PHY 416, Quantum Mechanics

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Contents

Chapter 1

First Class: Quantum Mechanics

Tuesday, August 26, 2008

1.1 Introduction

Welcome to Physics 416! Quantum Mechanics is, almost needless to say, an amazing subject! We will, of corse, see many amazing things in studying it.

Let me begin by briefly telling you about an example about the utility of quantum mechanics for us.

As we learned from Albert Einstein, energy and mass are interchangeable. Also, we now know that it is nuclear fusion that powers the sun. The following sequence of reactions is believed to contribute to this.

$$p + p \rightarrow {}_1H^2 + e^+ + \nu + 1.44MeV \tag{1.1}$$

$${}_1H^2 + p \rightarrow {}_2He^3 + \gamma + 5.49MeV \tag{1.2}$$

$${}_2He^3 + {}_2He^3 \rightarrow {}_2He^4 + p + p + 12.49MeV \tag{1.3}$$

Notice that this sequence is a chain reaction. It is called the proton-proton cycle, or the "p-p cycle". But, consider the first step: the protons in the core plasma of the sun repel each other according to Coulomb's law. Unless they are touching ($r \sim 10^{-15}$m).

Fig 1

We would like you to show that, at touching, the potential energy ∼1MeV (for a pair of protons, Coulomb P.E.).

Do the protons have this much energy? The sun's core is hot. According to quantum mechanics, we know how hot it is ($\approx 15.7 \times 10^6$K. Is this hot enough? Recall that, for independent particles in thermal equilibrium,

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}k_B T \tag{1.4}$$

where $k_B \equiv$ "Boltzmann's Constant" $= 1.381 \times 10^{-23} J/k = 8.617 \times 10^{-5} eV/k$ (recal that 1eV $= 1.6 \times 10^{-19} J$).

Now, the plasma at the center of the sum is roughly, we shall say, "like" an ideal gas of protons, neutrons, and electrons. Consider a proton in this plasma. For it

$$\left\langle \frac{1}{2}mv^2 \right\rangle \approx \left(8.7 \times 10^{-5}\frac{eV}{k}\right)\left(1.6 \times 10^7 K\right) \sim 1.4 \times 10^3 eV \ll 1MeV \tag{1.5}$$

Conclusion: According to classical physics, even in the core of the sun, it is too cold for nuclear fusion to occur; therefore, the sun should not shine! The protons should not penetrate the Coulomb barrier! Yet, according to quantum mechanics, particles can "appear" in forbidden regions – in fact, we use the theory to predict exactly the rate of this "forbidden appearance", and from this, the rate of the p-p cycle. From this, we can predict the mean power output of the sun ($\sim 3.8 \times 10^{26} W$), and from this, the mean expected temperature of the earth – and it works well!

Here is another example. Suppose we throw an eraser; it goes from "here" to "there" on a parabolic path.

fig2

You say that this follows Newton's law, but where is this from? Suppose a particle is observed to be at x_1 at time t_1, and later at x_2 at time t_2. How does it get from (x_1, t_1) to (x_2, t_2)?

According to orthodox quantum mechanics: Between the observations, the particle does not possess all the attributes of reality. In particular, it does not possess the attribute of position. Thus, there is no definite trajectory. Rather, "in potentia", all possible trajectories, even very wild ones, contribute to the result of the second observation.

fig3

As we will see, these trajectories **interfere** with each other in potentia. As we will also see, in the limit of macroscopic mass, the interference is destructive for all paths except those in a narrow band around the classical parabolic path. In this band, the "superposition of possibilities" is constructive.

fig4

Other examples

1. Light incident on glass
2. Photon counting in the lab

Clearly, an understanding of interference is important for embarking to understand quantum mechanics. We turn to a quick review of this next. For interest, we place this in a historical context.

1.2 Interference: Review of Evidence for the Wave Theory of Light – Thomas Young's Interference Experiment

Maxwell's equations and the theory of electrodynamics provide, as you know, very strong theoretical evidence for the electromagnetic wave nature of light (1865). However, the earlier results of Thomas Young are, from an experimental point of view, extremely important.

Background:

1. Newton: Corpuscular Theory of Light (1670's)
2. Huygen: Early Wave Theory of Light (1670's)

Situation in the 1700's: Great weight of Newton's opinion hung like a shroud over all of Europe.

Along comes 22 year old Thomas Young in 1802. He says that he can prove that light is a wave, and to boot that he can measure its wavelength! **How did he do this?** To understand, we must ask: What properties do waves have that is (are) different than those of particles? They can **interfere** e.g. You can have $\text{wave}_1 + \text{wave}_2 = 0$ if the crests of wave_1 overlap the troughs of wave_2. But, "particle + particle" cannot equal zero. Then Young had to face the issue of how to use this interference idea effectively to distinguish the two possibilities. for this, he resurrected Huygen's principle: all points on a wavefront can be considered as point sources for the production of a new ("secondary") spherical waves. After the elapsing of time, the new wavefront is the common surface of tangency to these secondary spherical waves.

fig5

The next ingenious idea was to attempt to effectively isolate only “two” spherical waves that would then be allowed to interfere with each other. It is presumably, mush easier to keep track of the interference of two waves than of an infinite number of waves. The idea then is to force the two waves to combine out of phase with each other by different amounts at different points on a viewing screen, thus causing the brightness of illumination along the screen to vary. To accomplish this, he used a setup that forced the two waves to start out in phase, but to meet out of phase due to an imposed difference in the distance traveled.

fig6

Let’s now fix these ideas semi-quantitatively

fig7

For P to be a max: $s_1 b = m\lambda$

$$d\sin(\theta) = m\lambda \quad or \quad \sin(\theta) = \frac{m\lambda}{d}, \quad m = 1, 2, \ldots \tag{1.6}$$

For P to be a min

$$d\sin(\theta) = (m+1)\lambda, \quad m = 1, 2, \ldots \tag{1.7}$$

som yound, knowing d and θ could find λ, thus proving that light is a wave! But, no one believed him.

About what is the wavelength of light? Example: green light

- Slit spacing: $d \approx 0.1mm$
- Distance to screen: $D \approx 20cm$
- First minimum found at 0.16°

$$\sin(\theta) = \frac{\frac{1}{2}\lambda}{d} = \frac{\lambda}{2d} \tag{1.8}$$

Therefore, $\lambda = 5460\mathring{A}$. World’s first (of course) determination of wavelength of light − now you see how we know it! (micro-world property − amazing for 1802!)

1.3 Two-slit interference, Quantitative Calculation of Intensity distribution at the Screen

At a given point on the screen we have the superposition of say, $E_1 = E_0 \sin(\omega t)$ and $E_2 = E_0 \sin(\omega t + \phi)$, $\quad \phi = \phi(\theta)$. We wish to add these:

$$E_p = E_1 + E_2 \quad = \quad E_0 \left[\sin(\omega t) + sin(\omega t + \phi)\right] \tag{1.9}$$

By using the trigonometry identity

$$\sin A + \sin B = 2 \sin\left(\frac{A+B}{2}\right) \cos\left(\frac{A-B}{2}\right) \tag{1.10}$$

by using this identity, one can obtain

$$E_p = 2E_0 \cos\left(\frac{\phi}{2}\right) \sin\left(\omega t + \frac{\phi}{2}\right) \tag{1.11}$$

The $2E_0 \cos\left(\frac{\phi}{2}\right)$ term depends only on ϕ, which depends on θ, so this is an amplitude that varies a P is moved along the screen. The $\sin\left(\omega t + \frac{\phi}{2}\right)$ term is a simple harmonic variation at the same frequency ω. Of course, the eye responds to intensity, not field. Recall that, for the electromagnetic wave, the intensity depends on the magnitude of the Poynting vector, $\vec{S}$, where

$$\vec{S} = \frac{1}{\mu_0} \vec{E} \times \vec{B} \tag{1.12}$$

For an electromagnetic wave in free space, $\vec{B} \perp \vec{E}$ and $B = \frac{E}{c}$, so

$$\vec{S} = \frac{1}{\mu_0 c} E^2 \tag{1.13}$$

Now S^2 varies in time according to its factor $\sin^2(\omega t + \alpha)$, which oscillates at the frequency, ω – some $10^{15} Hz$ – far to fast for the eye to follow. So, what we need is the time average over the resolution time of the eye. Since the variation is simple-harmonic, all cycles are the same, so it is suffices to average over one cycle. Thus, intensity at point P on the screen is

$$I_P = \frac{1}{\mu_0 c} 4E_0^2 \cos^2\left(\frac{\phi}{2}\right) \left\langle \sin^2(\omega t + \phi) \right\rangle_t \tag{1.14}$$

We drop the $\frac{1}{\mu_0 c}$ since we will be taking ratios for which it will cancel. Now, $\left\langle \sin^2(\omega t+\phi)\right\rangle_t = \frac{1}{2}$, so

$$I_P = 4E_0^2 \cdot \frac{1}{2} \cos\left(\frac{\phi}{2}\right) \tag{1.15}$$

Now again, $\phi = \phi(\theta)$. How? To find out, set up the ratio

$$\frac{\phi}{2\pi} = \frac{p.l.d}{\lambda} \Rightarrow \quad \frac{\phi}{2\pi} = \frac{d\sin)\theta)}{\lambda} \Rightarrow \quad \phi(\theta) = \frac{2\pi d\sin(\theta)}{\lambda} \tag{1.16}$$

thus, in its full glory (except for the supposed factor $\frac{1}{\mu_0 c}$),

$$I_P = \frac{1}{2} \cdot 4E_0^2 \cos^2\left(\frac{\pi d\sin(\theta)}{\lambda}\right). \tag{1.17}$$

It is often of important interest to compare the result for I_P when both slits are open to the intensity at P when only one slit is open and one is blocked. For this purpose, define$I_0(\theta)$ to be the intensity at $P(\theta)$ with only one slit open and the other blocked. Then

$$I_0(\theta) = \left\langle E_0 \sin^2(\omega t)\right\rangle_t \quad = \quad \frac{1}{2}E_0^2, \tag{1.18}$$

thus, the intensity with both slits open is

$$I_P = 4I_0 \cos^2\left(\frac{\phi}{2}\right) \tag{1.19}$$

This is interesting and very important. Let's plot it:

fig8

As we say, this is very important: If I_0 is the intensity with just one slit open, note that we do **not** get $2I_0 = I_0 + I_0$ (as you might expect)[1] by opening both slits. Rather, $I(\theta)$ varies between 0 and $4I_0$ as θ changes. It's as if $1+1=4$ or $1+1=0$!

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[1] You **do** get this if you use a flashlight instead of a laser as a source. Why is this?

Chapter 2

Second Class: More on the Behavior of Light

Thursday, August 28, 2008

2.1 Introduction

The wave picture of light, coupled with the interference idea, already leads us to conclusions like the possibilities of $1 + 1 = 4$ and $1 + 1 = 0$, which may seem natural in the wave picture, but which become very strange in the photon picture: it is the job of quantum mechanics to explain this.

There are other really amazing things. These occur with nearly monochromatic light (which is freed from the mixings and jumblings of everyday light). The laser is a good source of such light.

Suppose, for example, you illuminate a ball bearing with a indexlaser laser. With "true light", right at the center of the shadow, where you expect things to be the darkest (the "penumbra" of the shadow with ordinary light), there is a bright spot! This is evidence that true light does **not** "travel in straight lines", as we are led to believe! Some must have curved to get to the center!

fig1-5

These results are rather amazing! We do not expect these from geometrical optics. Maybe you don't believe them. That's o.k., you'll do it in lab sometime. Return to the shadow of the ball bearing, note the bright spot a the center – certainly weird. In 1818, Fresnel, a young Frenchman, (29 years old) presented an essay to the Paris academy. The judging committee had many of the prominent physicists of the day, including, Poisson, Arago, Laplace, and Biot. Poisson, an advocate of the corpuscular theory, worked out Fresnel's results and found the bright spot. This resulted in the corpuscular theory dying in one day, and was not revived again until the 20^{th} century.

Now back to the "expanding" behavior of light. We can get a first inkling from the following example. As a definite case, consider monochromatic plane waves incident on a single aperture of width a in one dimension (and width $\gg$a in the perpendicular direction, which is in and out of the page in figure 2.6). This figure shows what we call diffraction, which is really just the interference of many circular waves according to Huygen's principle.

fig6

2.2 Single Slit Diffraction, continued

Semi-quantitative Consideration

We could calculate the diffraction pattern quantitatively by summing (or integrating) over the infinite number of infinite similar-spaced points of emission along the slit. However, before we get involved, in detailed mathematics, let us see if we can figure out what we expect the answer to look like (roughly at least) in advance. Where possible, this procedure is always a good idea.

fig7

The point Q at the center will clearly be bright (Why?). Now consider a point P such that the following happens

fig8

Each point on top half is canceled by a point in the bottom half, therefore, we have found a minimum. So, $a\sin(\theta) = m\lambda$ are minima. Something happens at $m\lambda$. Now consider an angle θ such that the following is true

fig9

I cancels II, and the light reaching the screen at P is effectively $\frac{1}{3}$ of the total light from the slit. Therefore, we expect a maximum there[1], but not a bright as the central maximum. by this kind of preliminary logic, we expect an intensity pattern that looks something like this:

fig10

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[1] At least roughly midway between the first and second minima. It turns out that, in fact, the maxima are **not** exactly given by $a\sin(\theta) = \left(m + \frac{1}{2}\right)\lambda$. This will be addressed in the homework.

We now attempt to consider this more quantitively. The paradigm problem: A plane wave is incident on a small[2] aperature.

fig11

We want the calculate the result at P. To model the problem, try breaking the aperture into an infinite number of infinitesimal "subapertures"; each contributes a phasor of infinitesimal amplitude to P. So we must "add up" (or integrate) the contributions from all of the little "subslits". This means that we have to "add up" a very large number of harmonically varying electric fields (each with a different phase) at P. Although technically this is an integral, $E(P) \propto \int dy \sin(\omega t + \phi(y))$, we will develop a neat picture method instead

fig12

2.3 Method of Phasors

In order to understand our results, in a quantitative way, we will need an alternate, powerful method for adding sinusoidal oscillations of the same frequency. You will recall that we did this via "trigonometry identity" for $\sin(\omega t)+\sin(\omega t+\phi)$ for double slit interference. Let us consider that problem again. Consider an electric field, $E_1 = E_0 \sin(\omega t)$. This is the "vertical component" of the rotating vector in figure 13.a. Likewise, $E_2 = E_0 \sin(\omega t + \phi)$ is the "vertical component" of the rotating vector in figure 13.b. Consider then, the construction shown in figure 13.c. A moment's thought convinces you that the vertical component of $\vec{E}$, the vector sum, is the magnitude of $E_R = E_0 \sin(\omega t) + E_0 \sin(\omega t + \phi)$, which is what we want. Further, to find the phase of E_R, we can use simple geometry!

fig13a,b,c

fig14

We see that $\alpha = \frac{\phi}{2}$. Also, using the law of cosines, the magnitude,

$$\begin{aligned} E_R^2 &= E_0^2 + E_0^2 - 2E_0^2 \cos(180^\circ - \phi) \\ &= E_0^2(1 + \cos(\phi) \\ &= 4E_0^2 \cos\left(\frac{\phi}{2}\right) \end{aligned}$$

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[2] As we saw earlier, "small" means small compared to the wavelength of light

so,

$$E_R = 2E_0 \cos\left(\frac{\phi}{2}\right) \tag{2.1}$$

So

$$\begin{aligned} E_P &= \sin(\omega t) + \sin(\omega t + \phi) \\ &= 2E_0 \cos\left(\frac{\phi}{2}\right) \sin\left(\omega t + \frac{\phi}{2}\right) \end{aligned}$$

just as we had figured earlier by trigonometry identity. The great advantage of this technique is that it is easily extended to the addition of many harmonic oscillations of the same frequency – this would be very painful by trig identity, but if all else fails, with this method, you could do it graphically. It was invented by M Co?????, circa 1880.

fig 15

For our "single slit" problem, we will have essentially, to add together an infinite number of phasors, which is a tantamount to doing an integral "by pictures". In the following, we'll sketch how this works.

Now let us look at our "single slit" problem at the next level. We use the phasor method. An outline of this fllows:

- Divide slit up into many "elements"
- Adjacent elements have phase difference $\Delta\phi$

where,

$$\frac{\Delta\phi}{2\pi} = \frac{p.l.d}{\lambda} \Rightarrow \quad \Delta\phi = \frac{2\pi}{\lambda}\Delta x \sin(\theta) \tag{2.2}$$

fig16

Now let's look at the situation in the $\theta = 0$ direction. there, all path length are the same, so all the phasors point the same way and add up to something big – a very bright max of intensity.

fig17

Now we move P slightly up (or down) the screen. Then each successive ray has a slight path length difference from the previous one, so each successive phasor at P is inclined at a slightly greater angle. Thus, the resultant (E_θ in figure 18) is not as big as when all the phasors point in the same direction.

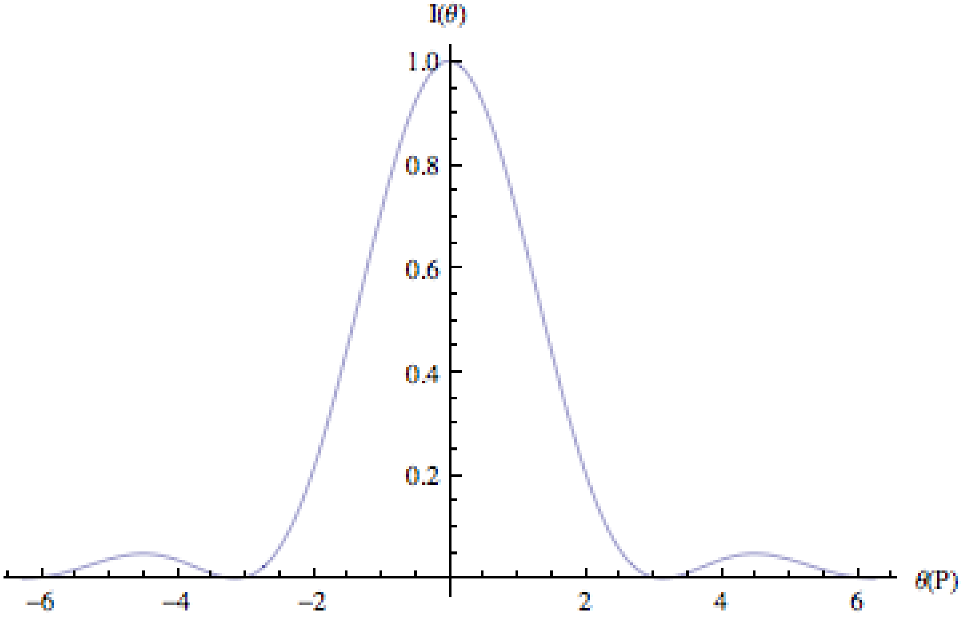

Figure 2.1: **Figure 21**: The intensity as a function of θ at point P.

fig18

And if θ increases further, so does $\delta\phi$ − until we reach a point when the phasors close in on themselves!

fig19

Then we have a minimum. And if we increase θ further,

fig20,

we reach a secondary maximum, with clearly less resultant than the straight ahead max. And so on, a pattern of maxima and minima, with the maxima getting dimmer and dimmer. our expectations from this again predict a curve that looks something like what is shown in figure 2.22.

But we still need to be more quantitative. Now we make a fully quantitative calculation − we “integrate by picture”. To see how this goes, consider the phasor situation at arbitrary θ

fig22

$$E_\theta = 2R\sin\left(\frac{\Phi}{2}\right) \tag{2.3}$$

but $S = r\theta$, so $E_m = R\Phi$ and $R = \frac{E_m}{\Phi}$ so

$$E_\theta = \frac{2E_m}{\Phi}\sin\left(\frac{\Phi}{2}\right) \Rightarrow \quad E_\theta = E_m\frac{\sin\left(\frac{\Phi}{2}\right)}{\left(\frac{\Phi}{2}\right)} \tag{2.4}$$

But, what is Φ?

$$\frac{\Phi}{2\pi} = \frac{p.l.d}{\lambda} \Rightarrow \quad \Phi = \frac{2\pi}{\lambda}a\sin(\theta) \tag{2.5}$$

So our final result for single-slit diffraction is

$$I(\theta) = I_{0^\circ}\left[\frac{\sin\left(\frac{\Phi}{2}\right)}{\left(\frac{\Phi}{2}\right)}\right]^2, \quad where \quad \frac{\Phi}{2} = \frac{\pi a}{\lambda}\sin(\theta) \tag{2.6}$$

The function $\left(\frac{\sin(x)}{x}\right)$ is called $\text{sinc}(x)$, so this is

$$I(\theta) = I_{0^\circ}\text{sinc}^2\left[\frac{\pi a}{\lambda}\sin(\theta)\right] \tag{2.7}$$

fig23

but, what is meant by "$I(\theta)$"? of course, the energy sent off at exactly angle θ is zero. What we mean is $I(\alpha)d\alpha$ = energy diffracted into the infinitesimal angular range $d\alpha$ centered on value α, where

$$\alpha \equiv \frac{\pi a}{\lambda}\sin(\theta). \tag{2.8}$$

We see that this function has the expected maxima and minima. **What are are minima?** We wish $\sin\left(\frac{\Phi}{2}\right) = 0$ so $\frac{\Phi}{2} = \pi, 2\pi, 3\pi, \cdots$ [3]

$$\frac{\pi a}{\lambda}\sin(\theta) = m\lambda \quad m = 1, 2, 3, \cdots \tag{2.9}$$

Therefore, the condition for minima in single slit diffraction is given by

$$a\sin(\theta) = m\lambda \tag{2.10}$$

which is as we anticipated.

Most Important 1 As it is obvious from the plot, most (almost all) of the light falls within $\theta < \theta_{first\ min}$. So, the angle of the first minimum is especially important. It is given by

$$\theta_{first\,\min} = \sin^{-1}\left(\frac{\lambda}{a}\right) \tag{2.11}$$

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[3] not $\frac{\Phi}{2} = 0$, since $\frac{\Phi}{2}$ is also in the denominator

Most Important 2 Note how this depends on the ration of λ to a. Three cases are plotted in figure 2.24.

fig24

Most Important 3 Remember the figure from earlier where it showed the waves diverging from apertures of widths $a = \lambda$, $a = 3\lambda$, and $a = 5\lambda$? Make sure that you understand the correlation between the situations shown in that figure and those shown in figure 24. This shows the effects of increasing and decreasing λ and a relative to each other. As you will see, that understanding is extremely important. A good rule of thumb to remember is **the half width of the central maximum is** $\sim \frac{\lambda}{a}$.

2.4 Position Resolution – Why $\Delta x \sim \lambda$

If we look at a very small object with light (or other electromagnetic radiation), the spatial resolution, Δx is approximately λ. This limiting resolution is due to diffraction! Let's understand this. We saw that, for monochromatic plane wave radiation incident on a long aperture of width a (single slit), the energy spreads in angle (diffracts), but is mostly contained within an angular range $\Delta\theta = 2\sin\left(\frac{\lambda}{a}\right)$ (the range between the first zeros). If the aperture is circular, the details of the results are different, but the main result is very similar – you get a diffraction pattern consisting of bright and dark bands (in this case, concentric rings). If the screen is far enough from aperture, the situation is called "Fraunhofer diffraction" results – in this case, for a circular aperture, you get a very strong and large central maximum surrounded by alternating light and dark rings. This is shown in figure 25.

fig25

For a circular aperture, under Fraunhofer conditions, the first minimum occurs, not exactly at $\theta = \sin^{-1}\left(\frac{\lambda}{a}\right)$, but rather at

$$\sin(\theta) = 1.22\frac{\lambda}{d} \tag{2.12}$$

where d is the diameter of the aperture. Now suppose you look at something with a lens – say you look at a point-like source (i.e. star at great distance) with a telescope. Say we concentrate on one wavelength component. Then, because of its very great distance, the light from the star is essentially a plane wave at the telescope's objective lens. This lens effectively "cuts out" a circular part of the plane wave fronts, passes them on, and rejects the rest. thus, in addition to its properties related to geometric optics, the lens acts like an aperture. Thus because its diameter is not infinite, the image formed on the "screen" is not a point, but rather is a somewhat spread out diffraction pattern.

fig26

Limit of Resolution This raises an interesting issue in resolution: suppose we look at two distance point sources. Then, if they are too closely spaced, if we look at both, they will not be individually resolved.

We will take as a resolution criterion "Rayleigh's criterion" (actually, one can do a bit better) – two objects are barely resolved if the central maximum of the diffraction pattern of one source falls on the first minimum of the diffraction pattern of the other. Thus, by this criterion, the minimum resolvable angular separation, or the angular limit of resolution is

$$\Delta\theta_{min} = 1.22\frac{\lambda}{d} \tag{2.13}$$

for aperture size d.

fig27

Let us look at this in a bit more detail. Suppose we have two objects (O_1 and O_2) to be imaged by a lens. Let the separation between them be δ; let the central maxima of their image blurs be centered at I_1 and I_2, respectively, as in figure 2.28. So, how far apart do O_1 and O_2 have to be for their distinct images I_1 and I_2 to be resolvable? We use Rayleigh's criterion – that the maximum of I_1 coincide with the first minimum of I_2. This means that O_2AI_1 differs in path length from O_2BI_2 by distance λ, To see where this condition comes from, recall that at the first minimum of a diffraction pattern, say from a rectangular slit, the rays coming from the extreme ends of the slit differ in bath length by λ (with this, dividing the slit into two zones ensured that for each ray in zone I, there is a corresponding ray in zone II that is π radians out of phase with it).

fig28

Now, from figure 227, O_2A is shorter than O_1A by length $\delta\sin\left(\frac{\alpha}{2}\right)$, and $O_1A = O_2B$, and O_1B is shorter than O_2B by $\delta\sin\left(\frac{\alpha}{2}\right)$. Thus, $O_2B - O_2A =$

$\delta \sin\left(\frac{\alpha}{2}\right) \approx O_2BI_1 - O_2AI_1$.Thus for O_1 and O_2 to be resolvable,

$$2\delta \sin\left(\frac{\alpha}{2}\right) \geq \lambda \Rightarrow \quad \delta \geq \frac{\lambda}{2\sin\left(\frac{\alpha}{2}\right)} \tag{2.14}$$

Thus, the limit of resolution is

$$\Delta x = \frac{\lambda}{2} \sin\left(\frac{\alpha}{2}\right) \tag{2.15}$$

of course, we can make this as small as we want by either using λ as small as possible (gamma rays) or by making α large (big diameter lens). However, if we insist on using long wavelength light, we have a price to pay in resolution. Since the largest $\frac{\alpha}{2}$ can be is $\frac{\pi}{2}$, we see that

$$\Delta x \sim \lambda \tag{2.16}$$

as claimed.

Chapter 3

Third Class: Quantum Bahavior

Tuesday, September 2, 2008

The notes for this section are taken directly from **The Feynman Lectures on Physics, Volume III**, Chapter 1 (Addison-Wesley, ©1965.

Chapter 4

Fourth Class: Double Slit and Quantum Mechanics

Thursday, September 4, 2008

4.1 Double Slit Experiment

Let us recall some features of the double slit experiment with electrons:

fig1

Recall salient features

1. **Hear clicks from a detector**: no half clicks
2. **Move detector around**: rate of clicking changes, but still no half clicks
3. **Lower gun temperature**: clicking slows down, still no half clicks
4. **Use two detectors at once**: never hear both go off simultaneously

Conclusion: Upon detection, the electron shows up like a particle – at one point in space, not spread out in space.

fig2

As we will see, in the case with photons, the "final picture" is not dimly present during the intermediate stages (as it would for a wave-caused buildup). Rather, each electron is detected at one place according to a probability rule. Yet, P_{12} results! P_{12} is a statistical pattern – it results from the accumulation of data over time – even if (and especially for the purposes of this experiment) the gun only sends one electron at a time.

Therefore, if we send in a single electron, we can't predict definitely where on the screen it will wind up. From $P_{12}(x)$ we can only predict the relative probability of winding up at different points. this illustrates the central feature of quantum mechanics – we cannot, even in principle, predict exactly where a given electron will wind up on the screen. We can only talk about relative probabilities. This is in marked contrast to classical physics where in principle, we could have followed the trajectory of a given bullet and then used Newton's laws to predict the subsequent trajectory.

Between creation at the electron gun and detection at a point at the screen, the electron seems to not exist as a particle, but propagates in accordance with the mathematics of wave motion. That is, it propagates **as if** it is statistically guided by a wave. (We will see later that the "wave" does not really exist as a spread out physical entity in space – it is a mathematical construct).

It is important to realize that over pattern P_{12}, though collected over many trials, reflects the interference of the wave function of a single electron with itself. Let us denote this "fictitious" or "proxy" wave function "guiding" the electron as $\Psi(x, y, x, t)$. That is, we will hypothesize that, before the position measurement at the screen, the electron is "represented" by the "state function" (or "wave function") $\Psi(x, y, z, t)$. After doing the experiment with a very, very large number of electrons and collecting the data, we will then hypothesize the following interpretation:

> Let dx be a very small distance along the screen centered at position x. Then we will say that the probability that any electron in a single trial of the experiment will materialize in dx, $P(x)dx$, is proportional to the intensity in that small region. In particular, we will take as a working postulate that:

$$P(x)dx = |\Psi(x)|^2 \, dx \tag{4.1}$$

where $P(x)$ is the probability for a single electron to materialize in dx centered on x.

This postulate ("Born probability rule") is clearly suggest by the results of the double-slit experiment for electrons.

4.2 Orthodox ("Copenhagen") Interpretation

As we say, before (in between) position measurement(s), the electron behaves as if "represented" by a wave function $\Psi(x, y, z, t)$. But there is, as we say, a crucial difference between this and the "water waves" case – as we say, Ψ is just a mathematical construct – for electrons, there is no real physical wave function in three dimensional space.

Further, the electron double-slit experiment results are consistent with the Copenhagen interpretation that we cannot say an object ("electron") even posses any definite position or partaken of any definite trajectory unless a measurement occurs (e.g. plug up one of the holes or use a light source to force a through only the one aperture). Likewise, according to the Copenhagen interpretation, the act of detection at the screen is a "position-materializing measurement" that forces the electron to "pick" a position along the screen to materialize at. In the words of another author[1] "If we cannot know the location of a particle **until** we actually look for it, it is hard to justify the claim that it even **has** a location until we look for it." this brings us to a major "philosophical" point in the modern consensus interpretation of quantum mechanics.

> According to the standard modern ("Copenhagen") interpretation of quantum mechanics, generally the particle **does not possess** a position until the act of measurement by detector forces to "materialize" at a fixed position (at a point – not spread out).
>
> This is because – according to current standard quantum mechanics, the electron does not exist in full reality between measurements with detection devices. It's not that the electron between detections is somewhere, but we just don't know where it is – **rather, generally, between detections the electron is "nowhere" because it does not exist in full reality**.

This is a definite break with all classical Western thought.

As Harris explains: "Early in the quantum age, many physicists, most notably, Albert Einstein himself, asserted that [the theory must then simply] be incomplete, that some modification is needed to allow 'real' quantities, such

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[1] R. Harris, p. 122 of **Modern Physics**, 2^{nd} Ed. (Pearson Addison-Wesley)

as [the] position [of a particle] to have definite values at all times. However, the modern consensus, known as the Copenhagen interpretation, is that until experiment actually localizes it, a particle simply does not have a location."

> Again, it is not that the electron is "somewhere" or even really physically spread out in space. Rather, we say that before the detection the electron generally **does not possess even the concept of position** ("partial reality"). In the orthodox quantum mechanics theory it is believed that the act of measurement **forces** the previously only "non-objectively real" electron to materialize in positional reality, selecting a position in the real world according to a certain "preassigned" probability function, $|\Psi(x, y, z, t)|^2$.

Its as if, before the detection measurement the electron is like a ghost holding a deck of cards, each card labeled with position in the real world. Consider an interval of positions dx starting at $x = x_a$, say then the number of cards holding this position in this interval is weighted compared to the number of cards holding positions in other intervals of equal width dx according to the electron's preassigned function $\psi^*(x)\psi(x) \equiv |\psi|^2$. The measurement apparatus then says to the ghostly electron – "Hurry and pick one of the cards at random – then appear in the world of humans at that point!"

Example: Suppose that before measurements, the state function of an electron is, in some region, say $0 \le x \le L$, at time t is

$$\Psi(x, y, z, t) = A \sin(kx) \mathrm{e}^{-i\omega t} \tag{4.2}$$

for some constants k and ω[2]. Where can the electron represented by this state function be forced into materialization, and with what relative probabilities, say at $t = 0$? **Answer**: Probability of materialization in a small interval, dx centered on x at time t is:

$$P(x, t)dx = |\Psi(x, t)|^2 \, dx \tag{4.3}$$

This is an example of a general rule:

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[2] At the moment, we do not worry about where this state function "comes from" or under what conditions it is valid. Of course, these are very important questions. We will deal with them at length later.

4.3 Probability Rule (Born, 1927)

Suppose that, between measurements of positions, the particle is represented by the state function, $\Psi(x,y,z,t)$. Then, upon a position measurement at time t, the probability that the particle will materialize in the small volume $(dx\ dy\ dz)$ centered on the point (x,y,z) is

$$P(x,y,z,t)\ dx\ dy\ dz = |\Psi(x,y,z,t)|^2\ dx\ dy\ dz. \tag{4.4}$$

In our example,

$$P(x,t=0) = |\Psi(x,t=0)|^2 = |A|^2 \sin^2(kx) \tag{4.5}$$

since $\mathrm{e}^{-i\omega 0} = 1$. We plot the relative probability to materialize at different points.

fig1

If governed by this state function, the particle will **definitely not** materialize at $x = 0, x = \frac{\pi}{k}, x = \frac{2\pi}{k}, \cdots$, In addition, the most likely places to materialize are $x = \frac{\pi}{2}k, \frac{3\pi}{2}k, \frac{5\pi}{2}k, \cdots$.

4.4 Normalization Condition

Now, the total probability of the particle's materializing **anywhere** in space on position measurement must be one (i.e. 100%). This, with Born's rule, leads to the normalization condition, leads to the equation

$$\int_{+\infty}^{+\infty}\int_{+\infty}^{+\infty}\int_{+\infty}^{+\infty} |\Psi(x,y,z,t)|^2\ dx\,dy\,dz = 1. \tag{4.6}$$

Adjusting unspecified constants in a candidate state function in called "normalizing" the state function; you will do an example of this in the homework.

4.5 Analogies with light

Let us now look at some experimental results with light[3]. As you know, in some experiments (e.g. double-slit interference, diffraction, etc.) light shows wavelike properties.

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[3] By "light", I mean monochromatic, coherent light.

From a reading of Einstein's 1905 paper, it appears (though it is not explicitly so stated) that by then he viewed a quantum of definite energy as being localized in space and used this to explain the photoelectric effect. By 1909, he seems to have arrived at a view that the localized energy packets ("photons") are guided statistically by the "associated" classical EM wave.

In this picture, which preceded the Copenhagen view, the intensity of radiation striking a surface is proportional to the number of photons incident per unit area per second on the surface. (Recall that $I = \left\langle \frac{\text{energy}}{\text{area}\cdot\text{sec}} \right\rangle$ and the energy of each photon of frequency f is fixed at value hf).

In this view, at any instant of time, the number of photons present in an (infinitesimal) volume, dV of space is proportional to the square of the electric field value there. Part of the reasoning leading to this: recall that, classically, the energy in dV is nhf (we assume a single frequency f), where n is the number of photons. Thus, $n(x, y, z, t) \propto E^2(x, y, z, t)$.

Thus, if a region of large E^2 moves through space (as around say a crest of the E field in a traveling sinusoidal EM wave), then the photons tend to follow along. Thus, this pre-Copenhagen view of Einstein's is a sort of "pilot-wave"/particle viewpoint − in it, the photon really exists all along as a localized bundle ("particle") and is statistically guided by the "really existing" associated wave.

Superficial support for this view comes from noting that detections in the double-slit experiment with the photons essentially come at "random" places one at a time, as is shown in figure 2, rather than from a dim version of the entire final pattern that gets progressively brighter, as it would if the classical EM wave theory were correct. Further support at this level seems to come from the development of images built up progressively again, the initial stages show seemingly randomly placed dots, rather than a dim replica of the final image.

fig2

Further evidence for the particle-like nature of light seems to come from further consideration of the double-slit experiment. If we line the screen with separate photon detectors, sending a very low level of light in, we find that **two detectors never fire at once**.

fig3

This is further evidence that, in interaction, light is not a wave. However, if we let the experiment accumulate data, we find a predictable statistical pattern of strikes. In particular, the relative number of strikes in any detector (compared to the others) when accumulated, follows the distribution expected from interference waves – e.g., there are detectors that never fire (located at positions of "destructive interference").

fig4

However, most[4] physicists now believe in accordance with the Copenhagen view: Although the pictures in figure 4 show that very dim light is detected "like a particle" ("photons"), the simple 'existing all along particle guided by an existing "pilot wave" ' is incorrect. Nowadays, this pilot-wave picture could be called a "semiclassical picture".

Although the orthodox Copenhagen interpretation has been mainstream since 1927-1928, it is only quite recently that we are approaching direct experimental evidence for it! Consider the experiments shown in figures 4.5 through 4.8.

First a "wide angle version of the double-slit experiment":

1. "Single-Photon, Wide-Angle Experiment[5]"

   fig5

2. Anti-coincidence Experiment: Consider the following experiment performed in 1986.

   fig6

   This is a "space-separated" analog of our "multiple detector detectors on the screen" thought experiment with the double-slit apparatus. Again, one photon is sent in at a time. Result: for any given event, either D_1 fires or D_2 fires, never both. This experiment shows the "particle nature of light".

3. Interferometer Experiment[6]

   a Showing wavelike behavior

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[4] But not all

[5] Lie and Diels, Journal of Optical Society of America B9, page 2290 (1992). The brief discussion here is from **Fundamentals of Physics**, 8^{th} Ed. by Halliday, Resnick, & Walker, pp. 1067-8.

[6] Discussion taken from **Physics**, 5^{th} Ed., by Halliday, Resnick, and Krane, p.p. 1024-1025

fig7

b Showing Particle-Like Behavior

fig8

c Delayed Choice Experiment: Experiments bearing on this very question have recently been done!

fig9

What can we conclude from this? Quoting[7] another author.

fig10

Thus, the probability wave has no physical existence. It is, so to speak, an artificial calculation device. Nor can the "photons" have a physical existence, like that of a little ball, while they are propagating ("in transit"). We will return to these issues later in the course.

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[7] Amit Goshamu in **Quantum Mechanics**, 2^{nd} Ed., p. 114 (Custom Publishing)

Chapter 5

Fifth Class: What Would Be a Valid State Function For a Free Particle?

5.1 Some Experimentation

We have seen interference effects with single electrons incident on a Young double-slit experiment (or its equivalent). So far as we now know, the electron is a fundamental particle, not composed of other "smaller" constituent particles. The questions then arises – would a composite system also show clearly predictable simple interference in a Young double-slit apparatus? Consider for example, the neutron, which is a composite bound state of quarks. Yet, they show predictable (according to their deBroglie wavelength) interference and diffraction:

fig1

fig2

Even entire atoms run through a double-slit apparatus show interference. This works for Neon and other relatively light atoms

fig3

However, for larger particles, interference is difficult to observe for at least two regions

1. The associated deBroglie wavelength becomes so short that the dimensions of the apparatus become impractically small
2. Decoherence effects (which quickly wash out "quantum behavior" and cause a system to behave in a Newtonian way) become very strong.

Let us recall deBroglie's proposal – it is that, associated with a free[1] particle of (definite) momentum, $\vec{p}$, and (definite) energy, E is a wavelength and frequency given by

$$\lambda = \frac{h}{p} \tag{5.1}$$

and

$$f = \frac{E}{h}. \tag{5.2}$$

Since $\omega \equiv 2\pi f$ and $k = \frac{2\pi}{\lambda}$, these are $p = \hbar k$ and $E = \hbar\omega$, where $\hbar \equiv \frac{h}{2\pi}$.

These relations argue that a plane wave is to be associated with a free particle of definite energy E and definite momentum $\vec{p}$. Of course, from the results of our interference experiments, we now know (at least in the orthodox Copenhagen interpretation) that the associated wave does not have a physical existence in real physical space, but rather is a probability wave ("state function"). Thus, we tentatively assume that the state function associated with a free particle of definite $(E, \vec{p} = p\hat{x})$ is

$$\Psi(x,t) = A\cos\left(\frac{p}{\hbar}x \pm \frac{E}{\hbar}t\right), \tag{5.3}$$

the choice of the sign depending on the direction of the momentum. Notice something interesting about this "wave function", it fills all space. (Its wavefronts are planes perpendicular to $\hat{x}$). This means that the position associated with such a state is "completely unknown" (or better, "completely does not exist"). On the other hand, for such a state (of nonobjective reality), the momentum, and hence the speed, is precisely known (partial reality state).

Now, if this plane wave (even though its not a real wave that actually exists in physical space – perhaps, we should call it the "proxy-wave") representing the state of a free electron of definite energy, E is to be a reasonable representation of the state, then its velocity should match the "velocity of the particle" calculated from $v_p = \frac{p}{m}$. Consider, though, as you know, the (proxy) wave velocity is

$$v_\phi = f\lambda = \frac{E}{h}\cdot\frac{h}{p} = \frac{E}{p} = \frac{\sqrt{c^2p^2 + m^2c^4}}{p} = c\sqrt{1 + \left(\frac{mc}{p}\right)^2} > c. \tag{5.4}$$

---

[1] By "free" particle, we mean one that is not subject to any forces of course, this is an idealization.

We seem to have a problem – the particle somehow "can't keep up with" the state function that is supposed to represent it. We must deal with this problem.

5.2 Partially Localized States

Another issue (which will turn out, as we'll see) to be related, also presents itself: While our deBroglie plane wave is useful as an idealization, it is "very rare" that the position of the particle it is to represent is **completely** nonexistent. Even in the most extreme case – if the universe is finite, the region of unknown position is also no infinite. thus, the plane state function is an idealization, never really occurring in practice. More typically, the position, while not defined within a certain range, is known to be zero (or very close to zero) outside this range. That is to say, upon the measurement, in most situation, the particle will not materialize "just anywhere", but only at a point within a certain range[2].

what would be a valid proxy wave representing a "moving, partially localized state?" Consider, for example, the possibility of a proxy wave that is a moving pulse, say

$$\Psi(x,t) = A\mathrm{e}^{\frac{-(x-vt)^2}{2\sigma^2}} \tag{5.5}$$

Now, the function

$$f(x) = A\mathrm{e}^{\frac{-x^2}{2\sigma^2}} \tag{5.6}$$

is a "Gaussian", or "bell-shaped" function of standard deviation, σ.

fig4

Then, by the rule for making rigidly moving pulses,

$$\Psi(x,t) = A\mathrm{e}^{\frac{-(x-vt)^2}{2\sigma^2}} \tag{5.7}$$

would represent this Gaussian shape moving rigidly down the x-axis at speed v.

Perhaps this is the sort of probability state function we should use in the theory to represent a free particle? It is the nice feature that adjusting σ

---

[2] e.g. the electron is somewhere within the resolution of a measuring instrument, etc.

adjusts the range of "unknownness" in the position. Interestingly, the answer to this question is **no**!

As we will see, not all functions are valid state functions in quantum mechanics – and this one is not. (As we will see, valid state functions must be solutions of a partial differential equation analogous to, but not the same as, the classical wave equation.) Since we do not yet (in this course) know this differential equation, we must look for another route to localized state functions for moving particles.

For this, we invoke the **principle of superposition**, which says that, under the right conditions, the sum of two valid state functions should also be a valid state function – evidence for this is the interference pattern we get at the screen in a double-slit electron experiment. ($\psi_t = \psi_1 + \psi_2$ is a solution; $|\psi_t|^2 = |\psi_1 + \psi_2|^2$, which shows the interference "cross term".)

So, to build more complicated solutions, which will hopefully lead to a degree of localization, we begin by superposing two of our basic deBroglie plane waves solutions, each corresponding to a definite, but different value of momentum.

$$\begin{aligned}\Psi(x,t) &= A\cos\left(\frac{p_1}{\hbar}x - \frac{E_1}{\hbar}t\right) + A\cos\left(\frac{p_2}{\hbar}x - \frac{E_2}{\hbar}t\right) && (5.8)\\ \Psi(x,t) &= A\cos\left(k_1x - \omega_1 t\right) + A\cos\left(k_2x - \omega_2 t\right) && (5.9)\end{aligned}$$

We note the trigonometry identity,

$$\cos(\alpha) + \cos(\beta) = 2\cos\left(\frac{\beta-\alpha}{2}\right)\cos\left(\frac{\beta+\alpha}{2}\right) \tag{5.10}$$

which tells us that

$$\Psi(x,t) = 2\cos\left(\frac{k_2x - \omega_2t - k_1x - \omega_1t}{2}\right)\cos\left(\frac{k_2x - \omega_2t + k_1x - \omega_1t}{2}\right) \tag{5.11}$$

$$\Psi(x,t) = 2\cos\left(\frac{\Delta k}{2}x - \frac{\Delta\omega}{2}t\right)\cos\left(\bar{k}x - \bar{\omega}t\right) \tag{5.12}$$

where $\Delta k \equiv k_2 - k_1$, $\Delta\omega \equiv \omega_2 - \omega_1$, $\bar{k} = \frac{1}{2}(k_1 + k_2)$, and $\bar{\omega} = \frac{1}{2}(\omega_1 + \omega_2)$.

Let us consider the case where $\omega_2$is only slightly greater than ω_1 and k_2 is only slightly greater than k_1. Then:

$$\Delta k \ll k_2 \text{ or } k_1, \quad \Delta k \ll \bar{k} \tag{5.13}$$

$$\Delta\omega \ll \omega_2 \text{ or } \omega_1, \quad \Delta\omega \ll \bar{\omega} \tag{5.14}$$

Then:

$$\Psi(x,t) = 2\cos\left(\frac{\Delta k}{2}x - \frac{\Delta\omega}{2}t\right)\cos\left(\bar{k}x - \bar{\omega}t\right) \tag{5.15}$$

The $2\cos\left(\frac{\Delta k}{2}x - \frac{\Delta\omega}{2}t\right)$ term is sinusoidal relatively long wavelength traveling "envelope" and the $\cos\left(\bar{k}x - \bar{\omega}t\right)$ term is a higher frequency "inside envelope" oscillations.

fig5,6

These are "groups" of wave. What is the speed of the wave? It is

$$\frac{\frac{\Delta\omega}{2}}{\frac{\Delta k}{2}} = \frac{\Delta\omega}{\Delta k} = v_{env} \tag{5.16}$$

This is **not the same** as the speed of the motion of the "inside oscillations", which is

$$v_{inside} = \frac{\bar{\omega}}{\bar{k}}. \tag{5.17}$$

This is still not very localizing, though – the groups repeat in space. To deal with this problem requires a bit more work, which we will do next.

5.3 A Single Moving Group – "Wave Packet"

It turns out[3] that if we suppose more (an infinite number) of sinusoidal traveling waves, we can arrange that there is basic constructive interference over a small Δx and essentially total destructive interference everywhere else. That is, we get **one** moving group only. Such a moving group is called a "wave packet".

fig7

This happens if you superpose an infinite number of different sine waves that span only a finite interval of wave numbers. That is, if δk is very small,

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[3] see or hear a course on a wave physics – e.g., late in the semester in PHY 301. We will also probably have a derivation of this a bit later in this course.

(likewise $\delta\omega$ is small),

$$\begin{aligned}\Psi(x,t) &= A\cos(k_1x-\omega_1t)+A\cos([(k_1+\delta k)x-(\omega_1+\delta\omega)t] \\ &+ A\cos\left[(k_1+2\delta k)x-(\omega_1+2\delta\omega)t\right] \\ &+ A\cos\left[(k_1+3\delta k)x-(\omega_1+3\delta\omega)t\right] \\ &+ \cdots \\ &+ A\cos[k_2x-\omega_2t],\end{aligned}$$

where $\omega=\omega(k)$. We really want the limit of this as $\delta k\to 0$, but k_1 and k_2 remain of the finite separation (in k). Then,

$$\Psi(x,t)=A\int_{k_1}^{k_2}\cos(kx-\omega t)\ dk \tag{5.18}$$

This gives us our wave packet.

fig8

The integral above is called a "Fourier integral[4]" In it, ω is a function of k. How so? We have

$$E=\frac{1}{2}mv_{particle}^2=\frac{p^2}{2m} \tag{5.19}$$

but, according to deBroglie,

$$\begin{aligned}E &= hf=\hbar\omega \\ p &= \frac{h}{\lambda}=\hbar k\end{aligned}$$

so,

$$\frac{\hbar^2k^2}{2m}=\hbar\omega \tag{5.20}$$

This leads to the "dispersion relation" for deBroglie waves for a free particle,

$$\omega=\frac{\hbar k^2}{2m} \tag{5.21}$$

---

[4] Parts of the more general fourier integral will be developed later in the course; for now, we are drawing on background from your previous exposure to the general concept from a "modern physics" course.

As is shown in a waves course (e.g. PHY 301), the group (region of constructive interference) moves a velocity

$$v_{group} = \lim_{\delta\omega \to +0} \frac{\delta\omega(k)}{\delta k} = \frac{d\omega(k)}{dk} \tag{5.22}$$

This is called the **group velocity** (V_g).

$$v_g = \frac{d\omega(k)}{dk} \tag{5.23}$$

Let us, following deBroglie, evaluate this "group velocity"

$$v_g = \frac{d\omega}{dk} = \frac{2\hbar k}{2m} = \frac{2p}{2m} \tag{5.24}$$

since $p = \frac{h}{\lambda} = \hbar k$

$$v_g = \frac{p}{m} = \frac{mv_{particle}}{m} = v_{particle}!! \tag{5.25}$$

I believe it was Einstein who called this, "the most amazing result of all time"!

5.4 Some Problems

Let us now return to considering the idealized basic plane-wave state function $\cos\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t + \phi\right)$. Several problems occur with it; among them are:

1. A free particle represented by this state function ought to have equal probability to materialize anywhere along the x-axis. But, as we've seen, this plane wave state function, at any time, represents bumps and valleys in spatial distribution of materialization probability.

2. Suppose we attempt to describe a free particle with momentum in the $+x$ direction by, say

   $$\Psi_{\rightarrow}(x,t) = A\sin(kx - \omega t), \qquad k = \frac{p}{\hbar}. \tag{5.26}$$

   Now, invoking the superposition principle,

   $$\Psi(x,t) = \Psi_{\rightarrow}(x,t) + \Psi_{\leftarrow}(x,t) = A\sin(kx - \omega t) + A\sin(kx + \omega t) \tag{5.27}$$

> then must be a possible state. By expanding out the right hand side, you can easily show that this is
>
> $$\Psi(x,t) = 2A\sin(kx)\cos(\omega t) \tag{5.28}$$
>
> (which is a standing wave). But, this is clearly not satisfactory, for at $t = \frac{\pi}{2\omega}$, this $\Psi(x,t)$ vanishes for all x, thus, violating the normalization condition! (A similar problem exists for $\Psi_{\leftarrow} = A\cos(kx + \omega t)$.)

Thus, we can only conclude that

$$f(x,t) = A\cos(kx \pm \omega t + \phi) \tag{5.29}$$

is not a valid free particle state function!

5.5 Toward a Governing Equation

So, we now have a catalog with zero valid state functions. Perhaps finding an equation that governs all state functions will help us find some that are valid.

Here is another reason why we need to have a governing equation for a state function:

> As we will discuss in a bit more detain later on, a measurement changes a state function. For example, a "perfectly accurate" (i.e. very small resolution) position-materializing measurement suddenly changes the state function to a tall, very narrow spike centered on the central measured value; this is shown in figure 5.9
>
> *fig9*
>
> This is called the "collapse of the state function"; it is usually taken as a postulate in the orthodox Copenhagen interpretation. The figure also shows that, after the measurement, while "on its own", that state function changes in time. **It is very important to understand how state functions change in time between measurements** ("time evolution of state function").

If the governing equation is a partial differential equation in the variables x and t, then presumably (if we can solve it), it will tell us exactly **how** state functions evolve in time. So we seek a governing equation. How can we find out if one exists, and if so, what it is? Let us think, we need:

1. A linear equation. This allows for the possibility that some solutions may be superpositions of other solutions. We saw that the double-slit experiment for electrons **requires** this.
2. We know that the energy of a particle is (nonrelativistically),

   $$E = \frac{1}{2}mv^2 + V(x,t) \tag{5.30}$$

   or

   $$E = \frac{p^2}{2m} + V(x,t) \tag{5.31}$$

   Now, in deBroglie language, this is

   $$\hbar\omega = \frac{\hbar^2 k^2}{2m} + V(x,t) \tag{5.32}$$

   This uses the dispersion relationship we found earlier. Our governing equation must be consistent with this.
3. Something that allows plane and spherical wave solutions

- Now the appearance of $V(x,t)$ in the dispersion relationship suggests that it must appear in the equation. It cannot appear alone because, for the sum of two solutions to be a solution of the equation must be homogeneous.So it must appear as

  $$V(x,t)\Psi^n(x,t). \tag{5.33}$$

  But, for the same reason, the equation must be linear; hence, $n = 1$. Thus, we expect a term

  $$V(x,t)\Psi(x,t). \tag{5.34}$$

- The $\hbar\omega$ in the dispersion relation (with a plane wave) suggests one derivative in time
- The $\frac{\hbar^2 k^2}{2m}$ suggests (again, with a plane wave) a second derivative in x.

Putting these ideas together, we try

$$a\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = b\frac{\partial\Psi(x,t)}{\partial t} \tag{5.35}$$

For a free particle, we would have $V = V_0$constant, which we could take as zero. Then, trying $\cos(kx-\omega t)$ or $\sin(kx-\omega t)$ in our trial governing equation, it doesn't work (as you can easily show). This is a good sign, since we already know from other arguments that these can't be valid state functions. For a free particle, let's try the superposition state

$$\Psi_{\rightarrow}(x,t) = \cos(kx-\omega t) + \gamma\sin(kx-\omega t) \tag{5.36}$$

where γ is unknown as yet (but hopefully, a constant). Then by using our trial governing equation:

$$\begin{aligned} -ak^2\cos(kx-\omega t) - a\gamma k^2\sin(kx &- \omega t) + V_0\cos(kx-\omega t) + \gamma V_0\sin(kx-\omega t) = \\ \omega b\sin(kx &- \omega t) - b\gamma\omega\cos(kx-\omega t). \end{aligned}$$

which, simplifies to

$$[-ak^2 + V_0 + b\gamma\omega]\cos(kx-\omega t) = [ak^2\gamma - V_0\gamma + b\omega]\sin(kx-\omega t). \tag{5.37}$$

For this to hold for all x and t, we must have

1. $-ak^2 + V_0 = -b\gamma\omega$
2. $-ak^2 + V_0 = \frac{b\omega}{\gamma}$

By subtracting both of these equations from each other,

$$\begin{aligned} 0 &= -\beta\gamma\omega - \frac{\beta\omega}{\gamma} && (5.38) \\ \gamma &= -\frac{1}{\gamma} && (5.39) \\ \gamma^2 &= -1 && (5.40) \end{aligned}$$

This is very interesting – we see that the imaginary number

$$i \equiv \sqrt{-1}$$

is required. However, for the moment, let us continue: we plug in $\gamma = \pm i$ back into our trial governing equation, getting

$$-ak^2 + V_0 = \mp ib\omega \tag{5.41}$$

Now this looks like a relation between ω and k, and so it must agree (if this form of the wave equation is to be consistent) with our original dispersion relation.

$$\frac{\hbar^2 k^2}{2m} + V_0 = \hbar\omega \tag{5.42}$$

Comparing these, we find

$$a = -\frac{\hbar^2}{2m} \tag{5.43}$$

$$b = \pm i\hbar \tag{5.44}$$

We will choose the positive sign for β; then our governing equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V_0\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{5.45}$$

We now assume that this promising-looking equation is valid wether V is constant or not. Then we have

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{5.46}$$

This is the famous Schrödinger equation. We will be dealing with it for the rest of the semester.

Chapter 6

Sixth Class: A Governing Equation

Thursday, September 11, 2008

Let's begin today by recalling where we have arrived. We saw that the basic candidate plane wave function $\cos\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t + \phi\right)$ for several reasons cannot be valid as a state function in quantum theory. Therefore, neither can superpositions of these be valid. And, as we remarked, nor is a rigidly moving shape, e.g., $f(x,t) = A\mathrm{e}^{\frac{-(x-vt)^2}{2\sigma^2}}$. Therefore, we have a catalogue of zero valid state functions. Our hope was that finding a "governing equation" might help us find valid state functions; presumably they are solutions of it.

6.1 Complex Plane Waves

A very interesting point has come up. In the process of our "derivation" we have seen that the original deBroglie form of the state function for a free particle of definite energy E and definite momentum p is **not valid**

$$\Psi(x,t) \neq A\cos\left(\frac{p_i}{\hbar}x - \frac{E_i}{\hbar}t\right) \tag{6.1}$$

for this case! Rather, the appropriate proxy wave function for this case is apparently

$$\Psi(x,t) = A\left[\cos\left(\frac{p_i}{\hbar}x - \frac{E_i}{\hbar}t\right) + i\sin\left(\frac{p_i}{\hbar}x - \frac{E_i}{\hbar}t\right)\right] \tag{6.2}$$

6.2 What is the Meaning of a Complex Wave Function?

It makes no sense to say "the length of this table is $27i$ inches" or "the voltage difference was $3i$ volts.;; Likewise, it makes not sense to say " the wave amplitude at this point of this stretched string is now $5i$ meters." So, how can we deal with a complex wave function in quantum mechanics? To quote another author who puts it sell:

fig1

Thus, the state function ("wave function") is a (generally) complex (in mathematical sense) function that represents (mathematically) the particle while it is in partial reality. We would like to write the equation in a more compact form; to do this, we recall Euler's formula:

$$\mathrm{e}^{i\theta} = \cos\theta + i\sin\theta \tag{6.3}$$

A convenient way to demonstrate this is by series expansions. We know

$$\mathrm{e}^{x} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \tag{6.4}$$

so,

$$\mathrm{e}^{i\theta} = 1 + i\theta + \frac{i^2\theta^2}{2!} + \frac{i^3\theta^3}{3!} + \frac{i^4\theta^4}{4!} + \cdots , \tag{6.5}$$

which is

$$\begin{aligned}
\mathrm{e}^{i\theta} &= 1 + i\theta - \frac{\theta^2}{2!} - \frac{i\theta^3}{3!} + \frac{\theta^4}{4!} + \frac{i\theta^5}{5!} \\
&= \left(1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \cdots\right) + i\left(\theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} - \cdots\right) \\
&= \cos\theta + i\sin\theta
\end{aligned}$$

Thus, the valid deBroglie plane wave for definite momentum and energy is

$$\Psi(x,t) = A\left[\cos(kx-\omega t) + i\sin(kx-\omega t)\right]$$

$$A\mathrm{e}^{i(kx-\omega t)} \tag{6.6}$$

6.3 Probabilities and Normalization Revisited

The probability of an occurrence must, of course, be real and ≥ 0. However, as we see from the Schrödinger equation, with its explicit $\sqrt{-1}$, state functions are, in general, complex. Now, earlier, to form the probability of materialization at position x^1 at time t we took $\Psi^2(x,t)dx$. But, if Ψ is complex, Ψ^2 will generally be complex as well; hence it cannot be used a probability density. For example, if

$$\Psi(x,t) = A\mathrm{e}^{-(kx-\omega t)}$$

then,

$$\Psi^2(x,t) = A^2\mathrm{e}^{2i(kx-\omega t)}$$

which is

$$\Psi^2(x,t) = A^2\left[\cos(2kx-2\omega t) + i\sin(2kx-2\omega t)\right]$$

which is not real except at certain instants.

