we saw last lecture that trapping a travelling wave in a potential set up interference. this is only constructive for certain wavelengths ie energies and sets up standing waves. If the potential is constant then the wavefunction is separable, we turn a single partial differential equation into 2 ordinary differential equations. One is easy, $T(t) = e^{-iEt/\hbar}$, the other is the time INDEPENDENT schroedinger equation. so to find our solutions, we have to specify $V(x)$, and solve the time INDEPENDENT schroedinger equation which is $H\psi = E\psi$ which is an eigenvalue/eigenvector equation (operator acting on some function returns that function multiplied by a constant - the equation sets BOTH the function and the energy) This typically gives an infinite number of solutions $\psi_E(x)$. for bound particles the energies are quantised so we can characterise these as $\psi_n(x)$ corresponding to energy E_n. Then the fully general solution to the time DEPENDENT schroedinger eqyation can be written as the linear sum of all the solutions $\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}$

3.3 Orthoganality of Eigenfunctions

$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}$ where c_n is the weighting of state n
so suppose we take one for n and another for m. Then we have

$$\hat{H}\psi_n(x) = E_n\psi_n(x)$$

integrate with ψ_m*

$$\int \psi_m^* \hat{H} \psi_n(x) dx = E_n \int \psi_m^* \psi_n(x) dx$$

But H is hermitian which means that $\int f^* H f dx = \int (Hf)^* f dx$. However, Hermitian means more generally (but its a bit formal see griffiths if you want) $\int g^* H f dx = \int (Hg)^* f dx$.

$$\int \psi_m^* \hat{H} \psi_n(x) dx = \int (H\psi_m)^* \psi_n(x) dx$$

But ψ_m is another of the eigenfunctions, this time with energy E_m so

$$\int (H\psi_m)^* \psi_n dx = E_m^* \int \psi_m^* \psi_n dx = E_m \int \psi_m^* \psi_n dx$$

bring it all together

1

$$\int (H\psi_m^*)\psi_n(x)dx = E_m\psi_m^*\psi_n dx = E_n \int \psi_m^*\psi_n(x)dx$$

so this requries $\int \psi_n\psi_m^* dx = 0$ for $n \neq m$ i.e. that energy eigenvectors are orthoganal. and normalised energy eigenvectors are orthonormal i.e. $\int \psi_m^*\psi_n dx = \delta_{mn}$

Hermitian operators give eigenvalues which are real and eigenvectors which form an orthoganal set.

we are also going to ASSUME they form a complete set i.e. they span the space so any function $f(x) = \sum_n c_n\psi_n$ can be written as a linear sum of the energy eigenfunctions - but this was the same condition for our general solution to the time dependent Schroedinger equation where we had $\Psi(x,t) = \sum c_n\Psi_n(x,t) = \sum_n c_n\psi_n(x)e^{-iE_n t/\hbar}$ so that at $t = 0$ we have $\Psi(x,t=0) = \sum c_n\psi_n(x)$

3.3.1 Example: the infinite square well

the energy eigenfunctions have the form

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin n\pi x/L \quad E = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

then if we have states n and m we have

$$\int \psi_n^*(x)\psi_m(x)dx = \frac{2}{L}\int_0^{+L}\sin(n\pi x/L)\sin(m\pi x/L)dx$$

Wolfram alpha
integrate Sin[n Pi x/L] Sin[m Pi x/L] from 0 to L
the indefinite integral form is actually the most useful

$$[\frac{L\sin(\pi(n-m)x/L)}{2\pi(n-m)} - \frac{L\sin(\pi(n+m)x/L)}{2\pi(n+m)}]_0^L$$

$$\frac{L\sin(\pi(n-m)x/L)}{2\pi(n-m)} - \frac{L\sin(\pi(n+m)x/L)}{2\pi(n+m)}$$

so the total is this $\times\frac{2}{L}$ i.e.

$$= \frac{\sin(\pi(n-m))}{\pi(n-m)} - \frac{\sin(\pi(n+m))}{\pi(n+m)}$$

when $n \neq m$ then both sin terms are for an integer times π so both are zero. when $n = m$ the denominator on the first term goes to zero and we have $\sin(\pi 0)/0 \to \pi$ (limit of $sin(ax)/x = a$ as $x \to 0$! so this is 1 when $n = m$ and so we can see explicitally that these are orthonormal.

we can also see that they span the space - we know from Fourier analysis that any function can be expressed as a sum of sin waves.

3.4   General solution: Wavefunctions with multiple states

so, our general solution is an arbitrary linear superposition of different stationary states given by the eigenfuctions $\psi_n(x)$ associated with energy E_n.

$$\Psi(x,0) = \sum_n c_n \psi_n(x)$$

and these eigenfunctions are mutually orthogonal. But if we MEASURE the system, it can only be in ONE of these eigenfunctions - the electron wave has to fit into the potential. so the multiple terms are telling us about the probability of finding the electron in a given state.

