3   Time independent Schroedinger equation

The Schroedinger equation is

$$\frac{-\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$$

This simplifies if $V(x,t) = V(x)$ i.e. the potential remains constant with time. Then the wavefunction is separable $\Psi(x,t) = \psi(x)T(t)$. Put this into the equation and:

$$\frac{-\hbar^2}{2m}\frac{\partial^2 [\psi(x)T(t)]}{\partial x^2} + V(x)\psi(x)T(t) = i\hbar\frac{\partial[\psi(x)T(t)]}{\partial t}$$

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

Divide by $\psi(x)T(t)$

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

The LHS is a function only of x, while the RHS is a function only of t. the only way these can be equal to each other is if NEITHER is a function of x or t i.e. if this is equal to a constant. We'll call this separation constant E as in a moment we'll see that it is!

$$E = i\hbar\frac{1}{T(t)}\frac{dT(t)}{dt}$$

$$\frac{E}{i\hbar}dt = -iE/\hbar dt = dT(t)/T(t)$$

cf the standard derivative $d(e^{ct})/dt = ce^{ct}$ so $T(t) = e^{-iEt/\hbar}$ on the other side we have

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

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

The time depenent Schroedinger equation is a partial differential equation and by separation of variables we turned it into two ordinary differential

equations, the time one was easy to solve as an exponential, the spatial one becomes an Eigenvalue equation. i.e. of the type $A(\hat{x})f(x) = af(x)$ where $\hat{A}$ is an operator and a is a number. In other words, the operator acting on a function returns the same function multiplied by a number. Ours is $A(\hat{x})\psi(x) = E\psi(x)$ where H is teh hamiltonian operator.

so we can use the whole set of mathematical machinary to solve the time independent schroedinger equation. and then we can completely specify the time dependent behaviour by multiplying ψ_E by $e^{-iEt/\hbar}$. $\psi_E(x)$ is termed the time independent wavefunction and E is the enery eigenvalue.

all we have to do for a time independent potential is to specify V. then we can solve the time independent Schroedinger equation to get $\psi_E(x)$ - where I've used the subscript E to describe the energy eigenfunction as there are typically multiple solutions, each corresponding to a different energy E. The full wavefunction for each eigenfunction, $\Psi_E(x,t)$ is simply found by multiplying $\psi_E(x)$ by $e^{-iEt/\hbar}$ where the E is specific to the ψ_E.

The general solution to the time dependent Schroedinger equation is the weighted sum of all of these separate wavefunctions.

$$\Psi(x,t) = \sum_E c_E \Psi_E(x,t) = \sum_E c_E \psi_E(x) e^{-iEt/\hbar}$$

though of course this total wavefunction is NOT a solution of the time independent Schroedinger equation, only each individual $\Psi_E(x,t)$ is.

3.1 Bound particles and standing waves

We are ultimately interested in the energy levels of hydrogen, so we are most interested in what happens with bound electrons. In these, the electron wave is trapped by a time independent potential. First we are going to look at this in a quite intuitive way. Then we will solve the time independent Schroedinger equation for it.

We can trap the free electron wave in the range 0-L, where now we are thinking of $L \sim \lambda$ by putting an infinite potential at these points.

Our wave moving from left to right in free space is $\Psi = Ae^{i(kx-\omega t)}$. But now it reflects off the other side of the potential, so there is another wave moving from right to left with $\Psi = -Ae^{i(-kx-\omega t)}$, and the two will interfere.

Our general wave function is the sum

$$\Psi = Ae^{i(kx-\omega t)} - Ae^{i(-kx-\omega t)}) = e^{-i\omega t}A(e^{ikx} - e^{-ikx})$$

$$= e^{-i\omega t} A[\cos(kx) + i\sin(kx) - \cos(-kx) - i\sin(-kx)]$$
$$= 2Ai\sin(kx) \quad \text{at } t = 0$$

$V(0) = V(L) = \infty$ so there is zero probability to find the electron at these points. $\Psi(0) = 0 = 2Ai\sin(0) = 0$ which is fine. But we also have $\Psi(L) = 0$ then $2iA\sin(kL) = 0$ so $k = n\pi/L$.

