Waves vs particles

QM notes #1

De Broglie's hypothesis can be applied to situations other than the Bohr atom.

Consider a well which has infinite walls separated by a length L.
Classically any energy is possible. Also, in fact, De Broglie's waves don't really say anything can't exist .... But let's look at the condition for standing waves in such a situation. (this is almost example 5.6)

For a well of length L, standing waves will occur with nodes at each wall. The lowest standing wave actually has the condition:

$$\tfrac{1}{2}\lambda_1 = L \Rightarrow \lambda_1 = 2L$$

According to the de Broglie hypothesis, we then have:

$$\lambda = \tfrac{h}{p} \Rightarrow p = \tfrac{h}{\lambda}$$

The momentum is related to the kinetic energy by:

$$E = \tfrac{p^2}{2m} \Rightarrow p = \sqrt{2mE}$$

Here, we're ignoring all other types of potential energies. This then gives:

$$2mE = \tfrac{h^2}{\lambda^2} \Rightarrow E = \tfrac{h^2}{2m\lambda^2}$$

We thus find the lowest-lying energy for a particle in a box to be given as:

$$E_1 = \frac{h^2}{2m\left(4L^2\right)} = \frac{h^2}{8mL^2}$$

We can obtain the condition for all standing waves in the box:

$$\lambda_n = \tfrac{2L}{n}$$

Each additional standing wave introduces one additional node. We thus have the result:

$$E_n = \frac{h^2}{2m\left(\frac{2L}{n}\right)^2} = n^2\frac{h^2}{8mL^2} = n^2 E_1$$

Each of these is called an energy level and if we impose standing wave following de Broglie's hypothesis, then in fact, we have an energy spectrum resulting.

I want to let you know that soon we're getting ready to apply quantum mechanics to this situation and we'll find that the result from quantum mechanics gives:

$$E_1 = \tfrac{\pi^2\hbar^2}{2mL^2} = \tfrac{h^2}{8mL^2}$$

with successive energy levels given by $E_n = n^2 E_1$ (see page 196). Notice that n=0 can not exist here since the well is not infinite in length.

Your author goes on to interpret things in terms of probability. I prefer not to do this here and instead to provide you now with an introduction to quantum mechanics.

The ultimate hypothesis was from Erwin Schrödinger (NP: 1933). There are alternative approaches to quantum mechanics but we'll follow Schrödinger's approach from 1926. The story is that a suggestion at a seminar in Berlin to Schrödinger was that particles must obey a wave equation of some sort if de Broglie's hypothesis was valid, which it seems that experimental evidence has shown. Now we can attempt to argue several plausible routes that may have led Schrödinger to his equation. I prefer not to do this. The wave equation which he proposed for 1-dimension is:

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V\psi(x,t) \quad (6.1)$$

I want to identify the important terms here:

$i \equiv \sqrt{-1}$; V is some potential; m=mass; ψ is a "wave function"

if we want to express this in 3-dimensions, the result is:

$$i\hbar \frac{\partial \psi(\vec{x},t)}{\partial t} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2 \psi(\vec{x},t)}{\partial x^2} + \frac{\partial^2 \psi(\vec{x},t)}{\partial y^2} + \frac{\partial^2 \psi(\vec{x},t)}{\partial z^2}\right] + V\psi(\vec{x},t) \quad (6.2)$$

Here, I've used the vector symbol to represent that the wave function is a function of x,y,z in order to condense notation.

Your author tries to compare this to the classical wave equation:

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

and you notice immediately that these don't really compare very well … in particular the classical equation involves a second derivative w/r to time combined with the second derivative w/r to x. Such a comparison is not going to be successful. Your author ultimately says this when he states "Equations (6.1) and (6.2) are the starting points that we will need for this chapter. We emphasize that the time-dependent Schrödinger wave equation has not been derived. There is no derivation because we need new physical principles."

The important point: (6.1) and (6.2) are a fundamental "law" new to physics as much as F=ma. I'll even be pretty blunt about it: you can't understand quantum mechanics unless you're going to be willing to work with the SWE. That is why I spent so much time showing you how to work with partial derivatives. In quantum mechanics, it's the starting point.

I will show you how to remove time from the SWE. I call 6.1 the 1DSWE. I call 6.2 the 3DSWE. After I show you how to remove time from these equations, we'll have what I will call the 1DTISWE and the 3DTISWE.

