QUANTUM MECHANICS

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Chapter 1

WAVE FUNCTION

Quantum Mechanics is such a radical and revolutionary physical theory that nowadays physics is divided into two main parts, namely *Classical Physics* versus *Quantum Physics*. Classical physics consists of *any* theory which does not incorporate quantum mechanics. Examples of classical theories are Newtonian mechanics (F = ma), classical electrodynamics (Maxwell's equations), fluid dynamics (Navier-Stokes equation), Special Relativity, General Relativity, etc. Yes, that's right; Einstein's theories of special and general relativity are regarded as classical theories because they don't incorporate quantum mechanics. Classical physics is still an active area of research today and incorporates such topics as chaos [Gleick 1987] and turbulence in fluids. Physicists have succeeded in incorporating quantum mechanics into many classical theories and so we now have Quantum Electrodynamics (combination of classical electrodynamics and quantum mechanics) and Quantum Field Theory (combination of special relativity and quantum mechanics) which are both *quantum* theories. (Unfortunately no one has yet succeeded in combining general relativity with quantum mechanics.)

I am assuming that everyone has already taken a course in Modern Physics. (Some excellent textbooks are [Tipler 1992, Beiser 1987].) In such a course you will have studied such phenomena as black-body radiation, atomic spectroscopy, the photoelectric effect, the Compton effect, the Davisson-Germer experiment, and tunnelling phenomena all of which cannot be explained in the framework of classical physics. (For a review of these topics see references [Tipler 1992, Beiser 1987] and chapter 40 of Serway [Serway 1990] and chapter 1 of Gasiorowicz [Gasiorowicz 1996] and chapter 2 of Liboff [Liboff 1992].)

The most dramatic feature of quantum mechanics is that it is a probabilistic theory. We shall explore this in much more detail later, however to get started we should review some of the basics of probability theory.

1.1 Probability Theory

(This section follows the discussion of Griffiths [Griffiths 1995].)

College instructors always have to turn in student grades at the end of each semester. In order to compare the class of the Fall semester to the class of the Spring semester one *could* stare at dozens of grades for awhile. It's much better though to average all the grades and compare the averages.

Suppose we have a class of 15 students who receive grades from 0 to 10. Suppose 3 students get 10, 2 students get 9, 4 students get 8, 5 students get 7, and 1 student gets 5. Let's write this as

$$\begin{array}{lll}
N(15)=0 & N(10)=3 & N(4)=0 \\
N(14)=0 & N(9)=2 & N(3)=0 \\
N(13)=0 & N(8)=4 & N(2)=0 \\
N(12)=0 & N(7)=5 & N(1)=0 \\
N(11)=0 & N(6)=0 & N(0)=0 \\
 & N(5)=1 &
\end{array}$$

where $N(j)$ is the number of students receiving a grade of j. The histogram of this distribution is drawn in Figure 1.1.

The total number of students, by the way, is given by

$$N = \sum_{j=0}^{\infty} N(j) \tag{1.1}$$

1.1.1 Mean, Average, Expectation Value

We want to calculate the average grade which we denote by the symbol $\bar{j}$ or $\langle j \rangle$. The *mean* or *average* is given by the formula

$$\bar{j} \equiv \langle j \rangle = \frac{1}{N} \sum_{\text{all}} j \tag{1.2}$$

where $\sum_{\text{all}} j$ means add them *all* up separately as

$$\begin{aligned}
\langle j \rangle &= \frac{1}{15}(10+10+10+9+9+8+8+8+8+7+7+7+7+7+7+5) \\
&= 8.0 \qquad (1.3)
\end{aligned}$$

Thus the mean or average grade is 8.0.

Instead of writing many numbers over again in (1.3) we could write

$$\bar{j} = \frac{1}{15}\left[(10 \times 3) + (9 \times 2) + (8 \times 4) + (7 \times 5) + (5 \times 1)\right] \tag{1.4}$$

This suggests re-writing the formula for average as

$$\langle j \rangle \equiv \bar{j} = \frac{1}{N}\sum_{j=0}^{\infty} jN(j) \tag{1.5}$$

where $N(j)$ = *number of times the value j occurs.* The reason we go from 0 to ∞ is because many of the $N(j)$ are zero. Example $N(3) = 0$. No one scored 3.

We can also write (1.4) as

$$\bar{j} = \left(10 \times \frac{3}{15}\right) + \left(9 \times \frac{2}{15}\right) + \left(8 \times \frac{4}{15}\right) + \left(7 \times \frac{5}{15}\right) + \left(5 \times \frac{1}{15}\right) \tag{1.6}$$

where for example $\frac{3}{15}$ is the *probability* that a random student gets a grade of 10. Defining the probability as

$$P(j) \equiv \frac{N(j)}{N} \tag{1.7}$$

we have

$$\langle j \rangle \equiv \bar{j} = \sum_{j=0}^{\infty} jP(j) \tag{1.8}$$

Any of the formulas (1.2), (1.5) or (1.8) will serve equally well for calculating the mean or average. However in quantum mechanics we will prefer using the last one (1.8) in terms of probability.

Note that when talking about probabilities, they must all add up to 1 $\left(\frac{3}{15} + \frac{2}{15} + \frac{4}{15} + \frac{5}{15} + \frac{1}{15} = 1\right)$. That is

$$\sum_{j=0}^{\infty} P(j) = 1 \tag{1.9}$$

Student grades are somewhat different to a series of actual *measurements* which is what we are more concerned with in quantum mechanics. If a bunch of students each go out and measure the length of a fence, then the j in (1.1) will represent each measurement. Or if *one* person measures the energy of an electron several times then the j in (1.1) represents each energy measurement. (do Problem 1.1)

In quantum mechanics we use the word expectation value. It means *nothing more* than the word *average* or *mean*. That is you have to make a *series* of measurements to get it. Unfortunately, as Griffiths points out [p.7, 15, Griffiths 1995] the name expectation value makes you think that it is the value you expect after making only one measurement (i.e. most probable value). This is not correct. *Expectation value is the average of single measurements made on a set of identically prepared systems.* This is how it is used in quantum mechanics.

1.1.2 Average of a Function

Suppose that instead of the average of the student grades, you wanted the average of the square of the grades. That's easy. It's just

$$\bar{j}^2 \equiv \langle j^2 \rangle = \frac{1}{N}\sum_{\text{all}} j^2 = \frac{1}{N}\sum_{j=0}^{\infty} j^2 N(j) = \sum_{j=0}^{\infty} j^2 P(j) \tag{1.10}$$

Note that in general the average of the square is not the square of the average.

$$\langle j^2 \rangle \neq \langle j \rangle^2 \tag{1.11}$$

In general for any function f of j we have

$$\langle f(j) \rangle = \sum_{j=0}^{\infty} f(j)P(j) \tag{1.12}$$

1.1.3 Mean, Median, Mode

You can skip this section if you want to. Given that we have discussed the mean, I just want to mention median and mode in case you happen to come across them.

The *median* is simply the *mid-point* of the data. 50% of the data points lie above the median and 50% lie below. The grades in our previous example were 10, 10, 10, 9, 9, 8, 8, 8, 8, 7, 7, 7, 7, 7, 5. There are 15 data points, so point number 8 is the mid-point which is a grade of 8. (If there are an even number of data points, the median is obtained by averaging the middle two data points.) The median is well suited to student grades. It tells you exactly where the middle point lies.

The *mode* is simply the *most frequently* occurring data point. In our grade example the mode is 7 because this occurs 5 times. (Sometimes data will have points occurring with the same frequency. If this happens with 2 data points and they are widely separated we have what we call a bi-nodal distribution.)

For a *normal* distribution the mean, median and mode will occur at the same point, whereas for a skewed distribution they will occur at different points.
(see Figure 1.2)

1.1.4 Standard Deviation and Uncertainty

Some distributions are more spread out than others. (See Fig. 1.5 of [Griffiths 1995].) By "spread out" we mean that if one distribution is more spread out than another then *most of its points are further away from the average* than the other distribution. The "distance" of a particular point from the average can be written

$$\Delta j \equiv j - \langle j \rangle \tag{1.13}$$

But for points with a value less than the average this distance will be negative. Let's get rid of the sign by talking about the *squared distance*

$$(\Delta j)^2 \equiv (j - \langle j \rangle)^2 \tag{1.14}$$

Then it doesn't matter if a point is larger or smaller than the average. Points an equal distance away (whether larger or smaller) will have the same squared distance.

Now let's turn the notion of "spread out" into a concise mathematical statement. If one distribution is more spread out than another then the *average* distances of all points will be bigger than the other. But we don't want the average to be negative so let's use squared distance. Thus if one distribution is more spread out than another then the *average squared distance* of all the points will be bigger than the other. This average squared distance will be our mathematical statement for how spread out a particular distribution is.

The *average* squared distance is called the *variance* and is given the symbol σ^2. The square root of the variance, σ, is called the *standard deviation*. The quantum mechanical word for standard deviation is *uncertainty*, and we usually use the symbol Δ to denote it. As with the word expectation value, the word uncertainty is misleading, although these are the words found in the literature of quantum mechanics. *It's* **much** *better (more precise) to use the words* **average** *and* **standard deviation** *instead of* **expectation value** *and* **uncertainty**. *Also it's much better (more precise) to use the symbol* σ *rather than* Δ, otherwise we get confused with (1.13). (Nevertheless many quantum mechanics books use expectation value, uncertainty and Δ.)

The average squared distance or variance is simple to define. It is

$$\begin{aligned} \sigma^2 \equiv \langle(\Delta j)^2\rangle &= \frac{1}{N}\sum_{\text{all}}(\Delta j)^2 \\ &= \frac{1}{N}\sum_{\text{all}}(j-\langle j\rangle)^2 \\ &= \sum_{j=0}^{\infty}(j-\langle j\rangle)^2 P(j) \end{aligned} \tag{1.15}$$

Note: Some books use $\frac{1}{N-1}$ instead of $\frac{1}{N}$ in (1.15). But if $\frac{1}{N-1}$ is used then equation (1.16) won't work out unless $\frac{1}{N-1}$ is used in the mean as well. For large samples $\frac{1}{N-1} \approx \frac{1}{N}$. The use of $\frac{1}{N-1}$ comes from a data set where only $N-1$ data points are independent. (E.g. percentages of people walking through 4 colored doors.) Suppose there are 10 people and 4 doors colored red, green, blue and white. If 2 people walk through the red door and 3 people through green and 1 person through blue then we *deduce* that 4 people *must* have walked through the white door. If we are making measurements of people then this last data set is *not* a valid independent measurement. However in quantum mechanics all of our measurements *are* independent and so we use $\frac{1}{N}$.

Example 1.1.1 Using equation (1.15), calculate the variance for the student grades discussed above.

Solution We find that the average grade was 8.0. Thus the "distance" of each $\Delta j \equiv j - \langle j\rangle$ is $\Delta 10 = 10 - 8 = +2$, $\Delta 9 = 1$, $\Delta 8 = 0$, $\Delta 7 = -1$, $\Delta 6 = -2$, $\Delta 5 = -3$ and the squared distances are $(\Delta 10)^2 = 4$, $(\Delta 9)^2 = 1$, $(\Delta 8)^2 = 0$, $(\Delta 7)^2 = 1$, $(\Delta 6)^2 = 4$, $(\Delta 5)^2 = 9$. The average of these are

$$\sigma^2 = \left(4 \times \frac{3}{15}\right) + \left(1 \times \frac{2}{15}\right) + \left(0 \times \frac{4}{15}\right)$$

$$
\begin{aligned}
& + \left(1 \times \frac{5}{15}\right) + \left(9 \times \frac{1}{15}\right) \\
= \;& 1.87
\end{aligned}
$$

However this way of calculating the variance can be a pain in the neck especially for large samples. Let's find a simpler formula which will give us the answer more quickly. Expand (1.15) as

$$
\begin{aligned}
\sigma^2 &= \sum \left(j^2 - 2j\langle j\rangle + \langle j\rangle^2\right) P(j) \\
&= \sum j^2 P(j) - 2\langle j\rangle \sum jP(j) + \langle j\rangle^2 \sum P(j)
\end{aligned}
$$

where we take $\langle j\rangle$ and $\langle j\rangle^2$ outside the sum because they are just *numbers* ($\langle j\rangle = 8.0$ and $\langle j\rangle^2 = 64.0$ in above example) which have already been summed over. Now $\sum jP(j) = \langle j\rangle$ and $\sum P(j) = 1$. Thus

$$\sigma^2 = \langle j^2\rangle - 2\langle j\rangle^2 + \langle j\rangle^2$$

giving

$$\sigma^2 = \langle j^2\rangle - \langle j\rangle^2 \tag{1.16}$$

Example 1.1.2 Repeat example 1.1.1 using equation (1.16).

Solution

$$
\begin{aligned}
\langle j^2\rangle &= \frac{1}{15}[(100 \times 3) + (81 \times 2) + (64 \times 4) + (49 \times 5) + (25 \times 1)] \\
&= 65.87 \\
\langle j\rangle^2 &= 8^2 = 64 \\
\sigma^2 &= \langle j^2\rangle - \langle j\rangle^2 = 65.87 - 64 = 1.87
\end{aligned}
$$

in agreement with example 1.1.1. (do Problem 1.2)

1.1.5 Probability Density

In problems 1.1 and 1.2 we encountered an example where a continuous variable (the length of a fence) rather than a discrete variable (integer values of student grades) is used. A better method for dealing with continuous variables is to use *probability densities* rather than *probabilities*. The probability that the value x lies between the values a and b is given by

$$P_{ab} \equiv \int_a^b \rho(x)dx \tag{1.17}$$

This equation *defines* the probability density $\rho(x)$ The quantity $\rho(x)dx$ is thus the *probability that a given value lies between x and $x+dx$*. This is just like the ordinary density ρ of water. The total mass of water is $M = \int \rho dV$ where ρdV is the mass of water between volumes V and $V + dV$.

Our old discrete formulas get replaced with new continuous formulas, as follows:

$$\sum_{j=0}^{\infty} P(j) = 1 \rightarrow \int_{-\infty}^{\infty} \rho(x)dx = 1 \tag{1.18}$$

$$\langle j \rangle = \sum_{j=0}^{\infty} jP(j) \rightarrow \langle x \rangle = \int_{-\infty}^{\infty} x\rho(x)dx \tag{1.19}$$

$$\langle f(j) \rangle = \sum_{j=0}^{\infty} f(j)P(j) \rightarrow \langle f(x) \rangle = \int_{-\infty}^{\infty} f(x)\rho(x)dx \tag{1.20}$$

$$\begin{aligned}\sigma^2 \equiv \langle (\Delta j)^2 \rangle &= \sum_{j=0}^{\infty} (j - \langle j \rangle)^2 P(j) \rightarrow \sigma^2 \equiv (\Delta x)^2 &&= \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 \rho(x)dx \\ &= \langle j^2 \rangle - \langle j \rangle^2 &&= \langle x^2 \rangle - \langle x \rangle^2\end{aligned} \tag{1.21}$$

In discrete notation j is the measurement, but in continuous notation the *measured variable is x*. (do Problem 1.3)

1.2 Postulates of Quantum Mechanics

Most physical theories are based on just a couple of fundamental equations. For instance, Newtonian mechanics is based on $F = ma$, classical electrodynamics is based on Maxwell's equations and general relativity is based on the Einstein equations $G_{\mu\nu} = -8\pi G T_{\mu\nu}$. When you take a course on Newtonian mechanics, *all* you ever do is solve $F = ma$. In a course on electromagnetism you spend all your time just solving Maxwell's equations. Thus these fundamental equations *are* the theory. All the rest is just learning how to solve these fundamental equations in a wide variety of circumstances. The fundamental equation of quantum mechanics is the Schrödinger equation

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

which I have written for a *single* particle (of mass m) moving in a potential U in *one* dimension x. (We will consider more particles and more dimensions later.) The symbol Ψ, called the *wave function*, is a function of space and time $\Psi(x, t)$ which is why partial derivatives appear.

It's important to understand that these fundamental equations *cannot* be derived from anywhere else. They are physicists' *guesses* (or to be fancy, *postulates*) as to how nature works. We *check* that the guesses (postulates) are correct by comparing their predictions to *experiment*. Nevertheless, you will often find "derivations" of the fundamental equations scattered throughout physics books. This is OK. The authors are simply trying to provide deeper understanding, but it is good to remember that these are *not* fundamental derivations. Our good old equations like $F = ma$, Maxwell's equations and the Schrödinger equation are *postulates* and that's that. Nothing more. They are sort of like the *definitions* that mathematicians state at the beginning of the proof of a theorem. They *cannot* be derived from anything else.

Quantum Mechanics is sufficiently complicated that the Schrödinger equation is not the only postulate. There are others (see inside cover of this book). The *wave function* needs some postulates of its own simply to understand it. The wave function Ψ is the *fundamental quantity* that we always wish to calculate in quantum mechanics.

Actually all of the fundamental equations of physical theories usually have a fundamental quantity that we wish to calculate given a fundamental *input*. In Newtonian physics, $F = ma$ is the fundamental equation and the acceleration a is the fundamental quantity that we always want to know given an input force F. The acceleration a is different for different forces F. Once we have obtained the acceleration we can calculate lots of other interesting goodies such as the velocity and the displacement as a function of time. In classical electromagnetism the Maxwell equations are the fundamental equations and the fundamental quantities that we always want are the electric ($\mathbf{E}$) and magnetic ($\mathbf{B}$) fields. These always depend on the fundamental input which is the charge (ρ) and current ($\mathbf{j}$) distribution. Different

ρ and $\mathbf{j}$ produce different $\mathbf{E}$ and $\mathbf{B}$. In general relativity, the fundamental equations are the Einstein equations ($G_{\mu\nu} = -8\pi G T_{\mu\nu}$) and the fundamental quantity that we always want is the metric tensor $g_{\mu\nu}$, which tells us how spacetime is curved. ($g_{\mu\nu}$ is buried inside $G_{\mu\nu}$). The fundamental input is the energy-momentum tensor $T_{\mu\nu}$ which describes the distribution of matter. Different $T_{\mu\nu}$ produces different $g_{\mu\nu}$.

Similarly the fundamental equation of quantum mechanics is the Schrodinger equation and the fundamental input is the potential U. (This is related to force via $\mathbf{F} = -\nabla U$ or $F = -\frac{\partial U}{\partial x}$ in one dimension. See any book on classical mechanics. [Chow 1995, Fowles 1986, Marion 1988, Goldstein 1980].) Different input potentials U give different values of the fundamental quantity which is the wave function Ψ. Once we have the wave function we can calculate all sorts of other interesting goodies such as energies, lifetimes, tunnelling probabilities, cross sections, etc.

In Newtonian mechanics and electromagnetism the fundamental quantities are the acceleration and the electric and magnetic fields. Now we all can agree on what the *meaning* of acceleration and electric field is and so that's the end of the story. However with the wave function it's entirely a different matter. We have to agree on what we mean it to be at the very outset. The meaning of the wave function has occupied some of the greatest minds in physics (Heisenberg, Einstein, Dirac, Feynman, Born and others).

In this book we will not write down all of the postulates of quantum mechanics in one go (but if you want this look at the inside cover). Instead we will develop the postulates as we go along, because they are more understandable if you already know some quantum theory. Let's look at a simple version of the first postulate.

Postulate 1:	To each state of a physical system there corresponds a wave function $\Psi(x,t)$.

That's simple enough. In classical mechanics each state of a physical system is specified by *two* variables, namely position $x(t)$ and momentum $p(t)$ which are both functions of the *one* variable time t. (And we all "know" what position and momentum mean, so we don't need fancy postulates to say what they are.) In quantum mechanics each state of a physical system is specified by only *one* variable, namely the wave function $\Psi(x,t)$ which is a function of the *two* variables position x and time t.

Footnote: In classical mechanics the state of a system is specified by $x(t)$

and $p(t)$ or $\Gamma(x, p)$. In 3-dimensions this is $\vec{x}(t)$ and $\vec{p}(t)$ or $\Gamma(x, y, p_x, p_y)$ or $\Gamma(r, \theta, p_r, p_\theta)$. In quantum mechanics we shall see that the uncertainty principle does not allow us to specify x and p simultaneously. Thus in quantum mechanics our good coordinates will be things like E, L^2, L_z, etc. rather than x, p. Thus Ψ will be written as $\Psi(E, L^2, L_z \cdots)$ rather than $\Psi(x, p)$. (E is the energy and L is the angular momentum.) Furthermore *all* information regarding the system resides in Ψ. We will see later that the expectation value of *any* physical observable is $\langle Q \rangle = \int \Psi^* \hat{Q} \Psi dx$. Thus the wave function will always give the values of *any* other physical observable that we require.

At this stage we don't know what Ψ *means* but we will specify its meaning in a later postulate.

Postulate 2: The time development of the wave function is determined by the Schrödinger equation

$$\boxed{\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U\right)\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)} \tag{1.22}$$

where $U \equiv U(x)$. Again this is simple enough. The equation governing the behavior of the wave function is the Schrödinger equation. (Here we have written it for a single particle of mass m in 1–dimension.)

Contrast this to classical mechanics where the time development of the momentum is given by $F = \frac{dp}{dt}$ and the time development of position is given by $F = m\ddot{x}$. Or in the Lagrangian formulation the time development of the generalized coordinates is given by the second order differential equations known as the Euler-Lagrange equations. In the Hamiltonian formulation the time development of the generalized coordinates $q_i(t)$ and generalized momenta $p_i(t)$ are given by the first order differential Hamilton's equations, $\dot{p}_i = -\partial H/\partial q_i$ and $\dot{q}_i = \partial H/\partial p_i$.

Let's move on to the next postulate.

Postulate 3: (Born hypothesis): $|\Psi|^2$ is the probability *density*.

This postulate states that the wave function is actually related to a probability density

Footnote: Recall that every complex number can be written $z = x + iy$ and that
$z^* z = (x - iy)(x + iy) = x^2 + y^2 \equiv |z|^2$.

$$\rho \equiv |\Psi|^2 = \Psi^* \Psi \tag{1.23}$$

where Ψ^* is the complex conjugate of Ψ. Postulate 3 is where we find out what the wave function really *means*. The basic postulate in quantum mechanics is that the wave function $\Psi(x,t)$ is *related* to the *probability for finding a particle at position* x. The actual probability for this is, in 1-dimension,

$$P = \int_{-A}^{A} |\Psi|^2 dx \tag{1.24}$$

P is the probability for finding the particle somewhere between A and $-A$. This means that

$|\Psi(x,t)|^2 dx =$ probability of finding a particle between position x and $x + dx$ at time t.

In 3-dimensions we would write

$$P = \int |\Psi|^2 d^3x \tag{1.25}$$

which is why $|\Psi|^2$ is called the probability *density* and not simply the probability. All of the above discussion is part of Postulate 3. The "discovery" that the symbol Ψ in the Schrödinger equation represents a probability density took many years and arose only after much work by many physicists.

Usually Ψ will be normalized so that the total probability for finding the particle somewhere in the universe will be 1, i.e. in 1-dimension

$$\int_{-\infty}^{\infty} |\Psi|^2 dx = 1 \tag{1.26}$$

or in 3-dimensions

$$\int_{-\infty}^{\infty} |\Psi|^2 d^3x = 1 \tag{1.27}$$

The probabilistic interpretation of the wave function is what sets quantum mechanics apart from all other classical theories. It is totally unlike anything you will have studied in your other physics courses. The acceleration or position of a particle, represented by the symbols $\ddot{x}$ and x, are well defined quantities in classical mechanics. However with the interpretation of the wave function as a probability density we shall see that the concept of the definite position of a particle no longer applies.

A major reason for this probabilistic interpretation is due to the fact that the Schrödinger equation is really a type of *wave equation* (which is why Ψ is called the wave function). Recall the classical homogeneous wave equation (in 1-dimension) that is familiar from classical mechanics

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} \tag{1.28}$$

Here $y = y(x,t)$ represents the height of the wave at position x and time t and v is the speed of the wave [Chow 1995, Fowles 1986, Feynman 1964 I]. From (1.22) the free particle (i.e. $U = 0$) Schrödinger equation is

$$\frac{\partial^2 \Psi}{\partial x^2} = -i\frac{2m}{\hbar}\frac{\partial \Psi}{\partial t} \tag{1.29}$$

which sort of looks a bit like the wave equation. Thus particles will be represented by wave functions and we already know that a wave is not localized in space but spread out. So too is a particle's wave property spread out over some distance and so we cannot say exactly where the particle is, but only the probability of finding it somewhere.

Footnote: The wave properties of particles are discussed in all books on modern physics [Tipler 1992, Beiser 1987, Serway 1990].

1.3 Conservation of Probability (Continuity Equation)

Before discussing conservation of probability it will be very helpful to review our knowledge of the conservation of charge in classical electromagnetism.

1.3.1 Conservation of Charge

In MKS (SI) units, Maxwell's equations [Griffiths 1989] are Gauss' electric law

$$\nabla \cdot \mathbf{E} = \rho/\epsilon_0 \tag{1.30}$$

and Gauss' magnetic law

$$\nabla \cdot \mathbf{B} = 0 \tag{1.31}$$

and Faraday s law

$$\nabla \times \mathbf{E} + \frac{\partial B}{\partial t} = 0 \tag{1.32}$$

and Ampère's law

$$\nabla \times \mathbf{B} - \frac{1}{c^2}\frac{\partial \mathbf{E}}{\partial t} = \mu_0 \mathbf{j} \tag{1.33}$$

Conservation of charge is *implied* by Maxwell's equations. Taking the divergence of Ampère's law gives

$$\nabla \cdot (\nabla \times \mathbf{B}) - \frac{1}{c^2}\frac{\partial}{\partial t}\nabla \cdot \mathbf{E} = \mu_0 \nabla \cdot \mathbf{j}$$

However $\nabla \cdot (\nabla \times \mathbf{B}) = 0$ and using Gauss' electric law we have

$$-\frac{1}{c^2}\frac{1}{\epsilon_0}\frac{\partial \rho}{\partial t} = \mu_0 \nabla \cdot \mathbf{j}$$

Now using $c^2 = \frac{1}{\mu_0 \epsilon_0}$ we get

Footnote:The form of the continuity equation is the same in all systems of units.

$$\boxed{\nabla \cdot \mathbf{j} + \frac{\partial \rho}{\partial t} = 0} \tag{1.34}$$

which is the continuity equation. In 1-dimension this is

$$\frac{\partial j}{\partial x} + \frac{\partial \rho}{\partial t} = 0 \tag{1.35}$$

The continuity equation is a local conservation law. The conservation law in integral form is obtained by integrating over volume.

Thus

$$\int \nabla \cdot \mathbf{j}\, d\tau = \oint \mathbf{j} \cdot d\mathbf{a} \tag{1.36}$$

by Gauss theorem and

$$\int \frac{\partial \rho}{\partial t} d\tau = \frac{d}{dt}\int \rho\, d\tau = \frac{dQ}{dt} \tag{1.37}$$

where

$$Q \equiv \int \rho\, d\tau \tag{1.38}$$

The step $\frac{d}{dt}\int \rho \, d\tau = \int \frac{\partial \rho}{\partial t} d\tau$ in (1.37) requires some explanation. In general ρ can be a function of position $\mathbf{r}$ and time t, i.e. $\rho = \rho(\mathbf{r}, t)$. However the integral $\int \rho(\mathbf{r}, t) d\tau \equiv \int \rho(\mathbf{r}, t) d^3\mathbf{r}$ will depend *only* on time as the $\mathbf{r}$ coordinates will be integrated over. Because the whole integral depends only on time then $\frac{d}{dt}$ is appropriate outside the integral. However because $\rho = \rho(\mathbf{r}, t)$ we should have $\frac{\partial \rho}{\partial t}$ inside the integral.

Thus the *integral* form of the *local* conservation law is

$$\boxed{\oint \mathbf{j} \cdot d\mathbf{a} + \frac{dQ}{dt} = 0} \tag{1.39}$$

Thus a change in the charge Q within a volume is accompanied by a flow of current across a boundary surface $d\mathbf{a}$. Actually $j = \frac{i}{\text{area}}$ so that $\oint \mathbf{j} \cdot d\mathbf{a}$ truly is a current

$$i \equiv \oint \mathbf{j} \cdot d\mathbf{a} \tag{1.40}$$

so that (1.39) can be written

$$i + \frac{dQ}{dt} = 0 \tag{1.41}$$

or

$$i = -\frac{dQ}{dt} \tag{1.42}$$

truly showing the conservation of the charge locally. If we take our boundary surface to be the whole universe then all currents will have died out at the universe boundary leaving

$$\frac{dQ}{dt} = 0 \tag{1.43}$$

where

$$Q \equiv Q_{\text{universe}}$$

which is the charge enclosed in the whole universe. Integrating (1.43) over time we either have $\int \frac{dQ}{dt} dt = \int O \, dt +$ constant $=$ constant which gives $Q =$ constant or we can write $\int_{Q_i}^{Q_f} \frac{dQ}{dt} dt = 0$ which gives $Q_f - Q_i = 0$ or $Q_f = Q_i$. Thus the global (universal) conservation law is

$$Q \equiv Q_{\text{universe}} = \text{constant}. \tag{1.44}$$

or

$$Q_f = Q_i \tag{1.45}$$

Our above discussion is meant to be general. The conservation laws can apply to electromagnetism, fluid dynamics, quantum mechanics or any other physical theory. One simply has to make the appropriate identification of $\mathbf{j}$, ρ and Q.

Finally, we refer the reader to the beautiful discussion by Feynman [Feynman 1964 I] (pg. 27-1) where he discusses the fact that it is relativity, and the requirement that signals cannot be transmitted faster than light, that forces us to consider *local* conservation laws.

Our discussion of charge conservation should make our discussion of probability conservation much clearer. Just as conservation of charge is *implied* by the Maxwell equations, so too does the Schrödinger equation *imply* conservation of probability in the form of a local conservation law (the continuity equation).

1.3.2 Conservation of Probability

In electromagnetism the charge density is ρ. In quantum mechanics we use the same symbol to represent the probability density $\rho = |\Psi|^2 = \Psi^*\Psi$. Calculate $\frac{\partial\rho}{\partial t}$.

$$\begin{aligned}
\frac{\partial\rho}{\partial t} &= \frac{\partial}{\partial t}(\Psi^*\Psi) \\
&= \Psi^*\frac{\partial\Psi}{\partial t} + \frac{\partial\Psi^*}{\partial t}\Psi
\end{aligned}$$

and according to the Schrödinger equation in 1-dimension

$$\frac{\partial\Psi}{\partial t} = \frac{1}{i\hbar}\left[-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + U\Psi\right] = \frac{i\hbar}{2m}\frac{\partial^2\Psi}{\partial x^2} - \frac{i}{\hbar}U\Psi$$

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

(assuming $U^* = U$) we can write

$$\begin{aligned}
\frac{\partial\rho}{\partial t} &= \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial^2\Psi}{\partial x^2} - \frac{\partial^2\Psi^*}{\partial x^2}\Psi\right) \\
&= \frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)\right]
\end{aligned}$$

Well that doesn't look much like the continuity equation. But it does if we define a *probability current*

$$j \equiv \frac{i\hbar}{2m}\left(\Psi\frac{\partial\Psi^*}{\partial x} - \Psi^*\frac{\partial\Psi}{\partial x}\right) \tag{1.46}$$

for then we have

$$\frac{\partial\rho}{\partial t} + \frac{\partial j}{\partial x} = 0 \tag{1.47}$$

which is the continuity equation in 1-dimension and represents our local law for conservation of probability.

Now let's get the global law for conservation of probability. In 1-dimension we integrate the continuity equation (1.47) over $\int_{-\infty}^{\infty} dx$ to get

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

In analogy with our discussion about the current located at the boundary of the universe, here we are concerned about the value of the wave function $\Psi(\infty)$ at the boundary of a 1-dimensional universe (e.g. the straight line). Ψ must go to zero at the boundary, i.e.

$$\Psi(\infty) = 0$$

Thus

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\Psi|^2 dx = 0 \tag{1.48}$$

which is our global conservation law for probability. It is entirely consistent with our normalization condition (1.26). Writing the total probability $P = \int \rho dx = \int |\Psi|^2 dx$ we have

$$\frac{dP}{dt} = 0 \tag{1.49}$$

analogous to global conservation of charge. The global conservation of probability law, (1.48) or (1.49), says that *once the wave function is normalized*, say according to (1.26) *then it always stays normalized.* This is good. We don't want the normalization to change with time.

1.4 Interpretation of the Wave Function

A beautifully clear description of how to interpret the wave function is found in Sec. 1.2 of [Griffiths 1995]. Read this carefully.

1.5 Expectation Value in Quantum Mechanics

(See pages 14, 15 of [Griffiths 1995]).

For a particle in state Ψ, the expectation value of y is

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\Psi|^2 dx \tag{1.50}$$

The meaning of expectation value will be written in some more postulates later on. Let's just briefly mention what is to come. *"The expectation value is the average of repeated measurements on an ensemble of identically prepared systems, not the average of repeated measurements on one and the same systems"* (Pg. 15, Griffiths [1995]).

1.6 Operators

In quantum mechanics, physical quantities are no longer represented by ordinary functions but instead are represented by *operators*. Recall the definition of total energy E

$$T + U = E \tag{1.51}$$

where U is the potential energy, and T is the kinetic energy

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{1.52}$$

where p is the momentum, v is the speed and m is the mass. If we multiply (16.1) by a wave function

$$(T + U)\Psi = E\Psi \tag{1.53}$$

then this is the Schrödinger equation (1.1) if we make the replacements

$$T \rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{1.54}$$

and

$$E \rightarrow i\hbar\frac{\partial}{\partial t} \tag{1.55}$$

The replacement (16.4) is the same as the replacement

$$p \rightarrow -i\hbar\frac{\partial}{\partial x} \tag{1.56}$$

(Actually $p \rightarrow +i\hbar\frac{\partial}{\partial x}$ would have worked too. We will see in Problem 1.4 why we use the minus sign.) Let's use a little hat ($\wedge$) to denote operators and write the *energy operator*

$$\boxed{\hat{E} = i\hbar\frac{\partial}{\partial t}} \tag{1.57}$$

and the *momentum operator*

$$\boxed{\hat{p} = -i\hbar\frac{\partial}{\partial x}} \tag{1.58}$$

What would the *position operator* or potential energy operator be? Well in the Schrödinger equation (1.1) U just sits there by itself with no differential operator. For a harmonic oscillator for example $U = \frac{1}{2}kx^2$ we just plug $\frac{1}{2}kx^2$ into the Schrödinger equation as

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right)\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \tag{1.59}$$

which is the Schrödinger equation for a harmonic oscillaor potential. Evidently these potentials *don't* get replaced with differential operators. They just remain as functions. We *could* write the harmonic oscillator operator as

$$\hat{U} = U(x) = \frac{1}{2}kx^2 \tag{1.60}$$

Now most potentials are just functions of position $U(x)$ so if $\hat{U} = U(x)$ it must follow that

$$\boxed{\hat{x} = x} \tag{1.61}$$

That is, the position opeator is just the position itself.

OK, we know how to write the expectation value of position. It's given in (1.50), but how about the expectation value of momentum? I can't just write $\langle p \rangle = \int_{-\infty}^{\infty} p|\Psi|^2 dx = \int_{-\infty}^{\infty} p\Psi^*\Psi dx$ because I don't know what to put in for p under the integral. But wait! We just saw that in quantum mechanics p is an operator given in (1.58). The proper way to write the expectation value is

$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} \Psi^* \left(-i\hbar\frac{\partial}{\partial x}\right)\Psi dx \tag{1.62}$$

$$= -i\hbar \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx \tag{1.63}$$

In fact the expectation value of *any* operator $\hat{Q}$ in quantum mechanics is

$$\boxed{\langle \hat{Q} \rangle \equiv \int \Psi^* \hat{Q} \Psi dx} \tag{1.64}$$

which is a *generalization* of (1.19) or (1.50).

This would give

$$\langle x \rangle = \int \Psi^* x \Psi dx$$

which gives the same result as (1.50).

But given an arbitrary quantity Q, how do we know how to write it in operator form? All we have so far are the operators for T, U, p and x. Well, it turns out that *any arbitrary operator $\hat{Q}$ can always be written in terms of $\hat{p}$ and $\hat{x}$.*

Example 1.6.1 Write down the velocity operator $\hat{v}$, and its expectation value.

Solution We have $\hat{p} = -i\hbar\frac{\partial}{\partial x}$ and $p = mv$. Thus we *define* the velocity operator

$$\hat{v} \equiv \frac{\hat{p}}{m}$$

Thus

$$\hat{v} = -\frac{i\hbar}{m}\frac{\partial}{\partial x}$$

The expectation value would be

$$\begin{aligned}\langle v\rangle &= \int \Psi^* \left(-\frac{i\hbar}{m}\frac{\partial}{\partial x}\right)\Psi\, dx \\ &= -\frac{i\hbar}{m}\int \Psi^* \frac{\partial \Psi}{\partial x} dx\end{aligned}$$

1.7 Commutation Relations

We are perhaps used to mathematical objects that *commute*. For example the integers commute under addition, such as $3+2=2+3=5$. The integers also commute under multiplication, such as $3\times 2=2\times 3=6$. Also matrices commute under matrix addition, such as

$$\begin{pmatrix}2 & 1\\ 1 & 2\end{pmatrix}\oplus\begin{pmatrix}1 & 3\\ 1 & 1\end{pmatrix}=\begin{pmatrix}1 & 3\\ 1 & 1\end{pmatrix}\oplus\begin{pmatrix}2 & 1\\ 1 & 2\end{pmatrix}=\begin{pmatrix}3 & 4\\ 2 & 3\end{pmatrix} \tag{1.65}$$

(Notice that I have used a special symbol $\oplus$ for matrix addition because it is very different from ordinary addition $+$ of real numbers.)