What the potential has done is take a travelling wave which could have any energy, reflect it so it interfers. Only for certain wavelengths which fit exactly into the potential can this interference be constructive and we get a STANDING WAVE. Otherwise we get nothing. The potential has fixed width, so there are only fixed wavelengths which fit into the potential, denoted by $k = 2\pi/\lambda = n\pi/L$ i.e. $\lambda = L/2n$. And each of these has its own energy since $E_n = k^2\hbar^2/2m = \frac{\hbar^2 n^2 \pi^2}{2mL^2} = E_1 n^2$ where $E_1 = \frac{\hbar^2\pi^2}{2mL^2}$ is the ground state

But this means that if a system is in one of its energy eigenfunctions, we get a DEFINITE answer for energy. which feels a bit weird as this is quantum mechanics, which is typically not definite about anything. But when you trap a wave by a potential, then reflections set up interference which mean that the matter wave which is the electron can only have one of a set of specfic energies - energy levels in Hydrogen (though its a fair way off) and if its in ones of these energy eigenstates, then this automatically means that all expectation values of any quantity are time independent

$$< A >= \int \Psi^* A \Psi dx = \int e^{iEt/\hbar} \psi^* A e^{-iEt/\hbar} \psi dx = \int \psi^* A \psi dx$$

And expectation values of the hamiltonian give a definite answer!! $< E >=< H >= E$.

3.2 Infinite square well energy eigenfunctions

$V = 0$ for $0 < x < L$ and ∞ elsewhere. so in the well we have

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

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x)$$

3

this is simply SHM $d^2\psi/dx^2 = -k^2\psi$ for $k = \sqrt{2mE}/\hbar$. So we know this has solution $\psi(x) = A\sin kx + B\cos kx$. Boundary conditions as before and $\psi(0)$ means $\psi(0) = A\sin 0 + B\cos 0 = B = 0$. The $\psi(L) = 0 = A\sin kx$ so $k = n\pi/L$ and it is quantised in $n = 1, 2 \ldots$. $\psi(x) = A\sin(n\pi x/L)$ and A is set by the normalisation condition $\int \psi^*\psi dx = 1$ giving $A = \sqrt{2/L}$.

These solutions are quantised in shape by quantum number n, and are quantised in energy $k = n\pi/L = \sqrt{2mE}/\hbar$ hence $E_n = n^2\pi^2\hbar^2/2mL^2 = n^2 E_1$. And it makes most sense to denote each different solution by n rather than by E because n is just a counter that goes from $1, 2, 3 \ldots$.

Then the spatial part of the energy eigenfunctions are $\psi_n(x) = \sqrt{2/L}\sin(n\pi x/L)$. we can make these into the full energy eigenfunctions by

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} e^{-iE_n t/\hbar} \sin(n\pi x/L)$$

so if the system is in a single energy eigenstate then all expectation values are time independnent

e.g. we saw an example of this already from our wavefunction in an infinite potential from 0 to L, but lets do t

$$\Psi(x, t) = e^{-i\omega t}\sqrt{\frac{2}{L}}\sin(n\pi x/L) = T(t)\psi(x)$$

we saw that

$$<x> = \int_0^L \Psi^* x \Psi dx = \int_0^L e^{i\omega t}\sqrt{\frac{2}{L}}\sin(n\pi x/L) x e^{-i\omega t}\sqrt{\frac{2}{L}}\sin(n\pi x/L)$$

$$= \frac{2}{L}\int_0^L x\sin^2(n\pi x/L)dx = \frac{2}{L}\frac{L^2}{4} = \frac{2}{L}$$

formally, for any eigenfunction, the probability of finding an electron within dx of x is

$$P(x, t)dx = \Psi^*(x, t)\Psi(x, t)dx = e^{iEt/\hbar}\psi^*(x)e^{-iEt/\hbar}\psi(x) = \psi^*(x)\psi(x)dx$$

i.e. is not time dependent.

And since the time terms cancel to unity, if ψ_n is normalised, then $\Psi_n = \psi_n e^{-iE_n t/\hbar}$ is automatically normalised too.

4

But physically, the important point here is that the probability distribution for the electron is not dependent on time - these are stationary states. Again, here is another moment of brilliance of QM. The big issue with electrons in atoms is why they did not radiate - circular motion of a point charge in an 'orbit' picture means that the charge density is accelerating, so the electron should radiate, lose energy and atoms shouldn't exist! Instead in QM, the idea is that allowed energy levels are STANDING waves, so they are stationary states. The charge distribution is not moving, so the electrons don't radiate.

the fully general solution to the time dependent Schroedinger equation is

$$\Psi(x, t) = \sum_n c_n \Psi_n(x, t) = \sum_n c_n \sqrt{\frac{2}{L}} e^{-iE_n t/\hbar} \sin(n\pi x/L)$$

where we choose the c_n so as to be able to normalise our total wave function so that $\int \Psi^*(x, t)\Psi(x, t)dx = 1$ as required.