Ok, now there is no way past it at this point: either you're going to work with the math and understand the results or you'll look at the results and always wonder how to get them. I prefer the first.

Here is the interpretation of the wave function that appears in the SWE:

(1) Ψ itself has no physical meaning ! Hu? yes you heard it directly from me.

ok, then what use is such a thing?

(2) $|\psi|^2$ has the physical interpretation of probability per unit length (1D) or probability per unit volume (3D) which is constant in time.

Ok, now I need to teach you one more thing. This is a second mathematical thing that is needed in order to work with the SWE.

Complex variables:

IMPORTANT TO UNDERSTAND: look at eq. 6.16 for example.

In general a complex number can be written as:

$$B = x + iy$$

x is called the real part of B and y is called the imaginary part of B.

Let me show you a bit of magic now:

$$(x+iy)(x-iy) = x^2 + ixy - ixy + y^2 = x^2 + y^2$$

This is how we define the magnitude of B:

$$|B| = \sqrt{x^2 + y^2}$$

which looks a whole lot like things you have seen before, only different.

That part (x-iy) looks like it is related to B , and it is almost B but not quite. We have a special name for that quantity: it is the COMPLEX CONJUGATE of B:

$$B=x+iy \Rightarrow B^* = x - iy$$

Now, we can also write complex numbers in another way: we can express them as a radius times a phase. Here is an example:

$$B = x + iy \Rightarrow B = Re^{i\varphi} = R\cos(\varphi) + iR\sin(\varphi)$$

$$R = \sqrt{x^2 + y^2}; \tan(\varphi) = \tfrac{y}{x}$$

It all looks pretty familiar. You can prove this by writing out the series expansion for sin and cosine and the exponential. I prefer that you know this and use this.

Now one more thing:

$$B = Re^{i\varphi} \Rightarrow B^* = Re^{-i\varphi}$$

It is important for you to force yourself to understand the complex conjugate, since we'll use it lots.

I could (and am tempted) to teach you a bit of complex algebra here … if we need it, I will do it. For now, be aware that you might think you understand algebra … you only understand ½ of it if you don't understand how to work with complex algebra.

Now let's look at what strings have to be connected to the wave function in order for interpretation (2) to be valid.

(a) it needs to be finite everywhere, otherwise the probability would be infinite.
(b) it must be single-valued since you can't have 2 probabilities for the same event.
(c) ψ and $\frac{d\psi}{dx}$ (or $\frac{\partial\psi}{\partial x}$) need to be continuous for finite potentials. Exceptions to this may be observed when potentials are approximated as becoming infinite.
(d) The probability of finding a particle somewhere in space must be equal to 1.
(e) Since (d) is the case, the wave function needs to vanish at infinity.

There are times when these rules are bent. One prime example that continually bothers people in physics is the quantum mechanical free particle. We'll worry about that later.

Condition (d) is called the "NORMALIZATION" condition. We want our wave functions to be properly normalized. If you gamble in Las Vegas, you want to have a probability of 1 that out of a deck of 52 cards, one of these cards will be the 7 of hearts. It's that kind of thing that we're talking about here.

We can express condition (d) mathematically. Here is the condition that it places upon the wave function:

1-D:

$$\int_{-\infty}^{+\infty} \psi\psi^* dx = 1$$

3-D:

$$\int_{\substack{\text{all}\\ \text{space}}} \psi\psi^* d^3\vec{x} = 1$$

Here is an important note: you have not completed your quantum mechanics problem until you have properly normalized your wave functions. You will also note, amazingly enough, that wave functions are not uniquely defined! There is always an arbitrary phase that is introduced. How can this be? It has to do with the meaning of the wave function (1) ... i.e. no physical meaning.

Now let me show you how to separate out the time from the 1DSWE to produce the 1DTISWE. Although I show you the details here, you will probably not need to worry too much if you don't follow all of them. Look for the place below where I say details stopped here, and start understanding again.