Matrices do *not* however commute under multiplication. For example

$$\begin{pmatrix}2 & 1\\ 1 & 2\end{pmatrix}\otimes\begin{pmatrix}1 & 3\\ 1 & 1\end{pmatrix}=\begin{pmatrix}3 & 6\\ 3 & 5\end{pmatrix} \tag{1.66}$$

but

$$\begin{pmatrix}1 & 3\\ 1 & 1\end{pmatrix}\otimes\begin{pmatrix}2 & 1\\ 1 & 2\end{pmatrix}=\begin{pmatrix}5 & 7\\ 3 & 3\end{pmatrix} \tag{1.67}$$

so that matrix multiplication is non-commutative.

Note also that our operators $\hat{x}$ and $\hat{p}$ do not commute. Now with operators they must always *operate* on something, and for quantum mechanics that something is the wave function Ψ. We already know that $\hat{p}\Psi = -i\hbar\frac{\partial\Psi}{\partial x}$ and $\hat{x}\Psi = x\Psi$, so now let's combine them. Thus

$$\begin{aligned}\hat{p}\hat{x}\Psi &= \hat{p}x\Psi = -i\hbar\frac{\partial}{\partial x}(x\Psi) \\ &= -i\hbar\left(\Psi + x\frac{\partial\Psi}{\partial x}\right)\end{aligned} \tag{1.68}$$

and

$$\hat{x}\hat{p}\Psi = -i\hbar\,\hat{x}\frac{\partial\Psi}{\partial x} = -i\hbar\,x\frac{\partial\Psi}{\partial x} \tag{1.69}$$

Thus $\hat{x}$ and $\hat{p}$ do not commute! That is $\hat{x}\hat{p} \neq \hat{p}\hat{x}$.

Let's now define the *commutator* of two arbitrary mathematical objects A and B as

$$\boxed{[A, B] \equiv AB - BA} \tag{1.70}$$

Where $AB \equiv A \circ B$ which reads A "operation" B. Thus for integers under addition we would have $[3, 2] \equiv (3 + 2) - (2 + 3) = 5 - 5 = 0$ or for integers under multiplication we would have $[3, 2] = (3 \times 2) - (2 \times 3) = 6 - 6 = 0$. Thus if two mathematical objects, A and B, commute then their commutator $[A, B] = 0$. The reason why we introduce the commutator is if two objects do *not* commute then the commutator tells us what is "left over". Note a property of the commutator is

$$[A, B] = -[B, A] \tag{1.71}$$

For our matrices $A \equiv \begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$ and $B \equiv \begin{pmatrix} 1 & 3 \\ 1 & 1 \end{pmatrix}$ that we had before, then the commutator is

$$[A, B] = AB - BA = \begin{pmatrix} 3 & 6 \\ 3 & 5 \end{pmatrix} - \begin{pmatrix} 5 & 7 \\ 3 & 3 \end{pmatrix} = \begin{pmatrix} 2 & 1 \\ 0 & -2 \end{pmatrix} \tag{1.72}$$

where we have used (1.66) and (1.67).

We are interested in the commutator $[\hat{x}, \hat{p}]$. In classical mechanics

$$[x, p]_{\text{classical}} = 0 \tag{1.73}$$

because x and p are just algebraic quantities, not operators. To work out quantum mechanical commutators we need to *operate* on Ψ. Thus

$$\begin{aligned} [\hat{x}, \hat{p}]\Psi &= (\hat{x}\hat{p} - \hat{p}\hat{x})\Psi \\ &= -i\hbar\, x\frac{\partial \Psi}{\partial x} + i\hbar\left(\Psi + x\frac{\partial \Psi}{\partial x}\right) \\ &= i\hbar\Psi \end{aligned} \tag{1.74}$$

Now "cancel" the Ψ and we have

$$\boxed{[\hat{x}, \hat{p}] = i\hbar}\,.$$

(1.75)

The commutator is a very fundamental quantity in quantum mechanics. In section 1.6 we "derived" the Schrödinger equation by saying $(\hat{T}+\hat{U})\Psi = \hat{E}\Psi$ where $\hat{T} \equiv \frac{\hat{p}^2}{2m}$ and *then* introducing $\hat{p} \equiv -i\hbar\frac{\partial}{\partial x}$ and $\hat{E} \equiv i\hbar\frac{\partial}{\partial t}$ and $\hat{x} \equiv x$. The *essence* of quantum mechanics are these operators. Because they are operators they satisfy (1.75).

An *alternative* way of introducing quantum mechanics is to *change* the *classical* commutation relation $[x, p]_{\text{classical}} = 0$ to $[\hat{x}, \hat{p}] = i\hbar$ which can *only* be satisfied by $\hat{x} = x$ and $\hat{p} = -i\hbar\frac{\partial}{\partial x}$.

Thus to "derive" quantum mechanics we **either** *postulate operator definitions (from which commutation relations follow)* **or** *postulate commutation relations (from which operator definitions follow).* Many advanced formulations of quantum mechanics *start* with the commutation relations and then later derive the operator definitions.

Figure 1.1: Histogram showing number of students $N(i)$ receiving a grade of i.

Figure 1.2: Location of Mean, Median, Mode

1.8 Problems

1.1 Suppose 10 students go out and measure the length of a fence and the following values (in meters) are obtained: 3.6, 3.7, 3.5, 3.7, 3.6, 3.7, 3.4, 3.5, 3.7, 3.3. A) Pick a random student. What is the probability that she made a measurement of 3.6 m? B) Calculate the expectation value (i.e. average or mean) using each formula of (1.2), (1.5), (1.8).

1.2 Using the example of problem 1.1, calculate the variance using both equations (1.15) and (1.16).

1.3 Griffiths Problem 1.6.

Hints: Some useful integrals are [Spiegel, 1968, pg.98]

$\int_0^\infty e^{-ax^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$

$\int_0^\infty x^m e^{-ax^2}dx = \frac{\Gamma[(m+1)/2]}{2a^{(m+1)/2}}$

Also note $\Gamma(3/2) = \frac{\sqrt{\pi}}{2}$

Properties of the Γ function are listed in [Spiegel, 1968, pg.101]

1.4 Calculate $\frac{d\langle x\rangle}{dt}$ and show that it is the same as the velocity expectation value $\langle v\rangle$ calculated in Example 1.6.1.

1.5 Griffiths Problem 1.12.

1.9 Answers

1.1 A) 0.2 B) 3.57

1.2 0.0181

1.3 Griffiths Problem 1.6. A) $A = \sqrt{\frac{\lambda}{\pi}}$ B) $\langle x \rangle = a$, $\langle x^2 \rangle = a^2 + \frac{1}{2\lambda}$, $\sigma = \frac{1}{\sqrt{2\lambda}}$

Chapter 2

DIFFERENTIAL EQUATIONS

Hopefully every student studying quantum mechanics will have already taken a course in differential equations. However if you have not, don't worry. The present chapter presents the very bare bones of knowledge that you will need for your introduction to quantum mechanics.

2.1 Ordinary Differential Equations

A differential equation is simply any equation that contains differentials or derivatives. For instance Newton's law

$$F = m\frac{d^2s}{dt^2} \tag{2.1}$$

is a differential equation because of the second derivative contained in the acceleration $a \equiv \frac{d^2s}{dt^2}$ and s is distance.

In what follows below, let's write the first derivative of the function $y(x)$ with respect to x as $y'(x) \equiv \frac{dy}{dx}$ and the second derivative as $y''(x) \equiv \frac{d^2y}{dx^2}$. We will not be considering higher order derivatives. The *order* of the differential equation is simply the degree of the highest derivative. For example

$$y'' + a_1(x)y' + a_2(x)y = k(x) \tag{2.2}$$

is called a second order differential equation because the highest derivative y'' is second order. If y'' wasn't there it would be called a first order differential equation.

Equation (2.2) is also called an *ordinary* differential equation because y is a function of only one variable x, i.e. $y = y(x)$. A *partial* differential equation occurs if y is a function of more than one variable, say $y = y(x, t)$ and we have derivatives in both x and t, such as the partial derivatives $\frac{\partial y}{\partial x}$ and $\frac{\partial y}{\partial t}$. We shall discuss partial differential equations later.

Equation (2.2) is also called an *inhomogeneous* differential equation because the right hand side containing $k(x)$ is not zero. $k(x)$ is a function of x only. It does not contain any y, y' or y'' terms and we usually stick it on the right hand side. If we had

$$y'' + a_1(x)y' + a_2(x)y = 0 \tag{2.3}$$

it would be a second order, ordinary, *homogeneous* differential equation. By the way, the reason I don't write say $a_0(x)y''$ in (2.2) or (2.3) is because the $a_0(x)$ can always be absorbed into the other coefficients.

Equation (2.2) is also called a differential equation with *non-constant coefficients*, because the $a_1(x)$ and $a_2(x)$ are *functions* of x. If they were not functions but just constants or ordinary numbers, it would be called a differential equation with constant coefficients.

Equation (2.2) is also called a *linear* differential equation because it is linear in y, y' and y''. If it contained terms like yy'', y^2, $y'y''$, y'^2, etc., it would be called a non-linear equation. Non-linear differential equations sure are fun because they contain neat stuff like chaos [Gleick 1987] but we will not study them here.

Thus equation (2.2) is called a second order, inhomogeneous, linear, ordinary differential equation with non-constant coefficients. The *aim* of differential equation theory is to solve the differential equation for the unknown function $y(x)$.

2.1.1 Second Order, Homogeneous, Linear, Ordinary Differential Equations with Constant Coefficients

First order equations are pretty easy to solve [Thomas 1996, Purcell 1987] and anyone who has taken a calculus course can work them out. Second order equations are the ones most commonly encountered in physics. Newton's law (2.1) and the Schrödinger equation are second order.

Let's start by solving the simplest second order equation we can imagine. That would be one which is homogeneous and has constant coefficients and is linear as in

$$y'' + a_1y' + a_2y = 0 \tag{2.4}$$

where now a_1 and a_2 are ordinary constants. The general solution to equation (2.2) is impossible to write down. You have to tell me what $a_1(x)$, $a_2(x)$ and $k(x)$ are before I can solve it. But for (2.4) I can write down the general solution without having to be told the value of a_1 and a_2. I can write the general solution *in terms* of a_1 and a_2 and you just stick them in when you decide what they should be.

Now I am going to just tell you the answer for the solution to (2.4). Theorists and mathematicians hate that! They would prefer to *derive* the general solution and that's what you do in a differential equations course. *But* it's not all spoon-feeding. You can *always* (and always *should*) *check* you answer by substituting back into the differential equation to see if it works. That is, I will tell you the general answer $y(x)$. You work out y' and y'' and substitute into $y'' + a_1y' + a_2y$. If it equals 0 then you know your answer is right. (It may not be unique but let's forget that for the moment.)

First of all try the solution

$$y(x) = r\ e^{rx} \tag{2.5}$$

Well $y'(x) = r^2e^{rx}$ and $y''(x) = r^3e^{rx}$ and upon substitution into (2.4) we get

$$r^2 + a_1r + a_2 = 0 \tag{2.6}$$

This is called the *Auxilliary Equation.* Now this shows that $y(x) = r\ e^{rx}$ will *not* be a solution for any old value of r. But if we pick r carefully, so that it satisfies the Auxilliary equation then $y(x) = r\,e^{rx}$ is a solution. Now the auxilliary equation is just a quadratic equation for r whose solution is

$$r = \frac{-a_1 \pm \sqrt{a_1^2 - 4a_2}}{2} \tag{2.7}$$

Now if $a_1^2 - 4a_2 > 0$ then r will have 2 distinct real solutions $r_1 = \frac{-a_1+\sqrt{a_1^2-4a_2}}{2}$ and $r_2 = \frac{-a_1+\sqrt{a_1^2-4a_2}}{2}$. If $a_1^2 - 4a_2 = 0$, then r will have 1 real solution $r_1 = r_2 = r = -\frac{a_1}{2}$. If $a_1^2 - 4a_2 < 0$ then r will have 2 complex solutions $r_1 \equiv \alpha + i\beta$ and $r_2 = \alpha - i\beta$ where $\alpha = -\frac{a_1}{2}$ and $i\beta = \frac{\sqrt{a_1^2-4a_2}}{2}$. We often just write this as $r = \alpha \pm i\beta$. We are now in a position to write down the general solution to (2.4). Let's fancy it up and call it a theorem.

Theorem 1. *The general solution of* $y'' + a_1y' + a_2y = 0$ *is*

$$\begin{aligned} y(x) &= Ae^{r_1x} + Be^{r_2x} \quad \text{if } r_1 \text{ and } r_2 \text{ are distinct roots} \\ y(x) &= Ae^{rx} + Bxe^{rx} \quad \text{if } r_1 = r_2 = r \text{ is a single root} \end{aligned}$$

Notes to Theorem 1

i) If $r_1 = r_2 = r$ is a single root then r must be real (see discussion above).

ii) If r_1 and r_2 are distinct and *complex* then they *must* be of the form $r_1 = \alpha + i\beta$ and $r_2 = \alpha - i\beta$ (see discussion above). In this case the solution is

$$\begin{aligned}
y(x) &= A\, e^{(\alpha+i\beta)x} + B\, e^{(\alpha-i\beta)x} \\
&= e^{\alpha x}(A\, e^{i\beta x} + B\, e^{-i\beta x}) \\
&= e^{\alpha x}(C\cos\beta x + D\sin\beta x) \\
&= e^{\alpha x} E\cos(\beta x + \delta) \\
&= e^{\alpha x} F\sin(\beta x + \gamma)
\end{aligned}$$

which are alternative ways of writing the solution. (do Problem 2.1) Generally speaking the exponentials are convenient for travelling waves (free particle) and the sines and cosines are good for standing waves (bound particle).

Example 2.1.1 Solve Newton's law ($F = ma$) for a spring force ($-kx$).

Solution In 1-dimension $F = ma$ becomes $-kx = m\ddot{x}$ ($\ddot{x} \equiv \frac{d^2x}{dt^2}$). Re-write as $\ddot{x} + \omega^2 x = 0$ where $\omega^2 \equiv \frac{k}{m}$. This is a second order differential equation with constant coefficients (and it's homogeneous and linear). The Auxilliary equation is

$$r^2 + \omega^2 = 0$$

(obtained by substituting $x(t) = r\, e^{rt}$ into the differential equation). The solution to the Auxilliary equation is

$$r = \pm i\omega$$

which gives $\alpha = 0$ and $\beta = \omega$ in Theorem 2.1.1. Thus the solution is

$$x(t) = B\, e^{i\omega t} + C\, e^{-i\omega t}$$

$$\begin{aligned} &= D\cos\omega t + E\sin\omega t \\ &= F\cos(\omega t + \delta) \\ &= G\sin(\omega t + \gamma) \end{aligned}$$

which is our familiar oscillatory solution for a spring.

Now let's determine the unknown constant. This is obtained from the *boundary condition*. Let's assume that at $t = 0$ the spring is at position $x = 0$ and at $t = \frac{T}{4}$ (T = period, $\omega = \frac{2\pi}{T}$) the spring attains its maximum elongation $x = A$ (A = Amplitude). Let's use the solution $x(t) = D\cos\omega t + E\sin\omega t$.

Then $x(0) = 0 = D$. Thus $D = 0$. And $x(\frac{T}{4}) = A = E\sin\frac{2\pi}{T}\frac{T}{4} = E\sin\frac{\pi}{2} = E$. Thus $E = A$. Therefore the solution consistent with boundary conditions is $x(t) = A\sin\omega t$ where A is the amplitude. Thus we see that *in the classical case the boundary condition determines the amplitude.*

(do Problem 2.2)

2.1.2 Inhomogeneous Equation

The next simplest differential equation to solve puts a function on the right hand side of (2.4) as

$$y'' + a_1 y' + a_2 y = f(x) \tag{2.8}$$

where $f(x)$ is called the inhomogeneous term.

We now have to distinguish between a *particular* solution and a *general* solution. A general solution to an equation contains everything, whereas a particular solution is just a little piece of a general solution. (A *very* crude example is the equation $x^2 = 9$. General solution is $x = \pm 3$. Particular solution is $x = -3$. Another particular solution is $x = +3$). Theorem 1 contains the general solution to the homogeneous differential equation (2.4).

Theorem 2 *The general solution of* $y'' + a_1 y' + a_2 y = f(x)$ *is*

$$y = y_P + y_H$$

where y_H is the general solution to the homogeneous equation and y_P is a particular solution to the inhomogeneous equation.

This is a really great theorem. We already have half of our solution to (2.8). It's y_H which is given in Theorem 2. If we can get y_P we have the complete solution. And y_P is easy to get!

Remember y_P is a particular solution so *any* old solution that you can find is a legitimate answer to y_P. There are 3 methods for find y_P. These are called i) Guessing, ii) method of Variation of Parameters and iii) method of Undetermined Coefficients.

Guessing is the best method. If you can guess the answer (for y_P) just add it to y_H (from Theorem 1) and you have the complete answer! ($y = y_P + y_H$).

The method of Variation of Parameters is also useful [Purcell 1987], but we will not use it.

We will use the method of Undetermined Coefficients, which I prefer to call the method of *Copying the Inhomogeneous Term.* Take a look at Table 2.1.

Table 2.1

<table>
<tr><th>if $f(x) =$</th><th>try $y_P =$</th></tr>
<tr><td>$b_m x^m + b_{m-1} x^{m-1} + \cdots b_1 x + b_0$</td><td>$B_m x^m + B_{m-1} x^{m-1} + \cdots B_1 x + B_0$</td></tr>
<tr><td>$be^{\alpha x}$</td><td>$Be^{\alpha x}$</td></tr>
<tr><td>$b \cos \beta x + c \sin \beta x$</td><td>$B \cos \beta x + C \sin \beta x \equiv A \cos(\beta x + \delta)$
$= F \sin(\beta x + \gamma)$ etc.</td></tr>
<tr><td colspan="2">Modification: if a term of $f(x)$ is a solution to the homogeneous equation then multiply it by x (or a higher power of x)</td></tr>
</table>

This Table gives you a summary of how to find y_P. For example if the differential equation is

$$y'' + 3y' + 2y = 3 \sin 2x$$

then the particular solution will be $y_P = B \sin 2x$. In other words just *change the constant in the inhomogeneous term and you have the particular solution.* That's why I like to call it the method of Copying the Inhomogeneous Term. There is one caveat however. If a function the same as the inhomogeneous term appears in the homogeneous solution then the method won't work. Try multiplying by x (or some higher power) to get y_P.

Example 2.1.2 Newton's law for a spring with a forcing function is $\ddot{x} + \omega^2 x = A\cos\alpha t$.

A) Find a particular solution and show that it satisfies the differential equation.

B) What is the general solution?

Solution

A) Copy the Inhomogeneous Term. Try $x_P = B\cos\alpha t$. Let's check that it works.

$$\begin{aligned}\dot{x}_P &= -B\alpha\sin\alpha t\\ \ddot{x}_P &= -B\alpha^2\cos\alpha t\end{aligned}$$

Substituting we get for the left hand side

$$\begin{aligned}\ddot{x}_P + \omega^2 x_P &= -B\alpha^2\cos\alpha t + \omega^2 B\cos\alpha t\\ &= B(\omega^2 - \alpha^2)\cos\alpha t\end{aligned}$$

which equals the right hand side *if* $A = B(\omega^2 - \alpha^2)$. Thus the Undetermined Coefficient is

$$B = \frac{A}{\omega^2 - \alpha^2}$$

and the particular solution is

$$x_P(t) = \frac{A}{\omega^2 - \alpha^2}\cos\alpha t$$

B) The general solution is just $x = x_H + x_P$ and we found x_H in Example 2.1.1. Thus the general solution is

$$x(t) = E\cos(\omega t + \delta) + \frac{A}{\omega^2 - \alpha^2}\cos\alpha t$$

(do Problem 2.3)

In a differential equations course you would *prove* Theorems 1 and 2 and then you would be happy and satisfied that the solutions I claimed are correct. If you have not taken a differential equations course you can *still* be happy and satisfied that the solutions are correct because you can always *check your answers by substituting back into the differential equation*! You should *always* do this anyway, just to make sure you haven't made a mistake. (See Problem 2.2) Thus if you have not yet studied differential equations then simply use Theorems 1 and 2 as a recipe for getting the answer. Then *check* your answer always to satisfy yourself that it is correct.

We have now finished our discussion of ordinary differential equations. We are not going to consider equations with non-constant coefficients.

If you are interested in *higher* order equations with constant coefficients then these are *easy* to solve once you know how to solve second order equations. See Purcell and Varberg [Purcell 1987].

2.2 Partial Differential Equations

Partial differential equations involve more than one variable such as $y(x,t)$ and involve partial derivatives such as $\frac{\partial y}{\partial x}$ and $\frac{\partial y}{\partial t}$ or $\frac{\partial^2 y}{\partial x \partial t}$ etc. The typical method of solution of a partial differential equation (PDE) involves the technique of *Separation of Variables*. For a function of two variables $y(x,t)$ this technique splits the single PDE into two ordinary differential equations! We solve these with our previous techniques. We call these the *separable* solutions because they are obtained with the technique of separation of variables.

However separable solutions are *not* general solutions of the PDE. *The general solution of a* PDE *is a linear combination of separable solutions.*

The technique of separation of variables is fairly easy to apply and we will study it using the Schrödinger equation as our example. But remember this technique will work on the wide variety of PDE's encountered in physics. (However the technique won't work on *all* PDE's such as the Wheeler-DeWitt equation for a scalar field.)

We wish now to show how the partial differential Schrödinger equation (1.1) gets reduced to two ordinary differential equations (ODE's). Notice that $\Psi(x,t)$ is a function of the two variables x and t. The fundamental technique in Separation of Variables is to write Ψ as a *product* of two separate functions $\psi(x)$ and $f(t)$ which are functions of a single variable. That is

$$\Psi(x,t) = \psi(x)f(t) \tag{2.9}$$

Now all you have to do is substitute this ansatz back into the original PDE and everything will fall out. We calculate $\frac{\partial\Psi}{\partial x} = \frac{d\psi}{dx}f(t)$ and $\frac{\partial^2\Psi}{\partial x^2} = \frac{d^2\psi}{dx^2}f(t)$ and $\frac{\partial\Psi}{\partial t} = \psi(x)\frac{df}{dt}$ to give

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}f(t) + U(x)\psi(x)f(t) = i\hbar\psi(x)\frac{df}{dt}$$

Divide the whole thing through by $\psi(x)f(t)$ and

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + U(x) = i\hbar\frac{1}{f}\frac{df}{dt}$$

But now notice that the left hand side is a function of x only and the right hand side is a function of t only. The *only* way two different functions of two different variables can always be equal is if they are both *constant.* Let's call the constant E and make both sides equal to it. Thus

$$\boxed{\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U\right)\psi = E\psi} \tag{2.10}$$

and

$$\frac{1}{f}\frac{df}{dt} = \frac{E}{i\hbar} = \frac{-i}{\hbar}E \tag{2.11}$$

and these are just two ordinary differential equations, which we know how to solve! Equation (2.10) is only a function of x and is called the *time-independent Schroödinger equation* (for 1 particle in 1 dimension). We shall spend a whole chapter on solving it for different potential energy functions $U(x)$. That is we will get different solutions $\psi(x)$ depending on what function $U(x)$ we put in. The second equation (2.11) can be solved right away because it doesn't have any unknown functions in it. It's just an easy first order ODE which has the solution

$$f(t) = Ce^{-\frac{i}{\hbar}Et} \tag{2.12}$$

(do Problem 2.4)

Thus the separable solution to the time dependent Schrödinger equation (1.1) is

$$\boxed{\Psi(x,t) = \psi(x)e^{-\frac{i}{\hbar}Et}} \tag{2.13}$$

(We will absorb normalization constants into $\psi(x)$.)

What is the constant E? Obviously it's the *total energy* because the kinetic energy operator is $T = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ and (2.10) is just

$$(T + U)\psi = E\psi$$

Compare to (16.3).

2.3 Properties of Separable Solutions

The separable solutions $\Psi(x)$ have many important properties which we shall now discuss.

2.3.1 General Solutions

When we actually solve (2.10) for a specific potential $U(x)$ in the next chapter we will see that a whole set of solutions $\psi(x)$ is generated, and each solution will correspond to a different value for the total energy. Let's use the subscript n to denote the different solutions $\psi_n(x)$ corresponding to the different energies E_n, where $n = 1, 2, 3 \ldots$.

The general solution to the time-dependent Schrödinger equation is a linear combination of separable solutions

$$\Psi(x,t) = \sum_n c_n \psi_n(x)e^{-\frac{i}{\hbar}E_n t} \tag{2.14}$$

where c_n are the expansion coefficients. We will see specifically what these are below.

2.3.2 Stationary States

A stationary state is one which never changes with time. Both the probability density and the expectation value of any variable are constant. The probability density

$$|\Psi(x,t)|^2 = \Psi^*\Psi = \psi^*(x)e^{\frac{i}{\hbar}Et}\psi(x)e^{-\frac{i}{\hbar}Et} = \psi^*(x)\psi(x) \tag{2.15}$$

is constant in time because the time dependence of the wave function cancels out. This also happens for any expectation value

$$\langle Q\rangle = \int \Psi^*(x,t)Q\Psi(x,t)dx = \int \psi^*(x)Q\psi(x)dx \tag{2.16}$$

because Q does not contain any time dependence. Remember all dynamical variables can be written as functions of x or p only $Q = Q(\hat{x},\hat{p}) = Q(x, -i\hbar\frac{d}{dx})$.

With equation (2.13) our normalization condition (1.26) can alternatively be written

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1 \tag{2.17}$$

2.3.3 Definite Total Energy

By the term *definite* total energy we mean that the total energy *uncertainty is zero.* Defining the Hamiltonian operator

$$\hat{H} \equiv -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x) \tag{2.18}$$

the time independent Schrödinger equation (2.10) is

$$\hat{H}\Psi = E\Psi \tag{2.19}$$

Thus from (2.16)

$$\langle H\rangle = \int \psi^*\hat{H}\psi dx = E\int \psi^*\psi dx = E \tag{2.20}$$

which is as we expect. Using (1.16) the uncertainty in the total energy operator $\hat{H}$ is

$$\sigma_H^2 = \langle H^2\rangle - \langle H\rangle^2 \tag{2.21}$$

Now

$$\begin{aligned}\langle H^2\rangle = \int \psi^*\hat{H}^2\psi dx &= \int \psi^*\hat{H}\hat{H}\psi dx = E\int \psi^*\hat{H}\psi dx \\ &= E^2\end{aligned} \tag{2.22}$$

so that

$$\sigma_H^2 = 0 \tag{2.23}$$

The uncertainty in the total energy is zero! Remember that the expectation value is the average of a set of measurements on an ensemble of identically prepared system. However if the uncertainty is zero then every measurement will be identical. *Every measurement will give the same value E.*

2.3.4 Alternating Parity

Recall that an even function obeys $f(x) = f(-x)$ and an odd function obeys $f(x) = -f(-x)$. We say that an even function possesses *even or positive parity* whereas an odd function possesses *odd or negative parity.*

For *even* potentials $U(x)$ [NNN only for even ???] the $n = 1$ solution has even parity, the $n = 2$ solution has odd parity, $n = 3$ even, $n = 4$ odd, etc. That is the parity alternates for each successive solution.

2.3.5 Nodes

A node is a point where the function $\psi(x)$ becomes zero (we are *not* including the end points here). As n increases the number of nodes in the wave function increases. In general the wave function $\psi_n(x)$, corresponding to E_n, will have $n - 1$ *nodes.*

Thus ψ_1 has 0 nodes, ψ_2 has 1 node, ψ_2 has 2 nodes. Thus the number of nodes in the wave function tells us which energy level E_n corresponds to it.

2.3.6 Complete Orthonormal Sets of Functions

Orthonormality

Let's first review a little bit about vectors. The scalar product, often called inner product, of two vectors is defined as

$$\mathbf{A} \cdot \mathbf{B} \equiv AB \cos\theta \tag{2.24}$$

where $A \equiv |\mathbf{A}|$ is the magnitude of $\mathbf{A}$ and θ is the angle between $\mathbf{A}$ and $\mathbf{B}$. We can write vectors in terms of basis vectors $\hat{e}_i$ as

$$\mathbf{A} = \sum_i A_i \hat{e}_i \tag{2.25}$$

where the expansion coefficients A_i are called the components of $\mathbf{A}$, with respect to the basis set $\{\hat{e}_i\}$. If the basis vectors are orthogonal to each other ($\hat{e}_i \cdot \hat{e}_j = 0$ for $i \neq j$) and are of unit length, i.e. normalized ($\hat{e}_i \cdot \hat{e}_j = 1$ for $i = j$) then we can write

$$\hat{e}_i \cdot \hat{e}_j = \delta_{ij} \tag{2.26}$$

for our *orthonormal* (orthogonal *and* normalized) basis. The Kronecker delta symbol is defined as

$$\delta_{ij} = \begin{cases} 1 & \text{if} \quad i = j \\ 0 & \text{if} \quad i \neq j \end{cases} \tag{2.27}$$

The Kronecker delta is an object which has the effect of *killing sums.* Thus

$$\sum_j C_j \delta_{ij} = C_i \tag{2.28}$$

(Prove this.)
The inner product of two arbitrary vectors (2.24) can be alternatively written

$$\mathbf{A}\cdot\mathbf{B} = \sum_i \sum_j A_i B_j \hat{e}_i \cdot \hat{e}_j = \sum_i \sum_j A_i B_j \delta_{ij} = \sum_i A_i B_i$$

Thus

$$\mathbf{A}\cdot\mathbf{B} = \sum_i A_i B_i \tag{2.29}$$

which could have served equally well as our definition of inner product.

The components or expansion coefficients A_i can now be calculated by taking the inner product between the vector $\mathbf{A}$ and the basis vector $\hat{e}_i$. Thus

$$\hat{e}_i \cdot \mathbf{A} = \sum_j \hat{e}_i \cdot A_j \hat{e}_j = \sum_j A_j \hat{e}_i \cdot \hat{e}_j = \sum_j A_j \delta_{ij} = A_i$$

giving

$$A_i = \hat{e}_i \cdot \mathbf{A} \tag{2.30}$$

Now let's look at functions. It turns out that the separable solutions form a function space which is a *complex infinite-dimensional vector space*, often called a *Hilbert space* [Byron 1969]. For an ordinary vector $\mathbf{A}$ the components A_i are labelled by the discrete index i. For a function f the components $f(x)$ are labelled by the continuous index x. The discrete index i tells you the number of dimensions, but x is a continuous variable and so the function space is infinite dimensional.

The inner product of two functions g and f is defined by [Byron 1969, Pg. 214]

$$\langle g \mid f\rangle \equiv \int_a^b g^*(x) f(x) dx \tag{2.31}$$

where we now use the symbol $\langle g \mid f\rangle$ instead of $\mathbf{A}\cdot\mathbf{B}$ to denote inner product. This definition of inner product is exactly analogous to (2.29), except that we have the complex component $g^*(x)$.

The word *orthonormal* means *orthogonal* and *normalized.* An orthonormal (ON) set of functions obeys

$$\int \psi_m^*(x)\psi_n(x) dx = \delta_{mn} \tag{2.32}$$

analogous to (2.26), where instead of distinguishing functions by different letters (f versus g) we distinguish them with different subscripts (ψ_m versus ψ_n). An orthogonal ($m \neq n$) set of functions obeys

$$\int \psi_m^*(x)\psi_n(x)dx = 0 \tag{2.33}$$

and a normalized ($m = n$) set of functions obeys

$$\int \psi_n^*(x)\psi_n(x)dx = 1 \tag{2.34}$$

which we had in (2.17).

Completeness

All separable solutions $\psi_n(x)$ form an orthonormal set and the vast majority are also complete. *A set of functions* $\{\psi_n(x)\}$ *is complete if* **any** *other function be expanded in terms of them* via

$$f(x) = \sum_n c_n \psi_n(x) \tag{2.35}$$

Now this looks exactly like the way we expand vectors in terms of basis vectors in (2.25), where the components A_i correspond to the expansion coefficients c_n. For this reason the functions $\psi_n(x)$ are called basis functions and they are *exactly analogous* to basis vectors.

Equation (2.30) tells us how to find components A_i and similarly we would like to know how to calculate expansion coefficients c_n. Looking at (2.30) you can *guess* the answer to be

$$c_n = \langle \psi_n \mid f \rangle = \int \psi_n^*(x) f(x) dx \tag{2.36}$$

which is just the inner product of the basis functions with the function.

(do Problem 2.5)

One last thing I want to mention is the so-called *completeness relation* or *closure relation* (Pg. 69 [Ohanian 1990]). But first I need to briefly introduce the Dirac delta function defined via

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)dx \equiv f(a) \tag{2.37}$$

which is nothing more than a generalization of the Kronecker delta symbol in equation (2.28). Whereas the Kronecker delta kills sums, the Dirac delta function is defined to *kill integrals*. (We shall discuss the Dirac delta in more detail later on.) Now recall that a complete set of basis functions allows us to expand any other function in terms of them as in (2.35), where the coefficients c_n are given in (2.36). Thus

$$\begin{aligned} f(x) &= \sum_n c_n \psi_n(x) \\ &= \sum_n \int \psi_n^*(x') f(x') dx' \psi_n(x) \\ &= \int f(x') \left[\sum_n \psi_n^*(x') \psi_n(x) \right] dx' \end{aligned} \tag{2.38}$$

and for the left hand side to equal the right hand side we *must* have

$$\boxed{\sum_n \psi_n^*(x') \psi_n(x) = \delta(x' - x)} \tag{2.39}$$

which is called the *completeness relation* or the *closure relation*. One can see that *if* a set of basis functions $\{\psi_n(x)\}$ satisfies the completeness relation *then* any arbitrary function $f(x)$ can be expanded in terms of them.

2.3.7 Time-dependent Coefficients

By the way, what if our arbitrary function $f(x)$ is instead a function of time also, like $f(x,t)$ or $\Psi(x,t)$ in (2.14)? This is easy to handle. Let's absorb the time dependence into the coefficient and write

$$c_n(t) \equiv c_n(0) e^{-\frac{i}{\hbar} E_n t} \tag{2.40}$$

where $c_n \equiv c_n(0)$. Then (2.14) is simply

$$\Psi(x,t) = \sum_n c_n(t) \psi_n(x) \tag{2.41}$$

or

$$\Psi(x,0) = \sum_n c_n(0) \psi_n(x) = \sum_n c_n \psi_n(x) \tag{2.42}$$

and therefore we still expand our function Ψ in terms of the complete set of basis functions $\psi_n(x)$.

2.4 Problems

2.1 Griffiths, Problem 2.19.

2.2 Refer to Example 2.1.1. Determine the constants for the other 3 forms of the solution using the boundary condition (i.e. determine B, C, F, δ, G, γ from boundary conditions). Show that *all* solutions give $x(t) = A\sin\omega t$.

2.3 Check that the solution given in Example 2.1.2 really does satisfy the differential equation. That is substitute $x(t) = E\cos(\omega t + \delta) + \frac{A}{\omega^2 - \alpha^2}\cos\alpha t$ and check that $\ddot{x} + \omega^2 x = A\cos\alpha t$ is satisfied.

2.4 Solve equation (2.11).

2.5 Prove that $c_n = \langle\psi_n \mid f\rangle$ (Equation (2.36)).

2.5 Answers

2.1

$$\begin{array}{llll} C = A + B, & D = i(A - B) & \text{for} & C\cos kx + D\sin kx \\ A = \frac{F}{2}e^{i\alpha}, & B = \frac{F}{2}e^{-i\alpha} & \text{for} & F\cos(kx + \alpha) \\ A = \frac{G}{2i}e^{i\beta}, & B = -\frac{G}{2i}e^{-i\beta} & \text{for} & G\sin(kx + \beta) \end{array}$$

2.2

$$\begin{array}{ll} B = \frac{A}{2i} & C = -\frac{A}{2i} \\ \delta = \frac{\pi}{2} & F = -A \\ \gamma = \pi & G = A \end{array}$$

2.3 $f(t) = Ae^{-\frac{i}{\hbar}Et}$ (equation (2.12)

Chapter 3

INFINITE 1-DIMENSIONAL BOX

One of the main things we are interested in calculating with quantum mechanics is the spectrum of the Hydrogen atom. This atom consists of *two* particles (proton and electron) and it moves about in *three* dimensions. The Schrödinger equation (2.10) is a *one* particle equations in *one* dimension. The mass of the particle is m moving in the x direction. We *will* eventually write down and solve the two body, three dimensional Schrödinger equation but it's much more complicated to deal with than the one particle, one dimensional equation. Even though the one particle, one dimensional equation is not very realistic, nevertheless it is *very* worthwhile to study for the following reasons. i) It is easier to solve and therefore we can get some practice with solutions before attacking more difficult problems. ii) It contains many physical phenomena (such as energy levels and tunnelling) that are found in the two particle, three dimensional problem and in the real world. It is much better to learn about these phenomena from a simple equation to begin with.