On the other hand, the interference pattern obtained in the double-slit electron experiment shows that that we must use a form bilinear in Ψ for the probability density function. What option then do we have?

Consider the function $\Psi^*(x,t)\Psi(x,t)$, where Ψ^* is the "complex conjugate" of Ψ.

> If a complex number, $z \equiv a + ib$, where a and b are real, then $z^* \equiv a - ib$. thus, if $f(x,t)$ is a complex-valued function of the real variables x and t, $f(x,t) \equiv u(x,t) + iv(x,t)$ where u and v are real valued functions, then $f^*(x,t) \equiv u(x,t) - iv(x,t)$. Then,
>
> $$\begin{aligned} f^*(x,t)f(x,t) \equiv |f(x,t)|^2 &= [u(x,t) - iv(x,t)]\,[u(x,t) + iv(x,t)] \\ &= u^2(x,t) - iv(x,t)u(x,t) + u(x,t)\cdot iv(x,t) + v^2(x,t) \end{aligned}$$
>
> Since, $(-i)(i) = i^2 = -(-1) = +1$. Thus,
>
> $$f^*(x,t)f(x,t) = u^2(x,t) + v^2(x,t) \qquad (6.7)$$

---

[1] we mean "in the dx centered on x."

> and note that this is always ≥ 0 since it is the sum of squares of real functions!

Consider also, the polar form of the representations:

$$f(x,t) = R\mathrm{e}^{i\theta(x,t)}$$

$$\begin{aligned} \mathrm{e}^{i\theta(x,t)} &= \cos\theta(x,t) + i\sin\theta(x,t) \\ \left(\mathrm{e}^{i\theta(x,t)}\right)^* &= \cos\theta(x,t) - i\sin\theta(x,t) \\ &= \mathrm{e}^{-i\theta(x,t)} \end{aligned}$$

where $\theta(x,t)$ is a real valued function of (x,t). Thus,

$$\left(\mathrm{e}^{i\theta}\right)^* = \mathrm{e}^{-\theta} = \frac{1}{\mathrm{e}^{i\theta}} \tag{6.8}$$

The complex conjugate of a product is, as you can easily show, the product of the conjugates. Thus, if $f(x,t) = R\mathrm{e}^{i\theta(x,t)}$ where R and θ are real, then, $f^*(x,t) = R^*\mathrm{e}^{-i\theta(x,t)}$. Thus, in this case,

$$|f(x,t)|^2 \equiv R^*\mathrm{e}^{-i\theta}R\mathrm{e}^{i\theta} = R^*R\mathrm{e}^{-i\theta}\mathrm{e}^{i\theta} = R^*R \equiv |R|^2 \tag{6.9}$$

(If all of this does not make full, familiar sense to you, get ahold of a standard undergraduate book with a section or chapter on complex numbers and review/learn it.)

With the above in mind, we consider the (bilinear) function $|\Psi(x,t)|^2 \equiv \Psi^*(x,t)\Psi(x,t)$ as a candidate for the positional probability density function. Since it is real and greater then or equal to zero, it is a good candidate, and, in fact, its use in this role shows agreement or consistency with all of the experiment data we have. In fact, formalizing this guess, in 1926, Max Born postulated the following, which has since been accepted as part of the standard orthodox interpretation of quantum mechanics: **Positional Probability Postulate (Born, 1926)**

> If, at time t, a position measurement is made for a particle associated with the state function $\Psi(x,t)$, then the probability that the particle will materialize in a small range, dx,centered on x is given by
>
> $$P(x,t)dx = \Psi^*(x,t)\Psi(x,t)\ dx \tag{6.10}$$

This means that out previously stated normalization condition must now be accordingly modified to

$$\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\ dx = 1 \tag{6.11}$$

at all times t.

6.4 Plane Wave and Uniformity of Space

Now we note another bonus of our complex plane wave states. With the real plane waves, e.g. $\cos(kx - \omega t)$, the probability density was bumpy"

fig2

This is a clear violation of the homogeneity of empty space[2], as we remarked some time ago. However, with the complex plane wave and the new probability rule,

$$P(x,t)dx = \Psi^*(x,t)\Psi(x,t) = \mathrm{e}^{-i(kx+\omega t)}\mathrm{e}^{i(kx-\omega t)} = 1. \tag{6.12}$$

This is constant in space, which accords with this basic principle of homogeneity of space.

6.5 A First Example of Using the Schrödinger Equation

We want to show a first example illustrating use of the Schrödinger equation to find what state functions are allowed for a specific situation. For this, we will use the familiar "particle-ini-a-box" (or "infinite square well"). The situation is familiar from a previous "modern physics" course, but the method we use here today is a little different:

> Say we have a certain force field that the particle is "in." Then, we have a potential energy profile, $V(x,t)$. Say, for example, the profile is that of the familiar infinite square well:
>
> $$V(x) = \begin{cases} 0 & \text{if } 0 \le x \le L, \\ \infty & \text{otherwise.} \end{cases} \tag{6.13}$$

---

[2] This is a cherished, basic principle of physics. Violation of it would be a very serious issue.

Then, inside the well, $V = 0$, so the Schrödinger equation is

$$-\frac{\hbar^2}{2}\frac{\partial^2\Psi(x,t)}{\partial x^2} = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{6.14}$$

inside the well.

How do we solve this? For now, instead of using formal mathematical methods, we note that inside the well the particle is free, so, if we assume a fixed, definite energy, E, the general solution should be a superposition of right and left moving quantum plane waves

$$\Psi_E \mathrm{e}^{(x,t)} = A\mathrm{e}^{i\frac{\sqrt{2mE}}{\hbar}x - i\frac{Et}{\hbar}} + B\mathrm{e}^{-i\frac{\sqrt{2mE}}{\hbar}x - i\frac{Et}{\hbar}} \tag{6.15}$$

We emphasize that this is the solution inside the well for only one energy. Solutions of this form for different energies can, by principle of superposition, be superposed; we will discuss that later on.

We are not done, however – recall that we have two boundary conditions:

1. $\Psi(x = 0, t) = 0$ for all t
2. $\Psi(x = L, t) = 0$ for all t

As you can show, application of the Schrödinger equation on our quantum plane waves leads to

$$\Psi_T = A\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right)\mathrm{e}^{-i\frac{Et}{\hbar}} \tag{6.16}$$

Them application of the second boundary conditions on this equation leads to

$$\sqrt{emE}\frac{L}{\hbar} = n\pi, \qquad n = 1, 2, 3\cdots \tag{6.17}$$

Which is the familiar **quantization of energy**

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}, \qquad n = 1, 2, 3, \cdots \tag{6.18}$$

Thus, the possible state functions for definite energy are

$$\Psi_n(x,t) = \begin{cases} A_n \sin\left(\frac{n\pi}{L}x\right)\mathrm{e}^{-\frac{in^2\pi^2\hbar}{2mL^2}t}, & 0 \le x \le L \\ 0, & x < 0, x > L \end{cases} \tag{6.19}$$

since the spatial parts of these state functions happen (in this case) to be purely real and we can plot them – they are plotted in figure 3, along with the associated probability density function $\Psi^*(x,t)\Psi(x,t)$ for each.

fig3

Note that, for the state function $\Psi_n(x,t)$ given by out possible state functions, the probability densities, while dependent on position (x) are all independent of time, since

$$\left|e^{-ict}\right|^2 = e^{+ict}e^{-ict} = 1 \tag{6.20}$$

for c real, as in our possible state function.

The coefficients $\{A_n\}$ can be found through the application of the normalization condition requiring $1 = \int \Psi^*(x,t)\Psi(x,t)\ dx$ here is

$$1 = |A_n|^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right)\ dx \tag{6.21}$$

SinceΨ is zero outside the well and since the time dependence from the exponential factor goes away in the probability density. Thus, the normalization condition is independent of time – it can be applied at any time to determine the normalization constant A_n, and once A_n is determined, it remains constant in time. (We will see later that there is a very beautiful theorem that ensures this time independence of the normalization is true for all state functions valid for single particles states in non-relativistic quantum mechanics.) Now, you can show,

$$\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)\ dx = \frac{L}{2} \tag{6.22}$$

for all integer n – note that it is independent of n. Thus, equation (6.21) tells us that for the infinite square well, $A_n = \sqrt{\frac{2}{L}}$ for all n. Thus, the state functions for definite energy are

$$\Psi_n(x,t) = \begin{cases} \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)e^{-\frac{in^2\pi^2\hbar}{2mL^2}t} & 0 \le x \le L \\ 0 & x < 0, x > L \end{cases} \tag{6.23}$$

Since the Schrödinger equation is linear and homogeneous, the sum of solutions – in fact, an arbitrary linear combination of solutions

$$\Psi(x,t) = \sum_{i=1}^{\infty} c_n \Psi_n(x,t) = \sum_{i=1}^{\infty} c_n \sin\left(\frac{n\pi x}{L}\right)e^{-\frac{iE_nt}{\hbar}} \tag{6.24}$$

is a solution inside the well. (of course, for "superposition solutions" like this, the c_n's must be scaled so that the overall $\Psi(x,t)$ is correctly normalized.) Of course, for this sort for superposition state function there is no single value of definite energy, since each Ψ_n in the sum corresponds to a distinct energy. This raises an important interpretational question about the meaning of superposition states like our superposition state. We have much to say about this later in the course. In fact, we'll also have much further to say about the definite-energy infinite square-well states and their physical meaning later. Here our purpose was to give you a first illustration of the use of the Schrödinger equation to find valid state function.

Chapter 7

Seventh Class: Time Dependence Through the Governing Equation

Tuesday, September 16, 2008

7.1 A Review of the Governing Equation

Our governing equation for state functions is the Schrödinger equation

$$\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) \tag{7.1}$$

Recall that the governing equation plays two (overlapping) roles:

1. It guides us in determining what state functions are permissible for what systems under what conditions and what what functions aren't permissible – i.e., any permissible state function must be a solution of the Schrödinger equation, and through this,
2. It tells us how the state function $\Psi(x,t)$ evolves between measurements (recall that measurements causes a sudden change, or "collapse", of the state function). This is so because the Schrödinger equation is providing the time-rate-of-change of $\Psi(x,t)$ (as long as the right-hand-side of the Schrödinger equation can be calculated).

We illustrated these roles by using the Schrödinger equation to find state functions of definite energy for a particle in an infinite square-well potential energy profile. In this case, the time evolution was through the factor $\mathrm{e}^{-\frac{iE_nt}{\hbar}}$ in each state function. Further, in this case, the probability density function, $P(x) = \Psi^*(x,t)\Psi(x,t)$, has no explicit time dependence since

$\left(\mathrm{e}^{\frac{+iE_nt}{\hbar}}\right)\left(\mathrm{e}^{\frac{-iE_nt}{\hbar}}\right) = 1$. Thus, in this case, at all x, the probability density is constant in time. As another example in the homework, you show that the functions $\mathrm{e}^{\frac{\pm iE_nt}{\hbar}}$ are valid free particle state functions provided a certain dispersion relationship is obeyed. As yet another example, some time ago we claimed that a rigidly moving "bell-shaped" curve,

$$f(x,t) = A\mathrm{e}^{-\frac{(x-vt)^2}{2\sigma^2}} \tag{7.2}$$

with v and σ real and constant is not a valid state function − and it is clear why not. Suppose that $f(x,t)$ is purely real for all x and all t. Then the application of the Schrödinger equation for $f(x,t)$ produces an imaginary function on one side and a real function on the other − and it is impossible for these to be equal to each (unless they are both zero). Since $f(x,t) = AE - \frac{(x-vt)^2}{2\sigma^2}$ with v and σ constant and real is purely real for all x and t, it is therefore not a valid quantum mechanical state function.

A situation that sometimes arises is one in which you know the state function at a specific time only (either by knowledge or by an assumption) and you want to find out how it changes in time. This is called the quantum initial value problem. Here is a quick example (without details) that will give you a first idea of how this sort of thing works. Suppose we have a free particle ($V(x,t) = 0$ all x and t) and we somehow know that at the specific time $t = 0$, the state function $\Psi(x,t)$, is Gaussian (bell-shaped).

$$\Psi(x, t=0) = A\mathrm{e}^{-\frac{x^2}{2\sigma^2}} \tag{7.3}$$

At a given instant, this can be a valid state function for a free particle. (In fact, as we will see in a few classes hence, any normalizable[1] continuous function $f(x)$ is a possible state function for a free particle at single instant of time[2]).

In fact, this is an example of the sort of state function that can result at the instant of position measurement, when the resolution of the measurement is 2σ. If σ is small, this looks like a tall, narrow spike of "width" 2σ, as shown in figure 1. Suppose $\Psi(x, t=0)$ is this. The question is − what happens to

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[1] "Normalizable" means $\int_{-\infty}^{+\infty} \Psi^*(x,t=0)\Psi(x,t=0)\, dx < \infty$

[2] Fourier theory will show this

Ψ as time goes by in the absence of or before another measurement? Must it change? (yes)

Fig1

Could it change in time by moving rigidly? As we've already seen, no. To find out how Ψ evolves in time, we need to find solution, $\Psi(x,t)$ to the Schrödinger equation that reduces down to equation (7.3) at $t = 0$.

Since the Schrödinger equation is first order in time, there is at most one linearly independent function that will do this. (see later if you are not familiar with this fact about first-order differential equations), In the near future, we'll see[3] (also from the theory of Fourier analysis) how to find this function, but that is not our goal here. Therefore, for now, I'll just tell you the answer, so we can work with it.

$$\Psi(x,t) = C\frac{\mathrm{e}^{-\frac{ax^2}{\left[1+\left(\frac{2i\hbar at}{m}\right)\right]}}}{\sqrt{1+\left(\frac{2i\hbar at}{m}\right)}} \tag{7.4}$$

where $a \equiv \frac{1}{2\sigma^2}$ and C is a constant. If you have the patience, you can verify that this equation works in free particle Schrödinger equation, and by setting t equal to zero, we see that it does reduce to our previous function at time equal to zero. So, this equation is correct. This question now is – how do we interpret it? A plot would help, but since $\Psi(x,t)$ is complex, we can't plot it. Anyway, what is more important than Ψ is the probability density function. By letting $\theta = \frac{2\hbar at}{m}$, we have

$$\Psi = C\frac{\mathrm{e}^{-\frac{ax^2}{(1+\theta)}}}{\sqrt{1+i\theta}} \quad \Rightarrow \quad \Psi^* = C^*\frac{\mathrm{e}^{-\frac{ax^2}{(1-\theta)}}}{\sqrt{1-i\theta}} \tag{7.5}$$

so,

$$P(x,t) = \Psi^*\Psi = |C|^2\frac{\mathrm{e}^{-ax^2\left[\frac{1}{1+i\theta}+\frac{1}{1-i\theta}\right]}}{\sqrt{1+\theta^2}} = \frac{|C|^2}{\sqrt{1+\theta^2}}\mathrm{e}^{-\frac{2ax^2}{(1+\theta^2)}} \tag{7.6}$$

To interpret this expression, we approximate by ignoring the denominator (i.e. approximate the denominator by 1. Show that this is valid to about

---

[3] if you are curious now, see Griffths problem 2.22, which assumes you can handle Fourier transforms.

10% accuracy as long as $t < \sqrt{\frac{m^2}{20\hbar^2 a^2}}$.) Then

$$P(x,t) \approx |C|^2 \mathrm{e}^{-\frac{ax^2}{\left(1+\frac{4\hbar^2 a^2 t^2}{m^2}\right)}} \tag{7.7}$$

which is again a Gaussian ("bell-shaped" curve) whose width increases in time. Thus, as we claimed in the last class, between position measurements the probability distribution spreads or "diffuses".

fig4

7.2 Persistence of Normalization

Suppose we have a state function $\Psi(x,t_0)$ and we normalize it at a particular time, say $t = t_0$. The state function changes in time according to the Schrödinger equation (since the Schrödinger equation has a $\frac{\partial}{\partial t}$). Then it would seem unlikely that Ψ remains normalized. But, if it doesn't, we have a problem! We investigate this: Let

$$P(t=t_0) = \int_{-\infty}^{+\infty} \Psi^*(x,t_0)\Psi(x,t_0)\ dx = 1. \tag{7.8}$$

Then

$$\begin{aligned} \frac{dP(t)}{dt} &= \frac{d}{dt}\int_{-\infty}^{+\infty} \Psi^*(x,t)\Psi(x,t)\ dx \\ &= \int_{-\infty}^{+\infty} \frac{\partial}{\partial t}\left[\Psi^*(x,t)\Psi\right]\ dx \\ &= \int_{-\infty}^{+\infty} \left[\frac{\partial \Psi^*(x,t)}{\partial t}\Psi + \Psi^*(x,t)\frac{\partial \Psi}{\partial t}\right]\ dx \end{aligned}$$

But, according to the Schrödinger equation,

$$\begin{aligned} \frac{\partial \Psi}{\partial t} &= \frac{i\hbar}{2m}\frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar}V\Psi \\ \frac{\partial \Psi^*}{\partial t} &= -\frac{i\hbar}{2m}\frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar}V\Psi^* \end{aligned}$$

By plugging these in, we get

$$\begin{aligned}\frac{dP(t)}{dt} &= \frac{i\hbar}{2m}\int_{-\infty}^{+\infty}\left(\Psi^*\frac{\partial^2\Psi}{\partial x^2}-\frac{\partial^2\Psi^*}{\partial x^2}\Psi\right)\,dx\\ &= \frac{i\hbar}{2m}\int_{-\infty}^{+\infty}\frac{\partial}{\partial x}\left[\Psi^*\frac{\partial\Psi}{\partial x}-\frac{\partial\Psi^*}{\partial x}\Psi\right]\,dx\\ &= \frac{i\hbar}{2m}\left[\Psi^*(x,t)\frac{\partial\Psi}{\partial x}-\frac{\partial\Psi^*}{\partial x}\Psi\right]_{-\infty}^{+\infty}\end{aligned}$$

Now, in any sensible theory, Ψ and $\Psi^* \longrightarrow 0$ as $x \longrightarrow \pm\infty$. Thus, $\frac{dP}{dt} = 0$, and "once normalized, always normalized" (unless measurement intervenes).

7.3 The Reason for the Persistence of the Normalization

We saw that, in the absence of measurement, if

$$P(t_0 = \int_{-\infty}^{+\infty}\Psi^*(x,t_0)\Psi(x,t)\ dx = 1, \tag{7.9}$$

then

$$\frac{dP(t)}{dt} = \frac{d}{dt}\int_{-\infty}^{+\infty}\Psi^*(x,t)\Psi(x,t)\ dx = 0. \tag{7.10}$$

Key to this proof was the use of the SchrödingerSchrödinger equation

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x,t)\Psi(x,t). \tag{7.11}$$

As you can convince yourself by going through the proof, again, what "made it work" is the SchrödingerSchrödinger equation is **first order in time**. As you can convince yourself (try it), if the SchrödingerSchrödinger equation were second order in time, $\frac{dP}{dt}$ would not by zero and then we would have problems. **Only a first order (in time) equation is consistent with conservation of probability**. Actually, this is pretty obvious (from the theory of differential equations) without going through the proof. A first order differential equation has only one "arbitrary constant" in its general solution and this is usually "$f(t=0)$". For example, consider say,

$$\begin{aligned}\frac{df(t)}{t} &= 2t \\ f(t) &= \int 2t\ dt = t^2 + \text{const.} \\ f(t) &= t^2 + f(t=0)\end{aligned}$$

or say,

$$\frac{df}{dt} = -3f(t) \quad \Rightarrow \quad f(t) = C\mathrm{e}^{-3t} \quad \Rightarrow \quad C = f(t=0).$$

So, for a first order equation, only $f(t=0)$ can be arbitrarily specified as an initial condition. However, a second order equation, say

$$\begin{aligned}\frac{d^2f(t)}{dt^2} &= 2t \\ f(t) &= \frac{1}{3}t^3 + at + b\end{aligned}$$

where a and b are constants.clearly, $b = f(0)$ and $a = f'(0)$. So for a unique time development $f(t)$, we need to specify both $f(t=0)$ and $f'(t=0)$. Or, say,

$$\begin{aligned}\frac{d^2f(t)}{dt^2} &= -\omega^2 f(t) \\ f(t) &= A\cos(\omega t + \phi) \\ &= C\sin(\omega t) + D\cos(\omega t)\end{aligned}$$

Then, $f(0) = D$ and $f'(0) = \omega C$. We see that, with second order differential equations, we can independently and arbitrarily specify both $f(0)$ and $f'(0)$ – and both are needed to specify a unique time development of $f(t)$. Thus, if the Schrödinger equation were second order in time, we could independently and arbitrarily specify $\Psi(x, t=0)$ and $\frac{\partial\Psi(x,t=0)}{\partial t}$. This would mean that we could set $\frac{\partial}{\partial t}\left[\Psi^*(x,t=0)\Psi(x,t=0)\right]$ and $\frac{d}{dt}\int_{-\infty}^{+\infty}\Psi^*(x,t=0)\Psi(x,t=0)\ dx$ to be nonzero. This would destroy conservation of probability; hence the Schrödinger equation **must** be first order in time!

7.4 Determinism in Quantum Mechanics – A Comment

It is often remarked that quantum mechanics has scarified the determinism (i.e. "predictability-in-principle") of Newtonian mechanics. While this is true, in another sense non-relativistic quantum mechanics, with its first order in time governing equation, is very deterministic for the state function itself. That is, it follows from our discussion of the last class that, in the absence of intervening measurement, knowledge of $\Psi(x, t_0)$ for all x at a single instant of time (t_0) is sufficient to determine $\Psi(x, t)$ anywhere for all $t > t_0$ [4]. Thus, the time evolution of the state function can be said to be deterministic.

Such a statement is not true for solutions of governing equations that are second order (or higher order) in time. Consider, for example, the familiar classical wave equation.

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \Psi(x,t)}{\partial t^2} \tag{7.12}$$

Which governs many classical wave phenomena (e.g. wave on dispersionless stretched string). For this case, (classical wave obeying the CWE) suppose that $\Psi(x, t = 0) = \cos(kx)$. Then, there are many possibilities for $\Psi(x, t)$ – among them, $\Psi_{\rightarrow} = \cos(kx - \omega t)$ and $\Psi_{\leftarrow} = \cos(kx + \omega t)$. For a second order (in time) equation, to be assured on a unique $\Psi(x, t)$, one must specify at $t = 0$ both Ψ and $\frac{\partial \Psi}{\partial t}$. Thus for a second order (in time) equation, knowledge of only Ψ at $t = 0$ is not enough to predict $\Psi(x, t > 0)$. All this being said, the question then arises as to wether one can write an explicit "general solution" of the Schrödinger equation valid for all potential energy profile functions $V(x, t)$ that directly express $\Psi(x, t)$ in terms of the values of Ψ at all points x' at an earlier time, say $t = 0$. Such an equation would be in the form of a general formula $\Psi(x, t) =??$, rather than in the form of a riddle (differential equation relating derivatives of Ψ to each other that must be solved). Based on what we have said above, in principle this is possible. Such an equation takes the form:

$$\Psi(x,t) = \int_{-\infty}^{+\infty} K(x', x, t)\Psi(x', t)\; dx' \tag{7.13}$$

---

[4] TO do this involves a sort of conversion of the Schrödinger equation to an integral equation. The results are fascinating and to be returned to if time allows.

where the function K is called the propagator, represents the influence of "old values" if Ψ at x' (i.e.$\Psi(x', 0)$) at the point x at the present time (t). [In this sense, $K(x', x, t)$ is like the contribution at point x at time t made by the state function at x' at the earlier time $t = 0$.] It turns out that the explicit form of the propagator is known for the case of a free particle

$$K_{free}(x', x, t) = \sqrt{\frac{m}{2\pi i\hbar t}} \mathrm{e}^{i\frac{(x-x')^2 m}{2\hbar t}} \tag{7.14}$$

This technique[5], while conceptually important, is uncommon in elementary courses, largely because the propagator is known in closed analytical form a sa function for only a few potential energy profiles (of course, including the free particle case $V(x, t) = 0$) and even in those cases, the mathematics involved can be quite formidable. For this reason, we will mostly or exclusively stay with the standard differential equation approach.

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[5] The propagator approach to quantum mechanics, largely pioneered by R. P. Feynman, is very important in modern quantum field theory. Nonrelativistic quantum mechanics is developed in his book **Quantum Mechanics and Path Integrals**.

Chapter 8

Eight Class: Probability

Thursday, September 18, 2008

8.1 Probability Current

In the last class, we looked into the rate of change of the total probability for materialization (or position measurement) anywhere on the x-axis and found that it was zero;

$$\frac{dP_{tot}}{dt} = \frac{i\hbar}{2m}\left[\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right]_{-\infty}^{+\infty} = 0 \tag{8.1}$$

by using the normalization boundary conditions,

$$\Psi(x,t) \to 0 \quad \frac{\partial\Psi(x,t)}{\partial x} \to 0 \quad \text{as} \quad x \to \pm\infty \tag{8.2}$$

Suppose, however that we consider the rate of change of the total probability to materialize in the finite region, say from x_1 to x_2. This would then be

$$\frac{\partial P(x_1,x_2,t)}{\partial t} = \frac{i\hbar}{2m}\left[\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right]_{x_1}^{x_2} \tag{8.3}$$

which in general, is not zero. In this case, we can define a function

$$J(x,t) = \frac{\hbar}{2mi}\left(\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x} - \Psi(x,t)\frac{\partial\Psi^*(x,t)}{\partial x}\right) \tag{8.4}$$

and then

$$\frac{\partial P(x_1,x_2,t)}{\partial t} = J(x_1,t) - J(x_2,t) \tag{8.5}$$

Interpretation: The rate of change of probability in $[x_1, x_2]$ is the rate at which probability enters $[x_1, x_2]$ at x_1, take away the rate at which probability leaves at x_2[1].

Thus, the quantity $J(x,t)$ represents the "flow of probability" (in the direction of increasing x) at position x at time t. It is called the **probability flux**. It is also often symbolized as $S(x,t) \equiv J(x,t)$

8.2 Choice of Free Particle Plane Wave States

We now return to look more closely at an issue we glossed over in the past. For a free particle, we've been using, as our basic "right-moving" plane-wave state,

$$\Psi^{(1)}_{\rightarrow}(x,t) = A\mathrm{e}^{i(kx-\omega t)}. \tag{8.6}$$

However, perhaps we should use for this purpose

$$\Psi^{(2)}_{\rightarrow}(x,t) = A\mathrm{e}^{i(kx-\omega t)} = A\mathrm{e}^{-ikx}\mathrm{e}^{+i\omega t} \tag{8.7}$$

or, can be use these "interchangeably" or even mix them in calculation? We also have different choices for "left-moving" plane-waves states:

$$\Psi^{(1)}_{\leftarrow}(x,t) = A\mathrm{e}^{i(kx-\omega t)} \quad \text{or} \quad \Psi^{(2)}_{\leftarrow}(x,t) = A\mathrm{e}^{-i(kx+\omega t)}. \tag{8.8}$$

Let's look into this: say we have the choice $\Psi^{(1)}_{\leftarrow} = A\mathrm{e}^{i(kx-\omega t)}$. With this, we could, for left-moving state, a príori still use either $\Psi^{(1)}_{\leftarrow}$ or $\Psi^{(2)}_{\leftarrow}$ above or both. Say we pick $\Psi^{(1)}_{\leftarrow}$ and $\Psi^{(1)}_{\rightarrow}$. Then, according to the principle of superposition,

$$\Psi(x,t) = \mathrm{e}^{i(kx-\omega t)} + \mathrm{e}^{i}(kx+\omega t) \tag{8.9}$$

should be a possible state. But this is

$$\Psi(x,t) = \mathrm{e}^{ikx}\left(\mathrm{e}^{i\omega t} + \mathrm{e}^{-i\omega t}\right) \quad = \quad 2\mathrm{e}^{ikx}\cos(\omega t), \tag{8.10}$$

which has the same problem we were trying to avoid, (namely, there is a time when $\Psi = 0$ everywhere). So, suppose we try $\Psi^{(1)}_{\rightarrow}(x,t) = A\mathrm{e}^{i(kx-\omega t)}$ and $\Psi^{(2)}_{\leftarrow}(x,t) = A\mathrm{e}^{-i(kx+\omega t)}$. Then the sum of these two is

$$\Psi(x,t) = \mathrm{e}^{i\omega t}\left(\mathrm{e}^{ikx} + \mathrm{e}^{-ikx}\right) \quad = \quad 2\cos(kx)\mathrm{e}^{-\omega t}, \tag{8.11}$$

---

[1] Note that because J can be a positive or negative at any point, the statement is equivalent to $[J(x_1,t) - J(x_2,t)]$, is the net rate at which probability enters $[x_1, x_2]$ at both ends minus the net rate at which probability leaves $[x_1, x_2]$ at both ends. Since this is equal to $\frac{\partial P(x_1,x_2,t)}{\partial t}$, probability is neither spontaneously created or destroyed in $[x_1, x_2]$; any change in it must follow in or out at the boundaries.

which avoids the problem! (Why?) Likewise, $\Psi^{(2)}_{\rightarrow}(x,t) = A\mathrm{e}^{i(kx-\omega t)}$ combined with $\Psi^{(1)}_{\leftarrow} = A\mathrm{e}^{i(kx-\omega t)}$ avoids this problem (show this).

What if sometimes use $\Psi^{(1)}_{\rightarrow}(x,t) = A\mathrm{e}^{i(kx-\omega t)}$ and sometimes we use $\Psi^{(2)}_{\rightarrow}(x,t) = A\mathrm{e}^{i(kx-\omega t)}$? This leads to trouble, as you can show by considering their superposition. So we need to make a choice, In this, we follow the **Quantum Mechanics Convention** for free particle plane wave states:

$$\Psi_{\rightarrow}(x,t) = A\mathrm{e}^{i(kx-\omega t)} \tag{8.12}$$

$$\Psi_{\leftarrow}(x,t) = A\mathrm{e}^{-i(kx+\omega t)} \tag{8.13}$$

Here is a quick way to remember this: the time part is always $\mathrm{e}^{-\frac{iEt}{\hbar}}$. (This is true in quantum mechanics for states of definite energy).

8.3 Circular and Spherical Definite Energy State Functions

Consider the case of a free (no force field acting on it) electron of definite energy E incident on a "pin-hole" aperture. On the downstream side of the aperture, the state function should be (in three dimension) a spherical wave

$$\Psi(\vec{r},t) = A(r)\mathrm{e}^{\frac{i(pr-Et)}{\hbar}} \tag{8.14}$$

where r is the distance from the pin-hole to the point $\vec{r}$ (origin taken as the pinhole). Note that A, the amplitude, depends on r – it must decrease with r, in fact. Why? Because the probability spreads out in space. For example, for the three dimensional case (spherical wave)

$$A(r) \propto \frac{1}{r} \tag{8.15}$$

while, for the two dimensional case, (circular wave)

$$A(r) \propto \frac{1}{\sqrt{r}}. \tag{8.16}$$

Thus, if we consider the electron double slit experiment with the slits as pin-holes, we have, downstream of the pin-hole plane

$$\Psi(\vec{r},t) = \Psi_1(\vec{r},t) + \Psi_2(\vec{r},t) \tag{8.17}$$

where Ψ_1 is a spherical wave centered on hole 1, and Ψ_2 is a spherical wave centered on hole 2. If we put a measurement device ("proximity device") near hole 1 to determine if the electron "went through" hole 1, then if the device registers a signal, after the measurement, $\Psi(\vec{r}, t)$ is "collapsed" to $\Psi(\vec{r}, t) = \Psi_1(\vec{r}, t)$.

For the case of a plane-wave state function incident on a long, infinitesimally narrow slit, the result downstream is a **cylindrical** wave state:

$$\Psi(\vec{r}, t) = \frac{A}{\sqrt{r}} \mathrm{e}^{i(kr-\omega t)} \tag{8.18}$$

where r is measured in cylindrical coordinates. An example of cylindrical waves is shown in figures 8.1 and 8.2.

fig1

fig2

As we see, for this case, r is just the direct perpendicular distance from the slit line to the nearest point on the wavefront.

8.4 Superposition States and Probabilities

Now let's consider a superposition state of plane waves:

$$\Psi(x, t) = A_1 \mathrm{e}^{i(k_1 x - \omega_1 t)} + A_2 \mathrm{e}^{i(k_2 x - \omega_2 t)} \tag{8.19}$$

Here, we have an interesting situation: each of the two components corresponds to a different, definite value of momentum ($p_1 \hbar k_1$, $p_2 = \hbar k_2$). Thus, the superposition state no longer corresponds to a definite value of momentum! What then happens if we measure the momentum for a particle represented by this superposition state function? Answer: If we do so, we definitely obtain

$$\begin{array}{lrcl} \text{either} & p_1 & = & \hbar k_1 \\ \text{or} & p_2 & = & \hbar k_2 \end{array}$$

How likely is each probability? In this case, the probability of getting result p_1 is:

$$\frac{|A_1|^2}{|A_1|^2 + |A_2|^2} \tag{8.20}$$

the probability of getting result p_2 is"

$$\frac{|A_2|^2}{|A_1|^2 + |A_2|^2} \tag{8.21}$$

and the probability of getting either p_1 or p_2 is:

$$\frac{|A_1|^2}{|A_1|^2 + |A_2|^2} + \frac{|A_2|^2}{|A_1|^2 + |A_2|^2} = \frac{|A_1|^2 + |A_2|^2}{|A_1|^2 + |A_2|^2} = 1 = 100\% \tag{8.22}$$

A similar sort of rule applies to superposition states having components corresponding to definite values of energy. As an example, consider the case of the infinite square-well. We found that the states of definite energy are

$$\Psi_n(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \mathrm{e}^{-\frac{iE_n t}{\hbar}} \tag{8.23}$$

However, since the Schrödinger equation is linear and homogeneous, superpositions of these are possible valid quantum states. Such superposition states will then not correspond to definite energy. Consider, for example, the superposition state

$$\Psi(x,t) = c_1\Psi_1(x,t) + c_2\Psi_2(x,t). \tag{8.24}$$

(Here, c_1 and c_2 must be chosen such that $\Psi(x,t)$ is normalized; we will worry about the details of how to choose c_1 and c_2 to ensure this, later.) Thus

$$\Psi(x,t) = c_1\sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \mathrm{e}^{-\frac{iE_1 t}{\hbar}} + c_2\sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \mathrm{e}^{-\frac{iE_2 t}{\hbar}} \tag{8.25}$$

If a measurement of energy is made on a particle represented by this state function, then we definitely obtain energy equal to either E_1 or E_2. Recall

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{8.26}$$

The probability of getting definite energy value E_1 is

$$E_1 = \frac{|c_1|^2}{|c_1|^2 + |c_2|^2} \tag{8.27}$$

and the probability of getting definite energy value E_2 is

$$E_2 = \frac{|c_2|^2}{|c_1|^2 + |c_2|^2} \tag{8.28}$$

and the probability of getting either E_1 or E_2 is

$$\frac{|c_1|^2}{|c_1|^2 + |c_2|^2} + \frac{|c_2|^2}{|c_1|^2 + |c_2|^2} = 1 = 100\%. \tag{8.29}$$

8.5 Packet States – Physical Meaning

In the past, we tried to construct localized moving "wave packets" by adding together many, very closely spaced (in wave number, or momentum) plane wave states. It is now clear that this must be done with complex exponentials, rather that with real cosines and/or sines. Thus, a general packet state would look (mathematically) like

$$\begin{aligned}
\Psi(x,t) &= \lim_{N\to\infty,\Delta k\to 0} \sum_{n=1}^{N} A_n \mathrm{e}^{i[(k_1+n(\delta k))x-(\omega_1+n(\delta\omega))t]} && (8.30)\\
&= \int_{k_1}^{k_2} A(k)\mathrm{e}^{i(kx-\omega t)}\, dk && (8.31)\\
& && (8.32)
\end{aligned}$$

Such a packet is made up of a whole band of different plane waves and therefore, a whole band of wave numbers. Thus, the possible results of measurement of momentum are spread over a band of width we call "Δp".

"Orthodox " Interpretation:

If we do measure the momentum, however, the particle will materialize one and only one value of momentum. The rule for this is the following:

$$\Psi(x,t) = \int_{k_1}^{k_2} A(k)\mathrm{e}^{i(kx-\omega t)}\, dk \tag{8.33}$$

where $k = \frac{p}{\hbar}$. Then, the probability of obtaining a value of momentum in a small range dp centered on p is

$$P(p)\; dp \propto |A(k)|^2\; dk \tag{8.34}$$

We'll work out the constant of proportionality later. Even without this, we can, of course, will work the relative probabilities (i.e., ratios of probabilities for which the constant of proportionality cancels).

Of course, for this to be really useful, we need to know how to calculate $A(k)$ for a given $\Psi(x,t)$. for that, we need Fourier analysis; we will see how that works in the next class.

Comment: "Materialization of momentum p" does not imply materialization at a definite position. In fact, there exists no state which simultaneously allows materializing atoms with precise p and precise x. (We will prove this later).

In the meantime, let us look at an example of something conceptually simpler – the evaluation of an integral like that in equation (8.33) to construct $\Psi(x,t)$.

Example:

> Suppose we want to evaluate the functional form (in x, say at $t = 0$) of an equal-amplitude mix of plane waves with equal amplitudes in some range $[k_1, k_2]$ and zero amplitudes for k outside this range. Thus, the "bandwidth in wave number" for this mix is $\Delta k = k_2 - k_1$. We suppose that the band of wave numbers is centered on $k = 0$, thus $k_1 = k_2$. Then $k_2 = \frac{\Delta k}{2}$ and $k_1 = -\frac{\Delta k}{2}$. A plot of $A(k)$ vs. k would then be flat from $= \frac{\Delta k}{2} \rightarrow +\frac{\Delta k}{2}$. Figure 8.3 shows this plot.
>
> *fig3*
>
> We chose the amplitude of $A(k)$ to be $\frac{1}{\sqrt{\Delta k}}$ so that the area under the plot is 1 for "neatness". Thus, this mix has half the plane waves propagating to the left (negative values of k) and, with equal

amplitudes, half to the right. We evaluate it at $t = 0$:

$$\begin{aligned}
\Psi(x, t=0) &= \frac{1}{\sqrt{\Delta k}} \int_{-\frac{\Delta k}{2}}^{+\frac{\Delta k}{2}} \mathrm{e}^{ikx}\ dk && (8.35)\\
&= \frac{1}{\sqrt{\Delta k}} \left[\frac{1}{ix}\mathrm{e}^{ikx}\right]_{-\frac{\Delta k}{2}}^{+\frac{\Delta k}{2}} && (8.36)\\
&= \frac{2}{x\sqrt{\Delta k}} \left[\frac{\mathrm{e}^{i\left(\frac{\Delta k}{2}\right)x} - \mathrm{e}^{-i\left(\frac{\Delta k}{2}\right)x}}{2i}\right] && (8.37)\\
&= \frac{2}{\sqrt{\Delta k}x} \sin\left(\frac{\Delta k}{2}x\right) && (8.38)\\
&= \frac{\sqrt{\Delta k}}{\left(\frac{\Delta k}{2}\right)x} \sin\left(\frac{\Delta k}{2}x\right) && (8.39)\\
&= \sqrt{\Delta k}\ \mathrm{sinc}\left(\frac{\Delta k}{2}x\right) && (8.40)
\end{aligned}$$

Schematically,

fig 4

Question for now. (Qualitatively), what do you expect will happen to the shape of $\Psi(x, t)$ as t increases from zero? Why?

Chapter 9

Ninth Class: Uncertainty in Quantum Mechanics

Tuesday, September 23, 2008

9.1 Certainty and Uncertainty

As we have explained, for a particle in "partial reality" and represented by state function $\Psi(x,t)$, generally it is unpredictable or "uncertain" where a single position-producing measurement will cause materialization[1]. The range of this uncertainty for position materialization, called "$2\Delta x$" (for the one-dimensional case) is defined or, in principle, is determined experimentally[2], as follows

9.1.1 Meaning of Δx

:

Imagine preparing an ensemble of very many[3] identical particles, all with the same state function, $\Psi(x,t)$. A position materialization measurement is performed for each system, Each particle materializes at a different position; the distribution of positions follows that of $\Psi^*(x,t)\Psi(x,t)$. Δx represents the standard deviation of this distribution of positions. Applied to the state function for a single particle before materialization on position measurement,

---

[1] Of course, the procedure described is as "in principle" or in the nature of a "thought experiment". Still, it defines the meaning of Δx.

[2] The only exception would be if the state function is an infinitely narrow spike function at the time of measurement, which never occurs in practice, but which represents an idealization we will further discuss later on.

[3] Technically, an infinite number

$2\Delta x$ represents the "uncertainty" in our knowledge of where we expect the particle to materialize. A schematic "cartoon" of this is shown in figure 1.

fig1

Note then, that in theory, Δx is equal to standard deviation of $\Psi^*(x,t)\Psi$, not that of Ψ.

It is also true, as we've seen, that for a particle in partial reality and represented by state function $\Psi(x,t)$, generally, if a momentum-producing measurement is made, the value of momentum materialized is unpredictable or "uncertain" over a ranger called $2\Delta p$. The "in-principle" experimental procedure for determining Δp is a follows.

9.1.2 Meaning of Δp

:

Imagine preparing an ensemble of very many identical particles, all with the same state function, $\Psi(x,t)$. A momentum materializing measurement is performed for each system. Generally each particle will materialize a different value of momentum. The symbol Δp represents the standard deviation of this distribution of momenta. Applied to a single particle with state function Ψ before momentum materialization, and $2\Delta p$ represents the "uncertainty" in our knowledge of what value of momentum we expect the particle to materialize with. Special cases are those of the plane waves states

$$\Psi(x,t) = A\mathrm{e}^{i\left(\frac{p}{\hbar}x-\frac{E}{\hbar}t\right)} \quad \text{and} \quad A\mathrm{e}^{-i\left(\frac{p}{\hbar}x+\frac{E}{\hbar}t\right)} \tag{9.1}$$

For each of these states the momentum is definite $\left(+\frac{p}{\hbar}\hat{x} \text{ and } -\frac{p}{\hbar}\hat{x}\right)$, respectively); thus for each of these states $\Delta p = 0$. We now come to something very important and fundamental. **Heisenberg Uncertainty Principle – Statement**

> There exists no valid state function in quantum mechanics for which the product $\Delta x \Delta p_x$ is less then $\frac{\hbar}{2}$. That is, for any valid state function
>
> $$\Delta x \Delta p_x \geq \frac{\hbar}{2} \tag{9.2}$$

In the next class we'll demonstrate the Heisenberg Uncertainty Principle (HUP) using Fourier analysis; in the meantime we will illustrate the result with a few preliminary examples.

9.2 Example: Plane-Wave states

Consider the plane wave states $\Psi(x,t) = A\mathrm{e}^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)}$ and $A\mathrm{e}^{-i\left(\frac{p}{\hbar}x + \frac{E}{\hbar}t\right)}$. As remarked earlier, for each, $\Delta p_x = 0$. However, for each $\Psi^*\Psi = |A|^2 =$ constant in x, $\Delta x = \infty$. Thus, for these states, $\Delta x \Delta p_x =$"$\infty \cdot 0$", which is not inconsistent with the Heisenberg Uncertainty Principle .

Example:

Consider the equal amplitude superposition of plane wave states we discussed in the last class – namely

$$\Psi(x, t=0) = \frac{1}{\sqrt{\delta k}} \int_{-\frac{\delta k}{2}}^{+\frac{\delta k}{2}} \mathrm{e}^{ikx}\; dk \tag{9.3}$$

Strictly speaking, we should use the standard deviation for the wave number distribution; as you can show[4], it is $\Delta k = \frac{2\delta k}{\sqrt{12}}$ for a flat distribution. Then, since for each plane wave component $p = hk \;\rightarrow\; \Delta p = \hbar \Delta k \;=\; \frac{2\hbar\delta k}{\sqrt{12}}$. As we saw last time, the integral evaluates to

$$\Psi(x, t=0) = \text{constant} \cdot \;\text{sinc}\left(\frac{\delta k}{2}x\right). \tag{9.4}$$

Thus,

$$|\Psi(x, t=0)|^2 \propto \;\text{sinc}^2\left(\frac{\delta k}{2}x\right) \tag{9.5}$$

Strictly speaking, for Δx we should use the standard deviation of $|\Psi(x, t = 0)|^2$. However, this would lead us into a (now) distracting side calculation – we seek an understanding, not exactness. Therefore, we will estimate Δx as the half-width to the first zero of $|\Psi|^2$ for this case. The first zero occurs at

$$\frac{\delta k}{2}x = \pi \quad \Rightarrow \quad x = \frac{2\pi}{\delta k}. \tag{9.6}$$

Calling this Δx, we have

$$\Delta x \approx \frac{2\pi}{\delta k} = \frac{4\pi}{\sqrt{12}\Delta k} \approx \frac{1.15\pi}{\Delta k} \approx \frac{\pi}{\Delta k} \tag{9.7}$$

---

[4] see later. Also, since the wave number distribution $A(k)$ is flat, the standard distribution for $|A(k)|^2$ ($\propto$ to probability of momentum $p = \hbar k$) is the same as that of $A(k)$.

i.e. $\Delta x \Delta k \approx \pi$. Thus,

$$\Delta p_x \Delta x = (\hbar \Delta k)(\Delta x) \approx \pi\hbar \geq \frac{\hbar}{2}, \tag{9.8}$$

consistent with the uncertainty principle.

Notice an interesting point: since $\Delta x \propto \frac{1}{\Delta p}$, the narrower we make wave number bandwidth Δk, the broader we make the positional uncertainty Δx^5. Conversely, the broader we make Δk, the narrower we make Δx. The Heisenberg Uncertainty Principle says that this is general – for any class of state functions

$$\begin{aligned} \Delta x &\geq \frac{\hbar}{2\Delta p} \propto \frac{1}{\Delta p_x} && (9.9) \\ \Delta p_x &\geq \frac{\hbar}{2\Delta x} \propto \frac{1}{\Delta x} && (9.10) \end{aligned}$$

More examples will be shown in the near future. Actually, the Heisenberg Uncertainty Principle holds in three dimensions – so there are really three relations

$$\begin{aligned} \Delta x \Delta p_x &\geq \frac{\hbar}{2} && (9.11) \\ \Delta y \Delta p_y &\geq \frac{\hbar}{2} && (9.12) \\ \Delta z \Delta p_z &\geq \frac{\hbar}{2} && (9.13) \end{aligned}$$

We illustrate today next with a physical example.

9.3 Example: Position Measurement by Aperture

Suppose we prepare an electron so that its state function is a plane wave of wave number k. This is accomplished by making a very [6] precise measurement of momentum – if the result $p = \hbar k$ is achieved, then the immediately afterward, the state function is the plane wave. We take this as

$$\Psi(x, t) = A\mathrm{e}^{i(kx-\omega t)} \tag{9.14}$$

---

[5] with a flat distribution, but a narrower Δk, you still get a sinc^2 function for $|\Psi|^2$, its just broader in x.

[6] actually, infinitely precise – this is an idealization

where $k = \frac{p}{\hbar}$, $\omega = \frac{E}{\hbar}$. In this state, $p_x = \hbar k$ (definitely) and p_y is definitely zero. However, $\Delta x = \infty$ and $\Delta y = \infty$ (plane waves extends over x and y). So $\Delta y \Delta p_y =$ "$\infty \cdot 0$", which is not inconsistent with the Heisenberg Uncertainty Principle $\Delta y \Delta p_t \geq \frac{\hbar}{2}$. Now suppose we attempt to measure y with an aperture:

fig2

Immediately after "passing through the aperture", $\Delta y = a$, the aperture size. Thus, we have reduced Δy. This means that the particle now has a new state function − this one with $\Delta y \geq a$. (This is general − a measurement or a disturbance on the particle causes a change in the state function. More on this later). In fact, we can reduce Δy as much a we like (by making a as small as we lke).

However, **in the new state function, Δp_y is no longer zero!** This is because the state function has diffracted thru the aperture!

fig3

The arrows show "possible trajectories" to points on the screen. (Remember, though, a single trajectory is not actually taken unless we force a one by measurement − recall the Feynman double-slit experiment − the situation is similar here.) But, $p = \frac{h}{\lambda}$, so, since $\Delta p_y = p\Delta\theta = p\frac{\lambda}{a}$, $\Delta p_y = \frac{h}{\lambda} \cdot \frac{\lambda}{a} = \frac{h}{a}$. Now, at any time after passage thru the aperture, $\Delta y > a$, so on the far side of the aperture, the new state function obeys

$$\Delta y \Delta py \geq h \geq \frac{\hbar}{2} \tag{9.15}$$

Thus, our attempt to reduce Δy in the new state function has been compensated with an increase in Δp_y, in accordance with Heisenberg Uncertainty Principle .

9.4 Expectation Values

We've established, that if you prepare an ensemble of very many identical particles all with the same state function $\Psi(x, t)$, position-producing measurements for each will generally produce different materialization places spread of a "range" $2\Delta x$. It is often important to know what average would be obtained if all these position measurements were (hypothetically) to be performed. This average is called the **expectation value of** x, denoted by $\langle x\rangle$ or $\bar{x}$.

It is easy to find a general formula for $\langle x\rangle$. As your text shows (p.p. 5-10), if $P(x)$ is the probability density function, then

$$\langle x\rangle = \int_{-\infty}^{+\infty} xP(x)\; dx \tag{9.16}$$

since $P(x) = \Psi^*(x,t)\Psi(x,t)$, $\langle x\rangle$ is a function of t and is

$$\langle x\rangle = \int_{-\infty}^{+\infty} x\left|\Psi(x,t)\right|^2\; dx = \int_{-\infty}^{+\infty} \Psi^*(x,t)x\Psi(x,t)\; dx \tag{9.17}$$

similarly,

$$\langle x\rangle^2 = \int_{-\infty}^{+\infty} \Psi^*(x,t)x^2\Psi(x,t)\; dx \tag{9.18}$$

and for an analytical function, $f(x)$,

$$\langle f(x)\rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t)f(x)\Psi(x,t)\; dx \tag{9.19}$$

What about the expectation value for momentum from momentum-producing measurements? For the time being, we will assume[7] that

$$\langle p\rangle = m\frac{d\left\langle x\right\rangle}{dt} \tag{9.20}$$

Now

$$\frac{d\left\langle x\right\rangle}{dt} = \frac{d}{dt}\int_{-\infty}^{+\infty} \left|\Psi(x,t)\right|^2\; dx \tag{9.21}$$

$$= \int_{-\infty}^{+\infty} x\left(\frac{\partial}{\partial t}\left|\Psi(x,t)\right|^2\right)\; dx \tag{9.22}$$

We've already seen that

$$\frac{\partial}{\partial t}\left|\Psi\right|^2 = \frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)\right] \tag{9.23}$$

---

[7] We will prove this assertion later, again, through Fourier analysis.

so

$$\frac{d\langle x\rangle}{dt} = \frac{i\hbar}{2m}\int_{-\infty}^{+\infty} x\frac{\partial}{\partial x}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)\,dx \tag{9.24}$$

Integrating this by parts and using $\Psi \to 0$ as $x \to \pm\infty$ (and also $\frac{\partial x}{\partial x} = 1$) yields

$$\frac{d\langle x\rangle}{dt} = -\frac{i\hbar}{2m}\int_{-\infty}^{+\infty}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)\,dx \tag{9.25}$$

The second term can be integrated by parts again, and again throwing away the boundary term, it is equal to the first term, so

$$\frac{d\langle x\rangle}{dt} = -\frac{i\hbar}{m}\int_{-\infty}^{+\infty}\Psi^*\frac{\partial\Psi}{\partial x}\,dx \tag{9.26}$$

so

$$\langle p\rangle = \frac{\hbar}{i}\int_{-\infty}^{+\infty}\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}\,dx \tag{9.27}$$

We can write this as

$$\langle p\rangle = \int_{-\infty}^{+\infty}\Psi^*(x,t)\cdot\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(x,t)\,dx \tag{9.28}$$

along with

$$\langle x\rangle = \int_{-\infty}^{+\infty} x\left|\Psi(x,t)\right|^2\,dx = \int_{-\infty}^{+\infty}\Psi^*(x,t)x\Psi(x,t)\,dx \tag{9.29}$$

From these we say that the "position basis" (what we are so far working in) the (multiplicative) "operator" $\hat{x} = x$ "represents" position, and the operator $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$ "represents" momentum. (We will see in the future that the utility of this operator concept, seemingly superfluous here, has significance far beyond that for these simple expectation values.)

Similarly, as you can show, if $f(p)$ is any polynomial in p (e.g. $KE = \frac{p^2}{2m}$), then

$$\langle f(p)\rangle = \int_{-\infty}^{+\infty}\Psi^*(x,t)f\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi(x,t)\,dx \tag{9.30}$$

Note also the action of $\hat{p}$ (or p_{op} or $\tilde{p}$) on a plane wave state:

$$\hat{p}\mathrm{e}^{i\left(\frac{p}{\hbar}x-\frac{E}{\hbar}t\right)} = \frac{\hbar}{i}\frac{\partial}{\partial x}\left[\mathrm{e}^{i\left(\frac{p}{\hbar}x-\frac{E}{\hbar}t\right)}\right] = \frac{\cancel{\hbar}}{\cancel{i}}\frac{\cancel{i}p}{\cancel{\hbar}}\left[\mathrm{e}^{i\left(\frac{p}{\hbar}x-\frac{E}{\hbar}t\right)}\right] \tag{9.31}$$

$$= p\mathrm{e}^{i\left(\frac{p}{\hbar}x-\frac{E}{\hbar}t\right)} \tag{9.32}$$

We see that, for a plane-wave state, $\hat{p}$ on it is equivalent to multiplication by the number p.

Now, any function of $\hat{p}$ is also an operator. For example, consider the kinetic energy $K = \frac{p^2}{2m}$. Then

$$\hat{K} = \frac{\hat{p}}{2m} = \frac{\hbar}{i}\frac{\partial}{\partial x}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{9.33}$$

Thus, (in one dimension),

$$\begin{aligned} \langle K \rangle &= \int_{-\infty}^{+\infty} \Psi^*(x,t)\hat{K}\Psi(x,t)\; dx & (9.34)\\ &= \int_{-\infty}^{+\infty} \Psi^*(x,t)\left(-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}\right)\; dx & (9.35)\end{aligned}$$

Which is

$$\langle K \rangle = -\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty} \Psi^*(x,t)\frac{\partial^2\Psi(x,t)}{\partial x^2}\; dx \tag{9.36}$$

Now consider the total energy $E = K + V$. Then,

$$\hat{E} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x,t) \tag{9.37}$$

And, consider the Schrödinger equation

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) \tag{9.38}$$

which is then

$$\hat{E}\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t) \tag{9.39}$$

Thus, the energy operator is also represented by

$$\hat{E} = i\hbar\frac{\partial}{\partial t} \tag{9.40}$$

so

$$\begin{aligned} \langle E \rangle &= \int_{-\infty}^{+\infty} \Psi^*(x,t)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial^2 x} + V(x,t)\right]\Psi(x,t)\; dx & (9.41)\\ &= -\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty} \Psi^*(x,t)\frac{\partial^2\Psi(x,t)}{\partial x^2}\; dx & (9.42)\\ &+ \int_{-\infty}^{+\infty} \Psi^*(x,t)V(x,t)\Psi(x,t)\; dx & (9.43)\end{aligned}$$

and also

$$\langle E \rangle = i\hbar \int_{-\infty}^{+\infty} \Psi^*(x,t) \frac{\partial \Psi(x,t)}{\partial t}\ dx \tag{9.44}$$

Chapter 10

Tenth Class: Heisenberg Uncertainty Principle and Fourier Analysis

Thursday, September 25, 2008

10.1 Heisenberg Uncertainty Principle – Another Example

Here is another example. Suppose that we prepare a particle in a plane wave state (or any other state with substantial Δx) and decide to see if we can force a violation of the Heisenberg Uncertainty Principle by actually "looking" at the particle with a "super-microscope" and "seeing" were it materializes. If we can do this to accuracy $\Delta x < \frac{\hbar}{2\Delta p}$, where Δp is the resulting uncertainty in momentum, then we would be able to violate the Heisenberg Uncertainty Principle . Let us see what we can do.

For this, we use the simplest "microscope" – one lens.

fig1

Now, because of the finite diameter of the lens, the probability density at the screen of materialized particle is, as you know, not a point, but rather a little diffraction pattern

fig2

As we saw in discussing physical optics, based on this diffraction distribution, two objects a distance δ apart can be resolved only if

$$2\delta \sin\left(\frac{\phi}{2}\right) \geq \lambda$$

$$\delta > \frac{\lambda}{2\sin\left(\frac{\phi}{2}\right)} \tag{10.1}$$

Thus, if the limit of resolution on where the electron materializes is

$$\Delta x = \frac{\lambda}{2\sin\left(\frac{\phi}{2}\right)} \tag{10.2}$$

Of course, we can make this as small as we want by either using λ as small as possible (gamma rays) or by making ϕ large (big diameter lens). In any case, the positional size of the electron wave packet after this observation is given by this equation (or is larger).

Now, let us inquire into the momentum of the electron after the viewing. In the initial state, we had $\Delta p = 0$. But, in the measurement, a certain amount of momentum is transferred to the electron. How much? To attempt to keep track of this, we assume a photon-electron collision (i.e. Compton scattering) of a **single** photon of known momentum ($p_\gamma = \frac{E}{c} = \frac{h}{\lambda}$)with the electron.

But, after the collision, the photon could have entered the lens anywhere, thus, the x-component of the photon momentum after the collision is uncertain by amount $\Delta p_x = \frac{h}{\lambda}\sin\theta$.

fig3

Thus, after the collision, the electron is in a packet state such that for it

$$\Delta p_x \geq \frac{h}{\lambda}\sin\theta \tag{10.3}$$

This is equal only if the initial e^- momentum is zero. Considering, then, the final packet state for the electron, we have

$$\Delta x \Delta p_x \geq \frac{\lambda}{2\sin\theta} \cdot \frac{h}{\lambda}\sin\theta \tag{10.4}$$

or

$$\Delta x \Delta p_x \geq \frac{h}{2} > \frac{\hbar}{2} \tag{10.5}$$

in full accord with the uncertainty principle.

In the context of this example, a key "reason" for the result is Einstein's photon hypothesis, according to which electromagnetic radiation is delivered (e.g., to the electron being forced to materialize at a point) is indivisible packets, each of momentum $p_x = \frac{h}{\lambda}$. If it were possible that $p_\gamma < \frac{h}{\lambda}$ for wavelength λ, then we could scatter photons from electrons with sufficient minimal unknowable x-momentum transfer to violate the Heisenberg Uncertainty Principle .

Many examples of this sort have been investigated; a real possibility of violating the Heisenberg Uncertainty Principle has never been found.

10.2 Fourier Analysis

Considering our general "wave packet"

$$\Psi(x,t) = \int_{k_1}^{k_2} A(k) \mathrm{e}^{i(kx-\omega t)}\, dk, \tag{10.6}$$

where $k = \frac{p}{\hbar}$ and $\omega = \frac{E}{\hbar}$. We mentioned that the probability of obtaining a value of momentum (on momentum measurement) in the infinitesimal range dp centered on p is

$$P(p)dp \propto |A(k)|^2\, dk, \qquad dk = \frac{dp}{\hbar} \tag{10.7}$$

As we remarked, in order for this to be really useful, we would like to find out how to deduce, for a given $\Psi(x,t)$, what function $A(k)$ is[1]. For this, we need Fourier analysis:

10.2.1 Basic Fourier Analysis

We will begin by recalling that any function $f(x)$ with period 2π can be expanded as

$$\begin{aligned} f(x) = \frac{a_0}{2} &+ a_1 \cos x + a_2 \cos(2x) + a_3 \cos(3x) + a_4 \cos(4x) + \cdots \\ &+ b_1 \sin x + b_2 \sin(2x) + b_3 \sin(3x) + b_4 \sin(4x) + \cdots \end{aligned}$$

or

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos(nx) + \sum_{n=1}^{\infty} b_n \sin(nx). \tag{10.8}$$

---

[1] Of course, we need also to be assured that, if given an arbitrary reasonable state function $\Psi(x,t)$, that $A(k)$ exists for it. Fourier analysis answers this question, as we will see.