Lets just go with 2 terms to start with

$$\psi(x,0) = c_1 \psi_1(x) + c_2 \psi_2(x)$$

we konw that we still need

$$\int \psi(x,0)^* \psi(x,0) dx = \int (c_1^* \psi_1^* + c_2^* \psi_2^*)(c_1 \psi_1 + c_2 \psi_2) dx$$

$$= c_1^2 \int \psi_1^* \psi_2 dx + c_1^* c_2 \int \psi_1^* \psi_2 dx + c_1 c_2^* \int \psi_2^* \psi_1 dx + c_2^2 \int \psi_2^2 dx = c_1^2 + c_2^2 = 1$$

so each state has a weighting of c_n^2 to the probability. And when we measure the energy, there are two possible values we can get - E_1 or E_2 - so we should see the c_n^2 the probability of finding the system in state n i.e. of measuring energy E_n.

so now we'll do this more formally. In order to normalise our total wavefunction we need

$$\int \psi^*(x)\psi(x)dx = 1$$

$$\int \sum_m c_m^* \psi_m^*(x) \sum_n c_n \psi_n(x) dx = 1$$

3

$$\sum_m \sum_n \int c_m^* c_n \psi_m^*(x) \psi_n(x) dx = 1$$

$$\sum_m \sum_n c_m^* c_n \delta_{nm} = 1$$

$$\sum_m |c_m|^2 = 1$$

so each state has a probability weighting of c_m^2

Quantum wierdness interpretation: this is the probability of measuring the system in this state i.e. of measuring an energy E_m

3.4.1 $\Psi(x,0) = N(2\psi_1 + \psi_2)$

The individual ψ_1, ψ_2 are alreay normalized so we just need to know how to normalise this weighted sum. We have $\sum_n c_n^2 = 1$ where $c_1 = 2N$ and $c_2 = N$. so $4N^2 + N^2 = 1$ or $N = 1/\sqrt{5}$.

hence $\Psi(x,0) = \frac{1}{\sqrt{5}}(2\psi_1 + \psi_2)$

the probability of measuring E_1 is $(2/\sqrt{5})^2 = 4/5$ and the probability of measuring E_2 is $1/5$.

3.5   Expectation for Energy in a system with wavefunction with multiple states

The average (expectation) value of the energy is

$$< E(t=0) > = \int \Psi(x,0)^* H \Psi(x,0) dx = \int \sum_m c_m^* \psi_m^*(x) H \sum_n c_n \psi_n(x) dx$$

$$= \sum_m \sum_n c_m^* c_n \int \psi_m^*(x) H \psi_n dx = \sum_m \sum_n c_m^* c_n \int \psi_m^*(x) E_n \psi_n dx$$

$$= \sum_m \sum_n c_m^* c_n E_n \delta_{mn} = \sum_m c_m^2 E_m$$

i.e. the expectation value of the energy is the probability weighted sum of the energies associated with each state.

3.5.1 $\Psi(x,0) = N(2\psi_1 + \psi_2)$

mean energy after multiple measurements of systems in this state is $4/5E_1 + 1/5E_2$. suppose this a system where $E_n = n^2E_1$ then $< E >= 4/5E_1 + 1/54E_1 = 1.6E_1$

No individual measurement will give this value - we get E_1 80 per cent of the time, and $4E_1$ the remaining 20 per cent of the time.

3.6   Time dependence of multiple states

$$\Psi(x,t) = \sum_n c_n\psi_n(x)e^{-iE_nt/\hbar}$$

so the contribution of the different energy states changes with time even though each one on its own is a stationary state.

We can see this explicitally by looking at the probability for a two state system $\Psi(x,t) = c_1\psi_1(x)e^{-iE_1t/\hbar} + c_2\psi_2(x)e^{-iE_2t/\hbar}$. and lets make it simple by choosing states that are real so $\psi^* = \psi$ and $c_n=c_n^*$

$$P(x,t) = \Psi^*\Psi = (c_1^*\psi_1^*e^{iE_1t/\hbar} + c_2^*\psi_2^*e^{iE_2t/\hbar})(c_1\psi_1e^{-iE_1t/\hbar} + c_2\psi_2e^{iE_2t/\hbar})$$

$$= |c_1|^2 * \psi_1^2 + |c_2|^2\psi_2^2 + c_1c_2\psi_1\psi_2e^{iE_1t/\hbar}e^{-iE_2t/\hbar} + c_1c_2\psi_1\psi_2^*e^{-iE_1t/\hbar}e^{iE_2t/\hbar}$$

so the last two terms contain $e^{\pm i(E_2-E_1)t/\hbar}$ i.e. they are oscillatory in time. Let $E_2 - E_1 = \hbar\omega$ and these go to $e^{\pm i\omega t} = \cos\pm i\omega t + i\sin\pm i\omega t$.

$$= |c_1|^2 * \psi_1^2 + |c_2|^2\psi_2^2 + c_1c_2\psi_1\psi_2(e^{-i\omega t} + e^{i\omega t})$$

$$= |c_1|^2 * \psi_1^2 + |c_2|^2\psi_2^2 + c_2\psi_1\psi_2(\cos\omega t - i\sin\omega t + \cos\omega t + i\sin\omega t)$$

$$= |c_1|^2 * \psi_1^2 + |c_2|^2\psi_2^2 + 2c_1c_2\psi_1\psi_2\cos\omega t$$

so the probability density IS a function of time.

it is still normalised so probablity of finding the particle SOMEWHERE $\int P(x,t) = 1$ as the orthoganality of eigenfunctions kills the time dependent term in the integral. but when we start asking for expectation values for systems which are NOT in an energy eigenstate then these CAN be time dependent.