

1 Basics of Quantum Mechanics

1.1 Admin

The course is based on the book Quantum Mechanics (2nd edition or new international edition NOT 1st edition) by Griffiths as its just genius for this level. There are copies in the library and college libraries, and my online lecture notes are pretty comprehensive, but it is a nice book to just buy and read.

The additional book is Quantum Mechanics, B.H. Bransden and C.J. Joachain (Prentice Hall, 2nd Edition). This is a more formal approach, so useful in defining the syllabus, but not much fun to read.

The whole point of the course is to do energy levels in Hydrogen, but we'll sneak up on it, building up the framework we need to calculate them! The course necessarily involves a lot of special functions - most of these you will meet in the maths course at some point. I'm not interested in them, I'm only really interested in what they tell us about the energy levels, so don't panic and think you need to memorise them. I do expect you to be able to use them once they are given to you though.

I'm more interested in building physical understanding. some of that necessarily comes from mathematical derivations, so there will be a lot of board-work in this course, but I want to stress what the equations mean, how to think about them, rather than getting you to memorize derivations!

1.2 The electron wavefunction and Schroedingers equation: a quick review of L1

The double slit experiment is one of the conceptually most important experiments of quantum mechanics.

The interference pattern when both slits are open means that the electron also have wavelike properties. The separation of the fringes gives us the wavelength of the electron waves, and we get the de Broglie relation $\lambda = h/p$ where p is momentum. If its a wave then we can describe it as a wave function $\Psi(\mathbf{r}, t)$ - in general can depend on both position and time.

But if its wavy, then we are automatically in trouble. A wave doesn't have a well defined position e.g. if $\Psi(x) = A \cos(kx)$ has wavelength $\lambda = 2\pi/k$.

This extends over the entire x axis so how do we define its position?
 If we were to add together two waves of different wavelengths we get beats - and you can see that this starts to localise the total wave. If we add together enough of them we can get something which starts to look like it might approximate to a classical mechanics notion of localisation. But we did this by adding lots of different wavelengths together. and in the quantum world $p = h/\lambda$ so we got to a well defined position only by having an increasingly poorly defined momentum. so we are not getting any close to a classical mechanics approach where when we have $x(t)$ (plus some boundary conditions) we automatically get $v = dx/dt$ and $p = mv = mdx/dt$ and $KE = T = mv^2/2 = p^2/2m$. we can get localise $x(t)$ at some time t but only at the expense of not knowing p very well at all. This is the Heisenburg Uncertainty principle (better to call it indeterminacy!) $\Delta x \Delta p \geq \hbar/2$ and it forms an absolute limit to our knowledge.

This is all very unlike classical mechanics!

Classical waves, waves on a string obeyed a wave equation. If the string is in the x direction then a transverse wave in the y direction is the solution of the 1D wave equation:

$$\frac{\partial^2 y(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y(x, t)}{\partial t^2}$$

a solution is $y(x, t) = A \cos(kx - \omega t)$ where $\omega = 2\pi f$ and $\lambda = 2\pi/k$. This is a wave moving in the +ve x direction (left to right) along a string, where $v = \lambda f = \omega/k$. This is the same velocity irrespective of wavelength, whereas we know that in the quantum world we have $p = mv = h/\lambda$ so the speed of an electron wave depends on its wavelength....

so what we are looking for is neither classical mechanics nor classical waves. which brings us to ...

Quantum mechanics Suppose our electron is also a wave, described by a wavefunction Ψ , travelling along the x axis. Then we could try a similar solution

$$\Psi(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t)$$

We know that its energy $E = \frac{1}{2}mv_x^2 + V$ so for a free particle $E = p_x^2/2m$ ($V = 0$). In a quantum world we also have $E = hf = h\omega/2\pi = \hbar\omega$ and $p = h/\lambda = hk/2\pi = \hbar k$. Merge these together and get $E = \hbar\omega = p_x^2/2m =$

$\hbar^2 k^2/2m$. But we can pretty easily determine k^2 as we know that

$$\begin{aligned}\frac{\partial^2 \Psi(x, t)}{\partial x^2} &= \frac{\partial}{\partial x} [-Ak \sin(kx - \omega t) + Bk \cos(kx - \omega t)] \\ &= -Ak^2 \cos(kx - \omega t) - Bk^2 \sin(kx - \omega t) = -k^2 \Psi(x, t) = -\frac{2mE}{\hbar^2} \Psi(x, t)\end{aligned}$$

so we could easily justify something like

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

so the spatial bit looks a lot like the classical wave equation.