If the function is periodic with a different period (call it $2L$), the the expansion becomes

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right) \tag{10.9}$$

We recall that the coefficients are found from

$$a_n = \frac{1}{L}\int_{-L}^{L} f(x)\cos\left(\frac{n\pi x}{L}\right)\, dx \tag{10.10}$$

$$b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\left(\frac{n\pi x}{L}\right)\, dx \tag{10.11}$$

where the integrals could be over any full period of f(x); I've arbitrarily chosen $-L \to L$. Recall also that, key to establishing the formulas for the coefficients are **orthogonality relations**

$$\int_{-L}^{L} \cos\left(\frac{m\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\, dx = 0 \quad \text{if } m \neq n \tag{10.12}$$

$$\int_{-L}^{L} \sin\left(\frac{m\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\, dx = 0 \quad \text{if } m \neq n \tag{10.13}$$

$$\int_{-L}^{L} \sin\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\, dx = 0 \quad \text{if } m \neq n \tag{10.14}$$

$$\int_{-L}^{L} \sin^2\left(\frac{n\pi x}{L}\right)\, dx = \int_{-L}^{L} \cos^2\left(\frac{n\pi x}{L}\right)\, dx = L \tag{10.15}$$

Thus, the set of functions

$$\left\{\frac{1}{\sqrt{2L}}, \frac{1}{\sqrt{L}}\sin\left(\frac{n\pi x}{L}\right), \frac{1}{\sqrt{L}}\cos\left(\frac{n\pi x}{L}\right)\right\} \tag{10.16}$$

form an **orthonormal set** on any interval of length $2L$.

10.2.2 Complex Orthogonal Functions

Consider two complex valued functions of the real variable x:

$$f(x) = u(x) + iv(x) \tag{10.17}$$

$$g(x) = w(x) + is(x) \tag{10.18}$$

where $u(x), v(x), w(x), s(x)$ are real. $f(x)$ and $g(x)$ are said to be **orthogonal** on the interval $[a, b]$ if

$$\int_a^b f^*(x)g(x)\ dx = \int_a^b g^*(x)f(x)\ dx = 0. \tag{10.19}$$

This is a direct generailization of the definition of orthogonality for real functions. It is interesting and easy to show that complex exponentials, also from an orthogonal set. To see this, consider (say, on interval $[0, 2\pi]$).

$$I = \int_0^{2\pi} y_n(x)y_m^*(x)\ dx \tag{10.20}$$

where $y_n(x) = \mathrm{e}^{inx}$. We have

$$I = \int_0^{2\pi} \mathrm{e}^{inx}\mathrm{e}^{-imx}\ dx \tag{10.21}$$

$$= \frac{1}{i(n-m)}\mathrm{e}^{i(n-m)x}|_0^{2\pi} \quad = 0 \quad \text{if } m \neq n. \tag{10.22}$$

If $n = m$,

$$\int_0^{2\pi} \mathrm{e}^{inx}\mathrm{e}^{-inx}\ dx = \int_0^{2\pi} 1\ dx = 2\pi \tag{10.23}$$

Thus, another orthonormal set on $[0, 2\pi]$ is

$$\left\{\frac{1}{\sqrt{2\pi}}\mathrm{e}^{inx}\right\}, \quad n = -\infty \to +\infty \quad \text{in integer steps.} \tag{10.24}$$

10.2.3 Complex Fourier Series on $[0, 2\pi]$

This leads us to an interesting conjecture – if $f(x)$ is an complex "arbitrary" periodic function of period 2π, perhaps we can expand this as

$$f(x) = c_0 + c_1\mathrm{e}^{ix} + c_{-1}\mathrm{e}^{-ix} + c_2\mathrm{e}^{2ix} + c_{-2}\mathrm{e}^{-2ix} + \cdots \quad ? \tag{10.25}$$

then,

$$f(x) = \sum_{n=-\infty}^{+\infty} c_n\mathrm{e}^{inx} \quad ? \tag{10.26}$$

Let us see if we can find coefficients c_n consistent with this. Assuming that equation (10.25) is true, by integrating both sides we get,

$$\frac{1}{2\pi}\int_0^{2\pi} f(x)\ dx = \frac{1}{2\pi}\int_0^{2\pi} c_0\ dx + \\ \frac{1}{2\pi}\int_0^{2\pi} c_1 \mathrm{e}^{ix}\ dx + \frac{1}{2\pi}\int_0^{2\pi} c_1 \mathrm{e}^{-inx}\ dx + \cdots$$

However, all integrals on the right except the first vanish.

$$\int_0^{2\pi} \mathrm{e}^{ix}\ dx = \frac{1}{i}\left[\mathrm{e}^{ix}\right]_0^{2\pi} = \frac{1}{i}\left[\mathrm{e}^{2\pi i} - \mathrm{e}^0\right] = \frac{1}{i}[1-1] = 0 \tag{10.27}$$

Thus,

$$c_0 = \frac{1}{2\pi}\int_0^{2\pi} f(x)\ dx \tag{10.28}$$

To find c_n, multiply equation (10.25) by e^{-inx} and integrate:

$$\begin{aligned}\frac{1}{2\pi}\int_0^{2\pi} f(x)\mathrm{e}^{-inx}\ dx &= \frac{c_0}{2\pi}\int_0^{2\pi} \mathrm{e}^{-inx}\ dx + \frac{c_1}{2\pi}\int_0^{2\pi} \mathrm{e}^{-inx}\mathrm{e}^{ix}\ dx \\ &+ \frac{c_{-1}}{2\pi}\int_0^{2\pi} \mathrm{e}^{-inx}\mathrm{e}^{-ix}\ dx + \cdots \\ &= \frac{c_0}{2\pi}\int_0^{2\pi} \mathrm{e}^{-inx}\ dx + \sum_{m=1, m\neq n}^{\infty}\int_0^{2\pi} \mathrm{e}^{i(m-n)x}\ dx \\ &+ \int_0^{2\pi} \mathrm{e}^{(n-n)x}\ dx\end{aligned}$$

These integrals are all zero except the last one, which is 2π; thus

$$c_n = \frac{1}{2\pi}\int_0^{2\pi} f(x)\mathrm{e}^{-inx}\ dx \tag{10.29}$$

10.2.4 Complex Fourier Series on $[-\ell, \ell]$, $[0, L]$

In the interval is $[-\ell, \ell]$, the series is $\pi \longrightarrow \frac{n\pi}{\ell}$

$$f(x) = \sum_{n=-\infty}^{+\infty} c_n \mathrm{e}^{\frac{in\pi x}{\ell}} \tag{10.30}$$

with

$$c_n = \frac{1}{2L}\int_{-\ell}^{\ell} f(x)\mathrm{e}^{\frac{-in\pi x}{\ell}}\ dx \tag{10.31}$$

From this, if the period is L (i.e. we are considering an “reasonable” complex-valued function of real variable x such that $f(x+L) = f(x)$), then the series can be gotten by the replacement in our above work of 2ℓ by L ($2\ell \to L$)

$$f(x) = \sum_{n=-\infty}^{+\infty} c_n \mathrm{e}^{\frac{2in\pi x}{L}} \tag{10.32}$$

with

$$c_n = \frac{1}{L}\int_{0}^{L} f(x)\mathrm{e}^{-\frac{2in\pi x}{L}}\ dx \tag{10.33}$$

It can be shown that these series converge for any “reasonable” $f(x)$. Thus, the set $\left\{\mathrm{e}^{inx}\right\}, n = -\infty, \cdots, \infty$ is a **complete** set.

10.2.5 Special Case of Real $f(x)$

If $f(x)$ is real, then

$$c_n^* = \left(\frac{1}{L}\int_0^L f(x)\mathrm{e}^{-\frac{2in\pi x}{L}}\ dx\right)^* = \frac{1}{L}\int_0^L f(x)\mathrm{e}^{\frac{2in\pi x}{L}}\ dx = c_n \tag{10.34}$$

In this case, our series

$$f(x) = \sum_{n=1}^{\infty} c_n \mathrm{e}^{\frac{2in\pi x}{L}} + \sum_{n=-\infty}^{0} c_{-n}\mathrm{e}^{-\frac{2in\pi x}{L}} \tag{10.35}$$

becomes

$$f(x) = \sum_{n=0}^{\infty}\left(c_n\mathrm{e}^{\frac{2in\pi x}{L}} + n_n^*\mathrm{e}^{-\frac{2in\pi x}{L}}\right) \tag{10.36}$$

Noting that in this case,

$$\begin{aligned}
c_n &= \frac{1}{L}\int f(x)\mathrm{e}^{-\frac{2in\pi x}{L}}\ dx \\
&= \frac{1}{L}\int f(x)\cos\left(\frac{2n\pi x}{L}\right) - \frac{i}{L}\int f(x)\sin\left(\frac{2n\pi x}{L}\right)
\end{aligned}$$

where $\frac{1}{L}\int f(x)\cos\left(\frac{2n\pi x}{L}\right)$ is a_n and $-\frac{i}{L}\int f(x)\sin\left(\frac{2n\pi x}{L}\right)$ is ib_n. Then

$$c_n = a_n - ib_n \tag{10.37}$$

and

$$c_n^* = a_n + ib_n \tag{10.38}$$

Then, equation (10.36) becomes

$$\begin{aligned} f(x) &= \sum_{n=0}^{\infty}\Bigg\{(a_n - ib_n)\left[\cos\left(\frac{2n\pi x}{L}\right) + i\sin\left(\frac{2n\pi x}{L}\right)\right] \\ &+ (a_n + ib_n)\left[\cos\left(\frac{2n\pi x}{L}\right) - i\sin\left(\frac{2n\pi x}{L}\right)\right]\Bigg\} \end{aligned}$$

which is

$$f(x) = \sum_{n=0}^{\infty} a_n\cos\left(\frac{2n\pi x}{L}\right) + b_n\sin\left(\frac{2n\pi x}{L}\right) \tag{10.39}$$

which itself is the familiar Fourier sine and cosine series for a real function f(x).

10.3 Fourier Expansion of Complex Non-periodic Functions – Fourier Transforms

For a complex function with a period L, we saw that the Fourier expansion

$$f(x) = \sum_{n=-\infty}^{+\infty} c_n \mathrm{e}^{\frac{2in\pi x}{L}} \tag{10.40}$$

and

$$c_n = \frac{1}{L}\int_0^L f(x)\mathrm{e}^{-\frac{2in\pi x}{L}} \tag{10.41}$$

is valid as long as $f(x)$ is "reasonable".

What if our expansion function $f(x)$ is not periodic? "Not periodic" means the same as "period → ∞". Therefore, we let $L \to \infty$ in our equations above, taking the interval (length L) as $\left[-\frac{L}{2}, \frac{L}{2}\right]$. Then, defining $k \equiv \frac{2n\pi}{L}$, and $\Delta k \equiv \frac{2\pi}{L}$,

$$f(x) = \sum_{k=-\infty}^{+\infty} c_n \mathrm{e}^{ikx} = \sum_{k-\infty}^{+\infty} \frac{L}{2\pi} c_n \mathrm{e}^{ikx}\Delta k \tag{10.42}$$

We now take the limit $L \to \infty$; the sum then becomes

$$f(x) = \int_{-\infty}^{+\infty} \frac{1}{\sqrt{2\pi}} \frac{Lc_n}{\sqrt{2\pi}} \mathrm{e}^{ikx} \, dk \tag{10.43}$$

Since,

$$c_n = \frac{1}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x') \mathrm{e}^{-\frac{2in\pi x'}{L}} \, dx', \tag{10.44}$$

$$f(x) = \int_{-\infty}^{+\infty} \frac{1}{\sqrt{2\pi}} \cdot \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x') \mathrm{e}^{-ikx'} \, dx' \right) \mathrm{e}^{ikx} \, dk \tag{10.45}$$

Let us define the quantity

$$g(k) \equiv \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) \mathrm{e}^{-ikx} \, dx \tag{10.46}$$

Then we see that we have established a very interesting and very important theorem: the **Fourier Transform Theorem**:

Theorem:
Suppose that $f(x)$ is a square-integrable function i.e.,

$$\int_{-\infty}^{+\infty} |f(x)|^2 \, dx < \infty \tag{10.47}$$

Then, there exists a function $g(k)$ such that

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k) \mathrm{e}^{ikx} \, dk \tag{10.48}$$

where

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) \mathrm{e}^{-ikx} \, dx \tag{10.49}$$

Chapter 11

Eleventh Class: Fourier Analysis and the Heisenberg Uncertainty Principle

Tuesday, September 30, 2008

11.1 Fourier Analysis

In the last class, we established the very important Fourier Transform theorem:

Theorem: Suppose that $f(x)$ is a complex-valued square integrable function of real variable x – i.e. $\int_{-\infty}^{+\infty} |f(x)|^2 \; dx < \infty$. Then, there exists a function $g(k)$ such that

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k) \mathrm{e}^{ikx} \; dk \tag{11.1}$$

where

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) \mathrm{e}^{-ikx} \; dx \tag{11.2}$$

Since quantum mechanical state functions are always square-integrable, we see that this theorem addresses our concerns about the existence of "$A(k)$" for any state function $\Psi(x, t_0)$ at any particular time t_0 – e.g. "$A(k)$" at time $t = 0$ is just $\frac{1}{\sqrt{2\pi}} g(k)$ above. (As we will see, for a free particle, $A(k)$ does not change in time. Of course, both $f(x)$ and $g(k)$ can be complex valued functions. We'll see later that if $f(x)$ is square-integrable, so is $g(k)$.

Example: Suppose that, at $t = 0$,

$$\Psi(x, t=0) = f(x) = \begin{cases} \frac{1}{\sqrt{a}} & |x| \leq \frac{a}{2} \\ 0 & |x| > \frac{a}{2} \end{cases} \tag{11.3}$$

fig 1

Then

$$\begin{aligned} g(k) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) \mathrm{e}^{-ikx}\, dx \\ &= \frac{1}{\sqrt{2\pi a}} \int_{-\frac{a}{2}}^{\frac{a}{2}} \mathrm{e}^{-ikx}\, dx \\ &= \frac{1}{\sqrt{2\pi a}} \left[-\frac{1}{ik} \mathrm{e}^{-ikx} \right]_{-\frac{a}{2}}^{\frac{a}{2}} \\ &= \frac{1}{\sqrt{2\pi a}} \frac{\sin\left(\frac{ka}{2}\right)}{\frac{k}{2}} \\ g(k) &= \sqrt{\frac{a}{2\pi}} \operatorname{sinc}\left(\frac{ka}{2}\right) \end{aligned}$$

fig 2

Now you might think – O.K. – let me check this – if I were to take this $g(k)$ and Fourier transform it, I should get $f(x)$ back – that is,

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \sqrt{\frac{a}{2\pi}} \frac{\sin\left(\frac{ka}{2}\right)}{\frac{ka}{2}} \mathrm{e}^{ikx}\, dk = \begin{cases} \frac{1}{\sqrt{a}} & \text{if } |x| \leq \frac{a}{2} \\ 0 & \text{if } |x| > \frac{a}{2} \end{cases} \tag{11.4}$$

This is true, but unfortunately, actually showing this by evaluating the integral on the left is not easy and requires an advanced technique called “contour integration”. We won’t get involved in that. Consider, however, an example (that we really did some time ago) that will serve as a kind of “complementary example” to the previous – say we now start with a flat distribution of wave numbers and ask what $f(x)$ this makes (“Fourier synthesis”)

fig 3

$$g(k) = \begin{cases} \frac{1}{\sqrt{\Delta k}} & \text{if } |k| < \frac{\Delta k}{2} \\ 0 & \text{if } |k| > \frac{\Delta k}{2} \end{cases} \tag{11.5}$$

Then

$$f(x) = \frac{1}{\sqrt{\Delta k}} \int_{-\frac{\Delta k}{2}}^{\frac{\Delta k}{2}} \frac{1}{\sqrt{\Delta k}} \mathrm{e}^{ikx}\, dk \tag{11.6}$$

$$= \frac{1}{\sqrt{2\pi\Delta k}} \operatorname{sinc}\left(\frac{x\Delta k}{2}\right) \tag{11.7}$$

fig 4

Let us look at an aspect of these examples: In the first, we have for the "full width" of $g(k)$ (spread between first zeros on either side of the center),

$$\Delta k = \frac{4\pi}{a} \tag{11.8}$$

If we take the full-width in x (call it Δx) as a, we then have, for this example,

$$\Delta k \Delta x = 4\pi \tag{11.9}$$

For the second example, as you easily show, we also have, for the full widths, $\Delta k \Delta x = 4\pi$. Thus in both examples,

$$\Delta k \propto \frac{1}{\Delta x} \tag{11.10}$$

and

$$\Delta k \Delta x \geq 1 \tag{11.11}$$

In order to see how general these are, let's look at another example.

Example: Suppose we take a Gaussian

$$f(x) = N\mathrm{e}^{-\frac{x^2}{2\sigma_x^2}} \tag{11.12}$$

fig 5

Here N is a normalization constant that we won't bother with yet, σ is the standard deviation. Then

$$g(k) = \frac{N}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx \mathrm{e}^{-\frac{x^2}{2\sigma_x^2}} \mathrm{e}^{ikx} \tag{11.13}$$

This integral is doable (we won't bother); the result is

$$g(k) = \frac{N}{\sqrt{2\pi}} \sqrt{\frac{\pi}{2\sigma_x^2}} \mathrm{e}^{-\frac{\sigma_x^2 k^2}{2}} \tag{11.14}$$

or

$$g(k) = \frac{N}{2\sigma_x} \mathrm{e}^{-\frac{\sigma_x^2 k^2}{2}} \tag{11.15}$$

This result is very interesting – we see that $g(k)$ is also a Gaussian! Let's find out what its standard deviation width (σ_k). To do this, we put the result ($g(k)$) into standard Gaussian form:

$$g(k) = N' \mathrm{e}^{-\frac{k^2}{2\sigma_k^2}} = \frac{N}{2\sigma_x} \mathrm{e}^{-\frac{\sigma_x^2 k^2}{k}} \tag{11.16}$$

Thus

$$\begin{aligned} \frac{k^2}{2\sigma_k^2} &= \frac{k^2 \sigma_x^2}{2} && (11.17) \\ \sigma_k^2 &= \frac{1}{\sigma_x^2} && (11.18) \\ \sigma_k &= \frac{1}{\sigma_x} && (11.19) \end{aligned}$$

Again the widths in x and k space are reciprocally related:

fig 6

We will have you work out a third example for homework: again you will find that $\Delta x \propto \frac{1}{\Delta k}$. This should make it plausible that this is general property. The statement $\sigma_x \sigma_k \sim 1$ is called the : "Fourier Bandwidth Theorem". Following, we will indicate a more general line of reasoning leading to this important mathematical result.

11.2 A More General Line of Reasoning Leading to the Fourier Bandwidth Theorem

Consider the function $f(x)$ synthesized as

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k) \mathrm{e}^{ikx} \, dk \tag{11.20}$$

where $g(k)$ is real and symmetrically peaked around $k = k_0$ with standard deviation δ_k. Then, as we know, schematically $f(x)$ looks like

fig 7

peaked at $x = 0$. Suppose we seek to understand the "qualitatively". We ask: **Why is $f(x)$ biggest at $x = 0$?** It's biggest at $x = 0$ since all contributions e^{ikx} for all the different k's in the wave number spectrum are in phase at $x = 0$ (all $\mathrm{e}^{ik\cdot 0} = 1$), so big resultant there. However, at any other $x \neq 0$, $f(x)$ must be smaller than $f(0)$. Why? Consider the synthesis at $x = x_0 \neq 0$. The integral

$$f(x_0) = \int_{-\infty}^{+\infty} g(k)\mathrm{e}^{ikx_0}\, dk \tag{11.21}$$

contains contributions from an infinite number of "phasors" $\mathrm{e}^{ikx_0}\, dk$one (of infinitesimal magnitude) for each value of k the integral sweeps over. But, if $x_0 \neq 0$, each such phasor carries a different phase, so there is a degree of destructive interference in the sum implied by the integral, and thus $f(x_0) < f(0)$. As we initially increase (or decrease) x_0 from 0, the greater the phase difference between "successive" phasors $\mathrm{e}^{ikx_0}\, dk$ (for neighboring k's) in the integral. Now suppose we go out to the "end of the packet in position space", i.e. $x = x_1$. There, the phasors $\left\{\mathrm{e}^{okx_1}\right\}$ for the different k's uniformly cover a phase interval of 2π – "for every phasor pointing in a given 'direction' (say 2 0'clock), there's another pointing opposite (8 o'clock); so we get cancellation". This is shown in figure 11.8.

fig 8

So, at x_1, $\Delta k x_1 = 2\pi$, where Δk is the full-bandwidth. Then if the full-width in x is $2x$, we have

$$\Delta x_{\mathrm{fw}} \approx \frac{2\pi}{\Delta k_{\mathrm{fw}}} \tag{11.22}$$

or

$$\Delta x_{\mathrm{fw}} \Delta k_{\mathrm{fw}} \approx 2\pi \tag{11.23}$$

Let's say that we want the product $\sigma_x \sigma_k$ instead of the product of full-widths. At least approximately, for symmetric $g(k)$ and $f(x)$, $\sigma_{x \text{ or } k} \approx \frac{1}{3}\Delta_{\mathrm{fw}}(\text{or } \Delta k_{\mathrm{fw}})$. Of course, the exact ratio of the standard deviations to full-widths depends on the exact shapes of $g(k)$ and $f(x)$; here we are only working toward a "rule-of-thumb" understanding. If we take $\sigma \sim \frac{1}{3}\Delta_{\mathrm{fw}}$, then we have

$$\sigma_x \sigma_k \sim \frac{2\pi}{9} \geq \frac{1}{2} \tag{11.24}$$

We will take $\sigma_x \sigma_k \geq \frac{1}{2}$ as our rule-of-thumb statement.

11.3 Heisenberg Uncertainty Principle

Let us now apply the forgoing to Quantum Mechanics. Let $\phi(k)$ be the Fourier transform of $\psi(x) \equiv \Psi(x, t_0)$ for some particular time t_0. Them we see that, in general, for state functions,

$$\Delta_\phi \propto \frac{1}{\Delta_\phi} \tag{11.25}$$

where Δx_ψ is the x-width of $\phi(x)$ and Δk_ψ is the k-width of $\phi(k)$. Now, for the Gaussian case, we saw that, if we use $\Delta x_\psi = \sigma_x$, $\Delta k_\psi = \sigma_k$, then $\Delta x_\psi \Delta_\psi = 1$ (Gaussian, for full-widths). It turns out that the Gaussian case achieves the minimum possible value for $\sigma_x \sigma_k$. (We will prove this later in the course). However, in quantum mechanics, the Heisenberg Uncertainty Principle refers to probabilities, not to state functions themselves. Now, the probability of materialization per unit x as a function of x is

$$\frac{dP(x)}{dx} = |\psi(x)|^2 \tag{11.26}$$

Likewise, the probability on momentum measurement of materializing of momentum p per unit interval of k is

$$\frac{dP(k)}{dk} = |\phi(k)|^2 \qquad \phi(k) \equiv g(k) \tag{11.27}$$

Now, for the Gaussian

$$\psi(x) = N\mathrm{e}^{-\frac{x^2}{2\sigma_x^2}} \;\Rightarrow\; |\psi(x)|^2 = |N|^2\,\mathrm{e}^{-\frac{x^2}{\sigma_x^2}} \tag{11.28}$$

Thus,

$$\sigma^x_{|\psi|^2} = \frac{1}{\sqrt{2}}\psi^x_\psi \tag{11.29}$$

Likewise

$$\sigma^x_{|\phi|^2} = \frac{1}{\sqrt{2}}\sigma^k_\phi \tag{11.30}$$

Thus letting,

$$\Delta x \;\equiv\; \sigma^x_{|\psi|^2} \tag{11.31}$$

$$\Delta k \;\equiv\; \sigma^x_{|\phi|^2} \tag{11.32}$$

We have

$$\Delta x \Delta k = \frac{1}{2} \tag{11.33}$$

since $p = \hbar k$, we have, for the Gaussian case,

$$\Delta x \Delta p_x = \frac{\hbar}{2} \tag{11.34}$$

As I remarked above, this product is minimum of all cases for the Gaussian. Thus, in general

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \tag{11.35}$$

This, again, is the Heisenberg Uncertainty Principle . We have already looked at physical examples (single-aperture, Bohr microscope, etc.) that explicate or illustrate its physical meaning.

Note: Note that Δx and Δp in the Heisenberg Uncertainty Principle refer to standard deviations (σ's), strictly, these are defined by $\Delta x = \left\langle (x - \bar{x})^2 \right\rangle^{\frac{1}{2}}$, where

$$\langle x \rangle = \bar{x} \;=\; \int \psi^*(x)\; x\; \psi(x)\; dx \tag{11.36}$$

$$\Delta x \;=\; \left[\int \psi^*(x)\;\; (x - \bar{x})\;\; \psi(x)\; dx \right]^{\frac{1}{2}} \tag{11.37}$$

similarly for $\Delta[$. For Gaussian distributions these definitions correspond to σ ("half-width"). Quoting another author, "The specific value of the number on the right hand side is not [so] important." What is important is the Heisenberg Uncertainty Principle viewed as an order-of-magnitude relation, inequality. (reciprocally proportional quantities)

11.4 A Square-Normalized $f(x)$ Implies a Square-Normalized $g(k)$

There is a handy little theorem, called Parseval's Theorem by mathematicians, that shows this. It follows easily from the Fourier Transform Theorem as follows:

$$\int_{-\infty}^{+\infty} g(^*(k) g(g)\; dk = \int_{-\infty}^{+\infty} g^*(k) \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) \mathrm{e}^{-ikx}\; dx \right]\; dk \tag{11.38}$$

As physicists we cavalierly interchange orders of integrations, thus

$$\begin{aligned}\int_{-\infty}^{+\infty} g^*(k)g(k)\ dk &= \int_{-\infty}^{+\infty}\left[\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} g^*(k)\mathrm{e}^{-ikx}\ dk\right] f(x)\ dx \qquad (11.39)\\ &= \int_{-\infty}^{+\infty} f^*(x)f(x)\ dx \qquad (11.40)\end{aligned}$$

Thus, if $f(x)$ is square-normalized, so is $g(k)$. And vice-versa. Nice this Parseval's theorem!

11.5 Fourier Analysis of "Arbitrary" $f(x,t)$

The Fourier theorem says that "any" $f(x)$ can be synthesized as

$$f(x) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} g(k)\mathrm{e}^{ikx}\ dk \qquad (11.41)$$

with

$$g(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} f(x)\mathrm{e}^{-ikx}\ dk \qquad (11.42)$$

Suppose you have an arbitrary continuous square -normalizable function of two variables $f(x,t)$. Think of $f(x,t)$ as defining a different function $f(x)$ for each t. Then, for each t, the pair of equations above are

$$f(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} g(k,t)\mathrm{e}^{ikx}\ dk \qquad (11.43)$$

where

$$g(k,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} f(x,t)\mathrm{e}^{-ikx}\ dx \qquad (11.44)$$

The "catch" is that g is now different at each time t; there is no general rule relating $g(k,t)$ to $g(k,t=0)$. Thus, it is, for example, not true that "any" function of x and t can be written as superposition of plane waves – i.e., there exists no $g(k)$ such that generally

$$f(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} g(k)\mathrm{e}^{i(kx-\omega t)}\ dk$$

for ω some function of k.

In quantum mechanics there is, however, one class of very important exceptions to this warning: As we will see shortly (in the coming section) "General Solution to Schrödinger equation for a free particle"', for a free particle (**only**) in quantum mechanics, $g(k,t)$ is easily predictable from $g(k,t=0)$, which (as we'll see) allows a plane wave expansion for any free particle state function $\Psi_{\text{free}}(x,t)$. That simplifies things considerably for the case of a free particle.

11.6 Dirac Delta Function

We found that, if $\psi(x)$ is a square-integrable function i.e., $\int_{-\infty}^{+\infty} |\psi(x)|^2 \; dx < \infty$, then there exists a function $g(k)$ such that

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k) \mathrm{e}^{ikx} \; dk \tag{11.45}$$

where

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \psi(x) \mathrm{e}^{-ikx} \; dx \tag{11.46}$$

f and g are Fourier transforms of each other. By combining the two above equations, we can write

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{e}^{ikx} \left[\int_{-\infty}^{+\infty} f(x') \mathrm{e}^{-ikx'} \; dx' \right] \; dk \tag{11.47}$$

by changing the order of integration[1] this is

$$f(x) = \int_{-\infty}^{+\infty} f(x') \left[\frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{e}^{ik(x-x')} \; dk \right] \; dx' \tag{11.48}$$

for the quantity in brackets we use the notation

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{e}^{-k(x-x')} \; dk = \delta(x'-x) \tag{11.49}$$

Thus equation (11.48) becomes

$$f(x) = \int_{-\infty}^{+\infty} \delta(x'-x) f(x') \; dx' \tag{11.50}$$

---

[1] again, as physicists we cavalierly do this, more on this later

We see that the object $\delta(x' - x)$ is the Dirac delta function, since equation (11.50) ("sifting property") defines the delta function.

For graduate students[2]: There is "another" way to see that equation (11.49) is a representation of the Dirac delta function. Consider the function

$$g_b(x) = \begin{cases} \frac{1}{b} & \text{for } |x| < \frac{b}{2} \\ 0 & \text{for } |x| > \frac{b}{2} \end{cases} \tag{11.51}$$

fig 9

For this function $\int_{-\infty}^{+\infty} g_b(x)\ dx = 1$. If we take the limit of this as $b \to 0$, we get $\delta(x)$:

$$\delta(x) = \lim_{b \to 0} g_b(x) \tag{11.52}$$

To check that this reproduces equation (11.50), note that the for "any" arbitrary function $f(x)$,

$$\lim_{b \to 0} \int_{-\infty}^{+\infty} g_b(x) f(x)\ dx = \lim_{b \to 0} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{1}{b} f(x)\ dx = f(0) \tag{11.53}$$

where we take the limit after closing the integral, instead of (as we "should") before doing the integral. (That is we can be cavalier like this about interchanging the order of integrals and limits was "creatively intuited" by Paul Dirac in his famous 1930 book on quantum mechanics; it was finally proved logically rigorous by Laurent Schwartz in the late 1930's.)

Now consider the Fourier transform of $g_b(x)$:

$$\begin{aligned} g_b(k) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g_b(x) \mathrm{e}^{-ikx}\ dx \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{1}{b} \mathrm{e}^{-ikx}\ dx \\ &= \frac{1}{\sqrt{2\pi}} \frac{\sin\left(\frac{kb}{2}\right)}{\frac{kb}{2}} \end{aligned}$$

thus

$$lim_{b \to 0} g_b(k) = \frac{1}{\sqrt{2\pi}} \tag{11.54}$$

---

[2] and also for interested undergrads

Now, if we take the Fourier transform of $\lim_{b\to 0} g_b(k)$, we must get back $\lim_{b\to 0} g_b(x) = \delta(x)$. Doing this:

$$\delta(x) = \mathcal{F}\left[\lim_{b\to 0} g_b(k)\right] = \mathcal{F}\left[\frac{1}{\sqrt{2\pi}}\right] = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} \frac{1}{\sqrt{2\pi}} \mathrm{e}^{ikx}\, dk \tag{11.55}$$

Which corroborates our previous result that

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{e}^{ikx}\, dk \tag{11.56}$$

similarly

$$\delta(x - x_0) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{e}^{ik(x-x_0)}\, dk \tag{11.57}$$

$$\delta(k - k_0) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{e}^{iu(k-k_0)}\, du \tag{11.58}$$

(end of section "for graduate students".)

11.7 The General Solution to Schrödinger's Equation for a Free Particle

As we know, all free-particle state functions must solve and obey the free particle Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{11.59}$$

In the past, we put together a fairly general solution of this as a superposition of plane waves,

$$\Psi(x,t) = \int_{k_1}^{k_2} A(k)\mathrm{e}^{i\left(kx - \frac{\hbar k^2}{2m}t\right)}\, dk \tag{11.60}$$

We now ask if all free-particle solutions are of this form, of if there are additional solutions. The following very nice treatment (from Ohanian[3]

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[3] Ohanian, Hans. **Principles of Quantum Mechanics. Benjamin Cummings**, 1989.

We will now find the general solution of the Schrödinger wave equation for a free particle. By Fourier's theorem, at one given time t, any normalizable wave function can be written as

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k,t) \mathrm{e}^{ikx} \, dk \tag{11.61}$$

We have indicated a time dependence in the Fourier transform $g(k,t)$, because although $\Psi(x,t)$ always can be expressed in the form given in the previous equation, the Fourier transforms at different times will be different. We call $g(k,t)$ the amplitude in momentum space. Next, we have to find $g(k,t)$. For this we substitute the above equation into the Schrödinger equation

$$-\frac{\hbar^2}{2m}\left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} -k^2 g(k,t) \mathrm{e}^{ikx} \, dk\right] = i\hbar \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} g(k,t) \mathrm{e}^{ikx} \, dk\right]$$

If we compare the Fourier transforms, or the coefficients of e^{ikx}, on both sides of this equation, we obtain

$$\frac{\hbar^2 k^2}{2m} g(k,t) = i\hbar \frac{\partial}{\partial t} g(k,t) \tag{11.62}$$

this has the obvious solution

$$g(k,t) = g(k,0)\mathrm{e}^{-\frac{i\hbar k^2 t}{2m}} \tag{11.63}$$

or

$$g(k,t) = g(k,0)\mathrm{e}^{-\frac{iEt}{\hbar}} \tag{11.64}$$

where

$$E = \frac{\hbar^2 k^2}{2m} \tag{11.65}$$

is the energy that corresponds to the momentum $p = \hbar k$. Equation (11-61) then becomes

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k,0) \mathrm{e}^{i\left(kx - \frac{\hbar k^2}{2m} t\right)} \, dk \tag{11.66}$$

This is the general solution of the Schrödinger's wave equation for a free particle. The amplitude $g(k,0)$ is arbitrary, but must satisfy the normalization condition

$$\int_{-\infty}^{+\infty} |g(k,0)|^2 \; dk = 1 \tag{11.67}$$

By Parseval's theorem, this will imply the correct normalization for $\Psi(x,t)$. Thus, according to equation (11.66), the general solution of the free particle Schrödinger equation is a (continuous) superposition harmonic waves. This means that the free-particle Schrödinger does not produce any solutions except those that can be directly constructed by superposition − the equation gives us nothing new.

If we chose the coefficients $g(k,0)$ in equation (11.66) correctly, we can construct a wave function Ψ that is nonzero only in some small region. Such a wave function is called a wave packet.

Chapter 12

Twelfth Class: Momentum Space

Thursday, October 2, 2008

12.1 Quantum Initial-Value Problem, Case of Free Particle

We showed that for a free particle (**only**) the most general state-function is (the most general solution to the free-particle Schrödinger equation)

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k,0) \mathrm{e}^{i\left(kx - \frac{\hbar k^2}{2m} t\right)} \, dk \tag{12.1}$$

where $g(k,0)$ is the Fourier transform of $\Psi(x,t=0)$. As we will illustrate by example shortly, this is clearly the formal solution to the free-particle initial value particle problem (find $\Psi(x,t)$ given $\Psi(x,t=0)$) in quantum mechanics. Prior to doing an example of this, we first note an interesting fact of it: Evaluating equation (12.1) at $t=0$ yields

$$\Psi(x,t=0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k,0) \mathrm{e}^{ikx} \, dk \tag{12.2}$$

But, by Fourier's theorem, any continuous square-normalizable function of x can be represented in this form with the proper $g(k,0)$. Therefore, we have now shown something we assumed in the past − that, for a free particle, $\Psi(x,t=0)$ can be (depending on the physical/experimential situation) any continuous square-normalizable function of x. (Of course, given $\Psi(x,t=0)$, $\Psi(x,t)$ is not arbitrary − it is controlled by the Schrödinger equation. Now we discuss examples of the initial value problem:

Example: Suppose $\Psi(x,t=0)=\cos(k_0x)$ and the represented particle is free. What is subsequent $\Psi(x,t)$?

Solution: Following our prescription, we Fourier analyze $\Psi(x,t=0)$ over the set $\left\{\mathrm{e}^{ikx}\right\}$. This Fourier analysis is

$$\cos(k_0x)=\frac{1}{2}\mathrm{e}^{ik_0x}+\frac{1}{2}\mathrm{e}^{-ik_0x} \tag{12.3}$$

Note: This also comes out of formal Fourier series: setting up

$$f(x)=\cos(k_0x)=\sum_{n=-\infty}^{+\infty}c_n\mathrm{e}^{ik_nx}$$

as you can show by evaluating, the integral expression for c_n, where $k_n=nk_0$. all $c_n=0$ except $c_1=c_{-1}=\frac{1}{2}$. You can also use the formal transform prescription $-$ if you evaluate

$$g(k)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\cos(k_0x)\mathrm{e}^{-ikx}\,dx$$

you will find

$$g(k)=\frac{1}{\sqrt{2\pi}}\left[\delta(k-k_0)+\delta(k+k_0)\right] \tag{12.4}$$

which implies plane wave contributions for $k=k_0$ and $k=-k_0$ only

Then

$$\begin{aligned}\Psi(x,t=0) &= \frac{\sqrt{2\pi}}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\frac{1}{2}\delta(k-k_0)\mathrm{e}^{ikx}\,dx+\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\frac{1}{2}\delta(k+k_0)\mathrm{e}^{ikx}\,dx\\ &= \frac{1}{2}\left[\mathrm{e}^{ik_0x}+\mathrm{e}^{-ik_0x}\right]\\ &= \cos(k_0x)\end{aligned}$$

so

$$\Psi(x,t)=\frac{1}{2}\left[\mathrm{e}^{i(k_0x-\omega_0t)}+\mathrm{e}^{-i(k_0+\omega_0t)}\right] \tag{12.5}$$

where $\omega_0=\frac{\hbar k_0^2}{2m}$, which of course, shows that $\Psi(x,t)\neq\cos(k_0x-\omega_0t)$.

Example: Free particle[1]

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[1] this is from Griffiths, worked example 2.6 pp 62-63

Suppose$\Psi(x, t=0)$ is a "flat-top function" of full-width $2a$ (perhaps result of measurement)

fig 1

Find $\Psi(x,t)$.

Solution: First, normalize: $A = \frac{1}{\sqrt{2a}}$. Then find $g(k,0)$:

$$g(k,0) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \int_{-a}^{a} \mathrm{e}^{-ikx} \, dx = \frac{1}{\sqrt{\pi a}} \frac{\sin(ka)}{k} = \sqrt{\frac{a}{\pi}} \operatorname{sinc}(ka) \tag{12.6}$$

then

$$\Psi(x,t) = \sqrt{\frac{a}{\pi}} \int_{-\infty}^{+\infty} \sin(ka) \mathrm{e}^{i\left(kx - \frac{\hbar k^2}{2m} t\right)} \, dk \tag{12.7}$$

The integral can be evaluated numerically, the result looks like we would expect

fig 2

Looking at limiting cases is instructive:

a) $\lim_{a\to 0} \Rightarrow \Psi(x, t=0)$ is a spike ($\Delta x \to 0$), $\Psi(x, t=0) = \delta(x - x_0)$ Then

$$\sin(ka) \approx ka$$

so

$$g(k) \approx \sqrt{\frac{a}{\pi}}$$

and this is flat ($\Delta k \to \infty$). Note that

$$\mathcal{F}\left[\delta(x - x_0)\right] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \delta(x - x_0) \mathrm{e}^{-ikx} \, dx = \mathrm{e}^{-ikx_0} \tag{12.8}$$

and this is flat.

b) $\lim_{a\to\infty}$, then

$$g(k,0) = \sqrt{\frac{a}{\pi}} \operatorname{sinc}(ka)$$

has max at $k = 0$, the first zero is at $ka = \pi \Rightarrow k_1 = \frac{\pi}{a} \to 0 \Rightarrow g(k,0) \propto \delta(k - k_0)$ ($\Delta x \to \infty$, $\Delta k \to 0$).

Example: In the past we had $\Psi(x, t=0) = A\mathrm{e}^{-ax^2}$, then I told you that $\Psi(x,t)$ was also a Gaussian, but with standard deviation, σ, that gets wider in time. (this is how I get it, (in fact, its Griffiths 2.22)).

12.1.1 State Function of Definite Momentum

A state of definite momentum $\hbar k_0$ must have $g(k,0) = A\delta(k - k_0)$ where A is a normalization we won't worry about. Let us see what this implies for a free particle,

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k,0) \mathrm{e}^{i\left(kx - \frac{\hbar k^2}{2m}t\right)}\, dk \tag{12.9}$$

$$\begin{aligned} \Psi(x,t) &= \frac{A}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \delta(k - k_0) \mathrm{e}^{i\left(kx - \frac{\hbar k^2}{2m}t\right)}\, dk && (12.10) \\ &= \frac{A}{\sqrt{2\pi}} \mathrm{e}^{i\left(k_0 x - \frac{\hbar k_0^2}{2m}t\right)} && (12.11) \end{aligned}$$

as we would expect. This shows the consistency of part of the theory.

12.1.2 State Function of Definite Position

This should be

$$\Psi(x, t = 0) = \delta(x - x_0) \tag{12.12}$$

(spike in position at x_0), again we don't yet worry about the normalization. Then

$$\begin{aligned} g(k) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \delta(x - x_0) \mathrm{e}^{-ikx}\, dx && (12.13) \\ &= \frac{A}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \delta(x - x_0) \mathrm{e}^{ikx}\, dx && (12.14) \\ &= \frac{A}{\sqrt{2\pi}} \mathrm{e}^{ikx_0} && (12.15) \end{aligned}$$

Therefore,

$$|g(k)|^2 = \frac{|A|^2}{2\pi} \tag{12.16}$$

this is flat in k, we we would expect by the bandwidth theorem. Futher, we should have

$$\begin{aligned}
A\delta(x-x_0) &= \Psi(x,t=0) \\
&= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} g(k,0)\mathrm{e}^{ikx}\ dk \\
&= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} \frac{A}{\sqrt{2\pi}}\mathrm{e}^{ik_0x}\mathrm{e}^{ikx}\ dk \\
&= \frac{A}{2\pi}\int_{-\infty}^{+\infty} \mathrm{e}^{i(-k_0)x}\ dk \\
&= A\delta(x-x_0)
\end{aligned}$$

since, as we showed in last class

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{e}^{i(k-k_0)x}\ dk = \delta(x-x_0) \tag{12.17}$$

12.2 Momentum-Space State Function – General Potential Energy Profiles

As mentioned in the last class, by Fourier's theorem, we can always Fourier analyze any state function (free-particle or not) at any time t as

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} g(k,t)\mathrm{e}^{ikx}\ dk \tag{12.18}$$

where

$$g(k,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} \Psi(x,t)\mathrm{e}^{-ikx}\ dx \tag{12.19}$$

Here, Parseval's theorem tells us that $g(k,t)$ is normalized at any time t if $\Psi(x,t)$ is normalized. $g^*(k,t)g(k,t)\ dk$ is not just proportional to, but is equal to the probability that, upon momentum producing measurement, the momentum will materialize in range $\hbar dk$ centered on $\hbar k$. We thus see that in our early work where we dealt with packets for a free particle of the form

$$\Psi(x,t) = \int A(k)\mathrm{e}^{i(kx-\omega t)}\ dk \tag{12.20}$$

that $|A(k)|^2$ is indeed proportional but not equal to it − we were merely missing the factor $\frac{1}{\sqrt{2\pi}}$ ($g(k) = \frac{1}{\sqrt{2\pi}}A(k)$ normalizes it).

now, in quantum mechanics, it is customary to recast equations (12.18) and (12.19) as integrals over a measurable quantity (momentum) rather then over k. If we do this, equations (12.18) and (12.19) are

$$\begin{aligned} \Psi(x,t) &= \frac{1}{\sqrt{2\pi}}\frac{1}{\hbar}\int_{-\infty}^{+\infty}(g\left[p(k),t\right]\mathrm{e}^{\frac{ip}{\hbar}x}\; dp \qquad (12.21)\\ g\left[p(k),t\right] &= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\Psi(x,t)\mathrm{e}^{-\frac{ip}{\hbar}x}\; dx \qquad (12.22) \end{aligned}$$

While correct, part of the symmetry is lost between equations (12.21) and (12.22) in this form. Therefore, it is conventional to rescale $g(k,t)$ by defining a function $\phi(p,t)$ as

$$\phi(p,t) \equiv \frac{1}{\sqrt{\hbar}}g(k,t) \qquad (12.23)$$

In terms of ϕ, we have then

$$\begin{aligned} \Psi(x,t) &= \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty}\phi(p,t)\mathrm{e}^{\frac{ip}{\hbar}x}\; dp \qquad (12.24)\\ \phi(p,t) &= \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty}\Psi(x,t)\mathrm{e}^{-\frac{ip}{\hbar}x}\; dx \qquad (12.25) \end{aligned}$$

which restores the symmetry. Since

$$\int_{-\infty}^{+\infty}|g(k,t=0)|^2\; dk = 1 \qquad (12.26)$$

it follows that

$$\int_{-\infty}^{+\infty}|\phi(p,t=0)|^2\; dp = 1 \qquad (12.27)$$

(show this) and also

$$\int_{-\infty}^{+\infty}|\phi(p,t)|^2\; dp = 1 \qquad (12.28)$$

Thus, $\phi^*(p,t)\phi(p,t)\; dp$ is the probability that the momentum will materialize in the range dp centered on p

The function $\phi(p,t)$ is called the "momentum-space state function" or "the state function in momentum-space". Since, by equation (12.24), we can reconstruct $\Psi(x,t)$ from knowledge of $\phi(p,t)$, $\phi(p,t)$ provides for any system, a description completely equivalent to that of Ψ. Thus, it is possible to completely do quantum mechanics in momentum space without ever mentioning Ψ. We do not pursue this in this course.

If a system is in state $\Psi(x,t)$ $[\phi(p,t)]$ and if a measurement is performed to produce momentum at time t, the probability that the momentum produced is in the infinitesimal interval dp centered on p is

$$P(p,t)\ dp = \phi^*(p,t)\phi(p,t)\ dp \tag{12.29}$$

We will take this as an axiom of quantum mechanics for the special case of free particle. We note that, since

$$\begin{aligned} \phi_{\text{free}}(p,t) &= \phi_{\text{free}}(p,0)\mathrm{e}^{-\frac{iE}{\hbar}t} & (12.30) \\ \phi^*_{\text{free}}(p,t)\phi_{\text{free}}(p,t) &= \phi^*_{\text{free}}(p,0)\phi_{\text{free}}(p,0) & (12.31) \end{aligned}$$

12.3 Expectation Value Revisited

Now, if the above interpretation of $\phi^*(p,t)\phi(p,t)$ is correct then we must be able calculate the expectation value of p from

$$\langle p\rangle = \int_{-\infty}^{+\infty} p\phi^*(p,t)\Psi(x,t)\ dp \tag{12.32}$$

Let us check this, say at $t=0$. Then if $\phi(p)\equiv\phi(p,t=0)$, we must have

$$\langle p\rangle_{t=0} = \int_{-\infty}^{+\infty} \phi^*(p)p\phi(p)\ dp \tag{12.33}$$

and likewise, for any analytic function of p, $s(p)$,

$$\langle s(p)\rangle = \int_{-\infty}^{+\infty} \phi^*(p)s(p)\phi(p)\ dp \tag{12.34}$$

where I've suppressed the $t=0$ subscript on $\langle\,\rangle$. Let us express equation (12.33) in terms of $\psi(x)\equiv\Psi(x,t=0)$. Using

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} \psi(x)\mathrm{e}^{-\frac{ip}{\hbar}x}\ dx \tag{12.35}$$

we have

$$\begin{aligned}
\langle p \rangle &= \int \left[\frac{1}{\sqrt{2\pi\hbar}} \int \psi(x) \mathrm{e}^{-\frac{ip}{\hbar}x}\ dx \right]^* p \left[\frac{1}{\sqrt{2\pi\hbar}} \int \psi(x') \mathrm{e}^{-\frac{ip}{\hbar}x'}\ dx' \right]\ dp \\
&= \frac{1}{2\pi\hbar} \int\int\int\ dx\ dx'\ dp\ \psi^*(x)\psi(x') p \mathrm{e}^{\frac{ip(x-x')}{\hbar}} \\
&= \frac{1}{2\pi\hbar} \int\int\int\ dx\ dp \psi^*(x)\psi(x') \left(-\frac{\hbar}{i}\frac{d}{dx'} \mathrm{e}^{\frac{ip(x-x')}{\hbar}} \right)\ dx'
\end{aligned}$$

integrating by parts on x' and using ψ, $\psi^* \to 0$ as $x \to \pm\infty$.

$$\begin{aligned}
\langle p \rangle &= \frac{1}{2\pi\hbar} \int\int\int\ dx\ dx'\ dp \psi^*(x) \mathrm{e}^{\frac{ip(x-x')}{\hbar}} \left(\frac{\hbar}{i}\frac{d}{dx'} \right) \psi(x') \\
&= \int\int\ dx\ dx' \psi^*(x) \delta(x-x') \left(\frac{\hbar}{i}\frac{d}{dx'} \right) \psi(x')
\end{aligned}$$

$$\langle p \rangle = \int_{-\infty}^{+\infty}\ dx \psi^*(x) \frac{\hbar}{i}\frac{d}{dx}\psi(x) \tag{12.36}$$

Likewise, as you can show, if $f(p)$ is any polynomial in p,

$$\langle f(p) \rangle = \int_{-\infty}^{+\infty}\ dx \psi^*(x) f\left(\frac{\hbar}{i}\frac{d}{dx} \right) \psi(x) \tag{12.37}$$

That these are the same results that we obtained some time ago shows the consistency of momentum probability density interpretation of $|\phi(p)|^2$.

12.4 Reality of $\langle p \rangle$

Now, in the coordinate representation, we have

$$\langle p \rangle_t = \int_{-\infty}^{+\infty} \Psi^*(x,t) \frac{\hbar}{i}\frac{\partial}{\partial x} \Psi(x,t)\ dx \tag{12.38}$$

which explicitly contains $i \equiv \sqrt{-1}$. On the othr hand, since $\langle p \rangle$ is a measurement result, it had better be real! Let us check this explicitly. From equation (12.38),

$$\langle p \rangle^* = \int_{-\infty}^{+\infty} \Psi(x,t) \left(\frac{\hbar}{-i}\frac{\partial \Psi^*}{\partial x} \right)\ dx \tag{12.39}$$

By integrating by parts,

$$\begin{aligned}
\langle p\rangle^* &= -\int_{-\infty}^{+\infty}\left(\frac{\hbar}{-i}\right)\frac{\partial\Psi}{\partial x}\Psi^*\ dx - \frac{\hbar}{i}\left[\Psi^*\Psi\right]_{-\infty}^{+\infty} && (12.40)\\
&= \int_{-\infty}^{+\infty}\frac{\hbar}{i}\Psi^*\frac{\partial\Psi}{\partial x}\ dx && (12.41)\\
\langle p\rangle^* &= \langle p\rangle && (12.42)
\end{aligned}$$

So, in spite of the i in the operator, $\langle p\rangle$ is real as it must be.

12.5 Hermitian Operators

In fact, the expectation value of any operator that represents a physical quantity (position, momentum, energy, angular momentum, etc.) must, of course, be real. Operators that have real expectation values for any permissible state function are called Hermitian operators.

Theorem: Let $\hat{\Omega}$ be a Hermitian operator. Then, for any admissible state function This is also true for $\hat{H}$. Let $\hat{\Omega} = \hat{H}$ or $\hat{p}$ or any other operator such that

$$\int_{-\infty}^{+\infty}\Psi^*\hat{\Omega}\Psi\ dx = \int_{-\infty}^{+\infty}\left(\hat{\Omega}\Psi\right)^*\Psi\ dx \qquad (12.43)$$

Proof: If $\hat{\Omega}$ is Hermitian,

$$\begin{aligned}
\left\langle\hat{\Omega}\right\rangle &= \left\langle\hat{\Omega}\right\rangle^*\\
\int\Psi^*\hat{\Omega}\Psi &= \left(\int\Psi^*\hat{\Omega}\Psi\right)^*\\
&= \int\Psi\left(\hat{\Omega}\Psi\right)^*\ dx\\
&= \int_{-\infty}^{+\infty}\left(\hat{\Omega}\Psi\right)^*\Psi\ dx
\end{aligned}$$

Theorem: If $\hat{\Omega}$ is a Hermitian operator, and if $\Psi_1(x,t)$ and $\Psi_2(x,t)$ are any two admissible state functions, then

$$\int_{-\infty}^{+\infty}\Psi_1^*\hat{\Omega}\Psi_2\ dx = \int_{-\infty}^{+\infty}\left(\hat{\Omega}\Psi_1\right)^*\Psi_2\ dx \qquad (12.44)$$

Proof: We sketch the proof; you can carry out the details: Consider $\Psi(x,t) = \Psi_1 + c\Psi_2$ for arbitrary complex constant c. Then

$$\begin{aligned}\int (\Psi_1^* + c^*\Psi_2^*)\,\hat{\Omega}\,(\Psi_1 + c\Psi_2) \;&=\; \int \Psi_1^*\Omega\Psi_1 + c^*c\int \Psi_2^*\Omega\Psi_2 \\ &+\; c\int \Psi_1^*(\Omega\Psi_2) + c^*\int \Psi_2^*(\Omega\Psi_1)\end{aligned}$$

must be real. The The first two terms on the right we know are real by the last theorem; consequently, the sum of third and forth terms must also be real and hence equal to its complex conjugate:

$$c\int \Psi_1^*(\Omega\Psi_2) + c^*\int \Psi_2^*(\Omega\Psi_1) = c^*\int \Psi_1(\Omega^*\Psi_2^*) + c\int \Psi_2(\Omega^*\Psi_1^*)$$

Applying this equation twice, once for real $c =$ a real constant b and once for $c = ib$ and adding yields:

$$\int \Psi_1^*\Omega\Psi_2\;dx = \int (\Omega\Psi_1)^*\Psi_2\;dx \tag{12.45}$$

which is the same as before.

12.6 Normalization of Free-Particle Definite Momentum States

Consider the free-particle definite momentum state at time $t = 0$:

$$\psi_p(x) = A\mathrm{e}^{\frac{ip}{\hbar}x} \tag{12.46}$$

several different normalizations are used, depending on circumstances. Two of them are discussed briefly in the following sections

12.6.1 “Box Normalization”

In this normalization scheme, we simply normalize to (large) length L. (“The universe is finite”, “My lab is finite”, etc.). Then we simply require

$$
\begin{aligned}
\int_{-\frac{L}{2}}^{\frac{L}{2}} \psi^* \psi \; dx &= 1 && (12.47) \\
|A|^2 \int_{-\frac{L}{2}}^{\frac{L}{2}} 1 \; dx &= 1 && (12.48) \\
A &= \frac{1}{\sqrt{L}} && (12.49) \\
\Psi_p(x, t=0) &= \frac{1}{\sqrt{L}} \mathrm{e}^{\frac{ip}{\hbar}x} && (12.50)
\end{aligned}
$$

12.6.2 “Dirac Normalization” of Free-Particle Definite Momentum State

Although technically $\psi_p(x) = A\mathrm{e}^{\frac{ip}{\hbar}x}$ is not square integrable, consider the inner product

$$(\psi_{p'}(x), \psi_p(x)) \equiv \langle \psi_{p'}(x) | \, \psi_p(x) \rangle = \int_{-\infty}^{+\infty} \psi_{p'}(x) \psi_p(x) \; dx \qquad (12.51)$$

$$
\begin{aligned}
&= |A|^2 \int_{-\infty}^{+\infty} \mathrm{e}^{\frac{i(p-p')}{\hbar}x} \; dx && (12.52) \\
&= |A|^2 \cdot 2\pi\hbar \delta(p - p') && (12.53)
\end{aligned}
$$

We pick $A = \frac{1}{\sqrt{2\pi\hbar}}$, then

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} \mathrm{e}^{\frac{ip}{\hbar}x} \qquad (12.54)$$

Then, as you can easily show, the normalization of $\psi_p(x)$ is

$$\langle \psi_{p'} \, | \, \psi_p \rangle = \delta(p - p') \qquad (12.55)$$

this is the continuum analogy of the Kronecker delta-orthonormality and is called “Dirac Normalization”

12.7 Normalization of a State of Definite Position

Let $\psi_{x_0}(x)$ be a state function of definite position $x = x_1$. Then

$$\psi_{x_1}(x) = A\delta(x - x_1) \tag{12.56}$$

Then consider the inner product for states of spike at x_1 and x_2:

$$\begin{aligned}
\langle \psi_{x_1} \,|\, \psi_{x_2} \rangle &= \int_{-\infty}^{+\infty} \psi^*_{x_1}(x)\psi_{x_2}(x)\; dx \\
&= |A|^2 \int_{-\infty}^{+\infty} \delta(x - x_1)\delta(x - x_2)\; dx \\
&= |A|^2\, \delta(x_1 - x_2)
\end{aligned}$$

we pick $A = 1$ Then

$$\langle \psi_{x_1} \,|\, \psi_{x_2} \rangle = \delta(x_1 - x_2) \tag{12.57}$$

This is Dirac Normalization of a state of definite position. Note that the set of states of definite position is a complete set: For any $\psi(x)$

$$\psi(x) = \int_{-\infty}^{+\infty} c(x_0)\delta(x - x_0)\; dx_0 \tag{12.58}$$

where $c(x_0)$ is the expansion coefficient and $\delta(x - x_0)$ is the basis vector. Therefore, $\{\psi_{x_0}(x)\}$ is a complete set. That the last expansion is valid can be seen by working with the right hand side:

$$\psi(x) = \int_{-\infty}^{+\infty} c(x_0)\delta(x - x_0)\; dx \tag{12.59}$$

comparing this to the known truth

$$\psi(x) = \int_{-\infty}^{+\infty} \psi(x_0)\delta(x - x_0)\; dx_0 \tag{12.60}$$

shows that $c(x_0)$ exists and is equal to $\psi(x_0)$.

12.8 Completeness of Free-Particle Definite Momentum States

The set

$$\left\{ \psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} \mathrm{e}^{\frac{ip}{\hbar}x} \right\} \tag{12.61}$$

is also a complete set − as we know from Fourier's theorem, any state function $\psi(x)$ can be expanded as

$$\psi(x) = \int_{-\infty}^{+\infty} c(p)\Psi_p(x,t)\ dp \tag{12.62}$$

with coefficient

$$c(p) = \frac{1}{\sqrt{2\pi\hbar}}\phi(p) \tag{12.63}$$

the the completeness statement is just

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} \phi(p)\mathrm{e}^{\frac{ip}{\hbar}x}\ dp \tag{12.64}$$

with $\phi(p)$ is the expansion coefficient and $\mathrm{e}^{\frac{ip}{\hbar}x}$ is the basis function. And we know this to be true!

These expansions are analogous to those of an ordinary vector in 3-space.

$$\vec{A} = A_x\hat{\imath} + A_y\hat{\jmath} + A_z\hat{k} \tag{12.65}$$

The expansion coefficients are

$$\begin{aligned} A_x &= \vec{A}\cdot\hat{\imath} \\ A_y &= \vec{A}\cdot\hat{\jmath} \\ A_z &= \vec{A}\cdot\hat{k} \end{aligned}$$

and $\hat{\imath}$, $\hat{\jmath}$, and $\hat{k}$ are the basis vectors.