In this chapter we are going to study the *single particle in an infinite 1-dimensional box*. This is one of the simplest examples to study in quantum mechanics and it lets us illustrate many of the unusual features of quantum theory via a simple example.

Another important reason for studying the infinite box at this stage is that we will then be able to understand the postulates of quantum mechanics much more clearly.

Imagine putting a marble in an old shoe box and then wobbling the box around so that the marble moves faster and faster. Keep the box on the floor and wobble it around. Then the marble will have zero potential energy U and its kinetic energy T will increase depending on how fast the marble moves. The total energy $E = T + U$ will just be $E = T$ because $U = 0$. In principle the marble can have *any* value of E. It just depends on the speed of the marble.

We are going to study this problem quantum mechanically. We will use an idealized box and let its walls be infinitely high. We will also restrict it to one dimension. (Even though this is an idealization, you could build such a box. Just make your box very high and very thin.) There is a picture of our infinite 1-dimensional (1-d) box in Figure 3.1.

What we want to do is to calculate the energy of a marble placed in the box and see how it compares to our classical answer (which was that E can be *anything*).

Even though Figure 3.1 looks like a simple drawing of a 1-d box it can also be interpreted as a *potential energy diagram* with a vertical axis representing $U(x)$ and the horizontal axis being x. Now inside the box $U = 0$ because the marble is just rattling around on the floor of the box. Because the box is infinitely high then the marble can never get out. An *equivalent* way of saying this is to say that $U(x \leq 0) = \infty$ and $U(x \geq a) = \infty$ for a box of width a.

3.1 Energy Levels

Let's now solve the Schrödinger equation inside the box where $U = 0$. (This is why the infinite box is a very easy example to start with. There's no *simpler* potential than $U = 0$, except for a completely free particle. More on this later.) Substitute $U = 0$ into (2.10) and we have

$$\frac{-\hbar^2}{2m}\psi'' = E\psi$$

where $\psi'' \equiv \frac{d^2\psi}{dx^2}$. Let's condense all of these annoying constants into one via

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \tag{3.1}$$

giving

$$\psi'' + k^2\psi = 0 \tag{3.2}$$

which is just a second order, homogeneous differential equation with constant coefficients. The Auxilliary equation is

$$r^2 + k^2 = 0 \tag{3.3}$$

which has solutions

$$r = \pm ik \tag{3.4}$$

According to Theorem 1 the solution is ($\alpha = 0$, $\beta = k$)

$$\psi(x) = C \cos kx + D \sin kx \tag{3.5}$$

(We could have picked any of the other solutions, e.g. $\psi(x) = E\cos(kx + \delta)$. These other solutions are explored in problem 3.2.) Thus $\psi(x)$ is a sinusoidal function! Let's try to figure out the unknown constants. We would assume it works just like the classical case (see Example 2.1.1) where the constants are determined from the boundary conditions.

What *are* the boundary conditions? Now we have to think quantum mechanically, not classically. In Figure 3.1 I have written $\psi = 0$ in the regions outside the infinite box. This is because if the walls are truly *infinite* the marble can never get out of the box. (It can't even tunnel out. See later.) Thus the *probability of finding the marble outside the box is zero. This* is our quantum mechanical boundary condition. Mathematically we write

$$\psi(x < 0) = \psi(x > a) = 0 \tag{3.6}$$

Now the marble is inside the box and so the probability of finding the marble inside the box is *not* zero.

$$\psi(0 < x < a) \neq 0 \tag{3.7}$$

OK, so we know the marble won't be outside the box, but it will be inside. But what happens *right at the edge* of the wall? Is the marble allowed to be there or not? $\psi(x)$ is supposed to be a well behaved mathematical function. That is, it is not allowed to have infinities, spikes and jumps (discontinuities). In fancy language we say that the *wave function and its derivatives must be continuous.* Thus the wave function outside the box must equal the wave function inside the box at the boundary. Therefore the wave function inside the box must be zero at the wall.

$$\psi(x = 0) = \psi(x = a) = 0 \tag{3.8}$$

This is the mathematical statement of our quantum mechanical boundary condition. Notice it says *nothing* about the *amplitude* of the wave function. Therefore, unlike the classical case of Example 2.1.1, the boundary condition will not tell us the amplitude. (We will see in a minute that we get the amplitude from the normalization condition (2.34).)

Combining (3.5) and (3.8) we have

$$\psi(x=0) = 0 = C \tag{3.9}$$

Thus $C = 0$ and therefore (3.5) becomes

$$\psi(x) = D \sin kx \tag{3.10}$$

Combining this with (3.8) gives

$$\psi(x=a) = 0 = D \sin ka \tag{3.11}$$

which means

$$\sin ka = 0 \tag{3.12}$$

(We don't pick $D = 0$, otherwise we end up with nothing. Actually nothing *is* a solution, but it's not very interesting.) This implies that $ka = 0$, $\pm\pi$, $\pm 2\pi \cdots$. The $ka = 0$ solution doesn't interest us because again we get nothing ($\psi = 0$). Also the negative solutions for ka are no different from the positive solutions because $\sin(-ka) = -\sin ka$ and the minus sign can be absorbed into the normalization. The *distinct* solution are

$$k = \frac{n\pi}{a} \qquad n = 1, 2, 3 \cdots. \tag{3.13}$$

Now from (3.1) this gives

$$E_n = \frac{\hbar^2 k^2}{2m} = n^2 \frac{\pi^2 \hbar^2}{2ma^2} \tag{3.14}$$

Thus the boundary condition tells us the energy! (not the amplitude). And see how interesting this energy is. It depends on the integer n. Thus the energy cannot be anything (as in the domial case) but comes in discrete steps according to the value of n. We say that the energy is *quantized*. Because there are only certain values of E allowed, depending on the value of n, I have added a subscript to E in (3.14) as E_n. Thus $E_1 = \frac{\pi^2\hbar^2}{2ma^2}$, $E_2 = 4\frac{\pi^2\hbar^2}{2ma^2} = 4E_1$, $E_3 = 9E_1$, $E_4 = 16E_1$ etc. Thus

$$E_n = n^2 E_1 \tag{3.15}$$

This *energy quantization* is one of the most important features of quantum mechanics. That's why it's called *quantum* mechanics. A picture of the allowed energy levels for the infinite box is shown in Figure 3.2. Another very important feature is the lack of a zero energy solution. $E = 0$ *is not allowed in quantum mechanics*. The quantum marble simply can never sit still.

What about the *classical limit*? Notice that if the box is very wide (a is large) then the infinite tower of energy levels will get very close together *and* $E_1 \approx 0$. If the levels are close together it will *appear* that the marble can have any value of energy because the closely spaced levels will look like a continuous distribution. (Do Problem 3.1)

3.2 Wave Function

Let's return to the wave function. From (3.10) and (3.13) we have

$$\psi(x) = D \sin \frac{n\pi}{a} x \tag{3.16}$$

but we still don't have D. This is determined not from the boundary conditions but from the normalization conditions (2.34), which for our example is written

$$\int_{-\infty}^{0} |\psi|^2 dx + \int_{0}^{a} |\psi|^2 dx + \int_{a}^{\infty} |\psi|^2 dx = 1 \tag{3.17}$$

However $\psi = 0$ outside the box, so that the first and third integrals are zero, leaving

$$D^2 \int_0^a \sin^2 \frac{n\pi}{a} x \, dx = 1 \tag{3.18}$$

which gives

Footnote:The integral is easily evaluated using $\cos 2\theta = 1 - 2\sin^2\theta$ where $\theta \equiv \frac{n\pi x}{a}$.

$D^2 \frac{a}{2} = 1$ giving $D = \sqrt{\frac{2}{a}}$. Thus our solution (3.16) is

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x \tag{3.19}$$

which we see is different for each value of n (which is why I add a subscript to ψ_n.) Several of these wave functions are plotted in Figure 3.3. Recall that the value of n characterizes the energy level E_n. Thus for every E_n there is a separate ψ_n. These are combined in Figure 3.4.

Example 3.1 Check that $\psi_2(x) = \sqrt{\frac{2}{a}} \sin \frac{2\pi}{a} x$ is normalized.

Solution We need to check that $\int_0^a \psi_2^* \psi_2 dx = 1$

$$\begin{aligned} \int_0^a \psi_2^*(x)\psi_2(x)dx &= \frac{2}{a}\int_0^a \sin^2 \frac{2\pi}{a} x \, dx \\ &= \frac{2}{a}\frac{a}{2} = 1 \end{aligned}$$

Example 3.2 Check that $\psi_2(x)$ and $\psi_1(x)$ are mutually orthogonal.

Solution We need to check that $\int_0^a \psi_2^*(x)\psi_1 dx = 0$

$$\text{Define } I \equiv \int_0^a \psi_2^*(x)\psi_1(x)dx = \frac{2}{a}\int_0^a \sin \frac{2\pi}{a} x \sin \frac{\pi}{a} x \, dx$$

$$= \frac{4}{a}\int_0^a \sin^2 \frac{\pi}{a} x \cos \frac{\pi}{a} x \, dx \qquad \text{using } \sin 2\theta = 2 \sin\theta \cos\theta$$

Let $u = \sin \frac{\pi}{a} x \quad \Rightarrow \quad du = \frac{\pi}{a} \cos \frac{\pi}{a} x \, dx.$

Thus $$I = \frac{4}{a}\frac{a}{\pi}\int_0^0 u^2 du = 0$$

because $u = 0$ for $x = 0$ and $u = 0$ for $x = a$.

In these exercises we checked orthonormality for some specific functions. We have already proved normality for *any* function via (3.19) and Griffiths (Pg. 27) proves orthogonality for *any* functions where $m \neq n$.

Figure 3.1: Infinite 1-dimensional Box with Width a.

Figure 3.2: Energy levels for Infinite 1-dimensional Box

Figure 3.3: Wave Functions for Infinite 1-dimensional Box

Figure 3.4: Energy Levels and Wave Functions for Infinite 1-dimensional Box

3.3 Problems

3.1 Consider the infinite 1-dimensional box. If the particle is an electron, how wide would the box have to be to approximate classical behavior?

(Hint: Classical behavior will pertain if the energy levels are "closely spaced" or if E_1 is close to zero. The latter condition is easier to quantify, but close to zero compared to what? The only "natural" energy side is the rest mass of the electron. Thus let's just say that classical behavior pertains if $E_1 = \frac{m_e c^2}{100}$.)

3.2 For the infinite 1-dimensional box, show that the same energy levels and wave functions as obtained in (3.14) and (3.19) also arise if the other solution $y(x) = Ae^{(\alpha+i\beta)x} + Be^{(\alpha-i\beta)x}$ is used from Theorem 1.

3.4 Answers

3.1 $a \approx 10,000 \text{ fm } = 10^{-11} \text{ m}$ (*approximately*)

Chapter 4

POSTULATES OF QUANTUM MECHANICS

We have already studied some of the postulates of quantum mechanics in Section 1.2. In this chapter we are going to develop the rest of the postulates and we shall also discuss the fascinating topic of *measurement* in quantum theory. Before getting to the other postulates however, we shall need a little bit more mathematical background.

4.1 Mathematical Preliminaries

4.1.1 Hermitian Operators

With all those i's floating around in the definitions of operators like $\hat{p} \equiv -i\hbar\frac{\partial}{\partial x}$ or $\hat{E} \equiv i\hbar\frac{\partial}{\partial t}$, we might wonder whether the expectation values of these operators are real. We *want* them to be real or otherwise the expectation values of $\hat{p}$ or $\hat{E}$ won't correspond to the momentum or energy that we actually measure in the real world.

Let's check that the expectation values of $\hat{p}$ and $\hat{E}$ *are* real.

Example 4.1.1 Show that the expectation value of the momentum operator is real (i.e. show that $\langle\hat{p}\rangle = \langle\hat{p}\rangle^*$).

Solution

$$\langle\hat{p}\rangle = -i\hbar\int_{-\infty}^{\infty}\Psi^*\frac{\partial\Psi}{\partial x}dx$$

$$\begin{aligned}
\text{therefore} \quad \langle \hat{p} \rangle^* &= i\hbar \int_{-\infty}^{\infty} \Psi \frac{\partial \Psi^*}{\partial x} dx \\
&= i\hbar \int_{-\infty}^{\infty} \Psi d\Psi^* \\
&= i\hbar \left\{ [\Psi \Psi^*]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \Psi^* d\Psi \right\}
\end{aligned}$$

where we have used integration by parts. The first boundary term is zero, giving

$$\begin{aligned}
\langle \hat{p} \rangle^* &= -i\hbar \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx \\
&= \langle \hat{p} \rangle
\end{aligned}$$

(do Problem 4.1)

Now an **operator which has a real expectation value is called an *Hermitian* operator**.

The operators that we have encountered so far, such as the momentum operator $\hat{p} \equiv -i\hbar \frac{\partial}{\partial x}$, the kinetic energy operator $\hat{T} \equiv -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$, the energy operator $\hat{E} \equiv i\hbar \frac{\partial}{\partial t}$ all have real expectation values and are therefore all Hermitian operators. In fact it seems eminently reasonable that all *observables* in quantum mechanics should be *real*.

4.1.2 Eigenvalue Equations

We have already seen what happens when operators act on functions. For the infinite 1-dimensional box the Hamiltonian operator inside the box ($U = 0$) was $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ acting on the wave function

$$\psi(x) = D \sin kx \qquad \text{where} \qquad k \equiv \frac{\sqrt{2mE}}{\hbar}$$

(see equation (3.1)). With $\hat{H}$ acting on ψ as in $\hat{H}\psi$ we have

$$\begin{aligned}
\hat{H}\psi &= -\frac{\hbar^2}{2m}(-Dk^2 \sin kx) = \frac{\hbar^2 k^2}{2m} D \sin kx \\
&= \frac{\hbar^2}{2m}\frac{2mE}{\hbar^2} D \sin kx \\
&= E \, D \sin kx \\
&= E\psi
\end{aligned}$$

This is kind of interesting if you think about it. A complicated operator $\hat{H}$ acts on a function ψ and *gives back the function ψ multiplied by a number E*!

Think about what might have happened instead. A general operator $\hat{B}$ might do all sorts of weird things to functions, ϕ. We might have

$$\hat{B}\phi = \phi^2$$

or

$$\hat{B}\phi = \phi + 7$$

or

$$\hat{B}\phi = \left(\frac{d\phi}{dx}\right)^2$$

or

$$\boxed{\hat{B}\phi = b\phi} \tag{4.1}$$

where b is a *number*. It's this last operator equation which is the special one and it's just like $\hat{H}\psi = E\psi$. In fact this last operator equation is so special that it's given a name. It's called an *eigenvalue equation*. An eigenvalue equation is one in which an operator $\hat{B}$ acts on a function ϕ and gives back simply the original function multiplied by a *number b*. In such a case the function ϕ is called an *eigenfunction* and the number b is called an *eigenvalue*. The eigenvalue and eigenfunctions need not be unique. There might be lots of them in which case we would write

$$\hat{B}\phi_i = b_i\phi_i \tag{4.2}$$

4.2 Postulate 4

Having discussed Hermitian operators and eigenvalue equations, we are ready to formulate our next postulate.

Postulate 4:	To every physical observable b there corresponds a Hermitian operator $\hat{B}$ such that $\hat{B}\phi_i = b_i\phi_i$.

This makes a lot of sense. In classical mechanics we have observbles like energy and momentum, but in quantum mechanics we don't have these any more. They get replaced by operators. But we still want to *observe* things so we say in the postulate that our observables are represented by operators. And they are special *Hermitian* operators to ensure that the observables are ordinary real numbers. The *observables* that we talked about in classical mechanics will now be *expectation values of Hermitian operators* which will be *real*. Furthermore these operators satisfy eigenvalue equations with the eigenvalue being the expectation value of the operator. Recall how this works for energy where the eigenvalue equation is $\hat{H}\Psi = E\Psi$ and the expectation value is (at fixed time)

$$\begin{aligned}
\langle H \rangle &= \int_{-\infty}^{\infty} \Psi^* \hat{H} \Psi \, dx \\
&= \int \sum_n c_n^* \psi_n^* \hat{H} \sum_m c_m \psi_m dx = \sum_n \sum_m c_n^* c_m \int \psi_n^* \hat{H} \psi_m dx \\
&= \sum_n \sum_m c_n^* c_m \int \psi_n^* E_m \psi_m dx = \sum_n \sum_m c_n^* c_m E_m \int \psi_n^* \psi_m dx \\
&= \sum_n \sum_m c_n^* c_m E_m \delta_{mn} = \sum_n |c_n|^2 E_n
\end{aligned}$$

for normalized eigenfunctions ψ_n. Thus Postulate 4 is hopefully eminently reasonable.

Finally notice that the *converse of Postulate 4 is not necessarily true.* Just because we can dream up a Hermitian operator, it doesn't mean that it corresponds to a new physical observable.

In summary, Postulate 4 is saying that *the only possible results of measurement are the eigenvalues of the corresponding operator.*

We have already seen that the energy observable has eigenvalue E, corresponding to the Hermitian operator $\hat{H}$. In that case we had $\hat{H}\psi_n = E_n\psi_n$ where the eigenvectors are ψ_n.

4.3 Expansion Postulate

Postulate 5:	(Expansion Postulate) *Any* wave function can be expanded in terms of ϕ_i, i.e. $\psi = \sum_i c_i \phi_i$.

In other words, the eigenfunctions of an observable (see Postulate 4) form basis functions for any wave function.

Postulate 5 can be stated differently:

Postulate 5′:	$\{\phi_i\}$ form a CON set, where the ϕ_i are eigenfunctions of observables.

We have also seen that this postulate makes sense. With the energy eigenfunctions $\psi_n(x)$ we are able to expand the general eigenfunctions as

$$\Psi(x,t)=\sum_n c_n\Psi_n(x,t)=\sum_n c_n\psi_n(x)e^{-\frac{i}{\hbar}E_nt} \tag{4.3}$$

(see Section 2.3.7). At t equal to some fixed time t_o we have

$$\boxed{\Psi(x,t_o)=\sum_n c_n'\psi_n(x)} \tag{4.4}$$

where

$$c_n'\equiv c_ne^{-\frac{i}{\hbar}E_nt_o}$$

with the time dependence absorbed into the constant. Equation (4.4) is very important. Let us think specifically about the infinite 1-dimensional box. The wave function for the *whole box* is $\Psi(x,t_o)$, which is a linear combination of all individual solutions $\psi_n(x)$. Equation (4.4) could easily be verified. Take each solution $\psi_n(x)$, and add them all up and you will still have a solution! Thus the *most general state* of the infinite 1-dimensional box is $\Psi(x)$.

4.4 Measurement Postulate

Postulate 6:	(Measurement Postulate) If the state of a system is ψ, then the *probability* that a measurement finds the system in state ϕ_j is $|c_j|^2$.

Again let us illustrate this with the 1-dimensional box. The box is in the general state $\Psi=\sum_n c_n\psi_n(x)$. If you make a measurement then the *probability* of finding the system in state $\psi_n(x)$ is $|c_n|^2$.

Recall the probability density is $|\Psi|^2$ so that

$$|\Psi|^2 = \Psi^*\Psi = \sum_n c_n^*\psi_n^* \sum_m c_m\psi_m e^{\frac{i}{\hbar}(E_m-E_n)t}$$

The probability is the integral of the probability density. Thus the normalization is

$$\begin{aligned} 1 = \int_{-\infty}^{\infty} |\Psi|^2 dx &= \sum_n\sum_m c_n^* c_m \int \psi_n^*(x)\psi_m(x)dx\, e^{\frac{i}{\hbar}(E_m-E_n)t} \\ &= \sum_n\sum_m c_n^* c_m \delta_{nm}\, e^{\frac{i}{\hbar}(E_m-E_n)t} \\ &= \sum_n c_n^* c_n = \sum_n |c_n|^2 \end{aligned}$$

showing that Postulate 6 is consistent with the probabilities adding up to 1 and indeed that it *is* reasonable to interpret each $|c_n|^2$ as a probability.

4.5 Reduction Postulate

Now we come to the most famous postulate in quantum mechanics.

Postulate 7:	(Reduction Postulate) A coherent superposition ψ collapses to an eigenfunction ϕ_j upon measurement.

Before we make a measurement on the particle in the box, the state is a coherent superposition $\psi = \sum\limits_n c_n\psi_n$. When we make the measurement we find the energy of the particle to be one of E_n, or the state to be one of ψ_n. (Recall, from postulate 6, that the probability to get a particular ψ_n or E_n is $|c_n|^2$.)

What happened when we made the measurement? The *act* of making the measurement forced the general state ψ to *collapse* to a particular state ψ_n. *This collapse must occur because otherwise an immediate second measurement might not yield the same* E_n.

This collapse of the wave function has mind-boggling philosophical implications. A nice quick discussion is given on Pages 2-4 of Griffiths [1994].

If we have two identically prepared 1-dimensional boxes then when a measurement is made the first box might collapse to ψ_3 and the second box might collapse to ψ_{10}. *Because* the wave function has collapsed then *immediate* subsequent measurements will still give ψ_3 and ψ_{10}. If the wave functions had not collapsed then we might have got ψ_5 and ψ_{13} on subsequent measurements. That is we would keep measuring a different energy for the system which is crazy.

4.6 Summary of Postulates of Quantum Mechanics (Simple Version)

We summarize our postulates for the 1-particle, 1-dimensional case.

1. To each state of a physical system there corresponds a wave function $\Psi(x,t)$.
2. The time development of the wave function is determined by the Schrödinger equation
$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\right)\Psi(x,t)=i\hbar\frac{\partial}{\partial t}\Psi(x,t)$$
3. (Born hypothesis) $|\Psi|^2$ is the probability *density*.
4. To every physical observable b there corresponds a Hermitian operator $\hat{B}$ such that $\hat{B}\phi_i = b_i\phi_i$.
5. (Expansion Postulate) $\{\phi_i\}$ from a CON set, such that *any* wave function can be written $\psi = \sum\limits_i c_i\phi_i$.
6. (Measurement Postulate) If the state of a system is ψ then the probability that a measurement finds the system in state ϕ_i is $|c_i|^2$.
7. (Reduction Postulate) A coherent superposition ψ collapses to an eigenfunction ϕ_i upon measurement.

We shall write a more fancy version later on in terms of quantities called *bras* and *kets*.

Example 4.6.1 This problem concerns the relationship between *expectation values* and *eigenvalues*. Assuming that $\hat{B}\phi_i = b_i\phi_i$, calculate the expectation value $\langle\hat{B}\rangle$.

Solution

$$\begin{aligned}
\langle\hat{B}\rangle &\equiv \int \Psi^*(x)\hat{B}\Psi(x)dx \qquad \text{(at fixed time)} \\
&= \int \sum_i c_i^*\phi_i^*\hat{B}\sum_j c_j\phi_j dx \qquad \text{using the Expansion postulate} \\
&= \sum_i\sum_j c_i^*c_j \int \phi_i^*\hat{B}\phi_j dx \\
&= \sum_i\sum_j c_i^*c_j \int \phi_i^* b_j\phi_j dx \\
&= \sum_i\sum_j c_i^*c_j b_j \int \phi_i^*\phi_j dx \\
&= \sum_i\sum_j c_i^*c_j b_j\delta_{ij} = \sum_i c_i^*c_i b_i \\
&= \sum_i |c_i|^2 b_i \qquad (4.5)
\end{aligned}$$

We previously found that $|c_i|^2$ is the *probability* of finding the system in state ϕ_i if the state of a system is ψ (see Postulate 6). Writing $P(i) \equiv |c_i|^2$ we see that

$$\langle\hat{B}\rangle = \sum_i P(i)b_i = \langle b\rangle$$

using our average formula from (1.8). Thus the *expectation value* is the *average* of the *eigenvalues*.

The *interpretation* of (4.5) is that if the state of a system is ψ then $|c_i|^2$ is the probability of a measurement yielding the eigenvalue b_i.

Thus in a measurement it is the **eigenvalues** *that are actually* **measured** (with a certain probability).

Example 4.6.2 If the state of a system ψ is *already* one of the eigenfunctions ϕ_i, then what is the expectation value $\langle\hat{B}\rangle$?

Solution

$$\psi = \phi_i$$

$$\begin{aligned}\langle\hat{B}\rangle &= \int \psi^* \hat{B} \psi \, dx \\ &= \int \phi_i^* b_i \phi_i \, dx \\ &= b_i \int \phi_i^* \phi_i \, dx \\ &= b_i\end{aligned}$$

Thus if the system is already in state ϕ_i with eigenvalue b_i, then a further subsequent measurement is *certain* to return the value b_i (unit probability).

The postulates of quantum mechanics tell us why we need to *perform measurements on a set of identically prepared systems, rather than a series of measurements on a single system.* When we make a measurement on a single system in state ψ, it *collapses* to state ϕ_i with eigenvalue b_i upon measurement. We just saw in the above examples that if we measure it again it will still be in state ϕ_i because it has already collapsed. Thus repeated measurements will keep giving us the measured eigenvalue b_i.

A different identically prepared system will also be in state ψ but on measurement it might collapse to state ϕ_j with eigenvalue b_j. Another system might collapse to ϕ_k with eigenvalue b_k. Thus the only way we are going to get a distribution of different eigenvalues, which we can subsequently average, is by using a set of identically prepared systems.

4.7 Problems

4.1 Show that the expectation value of the Hamiltonian or Energy operator is real (i.e. show that $\langle\hat{E}\rangle$ is real where $\hat{E} = i\hbar\frac{\partial}{\partial t}$).

4.2 Find the eigenfunctions of the momentum operator assuming that $\hat{P}\phi = p\phi$ where p is the momentum.

4.3 Griffiths Problem 2.8.

4.4 Griffiths Problem 2.9.

4.5 Griffiths Problem 2.10.

4.8 Answers

4.2 Griffiths Problem 2.8.

A)

$$A = \sqrt{\frac{30}{a^5}}$$

B)

$$\begin{aligned} \langle x \rangle &= \frac{a}{2} \\ \langle p \rangle &= 0 \\ \langle H \rangle &= \frac{5\hbar^2}{ma^2} \end{aligned}$$

4.4 Griffiths Problem 2.9.

$$\begin{aligned} c_i &= 0.99928 \\ c_2 &= 0 \\ c_3 &= 0.03701 \end{aligned}$$

Part I

1-DIMENSIONAL PROBLEMS

Chapter 5

Bound States

In physics most problems can either be considered as a *bound state* problem or a *scattering* problem. For example the orbits of planets constitute a bound state problem in gravity, whereas the paths of comets (those with hyberbolic trajectories, not periodic comets) constitute the scattering problem. Another example is that of electrons in orbit around a nucleus constituting the atomic bound state problem, whereas firing electrons at a nucleus in an accelerator is a scattering problem.

Quantum mechanical bound states are quite different to classical bound states. The table illustrates some of the differences.

Table 5.1 Properties of Bound States

Classical Bound State	Quantum Mechanical Bound State
Particle can have any energy, E	Particle can only take on certain discrete values of energy, E_n
Particle can have zero energy $E_1 = 0$	Particle cannot have zero energy $E_1 \neq 0$
Particle is trapped in the potential well if $E < U$ where U is the potential energy	Particle can escape (or tunnel) from the potential well even if $E < U$

The reason as to why we study such idealized simple problems as 1-dimensional potential wells (with only 1 particle) is that they exhibit the general properties listed in Table 5.1.

A very nice summary of the properties of potential wells and barriers can be found in Table 6-2 on Page 243 of Eisberg and Resnick (1974).

The *infinite* 1-dimensional well that we studied in Chapter 3 only admits *bound state* solutions. A particle could never *scatter* from the well because it is infinitely deep. It's a bit like a black hole. Once you fall in you can never get out.

The infinite 1-dimensional well was introduced in Chapter 3 so that we could better understand the postulates of quantum mechanics. In this chapter we shall study two more 1-dimensional bound state problems, namely the finite well and the harmonic oscillator. We will write the Schrödinger equation as

$$\boxed{\psi'' + \frac{2m}{\hbar^2}(E - U)\psi = 0} \tag{5.1}$$

5.1 Boundary Conditions

Suppose we have a boundary located at position as shown in Fig. 5.1. The left region of the boundary is designated as region I and the right side is region II. When we studied the infinite square well we assumed that the wave function was continuous across the boundary. That is

$$\psi_I(a) = \psi_{II}(a) \tag{5.2}$$

In this section we wish to discuss a second boundary condition that must be satisfied, namely that the first derivative of the wave function must be continuous at the boundary of a *finite* potential. That is

$$\psi'_I(a) = \psi'_{II}(a) \tag{5.3}$$

To see this again consider Fig. 5.1. The wave function drawn at the top of the figure certainly satisfies (5.2), yet it does not satisfy (5.3) and therefore is not allowed. Why not? The middle figure in Fig. 5.1 shows the first derivative ψ' on both sides of the boundary. Obviously then the second derivative ψ'' (shown at the bottom of Fig. 5.1) has an infinite spike at the boundary. The Schrödinger equation forbids this because U, E and ψ in the Schrödinger equation are all *finite* and therefore ψ'' must be finite as well. This means that (5.3) must hold at the boundary.

The only exception is when $U = \infty$, as in the case of the infinite square well. If $U = \infty$ then ψ'' can also be infinite and thus (5.3) was not used for the infinite square well.

5.2 Finite 1-dimensional Well

The *finite* 1-dimensional well admits *both* bound state *and* scattering solutions. If the well is say 20 MeV deep and you scatter in with 80 MeV then you might scatter out with 60 MeV. In this chapter however we will examine only the bound state solutions. The scattering solutions will be studied in the next chapter.

The finite 1-dimensional well is sketched in Fig. 5.1. For convenience we imagine the well to have a depth of $-U_0$ in the center of the well and $U = 0$ beyond both edges of the well located at $x = -a$ and $x = +a$. (We could have chosen $U = U_0$ beyond both edges and $U = 0$ in the center and $x = 0$ to $x = +a$. These other combinations are explored in the problems. Of course the energies and wave functions will always be equivalent.)

Because of the way we have drawn the finite square well potential in Fig. 5.2 the *bound states* will correspond to

$$\text{Bound States:}\quad E < 0 \tag{5.4}$$

whereas *scattering states* are

$$\text{Scattering:}\quad E > 0 \tag{5.5}$$

In this chapter we will only consider bound states, $E < 0$. In Regions I and III ($x < -a$ and $x > a$), we have $U = 0$ so that the Schrödinger equation (5.1) is

$$\psi'' + \frac{2mE}{\hbar^2}\psi = 0 \tag{5.6}$$

but despite the similarity to (3.1) and (3.2) it is *not* the same equation because here E is negative. Define

$$\bar{\kappa}^2 \equiv \frac{2mE}{\hbar^2} \tag{5.7}$$

and thus

$$\bar{\kappa} \equiv \frac{\sqrt{2mE}}{\hbar} \tag{5.8}$$

but remember now $\bar{\kappa}$ is *complex* because E is negative, whereas in (3.1) k was real. Proceeding write

$$\psi'' + \bar{\kappa}^2\psi = 0 \tag{5.9}$$

with Auxilliary equation

$$r^2 + \bar{\kappa}^2 = 0 \tag{5.10}$$

with solutions

$$r = \pm i\bar{\kappa} \tag{5.11}$$

yielding

$$\begin{aligned} \psi_I(x) &= A\,e^{i\bar{\kappa}x} + B\,e^{-i\bar{\kappa}x} \\ &= C\cos\bar{\kappa}x + D\sin\bar{\kappa}x \end{aligned} \tag{5.12}$$

However the $C\cos\bar{\kappa}x + D\sin\bar{\kappa}x$ solution doesn't make any sense because $\bar{\kappa}$ is complex. Actually (5.8) can alternately be written

$$\bar{\kappa} = i\sqrt{\frac{2m|E|}{\hbar}} \equiv i\kappa' \tag{5.13}$$

where κ' is *real*, and (5.11) becomes

$$r = \pm\kappa' \tag{5.14}$$

yielding

$$\psi_I(x) = A\,e^{\kappa' x} + B\,e^{-\kappa' x} \tag{5.15}$$

which is equivalent to (5.12) because $r = \pm i\bar{\kappa}$ is actually real. We can avoid the confusion above if we just agree to always choose κ or k or whatever to be *real* at the outset.

5.2.1 Regions I and III With Real Wave Number

Thus let's start again and write the Schrödinger equation as

$$\psi'' - \frac{(-2mE)}{\hbar^2}\psi = 0 \tag{5.16}$$

Because E is negative, $-E$ will be positive. Define

$$\kappa^2 \equiv -\frac{2mE}{\hbar^2} \tag{5.17}$$

or

$$\kappa \equiv \sqrt{-\frac{2mE}{\hbar^2}} \tag{5.18}$$

which is *real* because E is negative. Thus

$$\psi'' - \kappa^2\psi = 0 \tag{5.19}$$

with Auxilliary equation

$$r^2 - \kappa^2 = 0 \tag{5.20}$$

with real solutions

$$r = \pm\kappa. \tag{5.21}$$

Thus for Regions I and III

$$\psi(x) = A\,e^{\kappa x} + B\,e^{-\kappa x} \tag{5.22}$$

However, as it stands this wave function blows up for $x \to \infty$ and $x \to -\infty$. Thus in Region I we must have $B = 0$ and Region II must have $A = 0$. These are our boundary conditions. Thus

$$\psi_I(x) = A\,e^{\kappa x} \tag{5.23}$$

$$\psi_{III}(x) = B\,e^{-\kappa x} \tag{5.24}$$

which are now both finite for $x \to \pm\infty$.

We will need to impose further boundary conditions on ψ', so we note them now.

$$\psi_I'(x) = A\,\kappa e^{\kappa x} \tag{5.25}$$

$$\psi_{III}' = -B\,\kappa e^{-\kappa x} \tag{5.26}$$

5.2.2 Region II

In the region $-a < x < a$ we have $U = -U_0$ so that (5.1) becomes

$$\psi'' + \frac{2m}{\hbar^2}(E + U_0)\psi = 0 \tag{5.27}$$

Now even though $E < 0$ we will never have $E < U_0$ so that $E + U_0$ will remain positive. Thus we can define

$$k^2 \equiv \frac{2m}{\hbar^2}(E + U_0) \tag{5.28}$$

safe in the knowledge that

$$k \equiv \sqrt{\frac{2m(E + U_0)}{\hbar^2}} \tag{5.29}$$

is real. We use the same symbol for k here as in (3.1) because the Auxilliary equation and solutions are the same as before in Section 3.1. Equations (3.3)–(3.5) will be the same as here except with k defined as in (5.29). Thus

$$\psi_{II}(x) = C\cos kx + D\sin kx. \tag{5.30}$$

and the derivative is

$$\psi'_{II}(x) = -Ck\sin kx + Dk\cos kx \tag{5.31}$$

5.2.3 Matching Boundary Conditions

We have previously imposed the boundary conditions at infinity for ψ_I and ψ_{II}. Now we will match the wave functions and their derivatives at the boundaries between each of the three regions.

The requirement

$$\psi_I(-a) = \psi_{II}(-a) \tag{5.32}$$

yields

$$\begin{aligned} A\,e^{-\kappa a} &= C\cos(-ka) + D\sin(-ka) \\ &= C\cos ka - D\sin ka \end{aligned} \tag{5.33}$$

and

$$\psi'_I(-a) = \psi'_{II}(-a) \tag{5.34}$$

yields

$$\begin{aligned} A\kappa\,e^{-\kappa a} &= -Ck\sin(-ka) + Dk\cos(-ka) \\ &= Ck\sin ka + Dk\cos ka \end{aligned} \tag{5.35}$$

We have two equations (5.33) and (5.35) and three unknowns, A, C, D. Nevertheless let us solve for the two unknowns C and D in terms of A and let A be later determined from the normalization requirement. Equation (5.33) gives

$$C = \frac{A\,e^{-\kappa a} + D\sin ka}{\cos ka} \tag{5.36}$$

which is substituted into (5.35), which is then solved for D to give

$$D = A\,e^{-\kappa a}\left(\frac{\kappa}{k}\cos ka - \sin ka\right) \tag{5.37}$$

and substituting back into (5.36) gives

$$C = A\,e^{-\kappa a}\left(\cos ka + \frac{\kappa}{k}\sin ka\right) \tag{5.38}$$

Thus we now have

$$\begin{aligned}\psi_{II}(x) &= \frac{A}{k}e^{-\kappa a}[(\kappa\cos ka - k\sin ka)\sin kx \\ &\qquad +(k\cos ka + \kappa\sin ka)\cos kx] \qquad (5.39)\\ \psi'_{II} &= A\,e^{-\kappa a}[(\kappa\cos ka - k\sin ka)\cos kx \\ &\qquad -(k\cos ka + \kappa\sin ka)\sin kx] \qquad (5.40)\end{aligned}$$

with $\psi_I(x)$ still given in (5.23) and (5.25).