However, the time bit is going to be different from the classical wave equation as in quantum $p = mv = h/\lambda$ so the velocity depends on λ . So what happens w.r.t. time is different. Looking at the waveform you can see that you can get ω via a single derivative

$$\frac{\partial \Psi(x, t)}{\partial t} = \omega [A \sin(kx - \omega t) - B \cos(kx - \omega t)]$$

what we would really like for the term in square brackets to equal $C\Psi$

$$[A \sin(kx - \omega t) - B \cos(kx - \omega t)] = C[A \cos(kx - \omega t) + B \sin(kx - \omega t)]$$

equating coefficients of sine we get $A = CB$, while for cosine its $-B = CA$. Divide and get $-A/B = B/A$ i.e. $B^2 = -A^2$ and $B = \pm iA$. Take the +ve root. and firstly our electron wave is COMPLEX

$$\Psi = A[\cos(kx - \omega t) + i \sin(kx - \omega t)] = Ae^{i(kx - \omega t)}$$

Secondly, we get $C = -B/A = -i$ so $\partial \Psi / \partial t = -iE/\hbar \Psi$. Multiply both sides by $i\hbar$ and get $i\hbar \partial \Psi / \partial t = E\Psi$. We can now put everything together and our wave equation FOR A FREE PARTICLE MOVING IN ONE DIMENSION is

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = i\hbar \frac{\partial \Psi}{\partial t} = E\Psi$$

Since this is just simply saying $p_x^2/2m = \hbar\omega = E$ then we can easily see how to extend it to put an external Voltage, $V(x, t)$, as total energy is KE+PE so $p_x^2/2m + V(x, t) = \hbar\omega = E$

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

This is the time dependent Schroedinger equation in 1 dimension.

It is linear and homogeneous so the superposition principle holds i.e. if Ψ_1 and Ψ_2 are two different solutions of the Schroedinger equation, then their linear sum $\Psi = c_1\Psi_1 + c_2\Psi_2$ is also a solution.

It is also first order in the time derivative, with only $\partial/\partial t$ rather than the $\partial^2/\partial t^2$ of the classical wave equation. For classical waves we need both the wave function Ψ and its first derivative $\partial\Psi/\partial t$ in order to determine its behaviour as a function of time. Here, we only need the wave function at some time $t_0 = 0$ in order to completely specify the subsequent behaviour of the system.

1.3 Interpretation of Ψ

What can we do with a wave function? what does it tell us? The fact that we needed to use complex numbers in our justification for the Schroedinger equation shows immediately that we should not attempt to give wavefunctions a physical existence in the same way as water waves have a physical existence. complex quantities cannot be measured by any actual physical instrument. so we don't have to ask the questions what is waving and what is it waving in. And its questions like these that led to the aether in electromagnetism! but because our wave function here can be complex we are not tempted to make the same mistake again. wavefunctions are computational devices which have significance only in the context of the Schroedinger theory of which they are a part (this is a cop out, which we will look at in more detail in the final lecture!)

However, the wave function actually contains all in information which the uncertainty principle allows us to know. What is this information?

Going back to the double slit experiment, but turn down the intensity of the electron source so that only one electron comes through at a time. we can see the single hits on the screen where each electron lands (showing that individual electrons really are going through the slits). But after a while, when many 'single' particles have built up a pattern, we get the characteristic pattern of interference. Interference does not occur between electrons, but is a property of a single electron.