Chapter 13

Thirteenth Class

Tuesday, October 7, 2008 Exam 1

Chapter 14

Fourteenth Class:

Thursday, October 9, 2008 No Class

Chapter 15

Fifteenth Class: States of Definite Energy

Tuesday, October 14, 2008

15.1 Eigenstate Property

As we have seen, the Schrödinger equation is

$$\left[\frac{\hat{p}^2}{2m} + V(x,t)\right]\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{15.1}$$

The operator in the left, $\frac{\hat{p}^2}{2m} + V$, we call the "Hamiltonian", $(\hat{H})$ as it represents the total energy. Now, for any particular function $V(x,t)$, the Schrödinger equation has, in general, a large variety of solutions. How can we hope to be guided in identifying these solution? In the case of the free particle, we know that

1. Momentum is classically conserved ($\vec{F} = \frac{d\vec{p}}{dt}$, but $\vec{F} = 0$) and total energy is conserved
2. States of definite momentum are also states of definite energy − the plane waves states
3. The general solution of the Schrödinger equation is the general superposition of the definite energy and definite momentum states

However, if the particle is not free, the situation is quite different. For one, if the particle is not free($V(x,t) \neq$ constant in x and t), then momentum is not conserved (classically, $\frac{dp}{dt} = F = -\frac{\partial V}{\partial x}$, so $V = V(x) \Rightarrow \frac{dp}{dt} \neq 0$.) However, total energy still is conserved. This motivates us to see if we can identify or construct, from the maze of all solutions to the non-free Schrödinger equation, some general properties of solutions that represent definite energy.

As we will no show, the definite energy states obey the equation

$$\hat{H}\Psi_E(x,t) = E\Psi_E(x,t) \tag{15.2}$$

where E is the ("sharp" or definite) value of the energy associated with the state function $\Psi_E(x,t)$ that satisfies this equation. An equation in the general form

$$\hat{Q}\Psi_Q(x,t) = \mathcal{C}\Psi_Q(x,t) \tag{15.3}$$

where $\hat{Q}$ is any operator and where $\mathcal{C}$ is any constant (real or complex) is called an "eigenvalue equation" in the mathematical parlance. The constant C is called the "eigenvalue", and the states $\Psi_Q(x,t)$ are called the "eigenstates" (of operator Q). So, solutions to equation (15.2) are the eigenstates of the energy operator (Hamiltonian). In fact, we will show that a state function is sharp in energy **if and only if** it obeys equation (15.2).

To show that definite energy state function satisfy equation (15.2), we note that, for such a state, σ_E^2, the variance of the results of energy producing measurements, must be zero. Thus, if $\Psi_E(x,t)$ is sharp in energy,

$$\sigma_E^2 = \left\langle (E - \langle E\rangle)^2 \right\rangle = \int_{-\infty}^{+\infty} \Psi_E(x,t) \left[\hat{H} - \langle E\rangle\right]^2 \Psi_E(x,t)\; dx \tag{15.4}$$

Now, since $\hat{H}$ is a Hermitian operator and $\langle E\rangle$ is a constant, $\left(\hat{H} - \langle E\rangle\right)$ is also a Hermitian operator. Recall that if $\hat{Q}$ is a Hermitian operator, then

$$\langle Q\rangle^* = \langle Q\rangle \tag{15.5}$$

(reality of expectation value − required if the operator corresponds to a physical observable), which implies also that

$$\int_{-\infty}^{+\infty} \Psi(x,t) \left[\hat{Q}\Psi(x,t)\right]^*\; dx = \int_{-\infty}^{+\infty} \Psi^*(x,t)\hat{Q}\Psi(x,t)\; dx \tag{15.6}$$

for any valid state function $\Psi(x,t)$ (not just for eigenstates of $\hat{Q}$) and also

$$\int_{-\infty}^{+\infty} \Psi_1^*(x,t)\hat{Q}\Psi_2(x,t)\; dx = \int_{-\infty}^{+\infty} \left[\hat{Q}\Psi_1(x,t)\right]^* \Psi_2(x,t)\; dx \tag{15.7}$$

for **any pair** of valid quantum mechanical state functions $\Psi_1(x,t)$ and $\Psi_2(x,t)$. Thus, for the condition in equation (15.4) is,

$$0 = \int_{-\infty}^{+\infty} \Psi_E \left[\left(\hat{H} - \langle E \rangle \right) \left(\hat{H} - \langle E \rangle \right) \Psi_E \right] \, dx \tag{15.8}$$

where Ψ_E is like Ψ_1 is equation (15.7) and $\left(\hat{H} - \langle E \rangle \right) \Psi_E$ is like Ψ_2 is equation (15.7).

$$\begin{aligned} 0 &= \int_{-\infty}^{+\infty} \left[\left(\hat{H} - \langle E \rangle \right) \Psi_E \right]^* \left[\left(\hat{H} - \langle E \rangle \right) \Psi_E \right] \, dx && (15.9) \\ 0 &= \int_{-\infty}^{+\infty} \left| \left(\hat{H} - \langle E \rangle \right) \Psi_E \right|^2 \, dx && (15.10) \end{aligned}$$

Now, the integrand cannot be negative for any x, so the only way that the whole integral can vanish is if the integrand is zero for all x, which implies that

$$\left(\hat{H} - \langle E \rangle \right) \Psi_E = 0 \quad \Rightarrow \quad \hat{H} \Psi_E = \langle E \rangle \Psi_E \tag{15.11}$$

Since, for this state, $\langle E \rangle = E$ (sharp), we have established that if Ψ_E is a state of sharp E, then it satisfies the eigenvalue equation

$$\hat{H} \Psi_E(x,t) = E \Psi_E(x,t) \tag{15.12}$$

Now let us establish the converse, suppose that

$$\hat{H} \Psi(x,t) = \mathcal{C} \Psi(x,t) \tag{15.13}$$

where $\mathcal{C}$ is any constant. Consider then, $\langle E \rangle$ in such a state

$$\langle E \rangle = \int \Psi^* \hat{H} \Psi \, dx = \int \Psi^* \mathcal{C} \Psi \, dx = \mathcal{C} \int \Psi^* \Psi \, dx = \mathcal{C} \tag{15.14}$$

thus,

$$\mathcal{C} = \langle E \rangle \tag{15.15}$$

Consider, also the variance of measurements of the energy in such a state: Recall from chapter one of Griffith,

$$\sigma_E^2 = \sigma_{\hat{H}}^2 = \left\langle H^2 \right\rangle - \langle H \rangle^2 \tag{15.16}$$

Now,

$$\hat{H}^2\Psi = \hat{H}\hat{H}\Psi = \hat{H}\mathcal{C}\Psi = \mathcal{C}\hat{H}\Psi = \mathcal{C}\mathcal{C}\Psi = \mathcal{C}^2\Psi \tag{15.17}$$

Therefore

$$\left\langle E^2 \right\rangle = \int \Psi^* \hat{H}^2 \Psi \; dx = \mathcal{C}^2 \int \Psi^* \Psi \; dx = \mathcal{C}^2 \tag{15.18}$$

so

$$\sigma_E^2 = \left\langle E^2 \right\rangle - \left\langle E \right\rangle^2 = \mathcal{C}^2 - \mathcal{C}^2 = 0 \tag{15.19}$$

Thus, in such a state, the energy is sharp (variance zero) and $\mathcal{C} = E$.

So

$$\text{energy is sharp} \quad \Longleftrightarrow \quad \hat{H}\Psi_E(x,t) = E\Psi_E(x,t) \tag{15.20}$$

We see that Ψ obeys

$$\hat{H}\Psi_E(x,t) = E\Psi_E(x,t) \tag{15.21}$$

if and only if the energy is sharp. We note that the same sort of thing is true for momentum: $\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$ is the momentum operator. Then $\Psi(x,t)$ obeys the eigenvalue equation

$$\hat{p}\Psi(x,t) = p\Psi(x,t) \tag{15.22}$$

if and only if $\Psi(x,t)$ is a state of sharp momentum.

Proof:

> In our previous proofs for the operator $\hat{H}$, replace $\hat{H}$ by $\hat{p}$ and everything works analogously − in fact, the proof works for any Hermitian operator $\hat{Q}$. We will have more to say about this general property of Hermitian operators and their eigenstates later in the course. for now, except for the one example immediately following, we will worry about eigenstates of energy.

Example

For a free particle, the plane wave state

$$\Psi(x,t) = A\mathrm{e}^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)} \tag{15.23}$$

is an eigenstate of both the Hamiltonian ($\hat{H}$) and the momentum operator ($\hat{p}$): To see this, note

$$\hat{H}\left[A\mathrm{e}^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)}\right] - i\hbar\frac{\partial}{\partial t}\left[A\mathrm{e}^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)}\right] = i\hbar \cdot \frac{-i}{\hbar}E\Psi \tag{15.24}$$

or

$$\hat{H}\Psi = E\Psi \tag{15.25}$$

and

$$\hat{p}\left[A\mathrm{e}^{i\left(\frac{p}{\hbar}x-\frac{E}{\hbar}t\right)}\right] = \frac{\hbar}{i}\frac{\partial}{\partial x}\left[A\mathrm{e}^{i\left(\frac{p}{\hbar}x-\frac{E}{\hbar}t\right)}\right] = \frac{\hbar}{i}\cdot\frac{i}{\hbar}p\Psi \tag{15.26}$$

$$\hat{p}\Psi = p\Psi \tag{15.27}$$

It turns out that only for a free particle is an eigenstate of $\hat{H}$ also and eigenstate of $\hat{p}$.[1] We now return to our discussion of energy eigenstates.

15.2 Time Dependence of Energy Eigenstates

For eigenstates of energy

$$\hat{H}\Psi_E(x,t) = E\Psi_E(x,t) \tag{15.28}$$

which is

$$i\hbar\frac{\partial\Psi_E(x,t)}{\partial t} = E\Psi_E(x,t) \tag{15.29}$$

which is

$$\frac{\partial\Psi_E(x,t)}{\partial t} = -\frac{i}{\hbar}E\Psi_E(x,t) \tag{15.30}$$

or

$$\Psi_E(x,t) = f(x)\mathrm{e}^{-\frac{iEt}{\hbar}} \tag{15.31}$$

where $f(x)$ is a function of x only. **Notation**: We call $f(x)$, "$\psi(x)$". **Comment**: We see that $\psi(x) = \Psi(x, t = 0)$.

Terminology: $\psi(x)$ is called the eigenfunction (or more correctly, the **energy eigenfunction**) associated with $\Psi(x,t)$. We will see the reason for this terminology very soon. Thus,

$$\Psi_E(x,t) = \psi_E(x)\mathrm{e}^{-\frac{iEt}{\hbar}} \tag{15.32}$$

For Eigenstates only

---

[1] This makes sense in light of the fact that energy is conserved for a non-free particle, but momentum is not conserved. Thus, a state of definite energy for a non-free particle will have its momentum amplitude change in time.

15.3 Time Independent Schrödinger Equation

We now established an important property of the energy eigenfunctions, $\psi_E(x)$: Of course, $\Psi(x,t)$ must obey the Schrödinger equation

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) \tag{15.33}$$

thus, we can put equation (15.32) into the Schrödinger equation. We do this for the (most natural) case of $V(x)$ not depending on time. Then

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left[\psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}}\right] + V(x)\psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}} = i\hbar\left(-\frac{iE}{\hbar}\right)\psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}} \tag{15.34}$$

We can cancel the common exponential, then this is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{15.35}$$

This equation must be obeyed by the spatial factor $\psi(x)$ of an eigenstate of the Hamiltonian. It is called the **Time Independent Schrödinger Equation**

Here is another way of phrasing the same argument: Suppose that $\Psi_E(x,t)$ is an energy eigenstate and suppose that V depends on x but not on t. Then again

$$\hat{H}\Psi_E(x,t) = E\Psi_E(x,t) \tag{15.36}$$

Putting $\Psi(x,t) = \psi_e\mathrm{e}^{-\frac{iEt}{\hbar}}$ into this equation and canceling the $\mathrm{e}^{-\frac{iEt}{\hbar}}$ yields

$$\hat{H}\psi(x) = E\psi(x) \tag{15.37}$$

which is the time independent Schrödinger equation.

15.4 Energy Eigenstates are "Stationary States"

We now discuss an important general property of eigenstates, without reference to any particular example. First note that that for a general state $\Psi(x,t)$ that is not an eigenstate, the probability density at any point x generally depends on time and thus fluctuates:

$$P(x) = \Psi^*(x,t)\Psi(x,t) \tag{15.38}$$

depends on time, even though the integral

$$\int_{-\infty}^{+\infty} \Psi^*(x,t)\Psi(x,t)\ dx = 1 \tag{15.39}$$

does not depend on time.

However, for the eigenstates, $P(x)$ does not depend on time. (We say it is "stationary", hence eigenstates are also called "stationary states".)

Proof: If $\Psi(x,t)$ is an eigenstate, $\Psi(x,t) = \psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}}$ Thus,

$$\begin{aligned}
P(x) &= \Psi^*(x,t)\Psi(x,t) && (15.40)\\
&= \left(\psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}}\right)^* \left(\psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}}\right) && (15.41)\\
&= \psi^*(x)\mathrm{e}^{+\frac{iEt}{\hbar}}\psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}} && (15.42)\\
&= \psi^*(x)\psi(x)\mathrm{e}^{+\frac{iEt}{\hbar}}\mathrm{e}^{-\frac{iEt}{\hbar}} && (15.43)\\
&= \psi^*(x)\psi(x) && (15.44)
\end{aligned}$$

which clearly has not time dependence.

Thus, in a eigenstate, there can be no "left-right" motion of probability.

15.4.1 Normalization of $\psi(x)$

We already know that

$$\int_{-\infty}^{+\infty} \Psi^*(x,t)\Psi(x,t)\ dx = 1$$

If $\Psi(x,t)$ is an eigenstate of energy, the same logic we used above implies (as you can easily show) that

$$\int_{-\infty}^{+\infty} \psi^*(x)\psi(x)\ dx = 1 \tag{15.45}$$

is necessary; thus. the energy eigenfunctions obey the same normalization condition as does the state function.

15.5 A Possible Means to Further Solution? ("Separation of Variables")

We still only have certain solution (i.e. energy eigenstates) of the Schrödinger equation. We found that these solutions are factored in their space and time dependence − ie.

$$\Psi_E(x,t) = \psi_E(x)\mathrm{e}^{-\frac{iEt}{\hbar}} \tag{15.46}$$

Perhaps, there are other factorizable solutions,

$$\Psi(x,t) = f(x)g(t) \tag{15.47}$$

To find out, we put this equation into the Schrödinger equation an see what happens. It makes sense to try this separation of variables method, as it is a common mathematical technique for generating solutions of differential equation. Putting this equation into the Schrödinger equation yields

$$i\hbar\frac{dg(t)}{dt} = -\frac{\hbar}{2m}g(t)\frac{d^2f(x)}{dx^2} + V(x,t)f(x)g(t) \tag{15.48}$$

which is (divide through by $f(x)g(t)$

$$i\hbar\frac{1}{g(t)}\frac{dg(t)}{dt} = -\frac{\hbar^2}{2m}\frac{1}{f(x)}\frac{d^2f(x)}{dx^2} + V(x,t) \tag{15.49}$$

To make progress with this technique, we must again assume that V depends only on x and not on t. In that case, a very interesting thing happens − the left side of the equation depends only on t while the right side depends only on x. Thus, each side can only equal something that depends on neither x nor t − c constant − the same constant, so the equation can be split into two ordinary differential equations:

$$i\hbar\frac{1}{g(t)}\frac{dg(t)}{dt} = \mathcal{C} \tag{15.50}$$

and

$$-\frac{\hbar^2}{2m}\frac{d^2f(x)}{dx^2} + V(x)f(x) = \mathcal{C}f(x) \tag{15.51}$$

Now equation (15.51) is

$$\hat{H}f(x) = \mathcal{C}f(x) \tag{15.52}$$

Which we recognize as an energy eigenvalue equation; therefore, $\mathcal{C} = E$ and apparantly $f(x)$ is nothing but our energy eigenfunction $\psi(x)$ (or at least proportional to it). furthermore, the solution to equation (15.50) is

$$g(t) = g(t=0)\mathrm{e}^{-\frac{i\mathcal{C}t}{\hbar}} = g(t=0)\mathrm{e}^{-\frac{iEt}{\hbar}} \tag{15.53}$$

Now, $g(t = 0)$ is just a constant, so we may as well absorb it into $\psi(x)$ (which has to be normalized anyway). So, interestingly, we have found nothing new – **all time/space factorizable ("seperable") solutions to the Schrödinger equation are energy eigenstates**!

15.6 Spectrum of Eigenstates

In general, for a given Hamiltonian $\hat{H}$ (i.e. a given potential energy function $V(x)$), there are a number of eigenfunctions (solution to the time independent Schrödinger equation), say,

$$\psi_1(x), \psi_2(x), \psi_3(x), \cdots$$

In general, each of these will be a solution of the time independent Schrödinger equation for a different value of the energy. Thus, we have a spectrum of allowed energies

$$E_1, E_2, E_3, \cdots$$

(A concrete example of this is for the infinite square well. We will discuss this and other examples much further soon.

This means that the eigenstate solutions of the full (original) Time Dependent Schrödinger Equation

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

are many – in general (depending on the specific form of $V(x)$)

$$\begin{aligned}
\Psi_1(x,t) &= \psi_1(x) \mathrm{e}^{-\frac{iE_1 t}{\hbar}} \\
\Psi_2(x,t) &= \psi_1(x) \mathrm{e}^{-\frac{iE_2 t}{\hbar}} \\
\Psi_3(x,t) &= \psi_1(x) \mathrm{e}^{-\frac{iE_3 t}{\hbar}} \\
&\vdots
\end{aligned}$$

Again, how many linearly independent eigenfunctions (and hence eigenstates) there are in a given situation onthe potential energy profile $V(x)$.

15.7 General Solution to the Schrödinger Equation

Now look again at the Schrödinger equation

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

It is linear (in Ψ) – remember – we designed it that way. This means that the sum of two solutions is also a solution: If $\Psi_1(x,t)$ and $\Psi_2(x,t)$ are solutions, then $\Psi_{sum}(x,t) = \Psi_1(x,t) + \Psi_2(x,t)$ is also a solution. This can be shown by direct substitution.

In fact, since the equation is linear, any linear combination

$$\Psi(x,t) = \mathcal{C}_1\Psi_1(x,t) + \mathcal{C}_2\Psi_2(x,t) + \mathcal{C}_3\Psi_3(x,t) + \cdots$$

is also a solution.

Thus, for a given $V(x)$ there are N eigenstates, a quite general solution of the time dependent Schrödinger equation for this potential is

$$\Psi(x,t) = \sum_{n=1}^{N} c_n\Psi_n(x,t) = \sum_{n=1}^{N} c_n\psi_n \mathrm{e}^{-\frac{iE_nt}{\hbar}} \tag{15.54}$$

This is really "quite general" because for every time we change at least one of the c_b's. we get a different solution. Generally, $N = \infty$, and in fact, we assert (without proof for now) that **the most general solution to the time dependent Schrödinger equation is**

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\psi_n \mathrm{e}^{-\frac{-iE_nt}{\hbar}} \tag{15.55}$$

Thus, if you find all the eigenfunctions of the time independent Schrödinger equation, you have completely solved the time dependent Schrödinger equation!

Unfortunately, we only know how to do that analytically for a relatively very few cases!

The reader who has familiarity with wave physics will note the strong analogy to classical normal mode theory – the energy eigenstates are really the normal modes of the Schrödinger equation and the time independent

Schrödinger equation is nothing but its Helmholtz equation. one difference is that the mode time dependence in quantum mechanics is $\mathrm{e}^{-i\omega t}$ $\left(\omega \equiv \frac{E}{\hbar}\right)$ and not $\cos(\omega t)$ as in classical wave physics. Another difference, of course, is the probability interpretation of the quantum mechanical state functions.

15.7.1 Completeness

Let us look at the assertion of equation (15.55) in "another" way. If any valid state function $\Psi(x,t)$[2] can be written in the "eigenstate expansion form", (equation (15.55)), then at $t = 0$, any valid state function can be expressed as

$$\Psi(x, t=0) = \sum_{n=1}^{\infty} c_n \psi_n(x) \tag{15.56}$$

Thus, in principle, one way of solving the initial value problem for a non-free particle is the following: Given $\Psi(x, t = 0)$, solve the time independent Schrödinger equation for the relevant $V(x)$ − i.e, find all the eigenfunctions $\{\psi_i(x)\}$, then expand $\Psi(x, t = 0)$ over these eigenfunctions as in equation (15.56); then tack a factor $\mathrm{e}^{-\frac{iE_i t}{\hbar}}$ to each $\psi_i(x)$ and the result is the expansion in equation (15.55). Both equation (15.55) and (15.56) then, are statements of completeness. It may seem miraculous that one can always find the set $\{c_n\}$ for any $f(x) = \Psi(x, t = 0)$, but this completeness property can be proven[3] from the theory of "Storm-Liouville" equations.

15.8 A Concrete Example: The Infinite Square Well Revisited – Eigenfunctions

Fig 1

Here $V(x) = \infty$ unless $0 \le x \le L$, in which case $V(x) =$ constant (which we will take to be zero). You already found the eigenstates for this problem by combining traveling wave solutions of the time dependent Schrödinger equation; here we look at this through the time independent Schrödinger equation formalism. Outside the well (and at its boundaries $x = 0$ and $x = L$) clearly $\psi(x) = 0$, otherwise there would be considerable probability

---

[2] For a particular potential energy profile $V(x)$, of course.

[3] We won't do this, we'll just use the result. More on this next class.

for the particle to materialize at "±∞", which is not valid. inside the well, the time independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{15.57}$$

(since $V = 0$) or

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) \tag{15.58}$$

This is exactly the equation for harmonic oscillation in space, so

$$\psi(x) = \mathcal{C}\cos\left(\sqrt{\frac{2mE}{\hbar^2}}x + \phi\right) \tag{15.59}$$

where ϕ is a phase angle and where $\mathcal{C}$ is a constant. We rewrite this in the more convenient form

$$\psi(x) = A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}\right) + B\cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) \tag{15.60}$$

Applying the boundary condition $\psi(x = 0) = 0 \Rightarrow B = 0$ (why?) so

$$\psi(x) = A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) \tag{15.61}$$

Applying the boundary condition $\psi(x = L) = 0$, yields

$$\sqrt{\frac{2mE}{\hbar^2}} = n\pi, \quad n = 1, 2, 3, \cdots \tag{15.62}$$

(Why not $n = 0$?) Then

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{15.63}$$

The eigenstate of the infinite square well have the same shapes as those of the string, but their amplitude is fixed.

Fig 2

We see that the application of the boundary conditions has led to quantization of energy – only certain values of energy are allowed. (Of course, we reached the same conclusion in the past when we "solved" this problem using the original Schrödinger equation). We note, in particular, that the energy cannot be zero. Let us try to get some insight into this. The Heisenberg Uncertainty Principle tells us tat, for any state function,

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \tag{15.64}$$

Consider now the lowest energy state or "ground state". For it

$$\Delta x \approx L \tag{15.65}$$

Thus

$$\Delta p_x / ge \frac{\hbar}{2L} \tag{15.66}$$

But, inside the well $E = \frac{p^2}{2m}$ then, if $E = 0$, then p is definitely zero. But, if p is sharp at zero, then $\Delta p = 0$, in violation of the Heisenberg Uncertainty Principle . Hence, E cannot be sharp at value zero. The minimum energy,

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2} \tag{15.67}$$

is called the "zero-point" energy. In general, the ground state for any bound system has a zero-point energy that is not zero. As you can show, the normalization condition requires that, unlike the classical case of standing waves on a stretched string, the amplitude is not arbitrary; rather

$$A\sqrt{\frac{2}{L}} \tag{15.68}$$

Thus

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \tag{15.69}$$

Hence

$$\Psi_n(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \mathrm{e}^{-\frac{iE_n t}{\hbar^2}} \tag{15.70}$$

or

$$\Psi_n(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \mathrm{e}^{-i\frac{n^2\pi^2\hbar}{2mL^2}t} \tag{15.71}$$

inside the well. Now, the time dependent (i.e. "original") Schrödinger equation is linear, hence a more general solution of it for the infinite square well is, as we already mentioned some time ago,

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \mathrm{e}^{-i\frac{n^2\pi^2\hbar}{2mL^2}t} \tag{15.72}$$

if $0 \leq x \leq L$ and zero otherwise and c_n is an arbitrary complex constant.

Chapter 16

Sixteenth Class: Examples and Orthogonality

Thursday, October 16, 2008[1]

16.1 A Concrete Example of the Formalism: Infinite Square Well Revisited

Recall that definite energy state function can be written in factorized form as

$$\Psi_E(x,t) = \psi(x)\mathrm{e}^{-\frac{iEt}{\hbar}} \tag{16.1}$$

where $\psi(x)$, the (energy) eigenfunction, obeys the time independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{16.2}$$

if V is a function only of x (and not of t). The simplest example to try the formalism out on is the infinite square well $-$ recall that, for it $V(x) = \infty$ unless $0 \leq x \leq L$, in which case $V(x) =$ a constant (which for convenience we take to be zero).Working from the time dependent Schrödinger equation, we started with the assumption that the general definite energy state function inside the well is

$$\Psi(x,t) = A\mathrm{e}^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)} + B\mathrm{e}^{-i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)} \tag{16.3}$$

---

[1] This includes the "make-up" of the missed 14th class

In the eigenfunction approach, we start with the time independent Schrödinger equation. Inside the well, the time independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{16.4}$$

(since V=0) or

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) \tag{16.5}$$

This is exactly the equation for the harmonic oscillation in space, so

$$\psi(x) = \mathcal{C}\cos\left(\sqrt{\frac{2mE}{\hbar^2}}x + \phi\right) \tag{16.6}$$

where ϕ is a phase angle and where $\mathcal{C}$ is a constant. We rewrite this in the more convenient form

$$\psi(x) = \mathcal{A}\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) + \mathcal{B}\cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) \tag{16.7}$$

Note that, a priorí[2], $\psi(x)$ could be complex, and a priorí, $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ can all be complex. Note also that an alternative, and (as you can easily show) completely equivalent way to write the general solution to this free time independent Schrödinger equation is

$$\psi(x) = \mathcal{D}\mathrm{e}^{i\left(\frac{\sqrt{2mE}}{\hbar}x\right)} + \mathcal{F}\mathrm{e}^{-i\left(\frac{\sqrt{2mE}}{\hbar}x\right)} \tag{16.8}$$

for convenience, we will work with equation (16.7). Applying the boundary condition, $\psi(x=0)=0$, $\mathcal{B}=0$ (why?), so

$$\psi(x) = \mathcal{A}\sin\left(\frac{\sqrt{2mE}}{\hbar^2}x\right) \tag{16.9}$$

Applying the boundary condition $\psi(x=L)=0$, yields

$$\sqrt{\frac{2mE}{\hbar^2}}L = n\pi, \quad n = 1, 2, 3, \cdots \tag{16.10}$$

---

[2] without proof for now

(why not $n = 0$?) Solving for E, we obtain

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{16.11}$$

Thus, the energy eigenstates are

$$\psi_n(x,t) = \mathcal{A}_n \sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) \mathrm{e}^{-\frac{in^2\pi^2\hbar}{2mL^2}t} \tag{16.12}$$

where the normalization condition determine $\mathcal{A}_n$ to be $\sqrt{\frac{2}{L}}$ for all n. Figure 1 remind us of the shapes of the eigenfunctions and the associated probability density profiles; since the states are stationary, the probability density doesn't change in time. So,

$$\Psi_n(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \mathrm{e}^{-\frac{in^2\pi^2\hbar}{2mL^2}t} \tag{16.13}$$

fig 1

The analogous classical system is that of the stretched string which is bound down at both its ends ($x = 0, L$). The energy eigenstates here (normal modes of the Schrödinger equation) are almost exactly mathematically analogous to the normal modes of the classical string – the "only" mathematical differences are the mode amplitudes (fixed at $\sqrt{\frac{2}{L}}$ in quantum mechanics by probability normalization, arbitrary in the classical stretched string normal modes) and the time dependences ($\cos(\omega_n t + \phi_n)$) in the classical case, which means that $\Psi_n = 0$ for all x at certain times in the classical case (at those times the energy is all kinetic) and $\mathrm{e}^{i\omega_n t}$ i nthe quantum case, which prevents this from ever happening since it is never zero (as it must – otherwise conservation of total probability would be violated). That the mode amplitudes A_n are arbitrary in the classical case is a reflection that a given mode can possess arbitrary energy; in the quantum case, the amplitude is fixed and the energy in the mode is independent of it and is quantized since it is proportional to the quantized frequency. In the quantum case, the fixed amplitude of each node fixes the associated probability density profile.

16.2 The "Reason" for Energy Quantization

We see that the application of the boundary conditions has led to quantization of energy – only certain values of energy are allowed. (Of course, we reached the same conclusion in the past when we "solved" this problem using the original Schrödinger equation). It is easy to see the essence of the mathematical reason for the energy quantization – the Schrödinger time independent equation, being a second order ordinary differential equation, had two arbitrary constants in its general solution: "A" and "B" in

$$\psi(x) = \mathcal{A}\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) + \mathcal{B}\cos\left(\frac{\sqrt{2mE}}{\hbar}x\right) \tag{16.14}$$

But, there are **three** conditions to impose:

1. Boundary Condition I
$$\psi(x=0) = 0 \quad \Rightarrow \quad \mathcal{B} = 0$$
2. Overall normalization
$$A = \sqrt{\frac{2}{L}}$$
3. Boundary Condition II
$$\psi(x=L) = 0$$

To satisfy condition 3), E must be considered as "adjustable" to the condition – and hence, no longer arbitrary – thus, only certain values of E work. It should be plausible to you (we'll investigate the reasons more deeply later) that this same sort of thing occurs for an arbitrary potential – of course, the Schrödinger equation is different for each $V(x)$, but generally there are two linearly independent solutions (hence two adjustable constants) and three conditions,

1. $\psi(x) \to 0$ as $x \to +\infty$ (or some other point)
2. $\psi(x) \to 0$ as $x \to -\infty$ (or some other point)
3. $\int_{-\infty}^{+\infty} \psi^*(x)\psi(x)\, dx = 1$

Thus, it should be plausible to you at this stage that, in general, for a "bound state" scenario ($V(x) < 0$ in a region where, by convention, $V(x) \to 0$ as $x \to \pm\infty$) there are solutions to the time independent Schrödinger equation(i.e. eigenstates exist) only for certain values of the energy − the figure 2 schematically shows an example of this

fig 2

In order to try to get some preliminary insight into this, let's discuss the general situation just briefly now. Consider a general potential energy profile that would lead to bound states. (The phrase "bound state" means that the particle is permanently essentially[3] confined to a localized region of finite extent.)

fig 3

In figure 3, $V(x)$ is plotted and a possible energy value (E) on the same plot. First, let us review what would happen classically to a particle with the shown energy E moving in this potential energy profile. Whenever the potential energy changes with position there is a force given by the negative of its slope

$$F(x) = -\frac{dV(x)}{dx} \tag{16.15}$$

Thus, whenever the potential energy on the curve is becoming shallower, the particle is pushed back to the region of lower $V(x)$. Thus, the acceleration is greatest where the slope of $V(x)$ is greatest in magnitude. From the energy point of view, since $KE = E - V(x)$, the greater the difference $E - V$, the greater the kinetic energy. Thus, the points x_a and x_b, where the particle has zero kinetic energy, are classical turning points − approaching them, the particle slows, stops and turns around. Thus, classically, the particle oscillates between x_a and x_b and remains absolutely confined between these positions. Thus, in regions I and III in figure 3 are classically forbidden (in them $KE < 0$, which classically is nonsense) while region II is classically allowed. In quantum mechanics, the situation is somewhat different. The time independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{16.16}$$

---

[3] the reason for the qualifying "essentially" will become apparent shortly and clear later

must be obeyed in all regions, and hence, acceptable state functions subject to certain conditions[4].

1. $\psi(x)$ must everywhere be single-valued
2. $\psi(x)$ must everywhere be continuous
3. $\frac{d\psi(x)}{dx}$ must be single-valued everywhere
4. $\frac{d\psi(x)}{dx}$ must be continuous everywhere

The reason for condition (1) is that there must be a well defined probability density $\psi^*(x)\psi(x)$ at all x. The reason for condition (4) can be easily seen by rewriting the time independent Schrödinger equationas

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2}\left[V(x) - E\right]\psi(x) \tag{16.17}$$

Thus, for any finite and continuous $V(x)$, $\psi''(x)$ must be defined and finite as long as $\psi(x)$ is. For $\psi''(x)$ to be defined and finite at all places, $\psi'(x)$ must be single-valued, finite, and continuous; this thus establishes conditions (3) and (4). For $\psi'(x)$ to be finite and defined everywhere, $\psi(x)$ must be continuous, thus establishing condition (2). Generally, nonzero solutions to the time independent Schrödinger equationexist in all three regions, and these must join smoothly to each other to make a solution valid for all x that accords with conditions (1) through (4).

Example: Consider the finite square well. We consider the possibility of a bound state with $E < V_0$

fig 4

In region II, the time independent Schrödinger equationis

$$\frac{d^2\psi(x)}{dx^2} = -\frac{\sqrt{2mE}}{\hbar}\psi(x) \tag{16.18}$$

and the solution is sinusoidal

$$\psi_{II})(x) = \mathcal{A}\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) + \mathcal{B}\cos\left(\frac{\sqrt{2mE}}{\hbar}x\right) \tag{16.19}$$

---

[4] in addition to the normalization conditions mentioned earlier

while in regions I and III, the time independent Schrödinger equationis

$$\frac{d^2\psi(x)}{dx^2} = \frac{\sqrt{2m\,(V_0 - E)}}{\hbar}\psi(x) \tag{16.20}$$

Since $V_0 > E$, the coefficient of $\psi(x)$ on the right hand side is a positive number, and thus the solution to this equation are exponential:

$$\psi_{I,III}(x) = \mathcal{D}\mathrm{e}^{+\kappa x} + \mathcal{F}\mathrm{e}^{-\kappa x} \tag{16.21}$$

where $\kappa = \frac{\sqrt{2m(v_0-E)}}{\hbar} > 0$. In region I, $\mathcal{F}$ must be zero; in region III, $\mathcal{D}$ must be zero; otherwise $\psi(x)$ blows up as $x \to \pm\infty$. Thus

$$\begin{aligned}
\psi_{\mathrm{I}}(x) &= \mathcal{D}\mathrm{e}^{+\kappa x} && (16.22)\\
\psi_{\mathrm{II}}(x) &= \mathcal{A}\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) + \mathcal{B}\cos\left(\frac{\sqrt{2mE}}{\hbar}x\right) && (16.23)\\
\psi_{\mathrm{III}}(x) &= \mathcal{F}\mathrm{e}^{-\kappa x} && (16.24)
\end{aligned}$$

We will discuss how to match pieces up to make one continuous $\psi(x)$ extending from $x = -\infty$ to $x = +\infty$, but for now, our main points are $\psi(x)$ is not zero in the classically forbidden regions I and III and that the matching-up can be done. Thus, for example, the ground state eigenfunction for the finite square well looks like

fig 5

We will discuss the physical implications of the penetration of $\psi(x)$ into the nonclassical region later. Now return to consideration of the "general" potential $V(x)$. From elementary calculus, $\frac{d^2\psi(x)}{dx^2}$ represents the curvature of $\psi(x)$. Where $\frac{d^2\psi(x)}{dx^2} > 0$, $\psi(x)$ is concave up, where $\frac{d^2\psi(x)}{dx^2} < 0$, $\psi(x)$ in concave down. Thus, according to the time independent Schrödinger equation

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar}\left[V(x) - E\right]\psi(x) \tag{16.25}$$

in a classically allowed region ($E > V$), $\psi''(x)$ has the opposite sign as does $\psi(x)$ and hence always curves $\psi(x)$ toward the $\psi(x) = 0$ axis, when in a classically forbidden region ($E < V$) $\psi''(x)$ has the same size as $\psi(x)$ and hence always curves away from the axis; these possibilities are shown in figure 6.

fig 6

thus, for example, for the finite square well, the concavities of the ground-state eigenfunction segments are as marked in figure 7

fig 7

How do we know that this represents the ground state? In the classically allowed region the curvature is

$$\frac{d^2\psi(x)}{dx^2} = -E\psi(x) \tag{16.26}$$

and its magnitude is least when E is least (taking $V = 0$ to be the bottom of the well). Other ways to do the matching of segments are shown in figure 8. Clearly the curve marked $\psi_1(x)$ has the lest magnitude of curvature and is hence the ground state. (The other curves are $\psi_2(x)$ with $E_2 > E_1$ and $\psi_3(x)$ with $E_3 > E_2 (> E_1)$.)

fig 8

Also, it should be clear from the above considerations that, for the $V(x)$ profile shown in figure 9. We know this must be at lest qualitatively correct in depicting the shape of the ground state

fig 9

Armed with these insights, we can now understand the reason for the quantization of energy for cases other than the infinite square well. Consider again then, the symmetric potential energy profile shown below and its ground state eigenfunction.

fig 10

Suppose we attempt to solve the time independent Schrödinger equationfor an energy E just slightly lower then E_{ground}. Then, according to our discussion above, the curvature of the solution in the classically allowed region $-x_1 \to x_1$ is shallower than it was for $E_{textrmground}$. Consequently, the new solution (labelled "$\psi(x)$" for $E_t < E_{\text{ground}}$in the figure, and which we call $\psi_t(x)$ (t for "trial")), which we assume has the same amplitude at $x = 0$ as did the ground state eigenfunction $\psi_1(x)$, arrives at the turning point xm, with a higher amplitude than does $\psi_1(x)$. Now in region III, ψ_1 must also be concave up, but, since according the time independent Schrödinger equation

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar}\left[V(x) - E\right]\psi(x) \tag{16.27}$$

the curvature magnitude, $\frac{d^2\psi(x)}{dx^2} \propto \psi(x)$ and $\propto [V(x) - E]$, the region III curvature magnitude is greater than that of $\psi_1(x)$ on two counts. Thus, as shown in figure 10, the new trial solution diverges as $x \rightarrow +\infty$, and, by symmetry, also as $x \rightarrow -\infty$. This is unacceptable behavior. Now, since $\frac{d^2\psi(x)}{dx^2} \propto \psi(x)$, we could curve the divergent behavior by simply rescaling $\psi(x)$ − i.e., reducing the amplitude everywhere by the same factor f. It should be apparent that there does exist an f such that, for the new $E < E_{\text{ground}}$, $\psi_{\text{rescaled}} = f\psi_t$ does go smoothly to zero as $x \rightarrow \pm\infty$. This is perfectly acceptable behavior, bur now there is a new problem − ψ_{rescaled} does not obey the probability normalization condition! By this logic it is apparent that no energy near E_{ground} other than $E_{textrmground}$ itself is possible. Question to thing about: What would have gone wrong if we had tried raising the energy a bit instead of lowering it? If you look back now at our original statement (some time ago)

> generally, there are two linearly independent solutions (hence two adjustable constants) and three condition
>
> 1. $\psi(x) \rightarrow 0$ as $x \rightarrow +\infty$ (or some other point)
> 2. $\psi(x) \rightarrow 0$ as $x \rightarrow -\infty$ (or some other point)
> 3. $\int_{-\infty}^{+\infty} \psi^*(x)\psi(x)\, dx = 1$
>
> Thus, it should be plausible to you$\cdots$

as an intuitive explanation for energy quantization, you will see that the more detailed “numerical integration” argument given above, while increasing of our insight, is essentially the same argument. The situation “from here on” is well described by another author[5]:

quote

Example: The potential energy profile shown below below has the spectrum of energies shown on the same plot − discretely spaced bound state energies and a continuum of possible energies for $E > 0$.

fig 11

---

[5] Robert Scherrer in **Quantum Mechanics: An Accessible Introduction**, pp 57-58

16.3 Zero-Point Energy

Now back to the infinite square well: We note, in particular, that the energy cannot be zero. Let us try to get some insight into this. the Heisenberg Uncertainty Principle tells us that, for any state function

$$\Delta x \Delta p \geq \frac{\hbar}{2} \tag{16.28}$$

Consider now the lowest energy of "ground" state. For it,

$$\Delta x \leq \frac{L}{\sqrt{12}} = \frac{L}{2\sqrt{3}}^{6} \tag{16.29}$$

thus

$$\Delta p \geq \frac{\sqrt{3}\hbar}{L} \tag{16.30}$$

But, inside the well $E = \frac{p^2}{2m}$ if $E = 0$, then p is definitely zero. but if p is sharp at zero, then $\Delta p = 0$, in violation of our limitation on Δp in equation (16.16). Hence E cannot be sharp at value zero. The minimum energy

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2} \tag{16.31}$$

is called the "zero-point" energy. In general, the ground state for any bound system has a zero-point energy that is not zero. We can, in fact, use the Heisenberg Uncertainty Principle to estimate the ground state energy for a particle in a box. We have, for the ground state

$$E = E_K = \overline{E_K} = \frac{\overline{p^2}}{2m} \tag{16.32}$$

where $\overline{E} \equiv \langle E \rangle$. Now, from its definition,

$$\Delta p = \sqrt{\overline{p^2} - \overline{p}^2} \tag{16.33}$$

$\overline{p}$ is zero,since it would be equally likely to be positive as negative (homogeneity of space inside the well $-$ $V = 0$ everywhere inside). Thus

$$\Delta p = \sqrt{\overline{p^2}} \tag{16.34}$$

---

[6] $\Delta x_{ground} = \frac{L}{2\sqrt{3}}$ if $\psi^* \psi_{ground}$ is flat inside the well, since it is peaked, we expect $\Delta x_{ground} < \frac{L}{2\sqrt{3}}$; in actuality it works out to be $\Delta x \approx 0.18L$. Here we are only "estimating."

or

$$\frac{\overline{p^2}}{2m} = E = \frac{(\Delta p)^2}{2m} \tag{16.35}$$

using $\Delta p \geq \frac{\hbar\sqrt{3}}{L}$,

$$E_{\text{ground}} \geq \frac{3\hbar^2}{2mL^2} \tag{16.36}$$

which compare favorably with the actual value

$$E_{\text{ground}} = \frac{\pi^2\hbar^2}{2mL^2} \tag{16.37}$$

If one want to turn the logic around and use the ground state as an illustration of the Heisenberg Uncertainty Principle , one finds, after calculation

$$\begin{aligned} \Delta x &= \sqrt{\overline{x^2} - \overline{x}^2} \approx 0.181L \\ \Delta p &= \sqrt{\overline{p^2} - \overline{p}^2} = \frac{\pi\hbar}{L} \end{aligned}$$

so

$$\Delta x \Delta p = (0.181L)\left(\frac{\pi\hbar}{L}\right) \approx 0.569\hbar \geq \frac{\hbar}{2}. \tag{16.38}$$

As we have already mentioned, the (time dependent) Schrödinger equation is linear and homogeneous, thus, an arbitrary linear combination of eigenstates is also a solution. In fact, as we already mentioned on more than one occasion, the general solution to the time dependent Schrödinger equation is an arbitrary linear combination of the eigenstates; hence the general solution for the infinite square well potential is

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \mathrm{e}^{-\frac{in^2\pi 62\hbar}{2mL^2}t} \tag{16.39}$$

for $0 \leq x \leq L$ and 0 otherwise and the c_n's are determined (at least in ration) by the overall normalization requirement.

16.4 Orthogonality and Completeness of Eigenfunctions

From our general solution to the infinite square well potential. we can see that

$$\Psi(x,t=0) = \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi}{L}x\right) \tag{16.40}$$

From the theory of Fourier series, we know that the Fourier series on the right-hand side can, with appropriate b_n's represent any square-normalizable function that vanishes at $x = 0$ and $x = L$. Hence, as in the free particle case, $\Psi(x, t = 0)$ can be any square-normaliable function obeying the boundary conditions. As well we will see, a similar statement is true for any reasonable $V(x)$. We can get a first idea of why the last sentence is true for the orthogonality principle of eigenfunctions corresponding to different eigenfunctions that we now demonstrate for "general" $V(x)$.

> Remember – the completeness of $\hat{\imath}$, $\hat{\jmath}$, $\hat{k}$ in ordinary 3-space partly depends on their orthonormality – using $\hat{e}_1 \equiv \hat{\imath}$, $\hat{e}_2 \equiv \hat{\jmath}$, and $\hat{e}_3 \equiv \hat{k}$,
>
> $$\hat{e}_m \cdot \hat{e}_n = \delta_{m,n} \equiv \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases} \tag{16.41}$$

As we will see in the Fourier case, a key to the completeness is the orthogonality property:

> **Theorem**: For any continuous $V(x)$, eigenfunctions of $\hat{H}$ belonging to different eigenvalues are orthogonal – i.e.
>
> $$\int_{-\infty}^{+\infty} \psi_m^*(x)\psi_n(x)\,dx = 0 \quad \text{if } m \neq n. \tag{16.42}$$

Proof: $\psi_n(x)$ and $\psi_m(x)$ are respectively solutions to the time independent Schrödinger equation.

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} + V(x)\psi_n(x) &= E_n\psi_n(x) \\ -\frac{\hbar^2}{2m}\frac{d^2\psi_m(x)}{dx^2} + V(x)\psi_m(x) &= E_m\psi_m(x) \end{aligned}$$

Taking the complex conjugate of the lower equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_m^*(x)}{dx^2}+V(x)\psi_m^*(x)=E_m\psi_m^*(x)$$

We then multiply the the top equation by $\psi_m(x)$ and the above equation by ψ_n, then subtract them from each other and integrate

$$\frac{2m}{\hbar}\left(E_m-E_n\right)\int_{-\infty}^{+\infty}\psi_m^*(x)\psi_n(x)\ dx=\int_{-\infty}^{+\infty}\left[\psi_m^*\frac{d^2\psi_n(x)}{dx^2}-\psi_n\frac{d^2\psi_m^*(x)}{dx^2}\right]\ dx$$

This is

$$\frac{2m}{\hbar}\left(E_m-E_n\right)\psi_m^*(x)\psi_n(x)\,dx=\int_{-\infty}^{+\infty}\frac{d}{dx}\left(\psi_m^*(x)\frac{d\psi_n(x)}{dx}-\psi_n(x)\frac{d\psi_m(x)}{dx}\right)\ dx$$

The right hand side is

$$\left[\psi_m^*(x)\frac{d\psi_n(x)}{dx}-\psi_n(x)\frac{d\psi_m^*(x)}{dx}\right]_{-\infty}^{+\infty}=0 \tag{16.43}$$

thus since $E_m \neq E_n$,

$$\int_{-\infty}^{+\infty}\psi_m^*(x)\psi_n(x)\ dx=0 \quad \text{when } m\neq n \tag{16.44}$$

If the ψ_n's are normalized, then they form an orthonormal set

$$\int_{-\infty}^{+\infty}\psi_m^*(x)\psi_n(x)\ dx=\delta_{m,n} \tag{16.45}$$

where $\delta_{m,n}=0$ for $m\neq n$ and $\delta_{m,n}=1$ for $m=n$. Based on this, we now state a postulate: **Postulate**: For any continuous potential energy function $V(x)$, the set of eigenfunctions is a complete set – i.e. any function $f(x)$ obeying the boundary conditions associated with $V(x)$ can be expanded as

$$f(x)=\sum_{n=1}^{N}c_n\psi_n(x) \tag{16.46}$$

This is known as the completeness postulate.

Example: As we already remarked, the infinite square well eigenfunctions are complete.

Example: Consider the case $V(x) = 0$ everywhere (free particle). Then the eigenfunctions of $\hat{H}$ are the set $\left\{ \mathrm{e}^{ikx} \right\}$.

Proof:

$$\hat{H}\mathrm{e}^{ikx} = \frac{\widehat{p^2}}{2m}\mathrm{e}^{ikx} = \frac{1}{2m}\left(\frac{\hbar}{i}\right)^2 \frac{d^2}{dx^2}\left(\mathrm{e}^{ikx}\right) = -\frac{k^2\hbar^2}{2m}\mathrm{e}^{ikx} \tag{16.47}$$

or

$$\hat{H}\mathrm{e}^{ikx} = E\mathrm{e}^{ikx}. \tag{16.48}$$

The completeness of these eigenfunctions is just the statement

$$f(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \phi(k)\mathrm{e}^{ikx}\, dk \tag{16.49}$$

which we know already to be true.

Comments

1. The completeness postulate stated here (for any V) can actually be proved ("Sturm-Liouville Theory" in differential equation).
2. The completeness postulate stated here is actually a special case of a more general completeness postulate concerning eigenfunctions of any Hermitian operator.

16.5 The Quantum Initial Value Problem – Particle Not Free

The above considerations relate to the quantum initial value problem: determining $\Psi(x, t)$ from $\Psi(x, t = 0)$ for general $V(x)$. Now, as you recall, we already discussed and solved[7] this problem for the case of a free particle. There, the key was to expand $\Psi(x, t = 0)$ over a complete set of basis functions (i.e. the set $\left\{ \mathrm{e}^{ikx} \right\}$) and then evolve each basis function forward in time – this works if the basis functions do evolve independently in time and if we know how they evolve. For the case of "general" $V(x)$, it is now clear that we can attempt to proceed analogously: we begin, with license from the completeness postulate, by expanding the given $\Psi(x, t = 0)$ over

---

[7] at least in principle

the complete set of eigenfunctions of $\hat{H}(V)$.

$$\Psi(x,t=0)=\sum_{n=1}^{\infty} c_n \psi_n(x) \tag{16.50}$$

But: **How can we determine the coefficients c_n?**

Here we use the orthonormality condition. We first multiply both sides of this equation by $\psi_m(x)$ and integrate:

$$\begin{aligned}\int_{-\infty}^{+\infty} \psi_m^*(x)\Psi(x,t=0)\; dx &= \sum_{n=1}^{\infty} c_n \int_{-\infty}^{+\infty} \psi_m^* \psi_n(x)\; dx & (16.51)\\ &= \sum_{n=1}^{\infty} n_n \delta_{m,n} = c_m & (16.52)\end{aligned}$$

i.e.

$$c_m = \int_{-\infty}^{+\infty} \psi_m^*(x)\Psi(x,t=0)\; dx \tag{16.53}$$

Note that or expansion for $\Psi(x,t=0)$ and its derivation are exactly analogous to how we find Fourier coefficients − that is nothing but a special case of this! Thus, in general (i.e. for any continuous $V(x)$), we have

$$\Psi(x,t)=\sum_{n=1}^{\infty}\left[\int_{-\infty}^{+\infty}\psi_n^*(x')\Psi(x',0)\; dx'\right]\psi_n(x)\mathrm{e}^{-\frac{iE_n t}{\hbar}} \tag{16.54}$$

This is the formal solution to our problem. Note how it explicitly show that knowledge of $\Psi(x,t=0)$ at all x determines $\Psi(x,t)$.

Example (Griffiths example 2.2, infinite square well):

Say $\Psi(x,t=0)=Ax(a-x)$ for $0 \le x \le a$ (where a is the extent of the well)

Fig 2

What is $\Psi(x,t)$ for subsequent time t?

Normalizing, you find

$$A=\sqrt{\frac{30}{a^5}} \tag{16.55}$$

From Fourier,

$$
\begin{aligned}
c_n &= \int_0^a \Psi(x,t=0)\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)\ dx && (16.56)\\
&= \sqrt{\frac{2}{a}}\sqrt{\frac{30}{a^5}}\int_0^a x(a-x)\sin\left(\frac{n\pi}{a}x\right)\ dx && (16.57)
\end{aligned}
$$

which works out to

$$c_n = \frac{4\sqrt{15}}{(n\pi)^3}\left[\cos(0)-\cos(n\pi)\right] \tag{16.58}$$

which is

$$c_n = \begin{cases} 0 & n \text{ is even} \\ \frac{8\sqrt{15}}{n^3\pi^3} & n \text{ is odd} \end{cases} \tag{16.59}$$

So

$$\Psi(x,t) = \sqrt{\frac{30}{a}}\left(\frac{2}{\pi}\right)^3 \sum_{n=1,3,5,\cdots} \frac{1}{n^3}\sin\left(\frac{n\pi}{a}x\right)\mathrm{e}^{-\frac{n^2\pi^2\hbar}{2ma^2}t} \tag{16.60}$$

16.6 Energy Measurement

Let us turn now to another important issue. Suppose that, for some potential energy function $V(x)$, the system is in some state $\Psi(x,t)$. Suppose the energy is measured. What values are possible and what are their probabilities?

Expectation Value

We start by calculating $\langle E\rangle$ for the general superposition state

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\psi_n(x)\mathrm{e}^{-\frac{iE_nt}{\hbar}} \tag{16.61}$$

We have

$$
\begin{aligned}
\langle E\rangle = \left\langle \hat{H}\right\rangle &= \int_{-\infty}^{+\infty} \Psi^*(x,t)\hat{H}\Psi(x,t)\ dx \\
&= \int_{-\infty}^{+\infty}\left[\sum_m c_m^*\psi_m^*(x)\mathrm{e}^{+\frac{iE_mt}{\hbar}}\right]\hat{H}\left[\sum_n c_n\psi_n(x)\mathrm{e}^{-\frac{iE_nt}{\hbar}}\right]\ dx
\end{aligned}
$$

which is

$$\langle E\rangle = \int_{-\infty}^{+\infty} \sum_m \sum_n c_m^* c_n \psi_m^* \mathrm{e}^{\frac{iE_m t}{\hbar}} \mathrm{e}^{-\frac{iE_n t}{\hbar}} \hat{H}\psi_n \; dx \tag{16.62}$$

Now $\hat{H}\psi_n = E_n\psi_n$, so

$$\begin{aligned} \langle E\rangle &= \sum_m \sum_n c_m^* c_n E_n \mathrm{e}^{\frac{i(E_m - E_n)t}{\hbar}} \int_{-\infty}^{+\infty} \psi_m^*(x)\psi_n(x) \; dx && (16.63)\\ &= \sum_m \sum_n c_m^* c_n E_n \mathrm{e}^{\frac{i(E_m - E_n)t}{\hbar}} \delta_{m,n} && (16.64)\\ \langle E\rangle &= \sum_n |c_n|^2 E_n && (16.65) \end{aligned}$$

This suggests that, if you measure the energy, $|c_n|^2$ is at least proportional to the probability of materializing result E_n[8]. In fact, we can find the probability constant by finding the sum

$$\sum_{n=1}^{\infty} |c_n|^2 \tag{16.66}$$

We know that

$$\int_{-\infty}^{+\infty} \Psi^*\Psi(x,t) \; dx = 1 \tag{16.67}$$

which is

$$\begin{aligned} 1 &= \int_{-\infty}^{+\infty} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* \psi_m^*(x) \mathrm{e}^{\frac{iE_m t}{\hbar}} c_n \psi_n(x) \mathrm{e}^{-\frac{iE_n t}{\hbar}} && (16.68)\\ &= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \mathrm{e}^{\frac{i(E_m - E_n)t}{\hbar}} \int_{-\infty}^{+\infty} \psi_m^*(x)\psi_n(x) \; dx && (16.69)\\ &= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \mathrm{e}^{\frac{i(E_m - E_n)t}{\hbar}} \delta_{m,n} && (16.70)\\ 1 &= \sum_{n=1}^{\infty} |c_n|^2 && (16.71) \end{aligned}$$

Thus, the probabilities are normalized; hence: **If a particle is represented by the state function $\Psi(x,t)$ then, if a measurement of energy of**

---

[8] Because we should have , in analogy to finding the average of any discrete distribution, $\langle E\rangle = \frac{\sum_n |c_n|^2 E_n}{\sum |c_n|^2}$.

energy is made, one and only one of the eigenvalues E_n (for the given potential) materializes.

The probability of obtaining the result E_n is $|c_n|^2 = c_n^* c_n$, where

$$\Psi(x,t) = \sum_n c_n \psi_n(x) \mathrm{e}^{-\frac{iE_n t}{\hbar}} \tag{16.72}$$

This is taken as a postulate; actually it is a special case of a more general postulate concerning probabilities of eigenvalues of Hermitian operator. On the other hand, a similar argument can be made for the eigenvalues of any Hermitian operator (time permitting, we'll do this later in the course). For the case of momentum, for example, it strongly suggests the conclusion that we already assumed, namely, that the probability of obtaining momentum in the range dp centered on p at time t is

$$\phi(p,t)dp = \phi^*(p,t)phi(p,t) \tag{16.73}$$

where

$$\phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Psi(x,t) \mathrm{e}^{-\frac{ipx}{\hbar}} \; dx \tag{16.74}$$

Chapter 17

Seventeenth Class: Connections With Classical Physics and Optics

Tuesday, October 21, 2008

17.1 The Connection with Everyday Physics

This is a good question that one should continually ask – what is the connection between the quantum mechanics we've learned and the everyday real world of large objects? After all, classical physics must result as some limit of quantum mechanics; otherwise quantum mechanics is wrong! This is an issue we will return to in stages. Let us begin to think about this in the context of our infinite square well example. The stationary states and their resulting stationary probability densities are shown in figure 1

fig 1

We know ask: What is the connection of this with the behavior we expect? Classically, we expect the particle to bounce back and forth between the walls, moving at constant speed (since $V = 0$ inside the well).

fig 2

But, the behavior we've found doesn't look anything like this at all! In our normal modes, nothing moves right or left – the probability to materialize in any small region is constant in time ("stationary states"). We can make some progress on this problem as follows: We have

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}}\sin(k_n x)\mathrm{e}^{-i\omega_n t} \tag{17.1}$$

where $\omega_n = \frac{E_n}{\hbar}$. Now,

$$\sin\theta = \frac{\mathrm{e}^{i\theta} - \mathrm{e}^{-i\theta}}{2i} \tag{17.2}$$

So,

$$\Psi_n(x,t) = \frac{1}{2i}\sqrt{\frac{2}{a}}\left[\mathrm{e}^{i(k_n x - \omega_n t)} - \mathrm{e}^{-i(k_n x - \omega_n t)}\right] \tag{17.3}$$

This is a combination to oppositely directed traveling waves. (In fact, starting with this form was our first approach.) While this is somewhat comforting, it is still true that the probability density for this state is stationary. What we would really like to see is a moving "lump" of probability.

fig 3

Let us look at this issue from another point of view, however, our state functions give us information on the probability of materializing the particle in any small region dx in the box $[\psi^*(x)\psi(x)]$. Classically, this probability is proportional to the time spent (by the bouncing back-and-forth) particle in dx, call this dt. Then

$$dt = \frac{dx}{v_{\text{particle}}} = \text{constant} \tag{17.4}$$

call it $\mathcal{C}'$. So

$$P_{\text{classical}}(x) \propto \mathcal{C}' \tag{17.5}$$

call this

$$P_{\text{classical}} = \mathcal{C} \tag{17.6}$$

Now

$$\int_0^a P_{\text{classical}}(x)\ dx = 1 \ \Rightarrow\ \mathcal{C}\int_0^a\ dx = 1 \ \Rightarrow\ \mathcal{C} = \frac{1}{a} \tag{17.7}$$

so

$$P_{\text{classical}} = \frac{1}{a} \tag{17.8}$$

Now, quantum and classical physics are supposed to agree in the large n limit. This is known as the "correspondence limit". Let us think on this:

Example: An electron confined to a thin metal wire segment

fig4

mimics a quantum "particle in a box". If the segment is of macroscopic length (say 1cm), and the system is at equilibrium at room temperature, we expect to have a "classical limit" (if one is possible for trapped electrons). Here is an interesting example on this:

fig5

Conclusion: In any classical-like situation, n is huge! Figure 6 shows the plot of $\psi^*(x)\psi(x)$ for $n = 10$

fig 6

For n larger, the peaks get closer together, and if n is large enough, we can't resolve them. So, as $n \to \infty$, we see an average "flat" $\psi^*(x)\psi(x)$:

$$\begin{aligned}\langle P(x)\rangle_{\text{ave}} &= (\psi^*(x)\psi(x)) = \left\langle \frac{2}{a}\sin^2(k_n x)\right\rangle \\ &= \frac{2}{a}\left\langle \sin^2(k_n x)\right\rangle = \frac{2}{a}\cdot\frac{1}{2} \\ &= \frac{1}{a}\end{aligned}$$

which agrees with the classical prediction. Still, this is not yet really satisfying – we would still like to see a "moving lump" of probability.