Let us now match wave functions at the second boundary. For region II we now use (5.39) and (5.40) instead of (5.30) and (5.31).

The requirement

$$\psi_{II}(a) = \psi_{III}(a) \tag{5.41}$$

yields

$$\begin{aligned}&\frac{A}{k}e^{-\kappa a}[(\kappa\cos ka - k\sin ka)\sin ka + (k\cos ka + \kappa\sin ka)\cos ka] \\ &\qquad = B\,e^{-\kappa a} \qquad (5.42)\end{aligned}$$

and

$$\psi'_{II}(a) = \psi'_{III}(a) \tag{5.43}$$

yields

$$\begin{aligned}&A\,e^{-\kappa a}[(\kappa\cos ka - k\sin ka)\cos ka - (k\cos ka + \kappa\sin ka)\sin ka] \\ &\qquad = -B\kappa\,e^{-ka} \qquad (5.44)\end{aligned}$$

We have two equations (5.42) and (5.44) and four unknowns A, B, κ, k. Nevertheless let us solve for B from both equations and then combine the results. Equation (5.42) gives

$$B = \frac{A}{k}[2\kappa\cos ka\sin ka + k(\cos^2 ka - \sin^2 ka)] \tag{5.45}$$

and (5.44) gives

$$B = \frac{A}{\kappa}[2k\cos ka\sin ka - \kappa(\cos^2 ka - \sin^2 ka)] \tag{5.46}$$

Combining (5.45) and (5.46) yields

$$\kappa k(1-\tan^2 ka) = (k^2-\kappa^2)\tan ka \tag{5.47}$$

which is a quadratic equation for *either* unknown k or κ. Let us solve for κ in terms of k. Thus re-arranging (5.47) gives

$$\kappa^2 \tan ka + \kappa k(1-\tan^2 ka) - k^2 \tan ka = 0 \tag{5.48}$$

which has the quadratic solution

$$\kappa = \frac{-k(1-\tan^2 ka) \pm \sqrt{k^2(1-\tan^2 ka)^2 + 4k^2\tan^2 ka}}{2\tan ka} \tag{5.49}$$

which reduces to

$$\kappa = k\tan ka \tag{5.50}$$

or

$$\kappa = -k\cot ka \tag{5.51}$$

These are the same results as given in Griffiths (1995), equation (2.136), pg. 62 and in Gasiorowicz (1996), equation (5.63), pg. 90.

Recall the two equations (5.42) and (5.44) and four unknowns A, B, κ, k. The best we can do is eliminate two unknowns and solve for the other two. Equation (5.45) *or* (5.46) gives B in terms of A, κ and k. Equations (5.50) and (5.51) give κ in terms of k. Thus we have solved for B and κ in terms of the remaining two unknowns A and k. We expect to determine A separately from normalization, just as we did for the infinite square well.

Let us then summarize our solutions for the finite square well, inserting the constants we have solved for. We have

$$\begin{aligned}
\psi_I(x) &= A\, e^{\kappa x} && (5.52)\\
\psi_{II}(x) &= \frac{A}{k}e^{-\kappa a}[(\kappa\cos ka - k\sin ka)\sin kx \\
&\qquad\qquad + (k\cos ka + \kappa\sin ka)\cos kx] && (5.53)\\
\psi_{III}(x) &= \frac{A}{k}[2\kappa\cos ka\sin ka + k(\cos^2 ka - \sin^2 ka)] && (5.54)
\end{aligned}$$

with κ given by (5.50) or (5.51).

In writing $\psi_{III}(x)$ we used (5.45) but we could equally well have used (5.46). It does not matter.

Let us further simplify these wave functions by explicitly substituting (5.50) and (5.51). Upon substituting $\kappa = k \tan ka$ into (5.53) and (5.54) we obtain the following simplifications

$$\psi_I(x) = A\, e^{\kappa x} \tag{5.55}$$
$$\psi_{II}(x) = \frac{A}{k} e^{-\kappa a}(k \cos ka - \kappa \sin ka) \cos kx \tag{5.56}$$
$$\psi_{III}(x) = A\, e^{-\kappa x} \tag{5.57}$$

where we note that $\psi_{II}(x)$ is an *even* function. The other substitution $\kappa = -k \cot ka$ gives

$$\psi_I(x) = A\, e^{\kappa x}$$
$$\psi_{II}(x) = \frac{A}{k} e^{-\kappa a}(\kappa \cos ka - k \sin ka) \sin kx \tag{5.58}$$
$$\psi_{III}(x) = -A\, e^{-\kappa x} \tag{5.59}$$

where now $\psi_{II}(x)$ is an *odd* function. Also note that $\psi_{III}(x)$ in (5.59) is simply the *negative* of $\psi_{III}(x)$ given in (5.57).

5.2.4 Energy Levels

In the expressions for the wave function, equations (5.55)–(5.59) we have the one unknown constant A that will later be determined from normalization, just like the case of the infinite square well. (do Problems 5.1 and 5.2)

There are the two other constants κ and k. Actually only *one* of these are unknown because equations (5.17) and (5.28) imply that

$$\kappa^2 + k^2 = \frac{2mU_0}{\hbar^2} \tag{5.60}$$

Thus κ and k were related from the very beginning! There was really only *one* undetermined constant, *either* κ *or* k.

In the case of the infinite square well the value of k was determined to be $k = \frac{n\pi}{a}$ from the boundary conditions. This gave us energy quantization via $E_n = \frac{k^2\hbar^2}{2m}$.

For the finite well the boundary conditions gave us (5.50) and (5.51). Thus k (or κ) is determined! Thus the energy is already determined!

Look at it this way. Consider the even parity solution (5.50) *and* (5.60). They are two equations in two unknowns κ and k. Therefore both κ and k

are determined and consequently the energy E is calculated from (5.17) and (5.28).

The trouble is though that the two simultaneous equations (5.50) and (5.60) for κ and k cannot be solved analytically. We have to solve them numerically or graphically. This is done as follows. Equation (5.60) is the equation for a circle as shown in Fig. 5.3. The other equation (5.50) (for even parity) relating κ and k is shown in Fig. 5.4. The *solutions* of the two simultaneous equations (5.50) and (5.60) are the points where the two Figures 5.3 and 5.4 *overlap.* This is shown in Figure 5.5 where there are 4 points of intersection which therefore *corresponds to 4 quantized energy levels*, which are drawn on the potential energy diagram in Fig. 5.6. Notice that the radius of the circle in Fig. 5.3 is $\frac{\sqrt{2mU_0}}{\hbar}$. Thus the *radius depends on the strength of the potential* U_0. Looking at Fig. 5.5 then if the potential U_0 is very weak (small radius) then there might be zero bound states (zero intersections), whereas if the potential well is very *deep* (large U_0, thus large radius) then there may be *many* bound states (many points of intersection). Thus *the number of bound states depends on the depth of the potential well, or equivalently, on the strength of the potential.*

Similar considerations also hold for the odd parity solution (5.51).

5.2.5 Strong and Weak Potentials

Consider what happens if the potential is very strong, or equivalently if the well is very deep. From $k = \frac{\sqrt{2m(E+U_0)}}{\hbar}$ we will have $k \approx \frac{\sqrt{2mU_0}}{\hbar}$ so that the solution of (5.60) will be $\kappa = 0$. Then solving the even parity equations (5.50) yields

$$\tan ka = 0 \tag{5.61}$$

or

$$k = \frac{n\pi}{a} \tag{5.62}$$

Putting this back into $k = \frac{\sqrt{2m(E+U_0)}}{\hbar}$ gives

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} - U_0 \tag{5.63}$$

which is *identical* to the solution for the infinite square well. (For the infinite well we had $U = 0$ inside the well, whereas for the finite well we had $U = -U_0$ inside the well.)

Notice too that the wave functions become the same as for the infinite well.

Let us now consider the case of weak potentials or shallow wells.

Given that the number of energy levels depends on the number of intersection points, as shown in Fig. 5.5, which depends on the radius of the circle or the strength of the potential, we might expect that for a very weak potential there might be zero bound states. This is not the case however. *For a weak potential, there is always at least one bound state.* Again refer to Fig. 5.5. No matter how small the circle is, there will always be at least one intersection point or one bound state.

(do Problem 5.3)

5.3 Power Series Solution of ODEs

In the next section we consider the solution of the Schrödinger equation for the 1-dimensional harmonic oscillator potential $U = \frac{1}{2}kx^2$. Unfortunately the time-independent Schrödinger equation can no longer be solved with our standard methods. We will instead use the power series technique (Kreyszig, 1993).

In this section we shall review this technique and show how it can be used to obtain an answer that we already know, namely the solution to the infinite square well potential. The time-independent Schrödinger equation was

$$\psi'' + k^2\psi = 0 \tag{5.64}$$

and the solution was

$$\psi(x) = A\sin kx + B\cos kx \tag{5.65}$$

which is obtained *before* imposing boundary conditions and *before* specifying the coordinates of the well (which were subsequently specified as $x = 0$ and $x = a$).

Recall the Taylor series expansion [Spiegel, 1968, pg. 110] written as

$$f(x) = f(x_0) + (x - x_0)f'(x_0) + \frac{(x - x_0)^2}{2!}f''(x_0) + \frac{(x - x_0)^2}{3!}f'''(x_0) + \cdots \tag{5.66}$$

which specifies the expansion of the function $f(x)$ about the point $x = x_0$. Thus the wave function (5.65) is expanded about $x = x_0 = 0$ as

$$\psi(x) \quad = \quad A\left[kx - \frac{(kx)^2}{3!} + \frac{(kx)^5}{5!} - \frac{(kx)^7}{7!} + \cdots\right]$$

$$+B\left[1-\frac{(kx)^2}{2!}+\frac{(kx)^4}{4!}-\frac{(kx)^6}{6!}+\cdots\right] \tag{5.67}$$

which is *nothing* more than an alternative version of (5.65).

Let us now introduce the power series method of solution [Kreyszig 1993]. We expand $\psi(x)$ as a power series

$$\psi(x)=\sum_{m=0}^{\infty}a_m x^m \tag{5.68}$$

and calculate the derivatives

$$\psi'(x)=\sum_{m=1}^{\infty}m a_m x^{m-1} \tag{5.69}$$

$$\psi''(x)=\sum_{m=2}^{\infty}m(m-1)a_m x^{m-2} \tag{5.70}$$

which are substituted back into the differential equation (5.64) to give

$$\sum_{m=2}^{\infty}a_m[m(m-1)x^{m-2}+k^2x^m]+k^2(a_0+a_1x)=0 \tag{5.71}$$

We now simply write out all the terms in the sum explicitly and then equate like coefficients of x^m to 0. This yields

$$\begin{aligned}
2.1a_2 &\;+\; k^2a_0=0\\
3.2a_3 &\;+\; k^2a_1=0\\
4.3a_4 &\;+\; k^2a_2=0\\
5.4a_5 &\;+\; k^2a_3=0\\
6.5a_6 &\;+\; k^2a_4=0 \text{ etc.}
\end{aligned} \tag{5.72}$$

where $x\cdot y\equiv x\times y$. These equations can be solved in terms of only two unknown constants a_0 and a_1. Thus

$$\begin{aligned}
a_2 &= -\frac{k^2}{2.1}a_0=-\frac{k^2}{2!}a_0\\
a_3 &= -\frac{k^2}{3.2}a_1=-\frac{k^2}{3!}a_1\\
a_4 &= -\frac{k^2}{4.3}a_2=+\frac{k^4}{4!}a_0
\end{aligned}$$

$$\begin{aligned} a_5 &= -\frac{k^2}{5.4}a_3 = +\frac{k^4}{5!}a_1 \\ a_6 &= -\frac{k^2}{6.5}a_4 = -\frac{k^6}{6!}a_0 \\ a_7 &= -\frac{k^2}{7.6}a_5 = -\frac{k^6}{7!}a_1 \text{ etc.} \end{aligned} \tag{5.73}$$

These are substituted back into the solution (5.68) to yield

$$\begin{aligned} \psi(x) &= a_0 + a_1x + a_2x^2 + a_3x^3 + a_4x^4 + \cdots \\ &= a_0 + a_1x - \frac{k^2}{2!}a_0x^2 - \frac{k^2}{3!}a_1x^3 \\ &\quad + \frac{k^4}{4!}a_0x^4 + \frac{k^4}{5!}a_1x^5 + \cdots \\ &= a_0\left[1 - \frac{(kx)^2}{2!} + \frac{(kx)^4}{4!} - \frac{(kx)^4}{6!} + \cdots\right] \\ &\quad + \frac{a_1}{k}\left[kx - \frac{(kx)^3}{3!} + \frac{(kx)^5}{5!} - \frac{(kx)^7}{7!} + \cdots\right] \qquad (5.74) \\ &= a_0\cos kx + \frac{a_1}{k}\sin kx \qquad (5.75) \end{aligned}$$

which we recognize as our familiar solution (5.65) with $A \equiv \frac{a_1}{k}$ and $B \equiv a_0$!

5.3.1 Use of Recurrence Relation

The power series solution can be streamlined by using a recurrence relation, or recursion formula for the expansion coefficients.

In equation (5.70) note that m is simply a dummy variable which is summed over. Let's use a different dummy variable called $m+2$. Thus in (5.70) we make the replacement $m \to m+2$ to give

$$\begin{aligned} \psi''(x) &= \sum_{m+2=2}^{\infty}(m+2)(m+2-1)a_{m+2}x^{m+2-2} \\ &= \sum_{m=0}^{\infty}(m+2)(m+1)a_{m+2}x^m \end{aligned} \tag{5.76}$$

which is *exactly* the same as (5.70). Substituting both this and (5.68) back into the Schrödinger equation (5.64) gives

$$\sum_{m=0}^{\infty}[(m+2)(m+1)a_{m+2} + k^2a_m]x^m = 0 \tag{5.77}$$

instead of (5.71). The advantage of using the new sum in (5.76) is that it is *very straightforward* to equate like coefficients of x^m to 0 in equation (5.77). This yields

$$a_{m+2} = \frac{-k^2}{(m+2)(m+1)} a_m \tag{5.78}$$

which is called a *recurrence relation*, which is a compact formula for *each* of the expressions in equations (5.73).

5.4 Harmonic Oscillator

The harmonic oscillator potential is

$$U(x) = \frac{1}{2} m\omega^2 x^2 \tag{5.79}$$

The Schrödinger equation $\psi'' + \frac{2m}{\hbar^2}(E - U)\psi = 0$ gets quite messy with this potential so let's change variables. Define

$$y \equiv \sqrt{\frac{m\omega}{\hbar}} x \tag{5.80}$$

and

$$\epsilon \equiv \frac{2E}{\hbar\omega} \tag{5.81}$$

then the Schrödinger equation is

$$\frac{d^2\psi}{dy^2} + (\epsilon - y^2)\psi = 0 \tag{5.82}$$

We could use the power series method directly on this equation, but it will get very complicated. It's easier to write the wave function as another function multiplied by an asymptotic function.

By asymptotic we mean the region where x or y goes to infinity. For y very large the Schrödinger equation becomes

$$\frac{d^2\psi}{dy^2} - y^2\psi = 0 \tag{5.83}$$

which has the solution $\psi(y) = A\, e^{-y^2/2}$ where A is a constant. This can be checked by substitution.

Let's then write the solution to (5.82) as

$$\psi(y) \equiv h(y)e^{-y^2/2} \tag{5.84}$$

(NNN See Griffith footnote (14), pg. 38 and see Boas). Substituting this into the Schrödinger equation (5.82) we obtain a differential equation for the function $h(y)$ as

$$h'' - 2yh' + (\epsilon - 1)h = 0 \tag{5.85}$$

where $h' \equiv \frac{dh}{dy}$ and $h'' \equiv \frac{d^2h}{dy^2}$. We will solve *this* differential equation with the power series method. Writing

$$\begin{aligned} h(y) &= \sum_{m=0}^{\infty} a_m y^m && (5.86) \\ h'(y) &= = \sum_{m=1}^{\infty} m a_m y^{m-1} = \sum_{m=0}^{\infty} m a_m y^{m-1} && (5.87) \end{aligned}$$

$$\begin{aligned} h''(y) = \sum_{m=2}^{\infty} m(m-1)a_m y^{m-2} &= \sum_{m+2=2}^{\infty} (m+2)(m+2-1)a_{m+2}y^{m+2-2} \\ &= \sum_{m=0}^{\infty}(m+2)(m+1)a_{m+2}y^m \qquad (5.88) \end{aligned}$$

In (5.87) we have not made the replacement $m \to m+1$ because of the yh' term in (5.85) which will give $yh' \sim yy^{m-1} = y^m$, *without* having to make the $m \to m+1$ replacement. Substituting the above three equations into (5.85) we obtain

$$\sum_{m=0}^{\infty} [(m+2)(m+1)a_{m+2} - (2m+1-\epsilon)a_m]y^m = 0 \tag{5.89}$$

and equating like powers of y^m gives the recurrence relation

$$a_{m+2} = \frac{2m+1-\epsilon}{(m+2)(m+1)}a_m \tag{5.90}$$

Just as our power series solution for the infinite square well gave us two separate series for a_{odd} and a_{even} so too does the harmonic oscillator via (5.90). Obviously all of the a_{even} coefficients are written in terms of a_0 and the a_{odd} coefficients are written in terms of a_1.

But now we run into a problem. For very large m the recurrence relation is

$$a_{m+2} \approx \frac{2}{m} a_m \tag{5.91}$$

Thus the ratio of successive terms for the power series $h(y) = \sum_{m=0}^{\infty} a_m y^m$ for large m will be

$$\frac{a_{m+2} y^{m+2}}{a_m y^m} = \frac{(2m+1-\epsilon)}{(m+2)(m+1)} y^2 \approx \frac{2y^2}{m} \tag{5.92}$$

Now recall the series

$$e^x = \sum_{m=0}^{\infty} \frac{x^m}{m!} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \tag{5.93}$$

gives

$$\begin{aligned} e^{x^2} &= \sum_{m=0}^{\infty} \frac{x^{2m}}{m!} \\ &= 1 + x^2 + \frac{x^4}{2!} + \frac{x^6}{3!} + \frac{x^8}{4!} + \cdots \\ &= \sum_{m=0,2,4\ldots}^{\infty} \frac{x^m}{(m/2)!} \end{aligned} \tag{5.94}$$

which gives for the ratio of successive terms

$$\frac{x^{m+2}}{(m/2)x^m} = \frac{2x^2}{m} \tag{5.95}$$

the same as (5.92). *Thus* for large m we must have

$$h(y) = \sum_{m=0}^{\infty} a_m y^m \approx e^{y^2} \tag{5.96}$$

Therefore the wave function

$$\begin{aligned} \psi(y) &= h(y) e^{-y^2/2} = \left(\sum_{m=0}^{\infty} a_m y^m \right) e^{-y^2/2} \\ &\approx e^{y^2} e^{-y^2/2} = e^{y^2} \end{aligned} \tag{5.97}$$

which blows up for $y \to \infty$. That's out problem. The wave function is not normalizable.

This problem can *only* be solved if the series *terminates.* That is, at some value of m, the coefficient a_m and all the ones above it are zero. Then the series will *not* behave like e^{y^2} at large y (i.e. large x). Thus for some value $m \equiv n$, we must have

$$a_{m+2} \equiv a_{n+2} = 0 \tag{5.98}$$

If this is the case then the recurrence relation (5.90) tells us that all higher coefficients (eg. a_{n+4}, a_{n+6} etc.) will *also* be zero.

Now we have *no idea* as to the value of n. All we know is that it must be an integer like m. Our argument above will work for $n = 0$, $n = 1$, $n = 2$, $n = 3$ etc. That is, we will get finite normalizable wave functions for *any* integer value of n, and *all* of these wave functions will be *different* for each value of n because the series will terminate at different n values. (We can see quantization creeping in!)

There is another piece to this argument. We have noted that there are actually *two* independent power series for a_{even} and a_{odd}. The above argument only works for *one* of them. For example, if the even series terminates, it says *nothing* about the odd series, and vice versa. Thus if the even series terminates, then *all* of the coefficients of the odd series must be zero and vice versa. (We also expect this physically. For the infinite square well, a_{even} corresponded to $\cos kx$ and a_{odd} corresponded to $\sin kx$. See equation (5.64). We know from the properties of separable solutions that the eigenfunctions will alternate in parity. Thus it makes sense that for a particular value of n will correspond to *either* a_{even} or a_{odd} but not both.)

The requirement (5.98) together with (5.90) gives

$$2m + 1 - \epsilon \equiv 2n + 1 - \epsilon = 0 \tag{5.99}$$

yielding

$$\epsilon \equiv \frac{2E}{\hbar\omega} = 2n + 1 \tag{5.100}$$

or

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega} \quad n = 0, 1, 2, \ldots \tag{5.101}$$

which is our quantization of energy formula for the harmonic oscillator. Just as with the infinite and finite square wells, the energy quantization is a result of imposing boundary conditions. In the case of the harmonic oscillator, the boundary condition is that the wave function should be finite as $x \to \infty$.

An important feature of the harmonic oscillator energy levels is that they are *equally spaced*, as shown in Fig. 5.8. Contrast this to the infinite square well energy levels ($E_n = n^2 E_1$) in which the spacing gets bigger as n increases. See Fig. 3.2. (Note for the infinite well we had $n = 1, 2, 3, \ldots$, whereas for the harmonic oscillator we have $n = 0, 1, 2, 3 \ldots$).

Let us now turn our attention to the wave function. Recall $h(y) \equiv \sum_{m=0}^{\infty} a_m y^m$ which will be a different series for each value of n. Let us therefore distinguish each series using the notation

$$h_n(y) = \sum_{m=0}^{n} a_m y^m \tag{5.102}$$

and

$$\psi_n(y) = h_n(y) e^{-y^2/2} = \left(\sum_{m=0}^{n} a_m y^m \right) e^{-y^2/2} \tag{5.103}$$

Also the recurrence relation (5.90) now becomes

$$a_{m+2}^{(n)} = \frac{2(m-n)}{(m+2)(m+1)} a_m \tag{5.104}$$

where we have substituted (5.100) into (5.90). Thus the recurrence relation is *different* for different values of n. For $n = 0$, we have

$$h_0(y) = a_0 \tag{5.105}$$

and

$$\psi_0(y) = a_0 e^{-y^2/2}. \tag{5.106}$$

For $n = 1$ we have $a_0 = 0$ (even series is all zero) and

$$h_1(y) = a_1 y \tag{5.107}$$

and

$$\psi_1(y) = a_1 y \, e^{-y^2/2}. \tag{5.108}$$

For $n = 2$, we have all $a_{\text{odd}} = 0$ (odd series is all zero) and

$$h_2(y) = a_0 + a_2 y^2 \tag{5.109}$$

For $n = 2$ the recurrence relation (5.104) is

$$a^{(2)}_{m+2} = \frac{2(m-2)}{(m+2)(m+1)} a_m \tag{5.110}$$

giving

$$a^{(2)}_2 = -2a_0 \tag{5.111}$$

Thus

$$h_2(y) = a_0(1 - 2y^2) \tag{5.112}$$

and

$$\psi_2(y) = a_0(1 - 2y^2)e^{-y^2/2}. \tag{5.113}$$

For $n = 3$ we have $a_{\text{even}} = 0$ (even series all zero) and

$$h_3(y) = a_1 y + a_3 y^3 \tag{5.114}$$

with

$$a^{(3)}_{m+2} = \frac{2(m-3)}{(m+2)(m+1)} a_m \tag{5.115}$$

giving

$$a^{(3)}_3 = -\frac{2}{3} a_1 \tag{5.116}$$

Thus

$$h_3(y) = a_1 \left(y - \frac{2}{3} y^3 \right) \tag{5.117}$$

For $n = 4$ we have $a_{\text{odd}} = 0$ (odd series all zero) and

$$h_4(y) = a_0 + a_2 y^2 + a_4 y^4 \tag{5.118}$$

with

$$a^{(4)}_{m+2} = \frac{2(m-4)}{(m+2)(m+1)} a_m \tag{5.119}$$

giving

$$a^{(4)}_2 = -4a_0 \tag{5.120}$$

$$a^{(4)}_4 = -\frac{1}{3} a_2 = +\frac{4}{3} a_0 \tag{5.121}$$

Notice that for $n = 4$ we have $a_2 = -4a_0$, whereas for $n = 2$ we had $a_2 = -2a_0$. Thus you must be very careful to work out the recurrence relation separately for each value of n. Thus

$$h_4(y) = a_0 \left(1 - 4y^2 + \frac{4}{3} y^4 \right) \tag{5.122}$$

and

$$\psi_4(y) = a_0 \left(1 - 4y^2 + \frac{4}{3}y^4\right) e^{-y^2/2}. \tag{5.123}$$

The functions $h_n(y)$ are related to the famous Hermite polynomials $H_n(y)$, [Spiegel, 1968, pg. 151] the first few which are defined as

$$\begin{aligned}
H_0(y) &= 1 \\
H_1(y) &= 2y \\
H_2(y) &= 4y^2 - 2 \\
H_3(y) &= 8y^3 - 12y \\
H_4(y) &= 16y^4 - 48y^2 + 12
\end{aligned} \tag{5.124}$$

We can relate our $h_n(y)$ more directly to $H_n(y)$ by re-writing

$$\begin{aligned}
h_0(y) &= a_0(1) = a_0 H_0(y) \\
h_1(y) &= \frac{a_1}{2}(2y) = \frac{a_1}{2} H_1(y) \\
h_2(y) &= -\frac{a_0}{2}(4y^2 - 2) = -\frac{a_0}{2} H_2(y) \\
h_3(y) &= -\frac{a_1}{12}(8y^3 - 12y) = -\frac{a_1}{12} H_3(y) \\
h_4(y) &= \frac{a_0}{12}(16y^4 - 48y^2 + 12) = \frac{a_0}{12} H_4(y)
\end{aligned} \tag{5.125}$$

The Hermite polynomials satisfy Hermite's differential equation [Spiegel, 1968, pg. 151]

$$z'' - 2yz' + 2nz = 0 \tag{5.126}$$

where $n = 0, 1, 2 \ldots$ and $z' \equiv \frac{dz(y)}{dy}$ with solutions

$$z(y) \equiv H_n(y) \tag{5.127}$$

Recall we had $h'' - 2yh' + (\epsilon - 1)h = 0$ but with $\epsilon = 2n + 1$. Thus this becomes $h'' - 2yh' + 2nh = 0$ which is Hermite's ODE. That is the Hermite polynomials satisfy

$$H_n'' - 2yH_n' + 2nH_n = 0 \tag{5.128}$$

You can check simply by substituting each of (5.124) into (5.128). The Hermite polynomials also satisfy the following recurrence relations [Spiegel, 1968, pg. 151]

$$H_{n+1} = 2yH_n - 2nH_{n-1} \tag{5.129}$$

$$H_n' = 2nH_{n-1} \tag{5.130}$$

which again you can check by explicit substitution.

The Hermite polynomials can be obtained from *Rodrigue's formula* [Spiegel, 1968, pg. 151]

$$H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n}(e^{-y^2}) \tag{5.131}$$

$$e^{2ty-t^2} = \sum_{n=0}^{\infty} \frac{1}{n!} H_n(y) t^n \tag{5.132}$$

The function on the left is called a *generating function* of the Hermite polynomials. (This can be checked by expanding the generating function in terms of its Taylor series expansion.)

One of the most important properties of the Hermite polynomials is that they form an ON set. This is seen from the following integrals [Spiegel, 1968, pg.152]

$$\int_{-\infty}^{\infty} e^{-y^2} H_m(y) H_n(y) dy = 0 \;\text{ for } m \neq n \tag{5.133}$$

$$\int_{-\infty}^{\infty} e^{-y^2} H_n(y)^2 dy = 2^n n! \sqrt{\pi} \tag{5.134}$$

($H_n(y)$ can be Normalized simply by multiplying them by $\frac{1}{\sqrt{2^n n! \sqrt{\pi}}}$.) Again these two equations can be checked explicitly by substituting some of the $H_n(y)$ from (5.124).

Let us now return to our wave functions, which we wrote as $\psi(y) = h(y)e^{-y^2/2}$. We have found different $h(y)$ depending on n, and we should also put in a normalization factor. Thus the wave functions should be written as

$$\psi_n(y) = C_n h_n(y) e^{-y^2/2} \tag{5.135}$$

where C_n is a normalization. Using a different normalization A_n we can write ψ in terms of the Hermite polynomials

$$\psi_n(y) = A_n H_n(y) e^{-y^2/2} \tag{5.136}$$

Normalization requires

$$\begin{aligned}1 &= \int_{-\infty}^{\infty}\psi_n^*(x)\psi_n(x)dx = \sqrt{\frac{\hbar}{m\omega}}\int_{-\infty}^{\infty}\psi_n^*(y)\psi_n(y)dy \\ &= \sqrt{\frac{\hbar}{m\omega}}A_n^2\int_{-\infty}^{\infty}e^{-y^2}H_n(y)^2dy \\ &= \sqrt{\frac{\hbar}{m\omega}}A_n^2 2^n n!\sqrt{\pi} \qquad (5.137)\end{aligned}$$

where we have used $y \equiv \sqrt{\frac{m\omega}{\hbar}}x$ and $dx = \sqrt{\frac{\hbar}{m\omega}}dy$ and (5.134). This gives $A_n = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}$ so that the normalized Harmonic Oscillator wave functions are finally

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}H_n(y)e^{-y^2/2} \qquad (5.138)$$

where $y \equiv \sqrt{\frac{m\omega}{\hbar}}x$. This result together with the energy formula $E_n = (n+\frac{1}{2})\hbar\omega$ completes our solution to the 1-dimensional harmonic oscillator problem. The first few eigenfunctions and probabilities are plotted in Fig. 5.9. Note that for the odd solutions, the probability of the particle in the center of the well is zero. The particle prefers to be on either side. (See also Fig. 2.5, pg. 42 of [Griffiths, 1995].)

(do Problems 5.4–5.9)

5.5 Algebraic Solution for Harmonic Oscillator

In this section we shall solve the Schrödinger differential equation for the harmonic oscillator with an *alternative* method. This illustrates a very unique and novel approach to solving ODEs, and relies on algebra rather than calculus. The ideas presented here are used extensively in quantum field theory.

Recall the Schrödinger equation for the oscillator

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi \qquad (5.139)$$

Defining the Schrödinger equation in terms of the Hamiltonian operator

$$\hat{H}\psi = E\psi \qquad (5.140)$$

then

$$\hat{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{5.141}$$

for the harmonic oscillator Hamiltonian. (We are going to be lazy and just write p instead of $\hat{p}$ and x instead of $\hat{x}$.) Let us define two new operators

$$\hat{a} \equiv \frac{1}{\sqrt{2m\hbar\omega}}(m\omega\hat{x} + i\hat{p}) \tag{5.142}$$

and

$$\hat{a}^\dagger \equiv \frac{1}{\sqrt{2m\hbar\omega}}(m\omega\hat{x} - i\hat{p}) \tag{5.143}$$

or in our lazy rotation

$$\boxed{\left.\begin{matrix} a \\ a^\dagger \end{matrix}\right\} \equiv \frac{1}{\sqrt{2m\hbar\omega}}(m\omega x \pm ip)} \tag{5.144}$$

(Read $a^\dagger$ as "a dagger".) *Everyone* [Goswami, 19xx, pg. 143; Liboff, 1992, pg. 191; Ohanian, 1990, pg. 151; Gasiorowicz, 1996, pg 131] uses this definition *except* Griffiths [1995, pg. 33]. Also everyone uses the symbols a and $a^\dagger$, but Griffiths uses a_+ and a_-. Notice that

$$a^\dagger = a^* \tag{5.145}$$

which is called the *Hermitian conjugate* of a. In general the Hermitian conjugate of a matrix is the *complex conjugate of the transpose* matrix.

$$A^\dagger \equiv \tilde{A}^* \tag{5.146}$$

where $\tilde{A}$ is the transpose of A. Thus if $A \equiv \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}$ then $\tilde{A} = \begin{pmatrix} A_{21} & A_{22} \\ A_{11} & A_{12} \end{pmatrix}$ and $A^\dagger = \begin{pmatrix} A_{21}^* & A_{22}^* \\ A_{11}^* & A_{12}^* \end{pmatrix}$. A matrix is *Hermitian* if

$$A^\dagger = A \tag{5.147}$$

and it can be shown (see later) that Hermitian matrices have *real* eigenvalues. Our operator a is a 1-dimensional matrix so obviously we just have $a^\dagger = a^*$.

We shall pursue all of these topics in much more detail later. Let's return to our operators in (5.144).

The operators in (5.144) can be inverted to give

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger) \tag{5.148}$$

and

$$p = i\sqrt{\frac{m\hbar\omega}{2}}(a^\dagger - a) \tag{5.149}$$

(do Problem 5.10) Now the operators a and $a^\dagger$ do not commute. In fact using $[x, p] = i\hbar$, it follows that

$$[a, a^\dagger] = 1 \tag{5.150}$$

(do Problem 5.11) The Hamiltonian can now be written in three different ways as

$$\begin{aligned} H &= \frac{1}{2}(aa^\dagger + a^\dagger a)\hbar\omega \\ &= (aa^\dagger - \tfrac{1}{2})\hbar\omega \\ &= (a^\dagger a + \tfrac{1}{2})\hbar\omega \end{aligned} \tag{5.151}$$

Thus an *alternative* way to write the *Schrödinger equation* for the harmonic oscillator is

$$\boxed{(aa^\dagger - \tfrac{1}{2})\hbar\omega\psi = E\psi} \tag{5.152}$$

or

$$\boxed{(a^\dagger a + \tfrac{1}{2})\hbar\omega\psi = E\psi} \tag{5.153}$$

which are *entirely equivalent* ways of writing the Schrödinger equation compared to (5.139). A word of caution!

$$(aa^\dagger - \tfrac{1}{2})\hbar\omega a^\dagger\psi \neq Ea^\dagger\psi \tag{5.154}$$

and similarly for (5.153). The reason is because a and $a^\dagger$ do not commute. The correct statement is

$$\begin{aligned} & a^\dagger(aa^\dagger - \tfrac{1}{2})\hbar\omega\psi = Ea^\dagger\psi \\ & = (a^\dagger aa^\dagger - \tfrac{1}{2}a^\dagger)\hbar\omega\psi \\ & = (a^\dagger a - \tfrac{1}{2})\hbar\omega a^\dagger\psi \end{aligned} \tag{5.155}$$

which is quite different to (5.153). Note that (5.155) is *not* the Schrödinger equation. The Schrödinger equation is (5.152) or (5.153). To turn (5.155) into a Schrödinger equation we add $\hbar\omega a^\dagger\psi$ to give

$$(a^\dagger a - \tfrac{1}{2})\hbar\omega a^\dagger\psi + \hbar\omega a^\dagger\psi = Ea^\dagger\psi + \hbar\omega a^\dagger\psi$$

which is

$$(a^\dagger a + \tfrac{1}{2})\hbar\omega a^\dagger\psi = (E + \hbar\omega)a^\dagger\psi \tag{5.156}$$

Define $\psi' \equiv a^\dagger\psi$ and $E' \equiv E + \hbar\omega$ and we have

$$(a^\dagger a + \tfrac{1}{2})\hbar\omega\psi' = E'\psi'. \tag{5.157}$$

Thus we have the following "theorem".

Theorem 5.1 If ψ satisfies the Schrödinger equation with energy E, then $a^\dagger\psi$ and $a\psi$ satisfy the Schrödinger equation with energy $E + \hbar\omega$ and $E - \hbar\omega$ respectively.

The proof of the $a^\dagger\psi$ piece of this theorem is simply the collection of equations from (5.155) to (5.157). The $a\psi$ piece is done in the problems. (do Problem 5.13) The second Schrödinger equation corresponding to (5.156) is

$$(aa^\dagger - \tfrac{1}{2})\hbar\omega a\psi = (E - \hbar\omega)a\psi \tag{5.158}$$

Corollary If ψ satisfies the Schrödinger equation with energy E, then $a^{\dagger n}\psi$ and $a^n\psi$, where n is integer, satisfy the Schrödinger equation with energy $E + n\hbar\omega$ and $E - n\hbar\omega$ respectively.

I will leave you to prove this by induction. (do Problem 5.14) This means for example, that

$$(aa^\dagger - \tfrac{1}{2})\hbar\omega\, aaa\,\psi = (E - 3\hbar\omega)aaa\psi \tag{5.159}$$

or

$$(a^\dagger a + \tfrac{1}{2})\hbar\omega\, a^\dagger a^\dagger \psi = (E + 2\hbar\omega) a^\dagger a^\dagger \psi \tag{5.160}$$

Thus the operators $a^\dagger$ and a when applied to the wave function ψ either raise or lower the energy by an amount $\hbar\omega$. For this reason $a^\dagger$ is called the raising operator or creation operator and a is called the lowering operator or destruction operator or annihilation operator.