One single measurement does not have a predictable result - the electron hit can be anywhere in the pattern. only when we consider many identical systems do we get the full pattern. This suggests that for an individual

particle the process is of a statistical nature, so it is telling us something about the probability that the particle will hit the screen at a certain point. Since our wavefunction is complex, and probabilities must be real, this suggests that we associate a probability $\propto |\Psi(x, t)|^2$. This would be similar to classical waves where the intensity of a wave $I \propto \text{Amplitude}^2$. Then the probability of finding a particle between x and $x+dx$ is

$$P(x, t)dx \propto |\Psi(x, t)|^2 dx = \Psi^*(x, t)\Psi(x, t)dx$$

where the position probability density $P(x, t)$ has units $1/\text{length}$ and the wavefunction $\Psi(x, t)$ has units $(\text{length})^{1/2}$. This is always real even when our wavefunction is imaginary. Suppose $\Psi = a + ib$ where a, b are real. Then $\Psi^*\Psi = (a - ib)(a + ib) = a^2 + b^2$.

Thus the interpretation of the wavefunction is a statistical one. we talk about the wavefunction of an individual particle but it is more useful to think about it as describing the behaviour expected from an ensemble of identical systems.

1.4 Normalisation of a wavefunction

For a single particle, the probability to find this anywhere in space should be unity so this gives us a normalisation

$$\int P(x, t)dx = \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1$$

hence if we have some unnormalised function $f(x, t)$, which is a solution of Schroedinger equation, we can get its normalised version $\Psi(x, t)$ as $\Psi(x, t) = Nf(x, t)$ where N is some normalisation constant. Then we know that

$$\Psi(x, t)dx = 1 \quad \text{so} \quad \int (Nf)^*(Nf)dx = 1$$

$$|N|^2 \int f^* f dx = 1$$

$$|N|^2 = \frac{1}{\int f^* f dx} \quad \text{so} \quad N = \frac{1}{\sqrt{\int f^* f dx}}$$

so in full we have

$$\Psi(x, t) = \frac{f(x, t)}{\sqrt{\int_{-\infty}^{+\infty} |f(x, t)|^2 dx}}$$

1.4.1 Normalisation for free particle

So, lets go into this with our 1D Schrodinger equation for a free particle $\Psi(x, t) = Ae^{i(kx-\omega t)}$. Then

$$\int_{-\infty}^{+\infty} \Psi^*(x, t)\Psi(x, t)dx = A^2 \int_{-\infty}^{+\infty} e^{-i(kx-\omega t)}e^{i(kx-\omega t)}dx = A^2 \int_{-\infty}^{+\infty} dx = \infty$$

Thats not a good start. Its because a plane wave along the x axis is completely delocalised - there is constant probability to find it anywhere along the x-axis. In practice we'd confine it by the experiment to a box of length $L \gg \lambda$ (e.g. the size of the room!) so

$$A^2 \int_0^L e^{-i(kx-\omega t)}e^{i(kx-\omega t)}dx = A^2L = 1$$

so then $A^*A = 1/L$ so we are free to choose this to be any (complex) number where $A^2 = 1/L$ eg $A = 1/\sqrt{L}$ or $A = -1/\sqrt{L}$ or $A = i/\sqrt{L}$ or $A = -i/\sqrt{L}$ or.... so pick the one which makes life easy and go for $A = 1/\sqrt{L}$. we know that we don't have a physical meaning for the wavefunction itself, only its square, so this phase doesn't matter.

so our normalised wavefunction is $\Psi(x, t) = 1/\sqrt{L}e^{i(kx-\omega t)}$. The probability of finding it in any section from a to $a + da$ is then $\int_a^{a+da} \Psi^*(x, t)\Psi(x, t)dx = 1/L \int_a^{a+da} dx = 1/L(a + da - a) = da/L$ and there is equal probability of finding a particle with this wavefunction anywhere.

Summary of L1

The Schroedinger equation is just a statement that KE+PE=total energy. i.e. $p^2/2m + V = E$ but all multiplied by the wavefunction Ψ

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

Ψ is tricky, but Ψ^2 has a probabilistic interpretation. Hence we have to normalise it such that the probability of finding it anywhere in space is unity (the particle has to be somewhere)