The 1DSWE is:

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

Let us assume a solution of the form:

$$\psi(x,t) = \varphi(x)\,T(t)$$

Then if this is the solution to the 1DSWE, we have:

$$\frac{\partial\psi}{\partial t} = \varphi(x)\frac{\partial T(t)}{\partial t}$$

$$\frac{\partial^2\psi}{\partial x^2} = T(t)\frac{\partial^2\varphi(x)}{\partial x^2}$$

Substitute these into the 1DSWE:

$$i\hbar\varphi(x)\frac{\partial T(t)}{\partial t} = -\frac{\hbar^2}{2m}T(t)\frac{\partial^2\varphi(x)}{\partial x^2} + VT(t)\varphi(x)$$

Now divide both sides of the equation by the wave function:

$$i\hbar\frac{1}{T(t)}\frac{\partial T(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{\varphi(x)}\frac{\partial^2\varphi(x)}{\partial x^2} + V$$

Now notice that the left-hand side only depends upon time while the right hand side depends upon x. These can only be equal if both sides are equal to a constant. What this constant is will be obvious in a moment.

$$i\hbar\frac{1}{T(t)}\frac{\partial T(t)}{\partial t} = E; -\frac{\hbar^2}{2m}\frac{1}{\varphi(x)}\frac{\partial^2\varphi(x)}{\partial x^2} + V = E$$

Now notice that we can now write d’s instead of partials since the functions are of only one variable. Thus we have two equations to solve:

$$\frac{1}{T}\frac{dT}{dt} = -i\frac{E}{\hbar}; \frac{d^2\varphi}{dx^2} - \frac{2m}{\hbar^2}V\varphi = -\frac{2mE}{\hbar^2}\varphi$$

There is a little detail here:

sometimes V can get funny looking and it is safest to write it as I have written it.

Now we can solve for the time dependence very simply:

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

A note: in principle, there is a constant in front of this. I will let the constant be absorbed in the spatial part of the wave function.

Details ..

Now let’s look at the spatial equation:

$$\frac{d^2\varphi}{dx^2} - \frac{2m}{\hbar^2}V\varphi = -\frac{2mE}{\hbar^2}\varphi$$

At first glance, there is not much that will come out. So let’s take a second look. In particular, let’s look at the special case where V=0. This is a free particle, and if you have read closely, you know it’s not going to satisfy some condition somewhere. Be that as it may, let’s go ahead and see what happens:

$$V = 0 \Rightarrow \frac{d^2\varphi}{dx^2} = -\frac{2mE}{\hbar^2}\varphi \Rightarrow \frac{d^2\varphi}{dx^2} + \frac{2mE}{\hbar^2}\varphi = 0$$

This has very easy solutions: they are sins and cosines. I’m going to pick one:

$$\varphi(x) = A\sin(kx)$$

Now you can prove that this is a solution to the spatial equation by taking the second derivative:

$$\frac{d\varphi}{dx} = Ak\cos(kx); \frac{d^2\varphi}{dx^2} = -A(k)^2\varphi$$

Thus, we must have (for that suggested solution):

$$k^2 = \frac{2mE}{\hbar^2}$$

We can rewrite this as: $E = \frac{\hbar^2 k^2}{2m}$

Now what are the SI units of E?

$$[E] = \frac{\left[J^2 s^2\right]\left[\frac{1}{L^2}\right]}{\left[m^2\right]} = J\frac{Js^2}{mL^2} = J\frac{mL^2}{mL^2} = J$$

Ok, E has units of energy. You're beginning to understand why I picked this letter.

Let's compare this value to the value of a wave from the de Broglie wave length:

Suppose we have a particle described by:

$$\lambda = \frac{h}{p}$$

The wavelength is related to the wave vector k by:

$$k = \frac{2\pi}{\lambda}$$

If you compare the k in our spatial solutions to what we discussed about sinusoidal wave solutions, you can see that they are pretty much the same thing.

Thus, in terms of the wave vector, we have:

$$\lambda = \frac{2\pi}{k} = \frac{h}{p} \Rightarrow p = \frac{hk}{2\pi} = \hbar k$$

Hey, that's neat! that wave vector is actually related to momentum just like I might have mentioned to you! But look further:

$$KE = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

The kinetic energy looks a whole lot like the E for a particle in a potential-free region of space.

I would thus say that we are ready to state that E is the total energy of the particle.

Knowing this allows us to write the T equation as:

$$T(t) = e^{-i\omega t}$$

Where we recognize that the energy of the particle is

$$E = \hbar\omega$$

Now, so long as we can have time-independent potentials, we can separate the 1DSWE into two equations. The time equation will always have the same form that I've shown you (for several different energies, you'd need to add in different frequencies).