So by repeatedly applying the destruction operator a to ψ we keep lowering the energy. But this *cannot* go on forever! For the harmonic oscillator with the minimum of potential $U = 0$ at $x = 0$ we can never have $E < 0$. The harmonic oscillator *must* have a minimum energy E_0, with corresponding wave function ψ_0 such that

$$a\psi_0 = 0 \tag{5.161}$$

Now substitute this into the Schrödinger equation (5.153) to give

$$(a^\dagger a + \tfrac{1}{2})\hbar\omega\psi_0 = E_0\psi_0 \tag{5.162}$$

giving

$$E_0 = \tfrac{1}{2}\hbar\omega \tag{5.163}$$

because $a^\dagger a\, \hbar\omega\, \psi_0 = 0$ according to (5.161).

Corollary restated If ψ_0 satisfies the Schrödinger equation with energy $E_0 = \frac{1}{2}\hbar\omega$ (which we have just found that it *does*), then $a^{\dagger n}\psi_0$ satisfies the Schrödinger equation with energy $E_0 + n\hbar\omega = (n + \frac{1}{2})\hbar\omega$.

Thus the Schrödinger equation (5.153) can be written

$$(a^\dagger a + \tfrac{1}{2})\hbar\omega\psi_n = E_n\psi_n \tag{5.164}$$

where

$$\psi_n = \frac{A_n}{A_0} a^{\dagger n}\psi_0 \tag{5.165}$$

with A_n and A_0 being normalization constants. (We have written $\psi_n = \frac{A_n}{A_0} a^{\dagger n}\psi_0$ instead of $\psi_n = A_n a^{\dagger n}\psi_0$ because the latter expression gives $\psi_0 = A_0\psi_0$ for $n = 0$ which is no good.) Also

$$E_n = (n + \tfrac{1}{2})\hbar\omega \tag{5.166}$$

which is the same result for the energy that we obtained with the power series method.

Let's now obtain the wave functions ψ_n which can be obtained from $\psi_n = \frac{A_n}{A_0} a^{\dagger n} \psi_0$ once we know ψ_0. Using (5.161)

$$a\psi_0 = \frac{1}{\sqrt{2m\hbar\omega}}(m\omega x + ip)\psi_0 = 0 \tag{5.167}$$

we have (with $p = -i\hbar\frac{d}{dx}$)

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar} x\psi_0 \tag{5.168}$$

which is a *first* order ODE with solution

$$\begin{aligned} \psi_0 &= A_0\, e^{-\frac{m\omega}{2\hbar}x^2} \\ &= A_0\, e^{-y^2/2} = A_0 H_0(y) e^{-y^2/2} \end{aligned} \tag{5.169}$$

with $y \equiv \sqrt{\frac{m\omega}{\hbar}}x$ which is the same solution that we found for the power series method. (Recall $H_0(y) = 1$). To obtain ψ_n is now straightforward. We have

$$\psi_n = \frac{A_n}{A_0} a^{\dagger n}\psi_0 = A_n \left[\frac{1}{\sqrt{2m\hbar\omega}}\left(m\omega x - \hbar\frac{d}{dx}\right)\right]^n e^{-\frac{m\omega}{2\hbar}x^2} \tag{5.170}$$

However let's first write $a^\dagger$ a little more simply. Using $y \equiv \sqrt{\frac{m\omega}{\hbar}}x$ we have

$$\boxed{\left.\begin{matrix} a \\ a^\dagger \end{matrix}\right\} = \frac{1}{\sqrt{2}}\left(y \pm \frac{d}{dy}\right)} \tag{5.171}$$

(Exercise: Prove this.) Thus (5.170) is

$$\psi_n = \frac{A_n}{A_0} a^{\dagger n}\psi_0 = A_n \frac{1}{\sqrt{2^n}}\left(y - \frac{d}{dy}\right)^n e^{-y^2/2} \tag{5.172}$$

Example 5.5.1 Calculate ψ_1, without normalization.

Solution

$$\begin{aligned} \psi_1 = \frac{A_1}{A_0} a^\dagger \psi_0 &= A_1 \frac{1}{\sqrt{2}} \left(y - \frac{d}{dy} \right) e^{-y^2/2} \\ &= A_1 \frac{1}{\sqrt{2}} 2y e^{-y^2/2} = A_1 \frac{1}{\sqrt{2}} H_1(y) e^{-y^2/2} \end{aligned}$$

A very useful formula to use in calculating ψ_n is

$$H_{n+1} = 2yH_n - H_n' \tag{5.173}$$

obtained by combining (5.129) and (5.130).

Example 5.5.2 Calculate ψ_2, without normalization.

Solution

$$\begin{aligned} \psi_2(y) &= \frac{A_1}{A_0} a^\dagger a^\dagger \psi_0 = \frac{A_2}{A_1} a^\dagger \psi_1 \\ &= \frac{A_2}{A_1} A_1 \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} \left(y - \frac{d}{dy} \right) H_1(y) e^{-y^2/2} \\ &= A_2 \frac{1}{2} H_2(y) e^{-y^2/2} \end{aligned}$$

(do Problem 5.15)
From the above examples and from Problem 5.15 we have

$$\psi_0 = A_0 H_0(y) e^{-y^2/2} \tag{5.174}$$

$$\psi_1 = A_1 \frac{1}{\sqrt{2}} H_1(y) e^{-y^2/2} \tag{5.175}$$

$$\psi_2 = A_2 \frac{1}{2} H_2(y) e^{-y^2/2} \tag{5.176}$$

$$\psi_3 = A_3 \frac{1}{2\sqrt{2}} H_3(y) e^{-y^2/2} \tag{5.177}$$

$$\psi_4 = A_4 \frac{1}{4} H_4(y) e^{-y^2/2} \tag{5.178}$$

Obviously the generalization is

$$\psi_n = A_n \frac{1}{\sqrt{2^n}} H_n(y) e^{-y^2/2} \tag{5.179}$$

Let us now obtain the normalization constants.

Example 5.5.3 Calculate A_0.

Solution

$$\begin{aligned}
&\int_{-\infty}^{\infty} \psi_0^*(x)\psi_0(x)dx = 1 \\
&= \sqrt{\frac{\hbar}{m\omega}} \int_{-\infty}^{\infty} \psi_0^*(y)\psi_0(y)dy \\
&= \sqrt{\frac{\hbar}{m\omega}} A_0^2 \int_{-\infty}^{\infty} H_0(y)^2 e^{-y^2} dy \\
&= \sqrt{\frac{\pi\hbar}{m\omega}} A_0^2 \ \text{ using equation (5.123)}
\end{aligned}$$

Thus

$$A_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \tag{5.180}$$

Example 5.5.4 Calculate A_n for arbitrary n.

Solution

$$\begin{aligned}
&\sqrt{\frac{\hbar}{m\omega}} \int_{-\infty}^{\infty} \psi_n^*(y)\psi_n(y)dy = 1 \\
&= \sqrt{\frac{\hbar}{m\omega}} A_n^2 \frac{1}{2^n} \int_{-\infty}^{\infty} H_n(y)^2 e^{-y^2} dy \ \text{ using (5.181)} \\
&= \sqrt{\frac{\pi\hbar}{m\omega}} A_n^2 n! \ \text{ using (5.134)}
\end{aligned}$$

Thus

$$A_n = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{n!}}$$

giving

$$\frac{A_n}{A_0} = \frac{1}{\sqrt{n!}} \tag{5.181}$$

Thus we finally have from $\psi_n = \frac{A_n}{A_0} a^{\dagger n} \psi_0$,

$$\boxed{\psi_n = \frac{1}{\sqrt{n!}} a^{\dagger n} \psi_0} \tag{5.182}$$

and

$$\boxed{\psi_n = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(y) e^{-y^2/2}} \tag{5.183}$$

which is identical to the result we obtained with the power series method.

5.5.1 Further Algebraic Results for Harmonic Oscillator

We have obtained the energy and wave functions for the harmonic oscillator and thus we have completely solved the harmonic oscillator problem. In this section I just want to show you some other useful results that arise when one uses the creation and annihilation operators.

We previously found $E_n = (n + \frac{2}{2})\hbar\omega$. The Schrödinger equation is

$$H\psi_n = E_n \psi_n \tag{5.184}$$

with H given by any of the three expressions in (5.151). Choosing the third expression we have

$$(a^\dagger a + \tfrac{1}{2})\hbar\omega\psi_n = (n + \tfrac{1}{2})\hbar\omega\psi_n$$

or

$$a^\dagger a \psi_n = n\psi_n \tag{5.185}$$

Also the second expression gives $(aa^\dagger - \frac{1}{2})\hbar\omega\psi_n = (n + \frac{1}{2})\hbar\omega\psi_n$ to give

$$aa^\dagger \psi_n = (n+1)\psi_n \tag{5.186}$$

Defining the number operator

$$\hat{N} \equiv a^\dagger a \tag{5.187}$$

gives

$$\boxed{N\psi_n = n\psi_n} \tag{5.188}$$

which *is* the Schrödinger equation! Thus

$$H = (n + \tfrac{1}{2})\hbar\omega \tag{5.189}$$

Now some useful results are (do Problem 5.16 and 5.17)

$$\int_{-\infty}^{\infty} (a\psi_n)^* a\psi_n dx = \int \psi_n^* a^\dagger a\psi_n dx \tag{5.190}$$

and

$$\int (a^\dagger\psi_n)^* a^\dagger\psi_n dx = \int \psi_n^* a a^\dagger \psi_n dx \tag{5.191}$$

Before we had $\psi_n = \frac{A_n}{A_0} a^{\dagger n}\psi_0$ and we had to go to a lot of trouble to find that $\frac{A_n}{A_0} = \frac{1}{\sqrt{n!}}$. We can get this result here more quickly.

Example 5.5.5 Show that $a^\dagger\psi_n = \sqrt{n+1}\psi_{n+1}$.

Solution Writing

$$\psi_n = \frac{A_n}{A_0} a^{\dagger n}\psi_0$$

and

$$\psi_{n+1} = \frac{A_{n+1}}{A_0} a^\dagger a^{\dagger n}\psi_0 = \frac{A_{n+1}}{A_n} a^\dagger \psi_n$$

we have

$$\begin{aligned} &\int \psi_{n+1}^* \psi_{n+1} dx = 1 \\ &= \left(\frac{A_{n+1}}{A_n}\right)^2 \int (a^\dagger\psi_n)^*(a^\dagger\psi_n) dx \\ &= \left(\frac{A_{n+1}}{A_n}\right)^2 \int \psi_n^* a a^\dagger \psi_n dx \\ &= \left(\frac{A_{n+1}}{A_n}\right)^2 \int \psi_n^* (n+1) \psi_n dx \end{aligned}$$

which follows from (5.186), giving

$$\frac{A_{n+1}}{A_n} = \frac{1}{\sqrt{n+1}}$$

Thus

$$\boxed{a^\dagger \psi_n = \sqrt{n+1}\psi_{n+1}} \tag{5.192}$$

Actually instead of $\psi_{n+1} = \frac{A_{n+1}}{A_n} a^\dagger \psi_n$ we would just have written $\psi_{n+1} = C a^\dagger \psi_n$ because we know from Theorem 5.1 that this ψ_{n+1} satisfies the Schrödinger equation. As above we would then find $C = \frac{1}{\sqrt{n+1}}$.

Similarly it can be shown (do Problem 5.18) that

$$\boxed{a\psi_n = \sqrt{n}\psi_{n-1}} \tag{5.193}$$

which *is* consistent with $a\psi_0 = 0$.

Example 5.5.6 Show that $\psi_n = \frac{1}{\sqrt{n!}} a^{\dagger n} \psi_n$.

Solution We have

$$\begin{aligned}
\psi_n &= \frac{A_n}{A_0} a^{\dagger n} \psi_0 \\
&= \frac{A_n}{A_0} \left(a^\dagger\right)^{n-1} a^\dagger \psi_0 = \frac{A_n}{A_0} \left(a^\dagger\right)^{n-1} \psi_1
\end{aligned}$$

where we have used $a^\dagger \psi_0 = \sqrt{0+1}\psi_{0+1} = \psi_1$.

Continuing

$$\begin{aligned}
\psi_n &= \frac{A_n}{A_0} \left(a^\dagger\right)^{n-2} a^\dagger \psi_1 = \frac{A_n}{A_0} \left(a^\dagger\right)^{n-2} \sqrt{2}\psi_2 \\
&= \frac{A_n}{A_0} \left(a^\dagger\right)^{n-3} \sqrt{2} a^\dagger \psi_2 = \frac{A_n}{A_0} \left(a^\dagger\right)^{n-3} \sqrt{2}\sqrt{3}\psi_3 \\
&= \frac{A_n}{A_0} \left(a^\dagger\right)^{n-4} \sqrt{2}\sqrt{3} a^\dagger \psi_3 = \frac{A_n}{A_0} \left(a^\dagger\right)^{n-4} \sqrt{2}\sqrt{3}\sqrt{4}\psi_4
\end{aligned}$$

Thus we have

$$\psi_n = \frac{A_n}{A_0}\sqrt{n!}\psi_n$$

and we *must* therefore have $\frac{A_n}{A_0}\sqrt{n!} = 1$ or $\frac{A_n}{A_0} = \frac{1}{\sqrt{n!}}$ giving

$$\psi_n = \frac{1}{\sqrt{n!}} a^{\dagger n}\psi_0$$

Later we are going to introduce "Dirac notation." This involves, among other things, writing

$$\psi_n \equiv |n\rangle \tag{5.194}$$

Let us summarize our results in both notations. Thus

$$H = (N + \tfrac{1}{2})\hbar\omega \ \text{ and } \ N \equiv a^\dagger a \tag{5.195}$$

We have the Schrödinger equation

$$N\psi_n = n\psi_n \ \text{ or } \ N|n\rangle = n|n\rangle \tag{5.196}$$

and the creation and annihilation operators

$$a^\dagger\psi_n = \sqrt{n+1}\psi_{n+1} \ \text{ or } \ a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \tag{5.197}$$

$$a\psi_n = \sqrt{n}\psi_{n-1} \ \text{ or } \ a|n\rangle = \sqrt{n}|n-1\rangle \tag{5.198}$$

and

$$\psi_n = \frac{1}{\sqrt{n!}} a^{\dagger n}\psi_0 \ \text{ or } \ |n\rangle = \frac{1}{\sqrt{n!}} a^{\dagger n}|0\rangle \tag{5.199}$$

Finally, recall that $E_n = (n + \frac{1}{2})\hbar\omega$ resulted from

$$a\psi_0 \equiv 0 \quad \text{or} \quad a|0\rangle \equiv 0 \tag{5.200}$$

which is consistent with (5.198).

Chapter 6

SCATTERING STATES

In the previous chapter we studied bound state problems and in this chapter we shall study un-bound or scattering problems. For bound state problems, the most important things to know were the wave functions and discrete energy levels E_n. However for scattering problems the energy E is not discrete and can be anything. We are particularly interested in the wave functions which we shall use to determine the *transmission* and *reflection* coefficients T and R.

6.1 Free Particle

Conceptually, the simplest scattering state is the free particle where $U = 0$ everywhere. However, we will see that some care is required in specifying the wave functions.

If $U = 0$ everywhere and $E > 0$ then the solutions to the Schrödinger equation are the same as inside the infinite square well, namely

$$\begin{aligned} \psi(x) &= C\cos kx + D\sin kx \\ &= A\,e^{ikx} + B\,e^{-ikx} \end{aligned} \tag{6.1}$$

where

$$E \equiv \hbar\omega \equiv \frac{\hbar^2 k^2}{2m} \tag{6.2}$$

In the case of the infinite well we imposed boundary conditions and found that $\psi(x) = D\sin\frac{n\pi}{a}x$ and also that the energy was quantized. However for the free particle we have no such boundary conditions and thus the energy of the free particle can be anything.

Something we do need to specify for a free particle is whether it is travelling to the Left or Right. We need this because later we will consider scattering a free particle from a potential barrier and we want to know whether the *incident* particle is coming in from the Left or Right (in 1-dimension). The *outgoing* wave will typically be in both directions. Suppose the incident wave comes in from the Left. Then the *reflection* coefficient will be the Left outoing amplitude divided by the Left incoming amplitude and the *transmission* coefficient will be the Right outgoing amplitude divided by the Left incoming amplitude.

With the solution in (6.1) the notion of Left and Right is most easily expressed with the exponential solutions. Also the notion of a wave *travelling* to the Left or Right means we must bring in time dependence, thus

$$\begin{aligned} \Psi(x,t) &= \psi(x)e^{-i\omega t} \\ &= A\, e^{i(kx-\omega t)} + B\, e^{-i(kx+\omega t)} \end{aligned} \tag{6.3}$$

There are no boundary conditions and no quantization and so (6.3) is our solution. Recall the *wave equation* in 1-dimension from ordinary mechanics,

$$\frac{\partial^2 y}{\partial x^2} - \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} = 0$$

where $y = y(x,t)$ is the height of the wave at position x and time t and v is the speed of the wave [Feynman, 1964]. Solutions of the wave equation are (obviously) called *waves*. $\Psi(x,t)$ in (6.3) is a solution to the wave equation with wave speed

$$\boxed{v_p \equiv \pm\frac{\omega}{k}} = \sqrt{\frac{E}{2m}} \tag{6.4}$$

which we shall call the *phase velocity*. (This also just comes from $v = f\lambda$ with $\omega \equiv 2\pi f$ and $k \equiv \frac{2\pi}{\lambda}$ to give $v = \frac{\omega}{2\pi}\frac{2\pi}{k} = \frac{\omega}{k}$.) Exponential solutions of the type (6.3) are called *plane waves*. Another way to see where the phase velocity comes from, and how Left and Right moving waves enter the picture is to consider waves of *constant phase*. This means that

$$kx \pm \omega t = \text{constant}. \tag{6.5}$$

Thus

$$x = C \mp \frac{\omega}{k} t \tag{6.6}$$

and the wave speed

$$\frac{dx}{dt} = \mp\frac{\omega}{k} \tag{6.7}$$

in agreement with (6.4).

For $x = C - \frac{\omega}{k}t$, then as t *increases*, x decreases which is a wave travelling to the Left and $v_p \equiv \frac{dx}{dt} = -\frac{\omega}{k}$. For $x = C + \frac{\omega}{k}t$, then as t increases, x increases and the wave travels to the Right or $v_p \equiv \frac{dx}{dt} = +\frac{\omega}{k}$. Thus in (6.3)

$$\begin{array}{ll} e^{ikx} & \text{travels to Right} \\ e^{-ikx} & \text{travels to Left} \end{array}$$

We have seen that the free particle wave $A\,e^{ikx} + B\,e^{-ikx}$ travels to the Left or Right. To *specify* a wave travelling to the Left, we set $A = 0$, giving

$$\psi_L = B\,e^{-ikx} \tag{6.8}$$

and similarly for a wave travelling to the Right, $B = 0$ and

$$\psi_R = A\,e^{ikx} \tag{6.9}$$

Alternatively we can write k as negative or positive and write *only*

$$\psi = C\,e^{ikx} \tag{6.10}$$

and just identify

$$\begin{array}{ll} k > 0 & \text{wave travelling to Right} \\ k < 0 & \text{wave travelling to Left} \end{array}$$

What are we to make of our infinite square well bound state solution $\psi = D \sin k_n x$? Well write it as $\psi = D \sin k_n x = \frac{D}{2i}\left(e^{ik_n x} - e^{-ik_n x}\right)$ and we see that the *bound state solution is a superposition of Left and Right travelling waves that constructively interfere to produce a standing wave.* It's just like the way we get standing waves on a string. The travelling waves reflect from the boundaries to produce the standing wave.

Let's return to our discussion of the free particle. There are two difficulties with the above analysis. First consider a *classical* free particle where $U = 0$ so that $E = \frac{1}{2}mv^2 + 0$ giving

$$v_{\text{classical}} = \sqrt{\frac{2E}{m}} = 2v_p \tag{6.11}$$

which is *double* the quantum speed v_p! This seems very strange.

Secondly consider, for example, the Left wave.

$$\int_{-\infty}^{\infty} \psi_L^* \psi_L dx = B^2 \times \infty \tag{6.12}$$

Thus the Left and Right waves are not normalizable! But actually this is not really a problem because it's $\Psi(x,t)$ *not* $\psi(x)$ which is supposed to be normalizable.

Recall that for the bound discrete states E_n we had

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-\frac{i}{\hbar}E_n t} \tag{6.13}$$

and each $\psi_n(x)$ corresponded to a definite energy, and it turned out that each $\psi_n(x)$ *was* normalizable. $\Psi(x,t)$ does *not* contain a definite energy but a whole bunch of them. For the free particle, the fact that $\psi(x)$ is not normalizable means that "there is no such thing as a free particle with a definite energy." [Griffiths, 1995, pg. 45].

For the free particle $\psi(x)$ cannot be normalized but $\Psi(x,t)$ *can* be. Thus the normalized free particle wave function contains a whole bunch of energies, not just a single energy. Also these energies are continuous, so instead of $E = E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$ for the infinite well, let's write

$$E = E_k = \frac{\hbar^2 k^2}{2m} \tag{6.14}$$

where k now represents a *continuous* index (rather than E_n). Thus instead of (6.13) we now have

$$\begin{aligned} \Psi(x,t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\ \phi(k) \psi_k(x) e^{-\frac{i}{\hbar}E_k t} \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\ \phi(k) e^{i(kx-\omega t)} \end{aligned} \tag{6.15}$$

where $\int\limits_{-\infty}^{\infty} dk$ replaces $\sum\limits_n$ and k is allowed to be both positive and negative to include Left and Right waves. $\phi(k)$ replaces C_n. The factor $\frac{1}{\sqrt{2\pi}}$ is an arbitrary factor included for convenience. The definition (6.15) could be made without it.

$\Psi(x,t)$ in equation (6.15) is called a *wave packet* because it is a collection of waves all with different energies and speeds. Each of the separate waves travels at its own particular speed given by the *phase velocity.* A good picture of a wave packet is Figure 2.6 of Griffiths [1995, pg. 47].

Recall how we obtained the coefficients c_n in (6.13). We wrote

$$\Psi(x,0) = \sum_n c_n \psi_n(x) \tag{6.16}$$

and from the ON property of the basis set $\{\psi_n(x)\}$ we obtained

$$c_n = \langle \psi_n \mid \Psi(x,0)\rangle \equiv \int_{-\infty}^{\infty} \psi_n^*(x)\Psi(x,0)dx \tag{6.17}$$

Plancherel's theorem in *Fourier analysis* says that if

$$f(x) \equiv \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k)e^{ikx}dk \tag{6.18}$$

then

$$F(k) \equiv \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x)e^{-ikx}dk \tag{6.19}$$

$f(x)$ and $F(k)$ are called a *Fourier transform pair.* (If (6.18) did *not* have $\frac{1}{\sqrt{2\pi}}$ in front then $F(k)$ would have to have $\frac{1}{2\pi}$ in front.) Thus we can get the "expansion coefficient" $\phi(k)$. Write

$$\begin{aligned} \psi(x) \equiv \Psi(x,0) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\ \phi(k)\psi_k(x) \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\ \phi(k)e^{ikx} \end{aligned} \tag{6.20}$$

and Plancherel's theorem tells us that the "expansion coefficients" or Fourier transform is

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\Psi(x,0)e^{-ikx} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\psi(x)e^{-ikx} \tag{6.21}$$

which we could have *guessed* anyway by looking at (6.17) and identifying $\psi_k^*(x) = e^{-ikx}$.

6.1.1 Group Velocity and Phase Velocity

We have seen that the wave packet (6.15) consists of a collection of waves each with energy $E_k = \frac{\hbar^2 k^2}{2m}$ moving with phase velocity $v_p = \frac{\omega}{k}$. What then is the speed with which the whole wave packet moves? It turns out (see below) that the speed of the whole wave packet, called the *group velocity*, is given by

$$v_{\text{group}} = \frac{d\omega}{dk} \tag{6.22}$$

The *dispersion relation* is the formula that relates ω and k. From $E = \hbar\omega = \frac{\hbar^2 k^2}{2m}$, we see that the dispersion relation for the plane wave is

$$\omega(k) = \frac{\hbar k^2}{2m} \tag{6.23}$$

giving

$$\begin{aligned} v_{\text{group}} &= \frac{d\omega}{dk} = \frac{\hbar k}{m} \\ &= \frac{\hbar}{m}\frac{\sqrt{2mE}}{\hbar} = \sqrt{\frac{2E}{m}} = v_{\text{classical}} \end{aligned} \tag{6.24}$$

Evidently then it is the group velocity of the wave packet that corresponds to the classical particle velocity.

Example 6.1 Two waves differ by $d\omega$ in frequency and by dk in wave number. Superpose the waves and show that the *phase* speed is $\frac{\omega}{k}$ but the superposed wave speed (*group* speed) is $\frac{d\omega}{dk}$. (See [Beiser, 1987, pg. 96])

Solution

$$\begin{aligned} \text{Let } \psi_1 &= A\cos(\omega t - kx) \\ \text{and } \psi_2 &= A\cos[(\omega + d\omega)t - (k + dk)x] \end{aligned}$$

Using $\cos A + \cos B = 2\cos\frac{1}{2}(A+B)\cos\frac{1}{2}(A-B)$ we obtain

$$\begin{aligned} \psi &= \psi_1 + \psi_2 \\ &= 2A\cos\frac{1}{2}\left[(2\omega + d\omega)t - (2k + dk)x\right]\cos\frac{1}{2}(d\omega t - dkx) \\ &\approx 2A\cos(\omega t - kx)\cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right) \end{aligned}$$

Now $\cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right)$ has a tiny wavelength compared to $\cos(\omega t - kx)$ and thus $\cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right)$ represents a plane wave

$\cos(\omega t - kx)$ with amplitude *modulated* by the factor $\cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right)$. Thus the modulating factor is the wave packet speed given by $\frac{d\omega}{dk}$, whereas the phase speed is $\frac{\omega}{k}$. See Figure 3.4 of Beiser [1987, pg. 95].

6.2 Transmission and Reflection

We shall now consider *scattering* from some simple 1-dimensional potentials. In studying these problems *students are strongly encouraged to refer to Table 6-2 from Eisberg and Resnick [1974, pg. 243]. Students should learn this Table* because it summarizes so well many of the features of bound state and scattering problems.

In both bound and scattering problems we are interested in obtaining the wave functions. For bound states we are also interested in the discrete energy levels. For scattering we are also interested in the *transmission* and *reflection* coefficients, just as in classical electrodynamics. In fact it is *very worthwhile* at this stage to go back over the course you took in classical electrodynamics and review the discussion of transmission and reflection coefficients [Griffiths, 1989].

In quantum mechanics we define the reflection coefficient as

$$R \equiv \left|\frac{j_R}{j_i}\right| \tag{6.25}$$

where j_R is the reflected probability current density and j_i is the incident probability current density. The transmission coefficient is defined as

$$T \equiv \left|\frac{j_T}{j_i}\right| \tag{6.26}$$

where j_T is the transmitted probability current density. R and T are related always via

$$R + T = 1 \tag{6.27}$$

due to probability conservation. Recall the definition of probability current density from Chapter 1 as

$$j \equiv \frac{i\hbar}{2m}\left(\psi\frac{\partial\psi^*}{\partial x} - \psi^*\frac{\partial\psi}{\partial x}\right) \tag{6.28}$$

for 1-dimension. When actually *calculating* j it *saves time* to use the alternative expression

$$j = \frac{\hbar}{m} \text{ Im } \left(\psi^* \frac{\partial \psi}{\partial x} \right) \tag{6.29}$$

where Im stands for "Imaginary Part". For example $\text{Im}(a + ib) = b$. (do Problem 6.1)

6.2.1 Alternative Approach

There is an alternative way to calculating transmission and reflection coefficients based on *amplitude* and *speed*. Recall the local conservation of probability from Chapter 1 as

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 \tag{6.30}$$

or

$$\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0 \tag{6.31}$$

for 1-dimension, where ρ is the probability density and the probability $P = \int \rho \, dx$ for 1-dimension. Integrating (6.31) over $\int dx$ gives

$$j = -\frac{\partial P}{\partial t} \tag{6.32}$$

Now in scattering the incident, reflected and transmitted waves will *always* be of the form

$$\psi = Ae^{ikx} \tag{6.33}$$

(where k can be either negative or positive.) This is because the incident, reflected and transmitted waves will *always* be *outside* the range of the potential where $U = 0$, so that the Schrödinger equation will always be $\psi'' + k^2 \psi = 0$ with $k = \frac{\sqrt{2mE}}{\hbar}$ for incident, reflected and transmitted waves. This Schrödinger equation always has solution $Ae^{ikx} + Be^{-ikx}$. However the incident piece, the reflected piece and the transmitted piece will always either be travelling to the Left or Right and so will either be Ae^{ikx} or Be^{-ikx} but not both. This is accomplished in (6.33) by letting k be negative or positive. Using (6.33), the plane wave probability for incident, reflected and transmitted waves will be

$$P = \int \psi^* \psi dx = |A|^2 \int dx = |A|^2 x \tag{6.34}$$

Note that, unlike Chapter 1, we are *not* integrating over the whole universe and so j will not vanish. Thus from (6.32) we have

$$|j| = |A|^2 v \tag{6.35}$$

where $v = \frac{dx}{dt}$ is the speed of the wave. Thus the reflection and transmission coefficients become

$$R = \left|\frac{A_R}{A_i}\right|^2 \frac{v_R}{v_i} = \left|\frac{A_R}{A_i}\right|^2 \tag{6.36}$$

and

$$T = \left|\frac{A_T}{A_i}\right|^2 \frac{v_T}{v_i} = \left|\frac{A_T}{A_i}\right|^2 \sqrt{\frac{E_T}{E_i}} \tag{6.37}$$

using (6.11). Note that the reflected and incident wave will always be in the *same* region (or same medium) and so $v_R = v_i$ always. The above formulas are exactly analogous to those used in classical electrodynamics [Griffiths, 1989] and obviously (6.37) with the factor $\frac{v_T}{v_i}$ is just the *refractive index*. *If* the transmitted wave has the same speed as the incident wave then $T = \left|\frac{A_T}{A_i}\right|^2$.

6.3 Step Potential

The finite step potential is shown in Fig. 6.1. In region I ($x < 0$) there is no potential, $U = 0$, but in region II ($x > 0$) the potential is $U = U_0$ all the way out to infinity. ($U = U_0$ for $0 < x < \infty$).

The scattering problem we wish to consider is an incident particle coming in from the Left (*to* the Right) with energy $E < U_0$. Classically the particle would just bounce off the wall and return to $x = -\infty$. We shall see however that a quantum wave will slightly penetrate the barrier. (See Table 6-2 of Eisberg and Resnick [1974, pg. 243].)

In region I we have

$$\psi'' + k^2\psi = 0 \tag{6.38}$$

with

$$k = \frac{\sqrt{2mE}}{\hbar^2} \tag{6.39}$$

and solution

$$\begin{aligned} \psi_I(x) &= Ae^{ikx} + Be^{-ikx} \\ &\equiv \psi_i + \psi_R \end{aligned} \tag{6.40}$$

or we can write $\psi(x) = C\cos kx + D\sin kx$, however as mentioned before, the complex exponential solution enables us to specify the boundary condition (Left or Right) much more easily. The incident wave travels to the Right and the reflected wave to the Left. Thus in (6.40) we have made the identification

$$\psi_i = Ae^{ikx} \tag{6.41}$$

and

$$\psi_R = Be^{-ikx} \tag{6.42}$$

In region II we have

$$\psi'' + \frac{2m(E-U_0)}{\hbar^2}\psi = 0 \tag{6.43}$$

or

$$\psi'' - \frac{2m(U_0-E)}{\hbar^2}\psi = 0 \tag{6.44}$$

Now for our first problem we are considering $E < U_0$ and thus $2m(E-U_0)$ is negative, but $2m(U_0-E)$ is positive and thus we use the second equation (6.44) which is

$$\psi'' - \kappa^2\psi = 0 \tag{6.45}$$

with

$$\kappa \equiv \frac{\sqrt{2m(U_0-E)}}{\hbar} \tag{6.46}$$

which is *real* because $E < U_0$. The solution is

$$\psi(x) = Ce^{\kappa x} + De^{-\kappa x} \tag{6.47}$$

but for $x \to +\infty$ then $Ce^{\kappa x}$ blows up, so we must have $C = 0$. Thus

$$\psi_{II}(x) = De^{-\kappa x} \equiv \psi_T \tag{6.48}$$

which is the *transmitted* wave ψ_T. Let us now impose boundary conditions.

$$\psi_I(x=0) = \psi_{II}(x=0)$$

gives

$$A + B = D$$

and

$$\psi_I'(x=0) = \psi_{II}'(x=0)$$

gives

$$Aik - Bik = -\kappa D$$

Thus the wave functions become

$$\begin{aligned} \psi_I(x) &= \frac{D}{2}\left(1 + i\frac{\kappa}{k}\right) e^{ikx} + \frac{D}{2}\left(1 - i\frac{\kappa}{k}\right) e^{-ikx} \\ &\equiv \psi_i + \psi_R \end{aligned} \tag{6.49}$$

and $\psi_{II}(x)$ remains as given in (6.48).

Let us now calculate the reflection coefficient from (6.25) and (6.29). We have

$$\begin{aligned} j_R &= \frac{\hbar}{m} \text{ Im } \left(\psi_R^* \frac{\partial \psi_R}{\partial x}\right) \\ &= \frac{\hbar}{m}\frac{D^2}{4} \text{ Im } \left[\left(1 + i\frac{\kappa}{k}\right) e^{ikx}(-ik)\left(1 - i\frac{\kappa}{k}\right) e^{-ikx}\right] \\ &= -\frac{\hbar}{m}\frac{D}{2}k\left(1 + \frac{\kappa^2}{k^2}\right) \end{aligned}$$

and

$$j_i = \frac{\hbar}{m} \text{ Im } \left(\psi_i^* \frac{\partial \psi_i}{\partial x}\right) = \frac{\hbar}{m}\frac{D}{2}k\left(1 + \frac{\kappa^2}{k^2}\right)$$

giving

$$R = \left|\frac{j_R}{j_i}\right| = 1$$

which tells us that the wave is *totally reflected*. From equation (6.27) we expect $T = 0$, that is no transmitted wave. (Exercise: Show that you get the same result by evaluating $\left|\frac{B}{A}\right|^2$ directly.)

Example 6.2 Prove that $T = 0$ using (6.25).

Solution

$$\begin{aligned} j_T &= \frac{\hbar}{m} \text{ Im } \left(\psi_T^* \frac{\partial \psi_T}{\partial x}\right) \\ &= \frac{\hbar}{m} D^2 \text{ Im } [e^{-\kappa x}(-\kappa)e^{-\kappa x}] \\ &= 0 \end{aligned}$$

because ψ_T is purely real and has no imaginary part. Thus

$$T = \left|\frac{j_T}{j_i}\right| = 0$$

as expected.

Example 6.3 Prove $T = 0$ using (6.37).

Solution

$$\frac{E_T}{E_i} = \frac{E - U_0}{E}$$

but $E < U_0$ thus $\sqrt{\frac{E_T}{E_0}}$ is complex, which would give complex T which can't happen.

Thus $T = 0$ (see Griffith's Problem 2.33)

Even though the transmission coefficient is zero, the wave function still penetrates into the barrier a short distance. This is seen by plotting the wave function. (See Table 6-2 of Eisberg and Resnick [1976, pg. 243].)

(do Problem 6.2)

6.4 Finite Potential Barrier

The finite potential barrier is shown in Fig. 6.2. We shall analyze the problem for an incident particle with energy $E < U_0$.

