar^2 z_n^2/(ma^2)$
and then we can also write down the full wavefunction as we can then numerically solve for k and ρ and hence get the normalisation $D = Ae^{\rho a}\cos ka$ in terms of A.
and then of course we have to normalise the total wavefunction so that we get the value for A for which $\int \Psi^*\Psi dx = 1$. we have to do this in piecewise continuous fashion as our wavefunction is piecewise continuous. i.e. $\int_{-\infty}^{-a}\psi^*\psi dx + \int_{-1}^{a}\psi^*\psi dx + \int_{a}^{\infty}\psi^*\psi dx = 1$