Again. "so far, so good", but we would like to see a "moving lump" of probability. Can we somehow obtain this? We know that we are allowed to have superposition (of normal mode) states. We now look into this. We know we really should do this in the classical limit (n large), but to keep things simple, we consider only an equal amplitude superposition of the two lowest states:

$$\Psi(x,t) = A\sin\left(\frac{\pi}{L}x\right)\mathrm{e}^{-i\omega_1 t} + A\sin\left(\frac{2\pi}{L}x\right)\mathrm{e}^{-i\omega_2 t} \tag{17.9}$$

This superposition is shown for $t = 0$ along with its $P(x)$ in figure 6.

fig 7

Now, $E_2 = 4E_1$ ($E_n \propto n^2$), so $\omega_2 = 4\omega_1$. Also

$$T_1 = \frac{2\pi}{\omega_1} = \frac{2\pi}{\frac{E_1}{\hbar}} = \frac{2\pi\hbar}{E_1} = \frac{h}{E_1}$$

Thus at $t = \frac{1}{2}T_1 = \frac{h}{2E_1}$, the relative signs of the two modes reverse, as shown in figure 8.

fig 8

We thus see that, even for this low-n superposition, we do have a "lump of probability density" sloshing back and forth.

fig 9

However, we expect to be able to construct something that moves back and forth at the classical particle velocity. For this, we need to put a narrow wave packet state in the well, and it has to be a narrow wave packet that is carefully chosen: How can we do this? The method (in outline) should be as follows:

1. We choose an appropriate $\Psi(x, t = 0)$
2. We calculate $\Psi(x, t)$ from $\Psi(x, t = 0)$ via our "propagation formula"

$$\Psi(x,t) = \sum_n \left[\int_{-\infty}^{+\infty} \psi_n^*(x')\Psi(x',0)\ dx' \right] \psi_n(x) \mathrm{e}^{-\frac{iE_n t}{\hbar}} \tag{17.10}$$

Here

$$\Psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) & 0 \le x \le a \\ 0 & \text{otherwise} \end{cases} \tag{17.11}$$

3. We plot $|\Psi(x,t)|^2$ at various times t.

While this is easy to say, there are a number of subtleties involved in actually carrying this out: What do we choose for $\Psi(x, t = 0)$? We have two main requirements for it:

1. We want $\Psi(x, t = 0)$ to be a peaked function that is narrow compared to the well width (a).

   fig 10

2. We want $\Psi(x, t = 0)$ to have only right-moving (i.e. positive) momentum components

Of course, $\Psi(x, t = 0)$ must obey the boundary conditions (vanish at $x = 0$ and $x = L$). Therefore, it cannot be just a simple Gaussian function, since that has infinite tails. Rather, it is usual to start with

$$\Psi(x, t = 0) = \sum_n c_n \psi_n(x) \tag{17.12}$$

and choose the c_n's first so as to satisfy our second condition. This involves a fairly complicated procedure that we do not describe here. The results of such a procedure for a moderately tight "packet" initial state are shown on the web at site `http://www.optics.rochester.edu/~stroud/animations/`, click on **Decay of High Momentum Wave Packet** under section "infinite square well wave packets". It is fascinating to contemplate that such classical limit behavior results from a superposition of eigenstates (correctly chosen, of course) none of which individually involves any left or rightward motion.

It is further profound that what causes "bouncing off the wall" in the classical limit is not anything "put in by hand", but rather just the time evolution of superpositions of eigenstates, each involving its own phase factor $e^{-\frac{iE_n}{\hbar}t}$, and obeying the boundary conditions. From this, much of our "classical experience" results!

17.2 State Functions for Incidence on Abrupt but Finite Changes in V

As you know, any really successful theory of quantum mechanics must deal with the effects of forces on state functions. So far, we have only investigated this in one case – that where the change in potential energy is infinitely abrupt and also infinite in magnitude – infintie square well. Of course, both of these conditions represent idealizations. Consider, for example, a neutron approaching an atomic nucleus in the atmosphere of the sun. The potential energy profile it experiences may look like

fig 11

where the "change" occurs over a distance of order $1fm = 10^{-15}m$ – very abrupt on a macroscopic scale, not so abrupt compared to the size of the neutron, but still abrupt compared to the neutron's DeBroglie wavelength if its energy is low enough. To get a first handle on these sort of important practical (for physics), we consider possible state functions for the case of abrupt, but finite, changes in V. The simplest case is that of a sudden step-like change in the potential energy profile in x:

fig 12

$$V(x) = \begin{cases} 0 & x < 0 \quad (\text{“region I”}) \\ V_0 & x \geq 0 \quad (\text{“region II”}) \end{cases} \tag{17.13}$$

Now, we would like to deal with the realistic situation of a narrow packet state incident on the step, say from negative-x. (You will deal with incidence from the right (“potential-cliff” problem) in the homework). Since the packet state, at any given time, is a superposition of energy eigenstates (recall the completeness postulates), we first consider only the energy eigenstates. We then have two cases, $E < V_0$ and $E > V_0$. We treat the first case first: $E < V_0$

In region I, the time independent Schrödinger equationis

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_{\mathrm{I}}(x)}{dx^2} = E\psi_{\mathrm{I}}(x) \tag{17.14}$$

since $V = 0$ in region I. This is

$$\frac{d^2\psi_{\mathrm{I}}(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi_{\mathrm{I}}(x) \tag{17.15}$$

which has the general solution

$$\psi_{\mathrm{I}}(x) = \mathcal{A}\mathrm{e}^{ik_1x} + \mathcal{B}\mathrm{e}^{-ik_1x} \tag{17.16}$$

where $k_1 = \frac{\sqrt{2mE}}{\hbar}$ (any E is allowed $-$ we see here explicitly also, this is note a bound state). Note: this is the same as

$$\psi_{\mathrm{I}}(x) = \mathcal{C}\cos(k_1x + \phi) \tag{17.17}$$

Thus, the traveling wave form of $\Psi(x,t)$ in region I is

$$\Psi_{\mathrm{I}}(x,t) = \mathcal{A}\mathrm{e}^{i(k_1x-\omega t)} + \mathcal{B}\mathrm{e}^{-i(k_1x+\omega t)} \tag{17.18}$$

where $\omega = \frac{E}{\hbar}$. We see what “physical situation” this corresponds to: we would like to say that this is the situation of a plane wave state “incident’ from negative-x” and undergoing a degree of “reflection” at $x = 0$[1]. In region II, the time independent Schrödinger equationis

$$-\frac{\hbar^2}{2m} = \frac{d^2\psi(x)}{dx^2} + V_0\psi(x) = E\psi(x) \tag{17.19}$$

---

[1] More strictly speaking, however, the temporal ordering of “reflection following incidence” occurs with a superposition-state traveling wave packet incident from the left, but as I say, first we’ll just deal with the eigenstates $-$ for them, the math is simpler.

which is

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2}\left(V_0 - E\right)\psi(x) \tag{17.20}$$

since $V_0 > E$, the general solution to this is

$$\psi_{\mathrm{II}} = \mathcal{C}\mathrm{e}^{\kappa_2 x} + \mathcal{D}\mathrm{e}^{-\kappa_2 x} \tag{17.21}$$

where $\kappa_2 = \frac{\sqrt{2m(V_0-E)}}{\hbar}$ Now consider the behavior of this as $x \to \infty$. The first term blows up, which is not possible for the resulting probability density. Hence, $\mathcal{C} = 0$. Thus

$$\psi_{\mathrm{II}} = \mathcal{D}\mathrm{e}^{-\kappa_2 x} \tag{17.22}$$

and

$$\Psi_{\mathrm{II}}(x,t) = \mathcal{D}\mathrm{e}^{-\kappa_2 x}\mathrm{e}^{-\frac{iEt}{\hbar}} \tag{17.23}$$

The issue now is how to join ψ_1 and ψ_2 at the boundary $x = 0$. For this, we call on the following general theorem:

Theorem: To be acceptable, any eigenfunction $\psi(x)$ must obey

1. $\psi(x)$ must be finite for all x
2. $\frac{d\psi(x)}{dx}$ must be finite for all x
3. $\psi(x)$ must be continuous
4. $\frac{d\psi(x)}{dx}$ must be continuous

Proof: for the time being, we offer the following simple “proof”. this proof actually has a loophole, and there is a case in which that loophole is realized, but we’ll worry about that later. If $\psi(x)$ and $\frac{d\psi(x)}{dx}$ were not finite and continuous everywhere, then

$$S(x,t) = -\frac{i\hbar}{2m}\left[\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x} - \Psi(x,t)\frac{\partial\Psi^*(x,t)}{\partial x}\right] \tag{17.24}$$

would not be continuous everywhere. but, a discontinuity in $S(x,t)$ would require a source of “sink” of probability, which, in this theory makes no sense. We now return to our step potential problem. We have

$$\psi(x) = \begin{cases} \mathcal{A}\mathrm{e}^{ik_1 x} + \mathcal{B}\mathrm{e}^{-ik_1 x} & x < 0 \\ \mathcal{D}\mathrm{e}^{-\kappa_2 x} & x > 0 \end{cases} \tag{17.25}$$

continuity of $\psi(x)$ across $x = 0$ requires

$$\mathcal{A} + \mathcal{B} = \mathcal{D} \tag{17.26}$$

continuity of $\frac{d\psi(x)}{dx}$ requires

$$-\kappa_2 \mathcal{D}\, \mathrm{e}^{-\kappa_2 x}\Big|_{x=0} = ik_1 \mathcal{A}\, \mathrm{e}^{ik_1 x}\Big|_{x=0} - ik_1 \mathcal{B}\, \mathrm{e}^{-ik_1 x}\Big|_{x=0} \tag{17.27}$$

or

$$\frac{i\kappa_2}{k_1}\mathcal{D} = \mathcal{A} - \mathcal{B} \tag{17.28}$$

Subtracting equations (17.26) and (17.28) yields

$$\begin{aligned}
\mathcal{A} &= \frac{\mathcal{D}}{2}\left(1 + \frac{i\kappa_2}{k_1}\right) \\
\mathcal{B} &= \frac{\mathcal{D}}{2}\left(1 - \frac{i\kappa_2}{k_1}\right) \\
\mathcal{B} &= \frac{k_1 - i\kappa_2}{k_1 + i\kappa_2}\mathcal{A} \\
\mathcal{D} &= \frac{2k_1}{k_1 + i\kappa_2}\mathcal{A}
\end{aligned}$$

we choose to use the last two equations and let $\mathcal{A}$ be set by normalization. Thus, the eigenfunction for energy is

$$\psi(x) = \begin{cases} \mathcal{A}\mathrm{e}^{ik_1 x} + \left(\frac{k_1 - i\kappa_2}{k_1 + i\kappa_2}\right)\mathcal{A}\mathrm{e}^{-ik_1 x} & x \leq 0 \\ \frac{2k_1}{k_1 + i\kappa_2}\mathcal{A}\mathrm{e}^{-\kappa_2 x} & x \geq 0 \end{cases} \tag{17.29}$$

Thus

$$\Psi_{\mathrm{E}}(x,t) = \begin{cases} \mathcal{A}\mathrm{e}^{i\left(\frac{\sqrt{2mE}}{\hbar}x - \frac{E}{\hbar}t\right)} + \left(\frac{k_1 - i\kappa_2}{k_1 + i\kappa_2}\right)\mathcal{A}\mathrm{e}^{-i\left(\frac{\sqrt{2mE}}{\hbar}x + \frac{E}{\hbar}r\right)} & x \leq 0 \\ \frac{2k_1}{k_1 + i\kappa_2}\mathcal{A}\mathrm{e}^{-\frac{\sqrt{2m(V_0 - E)}}{\hbar}x}\mathrm{e}^{-\frac{iEt}{\hbar}} & x \geq 0 \end{cases} \tag{17.30}$$

We see that if $\Psi(x,t)$ has a component which is incident from the left, there is necessarily a reflected wave. The leads us to expect that $\Psi(x,t)$ is a standing wave in region I. Indeed it is; as you can show, the eigenfunction ψ_{I} can be rewritten as

$$\psi_{\mathrm{I}}(x) = \mathcal{D}\cos(k_1 x) - \mathcal{D}\frac{\kappa_2}{k_1}\sin(k_1 x) \tag{17.31}$$

which is

$$\psi_{\rm I}(x) = \mathcal{E}\cos(k_1 x + \phi) \tag{17.32}$$

(find $\mathcal{E}$ and ϕ in terms of $\mathcal{D}$, k_1, and κ_2). Finally, we show a plot of the eigenfunction for the case $\mathcal{D}$ real

fig 13

17.3 Reflection and Transmission Coefficients

Let us calculate the ratio of "reflected" probability flux to incident probability flux. we will cal this the "reflection coefficient" ($\mathcal{R}$). Now,

$$S(x,t) = -\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right) \tag{17.33}$$

For a general plane wave

$$\mathrm{e}^{i\left(kx - \frac{E}{\hbar}t\right)} \tag{17.34}$$

as you can easily show,

$$S(x,t) = \frac{\hbar k}{m}\mathcal{A}^*\mathcal{A} = \frac{p}{m}\left|\mathcal{A}\right|^2 = v\left|\mathcal{A}\right|^2 \tag{17.35}$$

Thus, for our eigenfunction in the region $x < 0$,

$$S_{\rm I}(x,t) = v\mathcal{A}^*\mathcal{A} - v\mathcal{B}^*\mathcal{B} \tag{17.36}$$

where $v \equiv \frac{\hbar k_1}{m}$. Thus,

$$\mathcal{R} = \frac{v\mathcal{B}^*\mathcal{B}}{v\mathcal{A}^*\mathcal{A}} = \frac{\mathcal{B}^*\mathcal{B}}{\mathcal{A}^*\mathcal{A}} = \frac{(k_1 - i\kappa_2)^*(k_1 - i\kappa_2)}{(k_1 + i\kappa_2)^*(k_1 + i\kappa_2)} \tag{17.37}$$

which is

$$\mathcal{R} = 1 \tag{17.38}$$

This agrees with the classical prediction, since classically the incident particle definitely reflects.

17.4 Classically Forbidden Region

We notice something strange, there is a region of nonzero probability of the particle to materialize in the classically forbidden region $x > 0$ where $E < V$! How can this be?

Firstly, the probability of materializing in the forbidden region is "considerable" only in the range of x, Δx of order $\frac{1}{2\kappa_2}$ (since $\psi_{\mathrm{II}}(x) \propto \mathrm{e}^{-\kappa_2 x} \Rightarrow \psi_{\mathrm{II}}^* \psi_{\mathrm{II}} \approx \mathrm{e}^{-2\kappa_2 x}$). Thus,

$$\Delta x \approx \frac{1}{2\kappa_2} = \frac{\hbar}{2\sqrt{2m(V_0 - E)}} \tag{17.39}$$

In the classical limit, (often but not always), $m(V_0 - E) \ggg \hbar^2$, so at least in that limit, this effect goes away. Suppose, however, that the situation is not "in the classical limit". Suppose measurement does force the particle to materialize in the forbidden region. Then, **after the measurement, there is new state function** associated with the "particle" **and for this new state function**

$$\Delta x \leq \frac{\hbar}{2\sqrt{2m(V_0 - E)}} \tag{17.40}$$

This means that for the new state function

$$\Delta p / ge \frac{\hbar}{\Delta x} \geq \sqrt{2m(V_0 - E_{\text{original}})} \tag{17.41}$$

Thus, for the new state function

$$\Delta E_{new} \sim \frac{(\Delta p)^2}{2m} \approx V_0 - E_{\text{original}} \tag{17.42}$$

Thus, it is no longer possible to say with certainty that $E_{\text{new}} < V_0$. In this way, the paradox "disappears". Upon contemplation, examples like this show how thin the edge is on which the consistency of theory hangs together. But, the universe depends on it.

Chapter 18

Eighteenth Class: More on the Potential Step

Thursday, October 23, 2008

18.1 More on Free-Particle Packet Motion and Group Velocity

In order to prepare for a discussion of a wave packet incident from $x = -\infty$ on a step potential, we need first to fill in some detail previously glossed over about the motion of free particle wave packets. As a start, in particular, back toward the beginning of the course I claimed that a reasonably tight packet envelope moves at the group velocity $v_g = \frac{dw}{dk}\Big|_{k=k+0}$ (where k_0 is the "central" value of k in the mix), but really only demonstrated this for the case of two plane waves (rather than an infinite number of plane waves). Thus, we consider the case of the packet state

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k) \mathrm{e}^{i(kx-\omega t)} \tag{18.1}$$

where $g(k)$ is at least fairly sharply and symmetrically peaked around a central value $k = k_0$. Our remarks will hold true for any continuous dispersion relation $\omega = \omega(k)$, hence, they apply e.g., to water wave packets, electromagnetic wave packets, etc., as well as deBroglie wave packets. Since ω is a continuous function of k, we can expand it around $k = k_0$:

$$\omega(k) = \omega(k_0) + \left.\frac{d\omega}{dk}\right|_{k=k_0} (k-k_0) + \frac{1}{2} \left.\frac{d^2\omega}{dk^2}\right|_{k=k_0} (k-k_0)^2 + \cdots \tag{18.2}$$

For our first approximation, we ignore all but the first two terms of this expansion. This this is not unreasonable approximation is justified by the assumed sharpness of $g(k)$ around k_0. Putting this into equation (18.1) we have

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k) \mathrm{e}^{ikx} \mathrm{e}^{-i\omega_0 t} \mathrm{e}^{-i\omega_0'(k-k_0)t} \, dk \tag{18.3}$$

It is convenient to change variables from k to $s \equiv k - k_0$ in this integral

$$\Psi(x,t) = \frac{\mathrm{e}^{-i\omega_0 t}}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k_0+s) \mathrm{e}^{i(k_0+s)x} \mathrm{e}^{-i\omega_0' s t} \, ds \tag{18.4}$$

Multiplying by $1 = \mathrm{e}^{ik_0\omega_0' t}\mathrm{e}^{-ik_0\omega_0' t}$, and this is

$$\Psi(x,t) = \frac{\mathrm{e}^{-i(\omega_0 - k_0\omega_0')t}}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k_0+s) \mathrm{e}^{i(k_0+s)x} \mathrm{e}^{-i\omega_0'(k_0+s)t} \, ds \tag{18.5}$$

or

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \mathrm{e}^{-i(\omega_0 t + k_0\omega_0' t)} \int_{-\infty}^{+\infty} g(k_0+s) \mathrm{e}^{i(k_0+s)(x-\omega_0' t)} \, ds \tag{18.6}$$

which tells us that

$$\Psi(x, t=0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k_0+s) \mathrm{e}^{-(k_0+s)x} \, ds \tag{18.7}$$

comparing equations (18.6) and (18.7), we see that

$$\Psi(x,t) = \mathrm{e}^{-i(\omega_0 - k_0\omega_0')t} \Psi(x - \omega_0' t, 0) \tag{18.8}$$

except for an uninteresting phase factor that accumulates (and which cancels out in the probability density $\Psi^*\Psi$ anyway), $\Psi(x,t)$ is the same as $\Psi(x - \omega_0' t, 0)$). Thus, in the approximation in which we ignore the quadratic term in the expansion of $\omega(k)$ around $k = k_0$, the packet moves rigidly without changing shape at velocity

$$v_g = \omega_0' = \left.\frac{d\omega}{dk}\right|_{k=k_0} \tag{18.9}$$

The effect of the quadratic term is then the spreading of the packet while it moves. As shown in the homework (set 6G), the effects of the quadratic term are ignorable as long as

$$t \ll \frac{m\,(\Delta x)_0^2}{\hbar} \tag{18.10}$$

where $(\Delta x)_0$ is the spatial extent of the packet at $t = 0$. This is the "coherence time" for the packet.

Now we are ready to consider the case of a fairly tight packet incident on a potential step with mean energy less than the step height

18.2 Wave Packet Incident on a Potential Step, case $E < V_0$

[This section of mathematics is for graduate students]

Let us consider a tightly peaked packet incident on the step from negative x[1]

fig 1

We arrange things so that the center of the packet reaches the step at $t = 0$. We consider the case where all energy components are less than V_0. We write the eigenfunction in region I as

$$\psi_{\mathrm{I}} = \mathcal{A}\mathrm{e}^{ik_1 x} + \mathcal{B}\mathrm{e}^{-ik_1 x} \tag{18.11}$$

we have seen that

$$|\mathcal{A}| = |\mathcal{B}| \tag{18.12}$$

therefore,

$$\mathcal{B} = \mathrm{e}^{i\phi(k_1)}\mathcal{A} \tag{18.13}$$

for some $\phi(k_1)$. It will convenient to write this as

$$\mathcal{B}(k_1) = \mathrm{e}^{-2i\theta(k_1)}\mathcal{A}(k_1) \tag{18.14}$$

where $\theta \equiv -\frac{\phi}{2}$. We will see that the phase difference between $\mathcal{B}$ and $\mathcal{A}$ can (surprisingly to some people) have an observable effect. Using

$$\frac{\mathcal{B}}{\mathcal{A}} = \frac{k_1 - i\kappa_2}{k_1 + i\kappa_2}, \quad k_1 = \sqrt{\frac{2mE}{\hbar^2}}, \quad \kappa_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \tag{18.15}$$

and defining $K_0 = \sqrt{\frac{2mV_0}{\hbar^2}}$, a little algebra leads to

$$\tan\left(\theta(k)\right) = \frac{\sqrt{K_0^2 - k^2}}{k} \tag{18.16}$$

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[1] I am partly following here the treatment of **Quantum Mechanics, Volume I**, by Cohen-Tannovdji, David Laloe (see list of books in syllabus), pp. 79-85.

Now let's put together a superposition (of energy eigenstates) wave packet. At time $t = 0$, this can be expressed as

$$\Psi_{\mathrm{I}}(x, t=0) = \frac{1}{\sqrt{2\pi}} \int_0^{k=K_0} g(k) \left[\mathrm{e}^{ikx} + \mathrm{e}^{-2i\theta(k)} \mathrm{e}^{-ikx} \right] \, dk \tag{18.17}$$

$$\Psi_{\mathrm{I}}(x, t=0) = \frac{1}{\sqrt{2\pi}} \int_0^{K_0} g(k) \mathrm{e}^{ikx} \, dk + \frac{1}{\sqrt{2\pi}} \int_0^{K_0} g(k) \mathrm{e}^{-i[kx - 2\theta(k)]} \, dk \tag{18.18}$$

we choose $g(k)$ to have a narrow peak centered on $k = k_0 < K_0$. We also choose $g(k)$ to be real (e.g. narrow Gaussian in k). Thus, by completing each "eigenfunction seed", using

$$\omega(k) = \frac{\hbar k^2}{2m} \tag{18.19}$$

$$\begin{aligned} \Psi(x,t) \; &= \; \frac{1}{\sqrt{2\pi}} \int_0^{K_0} g(k) \mathrm{e}^{i[kx - \omega(k)t]} \, dk \\ &+ \; \frac{1}{\sqrt{2\pi}} \int_0^{K_0} g(k) \mathrm{e}^{-[kx + \omega(k)t + 2\theta(k)]} \, dk \end{aligned}$$

Of these, the first is the incident packet; the second is the reflected packet. The incident packet moves in from $x = -\infty$ with speed $\frac{d\omega}{dk}\Big|_{k=k_0} = \frac{\hbar k_0}{m}$ thus its center $\overline{x_{\mathrm{inc}}}$ is $\overline{x_{\mathrm{inc}}} = \frac{\hbar k_0}{m} t$. This packet is thus "on course" to arrive at $x = 0$ at $t = 0$. Now consider the phase function $\theta(k)$. Since $g(k)$ is narrowly peaked around k_0, over the important range of k.

$$\theta(k) \approx \theta(k_0) + \frac{d\theta}{dk}\bigg|_{k=k_0} (k - k_0) \tag{18.20}$$

Thus, the reflected packet is

$$\Psi_{\mathrm{refl}}(x,t) = \frac{1}{\sqrt{2\pi}} \int_0^{K_0} g(k) \mathrm{e}^{i[kx + \omega(k)t + 2\theta_0 + 2\theta_0'(k - k_0)]} \tag{18.21}$$

where $\theta_0 \equiv \theta(k_0)$, $\theta_0' \equiv \frac{d\theta}{dk}\Big|_{k=k_0}$ Defining $\omega_0 \equiv \omega(k_0)$,

$$\Psi_{\mathrm{refl}}(x,t) \equiv \frac{1}{\sqrt{2\pi}} \mathrm{e}^{-2i\theta_0} \mathrm{e}^{i\omega_0 t} \int_0^{K_0} g(k) \mathrm{e}^{-i[kx + (\omega - \omega_0)t + 2\theta_0'(k - k_o)]} \, dk \tag{18.22}$$

Since the important range of k is narrow, for all important k

$$k - k_0 \equiv \delta k \approx \left.\frac{dk}{d\omega}\right|_{k=k_0} \delta\omega = \left.\frac{dk}{d\omega}\right|_{k=k_0} (\omega - \omega_0) \tag{18.23}$$

So

$$\Psi_{\text{refl}}(x,t) \approx \frac{1}{\sqrt{2\pi}} \mathrm{e}^{i(\omega_0 t - 2\theta_0)} \int_0^{K_0} g(k) \mathrm{e}^{-i\left[kx + (\omega-\omega_0)\left(t - \frac{2\theta_0'}{d\omega/dk|_{k=k_0}}\right)\right]}\, dk \tag{18.24}$$

or

$$\Psi_{\text{refl}}(x,t) \approx \frac{1}{\sqrt{2\pi}} \mathrm{e}^{2i(\omega_0 t - \theta_0)} \mathrm{e}^{i\left(\frac{2\theta_0'}{v_g}\right)} \int_0^{K_0} g(k) \mathrm{e}^{-i\left[kx + \omega\left(t - \frac{2\theta_0'}{v_g}\right)\right]}\, dk \tag{18.25}$$

where

$$v_g \equiv \left.\frac{d\omega}{dk}\right|_{k=k_0} \tag{18.26}$$

The phase factors in front do not affect the probability density $|\Psi|^2$, so

$$\Psi_{\text{refl}}(x,t) \sim \int_0^{K_0} g(k) \mathrm{e}^{-i\left[kx + \omega\left(t - \frac{2\theta_0'}{v_g}\right)\right]} \tag{18.27}$$

Now consider a hypothetical wave packet which leaves $x = 0$ at $t = 0$ and travels left; it would be

$$\Psi(x,t) \propto \int g(k) \mathrm{e}^{-i(kx - \omega t)}\, dk \tag{18.28}$$

Comparing equations (18.27) and (18.28), we see that the reflected packet moves in the x direction at the classical velocity $v_g = \left.\frac{d\omega}{dk}\right|_{k=k_0}$, but which is delayed in leaving $x = 0$ by an amount of time

$$\tau = \frac{2\theta_0'}{v_g} \tag{18.29}$$

(to see this, note that t in equation (18.28) is replaced in equation (18.27) by $t - \tau$). A little algebra shows that

$$\tau = \frac{2m}{\hbar k_0 \sqrt{K_0^2 - k_0^2}} \tag{18.30}$$

Thus, in disagreement with classical physics, the particle is not reflected immediately – it is said that "the particle spends time τ in the classically forbidden region ($x > 0$) before heading back." The following sequence of figures illustrates this.

fig 2

[end of graduate student section]

Note the relatively long interval of time during which the packet interacts with the step – this is a reflection (no pun intended) of the delay time τ.

The sharp interference "fringes" occur as a result of the extreme sharpness of the step – they are the result of interference between "incident" and "reflected" components of the packet. With a smoother change from $V = 0$ to $V = V_0$, the interference fringes are much less pronounced.

18.3 Particle "Incident" on Potential Step, Case $E > V_0$

fig 3

The eigenfunction for the energy E is of the form (as you should show)

$$\psi_{\mathrm{I}} = \mathcal{A}\mathrm{e}^{ik_1x} + \mathcal{B}\mathrm{e}^{-ik_1x} \quad k_1 = \frac{\sqrt{2mE}}{\hbar} \tag{18.31}$$

$$\psi_{\mathrm{II}} = \mathcal{C}\mathrm{e}^{ik_2x} + \mathcal{D}\mathrm{e}^{-ik_2x} \quad k_2 = \frac{\sqrt{2m(E-V_0)}}{\hbar} \tag{18.32}$$

For definiteness, we specify that a particle is "incident from the left", thus we set $\mathcal{D}$ ("there is nothing out at $x = +\infty$ to cause back reflections"). Thus we have three unknowns ($\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$). Continuity of ψ and ψ' give two equations, thus one unknown is unspecified. We take this one to be $\mathcal{A}$ (arbitrary incident amplitude). The algebra then yields

$$\mathcal{B} = \frac{k_1 - k_2}{k_1 + k_2}\mathcal{A} \tag{18.33}$$

$$\mathcal{C} = \frac{2k_1}{k_1 + k_2}\mathcal{A} \tag{18.34}$$

We define a “reflection coefficient” and a “transmission coefficient” as

$$R = \frac{S_{\text{reflected}}}{S_{\text{incident}}} = \frac{|\mathcal{B}|^2}{|\mathcal{A}|^2} \tag{18.35}$$

$$T = \frac{S_{\text{transmitted}}}{S_{\text{incident}}} = \frac{k_2\,|\mathcal{C}|^2}{k_1\,|\mathcal{A}|^2} = \frac{v_2\,|\mathcal{C}|^2}{v_1\,|\mathcal{A}|^2} \quad \text{since } k \propto v) \tag{18.36}$$

$$R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2 \tag{18.37}$$

$$T = \frac{4k_1k_2}{(k_1 + k_2)^2} \tag{18.38}$$

As it must be, the sum $R+T = 1$ (a given particle is either transmitted or it is reflected). Note the definite break with classical physics here − as we say, a given incident particle is either reflected or transmitted − it never splits. The probability of reflection is given by R, and R decreases with increasing incident energy. The probability of transmission T increases with incident energy (as you can see in figure 18.5). Note that, in the case $E < V_0$, $R = 1$ and $T = 0$. this makes good sense − $R = 1$since the reflected amplitude differs from the incident amplitude only by a phase factor, as we saw last class. $T = 0$ for $E < V_0$ since then ψ_{II} is not a traveling wave, so $S_{\text{II}} = 0$. forming an incident wave packet for the case $\overline{E_{\text{inc}}} > V_0$ leads to splitting of the packet − part is transmitted and part is reflected. Remember, however, that the reflected packet (or its modulus squared) represents the probability of reflection in a given case. If I send in a beam of identical particles all in the same packet state,

fig 4[2]

R is the fraction of particles reflected and T is the fraction transmitted. A given particle either reflects or transmits. How does a given particle “know” if it must reflect or transmit? Good question − this is quantum mechanics!

fig 5

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[2] Figure from Cohen-tannoudji et.al

Chapter 19

Nineteenth Class: The Barrier Potential

Thursday, October 30, 2008

19.1 Barrier Penetration – Theory

We last dealt with the "step potential"; now we terminate the step before $x \to \infty$ and thus consider the rectangular "barrier potential"

Fig 1

We consider today the case $E < V_0$ and treat the eigenfunction. Of course, a classical particle with energy $E < V_0$ and incident from the left would simply bounce back from the first wall with 100% probability. In quantum mechanics, as with the step potential, there is probability (but not 100%, as with the step) of reflection at the left barrier, but here there is, as we will see, finite probability that a traveling probability current will be excited in the region to the right of the barrier (region III in figure 19.1) in spite of the intervening classically forbidden region. As I mentioned to you, without the existence of this usually very, very small effect, called "quantum tunneling", the sun would not shine, and therefore, we would not live. Other applications of the effect abound, conduction of electrons in solids (tunneling of electrons through lattice ions, ammonia masers, radioactive decay, field emission process, new semiconductor devices, the "scanning tunneling microscope", etc.) Let us find the eigenfunction: the time independent Schrödinger equationis

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{19.1}$$

so, in region I, the Schrödinger equation becomes

$$\psi_{\mathrm{I}}''(x) = -\frac{2mE}{\hbar^2}\psi_{\mathrm{I}}(x) \tag{19.2}$$

with solution

$$\psi_{\mathrm{I}}(x) = \mathcal{A}\mathrm{e}^{ikx} + \mathcal{B}\mathrm{e}^{-ikx} \tag{19.3}$$

where $k = \frac{\sqrt{2mE}}{\hbar}$. In region II, the Schrödinger equation is

$$\psi''(x) = +\frac{2m(v_0 - E)}{\hbar^2}\psi(x) \tag{19.4}$$

with solution

$$\psi_{\mathrm{II}}(x) = \mathcal{C}\mathrm{e}^{-\kappa x} + \mathcal{D}\mathrm{e}^{+\kappa x} \tag{19.5}$$

with $\kappa = \frac{\sqrt{2m(V_0-E)}}{\hbar}$ here we must keep $\mathcal{C}$ since x does not go to infinity in region II. In region III,

$$\psi_{\mathrm{III}}(x) = \mathcal{F}\mathrm{e}^{ikx} + \mathcal{G}\mathrm{e}^{-ikx} \tag{19.6}$$

where $k = \frac{\sqrt{2mE}}{\hbar}$. The second part of this a reflection; since there is nothing out at infinity to cause this, we must have $\mathcal{G} = 0$. Now we must use the boundary conditions to stitch together the three parts of the eigenfunction. The boundary conditions are, of course

- continuity of ψ at $x = 0$
- continuity of ψ' at $x = 0$
- continuity of ψ at $x = a$
- continuity of ψ' at $x = a$

As you can easily show, applications of these four conditions leads to four equations

1. $\mathcal{A} + \mathcal{B} = \mathcal{C} + \mathcal{D}$
2. $ik\mathcal{A} - ik\mathcal{B} = -\kappa\mathcal{C} + \kappa\mathcal{D}$
3. $\mathcal{C}\mathrm{e}^{-\kappa a} + \mathcal{D}\mathrm{e}^{\kappa a} = \mathcal{F}\mathrm{e}^{ika}$
4. $-\kappa\mathcal{C}\mathrm{e}^{-\kappa a} + \kappa\mathcal{D}\mathrm{e}^{\kappa a} = ik\mathcal{F}\mathrm{e}^{ika}$

We have five unknowns and only four equations, so we could express $\mathcal{B}$, $\mathcal{C}$, $\mathcal{D}$, and $\mathcal{F}$ in terms of $\mathcal{A}$, which can later be set by the overall normalization condition[1]. However, since the algebraic situation is a little complicated here, it is best to focus on a more specific goal − of the greatest interest is determining the fraction of the probability current that leaks into region III, since that is a measure of the "tunneling". That fraction is the "transmission coefficient".

$$T = \frac{\text{current in region III}}{\text{current in region I}} = \frac{v_{\text{III}}\,|\mathcal{F}|^2}{v_{\text{I}}\,|\mathcal{A}|^2} = \frac{|\mathcal{F}|^2}{|\mathcal{A}|^2} \tag{19.7}$$

since $v_{\text{III}} = v_{\text{I}}$. Here is an outline[2] of a relatively quick route to this goal:

1. Eliminate $\mathcal{B}$: multiply our first boundary condition by ik and add the result to the second boundary condition, obtaining

$$2ik\mathcal{A} = (ik - \kappa)\mathcal{C} + (ik + \kappa)\mathcal{D} \tag{19.8}$$

2. Now multiply the third boundary condition by $-\kappa$ and add the result to the fourth boundary condition, we obtain

$$\begin{aligned} \mathcal{C} &= \frac{\kappa - ik}{2\kappa} \mathrm{e}^{\kappa a} \mathrm{e}^{ika} \mathcal{F} & (19.9) \\ \mathcal{F} &= \frac{\kappa + ik}{2\kappa} \mathrm{e}^{-\kappa a} \mathrm{e}^{ika} \mathcal{F} & (19.10) \end{aligned}$$

Now, putting both of these into equation (19.8), the result is

$$\frac{\mathcal{F}}{\mathcal{A}} = \frac{4i\kappa k}{[(\kappa + ik)^2 \mathrm{e}^{-\kappa a} - (\kappa - ik)^2 \mathrm{e}^{\kappa a}]} \mathrm{e}^{-ika} \tag{19.11}$$

thus

$$T(E) = \left|\frac{\mathcal{F}}{\mathcal{A}}\right|^2 = \frac{16\kappa^2 k^2}{|(\kappa - ik)^2 - (\kappa + ik)^2 \mathrm{e}^{-2\kappa a}|^2} \mathrm{e}^{-2\kappa a} \tag{19.12}$$

where $|\text{denominator}|^2 \equiv (\text{denominator})^*(\text{denominator})$, and where we've emphasized that T depends on E (through k and κ).

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[1] Thus, any value of $E < V_0$ is possible − the energy isn't quantized.

[2] from **Understanding Quantum Physics** by Michael Morrison, Prentice Hall, p.314

although equation (19.12) is fairly unwieldily form due to the $|\ |^2$ in the denominator, it will be useful to us. Further algebra leads to the form most commonly seen in textbooks:

$$T(E) = \left[1 + \frac{1}{4} \frac{\left(1 + \frac{k^2}{\kappa^2}\right)^2}{\frac{k^2}{\kappa^2}} \sinh\left(\kappa a\right) \right]^{-1} \tag{19.13}$$

As you can easily show, an alternate form of equation (19.13) that shows the dependence on the energy explicitly is

$$\begin{aligned} T(E) &= \left[1 + \frac{\sinh^2\left(\kappa a\right)}{4\left(\frac{E}{V_0}\right)\left(1 - \frac{E}{V_0}\right)} \right]^{-1} && (19.14) \\ &= \left[1 + \frac{\sinh^2\left(\sqrt{\frac{2mV_0a^2}{\hbar^2}\left(1 - \frac{E}{V_0}\right)}\right)}{4\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)} \right]^{-1} && (19.15) \end{aligned}$$

We'll look at a plot of this later, but for now, the main point is that $T > 0$ for $E < V_0$! The math reason "why" this occurs is that the combination of rising and decaying exponentials in region II is not dead at the door to region III.

The reflection coefficient, $R = \frac{|\mathcal{B}|^2}{|\mathcal{A}|^2}$ is not unity, as it is with the potential step, since the incoming current splits at the first wall – some goes on to region II, and some heads back. Thus, a given incident particle will definitely either reflect or tunnel; quantum mechanics can only tell us the probabilities.

Of course, this is highly nonclassical behavior for a particle, but it is familiar behavior with classical waves – in fact, the same phenomenon occurs in optics, as predicted by the wave theory (of optics) – Newton discovered that light can "tunnel" from one prism to another even with an air-gap in between – the wave is not traveling, but only "evanescent" on the air-gap – this interesting phenomenon is called "frustrated total internal reflection".

fig 2

In quantum mechanics, the reflection probability is

$$R(E) = 1 - T(E) \tag{19.16}$$

Let us now look at the probability density for this eigenfunction.

fig 3

$P(x,t)$ is constant in region III, since the eigenstate is a pure traveling wave there. Note how the amplitude is diminished there compared to region I – because of the exponential drop (essentially) in region II. In any case, we see clear possibility of "tunneling through the classically forbidden region". The "surviving" state function in region III is a pure traveling wave. Note that, in region I, $P(x,t)$ has peaks and valleys. This is because it is a mixture of right and left traveling waves. If the reflection coefficient were 1, as it is for the simple step potential, then this would be a pure standing wave and the valleys of $P(x,t)$ would go down to zero. But, here, $R \neq 1$ ($R = 1 - T$), so we don't get a pure standing wave – we get a mixed standing-traveling wave (in region I).

19.1.1 A Feel for the Numbers

Typical cases occur in atomic physics; there, energies and barrier heights are eV order, barrier widths are, say, molecular size ($\sim 0.5mm$).

Example[3]: Say electrons of kinetic energy 1eV encounter a barrier height 2eV and width 0.5nm. Then, the parameter $K \equiv \sqrt{\frac{2mV_0}{\hbar^2}}a$ which appears in T has value

$$K = \frac{\sqrt{2\left(0.511 \times 10^6 \frac{eV}{c^2}\right)(2eV)}}{197.3eV \cdot \frac{mm}{c}} \cdot (0.5mm) \approx 3.6 \tag{19.17}$$

Then for this case

$$T = \frac{1}{1 + \frac{\sinh^2\left(3.623\sqrt{1-0.5}\right)}{4(0.5)(0.5)}} \approx 0.024 \tag{19.18}$$

so, about 1 electron in 40 will penetrate the barrier.

19.2 Useful Approximations for Rectangular Barrier Penetration

Of course, one can always calculate $T(E)$ from equations (19.12) or (19.13) or (19.15) and get a numerical answer, but for insight in applications[4] it's

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[3] From Professor R. Hill's book manuscript **Basic Quantum Mechanics**

[4] one or two of which we'll discuss in the next class

useful to have simple − form approximations in each of two limiting cases. These are

19.2.1 “High and Wide Barrier”

(criterion $\kappa a \gg 1$) The criterion makes sense because

$$\kappa a = \sqrt{\frac{2mV_0}{\hbar^2}\left(1 - \frac{E}{V_0}\right)} \cdot a \tag{19.19}$$

In this case, by expanding the exponentials on the sinh in equation (19.15), and keeping only through the term factor linear in κa, we have (as you should verify)

$$T \approx 16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)\mathrm{e}^{-2\kappa a} \tag{19.20}$$

(high/wide approximation) When this approximation is valid, $T \ll 1$. (show this). In most applications involving “high and wide” barriers, the exponential factor is so tiny that the “prefactor” $16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)$ is relatively quite unimportant. For example, in applications reflecting the classical limit, even if the prefactor has value, say, 10^{-6}, the exponential is so much smaller than this that even an “error” of 6 orders of magnitude is unimportant in all but exact-seeking calculations. Thus, very often, if not usually,

$$T \sim \mathrm{e}^{-e\kappa a} \tag{19.21}$$

where $\sim$ no longer means “order of magnitude”, but means “is dominated by.”

19.2.2 “Thin Barrier”

(criterion $\kappa a \ll 1$) In this case

$$\mathrm{e}^{-2\kappa a} \approx 1 \tag{19.22}$$

In the limit of an extremely thin barrier of finite height ($\kappa a \to 0$), we expect $T \to 1$. From equation (19.12)

$$T \to \frac{16k^2\kappa^2}{|(\kappa - ik)^2 - (\kappa + ik)^2|^2} = \frac{16k^2\kappa^2}{16k^2\kappa^2} = 1 \tag{19.23}$$

However, we want a better approximation than this − T should be a bit less than 1, and we want an easy to use approximation that will tell us how much less than 1. For this, we use the following[5] method:

$$T = \frac{16k^2\kappa^2}{|(\kappa - ik)^2 - (\kappa + ik)^2 \mathrm{e}^{-2\kappa a}|^2}\mathrm{e}^{-e\kappa a} \tag{19.24}$$

we ignore the $\mathrm{e}^{-2\kappa a}$ in the denominator, but not the overall factor of $\mathrm{e}^{-2\kappa a}$. Then

$$T \approx \frac{16k^2\kappa^2}{16k^2\kappa^2}\mathrm{e}^{-2\kappa a} \approx \mathrm{e}^{-2\kappa a} \tag{19.25}$$

Therefore, the approximation of the transmission coefficient for the thin, finite square barrier is

$$T \approx \mathrm{e}^{-2\kappa a} \tag{19.26}$$

Thus, in the case of the thin, narrow barrier, the exponential $\mathrm{e}^{-2\kappa a}$ not only dominates T, but is actually approximately equal to it.

19.3 "Arbitrary" Shaped Barrier ($E < V_0$)

Now consider the case of an arbitrary shaped barrier[6]. This can be approximated as a sequence of thin barriers:

fig 3

The points x_1 and x_2 delineate the boundaries of the classically forbidden region. (Thus, the "barrier" extends from x_1 to x_2). In approximation[7] the overall transmission factor is, then

$$T \approx T_1 T_2 T_3 \cdots T_N \tag{19.27}$$

Here for T_i we use the thin barrier formula

$$T_i \approx \mathrm{e}^{-2\kappa_i \Delta x_i} \tag{19.28}$$

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[5] Hans C. Ohanian, **Principles of Quantum Mechanics**, pages 87-88

[6] We use the method of Ohanian, which is related to the original method of Ganow (1928). Ohanian's treatment is distinguished by it clarity; many unclear treatments exist in the literature, Amore rigorous treatment requires the WKB approximation (see Griffiths chapter 8 for more information)

[7] The simple combining of transmission factors we are doing ignores back and forth reflections within the barrier − we are assuming that once a reflection occurs, the particle has turned back.

thus

$$T \approx \prod_{i=1}^{N} \mathrm{e}^{-2\kappa_i \Delta x_i} = \mathrm{e}^{-2[\kappa_1 \Delta x_1 + \kappa_2 \Delta x_2 + \cdots + \kappa_N \Delta x_N]} \tag{19.29}$$

Taking the limit as $\Delta x_i \to 0$, $N \to \infty$, we have, for our approximation

$$T \approx \mathrm{e}^{-2\int_{x_1}^{x_2} \kappa(x)\ dx} \tag{19.30}$$

or

$$T \approx \mathrm{e}^{-\frac{2}{\hbar}\int_{x_1}^{x_2} \sqrt{2m[V(x)-E]}\ dx} \tag{19.31}$$

The formula above, Garnow's approximation, has many applications. Our derivation of it has been nonrigorous, but the same result is obtained using a somewhat more sophisticated approximation scheme called the "WKB Approximation", which is treated in an elementary way in chapter 8 of the Griffiths text.

Note: Many book derive Garnow's result for a high and wide but arbitrarily shaped barrier in a less rigorous way − by approximating the barrier as a sequence of "moderately wide" rectangular barriers, dropping the prefactor for the transmission for each, and then multiplying the T_i's and then pretending that the moderately wide sub-barriers are thin enough to take over to the integral in a "limit".

Chapter 20

Twentieth Class: Applications of Barrier Potentials

Tuesday, November 4, 2008

20.1 Applications of Gamow's Approximation

We developed Gamow's approximation for a non-rectangular high and wide barrier.

fig 1

$$T \approx \mathrm{e}^{-2\int_{x_1}^{x_2} \kappa(x)\ dx} \tag{20.1}$$

or

$$\boxed{T \approx \mathrm{e}^{-\frac{2}{\hbar}\int_{x_1}^{x_2} \sqrt{2m[V(x)-E]}\ dx}} \tag{20.2}$$

This approximation is especially useful in applications, for example, to types of radioactive decay (see following), to nuclear fusion, to field emission of electrons from a metal sample (see homework) and more. In many of these applications, one deals with the classically forbidden (but quantum-allowed) escape of a particle from a finite confined region in which it is free across a barrier of height greater than the energy of the particle and of substantial width.

fig 2

Figure 20.2 represents this schematically. In it, r_1 and r_2 are the classical turning points $-$ the positions at which a classical particle approaching the barrier from either classically allowed region would be turned back $-$ these are the places where $V(r) = E$, so the kinetic energy is zero. Frequently in applications one "starts" with the particle bound inside a finite classically allowed region (as mentioned above) in which the particle is "free", and one is interested in the probability per second of tunneling across the barrier. to the "outside world of freedom" ("escape rate"). In these applications, one often adopts a simple semiclassical picture in which the particle, in the initial confined region ($r = 0$ to $r = r_1$, as in figure 20.2) travels repeatedly back and forth due to "bounces" (reflection probability) off the "wall" of the well. In this semiclassical picture, the escape rate is given by

escape rate = (# of collisions with the "wall" per second) × (probability of tunneling per collision)

The "probability of tunneling per collision" is just the transmission coefficient $T(E)$ supplied, in approximation, by gamow's formula.

Of course, the semiclassical picture of a "bouncing back-and-forth particle in the well" is not rigorous – it is merely a semiclassical picture. The really correct way to approach the problem, however, is quite mathematical[1]. We use the semiclassical picture because it is simpler and because, to the estimation accuracy we are interested in, it works (e.g. the following discussion).

20.2 Application to Radioactive Alpha Decay

Many heavy atomic nuclei disintegrate ("decay") spontaneously, emitting particles (this is the phenomenon of radioactivity)[2]. One such type of decay, called alpha decay, occurs when a heavy nucleus emits an alpha particle (an intact Helium nucleus) and, in the process, becomes the (lighter) nucleus of another element. An example of this is

$$_{88}\mathrm{Ra}^{226} \rightarrow {}_{86}\mathrm{R}^{224} + {}_{2}\mathrm{He}^{4}$$

the half life (τ) for this is 1622 years! (this is incredibly long on what we now know as the typical time scale for nuclear interactions – the time it would take a light-speed impulse to cross a nucleus is $\sim 10^{-23}$ seconds!) but, some alpha emitting have much shorter half-lives e.g. $_{84}\mathrm{Po}^{212}$ has $\tau \approx 3 \times 10^{-7}$

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[1] see, e.g. **Quantum Theory** by David Bohm (Dover), chapter 12.

[2] Our discussion here is based on that of E. Wichmann (class handout); the original work was done by George Gamow around 1928.

seconds! at the other extreme, ${}_{92}\mathrm{U}^{238}$ has $\tau \approx 4.2 \times 10^9$ years! Any good theory will have to explain this enormous range of lifetimes!

Another fact: Each decaying isotope emits (usually) its alpha particle with a unique energy, usually in the range 4-10 MeV (K.E.) It was found that there is a rough correlation between the lifetime and the energy of the emitted alpha particle.

$$\log(\tau) \sim \frac{1}{\sqrt{E}} \quad \text{(roughly)} \tag{20.3}$$

A good theory should explain this also.

So, we have some incredibly daunting demands for any theory that seeks to "explain" alpha decay., This was the challenge that Gamow and Codon took up with the then fledgling theory of quantum mechanics.

20.2.1 The Basic Model

1. Pretend that the alpha particle exists intact inside the nucleus. It is held in by the very strong nuclear force, which presents a formidable barrier potential energy profile against the alpha particle leaving the nucleus.
2. The short-range strong nuclear force (range $\approx 10^{-15}$m), while essentially zero outside the parent nucleus, must be very strong inside and must vary strongly with position inside the nucleus. Nevertheless, for simplicity, the model assumes that the $V(r)$ that the "alpha particle inside the nucleus" is subject to is flat (constant) − in other words, replace the actual $V(r)$ inside the nucleus with its average value for $0 < r \leq R$ (R is the radius of the nucleus).
3. Since the strong nuclear force on an alpha particle is essentially zero if it is outside the nucleus, the force on the alpha-particle outside is purely electromagnetic. Since $Z_\alpha = 2$, if we let Z' be the charge of the daughter nucleus ($Z' = Z - 2$), then outside the nucleus,

$$V(r) = \frac{2e^2 Z'}{4\pi\epsilon_0 r} \quad r > R \tag{20.4}$$

thus, the picture in this simple model is the following: The alpha-particle is caught in a deep square well, inside of which it feels no force. Thus, in a semiclassical picture, it bounces back and forth between the boundaries of the parent nucleus. $V(r)$ looks like the (in the model)

fig 3

fig 4

Each time the alpha particle collides with the "nuclear wall", since it is "merely" very, but not infinitely high (in V) there is some small (very small) probability to leak out (transmission coefficient for penetration of the Coulomb barrier from inside the square well). With enough collisions with the wall, the accumulated chance to leak out should be "easily" relatable to the observed half-life for emission of the alpha-particle. Calculating this was Gamow's (and Codon's) program – it was a means, essentially, of testing quantum mechanics.

Let's take a moment to check the scale of figure 20.4 for $V(r)$. Let R_c be the classical turning point for a hypothetical particle of energy E (same as the emitted alpha particle energy) trying to get into the well from the outside. Then

$$E = \frac{1}{4\pi\epsilon_0}\frac{2Z'e^2}{R_c} \tag{20.5}$$

This can be solved for R_c:

$$R_x = \frac{1}{4\pi\epsilon_0}\frac{2Z'e^2}{E} \tag{20.6}$$

Let's see what this is for the case of the alpha decay of ${}_{88}\mathrm{Ra}^{226}$:

$$\begin{aligned} Z &= 88,\ Z' = 86,\ E = 4.8\ MeV \\ R_c &\approx 50 \times 10^{-13} cm = 50f \end{aligned}$$

Now, recall from Rutherford scattering

$$R \approx r_0 A^{\frac{1}{3}},\ r_0 = 1.2 \times 10^{-13} cm$$

so

$$A = 226\ \Rightarrow\ R \approx 7f < 50f \tag{20.7}$$

So, qualitatively, the picture is correct: however, the barrier should have drawn much thicker and much higher!

20.2.2 Summary of Goals for the Calculation

Before getting involved in the details of the calculation, let us summarize the main goals: We want to calculate, via the model, half-lives for alpha decay for radioactive nuclei and compare the predictions to the experimental data. To do this we need to

1. Calculate the approximate transmission coefficient $T(E)$ using Gamow's approximation
2. Multiply $T(E)$ by the factor f, the frequency of collisions with the barrier wall. (Of course, to do this, we first have to calculate, or estimate, f). The result of this is the decay rate $R = T \cdot f$

   escape probability per second = probability per "knock" ×# of knocks per second

3. We must the convert R to the half life. For this, we note that the mean lifetime $\tau = \frac{1}{R}$. The half life, $\tau_{1/2}$ is then related to τ by an arithmetical factor: since radioactive decay follows the exponential decay law, $N(t) = N(t = 0)e^{-t/\tau}$, as you can easily show, $\tau_{1/2}$ and τ are related by a factor of log(2).

20.2.3 Calculation of Collision Factor f

Following Gamow, we approximate as follows:

We pretend that the nucleus is a hallow and that the alpha particle before emission, bounces around inside it like a free particle[3] bouncing off the nuclear wall (i.e., we completely ignore the strong nuclear force of the alpha particle inside the nucleus!)

fig 5

At first sight, it may seem outrageous to "ignore" the strong force inside the nucleus. We can rationalize this somewhat, however, by noting that nucleons (protons and neutrons) in a nucleus are tightly packed, thus, an alpha particle in the interior of the nucleus might be imagined to feel equal forces in all directions, for a net force of zero. With this model, then, if R is

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[3] of energy E = the observed energy of the emitted alpha particle after the decay – i.e., about 6 MeV for the Ra decay we're taking as typical

the nuclear radius, the “back and forth time” (τ_0) is

$$\tau_0 = \frac{2R}{v} \tag{20.8}$$

where $v = \sqrt{\frac{2E}{m_\alpha}}$, so

$$\tau_0 = 2R\sqrt{\frac{m_\alpha}{E}} \tag{20.9}$$

The collision frequency f is $\frac{1}{\tau_0} = \frac{1}{2R}\sqrt{\frac{E}{m_\alpha}}$ in this model.

$$f = \frac{1}{\tau_0} = \frac{1}{2R}\sqrt{\frac{E}{m_\alpha}} \tag{20.10}$$

It is helpful to get an idea of the magnitude of f for a typical case. We take the case of ${}_{88}\mathrm{Ra}^{226}$:

$$f \approx \frac{C}{2R}\sqrt{\frac{E}{m_\alpha C^2}} \tag{20.11}$$

with

$$\begin{aligned} R &\approx 7\times 10^{-15}\ m \ \Rightarrow\ 2R \approx 1.4\times 10^{-14}\ m \\ E &\approx 4.8\ MeV \\ m_\alpha c^2 &\approx 4\ GeV = 4000\ MeV \end{aligned}$$

(since each alpha particle has 4 nucleons). Then,

$$f \approx \frac{3\times 10^8\ m/s}{1.4\times 10^{-14}\ m}\sqrt{\frac{4.8}{4000}} \sim 10^{21}\ Hz \tag{20.12}$$

We see that f, the “number of knocks per second” is typically very large.

20.2.4 Calculation of $T(E)$

(Gamow, 1928)

Recall that

$$\ln(T) \approx -\frac{2}{\hbar}\int_{x_1}^{x_2}\sqrt{2m\left[V(x)-E\right]}\,dx \tag{20.13}$$

Here, $V(r) = \frac{2e^2 Z'}{4\pi\epsilon_0 r}$ for the barrier region, so

$$\ln(T) \approx -\frac{2}{\hbar} \int_{r_1}^{r_2} \sqrt{2m_\alpha \left[\frac{2e^2 Z'}{4\pi\epsilon_0 r} - E\right]}\, dr \tag{20.14}$$

Here, r_1 and r_2 are the two turning points. Now, $E = \frac{1}{4\pi\epsilon_0} \frac{2Z'e^2}{r_2}$ (conservation of energy), so

$$\ln(T) \approx \frac{\sqrt{2mE}}{\hbar} \int_{r_1}^{r_2} \sqrt{\frac{r_2}{r} - 1}\, dr \tag{20.15}$$

This integral is doable, the result is

$$\ln(T) \approx \frac{\sqrt{2mE}}{\hbar} \left[r_2 \left(\frac{\pi}{2} - \sin^{-1}\left(\sqrt{\frac{r_1}{r_2}}\right)\right) - \sqrt{(r_2 - r_1)\, r_1}\right] \tag{20.16}$$

In our case, $r_1 \ll r_2$, so

$$\ln(T) \approx \frac{\sqrt{2mE}}{\hbar} \left[\frac{\pi}{2} r_2 - 2\sqrt{r_1 r_2}\right] \tag{20.17}$$

again using $E = \frac{1}{4\pi\epsilon_0} \frac{2Z'e^2}{r_2} \Rightarrow r_2 \frac{1}{4\pi\epsilon_0} \frac{2Z'e^2}{E}$ and evaluating the constants gives

$$\ln(T) \approx \left(\frac{e^2}{4\pi\epsilon_0} \frac{\pi\sqrt{2m}}{\hbar}\right) \cdot \frac{Z'}{\sqrt{E}} - \sqrt{\frac{e^2}{4\pi\epsilon}} \cdot \frac{4\sqrt{m}}{\hbar} \cdot \sqrt{Z' r_1} \tag{20.18}$$

or

$$\ln(T) \approx 1.980 \frac{Z'}{\sqrt{E}\ (\text{in MeV})} - 1.485\ f^{-1/2} \cdot \sqrt{Z' r_1} \tag{20.19}$$

where f=Fermi=10^{-15} meters. As a rough approximation to the above, we take $Z' \approx 86$, $R \approx 7.3f$ for all alpha-decaying nuclei. (Recall that $R \sim 1.1A^{1/3}f$ for all nuclei, for and archetypal nucleus ${}_{88}\text{Ra}^{226}$, $A = 226 \Rightarrow R \approx 7.3f$). converting, then, to base 10 logarithms (customary for plotting later), one winds up with, as a rough approximation,

$$\log_{10}(T) \approx -\frac{148}{\sqrt{E}\ (\text{in MeV})} + 32.5 \tag{20.20}$$

20.2.5 Comparison with Experiment

We not put the pieces together to compare with experimental data. We have τ=mean lifetime=$\frac{1}{R} = \frac{\tau_0}{T}$ (since $f = \frac{1}{\tau_0}$. As we remarked, the values of τ for diferent nuclear species subject to alpha decay vary over many orders of magnitude; therefore, for a global comparison it is good to deal with $\log(\tau)$ rather than τ. In fact, it is traditional to deal with $\log_{10}(\tau)$. thus, from the above,

$$\log_{10}(\tau) = \log_{10}(\tau_0) - \log_{10}(T) \tag{20.21}$$

From equation (20.20), this is

$$\log_{10}(\tau) = \log_{10}(\tau_0) + \frac{148}{\sqrt{E}\text{ (in MeV)}} - 32.5 \tag{20.22}$$

Now, as we saw, for the case of ${}_{88}\text{Ra}^{226}$, $f = \frac{1}{\tau_0} \sim 10^{21}$, so, for this case, $\log_{10}(\tau_0) = -21$. As you can convince yourself by looking at values of E for different parent nuclei, $\log_{10}(\tau_0)$ varies at most ± 1 or so from case to case; this variation is very minor compared to the other two terms of equation (20.22). Therefore, since we are only interested in an approximate answer, we may as well approximate $\log_{10}(\tau_0)$ as -21 in all cases. thus, the theory predicts,

$$\log_{10}(\tau) \approx \frac{148}{\sqrt{E}\text{ (in MeV)}} - 53.5 \tag{20.23}$$

In spite of some rough approximations on the way to equation (20.23), we[4] compare it to the data for known alpha emitters in figure 20.6.

fig 6

The results are a spectacular confirmation of quantum mechanics notice that the trend[5] of the theory is correct over 23 orders of magnitude!