In regions I and III, we have $U = 0$ and $E > 0$ so that the Schrödinger equation is

$$\psi'' + \frac{2mE}{\hbar^2}\psi = 0. \tag{6.50}$$

The solution is

$$\psi = Ae^{ikx} + Be^{-ikx} \tag{6.51}$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar^2} \tag{6.52}$$

We assume that the incident particle comes in from the Left. Thus in region III the wave will only be travelling to the right. Thus

$$\begin{aligned}\psi_I(x) &= Ae^{ikx} + Be^{-ikx} \\ &\equiv \psi_i + \psi_R \end{aligned} \tag{6.53}$$

and

$$\psi_{III}(x) = Ce^{ikx} \tag{6.54}$$

In region III we can write

$$\psi'' + \frac{2m(E-U_0)}{\hbar^2}\psi = 0 \tag{6.55}$$

or

$$\psi'' - \frac{2m(U_0-E)}{\hbar^2}\psi = 0 \tag{6.56}$$

but we will use the second equation because $U_0 > E$. Thus

$$\psi'' - \kappa^2\psi = 0 \tag{6.57}$$

with

$$\kappa \equiv \frac{\sqrt{2m(U_0-E)}}{\hbar} \tag{6.58}$$

which is real. Thus

$$\psi_{II}(x) = De^{\kappa x} + Ee^{-\kappa x} \tag{6.59}$$

The boundary conditions are

$$\psi_I(-a) = \psi_{II}(-a) \tag{6.60}$$

giving

$$Ae^{-ika} + Be^{ika} = De^{-\kappa a} + Ee^{\kappa a} \tag{6.61}$$

and

$$\psi'_I(-a) = \psi'_{II}(-a) \tag{6.62}$$

giving

$$ikAe^{-ika} - ikBe^{ika} = \kappa De^{-\kappa a} - \kappa Ee^{\kappa a} \tag{6.63}$$

and

$$\psi_{II}(a) = \psi_{III}(a) \tag{6.64}$$

giving

$$De^{\kappa a} + Ee^{-\kappa a} = Ce^{ika} \tag{6.65}$$

and

$$\psi'_{II}(a) = \psi'_{III}(a) \tag{6.66}$$

giving

$$\kappa D e^{\kappa a} - \kappa E e^{-\kappa a} = ikCe^{ika} \tag{6.67}$$

Equations (6.61), (6.63), (6.65) and (6.67) are the coupled equations we need to solve for the constants A, B, C, D, E. Let's plan a little strategy before jumping in. We want to calculate the *transmission* coefficient, which is

$$T = \left|\frac{C}{A}\right|^2 \tag{6.68}$$

Thus we only need C in terms of A (or vice versa) and hopefully the other constant will cancel. After all this algebra is done we get

$$T^{-1} = 1 + \frac{U_0^2}{4E(U_0 - E)} \sinh^2\left[\frac{2a}{\hbar}\sqrt{2m(U_0 - E)}\right] \tag{6.69}$$

(do Problem 6.3). The important point here is that *even with* $E < U_0$ *we have* $T \neq 0$. Classically the particle would bounce off the barrier and never undergo transmission. Yet quantum mechanically transmission occurs! This phenomenon is called *tunnelling*. It is again instructive to plot the wave functions from equations (6.53) and (6.54). This is done in Table 6-2 of Eisberg and Resnick [1974, pg. 243]. We can see that the wave function penetrates all the way through the barrier.

6.5 Quantum Description of a Colliding Particle

The Schrödinger equation does *not automatically* give us the concept of a particle. We saw that the Schrödinger equation gave us non-normalizable plane waves e^{ikx} as separable solutions with the complete solution being given in (6.20) as a wave packet. But we don't know the "expansion coefficients" $\phi(k)$ and so we don't know $\psi(x) \equiv \Psi(x,0)$. Actually *any* $\phi(k)$ will do and $\Psi(x,0)$ will be a solution to the Schrödinger equation. If we *knew* $\phi(k)$ we would have $\Psi(x,0)$ and vice versa, if we knew $\Psi(x,0)$ we could deduce $\phi(k)$ from (6.21). Both $\Psi(x,0)$ and $\phi(k)$ are *not* specified by the Schrödinger equation. We have to make them up.

We want to describe a localized particle and that's pretty hard to do when all you have are wave solutions. But wait! Think about classical solitons. Suppose somehow we had a wave packet as shown in Fig. 6.3. If such a localized wave packet moved to the left or right, it would be a pretty good *wave packet description of the concept of a classical particle.* Such a wave packet is represented by

$$\begin{aligned} \psi(x) \equiv \Psi(x,0) &= Ae^{-a(x-x_0)^2} \\ &\equiv \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \phi(k)\psi_k(x) \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \phi(k)e^{ikx} \end{aligned} \tag{6.70}$$

and is called a *Gaussian* wave packet. Such a Gaussian wave packet is widely used in quantum mechanics as a way to think about localized particles. You can think of (6.70) as specifying some sort of *initial conditions.* Since $\Psi(x,0)$ and $\phi(k)$ are arbitrary we are free to choose them to correspond to a particular physical system that we want to study. That's what we are doing with our Gaussian wave packet. We are choosing to study a localized wave. After all, there aren't any *other* boundary conditions we can use on the free particle solutions to the Schrödinger equation.

By the wave, in (6.70), the height of the wave packet is specified by A and the width of the packet is proportional to $1/a$. (Exercise: check this by plotting various Gaussian wave packets with different A and a.)

Now previously we found that the plane wave solutions $\psi_k(x) = e^{ikx}$ are not normalizable, but we claimed this didn't matter as long as $\Psi(x,t)$ is normalizable. Let's check this for our Gaussian wave packet. To do this you can use the famous Gaussian integral

$$\boxed{\int_{-\infty}^{\infty} dx\, e^{-ax^2+bx} = \sqrt{\frac{\pi}{a}} e^{b^2/4a}} \tag{6.71}$$

Of course we don't need the whole quadratic ax^2+bx+c because it's obvious, from (6.71), that

$$\int_{-\infty}^{\infty} dx\, e^{-ax^2+bx+c} = \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{4a}+c}$$

Example 6.4 Normalize the Gaussian wave packet.

Solution

$$\psi(x) \equiv \Psi(x,0) = A\, e^{-(x-x_0)^2}$$

$$\begin{aligned}
1 &= \int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx \\
&= A^2 \int_{-\infty}^{\infty} e^{-2a(x-x_0)^2} dx \\
&= A^2 e^{-2ax_0^2} \int_{-\infty}^{\infty} e^{-2ax^2+4ax_0x} dx \\
&= A^2 e^{-2ax_0^2} \sqrt{\frac{\pi}{2a}} e^{\frac{16a^2x_0}{8a}} \\
&= A^2 \sqrt{\frac{\pi}{2a}}
\end{aligned}$$

Thus

$$A = \left(\frac{2a}{\pi}\right)^{1/4}$$

and

$$\psi(x) \equiv \Psi(x,0) = \left(\frac{2a}{\pi}\right)^{1/4} e^{-a(x-x_0)^2} \qquad (6.72)$$

is the normalized Gaussian wave packet centered at $x = x_0$.

This example shows that even though plane waves are not normalizable, the superposed wave packet *is* normalizable.

6.5.1 Expansion Coefficients

The expansion coefficients $\phi(k)$ tell us the relative weightings of the *sines* and *cosines*, or plane waves e^{ikx}, that are added up to make the Gaussian wave packet. We get them using (6.21).

Example 6.5 Find $\phi(k)$ for the Gaussian wave packet.

Solution From (6.21) and (6.72) we have the Fourier transform

$$\begin{aligned}
\phi(k) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, \psi(x) e^{-ikx} \\
&= \frac{1}{\sqrt{2\pi}} \left(\frac{2a}{\pi}\right)^{1/4} \int_{-\infty}^{\infty} dx\, e^{-a(x-x_0)^2} e^{-ikx} \\
&= \frac{1}{\sqrt{2\pi}} \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax_0^2} \int_{-\infty}^{\infty} dx\, e^{-ax^2+(2ax_0-ik)x} \\
&= \frac{1}{\sqrt{2\pi}} \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax_0^2} \sqrt{\frac{\pi}{a}} e^{(2ax_0-ik)^2/4a}
\end{aligned}$$

Thus

$$\phi(k) = \frac{1}{(2\pi a)^{1/4}} e^{-\frac{k^2}{4a}-ikx_0} \tag{6.73}$$

Thus our Gaussian wave packet is

$$\begin{aligned}
\psi(x) \equiv \Psi(x,0) &= \left(\frac{2a}{\pi}\right)^{1/4} e^{-a(x-x_0)^2} \\
&= \left(\frac{a}{2\pi^3}\right)^{1/4} \int_{-\infty}^{\infty} dk\, e^{-\frac{k^2}{4a}} e^{ik(x-x_0)}
\end{aligned} \tag{6.74}$$

Note that (6.73) is also a Gaussian (ignore x_0 or set it to zero). Thus the Fourier transform of a Gaussian is a Gaussian.

6.5.2 Time Dependence

Our time dependent wave function is

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \phi(k) e^{i(kx-\omega t)} \tag{6.75}$$

with $E_k \equiv \hbar\omega = \frac{\hbar^2 k^2}{2m}$. This *should* tell us how our Gaussian wave packet behaves in time.

Example 6.6 Calculate $\Psi(x,t)$ and $|\Psi(x,t)|^2$ for the Gaussian wave packet.

Solution Using (6.75) and (6.73) we have

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\frac{1}{(2\pi a)^{1/4}}\int_{-\infty}^{\infty} dk\, \exp\,(-\frac{k^2}{4a} - ikx_0)\exp\,[i(kx - \frac{\hbar k^2}{2m}t)]$$

where we had to substitute the dispersion relation $\omega(k) = \frac{\hbar k^2}{2m}$ because we are doing an integral $\int dk$. Thus

$$\begin{aligned}\Psi(x,t) &= \frac{1}{\sqrt{2\pi}}\frac{1}{(2\pi a)^{1/4}}\int dk\, \exp\,[-\left(\frac{1}{4a} + i\frac{\hbar}{2m}t\right)k^2 + (ix - ix_0)k] \\ &= \frac{1}{\sqrt{2\pi}}\frac{1}{(2\pi a)^{1/4}}\sqrt{\frac{\pi}{\frac{1}{4a} + i\frac{\hbar}{2m}t}}\exp\,[(ix - ix_0)^2/4(\frac{1}{4a} + i\frac{\hbar}{2m}t)]\end{aligned}$$

finally giving

$$\Psi(x,t) = \left(\frac{2a}{\pi}\right)^{1/4}\sqrt{\frac{m}{m + i2a\hbar t}}\exp\,[\frac{-ma(x-x_0)^2}{m + i2a\hbar t}] \tag{6.76}$$

This yields

$$|\Psi(x,t)|^2 = \sqrt{\frac{2}{\pi}}\sqrt{\frac{m^2 a}{m^2 + 4a^2\hbar^2 t^2}}\exp\,[-2\frac{m^2 a}{m^2 + 4a^2\hbar^2 t^2}(x-x_0)^2] \tag{6.77}$$

for the probability density.

These are wonderful results! They tell us how the Gaussian wave packet changes with time. We can now *really* see the utility of calculating $\phi(k)$, plugging it into (6.75), doing the $\int dk$ integral and finally getting out some real answers!

The probability density (6.77) is very interesting. As time increases, the amplitude decreases and the width of the wave packet increases. The Gaussian wave packet "spreads out" over time. This is illustrated in Fig. 6.4. The wave packet *dissipates*. Initially the packet is well localized, and we "know" where the particle is, but after a long time the packet is so spread out that we don't know where the particle is anymore.

6.5.3 Moving Particle

The wave packet $\Psi(x,0) = Ae^{-a(x-x_0)^2}$ in (6.70) describes a wave *stationary* at $x = x_0$. However we want a *moving* particle, say a wave packet initially propagating to the Right. We might have hoped that tacking on the time dependence $e^{-i\omega t}$ in (6.75) would have given us a *moving* particle, but no luck! What the time dependence did tell us was that the wave packet dissipates, but our solutions (6.76) and (6.77) still won't budge. They are still clamped down at $x = x_0$.

We are back to our original problem discussed at the beginning of Section 6.5. The Schrödinger equation does *not* give us a particle and it also does not give us a *moving* particle. We have to put both things in by hand, or "specify initial conditions."

Actually this is easy to do. The particle is fixed at $x = x_0$, so let's just make x_0 move! A good way to do this is with

$$x_0 = \frac{p_0}{m}t \tag{6.78}$$

Thus our *moving* Gaussian wave is

$$e^{-a(x-\frac{p_0}{m}t)^2}$$

and now we have a *moving* wave. Just make the substitution (6.78) in all of the above formulas.

6.5.4 Wave Packet Uncertainty

(do Problems 6.4 and 6.5)

In Problem 6.4, the uncertainty in position and momentum for the Gaussian wave packet is calculated. The results are

$$\sigma_x = \sqrt{\frac{m^2 + 4a^2\hbar^2t^2}{4am^2}}$$

and

$$\sigma_p = \hbar\sqrt{a}$$

For $t = 0$ we see that

$$\sigma_x(t = 0) = \frac{1}{2\sqrt{a}}$$

but σ_x *gets larger as* t *increases*. This corresponds to the spreading of the wave packet as time increases and we are more and more uncertain of the position of the wave packet as time goes by (even thogh $\langle x\rangle = x_0$).

For $t = 0$ the product is

$$\sigma_x \sigma_p(t = 0) = \frac{\hbar}{2} \tag{6.79}$$

but for $t \neq 0$ we have

$$\sigma_x \sigma_p(t \neq 0) = \frac{\hbar}{2}\sqrt{1 + 4a^2\hbar^2 t^2/m^2} \tag{6.80}$$

which indicates that

$$\sigma_x \sigma_p(t \neq 0) > \frac{\hbar}{2} \tag{6.81}$$

We can combine the above results into

$$\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2}}$$

which is the famous Uncertainty Principle. Here we have shown how it comes about for the Gaussian wave packet. Later we shall prove it is general.

Chapter 7

FEW-BODY BOUND STATE PROBLEM

In previous chapters we have only considered the 1-body problem represented by a particle of mass m. However most problems in nature involve few or many bodies.

In this chapter we shall see that the two body problem can be *solved* for any potential $U(x)$. The few-body problem (i.e. more than 2 bodies) *cannot* be solved in general, but we shall see how the few-body problem *can* be solved for the harmonic oscillator potential. As we shall see, all of these statements apply to *both* classical mechanics *and* quantum mechanics.

It is very interesting to note that the 2-body problem cannot be solved in relativistic quantum mechanics. While the 2-body scattering problem can be solved with perturbative techniques (Feynman diagrams) if the interaction potential is weak, the strong interaction scattering problem and the bound state problems are described by the *Bethe-Salpeter* equation which cannot be solved in general.

[General Relativity]

7.1 2-Body Problem

One of the most important classical 2-body bound state problems is the Earth-Sun system. One of the important quantum 2-body bound states is the Hydrogen atom.

Before proceeding, we shall define some 2-body coordinates to be used below. Let x_1 be the coordinate of the first body and x_2 the coordinate of the second body. Define the *relative* coordinate

$$x \equiv x_1 - x_2 \tag{7.1}$$

and the *Center of Mass* (CM) coordinate

$$X \equiv \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \tag{7.2}$$

These of course can be inverted to give

$$x_1 = X + \frac{m_2}{M} x \tag{7.3}$$

and

$$x_2 = X - \frac{m_1}{M} x \tag{7.4}$$

where we have defined the *total mass*

$$M \equiv m_1 + m_2 \tag{7.5}$$

Also in what follows we *assume* that particles 1 and 2 interact via a potential U of the form

$$U = U(x_1 - x_2) = U(x) \tag{7.6}$$

This is a *crucial* assumption and it is the reason as to why we will be able to solve the 2-body problem for *any* potential of the form $U(x)$. Notice only the coordinate x enters the potential. That is the force *only* depends on the relative distance $x = x_1 - x_2$ between the particles. If U also depended on X then we would not be able to solve the 2-body problem.

7.1.1 Classical 2-Body Problem

Newton's Laws

Newton's second law of motion for bodies labelled 1 and 2 is

$$\Sigma F_1 = m_1 \ddot{x}_1 \tag{7.7}$$

and

$$\Sigma F_2 = m_2 \ddot{x}_2 \tag{7.8}$$

Assuming that the particles interact through the potential U then these equations become

$$-\frac{\partial U}{\partial x_1} = m_1\ddot{x}_1 \tag{7.9}$$

and

$$-\frac{\partial U}{\partial x_2} = m_2\ddot{x}_2 \tag{7.10}$$

Now with $U \equiv U(x_1 - x_2) = U(x)$ we have

$$\frac{\partial U}{\partial x_1} = \frac{\partial U}{\partial x}\frac{\partial x}{\partial x_1} = \frac{\partial U}{\partial x} \tag{7.11}$$

and

$$\frac{\partial U}{\partial x_2} = \frac{\partial U}{\partial x}\frac{\partial x}{\partial x_2} = -\frac{\partial U}{\partial x} \tag{7.12}$$

giving

$$-\frac{dU}{dx} = m_1\ddot{x}_1 \tag{7.13}$$

and

$$+\frac{dU}{dx} = m_2\ddot{x}_2 \tag{7.14}$$

Equations (7.9) and (7.10) or (7.13) and (7.14) are a set of *coupled* equations. They must be solved simultaneously to obtain a solution. But notice the following. With our new coordinates X and x we get

$$\ddot{X} = \frac{1}{M}(m_1\ddot{x}_1 + m_2\ddot{x}_2) = \frac{1}{M}\left(-\frac{dU}{dx} + \frac{dU}{dx}\right) = 0 \tag{7.15}$$

giving

$$\boxed{M\ddot{X} = 0} \tag{7.16}$$

and

$$\begin{aligned}\ddot{x} = \ddot{x}_1 - \ddot{x}_2 &= -\frac{1}{m_1}\frac{dU}{dx} - \frac{1}{m_2}\frac{dU}{dx} \\ &= -\frac{m_1 + m_2}{m_1 m_2}\frac{dU}{dx}\end{aligned} \tag{7.17}$$

Defining the *reduced mass*

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \tag{7.18}$$

we get

$$\boxed{-\frac{dU}{dx} = \mu\ddot{x}} \tag{7.19}$$

Thus equations (7.16) and (7.19) are *uncoupled* equations which we can solve *separately*. Thus we say that we have *solved the 2-body problem*! Notice also that these equations are *equivalent 1-body equations* for a "particle" of mass M and acceleration $\ddot{X}$ and another *separate* "particle" of mass μ and acceleration $\ddot{x}$ moving in the potential $U(x)$. We have also shown that the "particle" of mass M is the *center of mass "particle"* and it moves with *zero acceleration*.

Lagrangian Method

For a Lagrangian $L(q_i, \dot{q}_i)$ where q_i are the generalized coordinates, the equations of motion are

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0 \tag{7.20}$$

for *each* coordinate q_i. For our 2-body problem in 1-dimension we identify $q_1 \equiv x_1$ and $q_2 \equiv x_2$. The 2-body Lagrangian is

$$L(x_1, x_2, \dot{x}_1, \dot{x}_2) = \frac{1}{2}m_1\dot{x}_1{}^2 + \frac{1}{2}m_2\dot{x}_2{}^2 - U(x_1 - x_2) \tag{7.21}$$

Lagrange's equations are

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}_1}\right) - \frac{\partial L}{\partial x_1} = 0 \tag{7.22}$$

and

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}_2}\right) - \frac{\partial L}{\partial x_2} = 0 \tag{7.23}$$

which yield the coupled equations (7.9) and (7.10). (Exercise: Prove this.)

The trick with Lagrange's equations is to pick *different* generalized coordinates. Instead of choosing $q_1 = x_1$ and $q_2 = x_2$ we instead make the choice $q_1 \equiv X$ and $q_2 \equiv x$. Using equations (7.1) and (7.2) in (7.21) we obtain

$$L(x, X, \dot{x}, \dot{X}) = \frac{1}{2}M\dot{X}^2 + \frac{1}{2}\mu\dot{x}^2 - U(x) \tag{7.24}$$

(Exercise: Show this.) Lagrange's equations are

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{X}}\right) - \frac{\partial L}{\partial X} = 0$$

and

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) - \frac{\partial L}{\partial x} = 0$$

which yield (7.16) and (7.19) directly. (Exercise: Show this.)

To summarize, the trick with the Lagrangian method is to choose X and x as the generalized coordinates instead of x_1 and x_2.

7.1.2 Quantum 2-Body Problem

The time-independent Schrödinger equation is

$$H\psi = E\psi \tag{7.25}$$

and the 1-body Hamiltonian is

$$H = \frac{p_1^2}{2m_1} + U(x_1) \tag{7.26}$$

Making the replacement $p_1 \to -i\hbar\frac{d}{dx_1}$ gives

$$\left[-\frac{\hbar^2}{2m_1}\frac{d^2}{dx_1^2} + U(x_1)\right]\psi(x_1) = E\psi(x_1) \tag{7.27}$$

which is an *ordinary* differential equation that we have already studied extensively.

The 2-body Hamiltonian is

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + U(x_1 - x_2) \tag{7.28}$$

Obviously E is the total energy of the system $E = E_1 + E_2$. Thus we have

$$\left[-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} + U(x_1 - x_2)\right]\psi(x_1, x_2) = E\psi(x_1, x_2) \tag{7.29}$$

which is our 2-body Schrödinger equation. The *problem* now is not that we have 2 coupled equations, as in the classical case, but rather instead of the *ordinary* differential equation (for the variable x_1) that we had for the 1-body Schrödinger equation (7.27), we are now stuck with a *partial* differential equation (7.29) for the variables x_1 and x_2.

Fortunately it's easy to take care of. Consider an arbitrary function $f(x_1, x_2)$. Thus for example

$$\frac{\partial f}{\partial x_2} = \frac{\partial f}{\partial x}\frac{\partial x}{\partial x_2} + \frac{\partial f}{\partial X}\frac{\partial X}{\partial x_2} \tag{7.30}$$

giving

$$\frac{\partial}{\partial x_2} = \frac{\partial x}{\partial x_2}\frac{\partial}{\partial x} + \frac{\partial X}{\partial x_2}\frac{\partial}{\partial X} = -\frac{\partial}{\partial x} + \frac{m_2}{M}\frac{\partial}{\partial X} \tag{7.31}$$

Similarly

$$\frac{\partial}{\partial x_1} = +\frac{\partial}{\partial x} + \frac{m_1}{M}\frac{\partial}{\partial X} \tag{7.32}$$

Thus we obtain

$$\frac{\partial^2}{\partial x_2^2} = \frac{\partial^2}{\partial x^2} - 2\frac{m_2}{M}\frac{\partial^2}{\partial x \partial X} + \left(\frac{m_2}{M}\right)^2 \frac{\partial^2}{\partial X^2} \tag{7.33}$$

and

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial^2}{\partial x^2} + 2\frac{m_1}{M}\frac{\partial^2}{\partial x \partial X} + \left(\frac{m_1}{M}\right)^2 \frac{\partial^2}{\partial X^2} \tag{7.34}$$

Finally we have, upon substitution of (7.33) and (7.34),

$$\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2}{\partial x_2^2} = \frac{1}{\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{M}\frac{\partial^2}{\partial X^2} \tag{7.35}$$

where the "cross terms" $\frac{\partial^2}{\partial x \partial X}$ have cancelled out. Thus the Schrödinger equation (7.29) becomes

$$\left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + U(x)\right]\psi(X, x) = E\psi(X, x) \tag{7.36}$$

which is *still* a partial differential equation but now U depends on only one variable and we are now able to successfully apply the technique of separation of variables. Thus we define

$$\psi(X, x) \equiv W(X)w(x) \tag{7.37}$$

and

$$E = E_1 + E_2 \equiv E_X + E_x \tag{7.38}$$

which is a sum of center-of-mass and relative energy. Upon substitution of (7.37) and (7.38) into (7.36) we obtain

$$\boxed{-\frac{\hbar^2}{2M}\frac{d^2W(X)}{dX^2} = E_X W(X)} \tag{7.39}$$

and

$$\boxed{-\frac{\hbar^2}{2\mu}\frac{d^2w(x)}{dx^2} + U(x)w(x) = E_x w(x)} \tag{7.40}$$

which are now two uncoupled *ordinary* differential equations.

Just as in the classical case, where we found two equivalent 1-body equations (7.16) and (7.19), so too have we found in quantum mechanics two equivalent 1-body Schrödinger equations.

One is for the center of mass "particle" of mass M and one is for the reduced mass "particle" of mass μ. In the classical case, the center of mass equation was identical to a *free* particle equation (7.16) for mass M, so too in the quantum case we have found the center of mass Schrödinger equation is for a free particle of mass M. In the classical case the solution to (7.16) was

$$\ddot{X} = 0 \tag{7.41}$$

and in the quantum case the solution to (7.39) is

$$W(X) = Ae^{ikx} + Be^{-ikx} \tag{7.42}$$

which is the free particle plane wave solution where

$$K \equiv \frac{\sqrt{2ME_x}}{\hbar} \tag{7.43}$$

In the classical case, to get the relative acceleration equation we just make the replacement $x_1 \to x$ and $m_1 \to \mu$ to get the 2-body relative equation (7.19). We see that this identical replacement is *also* made for the quantum equation (7.40).

We can now go ahead and solve the 2-body quantum equation (7.40) using *exactly* the same techniques that we have used previously. In fact we just *copy* all our previous answers but making the replacement $m \to \mu$ and treating the variable x as $x \equiv x_1 - x_2$.

7.2 3-Body Problem

Part II

3-DIMENSIONAL PROBLEMS

Chapter 8

3-DIMENSIONAL SCHRÖDINGER EQUATION

The 2-body, 3-dimensional Schrödinger equation is

$$-\frac{\hbar^2}{2\mu}\nabla^2\Psi + U\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{8.1}$$

with $\Psi \equiv \Psi(\mathbf{r}, t)$ where $\mathbf{r}$ is a 3-dimensional relative position vector and the Laplacian operator in Cartesian coordinates is

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{8.2}$$

or in Spherical polar coordinates

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{8.3}$$

Using separation of variables $\Psi(\mathbf{r}, t) \equiv \psi(\mathbf{r})\chi(t)$ we obtain the 2-body, 3-dimensional time-independent Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + U\psi = E\psi \tag{8.4}$$

and with $\chi(t) = e^{-i/\hbar Et}$. The general solution is

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\chi(t) = \sum_n c_n\psi_n(\mathbf{r})e^{-i/\hbar E_n t} \tag{8.5}$$

In general the 2-body potential will be a function $U = U(r)$ and therefore it is preferable to use ∇^2 in spherical polar coordinates rather than Cartesian coordinates. Also $U = U(r)$ hints that we solve (8.4) using separation of variables according to

$$\psi(\mathbf{r}) \equiv \psi(r, \theta, \phi) \equiv R(r)Y(\theta, \phi)) \tag{8.6}$$

where we have separated out the radial and angular pieces. Substituting into (8.4) and dividing by RY gives

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}(E - U) = \frac{1}{Y}\frac{L^2 Y}{\hbar^2} \tag{8.7}$$

where the *angular momentum operator* is defined as

$$\hat{L}^2 \equiv -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{8.8}$$

In equation (8.7) the left hand side is a function of r only and the right hand side is a function of θ, ϕ only. Thus both sides must equal a constant defined as $l(l+1)$, giving

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}(E - U) = \frac{1}{Y}\frac{L^2 Y}{\hbar^2} \equiv l(l+1) \tag{8.9}$$

8.1 Angular Equations

Equation (8.9) gives the angular equation

$$L^2 Y = l(l+1)\hbar^2 Y \tag{8.10}$$

which is an eigenvalue equation. We separate variables again with

$$Y(\theta, \phi) \equiv \Theta(\theta)\Phi(\phi) \tag{8.11}$$

and dividing by $\Theta\Phi$ gives

$$\frac{1}{\Theta}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + l(l+1)\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} \tag{8.12}$$

Again the left side is a function of θ and the right side is a function of ϕ and so they must both be equal to a constant defined as m^2, giving

$$\frac{1}{\Theta}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + l(l+1)\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} \equiv m^2 \tag{8.13}$$

The equation easy to solve is

$$\frac{-1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m^2 \tag{8.14}$$

which has solution

$$\begin{aligned}\Phi(\phi) &= Ae^{im\phi} + Be^{-im\phi} \\ &\equiv A'e^{im\phi} \\ &= e^{im\phi}\end{aligned} \tag{8.15}$$

In the first line m is a fixed value, but in the second line we allow m to take on both positive and negative values. The third line arises because we will put all of the normalization into the $\Theta(\theta)$ solution.

The *periodic boundary condition* is

$$\Phi(\phi + 2\pi) = \Phi(\phi) \tag{8.16}$$

giving

$$e^{im(\phi+2\pi)} = e^{im\phi} \tag{8.17}$$

and thus

$$e^{i2\pi m} = 1 \tag{8.18}$$

implying

$$m = 0,\ \pm 1,\ \pm 2 \ldots \tag{8.19}$$

m is called the *azimuthal quantum number*. Equation (8.19) effectively means that the *azimuthal angle is quantized*! (Write $\Phi = e^{im\phi} \equiv e^{i\phi'}$ and thus ϕ' is quantized.)

The other angular equation becomes

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[l(l+1)\sin^2\theta - m^2\right]\Theta = 0 \tag{8.20}$$

Making the substitution

$$x \equiv \cos\theta \tag{8.21}$$

this reduces to

$$(1-x^2)\Theta'' - 2x\Theta' + \left[l(l+1) - \frac{m^2}{1-x^2}\right]\Theta = 0 \tag{8.22}$$

with $\Theta \equiv \Theta(\cos\theta)$ and $\Theta' \equiv \frac{d\Theta}{d\cos\theta}$ and $\Theta'' \equiv \frac{d^2\Theta}{d\cos^2\theta}$. Equation (8.22) is recognized as the famous *Legendre Associated Differential Equation* [Spiegel, 1968] which has as solutions the *Associated Legendre Functions of the First Kind*, $P_l^m(x)$. The properties of these functions, as well as specific values are given on pg. 149 of [Spiegel, 1968]. Note that l *is an integer* meaning effectively that the θ space is quantized. That is

$$\boxed{l = 0, 1, 2 \cdots} \tag{8.23}$$

A few points to note. Firstly, we could have solved (8.20) directly by the power series method. Using a cut-off would have quantized l for us, just like the cut-off quantized E for the harmonic oscillator. Secondly, for $m = 0$, the Legendre Associated Differential Equation becomes the Legendre Differential Equation with the *Legendre Polynomials* $P_l(x)$ as solutions, whereas above we have the Legendre function of the first kind $P_l^m(x)$. Thirdly we have already noted that l is required to be integer as given in (8.23). Fourthly, the properties of the Legendre function also requires

$$\boxed{m = -l, \cdots + l} \tag{8.24}$$

For example, if $l = 0$ then $m = 0$. If $l = 1$, then $m = -1, 0, +1$. If $l = 2$, then $m = -2, -1, 0, +1, +2$.

Thus we have found that the solutions of the angular equations are characterized by two discrete quantum numbers m and l. Thus we write (8.11) as

$$Y_l^m(\theta, \phi) = Ae^{im\phi} P_l^m(\cos\theta) \tag{8.25}$$

where A is some normalization. If we normalize the angular solutions to unity then the overall normalization condition will require the spatial part to be normalized to unity also. Let's do this. The result is [Griffith, 1995]

$$\boxed{Y_l^m(\theta, \phi) = \epsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}e^{im\phi} P_l^m(\cos\theta)} \tag{8.26}$$

where $\epsilon \equiv (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. These are normalized as in

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) = \delta_{ll'}\delta_{mm'} \tag{8.27}$$

8.2 Radial Equation

Using the substitution

$$u(r) \equiv rR(r) \tag{8.28}$$

the radial Schrödinger equation (8.9) becomes

$$\boxed{-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \left[U(r) + \frac{l(l+1)\hbar^2}{2\mu r^2}\right]u = Eu} \tag{8.29}$$

This is often called the *reduced* Schrödinger equation for the *reduced* wave function $u(r)$. ($R(r)$ is *the* radial wave function.) For $l = 0$ this is the *same* form as the 1-dimensional Schrödinger equation! For $l \neq 0$ it is still the same form as the 1-dimensional equation with an *effective potential*

$$U_{\text{effective}}(r) \equiv U(r) + \frac{l(l+1)\hbar^2}{2\mu r^2} \tag{8.30}$$

Note that precisely the same type of thing occurs in the classical case.

The normalization of the wave function is now the volume integral

$$\int d\tau \; |\Psi(\mathbf{r},t)|^2 = 1 \tag{8.31}$$

where the volume integral $\int d\tau$ is to be performed over the whole universe. In spherical coordinates we have

$$\int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \; |\Psi(r,\theta,\phi)|^2 = 1 \tag{8.32}$$

However $\Psi(r,\theta,\phi) \equiv R(r)Y(\theta,\phi)$ and $Y(\theta,\phi)$ is *already* normalized to unity via (8.27). This means that $R(r)$ must *also* be normalized to unity via

$$\int_0^\infty r^2 dr \; |R(r)|^2 = 1 \tag{8.33}$$

This procedure of separately normalizing $Y(\theta,\phi)$ and $R(r)$ is quite convenient because it follows that the $u(r)$ in (8.28) must be normalized as

$$\boxed{\int_0^\infty dr \; |u(r)|^2 = 1}$$

$$ \tag{8.34} $$

Remember, it is actually the $u(r)$ that we solve for in the radial Schrödinger equation (8.29). If the reduced wave functions $u(r)$ are normalized according to (8.34), then everything else is normalized.

8.3 Bessel's Differential Equation

Many times we will be interested in the solutions for a constant potential U_0. For example, consider the infinite spherical well defined as

$$\begin{aligned} U(r) &= 0 \quad \text{for} \quad r < a \\ &= \infty \quad \text{for} \quad r > a \end{aligned} \tag{8.35}$$

In both cases the potential is constant. For a *free particle* $U = 0$ everywhere and is another example of a constant potential. Another example is a finite spherical well defined as

$$\begin{aligned} U(r) &= 0 \quad \text{for} \quad r < a \\ &= U_0 \quad \text{for} \quad r > a \end{aligned} \tag{8.36}$$

In this section we wish to consider the solutions to a *constant potential U_0 in the classical region where $E > U_0$*. The equation we will end up with is the Bessel differential equation (BDE).

The equation that leads *directly* to the BDE is the Schrödinger equation for $R(r)$, and *not* the equation for $u(r)$. The solutions of the BDE are called Bessel functions. $R(r)$ is directly proportional to a Bessel function, whereas $u(r)$ is r *times* a Bessel function. Thus we shall find it convenient to directly solve the equation for $R(r)$ which we re-write as

$$r^2 R'' + 2rR' + [k^2 r^2 - l(l+1)]R = 0 \tag{8.37}$$

where $R = R(r)$ and $R' \equiv dR/dr$ and

$$k \equiv \frac{\sqrt{2\mu(E - U_0)}}{\hbar} \tag{8.38}$$

which is real in the classical region $E > U_0$. The above equations are valid for arbitrary $U(r)$, but the following discussion of solutions is only valid for the potential $U = U_0$ (or, of course, $U = 0$).

Now the BDE is [Spiegel, 1968, pg. 136]

$$\boxed{x^2 y'' + xy' + (x^2 - \nu^2)y = 0} \tag{8.39}$$

where $y = y(x)$, $y' \equiv \frac{dy}{dx}$ and $\nu \geq 0$. The solutions are [Spiegel, 1968, pg. 137, equation 24.14]

$$y(x) = A\, J_\nu(x) + B\, N_\nu(x) \tag{8.40}$$

where $J_\nu(x)$ are *Bessel* functions of order ν and $N_\nu(x)$ are *Neumann* functions of order ν. (The Neumann functions are often called Weber functions and given the symbol $Y_\nu(x)$. See footnote [Spiegel, 1968, pg. 136]. However $Y_\nu(x)$ is lousy notation for us, because we use Y for spherical harmonics.)

If the dependent variable is

$$\eta \equiv kr \tag{8.41}$$

rather than x, then the BDE is [Arfken, 1985, pg. 578]

$$\boxed{r^2 \frac{d^2 y}{dr^2} + r\frac{dy}{dr} + (k^2 r^2 - \nu^2)y = 0} \tag{8.42}$$

where $y = y(kr) = y(\eta)$. (Exercise: show this)

Now the radial Schrödinger equation (8.37) does not look like the Bessel equations (8.39) or (8.41). Introduce a new function [Arfken, 1985, pg. 623] defined as

$$w(\eta) \equiv \sqrt{\eta}\, R(r) \tag{8.43}$$

i.e.

$$w(kr) = \sqrt{kr}\, R(r) \tag{8.44}$$

Then the radial Schrödinger equation (8.37) becomes

$$\boxed{r^2 \frac{d^2 w}{dr^2} + r\frac{dw}{dr} + \left[k^2 r^2 - \left(l + \frac{1}{2}\right)^2\right] w = 0} \tag{8.45}$$

which is the BDE. (Exercise: show this)

Notice that the order of the Bessel and Neumann functions is

$$\nu = l + \frac{1}{2} \tag{8.46}$$

and we found previously that $l = 0, 1, 2, 3 \cdots$ giving therefore the half integer values

$$\nu = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \cdots \tag{8.47}$$

Comparing (8.45) to (8.42) and using (8.40) gives our solution as

$$w(\eta) = A\, J_{l+\frac{1}{2}}(\eta) + B\, N_{l+\frac{1}{2}}(\eta) \tag{8.48}$$

These Bessel and Neumann functions of half integer order are tabulated in [Spiegel, 1968, pg. 138]

Now these Bessel and Neumann functions of half integer order are usually re-defined as Spherical Bessel functions and Spherical Neumann functions of order l as follows [Arfken, 1985, pg. 623]

$$j_l(x) \equiv \sqrt{\frac{\pi}{2x}} J_{l+\frac{1}{2}}(x) \tag{8.49}$$

$$n_l(x) \equiv \sqrt{\frac{\pi}{2x}} N_{l+\frac{1}{2}}(x) \tag{8.50}$$

giving

$$w(\eta) = A' \sqrt{\frac{2\eta}{\pi}} j_l(\eta) + B' \sqrt{\frac{2\eta}{\pi}} n_l(\eta) \tag{8.51}$$

Thus using $R(r) = \frac{w(\eta)}{\sqrt{\eta}}$

$$R(r) = A\, j_l(\eta) + B\, n_l(\eta) \tag{8.52}$$

where $A \equiv A'\sqrt{\frac{2}{\pi}}$ and $B \equiv B'\sqrt{\frac{2}{\pi}}$. Introducing $u(r) \equiv rR(r)$ gives

$$u(r) = Ar\, j_l(kr) + Br\, n_l(kr) \tag{8.53}$$

in agreement with [Griffiths, 1995, equation 4.45, pg. 130].