Thus the 1DTISWE is what gives us the energies of a quantum mechanical particle:

$$\frac{d^2\varphi}{dx^2} - \frac{2m}{\hbar^2}V\varphi = -\frac{2mE}{\hbar^2}\varphi$$

In future work, we're going to be using this very important equation. But for now, I want to show you how to solve the problem of the square well of length L which one side at x=0 and the other side at x=L. The walls of the well are infinitely high, so that particle won't be leaving the well.

Outside of the well, the wave function vanishes ... otherwise an infinite probability would result. So the only place we have a wave function is inside the well.

Inside the well V=0 (I've made it that way by assumption).

The 1DTISWE is then:

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \pm\sqrt{\frac{2mE}{\hbar^2}}$$

$$\frac{d^2\varphi}{dx^2} - \frac{2m}{\hbar^2} V\varphi = -\frac{2mE}{\hbar^2}\varphi \Rightarrow \frac{d^2\varphi}{dx^2} = -\frac{2mE}{\hbar^2}\varphi$$

Now you know solutions to this are sin functions (cosines also work but they don't vanish at 0 like they need to do).

Thus:

$$\varphi(x) = A_n \sin(k_n x); k_n = \pm\sqrt{\frac{2mE_n}{\hbar^2}}$$

All I've done here that is new is to put the little n subscript on k and E. This is because I'm getting ready to show the formation of the energy spectrum.

At x=L, we require the wave function to vanish. This gives us:

$$\sin(k_n L) = 0 \Rightarrow k_n = \frac{n\pi}{L}; n = 1,2,3,\ldots$$

Oh ! wow, we suddenly have the energy spectrum of the particle in the well:

$$\frac{n^2\pi^2}{L^2} = \frac{2mE_n}{\hbar^2} \Rightarrow E_n = n^2\left[\frac{h^2}{8mL^2}\right] = n^2 E_1$$

This is exactly what de Broglie waves gave us! There is, however, one nasty detail left to do. We need to normalize the wave function. To do this, let me choose the + solution for k.

Watch how I do this so you'll be able to do it also.

$$1 = \int_{-\infty}^{+\infty} \varphi\varphi^* dx = \int_0^L A^2 \sin^2\left(n\pi \tfrac{x}{L}\right) dx$$

Transform the variables:

$$z \equiv n\pi \tfrac{x}{L} : x = L \Rightarrow z = n\pi; dz = n\pi \tfrac{dx}{L} \Rightarrow dx = \tfrac{L}{n\pi} dz$$

This means that we can write the integral as:

$$1 = A^2\left[\tfrac{L}{n\pi}\right] \int_{z=0}^{z=n\pi} \sin^2(z) dz$$

Now go to the integrator: http://integrals.wolfram.com/
and enter the input: Sin[x]*Sin[x] (treat z as x). The output is:

$$\int_0^{n\pi} \sin^2(z)dz = \left[\tfrac{z}{2} - \tfrac{1}{4}\sin(2z)\right]\Big|_0^{n\pi} = \tfrac{n\pi}{2}$$

(be careful looking at the image given back ... π and x are easy to confuse).

$$1 = A^2\left[\tfrac{L}{n\pi}\right]\tfrac{n\pi}{2} = A^2\tfrac{L}{2} \Rightarrow A = \pm\sqrt{\tfrac{2}{L}}$$

I'm going to choose + here. (remember the arbitrary phase of the wave function?)
Thus, the properly normalized wave function is:

$$\varphi_n(x) = \sqrt{\tfrac{2}{L}}\sin\left(n\pi\tfrac{x}{L}\right); E_n = n^2E_1; E_1 = \tfrac{h^2}{8mL^2}$$

There is now one really subtle point remaining ... you might be interested in looking at the time evolution of a wave function. It is not the case that the probability will change with time but indeed the wave function will change. And, in fact, the change is pretty subtle ... each energy eigenvalue (that is the name that each of these energies is called) will evolve differently. Hey! that's what happens in reality ... fast particles go faster than slow particles ... so let's see what the time dependence of one solution will be:

$$T_n(t) = e^{-i\omega_n t}$$

where,

$$E_n = \hbar\omega_n = n^2E_1 \Rightarrow \omega_n = n^2\tfrac{E_1}{\hbar} = n^2\omega_1$$

Thus the wave function of the nth eigenstate will vary as:

$$\psi_n(x,t) = \sqrt{\tfrac{2}{L}}e^{-i\left[n^2\omega_1 t\right]}\sin\left(n\pi\tfrac{x}{L}\right)$$

I will show you later what happens to the wave function after you've digested this part of QM.