The dotted line (theory prediction) is actually for the mean lifetime; whereas the experimental points are half-lives. As we remarked,

$$\tau_{1/2} = (\ln(2))\,\tau_{\text{mean}} \approx (0.69)\tau_{\text{mean}} \tag{20.24}$$

however, given the approximations of our discuaaion and the latitude in the plot from the dotted line, the factor $(\ln(2))$ is not worth bothering with here.

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[4] The plot in figure (20.6) is from **Quantum Mechanics** (Berkeley Physics Series, Volume IV) by Evyinf Wichmann (McGraw-Hill)

[5] of course, for individual cases (see plot) the erros can be order factor of 100 or even 1000, but the important thing is the trend

20.3 Another Application – Fusion in the Sun's Core

For fusion, protons have to get together to fuse, but, as we remarked in the beginning of the course, there is a $\sim 1MeV$ Coulomb barrier in the way, and, in the core of the Sun, the mean proton energy is only $\sim \frac{1}{1000}$ of this.

fig 7

Here we have the "opposite" of the alpha decay problem, we just treated a proton tries to get into the deep square well of attraction presented by the other proton from the outside, but in the way is a very high coulomb barrier! Now, even with quantum mechanics a simultaneous fusion of the 4 protons necessary is very unlikely – we must look for a chain. We believe that that correct chain for the sun is (Bethe)

$$\begin{aligned} {}^1_1\mathrm{H} + {}^1_1\mathrm{H} &\rightarrow {}^2_1\mathrm{H} + \mathrm{e}^+ + \nu \\ {}^2_1\mathrm{H} + {}^1_1\mathrm{H} &\rightarrow {}^3_2\mathrm{He} + \gamma \\ {}^3_2\mathrm{He} + {}^3_2\mathrm{He} &\rightarrow {}^4_2\mathrm{He} + {}^1_1\mathrm{H} + {}^1_1\mathrm{H} \end{aligned}$$

This is called p-p cycle.

the ν's produced in the core of the sun should escape (they interact so weakly that their mean free path in most matter is $\sim$ light years!). For the last 25 years, R. Davis has tried to detect these (actually these ν's are too low in energy – he looks for higher energy ν's from the p-p III cycle) in a shielded tank in Homestake Nums, S.D. filled with 100,000 gallons of C_2Cl_4 (cleaning fluid) via ${}^{37}\mathrm{Cl} + \nu \rightarrow {}^{37}A$, which is radioactive. Only one problem – he only sees about 35% of what he should! This is one of great unsolved problem of astrophysics (until recently).

20.4 Another Example of Barrier Penetration – Ammonia Molecule

Another (of many) example of barrier penetration is offered by the Ammonia molecule (NH_3. The location of the N ion is determined by the condition that there the energy is a minimum; there are two equivalent positions for this (as in figure 20.8). thus, in the region between the two minima there is a higher potential energy.

fig 8

The potential energy profile is shown in figure 20.9

fig 9

As we will see in the near future, a state with the N-ion "on one side" is not an eigenstate of the Hamiltonian for this potential energy profile. Consequently, if a measurement materializes the N on one side, the state function will change over the course of time. As we will see, the initial state function has a certain probability per unit time to "diffuse" through the forbidden region. and. given enough time, can end up almost completely on the other side – in fact, analysis shows that the N-ion will tunnel back and forth across the barrier at a fixed frequency! A calculation of this frequency (which we do not do here) shows it to be

$$f = 2.387 \times 10^{10} \text{ Hz} \tag{20.25}$$

This forms the basis of the Ammonia MASER. A maser of this sort was used in the discovery of the cosmic microwave background radiation that permeates the universe. Now, the N nucleus is charged, and as you know, classically, a charge moving back and forth in space emits radiation. This radiation, at this specific frequency, has been detected by radio telescopes as originating in interstellar space, thus signaling the presence of Ammonia molecules in the interstellar medium.

20.5 Another Application – Covalent Molecular Bonding

Consider, e.g., the H_2^+ molecule – two protons and one electron. An electron sees a Coulomb barrier between the protons

fig 10

Thus, classically, an electron "near" one proton must stay there. (by "near", we mean somehow localized by measurement). However, according to quantum mechanics, tunneling is possible and the probability density can flow back and forth, leading to the mechanism of the covalent bond.

Other applications of tunneling include:

- superconductors
- possible vaporization of cosmic back holes

- “scanning-tunneling microscope”, etc.

fig 11

Finally, the following sequence of figures shows the situation when a wave packet with $\overline{E} = \frac{1}{2}V_0$ is incident on a barrier. The strong interference fringes are an artifact of the sharpness of the barrier.

fig 12

Chapter 21

Twenty-first Class: Potential Barrier and Finite Square Well

Thursday, November 6, 2008

21.1 Potential Barrier, Case $E > V_0$

fig 1

For this case we have traveling wave eigenfunctions in all three regions:

$$\psi_{\mathrm{I}}(x) = \mathcal{A}\mathrm{e}^{ik_1x} + \mathcal{B}\mathrm{e}^{-ik_1x} \quad k_1 = \frac{\sqrt{2mE}}{\hbar} \tag{21.1}$$

$$\psi_{\mathrm{II}}(x) = \mathcal{C}\mathrm{e}^{ik_2x} + \mathcal{D}\mathrm{e}^{-ik_2x} \quad k_2 = \frac{\sqrt{2m(E-V_0)}}{\hbar} \tag{21.2}$$

$$\psi_{\mathrm{III}}(x) = \mathcal{F}\mathrm{e}^{ik_3x} + \mathcal{G}\mathrm{e}^{-ik_3x} \quad k_3 = k_1 \tag{21.3}$$

where $\mathcal{G} = 0$ because there is nothing at infinity to cause a reflection back. Above, we've assumed a plane wave incident from region I. Say, we want to know the transmission factor (T) to region III. We could go through the business of applying the boundary conditions to this, but we don't have to! We already done it! To see why, consider that the only difference in the form of our set of eigenfunctions to the eigenfunctions for the case $V < V_0$ seems to be in region II: For $E < V_0$ in region II we had

$$\psi_{\mathrm{II}}(x) = \mathcal{C}\mathrm{e}^{\kappa_2x} + \mathcal{D}\mathrm{e}^{-\kappa_2x} \quad \kappa_2 = \frac{\sqrt{2m(V_0-E)}}{\hbar} \tag{21.4}$$

This is still valid if $E > V_0$! ("The math doesn't know the difference"). However, if $E > V_0$, κ_2 is now imaginary:

$$\kappa_2 = \frac{\sqrt{2m(V_0 - E)}}{\hbar} = \frac{\sqrt{(-1)2m(E - V_0)}}{\hbar} = i\frac{\sqrt{2m(E - V_0}}{\hbar}$$

and now $(E - V_0) > 0$ so κ_2 is imaginary. Therefore, if we define $ik_2 \equiv \kappa_2$ with k_2 real, then indeed

$$\psi_{\text{II}}(x) = \mathcal{C}\text{e}^{ik_2x} + \mathcal{D}\text{e}^{-ik_2x} \tag{21.5}$$

Thus, we can take our old expression for $T_{E<V_0}$, nameley,

$$T_{E<V_0} = \left[1 + \frac{\sinh^2(\kappa_2 a)}{4\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)}\right]^{-1} \tag{21.6}$$

and wherever we see κ_2, replace it by ik_2, and we have $T_{E>V_0}$! Now

$$\sinh(\kappa_2 a) = \frac{\text{e}^{\kappa_2 a} - \text{e}^{-\kappa_2 a}}{2} \rightarrow \frac{\text{e}^{ik_2 a} - \text{e}^{-ik_2 a}}{2} = i\sin(k_2 a) \tag{21.7}$$

so

$$\sinh^2(\kappa_2 a) \rightarrow (i)^2 \sin^2(k_2 a) = -\sin^2(k_2 a) \tag{21.8}$$

so

$$T_{E>V_0} = \left[1 + \frac{\sin^2(k_2 a)}{4\frac{E}{V_0}\left(\frac{E}{V_0} - 1\right)}\right]^{-1} \tag{21.9}$$

(note that I changed the sign in the denominator) If you like, you can plug in $k_2 = \frac{\sqrt{2m(E-V_0)}}{\hbar}$. Again, R works out to (As it must) $R = 1T$.

Example: Photons incident on a slab of glass $-$ 4% are reflected back. This is barrier penetration with some probability of reflection. With wave packets, recall that the packet spits, but the particle is definitely either reflected or transmitted.

21.2 Resonance Transmission

Look at the expression for $T_{E>V_0}$:

$$T_{E>V_0} = \frac{1}{1 + \dfrac{\sin^2(k_2 a)}{4\frac{E}{V_0}\left(\frac{E}{V_0} - 1\right)}} \tag{21.10}$$

Notice that it has maxima ("resonances") when $\sin^2(k_2 a) = n\pi -$ then $T =$ 100% (perfect transmission – no reflection!)! Let us investigate this, these transmission resonances occur when

$$\begin{aligned} k_2 a &= n\pi \quad n = 1, 2, 3, \cdots & (21.11) \\ \frac{2\pi}{\lambda_2} a &= n\pi & (21.12) \\ \lambda_2 &= \frac{2a}{n} & (21.13) \end{aligned}$$

How can we understand this physically? Consider a DeBroglie plane wave incident from the left – part of it reflects at the "front wall" (call that part r_1) and part reflects at the back wall (call that part r_2).

fig 2

r_1 and r_2 combine and interfere with each other in region I – and their resultant is the net reflection off the barrier $^1/$ our condition for resonant transmission, $\lambda_2 = \frac{2a}{n}$, means that the two reflections r_1 and r_2 are in phase, and hence add, in region I. And so are higher order reflections ("back and forth") $r_3, r_4, \cdots$ But wait – that means that a resonance the reflections are max, which means that the transmission should be min, not max! So what is wrong? What is wrong is that we have neglected the fact that there is a 180° phase shift for r_2 when it is formed at the bounce off wall 2. Why is there a 180° phase shift there? To see why, let's look at a situation in classical wave physics. Say a wave pulse is incident from a less dense string to a more dense string. Then, at the junction, there is partial transmission and partial reflection – and, as you know, the reflection is inverted.

fig 3

---

[1] ignoring, for the moment, back and forth multiple reflections resulting in an $r_1 r_2 r_1$

The signal for inversion is an increase in wave number in growing from medium 1 to medium 2. You can check that k increases by noting that the phase velocity $v_\phi = \sqrt{\frac{F}{\mu}} = \lambda f = \frac{\omega}{k}$ decreases in going to medium 2, and since the frequency is the same in both media, k increases (λ decreases). (The same sort of thing happens when light waves travel from a medium with index of reflection n_1 to a medium with index n_2.) Now look at deBroglie waves. We have, for any region with constant V,

$$K = \frac{1}{\hbar}\sqrt{2m(E-V)} \tag{21.14}$$

Thus, the smaller V, the bigger k. So, for our barrier, $k_{\text{III}} > k_{\text{II}}$, and therefore, the reflection r_2 suffers "inversion" (180° phase shift). However, r_1 does not. (Why?). So at resonance, $r_{\text{net}} = 0 \Rightarrow T = 1$. Some plots showing the behavior of T are shown for typical cases in figure 21.4. Of course, at all values of $\frac{E}{V_0}$, $R = 1 - T$.

fig 4

21.3 The Finite Square Well

We now consider the effects of an attractive, rather then a repulsive, energy profile. We consider only rectangular profiles (called finite square wells); the potential energy profile is shown in figure 21.5.

fig 5

Some books[2] take the bottom of the well to be $V = 0$ and the top to be $V = V_0 > 0$; however, in many applications, it is more convenient to define the energy zero so that the top of the well (and hence, the "outside world") is at $V = 0$ – this makes sense in, e.g., scattering problems in nuclear and particle physics and is in accord with the convention that $V \to 0$ as $x \to \pm\infty$; we will thus follow this second convention[3]. With this, the bound-state energies are negative.

fig 6

As in classical physics, all observable results are the for either convention;

---

[2] e.g., R. Hill, to be referred to later. This convention is common in elementary books.

[3] so does your Griffith text (section 2.6) in accord with his particle physics background

to pass from one to the other, simply note that

$$E \rightarrow E + V_0 \tag{21.15}$$

On the left, E is positive and less than V_0, and on the right, E is positive and less than V_0 (since $E < 0$).

21.3.1 Finite Square Well, Incident Plane Wave State With $E > 0$

We consider

fig 7

We note that we choose to center the well at $x = 0$ (so it runs from $x = -a$ to $x = a$). This is done to simplify the search for solutions by taking advantage of "parity" – see later. And, consider the case of an incident plane wave with $E > 0$. Then, for the eigenfunction,

$$\begin{aligned}
\psi_{\mathrm{I}}(x) &= \mathcal{A}\mathrm{e}^{ik_1x} + \mathcal{B}\mathrm{e}^{-ik_1x} \quad k_1\frac{\sqrt{2mE}}{\hbar} && (21.16)\\
\psi_{\mathrm{II}}(x) &= \mathcal{C}\mathrm{e}^{ik_2x} + \mathcal{D}\mathrm{e}^{-ik_2x} \quad k_2\frac{\sqrt{2m(e+V_0)}}{\hbar} && (21.17)\\
\psi_{\mathrm{III}}(x) &= \mathcal{F}\mathrm{e}^{-k_1x} && (21.18)
\end{aligned}$$

The easiest way to derive the transmission coefficient $T \equiv \frac{|\mathcal{F}|^2}{|\mathcal{A}|^2}$ is to start with the expression for T for the potential barrier and replace.

fig 8

thus

$$T_{E>0} = \left[1 + \frac{\sin^2(2k_2a)}{4\frac{E}{V_0}\left(1 + \frac{E}{V_0}\right)}\right]^{-1} \tag{21.19}$$

this expression for T is in mixed notation $\left[k_2 = \frac{\sqrt{2m(E+V_0)}}{\hbar}\right]$. It also provides the ratio of transmitted to incident currents, and hence, the transmission probability, since $k_3 = k_1$. The reflected probability is, of course

$$R = 1 - T \tag{21.20}$$

We see that, as wit the repulsive barrier, there are situations in which the well is "transparent" − i.e., $T \to 1$ (and $R \to 0$), namely, when

$$\sin(2k_2 a) \to 0 \;\Rightarrow\; 2k_2 a = n\pi,\; n = 1, 2, 3, \cdots \tag{21.21}$$

Naturally, this is the same condition as for the square barrier, namely $n\lambda_2 = 4a$ = back and forth distance in region II. As you can show, this says that for incident energies,

$$E = -V_0 + \frac{n^2\pi^2\hbar^2}{8ma^2} \tag{21.22}$$

there is perfect transmission. This perfect transmission was first observed experimentally. In 1921 (before quantum mechanics was discovered!) by Ramsauer & Townsend when they scattered low energy electrons off of noble atoms (like xenon) nuclei − at the right values of energy (given by the last equation), the electrons essentially pass right though the nuclei as if it weren't there! Experiments electron energy of ≈ 1 eV, and then working backward though the formula showed that the effective well depth presented by the xenon ion is ≈ 10 eV. (We use $a \sim 2\mathring{A}$ − as the diameter of the ion.) for an attractive square well, depending of the ratio of well width to depth, the resonances on T can be very sharp, as in figure 21.9 and figure 21.10.

fig 9

fig 10

We conclude this section with a look at three cases (different mean energies) of Gaussian wave packets approaching and "scattering" from finite square wells. (in each case, $\overline{E} > 0$

fig 11

fig 12

fig 13

21.3.2 Bound States of the Finite Square Well

We take the well to "run from $-a$ to a" for bound states $E < 0$ (where the well depth is to $-V_0$.

fig 14

As we remarked some time ago, since $E < 0$, regions I and III are forbidden; we expect most of the state function amplitude to be in region II with (for eigenfunctions) only a bit of leakage into regions I and III. Thus, for example, we might expect an eigenfunction to look, say, something like this

fig 15

These states are bound states – they hang around in the well region.

21.3.3 Bound States for Finite Square Well – Qualitative Observations

Firstly, we note that the the solution to the time independent Schrödinger equation(i.e., the eigenfunction) in region II can be written equivalently in any of the following ways:

$$\psi_{\text{II}}(x) = \mathcal{F}\text{e}^{ikx} + \mathcal{G}\text{e}^{-ikx} \tag{21.23}$$
$$\psi_{\text{II}}(x) = \mathcal{A}\sin(kx) + \mathcal{B}\cos(kx) \tag{21.24}$$
$$\psi_{\text{II}}(x) = \mathcal{Y}\text{e}^{ikx} + \mathcal{Z}\cos(kx) \tag{21.25}$$

These are all equivalent. The first form is convenient for considering probability currents (since its composed of traveling wave pieces). However, for the bound states we are interested in, the net current must be zero (no left-right probability flux) and so the sin-cosine form is more convenient. Another reason the sine-cosine form is more convenient is that these (sin and cos) are functions of definite parity (odd and even). As in the case of the infinite well, if the ordinate axis is centered, the eigenfunctions must have definite parity. Mathematical proof of this assertion is in Professor Hill's book (section 4.11) however, a "physics proof" of it is simply the following: As you know, in an eigenstate, probability density at any x is independent of time. Since the potential energy is left-right symmetric around $x = 0$, then so must $\psi^*(x)\psi(x)$ – i.e., $\psi^*(x)\psi(x)$ must be an even function. There are only two ways for this to happen – either $\psi(x)$ or $\psi^*(x)$ is odd. Which possibility corresponds to the ground state? As noted above, in region II, $k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$. How E means lok k, which means long wavelength. We note, for example, that

fig 16

In either case, though, these have to map onto the region I and region III pieces of the eigenfunction.

21.3.4 Parity of Eigenfunctions

Recall that inside the well (region II), we choose to write the general form of the eigenfunctions as

$$\psi_{\mathrm{II}}(x) = \mathcal{A}\sin(kx) + \mathcal{B}\cos(kx) \tag{21.26}$$

This is especially convenient as the form in light of our recent result that, if $V(x)$ is symmetric around some point (call it $x = 0$, so well runs $-a$ to a), then the eigenfunctions must have definite (plus or minus) parity around this point. Sine and cosine both have definite parity. So in region II, either

$$\psi(x) = \mathcal{A}\sin(kx) \tag{21.27}$$

or

$$\psi(x) = \mathcal{B}\cos(kx) \tag{21.28}$$

but not any linear combination of both.

So, with the well centered on $x = 0$, the ground state must be of even parity, and hence, inside the well must be of the form $\cos(kx)$ with $k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$. In regions I and III, the time independent Schrödinger equationis

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \;\Rightarrow\; \frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}E\psi \tag{21.29}$$

has solutions that are exponential (since $E < 0$), namely

$$\begin{aligned} \psi_{\mathrm{I}}(x) &= \mathcal{A}\mathrm{e}^{+\kappa x} && (21.30)\\ \psi_{\mathrm{III}}(x) &= \mathcal{D}\mathrm{e}^{-\kappa x} && (21.31) \end{aligned}$$

where $\kappa = \frac{\sqrt{-2mE}}{\hbar} > 0$. Since $\mathrm{e}^{-\kappa x}$ blows up at $x \to -\infty$ and $\mathrm{e}^{+\kappa x}$ blows up as $x \to +\infty$. So the tails in the "forbidden" regions are simply exponentials sine the ground state is even, $\mathcal{D} = \mathcal{A}$. We choose the even cosine in region II (since it has the longest wavelength) and match it to the external exponential fall offs. So, the ground state looks like

fig 17

The first excited state has next shorter wavelength in the well, hence, by similar logic, it must look like

fig 18

Why does this state have higher (but still negative) energy than the ground state? Answer: The wavelength is shorter in region II, and $\lambda \propto \frac{1}{\sqrt{E}}$

$$\lambda = \frac{2\pi}{k_2}, \quad k_2 = \frac{\sqrt{-2m(E+V_0)}}{\hbar} \tag{21.32}$$

Thus, E_2 is more than infinitesimally greater than E_1. Similar logic shows that successively higher bound states will have successively higher energies (E_3, E_4, $\cdots$) all of which are still negative, and eigenfunctions that alternate in parity. Of course, only certain values of energy are “allowed”.

21.3.5 Finite Square Well, Quantitative Treatment of Bound States

fig 19

Based on our previous discussion[4]

$$\psi_{\mathrm{II}}(x) = \begin{cases} \mathcal{A}\cos(kx) & \text{even} \\ \mathcal{A}\sin(kx) & \text{odd} \end{cases} \tag{21.33}$$

$$\psi_{\mathrm{III}}(x) = \mathcal{B}\mathrm{e}^{-\kappa x} \tag{21.34}$$

$$\psi_{\mathrm{I}}(x) = \begin{cases} \psi_{\mathrm{III}}(-x) & \text{even} \\ -\psi_{\mathrm{III}}(-x) & \text{odd} \end{cases} \tag{21.35}$$

where $k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$ and $\kappa = \sqrt{\frac{-2mE}{\hbar^2}}$. Since we have definite parity for each eigenfunction, we need only apply the boundary conditions at $x = a$ and they are automatically taken care of at $x = -a$ (even or odd). We do the even case.

The continuity of $\psi(x)$:

$$\mathcal{A}\cos(ka) = \mathcal{B}\mathrm{e}^{-\kappa a} \tag{21.36}$$

The continuity of $\psi'(x)$:

$$-k\mathcal{A}\sin(ka) = -\kappa\mathcal{B}\mathrm{e}^{-\kappa a} \tag{21.37}$$

Dividing these,

$$k\tan(ka) = \kappa \quad \text{(even case)} \tag{21.38}$$

---

[4] Reference: **Basic Quantum Mechanics** by Professor R. Hill, Sections 7.8, 7.9, howver, we do not use his potential energy convention (as noted earlier)

which is really an (transcendental) equation for the energy:

$$\sqrt{\frac{2m(E+V_0)}{\hbar^2}}\tan\left(\sqrt{\frac{2m(E+V_0)}{\hbar^2}}a\right)=\sqrt{\frac{-2mE}{\hbar^2}}\quad\text{even case}\tag{21.39}$$

For the odd case (as you can easily verify),

$$-k\cot(ka)=\kappa\quad\text{(odd case)}\tag{21.40}$$

We now simplify that form of equation (21.38) and (21.40) by defining dimensionless energy and potential energy variables (following Professor Hill, but in our convention)

Let E' be the difference of E and the bottom of the well, i.e., $E'\equiv E+V_0$ *fig 20*

Then, define a new dimensionless variable ν by

$$\nu^2\equiv\frac{E'}{E^{\text{inf}}_{\text{gnd}}}\tag{21.41}$$

where $E^{\text{inf}}_{\text{gnd}}$ is the amount by which the ground-state energy in the equivalent width ($2a$) infinite square well is above the floor of that well.

$$E^{\text{inf}}_{\text{gnd}}=\frac{\pi^2\hbar^2}{2m(2a)^2}\tag{21.42}$$

thus

$$\nu^2=\frac{E'}{\frac{\pi^2\hbar^2}{8ma^2}}\tag{21.43}$$

We also define another dimensionless less variable ν by

$$\nu^2\equiv\frac{V_0}{E^{\text{inf}}_{\text{gnd}}}\tag{21.44}$$

Thus

$$\mu^2=\frac{8m}{\pi^2\hbar^2}V_0a^2\tag{21.45}$$

so μ is a measure of the "strength" of the well – i.e., $\mu\propto\sqrt{V_0}a$. μ is then also dimensionless. Equations (21.38) and (21.40) can then be written in terms of μ and ν as

$$\nu \tan\left(\frac{\pi}{2}\nu\right) = \sqrt{\mu^2 - \nu^2} \quad \text{even solutions} \tag{21.46}$$

$$-\nu \cot\left(\frac{\pi}{2}\nu\right) = \sqrt{\mu^2 - \nu^2} \quad \text{odd solutions} \tag{21.47}$$

These can be solved graphically (see figure 21.21) by plotting the left-hand sides of equations (21.46) and (21.47) and also their right hand side versus ν – solutions for each type (odd or even) are defined by where these curves intersect. One nice aspect of this is that , since μ is a constant ($\mu \propto \sqrt{V_0}a$, $\sqrt{\mu^2 - \nu^2}$ is a quarter circle of radius μ on such a plot.

fig 21

Figure 21.21 shows the situation for $\mu = 2.5$ so $V_0 = \frac{(2.5)^2\pi^2\hbar^2}{8ma^2}$. So

$$V_0 a^2 \approx 0.78\pi^2\hbar^2 \tag{21.48}$$

(in general. μ is, as we remarked earlier, a measure of $a\sqrt{V_0}$). We see that, for this value of μ (i.e., this product of $a\sqrt{V_0}$) thre are 3 bound ($E < V_0$) states. Based on our parity considerations, these bound states must look (at least semi-quantitatively) as shown in figure 21.22.

fig 22

To find the intersection points you can use trial and error with a pocket calculator, or, if you prefer, Newton-Raphson iteration in a spreadsheet such as Microsoft Excel. (This is explained in loving detail in section 7.9 of Professor Hill's book manuscript). From the values of ν at the intersection points you can easily obtain the energy for each bound state, and from that, the values of k and κ for the state. Thus, without bothering with the overall normalization, you can, if called to, write out the entire state functions. We note that, as we expected, the energies are always a bit lower than the corresponding energies for an infinite square well of the same width.

fig 23

We note an interesting point – by looking at figure 21.21 we see that, no matter how shallow the well (i.e., how small μ is) there is always at least one bound state. This, incidentally, is only true in one-dimensional wells – in the real world, three dimensional wells, there can be no bound states.

Chapter 22

Twenty-Second Class: The Finite Square Well

Tuesday, November 11, 2008

22.1 Brief Review of Quantitative Solutions for Finite Square Well

Let's recall some features of the path to our solution for the case $E < V_0$[1].

fig 1

The eigenfunctions must have definite parity (even or odd), thus

$$\psi_{\mathrm{II}}(x) = \begin{cases} \mathcal{A}\cos(kx) & \text{(even)} \\ \mathcal{A}\sin(kx) & \text{(odd)} \end{cases} \tag{22.1}$$

$$\psi_{\mathrm{III}}(x) = \mathcal{B}\mathrm{e}^{-\kappa x} \tag{22.2}$$

$$\psi_{\mathrm{I}}(x) = \begin{cases} \psi_{\mathrm{III}}(-x) & \text{(even)} \\ -\psi_{\mathrm{III}}(-x) & \text{(odd)} \end{cases} \tag{22.3}$$

Since higher energies implies more curvature of ψ, and since the odd solutions have $\psi = 0$ at $x = 0$,the ground state must be of even parity (cosine in the well) and hence the first excited state is of odd parity, etc. Since we have definite parity for each eigenfunction, we need only apply the boundary conditions at $x = a$ and they are automatically taken care of at $x = -a$ (even or odd). We do the even case.

Continuity of ψ: $\mathcal{A}\cos(ka) = \mathcal{B}\mathrm{e}^{-\kappa a}$

Continuity of ψ': $-k\mathcal{A}\sin(ka) = -\kappa\mathcal{B}\mathrm{e}^{-\kappa a}$

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[1] reference: **Basic Quantum Mechanics** by R. Hill, sections 7.8 and 7.9

or dividing

$$\begin{aligned} k\tan(ka) &= \kappa \quad \text{(even)} & (22.4)\\ -k\cot(ka) &= \kappa \quad \text{(odd)} & (22.5)\end{aligned}$$

We solved these transcendental equations graphically – we defined dimensionless variables

$$\nu^2 \equiv \frac{E'}{E^{\text{inf}}_{\text{gnd}}} \tag{22.6}$$

$$\mu^2 \equiv \frac{V_0}{E^{\text{inf}}_{\text{gnd}}} \tag{22.7}$$

where $E' = E - (-V_0) = E + V_0$ and $E^{\text{inf}}_{\text{gnd}}$ is the ground state energy of an infinite square well of same width ($2a$). ($\mu \propto \sqrt{V_0}a$). In terms of which the transcendental equations become

$$\nu\tan\left(\frac{\pi}{2}\nu\right) = \sqrt{\mu^2-\nu^2} \quad \text{(even)} \tag{22.8}$$

$$-\nu\cot\left(\frac{\pi}{2}\nu\right) = \sqrt{\mu^2-\nu^2} \quad \text{(odd)} \tag{22.9}$$

and the plotted left-hand sides and the right-hand side on one plot versus ν; from the intersection points you can easily deduce the energies.

fig 2

From knowing the energies you can then deduce the full form of each of the eigenstates $\psi_{\text{n}}(x,t)$; probability you will do an example of this in the homework.

22.2 Some Intuition

Let's now seek some intuition about why only certain energies are allowed. Of course, we already understand the basic reason for this[2], but here, we can provide a bit of additional insight for the finite square well. We consider the ground state. Inside the well the solution is a cosine; outside it is exponential . We must have both $\psi(x)$ and $\psi'(x)$ continuous across the two boundaries ($x = \pm a$).

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[2] section B of class notes for class of Thursday, October 16, especially the discussion of curvature of ψ and its implications therein.

Now, there is no problem in making ψ continuous at $x = \pm a$ for any wavelength (i.e., for any value of energy) in region II − both ψ_{I} and ψ_{III} have their own (same) constant multiplier that can be arbitrarily adjusted to match any amplitude at $x = a$ (the amplitude at $x = -a$ is the same as that at $x = a$ since ψ is even. However, in general, continuity of ψ' is not simultaneously achieved. To see this: If E is chosen too low[3], the slope of the exponential is too steep at the edge of the well (or, if you prefer, the slope of the cosine is not steep enough):

$$k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}} \; E \text{ to neg.} \Rightarrow \text{ low } k \Rightarrow \text{ low cosine slope} \tag{22.10}$$

$$\kappa = \sqrt{\frac{-2mE}{\hbar^2}} \; E \text{ too neg.} \Rightarrow \text{ high } \kappa \Rightarrow \text{ high exponential slope} \tag{22.11}$$

So, if E is too negative, the situation is shown in figure 22.3.

fig 3

Which has discontinuous slope at $x = \pm a$. If E is too high, the situation is shown in figure 22.4/

fig 4

which also has discontinuous slope. Only for a particular value of E do we get a ground state that is continuous in both ψ and ψ'

fig 5

Now let us think about the energies of the states. How do they compare to the energies of an infinite well of the same width? We expect they be a bit lower than those of the infinite square well. Why? Because in the ground state we don't fit half a wavelength in the well, whereas in the infinite well we do. So, for the finite well, the wavelength in the interior to the well region is a little longer than that for the infinite well, so the energy is a little lower. This is true for each eigenstate.

22.3 Applications

An understanding of the finite square well is extremely important for understanding many applications, both in nature and in technology. For example

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[3] i.e., too negative, or too little bigger than $-V_0$.

many of the properties of the conduction of electricity in metals (quantum theory of conduction) can be understood on the basis of the "quasi-free electron model"' in which "free" electrons are moving in a (three-dimensional) finite square well.

fig 6

Most of these applications involve three-dimensional wells and consideration of states of many particles in the well at once. We're not quite ready for these, so we defer detailed consideration of them to the next course. There is, however, one important application that we are about ready to briefly treat – that of a "free" neutron inside an atomic nucleus.

22.3.1 Application – Nuclear Potential and the Deuteron

A good application pertains to a simplified picture of a neutron inside the nucleus. We consider it relatively free to move about the interior of the (we assume spherical) nucleus, but it is pulled back strongly if it tries to reach the edge, which is at a few $\times 10^{-13}$ cm. We assume such a potential energy curve looks more or less like figure 22.7.

fig 7

The "smoothed out" version shown in figure 22.7, at least in rough approximation. For "simplicity", we assume that the neutron is in a spherical well (sharp edged)

$$V(r) = \begin{cases} -V_0 & 0 \le r \le b \\ 0 & r > b \end{cases} \tag{22.12}$$

For this we need the Schrödinger equation in three dimensions. We will develop this a pit later in the course, but so as to not get distracted by that development now. I will tell you that, for state functions with no dependence on direction (only depends on r, distance from an origin), if we define

$$u(r) \equiv r\psi(r) \tag{22.13}$$

then $u(r)$ obeys a very very familiar Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2u(r)}{dr^2} + V(r)u(r) = Eu(r) \tag{22.14}$$

which is identical to the one-dimensional time independent Schrödinger equationwe are used to. Here μ is the "reduced mass", which should be familiar from classical mechanics. (If it is not, just think of μ as the mass). So, for our problem of a "free" neutron inside a nucleus,

$$-\frac{\hbar^2}{2\mu}\frac{d^2u(r)}{dr^2} - V_0 u = -Bu \quad r \le b \tag{22.15}$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2u(r)}{dr^2} = -Bu \quad r > b \tag{22.16}$$

where B is the binding energy ($-B < 0$ is the actual energy of the neutron in the nucleus). Note that our finite well is now, of course, "one-sided":

fig 8

Now, for $r \le b$, the solution is

$$u(r) = \mathcal{A}\sin(kr) + \mathcal{B}\cos(kr) \tag{22.17}$$

where $k = \frac{\sqrt{2\mu[-B-(-V_0)]}}{\hbar} = \frac{\sqrt{2\mu(V_0-B)}}{\hbar}$. Note that the first boundary condition is

$$u(r) = 0atr = 0 \tag{22.18}$$

so the ground state cannot be cosine $-$ nor can cosine be present in any of the bound states[4] $- B = 0$, so

$$u(r) = \mathcal{A}\sin(kr) \tag{22.19}$$

since $u(r) = r\psi(r)$,

$$\psi_{\text{in}}(r) = \frac{\mathcal{A}}{r}\sin(kr) \quad r \le b \tag{22.20}$$

Now, for $r > b$, the solution is

$$u(r) = \mathcal{C}\mathrm{e}^{-\kappa r} + \mathcal{F}\mathrm{e}^{+\kappa r} \tag{22.21}$$

where $\kappa = \sqrt{\frac{2\mu B}{\hbar^2}}$. Since $\psi(r)$ must goto zero as r goes to infinity, $\mathcal{F} = 0$. Now, we have to match the solutions at $r = b$

1. Continuity of $\psi(r = b)$:

$$\frac{\mathcal{A}}{b}\sin(kb) = \frac{\mathcal{C}}{b}\mathrm{e}^{-\kappa b} \;\Rightarrow\; \mathcal{A}\sin(kB) = \mathcal{C}\mathrm{e}^{-\kappa b} \tag{22.22}$$

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[4] There is not problem with our "parity theorem" here the well is not symmetric around $r = 0$

2. Continuity of $\psi'(r=b)$:

$$k\mathcal{A}\cos(kB) = -\kappa\mathcal{C}\mathrm{e}^{-\kappa b} \tag{22.23}$$

dividing,

$$k\cot(kb) = -\kappa \tag{22.24}$$

This is exactly the same as the condition for the odd solutions of the one-dimensional finite square well. (as you will see by reading section 7.10 of Hill[5], this is not accident). It follows from this that a three dimensional well can be too shallow to have any bound states! If there is a bound state, the interior sine wave function $u(r)$ must pass $\pi/2$ in phase at $r = b$ so that it is falling and can connect on to the decreasing exponential outside as in figure 22.9.

fig 9

As a concrete example, we consider the deuteron (bound state of neutron and proton, nucleus of deuterium). We take $b \approx 1.4 \times 10^{-13}$ cm (recall that $R \sim 1.2A^{1/3}$ from Rutherford) and $B \approx 2.225$ MeV (measured as energy of the photon (γ) in $n + p \to d + \gamma$). (note: Here, the reduced mass, $\mu = \frac{m_p}{2}$ since $m_p \approx m_n$). Then our condition

$$k\cot(kb = -\kappa \tag{22.25}$$

becomes

$$\frac{\sqrt{2\mu(V_0 - B)}}{\hbar}\cot\left(\frac{\sqrt{2\mu(V_0 - B)}}{\hbar}b\right) = -\frac{\sqrt{2\mu B}}{\hbar} \tag{22.26}$$

As we will see in a moment, $V_0 \gg B$ (binding energy small compared to well depth – deuteron is "barely bound"). Therefore, to ger an idea of what is going on, we begin by setting $V_0 - B \approx V_0$. Then, our condition is

$$\frac{\sqrt{2\mu V_0}}{\hbar}\cot\left(\frac{\sqrt{2\mu V_0}}{\hbar}b\right) \approx -\frac{\sqrt{2\mu B}}{\hbar} \tag{22.27}$$

or

$$\cot\left(\frac{\sqrt{2\mu V_0}}{\hbar}b\right) \approx -\sqrt{\frac{B}{V_0}} \tag{22.28}$$

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[5] Please consider this a reading assignment

Since, $B \ll V_0$, as a first approximation

$$\cot\left(\frac{\sqrt{2\mu V_0}}{\hbar}b\right) \approx 0 \tag{22.29}$$

The bound state then corresponds to

$$\frac{\sqrt{2\mu V_0}}{\hbar}b \approx \frac{\pi}{2} \tag{22.30}$$

or

$$V_0 \approx \frac{\pi^2\hbar^2}{8\mu b^2} \approx \frac{\pi^2\hbar^2}{4m_p b^2} \tag{22.31}$$

Let's put some numbers into this: We have

$$\begin{aligned} \hbar^2 &\approx \left(6.6 \times 10^{-16}\ \text{eV}\cdot\text{s}\right)^2 \\ b &\approx 1.4 \times 10^{-15}\ \text{m} \\ \mu &\approx \frac{0.5\ \text{GeV}}{c^2} = \frac{5 \times 10^8\ \text{eV}}{c^2} \end{aligned}$$

($\mu \approx m_p/2$). So,

$$V_0 \approx \frac{(10)\left(44 \times 10^{-32}\right)\text{eV}^2 \cdot \text{s}^2 \left(9 \times 10^{16}\right)\text{m}^2/\text{s}^2}{4\left(10^9\text{eV}\right)\left(2 \times 10^{-30}\text{m}^2\right)} \tag{22.32}$$

$$V_0 \approx 50\text{MeV} \tag{22.33}$$

(believed to be about right) This confirms our approximation $V_0 \gg B$. Actually, $\cot\left(\frac{\sqrt{2\mu V_0}}{\hbar}b\right)$ is a little less than zero. Therefore, $\frac{\sqrt{2\mu V_0}}{\hbar}b$ is a little greater than zero, so $\frac{\sqrt{2\mu(V_0-B)}}{\hbar}b = kB$ is a little greater than $\pi/2$. As it must be to map onto the decaying exponential outside the well.

22.4 Further Intuition into Bound State Eigenfunctions

Frequently − usually, in real problems we have to deal with potential wells with non-square shapes. Very typically, the "bottom" of the well is not constant. Such problems, while ubiquitous in research, can be quite hard to solve analytically, and for this reason they are usually ignored in elementary texts[6] − this is unfortunate!

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[6] a notable exception is **Quantum Physics** by Edwin Taylor.

As a concrete example, consider the "simple" problem of a particle in an uniform force field − e.g., a particle in the gravitational field new earth's surface. Then $V(y) = mgy$. If the particle is confined to a region (y_1, y_2 boundaries), then the potential energy profile is shown in figure 22.10.

fig 10

Another example: consider the "free" electron in a metal wire segment running from x_1 to x_2. As we've already remarked, in the "quasi-free electron model", the electron in the metal are considered to be able to more freely in a finite potential well.

fig 11

Now suppose we apply a constant electric field − e.g., from a battery hooked up to the ends of the wire. Them the potential energy varies linearly along the length of the wire ($V = -kx \;\Rightarrow\; E = -\frac{dV}{dx} = k = \text{constant}$). The electrons are now in a linearly ramped well.

fig 12

Of course, this leads to the conduction of electric current. An understanding of the quantum mechanics of this problem leads to the first steps in understanding the quantum theory of conduction! While obviously very important, gaining a full understanding of this not simple, and today, we limit ourselves to just a few semi-quantitative first remarks about the $E < 0$ eigenfunctions in such a well. As a paradigm for this, take $V = gx$, where g is a constant. Then, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + gx\psi(x) = E\psi(x) \tag{22.34}$$

We can simplify the appearance of this by defining

$$\xi \equiv \left(x - \frac{E}{g}\right)\sqrt[3]{\frac{2mg}{\hbar^2}} \tag{22.35}$$

the the Schrödinger equation is

$$\frac{d^2\psi(\xi)}{d\xi^2} = -\xi\psi(\xi) \tag{22.36}$$

This equation looks very harmless, but, in fact, the solution to it cannot be written in terms of a finite number of elementary functions! The solution to equation (22.34) turns out to be the so-called "Airy Integral"

$$Ai(\xi) \equiv \frac{1}{\pi} \lim_{\varepsilon \to 0} \int_0^\infty \mathrm{e}^{-\varepsilon u} \cos\left(\frac{u^3}{3} + \xi u\right) \, du \tag{22.37}$$

In this course, we won't get involved with this function. however, it would be nice to know if we could intuit anything about the result without going through the mathematics. As I hope to show you, indeed we can, and our thought son this will apply much more generally than to just this problem.

22.5 Qualitative Eigenfunctions for Wells

Suppose first that we have a "split-level" well and we want the bound-state eigenfunction.

fig 13

Now, we could solve this exactly, but let's see what we can get by just "thinking".

1. In the internal regions (I and II), ψ is sinusoidal and

   $$k^2 = \frac{2m(E-V)}{\hbar^2} = \frac{2m}{\hbar^2}(K.E.) = \frac{2m}{\hbar^2}\frac{p^2}{2m} = \frac{p^2}{\hbar^2} = \frac{2\pi}{\lambda^2} \tag{22.38}$$

   Thus, large $E - V \;\Rightarrow\;$ small λ. So, $\lambda_{\mathrm{I}} < \lambda_{\mathrm{II}}$.

2. In the internal regions we can write, for some phases φ_i,

   $$\psi_i(x) = \mathcal{A}_i \sin(k_i x + \varphi_i) \quad i = \mathrm{I,II} \tag{22.39}$$

   Now consider the slope

   $$S_i = \frac{d\psi_i(x)}{dx} = k_i \mathcal{A}_i \cos(k_1 x + \varphi_i) \tag{22.40}$$

   so

   $$\frac{S_i}{k_1} = \mathcal{A}_i \cos(k_i x + \varphi_i) \tag{22.41}$$

   so

   $$\frac{S_i}{k_i} + \psi_i^2 = \mathcal{A}_i^2 \cos^2(k_i x + \varphi_i) + \mathcal{A}_i 62 \sin^2(k_i x + \varphi_i) = \mathcal{A}_i^2 \tag{22.42}$$

   now since $k_{\mathrm{II}} < k_{\mathrm{I}}$, and since both S and ψ are continuous across the step in the well bottom, it follows that $\mathcal{A}_{\mathrm{II}} > \mathcal{A}_{\mathrm{I}}$!

3. Number of nodes: We know that from our previous experience that ψ_n should have $n-1$ nodes inside the well. So suppose someone asks for the fifth lowest energy level in our split level well. We see in advance that it must look pretty muck like what is shown in figure 22.14.

   fig 14

Now, any shape well can be approximated by a succession of narrow step wells. Consider for example, the "ramp-bottom" well

fig 15

(the dotted line shows an approximation to it). Then, from our considerations, the say, fifth and seventh levels in this well have eigenfunctions that must look like figure 22.16.

fig 16

Here's a way of remembering that the amplitude is bigger in the shallower part of the well. Consider the classical limit in the sense of large n. The eigenfunction would then have a large number of zig zags. On which side of the well, shallow or deep, must ψ have greater amplitude? A classical particle spends more time where it is moving slowly. In the well in figure 22.16, the classical acceleration would be to the left ($F = -\frac{dV}{dx}$). Therefore, the classical particle spends more time (and is thus more likely to be found, in a randomly timed snapshot) on the right side. Hence $P(x) = \psi^*(x)\psi(x)$ must be greater on the right side, therefore, the amplitude of ψ is greater on the right side. Hence, shallower side of well ↔ greater amplitude for ψ. Something of a reversal of this logic gives us insight into where classical physics comes from: a narrow wave packet centered on very large n ("classical') accelerates on moving from the shallow to the deep end of the well – this is because that "local phase velocity" of any component of the packet is $v_\varphi(k,x) = \frac{\omega}{k(x)}$, and $k(x)$ increases for each component as the packet moves to the deep end of the well. (If the phase velocity of every component increases as the packet moves, then the center of the packet is accelerating.) Now, if $V = V(x)$, classically there is a force $F = -\frac{dV(x)}{dx}$ toward the deeper part of the well, so this looks like the center of the packet is obeying $a \propto F$ – i.e., this looks like Newton's second law $a = \frac{F}{m}$. Of course, we haven't shown that our "a" (we really mean $\frac{d^2\langle x\rangle}{dt^2}$) for that packet is proportional to $\frac{1}{m}$ and othr details, but, a bit later in our course we hope to show that, indeed, for this situation, as well as for many others

$$m\frac{d^2\left\langle x\right\rangle}{dt^2} = -\frac{d\left\langle V\right\rangle}{dx} \sim \text{“}F\text{”} \tag{22.43}$$

(The general result is called Ehrenfest's theorem). Now let us return to our constant force problem. If this is true in a limited region ($x = -a \rightarrow x = a$, say) as it always would be, then $V(x)$ looks like

fig 17

This is exactly what we just looked at! Now, let's look at the exact Airy function. It looks like figure 22.18.

fig 18

Note that we are plotting against $\xi = \text{constant} \times \left(x - \frac{E}{g}\right)$. $\psi(x) = \psi\left(\xi(x)\right)$ must be unravelled from this. Since we've using this problem only as a thought spring board, we won't worry about that.

Chapter 23

Twenty-third Class

Thursday, November 13, 2008 Exam 2

Chapter 24

Twenty-Forth Class: The Simple Harmonic Oscillator

Tuesday, November 18, 2008

24.1 Eigenstate in a Harmonic Oscillator Potential Energy Profile

We consider states for a potential energy profile that is quadratic, i.e.

$$V(x) = \frac{1}{2}kx^2 \tag{24.1}$$

where k is a constant.

fig 1

Classically, then, there is a return force

$$F(x) = -\frac{dV(x)}{dx} = -kx \tag{24.2}$$

which leads to

$$x(t) = \mathcal{A}\cos\left(\sqrt{\frac{k}{m}}t + \phi\right) \tag{24.3}$$

We define $\omega \equiv \sqrt{\frac{k}{m}}$, which is the classical frequency. In quantum mechanics, the Schrödinger equation for this case is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x) \tag{24.4}$$

To construct the general state function in this potential energy profile, we would start by finding the eigenstate through the solution of the Schrödinger equation.

24.1.1 Intuition

However, before we get involved in any detailed mathematically it is well to ask what we expect the eigenfunctions to look like. In our previous considerations of "split-level" wells with flat segments, we found rigorously that the amplitude is greater and the curvature less in the shallower part. Our quadratic potential is no composed of rectangular segments, so we cannot rigorously expect similar conclusions to apply to lowest-lying eigenfunctions here, but we can appeal to expectations for the classical limit − as we discussed, on these grounds, we expect the amplitude to be greater and the curvature less in the shallower parts of $V(x)$ (compared to E), certainly for high n. Also we expect ψ_n to have $(n-1)$ nodes, and for there to be leakage of probability onto the classically forbidden region. However, in the classical (large n) limit, the "percentage leakage" should go to zero (since in that limit, we must recover classical physics). Let us now think through that states "one-by-one".

1. **Parity**: Since $V(x)$ is even, all eigenfunctions must have definite parity (even or odd).
2. **Ground-State**: To minimize curvature (and hence, to minimize the energy), must be a smooth, continuous even function of x with no nodes. thus, for the ground state, the amplitude cannot be greater in the shallower parts of $V(x)$. However, that is not a contradiction since this is not large n and not a flat bottomed split-level well. So, the ground state must look something like

   fig 2

   where $\pm x_1$ are the classical turning points.
3. **First Excited State**: To minimize curvature (but be more curved than the ground state) must be a smooth continuous odd function of x with one node which must be at $x = 0$. Thus, again, it is not possible for the amplitude to be always greater in more shallow regions

   fig 3
4. **Second Excited State**: ψ must be even with two nodes, and hence

it is now geometrically possible for the amplitude to be greater in the shallow parts of the well (see figure 23.4)

5. **Further Excited States**: In summary, we expect that the eigenfunctions should qualitatively look like those shown in figure 23.4

   fig 4

   The vertical lines indicate that limits of the classically allowed region in each case. Note that the spacing increases as n does, since E increases as n does, so the intersection points of E with V move further apart (see figure 23.5).

fig 5

Figure 23.5 shows, of course, the actual eigenfunctions. It is clear that these look qualitatively as we expect (amplitudes for $n = 2,\ n = 3$ bigger in shallower parts of well, etc.). The figure 23.6 shows $|\psi_{100}(x)|^2$, and in it you can see both the expected amplitude increase and the expected "wavelength" decrease as you move to the shallower parts of the well for the fixed value of energy.

fig 6

24.1.2 Mathematical Treatment

Now that we have some intuition, we are ready for the math. We return to the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x) \tag{24.5}$$

Simplify the algebra, we define two dimensionless variables

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x \tag{24.6}$$

$$K \equiv \frac{2E}{\hbar\omega} \tag{24.7}$$

this leads to energy in units of $\frac{\hbar\omega}{2}$. In terms of these, the Schrödinger equation is

$$\frac{d^2\psi(\xi)}{d\xi^2} = \left(\xi^2 - K\right)\psi(\xi) \tag{24.8}$$

which is another of these simple-looking differential equations that is quite hard to solve directly. To approach this, we look at some limits to get some insight. Consider the limit of very large ξ (very large x). Then equation (23.8) becomes

$$\frac{d^2\psi(\xi)}{d\xi^2} \approx \xi^2\psi(\xi) \tag{24.9}$$

Even this equation cannot be solved exactly, but an approximate solution is

$$\psi(\xi) = \mathcal{A}\mathrm{e}^{\frac{\xi^2}{2}} + \mathcal{B}\mathrm{e}^{-\frac{\xi^2}{2}} \tag{24.10}$$

To check this, note

$$\frac{d^2\psi(\xi)}{d\xi^2} = \mathcal{A}\left(1+\xi^2\right)\mathrm{e}^{\frac{\xi^2}{2}} - \mathcal{B}\left(1-\xi^2\right)\mathrm{e}^{-\frac{\xi^2}{2}} \tag{24.11}$$

so, for $\xi \gg 1$

$$\frac{d^2\psi(\xi)}{d\xi^2} \approx \mathcal{A}\xi^2\mathrm{e}^{\frac{\xi^2}{2}} + \mathcal{B}\xi^2\mathrm{e}^{-\frac{\xi^2}{2}} = \xi^2\psi \tag{24.12}$$

Now, we want $\psi(\xi)$ to be well-behaved as $\xi \to \infty$, therefore, $\mathcal{A} = 0$, so for large ξ

$$\psi(\xi) \to \mathcal{B}\mathrm{e}^{-\frac{\xi^2}{2}} \tag{24.13}$$

Now we really want a solution to equation (23.8). Spurred by our insight in equation (23.13), let's factor $\mathrm{e}^{-\frac{\xi^2}{2}}$ out of ψ, so we write

$$\psi(\xi) \equiv h(\xi)\mathrm{e}^{-\frac{\xi^2}{2}} \tag{24.14}$$

Of course we sill don't know $h(\xi)$. Therefore, let us find the differential equation it obeys. Now $\psi(\xi)$ must obey equation (23.8). To get $\frac{d^2\psi}{d\xi^2}$ we work through $h(\xi)$

$$\begin{aligned} \frac{d\psi}{d\xi} &= \frac{dh}{d\xi}\mathrm{e}^{-\frac{\xi^2}{2}} - \xi h(\xi)\mathrm{e}^{-\frac{\xi^2}{2}} = \left(\frac{dh(\xi)}{d\xi} - \xi h(\xi)\right)\mathrm{e}^{-\frac{\xi^2}{2}} && (24.15) \\ \frac{d^2\psi}{d\xi^2} &= \left(\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + \left(\xi^2-1\right)h\right)\mathrm{e}^{-\frac{\xi^2}{2}} && (24.16) \end{aligned}$$

so equation (23.8) is

$$\frac{d^2h(\xi)}{d\xi^2} - 2\xi\frac{dh(\xi)}{d\xi} + (K-1)h(\xi) = 0 \tag{24.17}$$

Now this is an equation that is known to mathematicians and physicists. It was first studied by Charles Hermite in the 19^{th}century, and is therefore, called "Hermite's equation". To solve it, we use the method of power series: We try a power series solution.

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + a_3\xi^3 + \cdots = \sum_{j=0}^{\infty} a_j\xi^j \tag{24.18}$$

Our goal is to determine the a_j's. Now equation (23.18) leads to

$$\frac{dh}{d\xi} = \sum_{j=0}^{\infty} ja_j\xi^{j-1} \tag{24.19}$$

so

$$2\xi\frac{dh}{d\xi} = 2\sum_{j=0}^{\infty} ja_j\xi^j \tag{24.20}$$

and

$$\frac{d^2h}{d\xi^2} = \sum_{j=0}^{\infty}(j-1)(j)a_j\xi^{j-2} = \sum_{j=0}^{\infty}(j+1)(j+2)a_{j+2}\xi^j \tag{24.21}$$

since the first two terms of the left-hand sum are zero. We put these into equation (23.17), finding

$$\sum_{j=0}\infty\left[(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j\right]\xi^j = 0 \tag{24.22}$$

since this must be true for all ξ, the coefficient of each power of ξ is separately zero, so

$$(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j = 0 \tag{24.23}$$

for all j. This leads to

$$a_{j+2} = \frac{2j+1-K}{(j+1)(j+2)}a_j \tag{24.24}$$

A relation like this is called a recursion relation. From it, we can express all even-numbered a's in terms of a_0 and all odd-numbered a's in terms of a_1:

$$a_2 = \frac{1-K}{2}a_0, a_4 = \frac{5-K}{12}a_2 = \frac{(5-K)(1-K)}{24}a_0, \cdots \tag{24.25}$$

$$a_3 = \frac{3-K}{6}a_1, a_5 = \frac{7-K}{20}a_3 = \frac{(7-K)(3-K)}{120}a_1, \cdots \tag{24.26}$$

Thus, we have two independent series solution of equation (23.17); therefore, the general solution of (23.17) is a linear combination of them

$$h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi) \tag{24.27}$$

$$\begin{aligned} h_{\text{even}} &= a_0 + a_2\xi^2 + a_4\xi^4 + \cdots && (24.28) \\ h_{\text{odd}} &= a + 0\xi + a_3\xi^3 + a_5\xi^5 + \cdots && (24.29) \end{aligned}$$

These are called Hermite functions. However, notice a problem: consider the recursion relation from equation (23.24) for large j

$$a_{j+2} \approx \frac{2}{j} a_j \tag{24.30}$$

This is an algebraic equation with solution

$$a_j \approx \frac{C}{\left(\frac{j}{2}\right)!} \tag{24.31}$$

for any constant C.Now consider the behavior of the Hermite functions at large ξ. There, the higher powers of ξ dominate, so

$$h(\xi) \to C \sum \frac{1}{\left(\frac{j}{2}\right)!}\xi^j \approx C \sum \frac{1}{j!}\xi^{2j} \approx C\mathrm{e}^{\xi^2} \tag{24.32}$$

Then

$$\psi(\xi) = \mathrm{e}^{-\frac{\xi^2}{2}} h(\xi) \lim_{\xi\to\infty} \Rightarrow C\mathrm{e}^{\frac{\xi^2}{2}} \tag{24.33}$$

which diverges. Hence, neither Hermite function is a useful solution for us! How do we wiggle out of this problem? This leads to a loophole worthy of any attorney: the power series must terminate as polynomials!

There is some highest j for which $a_j \neq 0$. Then the recursion relation must lead to $a_{j+2} = 0$! Now, the recursion relation was

$$a_{j+2} = \frac{2j + 1 - K}{(j+1)(j+2)} a_j \tag{24.34}$$

so we require

$$2j + 1 - K = 0 \tag{24.35}$$

for $j = n$ (highest nonzero j). This leads to

$$K = 2n + 1 \tag{24.36}$$

but, $K \equiv \frac{2E}{\hbar\omega}$, so

$$\frac{2E}{\hbar\omega} = 2n + 1 \tag{24.37}$$

and by solving for the energy leads to

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad n = 1, 2, 3, \cdots \tag{24.38}$$

so, the allowed energies (energies of the eigenstates) are given by this formula!

24.2 Harmonic Oscillator Potential, Continued

We saw that for the potential energy profile $V(x) = \frac{1}{2}kx^2$. the energy values associated with the eigenstates are given by

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{24.39}$$

This is very basic and very important result in quantum mechanics. We see that the energy levels are equally spaced in units of $\hbar$ times the classical frequency, and that the ground state does not have zero energy, but rather energy $\frac{1}{2}\hbar\omega$ ("zero-point" energy) (n=0).

fig 7

Since so many potentials have minima, which are therefore locally quadratic (by Taylor expansion), "nothing is still" in quantum mechanics is a oft-repeated rule of thumb. Now let us look at our eigenfunctions. The recursion relation is

$$a_{j+2} = \frac{2j + 1 - K}{(j+1)(j+2)}a_j \tag{24.40}$$

and the series termination condition is

$$K = \frac{2E}{\hbar\omega} = 2n + 1 \tag{24.41}$$

leading to

$$a_{j+2} = \frac{2j + 1 - 2n - 1}{(j+1)(j+2)}a_j = -\frac{2(n-j)}{(j+1)(j+2)}a_j \tag{24.42}$$

We consider successive values of n in turn:

- $n = 0$: Then $a_2 = 0$. To kill the series h_{odd}, we choose $a_1 = 0$, so

  $$h_0(\xi) = a_0 \tag{24.43}$$

  and

  $$\psi_0(\xi) = a_0 \mathrm{e}^{-\frac{\xi^2}{2}} \tag{24.44}$$

  which means

  $$\psi_0(x) = a_0 \mathrm{e}^{-\frac{m\omega}{2\hbar}x^2} \tag{24.45}$$

  We see that the ground state is Gaussian in x (or in ξ). The normalized eigenfunction is

  $$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \mathrm{e}^{-\frac{m\omega}{2\hbar}x^2} \tag{24.46}$$

  since

  $$\int_{-\infty}^{+\infty} \mathrm{e}^{\frac{m\omega}{\hbar}x^2}\, dx = \sqrt{\frac{\pi\hbar}{m\omega}} \tag{24.47}$$

  Note that, as we expect, the ground state eigenfunction has no nodes. Note also there is significant penetration into the classically forbidden region.

  fig 8

- $n = 1$: We choose $a_0 = 0$ to kill off h_{even}. Then the recursion relation with $n = 1$, leads to $a_3 = 0$, so ξ,

  $$\begin{aligned} h_1(\xi) &= a_1\xi && (24.48)\\ \psi_1(\xi) &= a_1\xi \mathrm{e}^{-\frac{\xi^2}{2}} && (24.49) \end{aligned}$$

  From this point on, it is easier to leave ψ in terms of ξ. We see that $\psi_1(\xi)$ is an odd function with one node (at $\xi = 0$); both of these features we expect from our experience.

- $n = 2$: As you can easily show,

  $$\begin{aligned} h_2(\xi) &= a_0\left(1 - 2\xi^2\right) && (24.50)\\ \psi_2(\xi) &= a_0\left(1 - 2\xi^2\right)\mathrm{e}^{-\frac{\xi^2}{2}} && (24.51) \end{aligned}$$

  which is even and has two nodes.