8.3.1 Hankel Functions

Explicit formulas for the Spherical Bessel and Neumann functions are [Arfken, 1985, pg. 628; Griffiths, 1995, pg. 130]

$$j_l(x) = (-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\sin x}{x} \tag{8.54}$$

and

$$n_l(x) = -(-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\cos x}{x} \tag{8.55}$$

giving, for example,

$$j_o(x) = \frac{\sin x}{x} \tag{8.56}$$

and

$$n_o(x) = -\frac{\cos x}{x} \tag{8.57}$$

Thus $j_l(x)$ can be thought of as a *"generalized" sine* function and $n_l(x)$ as a *"generalized" cosine* function. Now if the solution of a differential equation can be written as

$$y = A' \sin kr + B' \sin kr \tag{8.58}$$

which is useful in bound state problems, it can also be written

$$y = A\, e^{ikr} + B\, e^{-ikr} \tag{8.59}$$

which is useful in scattering problems with

$$e^{ikr} = \cos kr + i \sin kr \tag{8.60}$$

and

$$e^{-ikr} = \cos kr - i \sin kr \tag{8.61}$$

Similarly the Hankel functions (of first and second kind) are defined as [Spiegel, 1968, pg. 138]

$$H_\nu^{(1)}(x) \equiv J_\nu(x) + i\, N_\nu(x) \tag{8.62}$$

and

$$H_\nu^{(2)}(x) \equiv J_\nu(x) - i\, N_\nu(x) \tag{8.63}$$

and are *also* solutions of the BDE, i.e. (8.40) can also be written

$$\boxed{\begin{aligned} y(x) &= A\, J_\nu(x) + B\, N_\nu(x) \\ &= C\, H_\nu^{(1)}(x) + D\, H_\nu^{(2)}(x) \end{aligned}} \tag{8.64}$$

In 3-d bound state problems (for arbitrary l) the Bessel and Neumann functions are useful, whereas in scattering the Hankel functions are more useful.

Footnote: Given that J and N (or j and n) are the generalized sine and cosine, then $H_\nu^{(1)}$ is actually like $ie^{-ikr} = \sin kr + i\cos kr$ and $H_\nu^{(2)}$ is like $-ie^{ikr} = \sin kr - i\cos kr$.

Similarly we can also define Spherical Hankel functions as

$$h_l^{(1)}(x) \equiv j_l(x) + i\, n_l(x) \tag{8.65}$$

and

$$h_l^{(2)}(x) \equiv j_l(x) - i\, n_l(x) \tag{8.66}$$

Thus, for example,

$$h_o^{(1)} = -i\frac{e^{ix}}{x} \tag{8.67}$$

and

$$h_o^{(2)}(x) = i\frac{e^{-ix}}{x} \tag{8.68}$$

Thus the solutions (8.52) and (8.53) to the Schrödinger equation can also be written

$$\boxed{\begin{aligned} R_l(r) &= A\, j_l(kr) + B\, n_l(kr) \\ &= C\, h_l^{(1)}(kr) + D\, h_l^{(2)}(kr) \end{aligned}} \tag{8.69}$$

or

$$\boxed{\begin{aligned} u_l(r) &= Ar\, j_l(kr) + Br\, n_l(kr) \\ &= Cr\, h_l^{(1)}(kr) + Dr\, h_l^{(2)}(kr) \end{aligned}} \tag{8.70}$$

Chapter 9

HYDROGEN-LIKE ATOMS

The hydrogen atom consists of one electron in orbit around one proton with the electron being held in place via the electric Coulomb force. Hydrogen-like atoms are any atom that has one electron. For example, in hydrogen-like carbon we have one electron in orbit around a nucleus consisting of 6 protons and 6 neutrons. The Coulomb potential for a hydrogen-like atom is

$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} \tag{9.1}$$

in MKS units. Here Z represents the charge of the central nucleus.

We shall develop the theory below for the 1-body problem of an electron of mass m_e interacting via a fixed potential. (We will do this so that we can pull out well known constants like the Bohr radius which involves m_e). If one wishes to consider the 2-body problem one simply replaces m_e with μ in all the formulas below.

9.1 Laguerre Associated Differential Equation

With the harmonic oscillator problem studied in Chapter 8, we solved the Schrödinger equation with the power series method and found that our solutions were the same as the Hermite polynomials. A different approach would have been to closely inspect the Schrödinger equation and observe that it was nothing more than Hermite's differential equation. We would then have immediately known that the solutions were the Hermite polynomials without having to solve anything. (Of course the way you find solutions to Hermite's differential equation *is* with the power series method.)

Many books [Griffiths, 1995] solve the Hydrogen atom problem with the power series method just as we did with the harmonic oscillator. They find that the solutions are the famous *Associated Laguerre Polynomials.* We shall instead follow the latter approach described above. We will closely inspect the Schrödinger equation for the Hydrogen atom problem and observe that it is nothing more than Laguerre's Associated Differential Equation (ADE). We then immediately conclude that the solutions are the Laguerre Associated Polynomials. (Of course all good students will do an exercise and *prove*, by power series method, that the Laguerre associated polynomials are, in fact, solutions to Laguerre's ADE.)

Inserting the Coulomb potential (9.1) into the reduced Schrödinger equation (8.29) gives

$$\frac{d^2u}{dr^2} + \left[-k^2 + \frac{2m_e}{\hbar^2}\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} - \frac{l(l+1)}{r^2}\right]u = 0 \tag{9.2}$$

where we have used m_e instead of μ and m_e is the mass of the electron. Also we have defined

$$k \equiv \frac{+\sqrt{-2m_eE}}{\hbar} \tag{9.3}$$

because the *bound* state energies E of the Coulomb potential are *negative* ($E < 0$). Now define a new variable

$$\rho \equiv 2kr \tag{9.4}$$

giving (9.2) as

$$\frac{d^2u}{d\rho^2} + \left[-\frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right]u = 0 \tag{9.5}$$

with

$$\lambda \equiv \frac{m_e}{\hbar^2}\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{k} \tag{9.6}$$

As with the harmonic oscillator we "peel off" the asymptotic solutions. For $\rho \to \infty$, equation (9.5) is approximately

$$\frac{d^2u}{d\rho^2} - \frac{1}{4}u = 0 \tag{9.7}$$

with solution

$$u(\rho) = Ae^{\frac{1}{2}\rho} + Be^{-\frac{1}{2}\rho} \tag{9.8}$$

but this blows up for $\rho \to \infty$ and thus we must have $A = 0$. Thus

$$u(\rho \to \infty) = Be^{-\frac{1}{2}\rho} \tag{9.9}$$

For $\rho \to 0$, equation (9.5) is approximately

$$\frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u = 0 \tag{9.10}$$

with solution

$$u(\rho) = C\rho^{l+1} + D\rho^{-l} \tag{9.11}$$

which can be checked by substitution. This blows up for $\rho \to 0$ and thus we must have $D = 0$. Thus

$$u(\rho \to 0) = C\rho^{l+1} \tag{9.12}$$

Thus we now define a new reduced wave function $v(\rho)$ via

$$u(\rho) \equiv \rho^{l+1}e^{-\frac{1}{2}\rho}v(\rho) \tag{9.13}$$

with the asymptotic behavior now separated out. Substituting this into (9.5), and after much algebra, we obtain (do Problem 9.1)

$$\rho v'' + (2l + 2 - \rho)v' + (\lambda - l - 1)v = 0 \tag{9.14}$$

with $v' \equiv \frac{dv}{d\rho}$ and $v'' \equiv \frac{d^2v}{d\rho^2}$. Laguerre's ADE is [Spiegel, 1968, pg. 155]

$$xy'' + (m + 1 - x)y' + (n - m)y = 0 \tag{9.15}$$

with $y' \equiv \frac{dy}{dx}$ and the solutions are the associated Laguerre polynomials $L_n^m(x)$, which are listed in [Spiegel, 1968, pg. 155-156] together with many useful properties, all of which can be verified similar to the homework done for the Hermite polynomials in Chapter 5. Note that *n and m are integers.* We see that the Schrödinger equation (9.14) is actually the Laguerre ADE and the solutions are

$$v(\rho) = L_{\lambda+l}^{2l+1}(\rho) \tag{9.16}$$

Thus our complete solution, from (9.13) and (9.14) is

$$u(r) = A\rho^{l+1}e^{-\frac{1}{2}\rho}L_{\lambda+l}^{2l+1}(\rho) \tag{9.17}$$

where we have inserted a normalization factor A. Note that this looks different [Griffiths, 1995] in many other quantum mechanics books because of different conventions. This is most clearly explained in [Liboff, 1992, pg. 439].

Before proceeding we need to make a very important observation about quantization. Recall that for the harmonic oscillator the *energy quantization condition followed directly from the series cut-off* which was required for finite solutions. When one solves the Laguerre ADE by power series method one also needs to cut off the series and that is where the *integer* n comes from in $L_n^m(x)$. Our solution is $L_{\lambda+l}^{2l+1}(\rho)$ and we already know that l is an integer. Therefore λ *must also be an integer*. Thus

$$\boxed{\lambda = n = 1, 2, 3\ldots} \tag{9.18}$$

which gives our energy quantization condition. Combining (9.18), (9.6) and (9.3) gives

$$\boxed{E_n = -\frac{m_e}{2\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2} \equiv -\frac{Z^2}{n^2}E_R \equiv \frac{E_1}{n^2}} \tag{9.19}$$

where the *Rydberg energy* is defined as

$$E_R \equiv \frac{m_e e^4}{2(4\pi\epsilon_0\hbar)^2} = 13.6 \text{ eV} \tag{9.20}$$

The energy levels are plotted in Fig. 9.1. Notice that the spacing *decreases* as n increases.

We now wish to normalize the reduced wave function (9.17), using (8.34). This is done in Problem 9.2 with the result that

$$A = \sqrt{\frac{Z}{an^2}\frac{(n-l-1)!}{[(n+l)!]^3}} \tag{9.21}$$

where the *Bohr radius* is defined as

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10}\text{m} \approx 1\mathring{A} \tag{9.22}$$

which is a characteristic size for the hydrogen atom. Thus k becomes

$$k = \frac{Z}{na} \tag{9.23}$$

Using $\frac{u(r)}{r} = 2k\frac{u(\rho)}{\rho}$ the final wave function is

$$\begin{aligned}\psi_{nlm}(r,\theta,\phi) &= R_{nl}(r)Y_{lm}(\theta,\phi) \\ &= \sqrt{\left(\frac{2Z}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\rho^l e^{-\frac{1}{2}\rho} L_{n+l}^{2l+1}(\rho)Y_{lm}(\theta,\phi)\end{aligned} \tag{9.24}$$

or

$$\boxed{\psi_{nlm}(r,\theta,\phi) = \sqrt{\left(\frac{2Z}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2Z}{na}r\right)^l e^{-\frac{Z}{na}r} L_{n+l}^{2l+1}\left(\frac{2Z}{na}r\right) Y_{lm}(\theta,\phi)} \tag{9.25}$$

which are the complete wave functions for Hydrogen like atoms.

9.2 Degeneracy

Let us summarize our quantum numbers. For the hydrogen like atom we have, from (9.19)

$$E_n = \frac{E_1}{n^2} \tag{9.26}$$

where n is the *principal quantum number* such that (see (9.18))

$$n = 1, 2, 3 \cdots \tag{9.27}$$

We already know from (8.23) that the *orbital quantum number* is

$$l = 0, 1, 2, \cdots \tag{9.28}$$

and from (8.19) and (8.24) that the *magnetic quantum number* is

$$m_l = 0,\ \pm 1,\ \pm 2 \cdots \pm l \tag{9.29}$$

However, looking at the wave function in (9.25) we see that in order to avoid (undefined) *negative factorials* we must also have, for hydrogen-like atoms, the condition

$$l = 0, 1, 2, \cdots n-1 \tag{9.30}$$

That is l cannot be bigger than $n-1$.

Thus the wave function is specified by 3 quantum numbers n, l, m subject to the conditions (9.27), (9.29) and (9.30) for hydrogen like atoms. (3 dimensions, 3 numbers!) Recall that for the 1 dimensional problem we had only the principal quantum number n. (1 dimension, 1 number!) The wave function ψ_{nlm} in (9.25) depends on *all 3 quantum numbers.* Thus the first few wave functions are

$$\begin{array}{ll} \text{for } n=1, & \psi_{100} \\ \text{for } n=2, & \psi_{200},\ \psi_{210},\ \psi_{21-1},\ \psi_{211} \\ \text{for } n=3, & \psi_{300},\ \psi_{310},\ \psi_{31-1},\ \psi_{311} \\ & \psi_{320},\ \psi_{32-1},\ \psi_{321},\ \psi_{32-2},\ \psi_{322} \end{array}$$

etc. However the energy E_n in (9.26) *depends only on the principal quantum number* n. Thus the energy level E_1 has only 1 wave function, but E_2 has 4 wave functions associated with it and E_3 has 9 wave functions. E_2 is said to be *4-fold degenerate* and E_3 is said to be 9-fold degenerate.

We shall see later that this degeneracy can be *lifted* by such things as external magnetic fields (Zeeman effect) or external electric fields (Stark effect). In the Zeeman effect we will see that the formula for energy explicitly involves *both* n and m_l.

Chapter 10

ANGULAR MOMENTUM

10.1 Orbital Angular Momentum

We *define* the orbital angular momentum *operator* as

$$\hat{L} \equiv \hat{r} \times \hat{p} \tag{10.1}$$

just as in the ordinary vector definition in classical mechanics. This gives

$$\begin{aligned} \hat{L}_x &= yp_z - zp_y \\ &\equiv -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \end{aligned} \tag{10.2}$$

and similarly

$$\begin{aligned} \hat{L}_y &= zp_x - xp_z \\ &\equiv -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \end{aligned} \tag{10.3}$$

and

$$\begin{aligned} \hat{L}_z &= xp_y - yp_x \\ &\equiv -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{aligned} \tag{10.4}$$

The above relations lead to the following angular momentum commutators

$$\boxed{[L_i, L_j] = i\hbar\epsilon_{ijk}L_k} \tag{10.5}$$

and

$$\boxed{[L^2, L_i] = 0} \tag{10.6}$$

where L_i is any of L_x, L_y, L_z and $L^2 \equiv L_x^2 + L_y^2 + L_z^2$. The Levi-Civita symbol is defined as

$$\epsilon_{ijk} = \begin{cases} +1 & \text{if } ijk \text{ are an even permutation of 1, 2, 3} \\ -1 & \text{if } ijk \text{ are an odd permutation of 1, 2, 3} \\ 0 & \text{if } ijk \text{ are not a permutation of 1, 2, 3} \end{cases} \tag{10.7}$$

(For example $\epsilon_{123} = +1$, $\epsilon_{231} = +1$, $\epsilon_{321} = -1$, $\epsilon_{221} = 0$.) These commutation relations are proved in the problems. (do Problems 10.1 and 10.2) Notice that in (10.5) a sum over k is *implied*. In other words

$$[L_i, L_j] = i\hbar \sum_k \epsilon_{ijk} L_k \tag{10.8}$$

In (10.5) we have made use of the Einstein summation convention in which a *sum is implied for repeated indices.* (Example: $\mathbf{A} \cdot \mathbf{B} = \sum\limits_i A_i B_i \equiv A_i B_i = A_1 B_1 + A_2 B_2 + A_3 B_3$.)

In spherical polar coordinates, the relation to Cartesian coordinates is

$$x = r \sin\theta \cos\phi \tag{10.9}$$
$$y = r \sin\theta \sin\phi \tag{10.10}$$
$$z = r \cos\theta \tag{10.11}$$

and by change of variables the angular momentum operators become

$$L_x = i\hbar \left(\sin\phi \frac{\partial}{\partial\theta} + \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right) \tag{10.12}$$
$$L_y = i\hbar \left(-\cos\phi \frac{\partial}{\partial\theta} + \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right) \tag{10.13}$$
$$L_z = -i\hbar \frac{\partial}{\partial\phi} \tag{10.14}$$

and

$$L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \tag{10.15}$$

which we previously defined in (8.8). Actually in (8.8) it was just a definition, whereas above we have shown that

$$L^2 = L_x^2 + L_y^2 + L_z^2 \tag{10.16}$$

Let us invent two additional operators defined as

$$L_\pm \equiv L_x \pm iL_y = \pm\hbar e^{\pm i\phi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\phi}\right) \tag{10.17}$$

We shall see the utility of these operators in a moment. It can now be shown that (do Problem 10.3)

$$L^2 Y_{lm}(\theta,\phi) = l(l+1)\hbar^2 Y_{lm}(\theta,\phi) \tag{10.18}$$

and

$$L_z Y_{lm}(\theta,\phi) = m\hbar Y_{lm}(\theta,\phi) \tag{10.19}$$

which are often written in Dirac notation as

$$\boxed{L^2 \mid lm\rangle = l(l+1)\hbar^2 \mid lm\rangle} \tag{10.20}$$

and

$$\boxed{L_z \mid lm\rangle = m\hbar \mid lm\rangle} \tag{10.21}$$

Thus we have found that the operators L^2 and L_z have *simultaneous eigenfunctions* $|lm\rangle = Y_{lm}$ such that $l = 0, 1, 2, 3\ldots$ and $m = -l\ldots + l$.

Commutator Theorem Two non-degenerate operators have simultaneous eigenfunction *iff* the operators commute.

Thus the fact that L^2 and L_z have simultaneous eigenfunctions is an instance of the commutator theorem. The question is, since say L^2 and L_x also commute, then won't they also have simultaneous eigenfunctions? The answer is *no* because L_x, L_y, and L_z do *not* commute among themselves and thus will never have simultaneous eigenfunctions. Thus L^2 will have simultaneous eigenfunctions with only *one of* L_x, L_y and L_z.

Equation (10.20) tells us that the magnitude of the angular momentum is

$$\boxed{L = \sqrt{l(l+1)}\hbar} \quad l = 0, 1, 2, \ldots \tag{10.22}$$

For example, for $l = 2$ then $L = \sqrt{2}\hbar$ (which *does* have the correct units for angular momentum). Because of the angular momentum quantum number we see that *angular momentum is quantized*. But this is fine. We have seen that energy is quantized and we now find that angular momentum is also quantized. But here's the crazy thing. The projection, L_z, of the angular momentum is *also* quantized via (10.21) with the magnitude of projection being

$$\boxed{L_z = m\hbar} \quad m = -l, \ldots + l \tag{10.23}$$

You see even if the magnitude L is quantized, we would expect classically that its projection on the z axis could be *anything*, whether or not L is quantized. The fact that L_z is also quantized means that the vector $\mathbf{L}$ can only *point* in certain directions! This is shown in Fig. 10.1. This is truly amazing! Thus, quite rightly, the quantization of L_z is referred to as *space quantization*.

The angular momentum raising and lowering operators have the property that

$$L_\pm Y_{lm}(\theta, \phi) = \hbar\sqrt{l(l+1) - m(m \pm 1)}Y_{lm\pm 1}(\theta, \phi) \tag{10.24}$$

or

$$\boxed{L_\pm \mid lm\rangle = \hbar\sqrt{l(l+1) - m(m \pm 1)} \mid l\, m \pm 1\rangle} \tag{10.25}$$

which raise or lower the value of n. (do Problem 10.4)

10.1.1 Uncertainty Principle

Recall our Uncertainty theorem from Chapter 6 which stated that if $[A, B] = iC$ then $\Delta A \Delta B \geq \frac{1}{2}|\langle C\rangle|$. The commutation relation (10.5) therefore implies

$$\Delta L_i \Delta L_j \geq \frac{\hbar}{2}|\langle\epsilon_{ijk}L_k\rangle| \tag{10.26}$$

For example $[L_x, L_y] = i\hbar L_z$ implies

$$\Delta L_x \Delta L_y \geq \frac{\hbar}{2}|\langle L_z \rangle| \tag{10.27}$$

10.2 Zeeman Effect

m_l is called the *magnetic* quantum number because its presence is felt when an atom is placed in a magnetic field. Each of the energy levels splits into smaller levels determined by m. This phenomenon is called the Zeeman effect. Let us see how it comes about.

Let's consider a hydrogen-like atom. The single electron is circulating around the nucleus and so it acts as a tiny magnetic dipole as shown in Fig. 10.2. If the atom is then placed in an external magnetic field then the dipole acquires some *potential energy.* This extra potential energy is acquired by the circulating electron and results in a *shift* of the electron energy levels. Thus we want to calculate this potential energy, which for a magnetic dipole μ placed in a field $\mathbf{B}$ is

$$U = -\mu \cdot \mathbf{B} = -\mu B \cos\theta \tag{10.28}$$

where θ is the angle between the dipole moment μ and the external magnetic field $\mathbf{B}$. Define the z direction to be in the direction of $\mathbf{B}$. Thus $\mu \cos\theta = \mu_z$ and

$$U = -\mu_z B \tag{10.29}$$

Thus we need to calculate μ_z now. The dipole moment for the current loop of Fig. 10.2 is

$$\mu = iA\hat{n} \tag{10.30}$$

where i is the current, A is the area of the loop and $\hat{n}$ is the vector normal to the plane of the loop. The magnitude is

$$\mu = iA = \frac{-e}{T}\pi r^2 \tag{10.31}$$

where $-e$ is the electron charge, T is the period and r is the radius of the loop. The angular momentum is

$$L = mvr = m\frac{2\pi r^2}{T} \tag{10.32}$$

and combining with (10.31) gives $\mu = \frac{-e}{2m} L$ or

$$\mu = -\left(\frac{e}{2m}\right)\mathbf{L} \equiv \gamma \mathbf{L} \equiv g\left(\frac{-e}{2m}\right)\mathbf{L} \tag{10.33}$$

where the *gyromagnetic ratio* γ is defined as the *ratio of* μ *to* $\mathbf{L}$ and we have also introduced the so-called *g-factor*. For the above example we have

$$\gamma = \frac{-e}{2m} \tag{10.34}$$

and

$$g = 1 \tag{10.35}$$

(Be careful because some authors call g the gyromagnetic ratio!) Thus

$$\mu_z = -\left(\frac{e}{2m}\right) L_z = -\left(\frac{e}{2m}\right) m_l \hbar \equiv -\mu_B m_l = -g\,\mu_B\, m_l \tag{10.36}$$

where the Bohr magneton is defined as

$$\mu_B \equiv \frac{e\hbar}{2m}. \tag{10.37}$$

Thus the interaction potential energy is

$$\boxed{U = m_l\, \mu_B\, B} = m_l \frac{e\hbar}{2m} B \tag{10.38}$$

where we don't need to worry about the $-$ sign because m_l takes on both $+$ and $-$ signs via $m_l = -l, \ldots +l$. Now there are $2l+1$ possible different values for m_l. Thus a spectral line of given l will be split into $2l+1$ separate lines when placed in an external magnetic field. (In the absence of a field they will not be split and will all have the same energy.) The *spacing* between *each* of the split lines will be $\mu_B B$. See Fig. 10.3.

Notice that the splitting of the spectral lines will be bigger for bigger magnetic fields. This is great because if we notice the Zeeman effect in the spectra of stars we can easily figure out the magnetic fields. In fact by observing the spectra of sunspots, people were able to find the strength of magnetic fields in the region of sunspots!

10.3 Algebraic Method

See [Griffiths, 1995, Section 4.3]

10.4 Spin

The Stern-Gerlach experiment performed in 1925 [Tipler, 1992] showed that the electron itself also carries angular momentum which has only 2 possible orientations. As nicely explained in [Griffiths, 1995] this angular momentum is *intrinsic* to the electron and does not arise from orbit effects. The half integral values of spin that we discovered above in the algebraic method are obviously suitable for the electron. The Stern-Gerlach experiment implies a spin $s = \frac{1}{2}$ for the electron with 2 projections $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$.

The theory of spin angular momentum is essentially a copy of the theory of orbital angular momentum. Thus we have (see (10.5) and (10.6)

$$[S_i, S_j] = i\hbar\epsilon_{ijk}S_k \tag{10.39}$$

and

$$[S^2, S_i] = 0 = [S^2, \mathbf{S}] \tag{10.40}$$

Similarly from (10.20) and (10.21) we have

$$S^2 \mid sm\rangle = s(s+1)\hbar^2 \mid sm\rangle \tag{10.41}$$

and

$$S_z \mid sm\rangle = m\hbar \mid sm\rangle \tag{10.42}$$

(Note that before our m meant m_l and here our m means m_s.) Finally from (10.23)

$$S_\pm \mid sm\rangle = \hbar\sqrt{s(s+1) - m(m\pm 1)} \mid s\ m\pm 1\rangle \tag{10.43}$$

where

$$S_\pm \equiv S_x \pm iS_y \tag{10.44}$$

Now in the theory of orbital angular momentum with the spherical harmonics, which were *solutions to the Schrödinger equation*, we only had $l = 0, 1, 2, \ldots$. But we saw from the algebraic method that half integer values can also arise (but there won't be solutions to the Schrödinger equation). In the theory of spin we use all values, that is

$$s = 0,\ \frac{1}{2},\ 1,\ \frac{3}{2},\ \ldots \tag{10.45}$$

and we still have

$$m = -s, \ldots + s. \tag{10.46}$$

10.4.1 Spin $\frac{1}{2}$

All of the quarks and leptons (such as the electron and neutrino) as well as the neutron and proton carry an intrinsic spin of $\frac{1}{2}$. Thus we shall study this now in some detail.

Now in our orbital angular momentum theory the eigenfunctions $|lm\rangle$ were just the spherical harmonic functions and the operators L^2, L_z were just angular differential operators. It turns out that for spin $\frac{1}{2}$ it is *not* possible to find functions and differential operators satisfying the algebra specified in equations (10.39)–(10.46), but it *is* possible to find *matrix* representations. The eigenfunctions are

$$\left|\frac{1}{2}\,\frac{1}{2}\right\rangle \equiv \chi_+ \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{10.47}$$

for spin "up" and

$$\left|\frac{1}{2}\,\frac{-1}{2}\right\rangle \equiv \chi_- \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{10.48}$$

for spin "down". *Now* we can work out the operators. This is done in [Griffiths, 1995, pg. 156]. I will just write down the answer which you can *check* by substituting.

Given the eigenstates (10.47) and (10.48) then the operators in (10.41) and (10.42) *must* be

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{10.49}$$

$$S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{10.50}$$

$$S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{10.51}$$

from which S^2 and $S_\pm$ can easily be deduced as

$$S^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{10.52}$$

$$S_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \tag{10.53}$$

$$S_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{10.54}$$

Actually the matrices S_i are often written

$$\mathbf{S} \equiv \frac{\hbar}{2}\mathbf{s} \tag{10.55}$$

where $\mathbf{s}$ are the famous Pauli Spin Matrices

$$\boxed{\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}} \tag{10.56}$$

$$\boxed{\sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}} \tag{10.57}$$

$$\boxed{\sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}} \tag{10.58}$$

In problems 10.5–10.8, it is shown very clearly that the spin $\frac{1}{2}$ operators S_i acting on $|sm\rangle$ obey exactly the same algebra as the operators L_i acting on $|lm\rangle = Y_{lm}$. Similar operators and states can also be found for all of the half integer values of spin angular momentum. (We only considered spin $\frac{1}{2}$, but arbitrary l).

10.4.2 Spin-Orbit Coupling

There are several classic experiments which demonstrate the reality of spin $\frac{1}{2}$ for the electron. These are the *Stern-Gerlack experiment*, the *anomalous Zeeman effect* and *hyperfine structure.* These are all discussed in most books on Modern Physics.

In this section we wish to briefly discuss another important piece of evidence for spin $\frac{1}{2}$ and that is the effect of *spin-orbit coupling* which is responsible for a *doubling splitting* of spectral lines.

Actually in the spectrum of hydrogen one observes *fine structure* and *hyperfine structure* which is the splitting of spectral lines. The fine structure is due to two effects, namely *relativity* and *spin-orbit* coupling. The hyperfine structure, which is about 1000 times smaller than fine structure, is due to a spin interaction with the nucleus. (One also observes the so-called *Lamb shift* which is a shift of the $2^2S_{1/2}$ state relative to the $2^2P_{1/2}$ state). The other effects such as the *Zeeman effect*, *anomalous Zeeman effect* and *Stark effect* are due to the presence of external *magnetic* and *relative* fields respectively.

Let us now consider the fine structure effect of spin-orbit coupling. From the point of view of the nucleus, the electron constitutes a current loop around it, but from the point of view of the electron, it sees a positively charged nucleus moving around it. Thus the electron feels a magnetic field due to the orbiting nucleus. The strength of this field is the same as the magnetic field at the center of a circular current loop, which from Ampere's law is

$$B = \frac{\mu_0 i}{2r} = \frac{\mu_0 ve}{4\pi r^2} \tag{10.59}$$

in MKS units where i is the current $\left(i = \frac{e}{T} = \frac{v}{2\pi r}e\right)$, v is the speed of the nucleus and r is the orbital radius.

So now our problem is like the normal Zeeman effect where the orbiting electron, with magnetic moment $\mu_z = -\left(\frac{e}{2m}\right)L_z$ interacted with the external magnetic field with interaction energy $U = -\mu_z B$. (See equations (10.36) and (10.29)). Similarly the spin-orbit effect is the *spin* magnetic moment

$$\mu_z \propto S_z \tag{10.60}$$

interaction with the magnetic field produced by the *orbiting* nucleus and the interaction energy again is

$$U = -\mu \cdot \mathbf{B} = -\mu B \cos\theta = -\mu_z B \tag{10.61}$$

except that now μ_z comes from (10.60) and the magnetic field from (10.59). In the Zeeman effect we used $L_z = m_l \hbar$ in (10.31) and so the interaction energy (10.38) was directly proportional to m_l. Thus if $l = 1$ the splitting was 3-fold ($m_l = 0$), or if $l = 2$ the splitting was 5-fold ($m_l = 0, \pm 1, \pm 2$), etc.

Similarly here we have

$$S_z = m_s \hbar$$

but for the electron m_s has only *two* values ($m_s = \pm\frac{1}{2}$) and so there will only be *double splitting of the spectral lines*, rather than the 3-fold, 5-fold, etc. splitting observed in the Zeeman effect. The actual magnitude of the splitting is calculated in equations (6.65) and (6.66) of [Griffiths, 1995]. The point of our discussion was simply to show that *spin* leads to a *double* splitting of spectral lines.

A more physical understanding of this double splitting can be seen from Fig. 10.4 and 10.5.

The spin-orbit effect occurs for *all* states *except* for S states ($l = 0$). This can be seen as follows. The magnetic field due to the proton is proportional to the electron angular momentum $\mathbf{L}$ as

$$\mathbf{B} \propto \mathbf{L}$$

or, more correctly, the angular momentum of the proton from the electron's point of view. The dipole moment of the electron is proportional to its spin

$$\mu \propto \mathbf{S}$$

Thus from $U = -\mu \cdot \mathbf{B}$ in (10.61) we have

$$\boxed{U \propto \mathbf{S} \cdot \mathbf{L}}$$

or

$$U \propto \mathbf{S} \cdot \mathbf{L} = S_z L = m_s l(l+1)\hbar$$

which is zero for $l = 0$ (S states). As shown in Fig. 10.5, the spin-orbit interaction splits the P state but not the S state.

10.5 Addition of Angular Momentum

Suppose we have a pion of spin 1 in orbit around a nucleon of spin $\frac{1}{2}$. The composite particle is called a delta particle. What will be the spin of the delta? The spin 1 particle has spin projections of 0, +1, −1 and the spin $\frac{1}{2}$ particle has projections $+\frac{1}{2}$, $-\frac{1}{2}$. Obviously the projections of the delta will be all combinations of these, namely

$$\begin{array}{rr} \frac{1}{2}, & -\frac{1}{2} \\ \frac{3}{2}, & \frac{3}{2} \\ -\frac{1}{2}, & -\frac{3}{2} \end{array}$$

These projections form naturally into the groups $M = \frac{1}{2}, +\frac{1}{2}$ and $M = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$ because we know that projections jump in integer steps. Thus, the total spin of the delta must be either $J = \frac{1}{2}$ or $J = \frac{3}{2}$.

We can always work out total spin combinations like this but it is easier to just use some simple rules.

For

$$\mathbf{j} \equiv \mathbf{j}_1 + \mathbf{j}_2 \tag{10.62}$$

then the magnitude of j is obtained from

$$\boxed{|j_1 - j_2| \leq j \leq j_1 + j_2} \tag{10.63}$$

with *j jumping in integer steps.* Here j_1 and j_2 are the magnitudes of the individual spins. Also

$$\boxed{m = m_1 \pm m_2} \tag{10.64}$$

because $j_z = j_{1z} \pm j_{2z}$. From our previous example with $j_1 = 1$ and $j_2 = \frac{1}{2}$ we have $|1 - \frac{1}{2}| \leq j \leq 1 + \frac{1}{2}$ giving $\frac{1}{2} \leq j \leq \frac{3}{2}$, implying $j = \frac{1}{2}$ or $\frac{3}{2}$.

The symbol $\mathbf{j}$ can be either *orbital* angular momentum $\mathbf{l}$ or *spin* angular momentum $\mathbf{s}$

Example 10.1 Two electrons have spin $\frac{1}{2}$. What is the total spin of the two electron system?

Solution

$$S_1 = \frac{1}{2}, \quad S_2 = \frac{1}{2}$$

$$\left|\frac{1}{2} - \frac{1}{2}\right| \leq S \leq \frac{1}{2} + \frac{1}{2}$$

$$O \leq S \leq 1$$

S jumps in integer steps, therefore $S = 0$ or 1.

Example 10.2 What are the possible spin projections in the previous example?

Solution

$$m_1 = +\frac{1}{2}, -\frac{1}{2} \quad m_2 = +\frac{1}{2}, -\frac{1}{2}$$

$$\begin{aligned} m = m_1 + m_2 &= \frac{1}{2} + \frac{1}{2} = 1 \\ \text{or} \qquad m &= \frac{1}{2} - \frac{1}{2} = 0 \\ \text{or} \qquad m &= -\frac{1}{2} + \frac{1}{2} = 0 \\ \text{or} \qquad m &= -\frac{1}{2} - \frac{1}{2} = -1 \end{aligned}$$

Evidently the $m = 0, \pm 1$ belong to $S = 1$ and the other $m = 0$ belongs to $S = 0$. $S = 1$ is called the *triplet* combination and $S = 0$ is called the *singlet* combination.

10.5.1 Wave Functions for Singlet and Triplet Spin States

From the previous two examples we have seen that by combining wave functions $|\frac{1}{2}\,\frac{1}{2}\rangle$ and $|\frac{1}{2}\,-\frac{1}{2}\rangle$ we can end up with singlet and triplet wave functions $|0\,0\rangle$ and $|1\,1\rangle$, $|1\,0\rangle$, $|1\,-1\rangle$. How are these all related to each other? Let's use the symbols

$$\left|\frac{1}{2}\;\frac{1}{2}\right\rangle \equiv \uparrow \tag{10.65}$$

and

$$\left|\frac{1}{2}\;-\frac{1}{2}\right\rangle \equiv \downarrow \tag{10.66}$$

The $|1\;-1\rangle$ state can only contain $\uparrow$ states. Thus

$$|1\;1\rangle = \uparrow\uparrow \tag{10.67}$$

and similarly

$$|1\;-1\rangle = \downarrow\downarrow \tag{10.68}$$

Note that both of these states are *symmetric* under interchange of particles 1 and 2. The $|0\ 0\rangle$ and $|1\ 0\rangle$ states must contain an equal admixture of ↑ and ↓ in order to get $M = 0$. Thus

$$|0\ 0\rangle = A(\uparrow\downarrow \pm \downarrow\uparrow) \tag{10.69}$$

and

$$|1\ 0\rangle = A'(\uparrow\downarrow \pm \downarrow\uparrow) \tag{10.70}$$

Now assuming each $|\frac{1}{2}\ \frac{1}{2}\rangle$ and $|\frac{1}{2} - \frac{1}{2}\rangle$ are separately normalized, i.e. $\langle\frac{1}{2}\ \frac{1}{2} \mid \frac{1}{2}\ \frac{1}{2}\rangle = (1\ 0)\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 1$, then we must have $A = A' = \frac{1}{\sqrt{2}}$. Thus the only difference between $|0\ 0\rangle$ and $|1\ 0\rangle$ can be in the ± sign. Now for the + sign the wave function will be symmetric under interchange of particles 1 and 2, while the − sign gives antisymmetry. Thus the + sign naturally belongs to the $|1\ 0\rangle$ state. Therefore our final composite wave functions are for the $S = 1$ *symmetric triplet*

$$|1\ 1\rangle = \uparrow\uparrow \tag{10.71}$$

$$|1\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \tag{10.72}$$

$$|1 - 1\rangle = \downarrow\downarrow \tag{10.73}$$

and for the $S = 0$ *antisymmetric singlet*

$$\boxed{|0\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)} \tag{10.74}$$

10.5.2 Clebsch-Gordon Coefficients

10.6 Total Angular Momentum

We have seen that there are two types of angular momentum, namely *orbital* angular momentum **L** and intrinsic *spin* angular momentum S. We have seen that the magnitude of **L** is

$$L = \sqrt{l(l+1)}\,\hbar \tag{10.75}$$

and

$$L_z = m_l \hbar \tag{10.76}$$

Also the magnitude of **S** is

$$S = \sqrt{s(s+1)}\,\hbar \tag{10.77}$$

and

$$S_z = m_s \hbar \tag{10.78}$$

We now define the *total* angular momentum **J** to be the sum of orbital and spin angular momenta as

$$\mathbf{J} \equiv \mathbf{L} + \mathbf{S} \tag{10.79}$$

Before we had L, L_z, S and S_z in terms of the *quantum numbers* l, m_l, s, m_s. Let us *define* new quantum numbers j and m_j such that the magnitude of **J** is

$$J \equiv \sqrt{j(j+1)}\,\hbar$$

and

$$J_z \equiv m_j\,\hbar$$

From (10.63) and (10.64) we obviously have

$$j = l \pm s$$

and

$$m_j = m_l \pm m_s$$

10.6.1 LS and jj Coupling

Suppose we have a whole collection of electrons orbiting a nucleus as in an atom. The electrons will each have individual spin $\mathbf{S}_i$ and individual orbital angular momenta $\mathbf{L}_i$. How do we figure out the total spin **J** for the whole collection of electrons? In other words what is the total angular momentum of the atom? There are at least two ways to do this.