We see that, for any n, $h_n(\xi)$ is an n^{th} order polynomial in ξ with only even or odd powers of ξ, according to whether n is even or odd. These polynomials are well-known in mathematics and in physics, and when their normalization is chosen to be such that the coefficient of the highest poser is 2^n, they are called Hermite polynomials. Some of these famous polynomials are listed below

$$\boxed{\begin{gathered} H_0(\xi) = 1 \\ H_1(\xi) = 2\xi \\ H_2(\xi) = 4\xi^2 - 2 \\ H_3(\xi) = 8\xi^3 - 12\xi \\ H_4(\xi) = 16\xi^4 - 48\xi^2 + 12 \\ H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi \end{gathered}}$$

In terms of these, the $\psi_n(\xi)$, properly normalized, are

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n(\xi) \mathrm{e}^{-\frac{\xi^2}{2}} \tag{24.52}$$

where $\xi = \sqrt{\frac{m\omega}{\hbar}}x$. The first five of these are plotted in figure 23.9.

fig 9

We see that these look more or less as we expect (smaller amplitude where $E - V$ is biggest, etc.).

Chapter 25

Twenty-Fifth Class: Further Properties of Harmonic Oscillator Eigenfunctions

Thursday, November 20, 2008

Recall that the eigenfunctions for the harmonic oscillator potential energy $V(x) = \frac{1}{2}kx^2$ are, once normalized,

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n(\xi) \mathrm{e}^{-\frac{\xi^2}{2}} \tag{25.1}$$

where $\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x$ and $\omega \equiv \sqrt{\frac{k}{m}}$. As we mentioned, the harmonic oscillator eigenfunctions, being eigenfunctions of Hermitian Hamiltonian, form an orthonormal set, i.e.,

$$\boxed{\int_{-\infty}^{+\infty} \psi_n(\xi)\psi_m(\xi)\ d\xi = \delta_{m,n}} \tag{25.2}$$

An interesting mathematical consequence that follows easily is that the Hermite polynomials themselves obey

$$\frac{1}{\sqrt{\pi}2^n n!} \int_{-\infty}^{+\infty} H_n(\xi)H_m(\xi)\mathrm{e}^{-\xi^2}\ d\xi = \delta_{m,n} \tag{25.3}$$

We say that that the Hermite polynomials are orthogonal "with respect to the 'weight function' $\mathrm{e}^{-\xi^2}$".

25.1 Expansion Postulate for Harmonic Oscillator

We saw quite a while ago that the eigenfunctions $\left\{\psi_n(x) = \mathcal{A}_n \sin\left(\frac{n\pi}{a}x\right)\right\}$ for the infinite square well potential form a complete set for the well boundary conditions – i.e. any "reasonable" $f(x)$ vanishing at $x = 0$ and at $x = a$ can be expanded as

$$f(x) = \sum a_n \psi_n(x) \tag{25.4}$$

this being nothing more than a Fourier sine expansion. This is then allowed solution of the "initial value problem" for the infinite square well potential: given an arbitrary $\Psi(x, t = 0)$, to find $\Psi(x, t)$, one technique is to expand

$$\Psi(x, t = 0) = \sum_n a_n \psi_n(x) \tag{25.5}$$

then

$$\Psi(x, t) = \sum_n a_n \psi_n(x) \mathrm{e}^{-\frac{iE_n}{\hbar}t} \tag{25.6}$$

The question is whether a similar result is true for the harmonic oscillator potential. You will also recall that we stated, some time ago, the expansion postulate of quantum mechanics, or at least, a special (but still very general) case of it – namely that:

Postulate: For any continuous potential energy function $V(x)$, the set of eigenfunctions is a complete set, i.e., and "reasonable" function $f(x)$ obeying the same boundary conditions as the eigenfunctions can be expanded as

$$f(x) = \sum_{n=1}^{\infty} a_n \psi_n(x) \tag{25.7}$$

Thus, the set of harmonic oscillator eigenfunctions

$$\left\{\psi_n(x) = C_n H_n(\xi) \mathrm{e}^{-\frac{\xi^2}{2}}\right\}, \quad C_n \equiv \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}, \ \xi \equiv \sqrt{\frac{m\omega}{\hbar}}x \tag{25.8}$$

is a complete orthonormal set. Thus, any square-integrable $f(x)$ on $(-\infty, \infty)$ can be expanded as

$$f(x) = \sum_{n=1}^{\infty} a_n \psi_n(x) \tag{25.9}$$

for this set. Assuming this, we can find the expansion coefficients: Multiply both sides of the expansion by ψ_k^* and inegrate

$$\begin{aligned}\int_{-\infty}^{+\infty} \psi_k^*(x) f(x)\ dx &= \sum_{n=1}^{\infty} a_n \int_{-\infty}^{+\infty} \psi_k^*(x)\psi_n(x)\ dx \\ \int_{-\infty}^{+\infty} \psi_k^* f(x)\ dx &= \sum_{n=1}^{\infty} a_n \delta_{k,n} = a_k\end{aligned}$$

$$a_k = \int_{-\infty}^{+\infty} \psi_k^*(x) f(x)\ dx \tag{25.10}$$

which is to say

$$a_k = C_n \int_{-\infty}^{+\infty} f(x) \mathrm{e}^{-\frac{m\omega}{2\hbar}x^2} H_k\left(\sqrt{\frac{m\omega}{\hbar}}x\right)\ dx \tag{25.11}$$

The condition that $f(x)$ be "reasonable" is the condition that the integral from of this equation for a_k exists. If $F(x)$ does not diverge more rapidly then $\mathrm{e}^{\pm\frac{m\omega}{4\hbar}x^2}$ as $x \rightarrow \pm\infty$, we do not need to worry about this.

25.1.1 Mathematical Aside

Since the Hermite polynomials themselves obey the orthogonality realtion

$$\frac{1}{\sqrt{\pi}2^n n!} \int_{-\infty}^{+\infty} H_n(x) H_m(x) \mathrm{e}^{-x^2}\ dx = \delta_{m,n} \tag{25.12}$$

it should be very plausible to you (and is, indeed true) that any square integrable $f(x)$ on $(-\infty, \infty)$ can be expanded in a Hermite series

$$f(x) = \sum_n a_n H_n(x) \tag{25.13}$$

with, as you can easily show

$$a_n = \frac{1}{2^n n! \sqrt{\pi}} \int_{-\infty}^{+\infty} \mathrm{e}^{-x^2} H_n(x) f(x)\ dx \tag{25.14}$$

such a series expansion is sometimes useful in mathematical physics.

25.2 Further Important Results

Returning to our wave function expansion, we have

$$f(x) = \Psi(x, t = 0) = \sum_n a_n \psi_n \tag{25.15}$$

with

$$a_n = \int_{-\infty}^{+\infty} \psi_n^*(x)\Psi(x, t = 0)\ dx \tag{25.16}$$

Since this is formally the same as what we had for the infinite square well, the same results follow:

1. $$\sum_{n=0}^{\infty} |a_n|^2 = 1 \tag{25.17}$$

   (proof same as on page 37 of Griffiths and in our previous notes)

2. $$\langle H \rangle = \sum_{n=0}^{\infty} |a_n|^2 E_n \tag{25.18}$$

3. $$\left\langle \sqrt{E} \right\rangle = \sum_{n=0}^{\infty} |a_n|^2 \sqrt{E_n} \tag{25.19}$$

   and

4. $$\Psi(x, t) = \sum_{n=0}^{\infty} a_n \psi_n(x) \mathrm{e}^{-\frac{iE_n}{\hbar} t} \tag{25.20}$$

   where

   $$E_n = \left(n + \frac{1}{2}\right) \hbar\omega \tag{25.21}$$

   with

   $$a_n = \int_{-\infty}^{+\infty} \psi_n^*(x)\Psi(x, t = 0)\ dx \tag{25.22}$$

   This formally solves the initial value problem.

Example: Suppose that $V(x) = \frac{1}{2}kx^2$ and that

$$\Psi(x, t = 0) = \sqrt{\frac{\beta}{\sqrt{\pi}}} \mathrm{e}^{-\frac{\beta^2(x-b)^2}{2}}, \ \beta \equiv \sqrt{\frac{m\omega}{\hbar}}, \ \omega \equiv \sqrt{\frac{k}{m}} \tag{25.23}$$

(this function is just like the harmonic oscillator ground state, except that it is centered at $x = b$ rather than at $x = 0$)

fig 1

If the energy is measured, what is the probability of finding $\frac{\hbar\omega}{2}$? $\frac{3\hbar\omega}{2}$

What is $\Psi(x, t)$?

This may be a homework problem.

25.3 The Classical Limit in the Harmonic Potential –A First Look

We can make a first pass at trying understand the classical limit by looking, still at eigenfunctions only, but those for very large n. Let us first ask what we expect in the classical limit. Classically, the oscillator should spend more time where it moves more slowly – near the edges of the classically allowed region. Also, the "leakage trail" into the forbidden region should become negligible.

fig 2

We note that even for very low n ($n = 4$), the amplitude of ψ_n is smaller near the center $x = 0$, and indeed, this is what we expect from our observations last week in class. At large n, this behavior persists – the situation for "low intermediate" n ($n = 100$) is shown in figure 25.3.

fig 3

Let us calculate the classical probability distribution. Let the classical period $\tau = \frac{2\pi}{\omega}$. Then

$$P_{\text{classical}}(x)\Delta x = \frac{\Delta t}{\tau} = \frac{\omega}{2\pi}\frac{2\Delta x}{v(x)} \tag{25.24}$$

where v is the classical speed. Now,

$$x_{\text{classical}} = A\cos(\omega t) \tag{25.25}$$

where we ignore the phase, and where $A = \sqrt{\frac{2E}{m\omega^2}}$ where E is the energy. Thus,

$$\begin{aligned} v(x) &= -\omega A \sin(\omega t) \\ &= -\omega \left[\sqrt{1-\cos^2(\omega t)}\right] \end{aligned}$$

$$v(x) = \omega A \left(1 - \frac{x^2}{A^2}\right)^{\frac{1}{2}} \tag{25.26}$$

which gives us v as a function of x. Thus,

$$P_{\text{classical}} \Delta x = \frac{1}{\pi A} \frac{1}{\left(1 - \frac{x^2}{A^2}\right)^{\frac{1}{2}}} \Delta x \tag{25.27}$$

$$P_{\text{classical}} = \frac{1}{\pi A} \frac{1}{\left(1 - \frac{x^2}{A^2}\right)^{\frac{1}{2}}} \tag{25.28}$$

and this is plotted as the dashed line in figure 25.3. So, in the limit of large n, the agreements of the probability distributions is very good. Now, what about leakage into the forbidden region? We note that the exponential factor $\mathrm{e}^{-\frac{\xi^2}{2}}$ is the same for all n; however, the classically allowed region get wider (why?) as n increases, so the probability leakage fraction does get less. Of course, we would like to see a probability lump moving back and forth harmonically in the classical limit, and, of course, we cannot get that just considering solely eigenfunctions (why not?). So, we need to understand the motion of a peaked wave packet in a harmonic oscillator potential.

25.4 Behavior of Harmonic Oscillator Superposition States

As a start toward this, we can consider the behavior over time of an equal superposition o the ground and first excited states

$$\Psi(x, t=0) = \frac{1}{\sqrt{2}} \left[\psi_0(x) + \psi_1(x)\right] \tag{25.29}$$

Notice that these are the two must non-classical states! However, as you will show in the homework, a plot of the probability density as a function of time oscillates as shown in figure 25.4.

fig 4

We note, in fact, that any packet or superposition state in a harmonic oscillator potential (only) is periodic (and will therefore be in the same place and look the same after one or an integral number of periods). To see this, note that, by the completeness theorem, any initial state $\Psi(x,t=0)=f(x)$ can be expanded as

$$\Psi(x,t=0)=\sum_{n=0}^{\infty}c_n\psi_n(x) \tag{25.30}$$

so

$$\Psi(x,t)=\sum_{n=0}^{\infty}c_n\psi_n(x)\mathrm{e}^{-\frac{iE_n}{\hbar}t} \tag{25.31}$$

Then the probability density is

$$P(x,t)=|\Psi(x,t)|^2=\sum_{k=0}^{\infty}\sum_{n=0}^{\infty}c_k^*c_n\psi_k^*(x)\psi_n(x)\mathrm{e}^{-(k-n)\omega t} \tag{25.32}$$

where $\omega\equiv\sqrt{\frac{k}{m}}$. Each term in this sum oscillates in time at an integral multiple $(k-n)$ of the classical frequency ω. Hence the whole series is periodic in time at the classical frequency. Of course, this doesn't mean that the superposition state moves in simple harmonic motion. So, we must look into this more deeply.

25.4.1 Motion of Gaussian Wave Packet in Harmonic Potential

We consider starting with a packet state initially centered at the point $x=0$ and having $\langle p\rangle$ positive. A good choice would be a Gaussian in momentum

$$\phi(p)\sim\mathrm{e}^{-\frac{p-p_0}{2\sigma_p^2}} \tag{25.33}$$

where $\langle p\rangle=p_0$. As you know, a Gaussian $\phi(p)$ leads to a Gaussian $\psi(x)$ in position; so

$$\Psi(x,t=0)=\frac{1}{\sqrt{\sqrt{\pi}\sigma_x}}\mathrm{e}^{-\frac{x^2}{2\sigma_x^2}}\mathrm{e}^{\frac{ip_0}{\hbar}x} \tag{25.34}$$

fig 5

This packet has $\langle p\rangle = p_0$. If it were in free space (i.e. $V = 0$), such as packet would move to positive x continuously, always spreading. but, the packet is not in free space. To find out what happens over the course of time, we use the completeness theorem:

$$\Psi(x,t) = \sum_{n=0}^{\infty} c_n \psi_n(x) \mathrm{e}^{-\frac{iE_n}{\hbar}t} \tag{25.35}$$

where

$$c_n = \int_{-\infty}^{+\infty} \psi_n^*(x')\Psi(x',0)\ dx' \tag{25.36}$$

Recall that we rewrote this expansion in the form

$$\Psi(x,t) = \int_{-\infty}^{+\infty} \Psi(x', t=0) K(x', x, t)\ dx' \tag{25.37}$$

where K is the "propagator" is iven by

$$K(x', x, t) = \sum_{n=0}^{\infty} \psi_n^*(x')\psi_n(x) \mathrm{e}^{-\frac{iE_n}{\hbar}t} \tag{25.38}$$

For the harmonic potential, as we know

$$\begin{aligned} E_n &= \left(n + \frac{1}{2}\right)\hbar\omega \\ \psi_n(x) &= \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \mathrm{e}^{-\frac{m\omega}{2\hbar}x^2} \end{aligned}$$

thus, in this case. the propagator is very complicated. However, this is one of the very few cases in which it has been evaluated in closed form! The result, after much work, is for the harmonic oscillator,

$$K(x', x, t) = \sqrt{\frac{m\omega}{2i\pi\hbar\sin(\omega t)}} \mathrm{e}^{\frac{im\omega}{\hbar}\frac{(x^2+x'^2)\cos(\omega t) - 2xx'}{2\sin(\omega t)}} \tag{25.39}$$

which itself is not at all simple. By solving for $\Psi(x,t)$, it has been found (again, after much work) that, for an initial state as in equation (25.34),

$$|\Psi(x,t)|^2 = \frac{1}{\sqrt{\pi}\Delta(t)} \mathrm{e}^{-\frac{\left[x - \frac{p_0}{m\omega}\sin(\omega t)\right]}{\Delta^2(t)}} \tag{25.40}$$

where

$$\Delta(t) \equiv \sqrt{\sigma_x^2 \cos^2(\omega t) + \left(\frac{\hbar}{m\omega\sigma_x}\right)^2 \sin^2(\omega t)} \tag{25.41}$$

This result is remarkably simple: We see that the probability packet remains Gaussian in shape, although the center moves, at time t it is apparently centered at coordinate x_c given by

$$\begin{aligned} x_c &- \frac{p_0}{m\omega}\sin(\omega t) = 0 && (25.42) \\ x_c &= \frac{p_0}{m\omega}\sin(\omega t) && (25.43) \end{aligned}$$

Thus, we see that the center of the packet oscillates harmonically in position at exactly the classical frequency! Let us attempt a more detailed comparison with a classical mass-spring oscillator: Classically, the energy and amplitude are related by

$$E = \frac{1}{2}kA^2 \;\Rightarrow\; A = \sqrt{\frac{2E}{m\omega^2}} \tag{25.44}$$

using the classical relation $p_{\text{max}} = \sqrt{\frac{2E}{m}}$, we have

$$A_{\text{classical}} = \frac{p}{m\omega} \tag{25.45}$$

therefore,

$$x(t) = \frac{p_{\text{max}}}{m\omega}\sin(\omega t) \tag{25.46}$$

In the quantum expression, we recall that $p_0 = \langle p \rangle$, so

$$x_{\text{class,quantum}} = \frac{\langle p \rangle}{m\omega}\sin(\omega t) \tag{25.47}$$

We see that close correspondence. Note also that the width of the packet $\Delta(t)$ also oscillates in time. As yo can easily show, the frequency for this is twice the classical frequency. Thus, the packet itself moves back and forth, it breathes!. An interesting special case occurs when σ_x is chosen for the initial packet as $\sigma_x = \sqrt{\frac{\hbar}{m\omega}}$; then, the packet width, $\Delta(t)$, is independent of time. This special packet, called a "coherent state" oscillates rigidly back and forth at frequency ω much like a classical particle.

25.5 The Time Dependence of Expectation Values

We will see that an understanding of how expectation values change in time will greatly help our understanding of how classical physics comes from quantum mechanics. We are interested in the general case −i.e., not just the case of a harmonic potential or “particle in a box”, etc. With this in mind, we now consider the time dependence of $\left\langle \widehat{Q} \right\rangle$, where $\widehat{Q}$ is any operator ($\hat{x}, \hat{p}, \hat{L}$, etc.) We keep in mind that $\left\langle \widehat{Q} \right\rangle$ may have derivatives with respect to x (e.g. $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$), In any case, $\widehat{Q}$ acts on functions of x to yield ther functions of x. Now

$$\left\langle \widehat{Q} \right\rangle_t = \int_{-\infty}^{+\infty} \Psi^*(x,t)\widehat{Q}\Psi(x,t)\ dx \tag{25.48}$$

We seek $\frac{d}{dt}\left\langle \widehat{Q} \right\rangle$. Then

$$\begin{aligned} \frac{d}{dt}\left\langle \widehat{Q} \right\rangle &= \frac{d}{dt}\int_{-\infty}^{+\infty} \Psi^*(x,t)\widehat{Q}\Psi\ dx \\ &= \int_{-\infty}^{+\infty} \left(\frac{\partial \Psi^*}{\partial t}\widehat{Q}\Psi + \Psi^*\widehat{Q}\frac{\partial \Psi}{\partial t} \right)\ dx \end{aligned}$$

Now, the Schrödinger equation is

$$\widehat{H}\Psi = i\hbar\frac{\partial \Psi}{\partial t} \ \Rightarrow\ \frac{\partial \Psi}{\partial t} = \frac{1}{i\hbar}\widehat{H}\Psi = -\frac{i}{\hbar}\widehat{H}\Psi \tag{25.49}$$

and its conjugate is

$$\widehat{H}\Psi^* = -i\hbar\frac{\partial \Psi^*}{\partial t} \ \Rightarrow\ \frac{\partial \Psi^*}{\partial t} = \frac{i}{\hbar}\widehat{H}\Psi^* \tag{25.50}$$

so

$$\frac{d}{dt}\left\langle \widehat{Q} \right\rangle = \frac{i}{\hbar}\int_{-\infty}^{+\infty} \left(\widehat{H}\Psi\right)^* \widehat{Q}\Psi\ dx \tag{25.51}$$

Now, $\widehat{H}$ is a Hermitian operator. Recall that, for any Hermitian operator, $\widehat{O}$, by definition, for any two allowed state functions Ψ_1 and Ψ_2,

$$\int_{-\infty}^{+\infty} \Psi_1^* \left[\widehat{O}\Psi_2\right]\ dx = \int_{-\infty}^{+\infty} \left[\widehat{O}\Psi_1\right]^* \Psi_2\ dx \tag{25.52}$$

Thus,

$$\int_{-\infty}^{+\infty}\left(\widehat{H}\Psi\right)^*\left(\widehat{Q}\Psi\right)\,dx=\int_{-\infty}^{+\infty}\Psi^*\widehat{H}\left(\widehat{Q}\Psi\right)\,dx \tag{25.53}$$

Thus, equation (25.51) is

$$\frac{d}{dt}\left\langle\widehat{Q}\right\rangle=\frac{i}{\hbar}\int_{-\infty}^{+\infty}\Psi^*\left[\widehat{H}\widehat{Q}-\widehat{Q}\widehat{H}\right]\Psi\,dx \tag{25.54}$$

Now the combination of operators $\widehat{A}\widehat{B}-\widehat{B}\widehat{A}$ is very common in quantum mechanics; it is denoted as

$$\left[\widehat{A},\widehat{B}\right]\equiv\widehat{A}\widehat{B}-\widehat{B}\widehat{A} \tag{25.55}$$

and given a special name − it is called “the commutator of $\widehat{A}$ and $\widehat{B}$”. So

$$\frac{d}{dt}\left\langle\widehat{Q}\right\rangle=\frac{i}{\hbar}\int_{-\infty}^{+\infty}\Psi^*\left[\widehat{H},\widehat{Q}\right]\Psi\,dx=\frac{i}{\hbar}\left\langle\left[\widehat{H},\widehat{Q}\right]\right\rangle \tag{25.56}$$

$$\boxed{\frac{d}{dt}\left\langle\widehat{Q}\right\rangle=\frac{i}{\hbar}\left\langle\left[\widehat{H},\widehat{Q}\right]\right\rangle} \tag{25.57}$$

As we will shortly get at least a first idea of this is a very important relation in quantum mechanics.

Note: In rare cases, an operator may also have an explicit time dependence. An example might be a harmonic potential energy in which the “spring constant” (and hence the classical frequency) changes in time − then $\widehat{H}$ for this system changes in time ($\widehat{H}=\frac{\widehat{p^2}}{2m}+\frac{1}{2}k(t)x^2=\widehat{H}(t)$). In such cases, the time derivative of the expectation value is modified to

$$\frac{d}{dt}=\frac{\partial\widehat{Q}}{\partial t}+\left\langle\left[\widehat{H},\widehat{Q}\right]\right\rangle \tag{25.58}$$

In this course, we do not deal with such cases. We now reap our first result from this theorem: **Conservation of Energy** Let $\widehat{Q}$ be the Hamiltonian $\widehat{H}$. Then

$$\left[\widehat{H},\widehat{Q}\right]=\left[\widehat{H},\widehat{H}\right]=\widehat{H}\widehat{H}-\widehat{H}\widehat{H}=0 \tag{25.59}$$

Then

$$\frac{d}{dt}\left\langle\widehat{H}\right\rangle=0\;\Rightarrow\;\frac{d}{dt}\langle E\rangle=0 \tag{25.60}$$

Thus, we have derived conservation of energy of energy as a statistical result.

Relation between $\hat{x}$ and $\hat{p}_x$ We now consider the very fundamental commutator:

$$[\hat{x}, \hat{p}_x] \tag{25.61}$$

To find out what this is, we operate with it is a function $f(x)$:

$$\begin{aligned}
[\hat{x}, \hat{p}_x] f(x) &= \\
&= \hat{x}\hat{p}_x f(x) - \hat{p}_x \hat{x} f(x) \\
&= x\frac{\hbar}{i}\frac{\partial f(x)}{\partial x} - \frac{\hbar}{i}\frac{\partial}{\partial x}\left[x f(x)\right] \\
&= x\frac{\hbar}{i}\frac{\partial f(x)}{\partial x} - \frac{\hbar}{i}\left(f(x) + x\frac{df}{dx}\right) \\
&= \frac{\hbar}{i}x\frac{\partial f}{\partial x} - \frac{\hbar}{i}f(x) - \frac{\hbar}{i}x\frac{df}{dx} \\
&= i\hbar f(x)
\end{aligned}$$

since this is true for any $f(x)$,

$$\boxed{[\hat{x}, \hat{p}_x] = i\hbar} \tag{25.62}$$

As we will see later, this result is very fundamental in quantum mechanics.

Relation between $\langle x \rangle$ and $\langle p_x \rangle$: We had, for the time development of expectation values,

$$\boxed{\frac{d}{dt}\langle Q \rangle = \frac{i}{\hbar}\int_{-\infty}^{+\infty} \Psi^* \left[\widehat{H}, \widehat{Q}\right] \Psi \; dx \equiv \frac{i}{\hbar}\left\langle \left[\widehat{H}, \widehat{Q}\right] \right\rangle} \tag{25.63}$$

Suppose $\widehat{Q} = \hat{x}$. Now

$$\begin{aligned}
\left[\widehat{H}, \hat{x}\right] &= \left[\left(\frac{\widehat{p_x^2}}{2m} + V(x)\right), \hat{x}\right] \\
&= \frac{1}{2m}\left[\widehat{p_x^2}, \hat{x}\right] \\
&= \frac{1}{2m}\left[\widehat{p_x}\widehat{p_x}, \hat{x}\right]
\end{aligned}$$

Now, as you will show in the homework, for any three operators $\hat{A}, \hat{B}$, and $\hat{C}$,

$$\left[\hat{A}\hat{B}, \hat{C}\right] = \hat{A}\left[\hat{B}, \hat{C}\right] + \left[\hat{A}, \hat{C}\right]\hat{B}$$

also,

$$\left[\hat{A}, \hat{B}\hat{C}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right]$$

so

$$\left[\widehat{p_x^2}, \hat{x}\right] = \widehat{p_x}\left[\widehat{p_x}, \hat{x}\right] + \left[\widehat{p_x}, \hat{x}\right]\widehat{p_x} \tag{25.64}$$

now

$$\left[\hat{A}, \hat{B}\right] = -\left[\hat{B}, \hat{A}\right]$$

$$\left[\widehat{p_x^2}, \hat{x}\right] = -i\hbar\widehat{p_x} - i\hbar\widehat{p_x} = \frac{2\hbar}{i}\widehat{p_x} \tag{25.65}$$

so

$$m\frac{d}{dt}\langle x\rangle = \langle\widehat{p_x}\rangle \tag{25.66}$$

which shows that the classical connection between momentum and position is true, on average, even though both can't be known exactly together!

Newton's Second Law In classical mechanics, this is

$$\frac{dp_x}{dt} = -\frac{\partial V}{\partial x} \tag{25.67}$$

So we consider $\frac{d}{dt}\langle\widehat{p_x}\rangle$. This is

$$\frac{d}{dt}\langle\widehat{p_x}\rangle = \frac{i}{\hbar}\left\langle\left[\widehat{H}, \widehat{p_x}\right]\right\rangle \tag{25.68}$$

Now,

$$\left[\widehat{H}, \widehat{p_x}\right] = \left[\frac{\widehat{p^2}}{2m} + V, \widehat{p_x}\right] = \frac{1}{2m}\left[\widehat{p_x^2}, \widehat{p_x}\right] + \left[\widehat{V}, \widehat{p_x}\right] \tag{25.69}$$

now

$$\left[\widehat{p_x^2}, \widehat{p_x}\right] = \left[\widehat{p_x}\widehat{p_x}, \widehat{p_x}\right] = 0 \tag{25.70}$$

To find $[V(x), \widehat{p_x}]$, consider

$$\begin{aligned}
\left[V(x), \widehat{p_x}\right]\psi(x) &= V(x)\frac{\hbar}{i}\frac{\partial\Psi}{\partial x} - \frac{\hbar}{i}\frac{\partial V\Psi}{\partial x} \\
&= \frac{\hbar}{i}\left[V\frac{\partial\Psi}{\partial x} - \frac{\partial V}{\partial x}\Psi - V\frac{\partial\Psi}{\partial x}\right] = i\hbar\frac{\partial V}{\partial x}\Psi
\end{aligned}$$

so

$$\left[V(x), \widehat{p_x}\right] = i\hbar\frac{\partial V}{\partial x} \tag{25.71}$$

Thus,

$$\left[\widehat{H}, \widehat{p_x}\right] = i\hbar \frac{\partial V}{\partial x} \tag{25.72}$$

Hence

$$\boxed{\frac{d}{dt}\left\langle \widehat{p_x} \right\rangle = -\left\langle \frac{dV(x)}{dx} \right\rangle} \tag{25.73}$$

Equations (25.66) and (25.73) together are called Ehrenfest's theorem (1927). Note that they are true for any continuous $V(x)$ and for any superposition (or eigen-) state. We note, of course, that equation (25.73) looks a lot like Newton's second law for expectation values. Thus, it looks like our long sought general connection between quantum and classical physics. It is not quite that. For "Newton's Second Law for the expectation values", we would like

$$\frac{d}{dt}\left\langle \widehat{p_x} \right\rangle = -\frac{d}{dx} V\left(\langle x \rangle\right) \tag{25.74}$$

since

$$-\frac{d}{dx} V\left(\langle x \rangle\right) = F\left(\langle x \rangle\right) \tag{25.75}$$

but, equations (25.73) and (25.74) are generally not the same since, in general,

$$\left\langle \frac{dV(x)}{dx} \right\rangle \neq \frac{d}{d\langle x \rangle} V\left(\langle x \rangle\right) \tag{25.76}$$

or

$$\langle F(x) \rangle \neq F\left(\langle x \rangle\right) \tag{25.77}$$

Proof:

$$\begin{aligned}
\left\langle \frac{dV(x)}{dx} \right\rangle &= \int_{-\infty}^{+\infty} \Psi^*(x,t) \frac{\partial V}{\partial x} \Psi(x,t)\ dx && (25.78) \\
\frac{d}{dx} V\left(\langle x \rangle\right) &= \frac{d}{dx}\left\{ V\left(\int_{-\infty}^{+\infty} \Psi^*(x,t) x \Psi(x,t)\ dx \right) \right\} && (25.79)
\end{aligned}$$

and these two are not equal in general. Of course, this somewhat deepens (or muddies, depending on your point of view) to gap (or connection) between quantum and classical physics.

25.6 When Does Classical Mechanics Apply?

When, then does classical mechanics apply? Must the system be macroscopic? The answer is no – for example, motion of electrons in an accelerator beam are well described by the classical law

$$m_e \frac{d^2\vec{x}}{dt^2} = q\vec{E} + q\vec{V} \times \vec{B} \tag{25.80}$$

in accelerator guide fields. One key is that $V(x)$ is a "slowly varying" (compared with the mean deBroglie wavelength in the packet under consideration) function of x. To see this, we expand $f(x) = -\frac{dV(x)}{dx}$ around $x = \langle x \rangle$:

$$F(x) = F\left(\langle x \rangle\right) + \left(x - \langle x \rangle\right) \frac{dF\left(\langle x \rangle\right)}{dx} + \frac{\left(x - \langle x \rangle\right)^2}{2!} \frac{d^2F\left(\langle x \rangle\right)}{dx^2} + \cdots \tag{25.81}$$

If $\left(x - \langle x \rangle\right) \frac{dF(\langle x \rangle)}{dx} \ll F\left(\langle x \rangle\right)$ for all $\left(x - \langle x \rangle\right)$ occupied by the packet at all times t under consideration, then we can drop all terms but the first and

$$F(x) \approx F\left(\langle x \rangle\right) \;\Rightarrow\; \frac{dV}{dx} \approx \frac{dV\left(\langle x \rangle\right)}{d\langle x \rangle} \tag{25.82}$$

Under these conditions,

$$m\frac{d^2\langle x \rangle}{dt^2} \rightarrow -\frac{\partial V\left(\langle x \rangle\right)}{\partial \langle x \rangle} \tag{25.83}$$

25.6.1 Exceptions

Consider the harmonic potential $V(x) = \frac{1}{2}kx^2$. Then

$$\frac{dV}{dx} = kx \left\langle \frac{dV}{dx} \right\rangle = \langle kx \rangle = k\langle x \rangle \tag{25.84}$$

Then, Newton's second law can be written as

$$m\frac{d^2\langle x \rangle}{dt^2} = -k\langle x \rangle \tag{25.85}$$

Which has as solution

$$\langle x \rangle = A\cos\left(\sqrt{\frac{k}{m}}t + \phi\right) \tag{25.86}$$

Note that this is true for any state for any value of k (which controls how fast V varies with x). Thus, for the harmonic potential, $\langle x \rangle$ always obeys equation (25.85), which leads to "classical behavior".

Question: What about for an eigenstate in this potential? is equation (25.86) obeyed? Is equation (25.85) obeyed?

As you can show, $\langle x \rangle$ always obeys a classical equation of motion of $V(x) = Cx^n$ as long as n is a positive integer greater than 2.

Question: Why doesn't this work if $n = 1$?

25.7 Another Example of an Operator – Angular Momentum

In classical physics, the orbital angular momentum of a particle around an origin is

$$\vec{L} = \vec{r} \times \vec{p} \tag{25.87}$$

In cartesian coordinates, this is

$$\begin{aligned} L_x &= yp_z - zp_y & (25.88) \\ L_y &= zp_x - xp_z & (25.89) \\ L_z &= xp_y - yp_x & (25.90) \end{aligned}$$

The normal procedure is now the following: For every dynamical variable of classical physics, we have an operator in quantum mechanics constructed according to the prescription $p_x \to \frac{\hbar}{i}\frac{\partial}{\partial x}$, etc. Thus, in quantum mechanics, we have

$$\begin{aligned} \widehat{L_x} &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) & (25.91) \\ \widehat{L_y} &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) & (25.92) \\ \widehat{L_z} &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) & (25.93) \\ & & (25.94) \end{aligned}$$

As we will see, these three operators are very important. However, in nature, quantum mechanics does not "come from" classical physics, rather, we believe that it is somewhat the other way around. Thus, really, we believe that the classical quantities (“momentum”, “position”, “angular momentum”, etc.) do not exist as quantities except in a certain limit. Rather, there are only operators and states, and in the “classical limit” certain superposition states behave as if certain quantities are conserved.

Chapter 26

Twenty-Sixth Class: Quantum Mechanics and the Hydrogen Atom

Tuesday, December 2, 2008

26.1 An Introduction

We ow begin application of quantum mechanics to atomic physics – specifically, to the simplest atom – that of hydrogen. To prepare, let us raise three questions:

1. What determines the size of an atom? What sets the scale? Classical orbits (e.g., planets around the sun) can occur with any radius. Is this true in quantum mechanics?
2. Why is the atom stable? Why does it not decay, as predicted by classical mechanics?
3. Associated with atoms are their atomic spectra. For example, for hydrogen, the Balmer series wavelengths are well-known. But, why should atom emit photons at all? Is it possible to derive, from "first principles", the Balmer formula for the wavelengths?

These are excellent questions. To refresh our memories, let us recall some facets of the semiclassical Bohr model. In his original model, Bohr assumed circular, classical orbits. He also assumed, ad-hoc, that the orbital angular momentum of the electron is restricted to values

$$L = n\hbar, \quad n = 1, 2, 3, \cdots \tag{26.1}$$

This led to "results":

1. That the ground state orbit has radius

$$a_0 = 4\pi\varepsilon_0 \frac{\hbar^2}{m_e e^2} \approx 0.529 \times 10^{-10} \text{ m} \tag{26.2}$$

   ("Bohr radius")

2. That the energy of the ground state is

$$E_1 = -\left(\frac{1}{4\pi\varepsilon_0}\right)^2 \frac{m_e e^4}{2\hbar^2} = -13.6 \text{ eV} \tag{26.3}$$

   in agreement with the experimental value of the ionization energy.

3. That the energy of state n is

$$\boxed{E_n = \frac{E_1}{n^2}} \tag{26.4}$$

   so, $E_n \propto \frac{1}{n^2}$, which is the assumption of photon emission accompanying "transitions" between energy levels, reproduces the Balmer series formula. Still, due to the ad-hoc nature of its assumption, the Bohr model is unsatisfactory.

Now we see what the Schrödinger equation quantum mechanics has to say. We consider an electron, still not in fully objective reality, but in the Coulomb field of the proton − the latter considered as a classical object that is infinitely heavy and sets stationary at the origin. figure 26.1 shows one possible point that the electron could materialize at upon position measurement.

fig 1

Thus, the electron has a state function that depends on all three of its coordinates and the time

$$\Psi(z, y, z, t) \equiv \Psi(\vec{r}, t) \tag{26.5}$$

As we know, the time dependent Schrödinger equationfor this is

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}) \Psi \vec{r}, t) \tag{26.6}$$

We look for the normal-mode or standing wave or eigenstates:

$$\Psi(\vec{r},t) = \psi(\vec{r})\mathrm{e}^{-i\frac{E}{\hbar}t} \tag{26.7}$$

where

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \tag{26.8}$$

Here, $V(x,y,z)$ is the Coulomb potential due to the proton at each "potential position" (x,y,x) of the electron

$$V(\vec{r}) = V(x,y,z) = -\frac{e^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}} = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{26.9}$$

Clearly, spherical coordinates are more convenient for us here than the Cartesian coordinates. So, we re-express

$$\psi(x,y,z) = \psi(r,\theta,\phi) \tag{26.10}$$

Now we need the Schrödinger equation (which we have in Cartesian coordinates) in spherical coordinates. We need to transform

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{26.11}$$

to spherical coordinates. This is done in multivariable calculus, and the result is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin\theta}\frac{\partial^2}{\partial\phi^2} \tag{26.12}$$

With this, the time independent Schrödinger equationis[1]

$$\begin{aligned} -\frac{\hbar^2}{2m}\left\{\frac{\partial^2\psi(r,\theta,\phi)}{\partial r^2} + \frac{2}{r}\frac{\partial\psi(r,\theta,\phi)}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right)\right. \\ \left. + \frac{1}{r^2\sin^\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial\phi^2}\right\} - \frac{e^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi) \end{aligned} \tag{26.13}$$

We seek solutions of this monstrous-looking equation.

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[1] where I've expanded out the term $\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$ using the product rule for derivatives.

26.2 Spherically Symmetric Solutions

Before getting involved in the more complicated business of trying to find rather general solution of equation (26.13), let us first see if we can somehow find (or guess) a few simple solutions. For example, let's see if we can find any solutions for which ψ depends only or r (and not on θ or ϕ).[2]. Then, equation (26.13) becomes

$$\frac{d^2\psi(r)}{dr^2} + \frac{2}{r}\frac{d\psi(r)}{dr} + \frac{2mke^2}{\hbar^2 r}\psi(r) = -\frac{2m}{\hbar^2}E\psi(r) \tag{26.14}$$

where $k \equiv \frac{1}{4\pi\varepsilon_0}$. This ordinary differential equation still looks formidable. Can we guess a solution? We know that the probability that the electron will materialize at points for $r \to \infty$ must go to zero. So, we look for a $\psi(r)$ that decreases when r is large and increasing. This still seems like a formidable "guessing problem". However, notice an interesting feature of the differential equation. Let us rewrite it as

$$\frac{d^2\psi(r)}{dr^2} + \frac{2}{r}\frac{d\psi(r)}{dr} = -\frac{2m}{\hbar^2}\left(E + \frac{ke^2}{r}\right)\psi(r) \tag{26.15}$$

Now, the two pieces that look troublesome (one on the left and one on the right) both have $\frac{1}{r}$ factors. How nice it would be if they were equal – then we could just cancel them! So, we can't resist trying – just trying

$$\frac{2}{r}\frac{d\psi(r)}{dr} = -\frac{2m}{\hbar^2}\frac{ke^2}{r}\psi(r) \tag{26.16}$$

Then

$$\frac{d\psi(r)}{dr} = -\frac{mke^2}{\hbar^2}\psi(r) \tag{26.17}$$

But this we can solve – the solution is

$$\psi(r) = \mathcal{A}\mathrm{e}^{-br} \tag{26.18}$$

where $b = \frac{ke^2m}{\hbar^2}$. Note incidentally that this "play function" at least agrees with our observation that $\psi(r)$ decreases at large r. Of course, if life were so

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[2] Such solutions would then be spherically symmetric.

simple, then this same function,$\psi(r) = \mathcal{A}\mathrm{e}^{-br}$, would also have the solve the rest of equation (26.14), namely,

$$\frac{d^2\psi(r)}{dr^2} = -\frac{2m}{\hbar^2}E\psi(r) \tag{26.19}$$

This looks a bit familiar. Is it an oscillator equation? No − since $E < 0$ (why?) the right hand side is positive, not negative. That means that tis solution is also a decaying exponential

$$\psi(r) = \mathcal{B}\mathrm{e}^{-\left(\frac{2mE}{\hbar^2}\right)^{1/2}r} \tag{26.20}$$

so

$$\psi(r) = \mathcal{A}\mathrm{e}^{+\sqrt{\frac{-2mE}{\hbar^2}}r} + \mathcal{B}\mathrm{e}^{-\sqrt{\frac{-2mE}{\hbar^2}}r} \tag{26.21}$$

but we must have $\mathcal{A} = 0$ (why?). Of course, now we have two different functions $\psi(r)$, each solving an additive piece of the differential equation. Let's just try to equate them − is this possible? It is if

$$\begin{aligned}
\mathrm{e}^{-\left(\frac{-2mE}{\hbar^2}\right)^{1/2}r} &= \mathrm{e}^{-\frac{ke^2m}{\hbar^2}r} && (26.22)\\
\left(-\frac{2mE}{\hbar^2}\right)^{1/2} &= \frac{ke^2m}{\hbar^2} && (26.23)\\
-\frac{2mE}{\hbar^2} &= \frac{\left(ke^2m\right)^2}{\hbar^4} && (26.24)\\
E &= -\frac{k^2me^4}{2\hbar^2} && (26.25)
\end{aligned}$$

which, amazingly, is exactly the ground state Bohr model energy (and it is equal to −13.6 eV)! So let us look at our solution:

$$\psi(r) = \mathrm{e}^{-br} \tag{26.26}$$

where $b = \frac{ke^2m}{\hbar^2}$ This is a simple exponential fall off with "$\frac{1}{e}$" distance of $\frac{1}{b}$.

fig 2

But,

$$\frac{1}{b} = \frac{1}{k}\frac{\hbar^2}{me^2} = 4\pi\varepsilon_0\frac{\hbar^2}{m_e e^2} \tag{26.27}$$

which is nothing but the Bohr radius a_0!

$$a_0 = 4\pi\varepsilon_0 \frac{\hbar^2}{m_e e^2} \tag{26.28}$$

So our solution is

$$\psi(r) = \mathcal{B}\mathrm{e}^{-\frac{r}{a_0}} \tag{26.29}$$

which we expect top be the ground-state eigenfunction. This turns out to be correct.

26.3 Other Spherically Symmetric Solutions

As you can show for yourself, another spherically symmetric solution to equation (26.15) is

$$\psi_2(r) = \left(2 - \frac{r}{a_0}\right)\mathrm{e}^{-\frac{r}{2a_0}} \tag{26.30}$$

fig 3

If you go through the algebra, you will find tat his is a solution only if

$$E = E_2 = \frac{E_1}{4} = -\frac{13.6\text{ eV}}{4} \tag{26.31}$$

again agreeing with the Bohr theory. In fact, there is an entire series of solutions to equation (26.15)

$$\psi_1(r), \psi_2(r), \psi_3(r), \psi_4(r), \cdots$$

$$\psi_3(r) = \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right)\mathrm{e}^{-\frac{r}{3a_0}} \tag{26.32}$$

fig 4

with energies

$$E_n = \frac{-13.6\text{ eV}}{n^2} \tag{26.33}$$

This is a fantastic result! It shows that, although the Bohr model is really wrong, the Bohr formula for the energies

$$E_n = -\left(\frac{mk^2e^4}{2\hbar^2}\right)\frac{1}{n^2} \tag{26.34}$$

is apparently correct in Schrödinger quantum mechanics! From this point of view, it is interesting to contemplate the far from obvious fact that equation (26.15) is apparently equivalent to the Balmer formula.

Of course, there is one aspect of the procedure we used above to find solutions that is, perhaps, a bit unsatisfying – we guessed we guessed the solutions beyond ψ_1. This raises the question – is there a systematic method of finding these and also non-spherical symmetric eigenfunctions? The answer is yes – and in the following we use methods of differential equations to show this and to find them.

26.4 The Road to More General Hydrogen Atom Eigenfunctions

The hydrogen atom still holds more secrets. Thus, we return to equation (26.13)

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\left(\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right)\right\}+$$
$$\frac{1}{r^2\sin^2\theta}\frac{\partial\psi(r,\theta,\phi)}{\partial\phi}+\frac{2m}{\hbar^2}\left[\frac{e^2}{4\pi\varepsilon_0 r}-E\right]\psi(r,\theta,\phi)=0 \tag{26.35}$$

We try separation of variables: Search for solutions of the form

$$\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi) \tag{26.36}$$

we plug this into the Schrödinger equation. This yields

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\left[R\Theta\Phi\right]}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\left[R\Theta\Phi\right]}{\partial\theta}\right)+\right.$$
$$\left.\frac{1}{r^2\sin^2\theta}\frac{\partial^2\left[R\Theta\Phi\right]}{\partial\phi^2}\right]+V(r)R\Theta\Phi=ER\Theta\Phi \tag{26.37}$$

Now,

$$\frac{\partial\left[R\Theta\Phi\right]}{\partial r} = \Theta\Phi\frac{dR}{dr} \tag{26.38}$$
$$\frac{\partial\left[R\Theta\Phi\right]}{\partial\theta} = R\Phi\frac{d\Theta}{d\theta} \tag{26.39}$$
$$\frac{\partial^2\left[R\Theta\Phi\right]}{\partial\phi^2} = R\Theta\frac{d^2\Phi}{d\phi^2} \tag{26.40}$$

so the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\left[\frac{\Theta\Phi}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R\Phi}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\right.$$
$$\left.\frac{R\Theta}{r^2\sin^2\theta}\frac{d^2\Phi}{d\phi^2}\right]+V(r)R\Theta\Phi=ER\Theta\Phi \tag{26.41}$$

Now we divide by $R\Theta\Phi$ and multiply by $-2\mu r^2\sin^\theta$ (from now on, we let μ stand for m_e)

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-$$
$$\frac{2\mu}{\hbar^2}r^2\sin^2\theta\left[E-V(r)\right] \tag{26.42}$$

In spite of the complication, the above echoes a by now familiar situation – the left hand side depends only on one variable (ϕ while the right hand side does not depend on this variable at all. Therefore, each side must equal a constant, which for later connivence, we denote as "$-m_\ell^2$"[3]. (At this stage, this is completely general – so far "$-m_\ell^2$" can be any complex number). So we now have two simpler equations.

$$\frac{1}{\Phi(\phi)}\frac{d^2\Phi}{d\phi^2}=-m_\ell^2 \tag{26.43}$$

and

$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)=\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{2\mu}{\hbar^2}r^2\left[E-V(r)\right]=$$
$$-\frac{m_\ell^2}{\sin^2\theta} \tag{26.44}$$

which is

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left[E-V(r)\right]=\frac{m_\ell^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) \tag{26.45}$$

Again, the same sort of thing has happened – one side depends only on one variable (θ) and the other only on another (r). So again, each side is equal to

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[3] The notation for the constant is conventional; the reason for the "ℓ" subscript will become apparent in the subsequent lectures.

a constant, call it "α". So now we have three ordinary differential equations, each of which is much simpler than the original partial differential equation:

$$\begin{aligned}
\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-V(r)\right] &= \alpha\frac{R}{r^2} && (26.46)\\
-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{m_\ell^2\Theta}{\sin^2\theta} &= \alpha\Theta && (26.47)\\
\frac{d^2\Phi}{d\phi^2} &= -m_\ell^2\Phi && (26.48)
\end{aligned}$$

In these equations lie locked the secrets of the hydrogen atom!

26.5 Hydrogen Atom Eigenstate Functions

We assumed separation of variables for the time independent Schrödinger equation

$$\psi(r,\theta\phi)=R(r)\Theta(\theta),\Phi(\phi) \tag{26.49}$$

and broke the time independent Schrödinger equationup into three ordinary differential equations:

$$\begin{aligned}
\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-V(r)\right] &= \alpha\frac{R}{r^2}\\
-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{m_\ell^2\Theta}{\sin^2\theta} &= \alpha\Theta\\
\frac{d^2\Phi}{d\phi^2} &= -m_\ell^2\Phi
\end{aligned}$$

While we have no guarantee yet that we can cover all solutions of the time independent Schrödinger equationby this procedure, we proceed anyway. The ϕ-equation is easiest; it is an "oscillator equation", with general solution expressible as

$$\Phi(\phi)=\mathcal{A}\cos\left(m_\ell\phi\right)+\mathcal{B}\sin\left(m_\ell\phi\right) \tag{26.50}$$

or as

$$\Phi(\phi)=\mathcal{C}\mathrm{e}^{im_\ell\phi}+\mathcal{D}\mathrm{e}^{-im_\ell\phi} \tag{26.51}$$

To remove any lingering doubt as to the equivalence of these solutions (bear in mind that $\mathcal{A}, \mathcal{B}, \mathcal{C}, \mathcal{D}$ are all allowed to range over all complex numbers), we expand that last form by Euler's theorem:

$$\begin{aligned}\Phi(\phi) &= \mathcal{C}\left[\cos\left(m_\ell \phi\right) + i \sin\left(m_\ell \phi\right)\right] + \mathcal{D}\left[\cos\left(m_\ell \phi\right) - i \sin\left(m_\ell \phi\right)\right] \\ &= \left(\mathcal{C} + \mathcal{D}\right)\cos\left(m_\ell \phi\right) + i\left(\mathcal{C} - \mathcal{D}\right)\sin\left(m_\ell \phi\right)\end{aligned}$$

where we define $(\mathcal{C} + \mathcal{D})$ to be $\mathcal{A}$ and $i\,(\mathcal{C} - \mathcal{D})$ to be $\mathcal{B}$. We can allow for both terms by allowing m_ℓ to be either positive or negative, so we take

$$\Phi(\phi) = \mathcal{C}\mathrm{e}^{i m_\ell \phi} \tag{26.52}$$

26.5.1 Boundary Conditions on $\Phi(\phi)$

This is not all with this equation, however. Since changing an azimuthal angle by 2π brings one back to the same point in space, we should require

$$\Phi\left(\phi + 2\pi\right) = \Phi\left(\phi\right) \tag{26.53}$$

This means

$$\begin{aligned}\mathrm{e}^{i m_\ell (\phi + 2\pi)} &= \mathrm{e}^{i m_\ell \phi} \\ \mathrm{e}^{-m_\ell \phi}\mathrm{e}^{2\pi i m_\ell} &= \mathrm{e}^{i m_\ell \phi} \\ \mathrm{e}^{2\pi i m_\ell} &= 1 \\ \cos\left(2\pi m_\ell\right) + i \sin\left(2\pi m_\ell\right) &= 1 + 0i \\ \cos\left(2\pi m_\ell\right) &= 1 \\ \sin\left(2\pi m_\ell\right) &= 0\end{aligned}$$

$$m_\ell = 0, \pm 1, \pm 2, \pm 3, \cdots \tag{26.54}$$

We see that m_ℓ is restricted to be zero or a positive or negative integer, and that

$$\Phi_{m_\ell}(\phi) = \mathrm{e}^{-m_\ell \phi} \tag{26.55}$$

No other values of m_ℓ produce acceptable solutions.

26.6 The Θ Equation

We have

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{m_\ell^2\Theta}{\sin^2\theta}=\alpha\Theta \tag{26.56}$$

This is an equation that is well known to physicists and mathematicians. It cvan be solved by standard power series methods[4]; as with the harmonic oscillator, the solutions that do blow up at $\theta = 0$ and/or $\theta = \pi$ are polynomials times well behaved functions of θ; these exist for integer values of of two indices (ℓ, m_ℓ) where $\alpha = \ell(\ell+1)$

$$\Theta_{\ell,m_\ell}(\theta)=\mathcal{A}P_\ell^m(\cos\theta) \tag{26.57}$$

where $P_\ell^m(\cos\theta)$ is the "associated Legendre function", is

$$P_\ell^m(\cos\theta)\equiv\left(1-\cos^2\theta\right)^{|m_\ell|/2}\left(\frac{d}{dx}\right)^{|m_\ell|}P_\ell(\cos\theta) \tag{26.58}$$

where $P_\ell(\cos\theta)$ is the ℓ^{th} Legendre polynomial, given by

$$P_\ell(x)=\frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell\left(x^2-1\right)^\ell \tag{26.59}$$

where the first few Legendre polynomials are

$$\begin{aligned}
P_0(x) &= 1\\
P_1(x) &= x\\
P_2(x) &= \frac{1}{2}\left(3x^2-1\right)\\
P_3(x) &= \frac{1}{2}\left(5x^3-3x\right)\\
P_4(x) &= \frac{1}{8}\left(35x^4-30x^2+3\right)\\
&\vdots
\end{aligned}$$

Some mathematical properties they obey: The Legendre polynomials are orthogonal on the interval $[-1,1]$:

$$\int_{-1}^{1}P_m(x)P_n(x)\;dx=\begin{cases}0 & m\neq n\\ \frac{2}{2n+1} & m=n\end{cases} \tag{26.60}$$

---

[4] see any decent differential equations book.

They also form a complete set on this interval: Any “arbitrary” function $f(x)$ on $[-1, 1]$ can be expressed as

$$f(x) = \sum_{n=0}^{\infty} a_n P_n(x) \tag{26.61}$$

where, from the orthogonality relation above,

$$a_n = \left(n + \frac{1}{2}\right) \int_{-1}^{1} f(x) P_n(x)\ dx \tag{26.62}$$

You can verify that equation (26.57)is a solution of equation (26.56) by simply “plugging it in”. Note that for equation (26.59) to exist, ℓ has to be positive integer. Further, if $|m_\ell| > \ell$, $|m_\ell| \leq \ell$. Thus acceptable solutions exist only for

$$\begin{aligned} \ell &= 0, 1, 2, 3, 4, \cdots & (26.63) \\ m_\ell &= -\ell, -\ell+1, -\ell+2, \cdots, -1, 0, 1, \cdots, \ell-1, \ell & (26.64) \end{aligned}$$

Now, as a second order differential equation (26.56) has two linearly independent solutions for any ℓ and any m_ℓ, integer or not; the point is that these diverge at $\theta = 0$ and/or $\theta = \pi$ unless equation (26.63) and equation (26.64) are satisfied.

26.7 Spherical Harmonics

Putting these together, we define (dropping the subscript on m_ℓ)

$$Y_\ell^m(\theta, \phi) = N \Theta(\theta) \Phi(\phi) \tag{26.65}$$

where N is normalization constant. The determine N, we note that the volume element in spherical coordinates is $d^3\vec{r} = r^2 \sin\theta\ dr\ d\theta\ d\phi$; thus, to normalize Y_ℓ^m, we require

$$\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} |Y_\ell^m|^2 \sin\theta\ d\theta\ d\phi = 1 \tag{26.66}$$

This works out to be

$$Y_\ell^m(\theta, \phi) = \epsilon \sqrt{\frac{(2\ell+1)}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!}} \mathrm{e}^{im\phi} P_\ell^m(\cos\theta) \tag{26.67}$$

where $\epsilon = (-1)^m$ for $m \geq 0$, $\epsilon = 1$ for $m \leq 0$. These are orthogonal; they are listed (for low ℓ, m) in the following tables. The orthogonality of the spherical harmonics requires that

$$\int_0^{2\pi} \int_0^{\pi} \left[Y_\ell^m(\theta, \phi)\right]^* \left[Y_{\ell'}^{m'}(\theta, \phi)\right] \sin\theta \; d\theta \; d\phi = \delta_{\ell,\ell'} \delta_{m,m'} \tag{26.68}$$

$$\boxed{\begin{aligned}
Y_0^0 &= \left(\frac{1}{4\pi}\right)^{1/2} \\
Y_0^1 &= \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \\
Y_1^{\pm 1} &= \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \mathrm{e}^{\pm i\phi} \\
Y_2^0 &= \left(\frac{5}{16\pi}\right)^{1/2} \left(3\cos^2\theta - 1\right) \\
Y_2^{\pm 1} &= \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta \mathrm{e}^{\pm i\theta} \\
Y_2^{\pm 2} &= \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta \mathrm{e}^{\pm 2i\phi} \\
Y_0^3 &= \left(\frac{7}{16\pi}\right)^{1/2} \left(5\cos^3\theta - 3\cos\theta\right) \\
Y_3^{\pm 1} &= \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta \left(5\cos^2\theta - 1\right) \mathrm{e}^{\pm i\pi} \\
Y_3^{\pm 2} &= \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta \mathrm{e}^{\pm 2i\phi} \\
Y_3^{\pm 3} &= \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta \mathrm{e}^{\pm 3i\phi}
\end{aligned}}$$

Essentially due to their orthogonality,the spherical harmonics are also complete − any behaved function of θ and ϕ, $f(\theta, \phi)$ can be expanded as

$$f(\theta, \phi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} a_{\ell,m} Y_\ell^m(\theta, \phi) \tag{26.69}$$

while we do not prove this here, it is not terribly surprising since

$$Y_\ell^m(\theta,\phi) \propto \mathrm{e}^{-m\phi} P_\ell^m(\cos\theta) \tag{26.70}$$

and since the set $\left\{\mathrm{e}^{im\phi}\right\}$ is complete for functions of ϕ (it is just the complex Fourier series set) and the set $\{P_\ell(\cos\theta)\}$ is complete for functions of θ. (The same turns out to be true for associated Legendre functions $\{P_\ell^m(\cos\theta)\}$). The completeness of the $\{Y_\ell^m\}$ is very useful in slightly more advanced courses, however, we mention it now as a theoretical point.

Chapter 27

Twenty-Seventh Class: More on the Hydrogen Atom

Thursday, December 4, 2008

27.1 The Radial Equation

The radial equation for the hydrogen atom is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-V(r)\right]=\alpha\frac{R}{r^2} \tag{27.1}$$

Since $\alpha=\ell(\ell+1)$,this is

$$\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)-\frac{2mr^2}{\hbar^2}\left[V(r)-E\right]R(r)=\ell(\ell+1)R(r) \tag{27.2}$$

We have already some experience with this for the case $\ell=0$; in any case, before jumping into mathematics, let's try to further our intuition. In dealing with the semi-infinite square well in three dimensions (for the binding energy of the deuteron problem), I mentioned that the three dimensional Schrödinger equation for spherically symmetric states (ψ depends only on r) looks like the one-dimensional Schrödinger equation if we write it in term of the new variable $u(r)\equiv r\psi(r)$. So we try the same trick here. We define

$$u(r)\equiv rR(r) \tag{27.3}$$

then the radial equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2}+\left[V(r)+\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u(r)=Eu(r) \tag{27.4}$$

Note that this is the same as a one-dimensional time independent Schrödinger equationexcept for the appearance of a "new piece" $\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$ added to the potential energy. This "new piece" is called the centrifugal potential; it should be familiar from classical mechanics. To connect with this, consider the energy of, say, an orbiting planet in classical mechanics.

fig 1

The energy of this situation is

$$E = \frac{1}{2}mv^2 + V(r) \tag{27.5}$$

Now, in polar coordinates (since the orbit is in a plane)

$$\vec{v} = \dot{r}\hat{r} + r\dot{\theta}\hat{\theta} \tag{27.6}$$

so

$$v^2 = \dot{r}^2 + r^2\dot{\theta}^2 \tag{27.7}$$

so, the kinetic energy is

$$K.E. = \frac{1}{2}mv^2 = \frac{1}{2}m\dot{r}^2 + \frac{1}{2}mr^2\dot{\theta}^2 \tag{27.8}$$

The $\frac{1}{2}m\dot{r}^2$ term is the radial term and the $\frac{1}{2}mr^2\dot{\theta}^2$ term is the centrifugal term. Note that the kinetic energy is the "one-dimensional" "radial kinetic energy" plus a "centrifugal" piece. Thus

$$E = \frac{1}{2}m\dot{r}^2 + V(r) + \frac{1}{2}mr^2\dot{\theta}^2 \tag{27.9}$$

is the equivalent one-dimensional form of the energy. We now rewrite the centrifugal term in terms of the orbital angular momentum L. We have, from $\vec{L} = \vec{r} \times \vec{p}$,

$$L = m\left|\vec{v} \times \vec{r}\right| = mrv_\theta = mr \cdot r\dot{\theta} = mr^2\dot{\theta} \tag{27.10}$$

so

$$\frac{L^2}{2mr^2} = \frac{m^2r^4\dot{\theta}^2}{2mr^2} = \frac{1}{2}mr^2\dot{\theta}^2 \tag{27.11}$$

Comparing equations (27.1) and (27.11), we get

$$\boxed{E = \frac{1}{2}m\dot{r}^2 + V(r) + \frac{L^2}{2mr^2}} \tag{27.12}$$

Written in the last form, the centrifugal term $\frac{L^2}{2mr^2}$ looks like an addition to the potential energy; for this reason it is often called the "centrifugal potential"[1]. This makes us suspect that our term in the Schrödinger equation

$$\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} \tag{27.13}$$

is somehow the value of $\frac{L^2}{2mr^2}$ (i.e., $L^2 = \ell(\ell+1)\hbar^2$) for the eigenstates we will find with "quantum numbers" ℓ and m_ℓ. As we will see next week, this conjecture is exactly correct. Notice that the centrifugal potential acts like a classical "force" that is repulsive from the origin and is very strong at small r – this is like the centrifugal force in a rotating frame of reference in classical mechanics

$$-\frac{\partial V_{\text{cent}}}{\partial r} = +\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^3} \tag{27.14}$$

the + sign shows that this force is repulsive to + r and the $\frac{1}{r^3}$ term grows strongly with decreasing r.

27.2 More on the Hydrogen atom Radial Equation

With $u(r) \equiv rR(r)$, our radial equation (from any spherically symmetric potential $V(r)$) is

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu \tag{27.15}$$

For the hydrogen atom this becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu \tag{27.16}$$

To handle this, first we tidy it up (following Griffith's notation) by putting it in terms of a dimensionless dependent variable. We define

$$\kappa = \frac{\sqrt{-2mE}}{\hbar}, \quad \rho \equiv \kappa r, \quad \rho_0 \equiv \frac{me^2}{2\pi\varepsilon_0\hbar^2\kappa} \tag{27.17}$$

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[1] In classical physics, the "force" $-\frac{\partial V_{\text{cent}}}{\partial r}$ associated with V_{cent} is called the "inertial" or "fictitious" force.

then the equation is

$$\frac{d^2u(\rho)}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u(\rho) \tag{27.18}$$

It is tempting to try a direct power series solution of this,

$$u(\rho) = \sum_{n=0}^{\infty} a_n \rho^n$$

but this does not work. From your reading for today, you know that a method around this is to extract the behavior of $u(\rho)$ in the limits $\rho \to 0$ and $\rho \to \infty$, factoring these, then, we define a function $v(\rho)$ by

$$u(\rho) \equiv \rho^{\ell+1} \mathrm{e}^{-\rho} v(\rho) \tag{27.19}$$

then

$$\rho \frac{d^2 v}{d\rho^2} + 2(\ell + 1 - \rho)\frac{dv}{d\rho} + \left[\rho_0 - 2(\ell+1)\right] v = 0 \tag{27.20}$$

A simple power series trial

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

as a solution of equation (27.20) does not obviously fail, it leads to the recursion relation

$$c_{j+1} = \left[\frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)}\right] c_j \tag{27.21}$$

As you know from your reading, here we again encounter the same kind of problem we had for the harmonic oscillator problem – namely, the series solution represented by equation (27.21) diverges as $\rho \to \infty$ – and it badly enough to make $u(\rho) = \rho^{\ell+1}\mathrm{e}^{-\rho} v(\rho)$ also diverge as $\rho \to \infty$. Interestingly, "the same problem has the same solution" – our loophole (for the the atom to exist) is the terminate the series into polynomials. Then, equation (27.21) says for a given ρ_0, there must be a "j_{max}" such that

$$2\left(j_{\mathrm{max}} + \ell + 1\right) - \rho = 0 \tag{27.22}$$

Letting $n \equiv j_{\mathrm{max}} + \ell + 1$, then the termination condition is

$$2n = \rho_0 \tag{27.23}$$

which is

$$2n = \frac{me^2}{2\pi\varepsilon_o\hbar^2}\frac{\hbar}{\sqrt{-2mE}} \tag{27.24}$$

or

$$\sqrt{-2mE} = \frac{m_e e^2}{4\pi\varepsilon_0 n\hbar} \tag{27.25}$$

or

$$E_n = -\left(\frac{1}{4\pi\varepsilon_0}\right)^2 \frac{me^4}{2n^2\hbar^2} \tag{27.26}$$

therefore,

$$E_n = \frac{E_1}{n^2}, \quad E_1 = -\left(\frac{1}{4\pi\varepsilon_0}\right)^2 \frac{m_e e^4}{2\hbar^2} \tag{27.27}$$

these are exactly the Bohr energies! Further,

$$\kappa = \frac{\sqrt{-2mE}}{\hbar} = \left(\frac{1}{4\pi\varepsilon_0}\frac{m_e^2}{\hbar^2}\right)\frac{1}{n} = \frac{1}{a_0 n} \tag{27.28}$$

where $a_0 = 4\pi\varepsilon_0\frac{\hbar^2}{m_e e^2}$ is the Bohr radius.

27.3 A check

Let us pause before going on to state our result in generality and check that what we have makes sense. We consider the ground state. the question is – how do we identify it? Recall our termination condition

$$n = j_{\max} + \ell + 1 \tag{27.29}$$

The lowest energy is the minimum n, $n = 1$, and this means that $j_{\max} = \ell = 0$. Recalling that this only allows only $m_\ell = 0$ (m_ℓ ranges from $-\ell$ to ℓ), we see that our set of quantum numbers for the ground state is $n = 1, \ell = 0, m_\ell = 0$. So, we are looking at

$$\psi_{100}(r, \theta, \phi) = R_{1,0}(r) Y_0^0(\theta\phi) \tag{27.30}$$

Since Y_0^0 is a constant, all we need is $R_{1,0}(r)$. Now equation (27.21) with $j = 0$

$$c_1 = \frac{2(0+0+1-1)}{(0+1)(0+0+2)} = 0$$

so for $R_{1,0}$ only c_0 is not zero. Then from equation (27.16),

$$R_{1,0}(r) = \frac{u_{1,0}}{r} = \frac{\rho^{0+1}\mathrm{e}^{-\rho}v_{1,0}(\rho)}{r} \tag{27.31}$$

with $v_{1,0}(\rho) = c_0$ (a constant). Now, $\rho \equiv \kappa r$, and recalling that $\kappa = \frac{1}{a_0 n}$, here, $n = 1$

$$R_{1,0}(r) = c_0\frac{r}{a_0 r}\mathrm{e}^{-\frac{r}{a_0}} = \frac{c_0}{a_0}\mathrm{e}^{-\frac{r}{a_0}} = \text{constant} \times \mathrm{e}^{-\frac{r}{a_0}} \tag{27.32}$$

which is the same as we had by our original "easier method" early last week. Properly normalized (we'll see how to do this shortly),

$$\psi_{1,0,0}(r\theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}}\mathrm{e}^{-\frac{r}{a_0}} \tag{27.33}$$

Now consider the next energy level − $n = 2$. Referring to our definition of n, $n \equiv j_{\max} + \ell + 1$, we see that there two possible values of ℓ

$$\ell = 0 \;\Rightarrow\; j_{\max} = 1 \tag{27.34}$$

and

$$\ell = 1 \;\Rightarrow\; j_{\max} = 0 \tag{27.35}$$

This means that there are actually four different states with this energy: for $\ell = 1$, m_ℓ can be $-\ell, 0$, or $+1$! If $\ell = 0$ equation (27.21) says $c_1 = -c_0$, $c_2 = 0$, so all higher $c_n = 0$. Then, $v(\rho) = c_0 + c_1\rho = c_0(1 - \rho)$, so

$$R_{2,0}(r) = \frac{c_0}{2a_0}\left(1 - \frac{r}{2a_0}\right)\mathrm{e}^{-\frac{r}{2a_0}} \tag{27.36}$$

If $\ell = 1$, $j_{\max} = 0 \;\Rightarrow\; v(\rho) = c_0$

$$R_{2,1}(r) = \frac{c_0}{4a_0^2} r\mathrm{e}^{-\frac{r}{2a_0}} \tag{27.37}$$

so, you see how this thing works: for any n, $n = j_{\max} + \ell + 1$ tell us that the possible values of ℓ are

$$\ell = 0, 1, 2, 3, \cdots, n - 1 \tag{27.38}$$

and we already know that for any ℓ,

$$m_\ell = -\ell, -\ell + 1, -\ell + 2, \cdots, -1, 0, 1, \cdots, \ell - 1, \ell \tag{27.39}$$

(there are $2\ell+1$ values). Thus, level n has degeneracy

$$\sum_{\ell=0}^{n-1}(2\ell+1) = n^2 \tag{27.40}$$

In general,

$$\begin{aligned}
\psi_{n,\ell,m_\ell}(r,\theta,\phi) &= R_{n,\ell}(r)Y_\ell^{m_\ell}(\theta,\phi) && (27.41)\\
&= \frac{1}{r}\rho^{\ell+1}\mathrm{e}^{-\rho}v_{n,\ell}(\rho)Y_\ell^{m_\ell}(\theta,\phi) && (27.42)\\
&= \frac{1}{r}\left(\frac{r}{a_0 n}\right)^{\ell+1}\mathrm{e}^{-r/(a_0 n)}v_{n,\ell}\left(\frac{r}{a_0 n}\right)Y_\ell^{m_\ell}(\theta,\phi) && (27.43)
\end{aligned}$$

27.4 Hydrogen Atom – Eigenstates, Completeness, Probabilities

For the hydrogen atom,

$$\begin{aligned}
\psi_{n,\ell,m_\ell}(r,\theta,\phi) &= R_{n,\ell}(r)Y_\ell^{m_\ell}(\theta,\phi) && (27.44)\\
&= \frac{1}{r}\rho^{\ell+1}\mathrm{e}^{-\rho}v_{n,\ell}(\rho)Y_\ell^{m_\ell}(\theta,\phi) && (27.45)\\
&= \frac{1}{r}\left(\frac{r}{a_0 n}\right)^{\ell+1}\mathrm{e}^{-r/(a_0 n)}v_{n,\ell}\left(\frac{r}{a_0 n}\right)Y_\ell^{m_\ell}(\theta,\phi) && (27.46)
\end{aligned}$$

$V_{n,\ell}(\rho)$ is a polynomial of order $(n-\ell-1)$:

$$n_{n,\ell}(\rho) \equiv L_{n-\ell-1}^{2\ell+1}(2\rho) \tag{27.47}$$

where

$$L_{q-p}^{p}(x) \equiv (-1)^p\left(\frac{d}{dx}\right)^p L_q(x) \tag{27.48}$$

where

$$L_q(x) \equiv \mathrm{e}^x\left(\frac{d}{dx}\right)^q\left(\mathrm{e}^{-x}x^q\right) \tag{27.49}$$

$L_q(x)$ is called the "q^{th} Laguerre polynomial", and $L_{q-p}^{p}(x)$ is called the "associated Laguerre polynomial". Some of the Laguerre polynomials (L_q) are listed below.

$$\boxed{\begin{gathered}L_0 = 1\\ L_1 = -x + 1\\ L_2 = x^2 - 4x + 2\\ L_3 = -x^3 + 9x^2 - 18x + 6\\ L_4 = x64 - 16x^3 + 72x^2 - 96x + 24\\ L_5 = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120\\ L_6 = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720\end{gathered}}$$

Some of the associated Laguerre polynomials (L^p_{q-p}) are listed below

$$\boxed{\begin{gathered}L^0_0 = 1\\ L^0_1 = -x + 1\\ L^0_2 = x^2 - 4x + 2\\ L^1_0 = 1\\ L^1_1 = -2x + 4\\ L^1_2 = 3x^2 - 18x + 18\\ L^2_0 = 2\\ L^2_1 = -6x + 18\\ L^2_2 = 12x^2 - 96x + 144\\ L^3_0 = 6\\ L^3_1 = -24x + 96\\ L^3_2 = 60x^2 - 600x + 1200\end{gathered}}$$

With the normalization, the wave functions are

$$\psi_(n, \ell, m_\ell) =$$

$$\sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n\left[(n+\ell)!\right]^3}} \mathrm{e}^{-r/(na_0)} \left(\frac{2r}{na_0}\right)^\ell \left[L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{na_0}\right)\right] Y^m_\ell(\theta, \phi) \quad (27.50)$$

which is very complicated looking. Combining the orthonormality of the Y_ell^m's with that of the associated Laguerre polynomials yields (we don't show this) the result that the $\{\psi_{n,\ell,m}\}$ is a complete orthonormal set; the orthonormality relation is

$$\int \psi^*_{n,\ell,m}(r,\theta,\phi)\psi_{n',\ell',m'}(r,\theta,\phi)r^2\sin\theta\; dr\; d\theta\; d\phi = \delta_{n,n'}\delta_{\ell,\ell'}\delta_{m,m'} \tag{27.51}$$

The completeness property means that we can be assured that we have not "left out" any solution of the Schrödinger equation by looking for product solutions; any behaved function $f(r,\theta,\phi)$ can be expanded as

$$f(r,\theta,\phi) = \sum_{n=1}^{\infty}\sum_{\ell=0}^{\infty}\sum_{m_\ell=-\ell}^{\ell} a_{n,\ell,m_\ell}\psi_{n,\ell,m_\ell}(r,\theta,\phi) \tag{27.52}$$

In the next classes, we will try to make physical sense of our complicated looking results.

Chapter 28

Twenty-Eigth Class: Resolutions of Paradoxes

Tuesday, December 9, 2008

28.1 The Location of the Electrons in the Hydrogen Atom

We have our eigenstates for the Schrödinger hydrogen atom, but let's now look again at the most basic solution – the ground state. According to the Bohr model, the electron orbits at definite radius $a_0 \approx 0.5 \times 10^{-11}$ m. However, in the Schrödinger theory

$$\psi_{1,0,0} = \mathcal{C}_{1,0,0} \mathrm{e}^{-r/a_0} \tag{28.1}$$

This then means that the probability density of $\psi^* \psi$,

$$\psi^* \psi = |\mathcal{C}|^2 \, \mathrm{e}^{-2r/a_0} \tag{28.2}$$

peaks at $r = 0$ (inside the nucleus!)

fig 1

This seems to make no sense! Let us then, recall the volume element in spherical coordinates.

fig 2

Thus, probability of materializing in dV is

$$\mathrm{Prob}_{indV(r,\theta,\phi)} = \psi^*(r, \theta, \phi) \psi(r, \theta, \phi) r^2 \sin\theta \; dr \; d\theta \; d\phi \tag{28.3}$$

Let us ask, then for the total probability that the electron will materialize "between r and $r + dr$." Since we are dealing here with a spherically symmetric state ($\psi^* \psi$ is independent of θ and ϕ depends only on r), all we have to do in this case is multiply $\psi^*\psi$ by differential volume between r and $r + dr$ $dV = 4\pi r^2\ dr$. (hatched volume in figure 28.3.

fig 3

Thus

$$P(r)\ dr = \psi^*(r)\psi(r) \cdot 4\pi r^2\ dr \tag{28.4}$$

this is for s-states only[1]. We now see the resolution of our paradox:

$$P_{1,0,0}(r)\ dr = 4\pi \mathrm{e}^{-2r/a_0} r^2\ dr \propto r^2 \mathrm{e}^{-2r/a_0} \tag{28.5}$$

The factor r^2 vanishes at the nucleus; thus the plot of $P_{1,0,0)}(r)\ dr$ is shown in figure 28.4.

fig 4

Let us ash where this function peaks. To do this, we set

$$\begin{aligned}
\frac{dP(r)}{dr} &= 0 \\
\frac{d}{dr}\left(r^2 \mathrm{e}^{-2r/a_0}\right) &= 0 \\
r^2\left(-\frac{2}{a_0}\right) \cdot \mathrm{e}^{-2r/a_0} + 2r\mathrm{e}^{-2r/a_0} &= 0 \\
\frac{r^2}{a_0} &= r
\end{aligned}$$

therefore,

$$r = a_0 \tag{28.6}$$

Thus, for the ground state ($\psi_{1,0,0}$), the most likely small range of r that the electron can materialize in is centered on $r = a_0$!

28.2 Probability Distributions for Excited States

Now, unlike the ground state, generally the excited state functions depend on θ and ϕ (unless, of course, $\ell = 0$, in which cases the procedure is similar to that for the ground state.

$$\psi^*_{n,\ell,m_\ell}(r,\theta,\phi)\psi_{n,\ell,m_\ell}(r,\theta,\phi) = R^*_{n,\ell}\Theta^*_{\ell,m_\ell}\Phi^*_{m_\ell}R_{n,\ell}\Theta_{\ell,m_\ell}\Phi_m \tag{28.7}$$

---

[1] "s-states" are eigenstates with $\ell = 0$. The notation "s" is historical, but still widely used.

subject to the normalization condition

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^*_{n,\ell,m_\ell}(r,\theta,\phi)\psi_{n,\ell,m_\ell}(r,\theta,\phi) r^2 \sin\theta \; dr \; d\theta \; d\phi = 1 \tag{28.8}$$

often,however, we are not interested in keeping track of the angular dependence − we often only want to know about the radial probability distribution − e.g., about $\frac{dP}{dr}\,dr$, the probability of materialization in dr centered on r irrespective of θ and ϕ, or the total probability to materialize between distances r_1 and r_2 from the nucleus, irrespective of θ and ϕ, etc. If we are interested in the radial probability density, we want[2].

$$\begin{aligned} P_{n,\ell}(r)\;dr &= \int_0^\pi \int_0^{2\pi} \psi^*\psi r^2 \sin\theta \; dr \; d\theta \; d\phi \\ &= r^2 R^*_{n,\ell}(r) R_{n,\ell}(r)\;dr \int_0^\pi \Theta^*_{\ell,m}\Theta_{\ell,m}\sin\theta\;d\theta \int_0^{2\pi}\Phi^*\Phi\;d\phi \end{aligned}$$

Now the Θ and Φ functions are separately normalized so that the integrals above involving them are each equal to one. Thus,

$$P_{n,\ell}(r)\;dr = r^2 R^*_{n,\ell}(r) R_{n,\ell}(r)\;dr \tag{28.9}$$

We note that this is independent of m_ℓ. Of course

$$\int_0^\infty P_{n,\ell}(r)\;dr \tag{28.10}$$

for any n and ℓ. Thus, for example, in state n,ℓ,m $\langle r\rangle$ is found from

$$\langle r_{n,\ell}\rangle = \int_0^\infty r P_{n,\ell}(r)\;dr \tag{28.11}$$

Here is a way of remembering the r^2 factor in $P_{n,\ell}(r)$: $P(r)$ is the probability of finding the electron anywhere in the spherical shell of thickness dr centered on r − this is $\psi^*\psi$ × shell volume.

$$\begin{aligned} &= \psi^*\psi \cdot \text{surface area} \times \text{shell thickness} \\ &= \psi^*\psi \cdot 4\pi r^2 \; dr \end{aligned}$$

---

[2] $P_{n,\ell}(r)\;dr \equiv \frac{dP}{dr}\;dr$ for the state n,ℓ,m_ℓ

The 4π is absorbed in the conversion from ψ to R and the angular integrations. To see this, consider, e.g., the $1-s$ state

$$\psi_{1,0,0}(r) = \frac{1}{\sqrt{4\pi}} R(r) = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} \mathrm{e}^{-r/a_0} \tag{28.12}$$

with probability

$$\begin{aligned} P(r)\ dr &= |\psi|^2 \cdot 4\pi r^2\ dr & (28.13)\\ &= \frac{1}{4\pi} |R(r)|^2 \cdot 4\pi r^2\ dr & (28.14)\\ &= r^2 |R(r)|^2\ dr & (28.15) \end{aligned}$$

In any case, equation (28.9) on page 253 is correct for any eigenstate ψ_{n,ℓ,m_ℓ}. The factor r^2 in $r^2 |R_{n,\ell}|^2$ is important for any radial probability calculation and must not be omitted. Figure 28.5 shows plots for the $n = 1, 2$ and 3 states.

fig 5

The small vertical arrows indicate the position of $\langle r \rangle$ in units of a_0; note that, in general $\langle r \rangle \neq r_{\text{peak of dP/dr}}$. The expectation value is, of course, calculated from

$$\begin{aligned} \langle r_{n,\ell} \rangle &= \int_0^\infty r P_{n,\ell}(r)\ dr \\ &= \int_0^\infty r \cdot r^2 |R_{n,\ell}|^2\ dr \\ &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^*_{n,\ell,m} r \psi_{n,\ell,m} r^2 \sin\theta\ dr\ d\theta\ d\phi \end{aligned}$$

These expectation values have been evaluated; they are

$$\langle r_{n,\ell} \rangle = n^2 a_0 \left\{ 1 + \frac{1}{2} \left[1 - \frac{\ell(\ell+1)}{n^2} \right] \right\} \tag{28.16}$$

we see from this that the ℓ-dependence is suppressed by the factor $\frac{1}{2n^2}$; a qualitatively similar conclusion holds for the peaks. Thus, we see that the peaks for $n = 2$ are at larger r than that for $n = 1$, and for $n = 3$ at still larger r. Further, all the $n = 2$ functions peak near $r = 4a_0$ (most exact for $n = 2, \ell = 1$); all the $n = 3$ functions peak at $r \sim 9a_0$ (most exact for $n = 3, \ell = 2$), etc. This is roughly in agreement with the Bohr model ($R_n = n^2 a_0$) and provides support for a shell model of the atom. In order order to make much sense of the angular probability distributions, it is good to first discuss the connection with the angular momentum in quantum mechanics, and that we turn to next.

28.3 Angular Momentum and Hydrogen Atom States

We have, in cartesian coordinates,

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \tag{28.17}$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \tag{28.18}$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \tag{28.19}$$

As we have discussed, in quantum mechanics, classical quantities "do not exist", rather they are represented by operators. Since $p_x = - - \hbar\frac{\partial}{\partial x}$, etc., we have

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{28.20}$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{28.21}$$

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right) \tag{28.22}$$

As we are working in spherical coordinates, we need to transform these. If we do this, one finds

$$\hat{L}_x = -\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \tag{28.23}$$

$$\hat{L}_y = -\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \tag{28.24}$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \tag{28.25}$$

We will also be interested in $\widehat{L^2} = \widehat{L_x^2} + \widehat{L_y^2} + \widehat{L_z^2}$; in spherical coordinates this works out to be

$$\widehat{L^2} = -\hbar \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \tag{28.26}$$

Let us consider finding the eigenfunctions of $\hat{L}_z$ and $\widehat{L^2}$. Recall that, for any operator $\hat{Q}$, the function $f(\vec{r})$ is an eigenfunction of $\hat{Q}$ if and only if

$$\hat{Q} f(\vec{r}) = \text{constant} \times f(\vec{r}) \tag{28.27}$$

the constant is then the eigenvalue corresponding to the eigenfunction $f(\vec{r})$ of $\hat{Q}$. Consider, then, the eigenfunction problem for $\hat{L}_z$:

$$-i\hbar \frac{\partial}{\partial\phi} f(\phi) = c f(\phi) \Rightarrow \frac{df(\phi)}{d\phi} = \frac{ic}{\hbar} f(\phi)$$

therefore,

$$f(\phi) = \mathcal{A} \mathrm{e}^{\frac{ic}{\hbar}\phi} \tag{28.28}$$

any function $f(\phi)$ of this form is an eigenfunction of $\hat{L}_z$. Now consider the functions $\mathrm{e}^{-m_\ell \phi}$ from the hydrogen atom. Clearly

$$\hat{L}_z \mathrm{e}^{i m_\ell \phi} = m_\ell \hbar \mathrm{e}^{i m_\ell \phi} \tag{28.29}$$

since

$$Y_\ell^m(\theta, \phi) \propto P_\ell^m (\cos\theta)\, \mathrm{e}^{i m_\ell \phi} \tag{28.30}$$

$$\hat{L}_z Y_\ell^m(\theta, \phi) = m_\ell \hbar Y_\ell^m(\theta, \phi) \tag{28.31}$$

Further since

$$\begin{aligned} \hat{L}_z \psi_{n,\ell,m_\ell}(r, \theta, \phi) &= -i\hbar \frac{\partial}{\partial\phi} \\ &= R(r) \left[-i\hbar \frac{\partial}{\partial\phi} Y_\ell^m(\theta, \phi) \right] \\ &= m_\ell \hbar \left[R(r) Y_\ell^m(\theta, \phi) \right] \\ &= m_\ell \hbar \psi_{n,\ell,m}(r, \theta, \phi) \end{aligned}$$

thus, $\psi_{n,\ell,m}(R, \theta, \phi)$ is an eigenfunction of $\hat{L}_z$ with eigenvalue $m_\ell \hbar$. Now consider equation (28.3)

$$\widehat{L^2} = -\hbar \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$$

The right hand side of this looks kind of familiar. Recall the "Θ-equation" for the hydrogen atom eigenstates; it is

$$\left[-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{m_\ell^2}{\sin^2\theta}\right]=\ell(\ell+1)\Theta(\theta) \tag{28.32}$$

This is solved by $\Theta_{\ell,m_\ell}(\theta)$. Consider, then

$$\widehat{L^2}\psi_{m,\ell,m_\ell}=-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]\psi_{n,\ell,m_\ell}-\frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\psi_{n,\ell,m_\ell} \tag{28.33}$$

since

$$\frac{\partial^2}{\partial\phi^2}\psi_{n,\ell.m_\ell}=R(r)\Theta(\theta)\frac{\partial^2}{\partial\phi^2}\mathrm{e}^{im_\ell\phi}=(im_\ell)^2\,R(r)\Theta(\theta)\Phi(\phi)$$

$$\widehat{L^2}\psi_{n,\ell,m_\ell}=-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]\psi_{n,\ell,m_\ell}-\frac{m_\ell^2}{\sin^2\theta}\psi_{n,\ell,m_\ell} \tag{28.34}$$

therefore,

$$\widehat{L^2}\psi_{n,\ell,m_\ell}=-\hbar^2R_{n,\ell}(r)\Phi_{m_\ell}(\phi)\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)-\frac{m_\ell^2}{\sin^2\theta}\right]\Theta(\theta) \tag{28.35}$$

by using equation (28.32), this is

$$\widehat{L^2}\psi_{n,\ell,m_\ell}=\hbar^2\ell(ell+1)\psi_{n,\ell,m_\ell} \tag{28.36}$$

i.e., $\psi_{n,\ell,m_\ell}(r,\theta,\phi)$ is an eigenfunction of $\widehat{L^2}$ with eigenvalue $\ell(\ell+1)\hbar^2$

Thus, in addition to to being an eigenfunction of the hydrogen atom Hamiltonian with eigenvalue E_n

$$\widehat{H}\psi_{n,\ell,m_\ell}=E_n\psi_{n,\ell,m_\ell} \tag{28.37}$$

ψ_{n,ℓ,m_ℓ} is simultaneously also an eigenfunction of $\widehat{L^2}$ and $\hat{L}_z$

As we will see, the consequences of this are interesting are profound. However, already we see the physical meaning of the quantum numbers of ℓ and m_ℓ. Thus, if the state function is ψ_{n,ℓ,m_ℓ} If we measure the energy, we definitely get the value E_n. If we measure the magnitude of the "orbital" angular momentum, we definitely get the value $\sqrt{\ell(\ell+1)}\hbar$. If we measure the z-component of the angular momentum, we definitely get the value $m_\ell\hbar$. If the state function is a superposition state, then the probabilities follow the usual statistical rules we've developed.

28.4 Compatible and Incompatible Quantities

We have established[3] that the following three operators commute with each other:

$$\left[\widehat{H}, \widehat{L^2}\right] = \left[\widehat{H}, \hat{L}_z\right] = \left[\widehat{H}, \hat{L}_z\right] \tag{28.38}$$

Further, we have seen that the ψ_{n,ℓ,m_ℓ} are simultaneously, eigenfunctions of all three of these operators. This means that the values of of E, L^2, and L_z are sharp for any state ψ_{n,ℓ,m_ℓ}. These results illustrate a general theorem in quantum mechanics

Theorem: If observable operators $\hat{A}$ and $\hat{B}$ commute ($\left[\hat{A}, \hat{B}\right] = 0$), then there exists a complete set of functions $\{\psi_{A,B}\}$ that are simultaneously eigenfunctions of $\hat{A}$ and eigenfunctions of $\hat{B}$ – i.e.,

$$\begin{aligned} \hat{A}\psi_{A,B} &= A\psi_{A,B} \\ \hat{B}\psi_{A,B} &= B\psi_{A,B} \end{aligned}$$

thus, in such a state, the quantities corresponding to both $\hat{A}$ and $\hat{B}$ are sharp. We will not have time to prove this theorem in general, but, we note that the operators $\widehat{H}$, $\widehat{L^2}$, and $\hat{L}_z$ for the hydrogen atom provide an example.

On the other hand, the inverse of the theorem is also true – i.e., If $\hat{A}$ and $\hat{B}$ do not commute ($\left[\hat{A}, \hat{B}\right] \neq= 0$), then other than the zero function, there exists no function that is simultaneously an eigenfunction of $\hat{A}$ and also an eigenfunction of $\hat{B}$. Thus, if $\left[\hat{A}, \hat{B}\right] \neq 0$, there exists no state (other than $\psi = 0$) for which A and B are both sharp.

Example: Consider $\hat{x}$ and $\hat{p}_x$

We know that $[\hat{x}, \hat{p}_x] = i\hbar \neq=$. We also already know that there does not exist any states for which x and p_x are simultaneously sharp – the Heisenberg Uncertainty Principle forbids this. Now, we begin to see why.

In fact, in any state, the product of the statistical uncertainties $\sigma_A\sigma_B$ of A and B is determined by the extent of the noncommutation:

$$\boxed{\sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}\left\langle\left[\hat{A}, \hat{B}\right]\right\rangle\right)^2} \tag{28.39}$$

---

[3] You can easily show these

where $\langle[\,]\rangle$ is the expectation value of the commutator $\left[\hat{A}, \hat{B}\right]$. Equation (28.39)is the generalized uncertainty principle. It is proved in the appendix to this lecture.

Example: $[\hat{x}, \hat{p}_x]$ according to equation (28.39)

$$\sigma_x^2 \sigma_p^2 \geq \left(\frac{1}{2i} \cdot i\hbar\right)^2 = \left(\frac{\hbar}{2}\right)^2 \Rightarrow \sigma_x \sigma_p \geq \frac{\hbar}{2} \tag{28.40}$$

Now, we know, e.g., that (similarly, one can show that)

$$\boxed{\begin{aligned} \left[\hat{L}_x, \hat{L}_y\right] &= i\hbar L_z \\ \left[\hat{L}_y, \hat{L}_z\right] &= i\hbar L_x \\ \left[\hat{L}_z, \hat{L}_x\right] &= i\hbar L_y \end{aligned}} \tag{28.41}$$

This means that there is no state (other than $\psi = 0$) that is sharp in more than one cartesian component of L.

Example: $\psi_{n,\ell,m}$ is sharp in L_z ($L_z = m_\ell \hbar$).

Therefore, it is not sharp in L_x and not sharp in L_y.

Question: Suppose then that the state function is $\psi_{n,\ell,m}$ and we measure L_x. What possible results can you obtain? What is the probability of each result?.

Answer:

To answer this, one must expand the state function $\psi_{n,\ell,m}$ over the complete set of eigenfunctions of the operator $\hat{L}_x$. (Since $\hat{L}_x$ is a Hermitian operator, like all other Hermitian operators it possesses a complete set of eigenfunctions). Let us call these functions $\{f_{L_x}\}$. Then our expansion is

$$\psi_{n,\ell,m} = \sum_k c_k f_{L_x,k} \tag{28.42}$$

where

$$\hat{L}_x f_{L_x,k} = L_x f_{L_x,k}$$

The probability of obtaining the result $L_{x,k}$ is $|c_k|^2$.

We will now inquire as to the nature of the eigenfunctions of $\hat{L}_x$. We will note, however, (without proof) that the eigenvalues of $\hat{L}_x$ are integer multiples of $\hbar$, as are the eigenvalues of $\hat{L}_z$ (and $\hat{L}_y$). For this reason, $\hbar$ is the fundamental unit of angular momentum

28.5 Angular Dependence of States and Probabilities

We now return to the angular dependence of probabilities. We note that

$$\psi^*_{n,\ell,m_\ell}\psi_{n,\ell,m_\ell} = R^*_{n,\ell}R_{n,\ell}\Theta^*_{\ell,m_\ell}\Theta_{\ell,m_\ell}\Phi^*_{m_\ell}\Phi_{m_\ell} \tag{28.43}$$

but,

$$\Phi^*_{m_\ell}\Phi_{m_\ell} = \mathrm{e}^{im_\ell\phi}\mathrm{e}^{im_\ell\phi} = 1 \tag{28.44}$$

consequently, for state ψ_{n,ℓ,m_ℓ}, the probability density does not depend of ϕ. Thus, to study the angular dependence of probabilities for the eigenstates, we need only study $\Theta^*_{\ell,m_\ell}\Theta_{\ell,m_\ell}$. A simplified way of studying this involves a polar diagram (see figure 28.6); the origin is at the nucleus, and the z-axis is taken alone the direction from which θ is measured. The distance from the origin to the curve, at angle θ is proportional to $\Theta^*_{\ell,m_\ell}(\theta)\Theta_{\ell,m_\ell}(\theta)$.

fig 6

Let is look at a few of the states in more detail. The $1s$ and $2s$ states are, of course, spherically symmetric. However, consider the $2p$ states.

$$\psi_{2,1,0} = C_{2,1,0}\left(\frac{r}{a_0}\right)\mathrm{e}^{\frac{r}{2a_0}}\cos\theta \tag{28.45}$$

$$\psi_{2,1,\pm1} = C_{2,1,1}\left(\frac{r}{a_0}\right)\mathrm{e}^{-\frac{r}{2a_0}}\sin\theta\mathrm{e}^{\pm i\phi} \tag{28.46}$$

The angular probability densities $\Theta^*\Theta$ behaves as

$$\Theta^*_{1,0}\Theta_{1,0} \propto \cos^2\theta \tag{28.47}$$

$$\Theta^*_{1,\pm1}\Theta_{1,\pm1} \propto \sin^2\theta \tag{28.48}$$

(where θ is measured from the z-axis). Computer plots in which the density of the dots gives an indication of the r-dependence of the probability density are shown in figures 28.7 through 28.12.

fig 7-12

Appendix

28.6 Schwarz Inequality

to proceed we need to establish a result called the "Schwarz Inequality". This say that, for any two normalizable functions $f(x)$ and $g(x)$, and any interval $[a, b]$,

$$\left(\int_a^b |f|^2 \ dx\right)\left(\int_a^b |g|^2 \ dx\right) \geq \left|\int_a^b f^*(x)g(x) \ dx\right|^2 \tag{28.49}$$

In our more compact notation, this is

$$\langle f \mid f\rangle \langle g \mid g\rangle \geq |\langle f \mid g\rangle|^2 \tag{28.50}$$

Before we prove this, first let's get some intuition on it in ordinary three dimensional space. SUppose that, in ordinary three dimensional space, we have two vectors, $\vec{A}$ and $\vec{B}$. Then

textitfig 13

$$\langle A \mid B\rangle \equiv \vec{A} \cdot \vec{B} = AB\cos\theta \leq AB \tag{28.51}$$

therefore,

$$|\langle A \mid B\rangle|^2 \leq |A|^2 |B|^2 \tag{28.52}$$

The Schwartz inequality say "the same thing" on the infinite dimensional function space.

Proof

1. **Lemma**: For any normalizable function $f(x)$, $\langle f \mid f\rangle \geq 0$.

   Proof: Using completeness, expand in the complete set of eigenfunctions of any hermitian observable

$$f(x) = \sum_n c_n \psi_n \tag{28.53}$$

Then,

$$\begin{aligned}
\langle f \mid f\rangle &= \left\langle \sum_{i=1}^{N} c_i\psi_i \mid \sum_{j=1}^{N} c_j\psi_j \right\rangle \\
&= \sum_{i=1^N} \sum_{j=1}^{N} c_i^* c_j \langle \psi_i \mid \psi_j\rangle \\
&= \sum_{i=1}^{N} \sum_{j=1}^{N} c_i^* c_j \delta_{i,j} \\
&= \sum_{i=1}^{N} |c_i|^2 \geq 0
\end{aligned}$$

2. Now let $\psi = f + bg$ where b is an arbitrary complex number.

   By our lemma,

   $$0 \leq \langle \mid \psi\rangle = \langle f + bg \mid f + bg\rangle \tag{28.54}$$

   Therefore,

   $$0 \leq \langle f \mid f\rangle + b\langle f \mid g\rangle + b^* \langle g \mid f\rangle + bb^* \langle g \mid g\rangle \tag{28.55}$$

   To minimize the right hand side, we differentiate with respect to b and set the result equal to zero.

   $$0 = \frac{d}{db}\langle \psi \mid \psi\rangle = \langle f \mid g\rangle + b^* \langle g \mid g\rangle \tag{28.56}$$

   therefore,

   $$b^* = -\frac{\langle f \mid g\rangle}{\langle g \mid g\rangle} \tag{28.57}$$

   and

   $$b = -\frac{\langle g \mid f\rangle}{\langle g \mid g\rangle} \tag{28.58}$$

   By putting these into equation (28.55), we get

   $$0 \leq \langle f \mid f\rangle - \frac{\langle g \mid f\rangle}{\langle g \mid g\rangle}\langle f \mid g\rangle - \frac{\langle f \mid g\rangle}{\langle g \mid g\rangle} + \frac{\langle g \mid f\rangle \langle f \mid g\rangle}{\left|\langle g \mid g\rangle\right|^2} \tag{28.59}$$

Therefore,

$$0 \leq \langle f \mid f \rangle - \frac{|\langle f \mid g \rangle|^2}{\langle g \mid g \rangle} + \frac{|\langle f \mid g \rangle|^2}{\langle g \mid g \rangle} \tag{28.60}$$

Therefore,

$$\langle f \mid f \rangle \langle g \mid g \rangle \geq |\langle f \mid g \rangle|^2 \tag{28.61}$$

28.7 The Uncertainty Principle – Proved

Suppose we have an ensemble of systems, all in the same state Ψ, and we consider measurements of two observables, A and B. From our previous discussions, the variances are

$$\begin{aligned} \sigma_A^2 &= \left\langle \left(\hat{A} - \langle A \rangle\right)^2 \right\rangle \\ &= \left\langle \Psi \mid \left(\hat{A} - \langle A \rangle\right) \left(\hat{A} - \langle A \rangle\right) \Psi \right\rangle \\ &= \left\langle \left(\hat{A} - \langle A \rangle\right) \Psi \mid \left(\hat{A} - \langle A \rangle\right) \Psi \right\rangle \end{aligned}$$

Therefore,

$$\sigma_A^2 = \langle f \mid f \rangle \tag{28.62}$$

where $f(x) \equiv \left(\hat{A} - \langle A \rangle\right) \Psi$. Likewise,

$$\sigma_B^2 = \langle g \mid g \rangle \tag{28.63}$$

where $g(x) \equiv \left(\hat{B} - \langle B \rangle\right) \Psi$

Consider now

$$\sigma_A^2 \sigma_B^2 = \langle f \mid f \rangle \langle g \mid g \rangle \tag{28.64}$$

By the Schwarz inequality, the right hand side of this is greater than $|\langle f \mid g \rangle|^2$, hence

$$\sigma_A^2 \sigma_B^2 \geq |\langle f \mid g \rangle|^2 \tag{28.65}$$

Now $\langle f \mid g \rangle$ is some complex number; call it z. Since for any complex number,

$$\begin{aligned} |z|^2 = z^* z &= [Re(z) - iIm(z)]\,[Re(z) + iIm(z)] \\ &= [Re(z)]^2 + [Im(z)]^2 \geq [Im(z)]^2 \\ &= \left[\frac{z - z^*}{2i}\right]^2 \end{aligned}$$

We have

$$\boxed{\sigma_A^2 \sigma_B^2 \geq \left[\frac{\langle f \mid g\rangle - \langle g \mid f\rangle}{2i}\right]^2} \tag{28.66}$$

Let us work this out in terms of $\hat{A}$ and $\hat{B}$

$$\begin{aligned}
\langle f \mid g\rangle &= \left\langle \left(\hat{A} - \langle A\rangle\right)\Psi \mid \left(\hat{B} - \langle B\rangle\right)\Psi\right\rangle \\
&= \left\langle \Psi \mid \left(\hat{A} - \langle A\rangle\right)\left(\hat{B} - \langle B\rangle\right)\Psi\right\rangle \\
&= \left\langle \Psi \mid \left\{\hat{A}\hat{B} - \langle A\rangle \hat{B} - \hat{A}\langle B\rangle + \langle A\rangle\langle B\rangle\right\}\Psi\right\rangle \\
&= \left\langle \Psi \mid \left(\hat{A}\hat{B}\right)\Psi\right\rangle - \langle A\rangle\left\langle \Psi \mid \hat{B}\Psi\right\rangle - \langle B\rangle\left\langle \Psi \mid \hat{A}\Psi\right\rangle + \langle A\rangle\langle B\rangle\langle \Psi \mid \Psi\rangle \\
&= < \langle AB\rangle - \langle A\rangle\langle B\rangle - \langle B\rangle\langle A\rangle + \langle A\rangle\langle B\rangle \\
&= \langle AB\rangle - \langle A\rangle\langle B\rangle
\end{aligned}$$

Likewise,

$$\langle g \mid f\rangle = \langle f \mid g\rangle^* = \langle BA\rangle - \langle A\rangle\langle B\rangle$$

Therefore, equation (28.66) says

$$\sigma_A^2 \sigma_B^2 \geq \left[\frac{\langle AB\rangle - \langle BA\rangle}{2i}\right]^2 = \left[\frac{\langle AB - BA\rangle}{2i}\right]^2 \equiv \left[\frac{\left\langle\left[\hat{A}, \hat{B}\right]\right\rangle}{2i}\right]^2 \tag{28.67}$$

Thus, the generalized uncertainty principle is

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{\left\langle\left[\hat{A}, \hat{B}\right]\right\rangle}{2i}\right)^2 \tag{28.68}$$

this gives a quantitative expression to “how incompatible” A and B are when they don’t commute.

Example: Suppose $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p_x} = \frac{\hbar}{i}\frac{\partial}{\partial x}$.

As you know, $[\hat{x}, \hat{p}_x] = -\hbar$. Therefore, equation (28.68) says that, for any state Ψ

$$\sigma_x^2 \sigma_{p_x}^2 \geq \left(\frac{i\hbar}{2i}\right)^2 = \left(\frac{\hbar}{2}\right)^2 \tag{28.69}$$

or

$$\sigma_x \sigma_{p_x} \geq \frac{\hbar}{2} \tag{28.70}$$

Which you recognize as the original Heisenberg Uncertainty Principle , now proved. However, we now see that this is just one case a much more general (and deeper) principle. We will discuss one consequence of this in the next class.

Chapter 29

Twenty-Ninth Class: Four Last Things

Friday, December 2, 2008

29.1 What's Special About the z-Axis?

Look back at our polar plots of the angular dependence of the hydrogen atom eigenstate probability densities. We see that in these plots that, for a given state with $\ell \neq 0$, there are conical "nodal surfaces" on which the electron can never materialize. This is very strange, you might think. You might say − prepare a million different hydrogen atoms in the same state, then measure the position of the electron for each. This would then locate the nodal surfaces, from which one could locate the z-axis. But, this should be impossible − since $V(r)$ is spherically symmetric, this would amount to finding a preferred direction in space, which is a violation of a very basic physical principle. Thus, it appears that we have a serious paradox undermining the entire Schrödinger theory of the hydrogen atom on our hands. Let us think on this.

Consider any one of the $n = 2$ states, for example, $\psi_{2,1,1}$. How could one set a system into this state? We need to perform three measurements − energy (to segregate for further measurements later all atoms materializing the $n = 2$ energy level), magnitude of angular momentum (to segregate all atoms with $\ell = 1$ in addition to $n = 2$), and L_z (to finally define $L_z = 1\hbar$). Consider, for example, the least measurement. To accomplish it requires an external magnetic field set up to point in the direction we wish to call "z". thus, to make the measurement requires the positive setting up of a special direction in space, thus destroying the isotropy. Without destroying the isotropy of space by forcing a "special direction" it is not possible to measure L_z. Thus, without destroying the isotropy of space, all we an say is that an atom could be in any of $\psi_{2,1,-1}$, $\psi_{2,1,0}$, $\psi_{2,1,1}$, or any superposition of these. Thus, on average, a large ensemble would correspond to an equal weight superposition of these states; thus

$$\psi^*\psi_{\text{effective}} = \frac{1}{3}\left[\psi^*_{2,1,-1}\psi_{2,1,-1} + \psi^*_{2,1,1}\psi_{2,1,1} + \psi^*_{2,1,0}\psi_{2,1,0}\right] \tag{29.1}$$

Two of these terms are proportional to $\frac{1}{2}\sin^2\theta$, and one is proportional to $\cos^2\theta$. Therefore, the sum is spherically symmetric ($\sin^2\theta + \cos^2\theta =$ no θ dependence).

This logic shows that at least, we cannot "force" the paradox to appear experimentally. To further resolve the paradox conceptually, we must realize again that the "wave function" ψ is not a real thing that exists in real space. (In fact, this paradox demonstrates one of the major problems with such a naive "realism" interpretation of ψ.

29.2 A Brief Basis for Chemical Bonding – Atomic "Orbital" in Different Directions

We have, for p-states for any $n > 1$,

$$\begin{aligned}
\psi_{n,1,1})r,\theta,\phi) &= -\sqrt{\frac{3}{8\pi}}R_{n,1}(r)\sin\theta \mathrm{e}^{i\phi} && (29.2)\\
\psi_{n,1,0}(r,\theta,\phi) &= \sqrt{\frac{3}{4\pi}}R_{n,1}(r)\cos\theta = \sqrt{\frac{3}{4\pi}}R_{n,1}(r)\frac{z}{r} && (29.3)\\
\psi_{n,1,-1}(r,\theta,\phi) &= \sqrt{\frac{3}{8\pi}}R_{n,1}(r)\sin\theta \mathrm{e}^{-i\phi} && (29.4)
\end{aligned}$$

These three states are degenerate (correspond to the same energy). Now, chemical bonding in a molecule is greatly enhanced when the electron's wave function overlap from the atom's is maximally dense. The state $\psi_{n,1,0}$ is suited for this since its "lobes" stick out purely along z; however, the high density region for the other two states is distributed all around the equator, and hence is "diluted". With this in mind, we investigate the possibility of forming new eigenstates that have a more "centered" probability density than do $\psi_{2,1,1}$ and $\psi_{2,1,-1}$. to begin to understand how this works, we consider the following statement: Any linear combination of eigenstates corresponding to the same energy for a given Hamiltonian $\widehat{H}$ is also an eigenstate of $\widehat{H}$ for that same energy.

Proof: Suppose $\widehat{H}\psi_i = E\psi_1$ and $\widehat{H}\psi_2 = E\psi_2$. Let c_1 and c_2 be any complex numbers. Then

$$\begin{aligned} c_1\widehat{H}\psi_1 &= \widehat{H}(c_1\psi_1) = c_1E\psi_1 = Ec_1\psi_1 && (29.5) \\ c_2\widehat{H}\psi_2 &= \widehat{H}(c_2\psi_2) = c_2E\psi_2 = Ec_2\psi_2 && (29.6) \\ & && (29.7) \end{aligned}$$

(since $\widehat{H}$ is linear). Adding these

$$\widehat{H}\left(c_1\psi_1 + c_2\psi_2\right) = E\left(c_1\psi_1 + c_2\psi_2\right) \tag{29.8}$$

(again using the linearity of $\widehat{H}$). Therefore, $c_1\psi_1+c_2\psi_2$ is also an eigenfunction of $\widehat{H}$ with eigenvalue E.

with this in mind, let us consider the following three linear combinations of $\psi_{n,1,0}$, $\psi_{n,1,1}$, and $\psi_{n,1,-1}$

$$\begin{aligned} p_z &= \psi_{n,1,0}(\vec{r}) = \sqrt{\frac{3}{4\pi}}R_{n,1}(r)\frac{z}{r} && (29.9) \\ p_x &= -\frac{1}{\sqrt{2}}\left[\psi_{n,1,1}(\vec{r}) - \psi_{n,1,-1}(\vec{r})\right] = \sqrt{\frac{3}{4\pi}}R_{n,1}(r)\frac{x}{r} && (29.10) \\ p_y &= \frac{i}{\sqrt{2}}\left[\psi_{n,1,1}(\vec{r}) + \psi_{n,1,-1}(\vec{r})\right] = \sqrt{\frac{3}{4\pi}}R_{n,1}(r)\frac{y}{r} && (29.11) \end{aligned}$$

These new eigenfunctions ("orbitals" to chemists) are shown in figure 29.1.

fig 1

In each of these we have two regions of relatively high electron probability density, which is god for chemical bonding. An example wherein nature "makes use of this" is in the crucially important H_2O molecule. In the oxygen atom (at the "center" (total 8 electrons), the $1s$ state is filled (uses two electrons, spin up and spin down). the $2s$ state is also filled (uses 2 more electrons), one $2p$ orbital is fully occupied (uses 2 more electrons) and the remaining two $2p$ orbitals are each only half full (1 electron each) and so each can join with a $1s$ orbital from a hydrogen atom in its ground state to form what are "$sp\sigma'$' bonding orbitals (shown in figure 29.2). In this, essentially the $2p_x$ and $2p_y$ orbitals of the oxygen are used.

fig 2

29.3 The Necessary "Bohr-Limit"

We wish to further investigate the classical limit of the quantum mechanics of the hydrogen atom. Ultimately, we would like to be able to construct tight wave packets that circle the nucleus in orbitals,part of this is implied by Ehrenfest's theorem, which tells us that $\langle\vec{r}\rangle$ for the electron follows the classical path. As a conceptual step along the way, we could ask $-$ to what extent are certain of the eigenfunctions ψ_{n,ℓ,m_ℓ} Bohr-like? Now we're already seen that the radial probability distributions peak around n^2a_0 (with sub-peaks in case for which $\ell < n-1$); as a reminder, a figure corresponding to this is shown figure 29.3.

fig 3

The states with the "single bump in r" are the most Bohr-like. It is interesting that these occur for the highest possible ℓ-values for each n (i.e., $\ell = n-1$). This is explained in the following

text

Classical Limit: One can imagine "setting up" a superposition state function $\Psi(x, t=0)$ that is the sum of large n and $\ell = n-1$ eigenfunctions, and one that is localized to a small azimuthal range $\Delta\phi$. (For large n and $\ell = n-1$, $\Psi(x, t=0)$ is already very localized around $\theta = \frac{\pi}{2}$ and in r), If the time dependence for each term is included, then, presumably, the following is what would unfold over over the course of time: the packet would "split" into two pieces, each of which orbits the point at the proton in the opposite direction. This, presumably represents the classical limit.

29.4 If an Eigenstate is Forever, Why Do Atoms Radiate?

Consider an electron in a hydrogen atom; say in a $2p$ state. After a mean lifetime $\tau \sim 10^{-8}$ seconds in this state, the atom "decays" to the ground state, with the emission of a photon of frequency corresponding to the energy difference between $2p$ and $1s$. But why? $2 - p$ is an eigenstate, and according to our work so far, eigenstates should last forever.

The classical theory, on the other hand, seems to present the opposite problem. According to Maxwell;'s equations, whenever a charge accelerates, the vacuum is obliged to emit electromagnetic radiation; since electrons in classical orbits accelerate, they should always radiate. We will sketch the answer to the answer to the "eigenstates should live forever" question shortly. In the meantime, to get a physical picture (again, we'll justify this shortly) we will assume that "during the transition", the state function is a time dependent superposition of the initial and final atomic eigenstates

$$\Psi(\vec{r}, t) = a_i(t)\psi_i(\vec{r})\mathrm{e}^{-E_i t/\hbar} + a_f(t)\psi_f(\vec{r})\mathrm{e}^{-iE_f t/\hbar} \tag{29.12}$$

Note that the coefficients a_i and a_f are time dependent where $a_i(t) = 1$ before the transition and zero after the transmission and $a_f(t) = 0$ before the transition and one after the transition. Now consider $\langle \vec{r} \rangle$ for the electron during the transition

$$\begin{aligned}
\langle \vec{r} \rangle_t &= \int \Psi^*(\vec{r}, t)\vec{r}\Psi(\vec{r}, t)\ d^3\vec{r} \\
&= a_1^* a_i \int \vec{r}\,|\psi_i|^2\ d^3\vec{r} + a_f^* a_f \int \vec{r}\,|\psi_f|^2\ d^3\vec{r} \\
&+\ a_i^* a_f \left(\int \psi_i^* \vec{r} \psi_f\ d^3\vec{r} \right) \mathrm{e}^{+i(E_i - E_f)t/\hbar} \\
&+\ a_f a_f^* \left(\int \psi_f^* \vec{r} \psi_i\ d^3\vec{r} \right) \mathrm{e}^{-i(E_i - E_f)t/\hbar}
\end{aligned}$$

Now, since ψ_i and ψ_f are eigenstates ψ_{n,ℓ,m_ℓ}, the first two integrals vanish. The third and fourth terms are complex conjugates, so their sum is

$$\langle \vec{r} \rangle_t = 2Re \left\{ \left(a_f^* a_i \right) \left(\int \psi_f^* \vec{r} \psi_i\ d^3\vec{r} \right) \mathrm{e}^{-i(E_i - E_f)t/\hbar} \right\} \tag{29.13}$$

This expression has three factors. The middle factor is called "the matrix element of $\vec{r}$"; it is an overlap integral involving the final and initial states; it is a measure of the amplitude of the oscillation defined by the real part of the last factor, $\cos\left(\frac{E_i - E_f}{\hbar}t\right)$. Thus, in this picture, during the transition, the position of the electron expectation value undergoes simple harmonic motion of frequency $\frac{E_i - E_f}{\hbar} = \frac{E_2 - E_1}{\hbar}$; semi-classically, this would require the emission of electromagnetic radiation of this frequency.

Now, why should the state function during the transition be a superposition of hydrogen atom eigenstates? The answer is deep, and have time only to sketch it here. The point is that, according to quantum field theory, the Hamiltonian of the electron is the atom is not the whole story! Rather, the real Hamiltonian has three pieces, the Hamiltonian for the electron in the hydrogen atom, the Hamiltonian for the vacuum radiation filed, and the Hamiltonian for the interaction between the electron and the vacuum radiation field. Thus, the total Hamiltonian for the hydrogen atom is the sum of these

$$\widehat{H}_{e^-} \equiv \widehat{H}_1 + \widehat{H}_2 + \widehat{H}_3 \tag{29.14}$$

The eigenstates of $\widehat{H}_1$ are the ψ_{n,ℓ,m_ℓ}'s. The eigenstates of $\widehat{H}_2$ are the existence of various numbers and frequencies of photons in the vacuum.

But, what can be said about $\widehat{H}_3$? Electrodynamics shows that it is of the form

$$\widehat{H}_{int} = -\frac{e}{2m_e}\left(\hat{\vec{p}} \cdot \hat{\vec{A}} + \hat{\vec{A}} \cdot \hat{\vec{p}}\right) \tag{29.15}$$

where $\hat{\vec{p}}$ is the electron momentum operator and $\hat{\vec{A}}$ is the operator for the electromagnetic vector potential.

At this point,you might think that, in "darkness" (atom in vacuum), $\vec{A} = 0$, so nothing will happen, but quantum field theory shows this to be wrong! The background quantum vector potential field, whose excited modes are photons, looks like an infinite collection of quantum oscillators. According to quantum mechanics, each oscillator mode (photon) has a nonzero "zero-point energy" (recall that this is $\frac{1}{2}\hbar\omega$ for a quantum oscillator), so even in "darkness", $\widehat{H}_{int}$ is always nonzero.

Now consider the atom in the $2p$ state. this is an eigenstate of $\widehat{H}_1$, but it is not an eigenstate of $\widehat{H}_{full} = \widehat{H}_1 + \widehat{H}_2 + \widehat{H_3}$. Therefore, its real time dependence is not $\mathrm{e}^{-iE_2t/\hbar}$, where E_2 is the energy of $2p$. Rather, its best to just write it as $\Psi(\vec{r},t)$.

So, what is $\Psi(\vec{r},t)$? According to the completeness theorem (again!), whatever the eigenstates, ψ_{n,ℓ,m_ℓ} are a complete set, so

$$\Psi(\vec{r},t) = \sum a_{n,\ell,m_\ell}(t)\psi_{n,\ell,m_\ell}\mathrm{e}^{-iE_nt/\hbar} \tag{29.16}$$

where the expansion coefficients $a_{n,\ell,m_\ell}(t)$ depend on time. We note that equation (29.16) is of the form of equation (29.12). Detailed analysis shows that only the initial $2p$ and the ground state $1s$ states contribute to equation (29.16), so equation (29.12) does indeed result.

29.5 Transition Rates and Spin Angular Momentum of Photons

We have seen that the transition rate (probability of decay from excited state to ground state with emission of electromagnetic radiation, per second) should be proportional to the square of the "matrix element" between the initial and final electron states, i.e.,

$$R \propto |P_{fi}|^2, \quad P_{fi} \equiv \int \psi_f^* e\vec{r}\psi_i \; d\tau \tag{29.17}$$

where $d\tau \equiv \; d^3\vec{r}$. A rigorous treatment from quantum electrodynamics corroborates this conjecture. Now, P_{fi} can be evaluated for every pair of eigenstates for the hydrogen atom. When this is done, it is found that $P_{fi} = 0$ unless

$$\boxed{\begin{gathered}\Delta\ell = \pm 1\\ \Delta m_\ell = 0, \pm 1\end{gathered}} \tag{29.18}$$

for the transition. These are known as the "selection rules". Thus, unless these "selection rules" are obeyed, the rate for the transition is much suppressed (in fact, in our approximate treatment the rate would be zero.) Such transitions are called "dipole forbidden". We can get some insight into the $\Delta\ell \pm 1$ rule by noting that $\psi_{n,\ell,m_\ell} \propto Y_\ell^{m_\ell}(\theta,\phi)$ and the space reflection on parity of $Y_\ell^{m_\ell}$ is (-1)! That is, if $\vec{r} \to -\vec{r}$, then $Y_\ell^{m_\ell}(\theta,\phi) \to (-1)^\ell Y_\ell^{m_\ell}(\theta',\phi') \Rightarrow \psi_{n,\ell,m_\ell} \to (-1)^\ell \psi_{n,\ell,m_\ell}(r,-\theta,-\phi)$. Now consider

$$P_{fi} = e\int \psi_f^* \vec{r}\psi_i \; d\tau \tag{29.19}$$

Under reflection $\vec{r} \to -\vec{r}$. Thus, if $\psi_f^* \psi_i \to +\psi_f^* \psi_i$, the integrand is off and $P_{fi} = 0$. But $\psi_f^* \psi_i \to (-1)^{\ell_f}(-1)^{\ell_i} \Rightarrow \psi_f^* \psi_i$ is even if $\Delta\ell = 0, 2$ and $\psi_f^* \psi_i$ is odd if $\Delta\ell = \pm 1$. If $\Delta\ell = 1$, it is fair to ask what happens to the "disappeared" angular momentum. The theory of relativity plus quantum mechanics shows that the photon carries a "spin" or intrinsic angular momentum of either $+1\hbar$ or $-\hbar$ in the propagation direction, these are "right circularly" and "left circularly" polarized photons.

a slightly more detailed discussion follows[1]

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[1] From R. Eisberg and R. Resnick, **Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles** (Wiley), 2nd Edition.

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