In the *LS coupling scheme* the $\mathbf{L}_i$ and $\mathbf{S}_i$ are added separately as in

$$\mathbf{L} \equiv \sum_i \mathbf{L}_i \tag{10.80}$$

$$\mathbf{S} \equiv \sum_i S_i \tag{10.81}$$

$$\mathbf{J} \equiv \mathbf{L} + \mathbf{L} \tag{10.82}$$

In the LS coupling scheme the total angular momentum state is usually expressed in spectroscopic rotation

$$^{2s+1}L_J \tag{10.83}$$

where the letters S, P, D, F or s, p, d, f etc. are used to denote the states $L = 0, 1, 2, 3$, etc.

In the *jj coupling scheme* we have each individual $\mathbf{L}_i$ and $\mathbf{S}_i$ added to give an individual bfJ_i, as in

$$\begin{aligned} \mathbf{J}_i &\equiv \mathbf{L}_i + \mathbf{S}_i \\ \mathbf{J} &\equiv \sum_i \mathbf{J}_i \end{aligned}$$

LS coupling holds for most atoms and for weak magnetic fields. jj coupling holds for heavy atoms and strong magnetic fields. jj coupling also holds for most nuclei. [Beiser, pg. 264-267, 1987; Ziock, pg. 139, 1969]

The physical reasons as to why LS coupling holds versus jj coupling can be found in these two references. The basic idea is that internal electric forces are responsible for coupling the individual $\mathbf{L}_i$ of each electron into a single vector $\mathbf{L}$. Strong magnetic fields can destroy this cooperative effect and then all the spins act individually. Normally a single electron "cooperates" with all other electrons giving $\mathbf{L} = \sum_i \mathbf{L}_i$ and $S = \sum_i S_i$. However in a strong magnetic field (internal or external), all the electrons start marching to the orders of the strong field and begin to ignore each other. Then we get $\mathbf{L}_i = \mathbf{L}_i + \mathbf{S}_i$.

Example 10.3 If one electron is in a P state and another is in a D state what is the total spin on both LS and jj coupling? In LS coupling what is $^{2s+1}L_J$?

Solution

$$S_1 = \frac{1}{2}, \quad S_2 = \frac{1}{2}$$

$$l_1 = 1 \text{ (P state)} \quad l_2 = 2 \text{ (D state)}$$

LS Coupling:

$$\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$$

$$|L_1 - L_2| \leq L \leq L_1 + L_2$$
$$|1-2| \leq L \leq 1+2 \Rightarrow L = 1, 2, 3$$
$$\mathbf{S} = \mathbf{S}_1 + \mathbf{L}_2$$
$$|S_1 - S_2| \leq S \leq S_1 + S_2$$
$$|\tfrac{1}{2} - \tfrac{1}{2}| \leq S \leq \tfrac{1}{2} + \tfrac{1}{2} \Rightarrow S = 0, 1$$
$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$
$$|L - S| \leq J \leq L + S$$

S	L	J	${}^{2s+1}L_J$
0	1	1	${}^1P_1$
	2	2	${}^1D_2$
	3	3	${}^1F_3$
1	1	$0, 1, 2$	${}^3P_0\ {}^3P_1\ {}^3P_2$
	2	$1, 2, 3$	${}^3D_1\ {}^3D_2\ {}^3D_3$
	3	$2, 3, 4$	${}^3F_2\ {}^3F_3\ {}^3F_4$

jj Coupling:

$$\mathbf{J} = \mathbf{L}_1 + \mathbf{S}_1$$
$$|L_1 - S_2| \leq J_1 \leq L_1 + S_1$$
$$|1 - \tfrac{1}{2}| \leq J_1 \leq \tfrac{1}{2} \Rightarrow J_1 = \tfrac{1}{2}, \tfrac{3}{2}$$
$$|L_2 - S_2| \leq J_2 \leq L_2 + S_2$$
$$|2 - \tfrac{1}{2}| \leq J_2 \leq 2 + \tfrac{1}{2}$$
$$\tfrac{3}{2} \leq J_2 \leq \tfrac{5}{2} \Rightarrow J_2 = \tfrac{3}{2}, \tfrac{5}{2}$$
$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$$
$$|J_1 - J_2| \leq J \leq |J_1 + J_2|$$

J_1	J_2	J
$\frac{1}{2}$	$\frac{3}{2}$	$1, 2$
$\frac{1}{2}$	$\frac{5}{2}$	$2, 3$
$\frac{3}{2}$	$\frac{3}{2}$	$0, 1, 2, 3$
$\frac{3}{2}$	$\frac{5}{2}$	$1, 2, 3, 4$

Note that the notation ${}^{2s+1}L_J$ is meaningless in jj coupling.

(do Problem 10.10)

Chapter 11

SHELL MODELS

Clearly atoms and nuclei are very complicated many body problems. The basic idea of any shell model is to replace this difficult many body problem by an effective 1-body problem.

In the case of atoms, instead of focusing on the very complicated behaviors of all the electrons we instead follow the behavior of 1 electron only. The *shell model approximation* is to regard this single electron as moving in an overall effective potential which results from all of the other electrons and the nucleus. This is often called the *mean field approximation*, an it is often a surprisingly good method. The same idea holds in the nuclear shell model where a single nucleon's behavior is determined from the mean field of all the other nucleons.

11.1 Atomic Shell Model

11.1.1 Degenerate Shell Model

For the moment, let us imagine that the mean field is just the Coulomb potential. We have found that $n = 1, 2, 3 \cdots$ and $l = 0, 1, 2 \cdots n - 1$ and $m_l = -l \cdots + l$. Thus for $n = 1$ we have $l = 0(s)$ and $m_l = 0$. For $n = 2$ we have $l = 0(s)$ or $1(p)$ and $m_l = 0$ or $0, \pm 1$, etc. Thus for the Coulomb potential, the $n = 1, 2, 3 \cdots$ *shells* consist of the following *subshells*:

$$\begin{array}{llll} 1s & & & \\ 2s & 2p & & \\ 3s & 3p & 3d & \\ 4s & 4p & 4d & 4f \end{array}$$

Now the s subshells have $l = 0$ and $m_l = 0$. Electrons have $m_s = \pm\frac{1}{2}$ and recall that the Pauli principle states that no two fermions (electrons) can have the same quantum numbers. Thus it is possible for two electrons to have quantum numbers n and $l = 0$ but not three. Similarly 6 electrons can have quantum numbers n, $l = 1$ but not 7 or 8. This is symbolized with $(s)^2$, $(p)^6$, $(d)^{10}$, $(f)^{14}$. Notice that *the numbers keep increasing by 4.*

Thus if we keep putting electrons into the Coulomb mean field we might get a configuration as shown in Fig. 11.1 for 60 electrons.

11.1.2 Non-Degenerate Shell Model

Actually the atomic shell model doesn't work quite like that discussed above. The reason is that the mean field is not exactly a Coulomb potential. As pointed out by [Shankar, pg. 379, 1980], if all the electron orbitals were circular, we might expect a mean Coulomb potential, with the inner electrons merely shielding the inner nuclear charge to produce a net reduced charge. However only $s(l = 0)$ orbitals are circular and the potential is no longer a purely $\frac{1}{r}$ potential. The effect of this is to lift the degeneracy in l.

From plots of the spherical harmonics we see that an electron in a low l orbit spends more time near the nucleus than an electron with high l. Thus an electron with large l will have the nuclear charge more screened out and therefore will feel a reduced nuclear charge resulting in a larger energy. Thus *for a given n, states with higher l have higher energy.* [Shankar, pg. 379-380, 1980].

This lifting of degeneracy is shown in Fig. 11.2.

11.1.3 Non-Degenerate Model with Surface Effects

It might seem very peculiar that, for example, the $3p$ electrons in Fig. 11.2 can really be considered to move in a Coulomb mean field. That this is really so is beautifully illustrated in Fig. 11.3 which shows that *for a typical electron not near the edge of the atom, the effects of all the electrons cancel out. Thus for intermediate distance electrons the non-degenerate shell model of Fig. 11.2 is basically correct.* Fig. 11.3 clearly shows that the reason the many-body problem reduces to a 1-body problem is because the effects of the many bodies cancel out.

However for electrons near the edge of the atom, surface effects come into play and the Coulomb mean field picture breaks down. The reason for this is shown in Fig. 11.3. Thus the shell model picture of Fig. 11.2 is *not* correct for the outermost electrons.

The way that the outer shells are filled is shown in Fig. 11.5. Thus for $_{60}Nd$ the outer *shell* is not $(4s)^2\,(4p)^6\,(4d)^{10}\,(4f)^{14}$ but rather $(4s)^2\,(4p)^6\,(4d)^{10}\,(5s)^2\,(5p)^6\,(6s)^2\,(4f)^4$.

Fig. 11.5 neatly explains the Periodic Table. All students should fill all the shells in Fig. 11.5 and watch how the periodic table arises. (Exercise: do this). Fig. 11.5 is often represented in tabular form as shown in Table 11.1.

Fig. 11.5 and Table 11.1 are very misleading. They show you correctly how the outer shells fill, but Fig. 11.5 does **not** *represent the energy level diagram of* **any** *atom. The outer electrons are arranged according to Table 11.1 and Fig. 11.5 but the inner electrons of a particular atom are arranged according to Fig. 11.2. The clearest representation of this is shown in Fig. 11.6 which correctly shows the outer electrons and the inner electrons.*

Why then do people use misleading figures like Fig. 11.5 and Table 11.1? The chemical properties of atoms only depend on the outer electrons. The inner electrons are essentially irrelevant, and so who cares how they are arranged? It doesn't really matter.

In order to avoid confusion it is highly recommended that Fig. 11.6 be studied carefully.

11.1.4 Spectra

We have seen that the outer shells are filled according to Fig. 11.5, but that the inner shells are more properly represented in Fig. 11.2. (And both figures are combined in Fig. 11.6). What figure are we to use for explaining the spectrum of an atom? Well the spectrum is always due to excitations of the outer electrons and so obviously we use Fig. 11.5. (This supports what we said earlier. Neither the chemical properties *or* the spectra care about the inner electrons. It's the outer electrons, hence Fig. 11.5, that determine all the interesting behavior.) We summarize this in Table 11.2.

The ground state configuration of Hydrogen is $(1s)^1$. For Sodium it is $(1s)^2(2s)^2(2p)^6(3s)^1$. The *spectrum of Hydrogen* is determined by transitions of the $(1s)^1$ electron to the higher states such as $(2s)^1$ or $(2p)^1$ or $(3s)^1$ or $(3p)^1$ or $(3d)^1$, etc. The *spectrum of Sodium* is determined by transitions of the $(3s)^1$ electron to states like $(3p)^1$ or $(4s)^1$ etc. (Actually energetic transitions also occur by promoting say one of the $(2p)^6$ electrons to say $(3s)^1$ or higher).

When electronic transitions occur, a photon carries off the excess energy and *angular momentum* according to certain selection rules. Thus we need to know the angular momenta of the atomic states undergoing transitions. Let us look at Hydrogen and determine the angular momenta of the ground and excited states.

Example 11.1 Determine the angular momentum for the $n = 1, 2$ levels of Hydrogen.

Solution

$$\begin{aligned}
&\text{The ground state of } H \text{ is } (1s)^1 \\
&\text{Thus } l = 0 \;\; s = 1/2 \Rightarrow j = 1/2 \\
&\;\Rightarrow n^{2S+1}L_J = 1^2S_{1/2} \\
&\text{The first excited states are } (2s)^1 \text{ or } (2p)^1 \\
&(2s)^1 \; : \; l = 0 \;\; s = 1/2 \Rightarrow j = 1/2 \\
&\;\Rightarrow n^{2S+1}L_J = 2^2S_{1/2} \\
&(2p)^1 \; : \; l = 1 \;\; s = \frac{1}{2} \Rightarrow j = 1/2, 3/2 \\
&\;\Rightarrow n^{2S+1}L_J = 2^2P_{1/2}, 2^2P_{3/2}
\end{aligned}$$

(do Problem 11.1)

These excited states and possible transitions are shown in Fig. 11.7. The figure shows how the $2^2P_{1/2}$ and $2^2P_{3/2}$ states are split by the spin-orbit interaction (which does not affect the S state). Also the higher states are also split by the spin-orbit interaction. The figure also shows how the $^2S_{1/2}$ and $^2P_{1/2}$ states are split. This is called the *Lamb Shift* and is a result of quantum fluctuations of the vacuum. (See [Beiser, pg. 268, 1987; Ziock, pg. 139-140, 1969]).

11.2 Hartree-Fock Self Consistent Field Method

See [Matthews, pg. 44, 1986].

11.3 Nuclear Shell Model

The effect of spin-orbit coupling in atoms is rather small and has no effect on the ground state configurations in the periodic table. However in nuclei, Mayer and Jensen showed in 1949 that the nuclear spectra would only be explained by assuming a rather large spin-orbit interaction. [Beiser, pg. 430, 1987].

The nuclear shell model is shown in Fig. 11.8 which represents the filling of the *outer shells* and does *not* represent the energy level diagram of any *particular* nucleus [Eisberg and Resnick, pg. 585, 1974]. Thus the Fig. 11.8 is "analogous to the diagram that could be constructed for atoms using only the left side" of Fig. 11.6 [Eisberg and Resnick, pg. 585, 1974].

The left side of Fig. 11.8 is analogous to the right side of Fig. 11.5, both of which contain no spin-orbit coupling. If spin orbit coupling *was* large in atoms, then the right side of Fig. 11.5 would be further split as in the right side of Fig. 11.8. In atoms we have only one type of particle, namely electrons. However in nuclei we have two types of particle, namely protons and neutrons. Thus we have a *double* copy of Fig. 11.8; one for protons and one for neutrons.

11.3.1 Nuclear Spin

For most atoms and weak magnetic fields the LS coupling scheme is used to figure out the total spin of the atomic ground states and excited states. However for the majority of nuclei it is the jj coupling scheme which holds [Beiser, pg. 430, 1987]. Actually LS coupling holds only for the lightest nuclei.

Much of nuclear physics research is devoted to a study of nuclear excited states. In atoms these are generally due to single or multiparticle excitations of atomic shell orbitals. The same is true for nuclear physics, but many nuclei are not spherical in shape and so one has to work out the shell model scheme *without the assumption of spherical symmetry.* Such a shell model scheme as a function of nuclear deformation is shown in Fig. 11.9.

Consider the nuclear energy level diagram for the excited states of ^{41}Ca shown in Fig. 11.10. From Fig. 11.8 we see that ^{41}Ca has the major core ^{40}Ca with 1 nucleon in the $4f_{7/2}$ state. This is confirmed in the energy level diagram of Fig. 11.10 where the ground state is 7/2. The next level in Fig. 11.8 is the $3p_{3/2}$ state and we would expect the first excited state of ^{41}Ca to have the nucleon promoted to this state. This is indeed true. The first excited state in Fig. 11.10 is indeed 3/2.

However the excited states of nuclei involve much more than simple excitation to shell model states. Nuclei vibrate and rotate and so have excited states corresponding to these modes, some of which appear in the energy level diagram of Fig. 11.10. Vibrational and rotational modes are not that important in atoms, but they *are* quite important in the spectra of *molecular* as well as nuclei.

11.4 Quark Shell Model

Chapter 12

DIRAC NOTATION

12.1 Finite Vector Spaces

12.1.1 Real Vector Space

A vector space consists of a set of vectors which can be added to each other or multiplied by scalars to produce other vectors. (See pg. 76 of [Griffiths, 1995] for a formal definition.) The scalars are real numbers and thus we have a real vector space.

A vector **A** can be written in terms of components A_i and unit vectors $\hat{e}_i$ as

$$\mathbf{A} = \sum_i A_i \hat{e}_i \tag{12.1}$$

Here is an example of a scalar A_i multiplying a vector $\hat{e}_i$ to produce another vector **A**. The components A_i are real numbers.

We can also write this in *Dirac notation* as

$$|A\rangle = \sum_i A_i \mid \hat{e}_i\rangle \equiv \sum_i A_i \mid i\rangle \tag{12.2}$$

where $|A\rangle \equiv \mathbf{A}$ and $|\hat{e}_i\rangle \equiv |i\rangle \equiv \hat{e}_i$. We are just using different symbols. Another way to write this is

$$\langle A| \equiv \sum_i A_i \langle i| \tag{12.3}$$

and for real vector spaces there is no distinction between $|\ \ \rangle$ or $\langle\ \ |$.

The *inner product* (often called the scalar product) of two vectors is

$$\begin{aligned}\mathbf{A}\cdot\mathbf{B} &= \sum_i\sum_j A_iB_j\hat{e}_i\cdot\hat{e}_j \\ &\equiv \sum_i\sum_j A_iB_jg_{ij} \qquad (12.4)\end{aligned}$$

where the *metric tensor* is defined as

$$g_{ij}\equiv\hat{e}_i\cdot\hat{e}_j \qquad (12.5)$$

For orthonormal unit vectors, $g_{ij}=\delta_{ij}$ and

$$\mathbf{A}\cdot\mathbf{B}=\sum_i A_iB_i \qquad (12.6)$$

which gives *Pythagoras' theorem* as

$$A^2\equiv\mathbf{A}\cdot\mathbf{A}=\sum_i A_i^2=A_x^2+A_y^2 \qquad (12.7)$$

in two dimensions. In Dirac notation we write

$$\mathbf{A}\cdot\mathbf{B}\equiv\langle\mathbf{A}\mid\mathbf{B}\rangle \qquad (12.8)$$

In ordinary notation components A_i are found according to

$$\hat{e}_i\cdot\mathbf{A}=\sum_j A_j\hat{e}_i\cdot\hat{e}_j=A_i \qquad (12.9)$$

where we have used $\hat{e}_i\cdot\hat{e}_j=\delta_{ij}$. In Dirac notation this is

$$g_{ij}\equiv\hat{e}_i\cdot\hat{e}_j=\boxed{\langle i\mid j\rangle=\delta_{ij}} \qquad (12.10)$$

giving

$$\langle i\mid A\rangle=\sum_j A_j\langle i\mid j\rangle=A_i \qquad (12.11)$$

Finally in ordinary notation we can write

$$\mathbf{A}=\sum_i A_i\hat{e}_i=\sum_i\hat{e}_i\cdot\mathbf{A}\hat{e}_i=\sum_i\hat{e}_i\hat{e}_i\cdot\mathbf{A} \qquad (12.12)$$

and because we must have left hand side = right hand side we have the identity

$$\sum_i \hat{e}_i \hat{e}_i \cdot = 1 \tag{12.13}$$

Similarly

$$|A\rangle = \sum_i A_i \mid i\rangle = \sum_i \langle i \mid A\rangle \ |i\rangle = \sum |i\rangle\langle i \mid A\rangle$$

yielding

$$\boxed{\sum_i |i\rangle \ \langle i| = 1} \tag{12.14}$$

which is called the *completeness* or *closure* relation because of its similarity to (**??**). The usefulness of (12.14) is that it can always be sandwiched between things because it is unity. For example

$$\langle A \mid B\rangle = \sum_i \langle A \mid i\rangle\langle i \mid B\rangle = \sum_i A_i B_i \tag{12.15}$$

In old notation this would be

$$\mathbf{A} \cdot \mathbf{B} = \sum_i \mathbf{A} \cdot \hat{e}_i \hat{e}_i \cdot \mathbf{B} = \sum_i A_i B_i \tag{12.16}$$

Similarly writing a vector in terms of components,

$$|A\rangle = \sum_i |i\rangle \ \langle i \mid A\rangle = \sum_i A_i \mid i\rangle \tag{12.17}$$

or

$$\mathbf{A} = \sum_i \hat{e}_i \hat{e}_i \cdot \mathbf{A} = \sum_i A_i \hat{e}_i \tag{12.18}$$

12.1.2 Complex Vector Space

In a complex vector space the scalars can be complex numbers. That is, components can be complex. Recall that complex numbers can be represented as

$$z = x + iy \tag{12.19}$$

Now $zz = x^2 + i2xy - y^2$ whereas

$$|z|^2 \equiv z^* z = x^2 + y^2 \tag{12.20}$$

which looks like Pythagoras' theorem. This will help us define an inner product for complex vectors.

Let's consider a two-dimensional complex vector

$$\mathbf{z} \equiv z_1 \hat{e}_1 + z_2 \hat{e}_2 \tag{12.21}$$

where z_1 and z_2 are complex components. That is $z_1 = x_1 + iy$, and $z_2 = x_2 + iy_2$. The inner product of $\mathbf{z}$ with itself should give Pythagoras' theorem as in (12.7). But if we use the formula (12.7) as $z^2 = \mathbf{z} \cdot \mathbf{z} = \sum\limits_i z_i^2$ we get

$$z^2 = \mathbf{z} \cdot \mathbf{z} = \sum_i z_i^2 = z_1^2 + z_2^2 = x^2 - y^2 \tag{12.22}$$

which is the wrong sign. Thus *instead* of (12.6) as the scalar product, we define the scalar product for a complex vector space as

$$\boxed{\mathbf{A} \cdot \mathbf{B} \equiv \langle A \mid B \rangle \equiv \sum_i A_i^* B_i} \tag{12.23}$$

In 2-dimensions this gives $\mathbf{A} \cdot \mathbf{B} = \langle A \mid B \rangle = A_1^* B_1 + A_2^* B_2$ which results in

$$z^2 = \mathbf{z} \cdot \mathbf{z} = \langle z \mid z \rangle = \sum_i z_i^* z_i = x^2 + y^2 \tag{12.24}$$

which *does* give Pythagoras theorem.

Now we see the *advantage of Dirac notation.* For complex vectors (in 2-dimensions) define

$$|A\rangle \equiv A_1 \hat{e}_1 + A_2 \hat{e}_2 \tag{12.25}$$

but define

$$\langle A| \equiv A_1^* \hat{e}_1 + A_2^* \hat{e}_2 \tag{12.26}$$

which automatically gives $\langle A \mid B \rangle = A_1^* B_1 + A_2^* B_2$. *The distinction between (12.25) and (12.26) cannot be made with ordinary vector notation* $\mathbf{A}$. More generally

$$\boxed{|A\rangle \equiv \sum_i A_i \mid i\rangle} \tag{12.27}$$

and

$$\boxed{\langle A| \equiv \sum_i A_i^* \langle i|} \tag{12.28}$$

from which *follows*

$$\begin{aligned}\langle A \mid B\rangle &= \sum_i \sum_j A_i^* B_j \langle i \mid j\rangle = \sum_i \sum_j A_i^* B_j \delta_{ij} \\ &= \sum_i A_i^* B_i \end{aligned} \tag{12.29}$$

With ordinary vector notation we have to *define* the scalar product in (12.23). But with Dirac notation (12.27) and (12.28) *imply* the scalar product $\langle A \mid B\rangle = \sum\limits_i A_i^* B_i$. Thus in defining a complex vector space from scratch one can either start with $\langle A \mid B\rangle \equiv \sum\limits_i A_i^* B_i$ *or* one can start with $|A\rangle \equiv \sum\limits_i A_i \mid i\rangle$ and $\langle A| \equiv \sum\limits_i A_i\ \langle i|$. We prefer the latter.

Notice that

$$\boxed{\langle A \mid B\rangle = \langle B \mid A\rangle^*} \tag{12.30}$$

(do Problem 12.1) Actually we could start with *this* as a definition of our complex vector space. (do Problem 12.2). Also note that

$$\boxed{\langle A \mid xB\rangle = x\ \langle A \mid B\rangle} \tag{12.31}$$

and

$$\boxed{\langle xA \mid B\rangle = x^*\ \langle A \mid B\rangle} \tag{12.32}$$

where x is a (complex) scalar. (Exercise: prove these relations)

12.1.3 Matrix Representation of Vectors

For real vector spaces we can also represent the vectors as matrices. For example, in 2-dimensions

$$\mathbf{B} \equiv |B\rangle \equiv \begin{pmatrix} B_1 \\ B_2 \end{pmatrix} \tag{12.33}$$

For the inner product $\mathbf{A} \cdot \mathbf{B}$ we *want* our answer to be $\mathbf{A} \cdot \mathbf{B} \equiv \langle A \mid B\rangle = A_1B_1 + A_2B_2$. This will work *if*

$$\langle A| \equiv (A_1 \quad A_2) \tag{12.34}$$

because then

$$\mathbf{A} \cdot \mathbf{B} = \langle A \mid B\rangle = (A_1 \quad A_2)\begin{pmatrix} B_1 \\ B_2 \end{pmatrix} = A_1B_1 + A_2B_2 \tag{12.35}$$

Thus again we see the *advantage of Dirac notation.* Ordinary vector notation $\mathbf{A}$ provides us with no way to distinguish (12.33) and (12.34). Notice above that $(A_1 \quad A_2) = \langle A|$ is the *transpose* of $|A\rangle = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$.

For complex vector spaces we keep (12.33). For the inner product $\mathbf{A} \cdot \mathbf{B}$ we *want* our answer to be $\mathbf{A} \cdot \mathbf{B} \equiv \langle A \mid B\rangle = A_1^*B_1 + A_2^*B_2$. This will work *if*

$$\langle A| \equiv (A_1^* \quad A_2^*) \equiv |A\rangle^\dagger \tag{12.36}$$

which is the *transpose conjugate* of $|A\rangle = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$, often called the *Hermitian conjugate.* For a general matrix C the Hermitian conjugate $C^\dagger$ is defined as

$$C^\dagger \equiv C_{ji}^* \tag{12.37}$$

(interchange rows and columns and take the complex conjugate of everything.) A matrix H is called *Hermitian* if

$$H^\dagger = H \tag{12.38}$$

12.1.4 One-Forms

Note that in our matrix representation of real vectors we found that $|A\rangle = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$ and $\langle A| = (A_1 \quad A_2)$ are rather different objects. For complex vectors

$|A\rangle = \sum_i A_i \mid i\rangle$ and $\langle A| = \sum_i A_i \ \langle i|$ are also different objects. We seem to have come across *two* different types of vector.

In general $|A\rangle$ is called a *vector* and $\langle A|$ is called a *covector*. Other names are $|A\rangle$ is a *contravariant vector* and $\langle A|$ is a *covariant vector* or *one-form*. This *dual* nature of vector spaces is a very general mathematical property. $|A\rangle$ is a space and $\langle A|$ is the *dual space*.

By the way, in Dirac notation $\langle A|$ is called a *bra* and $|A\rangle$ a *ket*. Thus $\langle A \mid B\rangle$ is a *braket*.

12.2 Infinite Vector Spaces

In the previous section the index i occurring in $\mathbf{A} = |A\rangle = \sum_i A_i \mid i\rangle$ counted the dimensions. For a 2-dimensional space i has values $i = 1, 2$ and for 3-dimensions values $i = 1, 2, 3$ and so on. We can imagine an infinite number of dimensions, but it is more convenient to use a *continuous index* x rather than a discrete index i, and integrals rather than sums. Thus (using a different symbol ψ instead of A)

$$\psi = \sum_i \psi_i \hat{e}_i = \int_{-\infty}^{\infty} dx \ \psi(x)\hat{e}(x) \tag{12.39}$$

is the appropriate generalization. $\psi(x)$ are the infinite number of components of ψ and $\hat{e}(x)$ are the infinite number of basis vectors. In Dirac notation this is

$$\boxed{|\psi\rangle = \sum_i \psi_i \mid i\rangle = \int_{-\infty}^{\infty} dx \ \psi(x) \mid x\rangle} \tag{12.40}$$

We have written the infinite number of components as $\psi(x)$ to purposely suggest the connection with *functions*. Thus the infinite components of the abstract vector $|\psi\rangle$ are nothing more than ordinary functions! This is where vector space theory and analysis meet!

Also as all students know, *the components of a vector depend on the basis chosen.* $|\psi\rangle$ is the abstract vector but ψ_i change depending on whether the basis vectors $|i\rangle$ are say Cartesian $(\hat{i}, \hat{j}, \hat{k})$ or Spherical $(\hat{e}_r, \hat{e}_\theta, \hat{e}_\phi)$. Similarly for infinite vectors the components depend on the basis. Equation (12.40) can be written

$$|\psi\rangle = \int_{-\infty}^{\infty} dx\ \psi(x) \mid x\rangle = \int_{-\infty}^{\infty} dp\ \psi(p) \mid p\rangle \tag{12.41}$$

$\psi(x)$ is the functional representation of $|\psi\rangle$ in coordinate space ($|x\rangle$) whereas $\psi(p)$ is the representation in momentum space ($|p\rangle$). $\psi(x)$ and $\psi(p)$ are related via a Fourier transform. We shall have more to say about this later.

Let's not bother with real infinite vectors but instead consider *complex infinite vector space* often called *Hilbert space.* This is the space where quantum mechanics belongs because the wave functions $\psi(x)$ can be real or complex $\psi^*(x)$. Thus generalize (12.28) and (12.40) to

$$\boxed{\langle\psi| = \sum_i \psi_i^*\ \langle i| = \int_{-\infty}^{\infty} dx\ \psi^*(x)\langle x|} \tag{12.42}$$

The generalization of $\langle i \mid j\rangle = \delta_{ij}$ is

$$\boxed{\langle x \mid x'\rangle = \delta(x - x')} \tag{12.43}$$

where $\delta(x - x')$ is the Dirac delta function, defined as

$$\int_{-\infty}^{\infty} f(x')\delta(x - x')dx' \equiv f(x) \tag{12.44}$$

The inner product follows as

$$\begin{aligned}
\langle\phi \mid \psi\rangle &= \int dx\ \phi^*(x)\ \langle x| \int_{-\infty}^{\infty} dx'\ \psi(x') \mid x'\rangle \\
&= \int dx \int dx'\ \phi^*(x)\psi(x')\ \langle x \mid x'\rangle \\
&= \int dx\ \phi^*(x)\psi(x)
\end{aligned} \tag{12.45}$$

Thus the "length" or *norm* of the vector $|\psi\rangle$ is

$$\boxed{|\psi|^2 \equiv \langle \psi \mid \psi \rangle = \int dx\ \psi^*(x)\psi(x)} \tag{12.46}$$

The components are obtained in the usual way. Using (12.40) gives

$$\begin{aligned} \langle x \mid \psi \rangle &= \langle x| \int_{-\infty}^{\infty} dx'\ \psi(x') \mid x' \rangle \\ &= \int dx'\ \psi(x')\ \langle x \mid x' \rangle \\ &= \psi(x) \end{aligned}$$

Thus the components are

$$\boxed{\langle x \mid \psi \rangle = \psi(x)} \tag{12.47}$$

and

$$\boxed{\langle \psi \mid x \rangle = \psi^*(x)} \tag{12.48}$$

Therefore the completeness or closure relation is

$$\boxed{\int dx\ |x\rangle\ \langle x| = 1} \tag{12.49}$$

analogous to (12.14). (do Problem 12.3 and 12.4)

Everyone should now go back and review Section 2.3.6.

12.3 Operators and Matrices

12.3.1 Matrix Elements

Suppose we have an operator $\hat{A}$ turning an old vector $\mathbf{x}$ into a new vector $\mathbf{x}'$ as in

$$\mathbf{x}' = \hat{A}\mathbf{x} \tag{12.50}$$

We would like to know how the components transform. We already know that $\langle e_i \mid \mathbf{x}\rangle \equiv \langle i \mid \mathbf{x}\rangle = x_i$. Thus

$$\begin{aligned} \langle e_i \mid \mathbf{x}'\rangle \equiv \langle i \mid \mathbf{x}'\rangle \equiv x_i' &= \langle e_i \mid A\mathbf{x}\rangle \\ &= \langle e_i \mid A\sum_j x_j \mid e_j\rangle \\ &= \sum_j \langle e_i \mid A \mid e_j\rangle x_j \qquad (12.51) \\ &\equiv \sum_j \langle i \mid A \mid j\rangle x_j \end{aligned}$$

Defining

$$\boxed{\langle e_i \mid \hat{A} \mid e_j\rangle \equiv \langle i \mid A \mid j\rangle = A_{ij}} \qquad (12.52)$$

gives

$$x_i' = \sum_j A_{ij} x_j \qquad (12.53)$$

for the transformation of components. We have had to introduce matrix elements A_{ij} in (12.52). Notice that *the matrix elements* A_{ij} *of the operator* A *depend on what basis* $|\hat{e}_i\rangle$ *is chosen.* This is exactly analogous to our previous result where we found that vector components x_i depend on the chosen basis. Equation (12.52) is a *matrix representation of the operator.*

Just as a vector $\mathbf{x}$ can be represented by components x_i so too is an operator $\hat{A}$ represented by components A_{ij}.

We can work out similar results for our Hilbert space. The analog of (12.50)

$$|\psi'\rangle = \hat{A} \mid \psi\rangle \equiv |\hat{A}\psi\rangle \qquad (12.54)$$

To work out how the components $\psi(x) \equiv \langle x \mid \psi\rangle$ transform we write

$$\begin{aligned} \langle x \mid \psi'\rangle \equiv \psi'(x) &= \langle x \mid \hat{A}\psi\rangle \\ &= \langle x \mid \hat{A}\int dx'\ \psi(x') \mid x'\rangle \\ &= \int dx'\ \langle x \mid \hat{A} \mid x'\rangle\ \psi(x') \qquad (12.55) \end{aligned}$$

which *is* our formula for how the components transform and $\langle x \mid \hat{A} \mid x'\rangle$ is an *infinite-dimensional matrix element.*

Example 12.1 Work out the formulae for transformation of components using the closure relations.

Solution A) Let's first do the finite-dimensional case.

$$\mathbf{x}' = \hat{A}\ \mathbf{x}$$

$$\begin{aligned} x_i' = \langle i \mid \mathbf{x}' \rangle &= \langle i \mid \hat{A}\mathbf{x} \rangle \\ &= \sum_j \langle i \mid \hat{A} \mid j \rangle\ \langle j \mid \mathbf{x} \rangle \\ &= \sum_j A_{ij}\ x_j \end{aligned}$$

B) Now the Hilbert space.

$$|\psi' \rangle = \hat{A} \mid \psi \rangle$$

$$\begin{aligned} \psi'(x) = \langle x \mid \psi' \rangle &= \langle x \mid \hat{A} \mid \psi \rangle \\ &= \int dx'\ \langle x \mid \hat{A} \mid x' \rangle\ \langle x' \mid \psi \rangle \\ &= \int dx'\ \langle x \mid \hat{A} \mid x' \rangle\ \psi(x') \end{aligned}$$

We see that this method is a little easier and clearer.

Finally we examine matrix multiplication. Suppose we have operators $A = BC$. We can get matrix elements as follows.

$$\begin{aligned} A_{ij} &\equiv \langle i \mid A \mid j \rangle = \langle i \mid BC \mid j \rangle \\ &= \sum_k \langle i \mid B \mid k \rangle\ \langle k \mid C \mid j \rangle \\ &= \sum_k B_{ik} C_{kj} \qquad (12.56) \end{aligned}$$

which is the usual matrix multiplication formula which we have obtained with the closure relation. Similarly for Hilbert space

$$\begin{aligned} \langle x \mid A \mid x' \rangle &= \langle x \mid BC \mid x' \rangle \\ &= \int dx''\ \langle x \mid B \mid x'' \rangle\ \langle x'' \mid C \mid x' \rangle \qquad (12.57) \end{aligned}$$

which is our matrix multiplication formula in Hilbert space.

12.3.2 Hermitian Conjugate

The Hermitian conjugate $A^\dagger$ of a matrix A is defined as the complex transpose

$$A^\dagger \equiv \tilde{A}^* \tag{12.58}$$

where $\tilde{A}$ is the transpose. In component form this is

$$A^\dagger_{ij} = A^*_{ji} \tag{12.59}$$

or

$$\langle i \mid A \mid j\rangle^\dagger = \langle j \mid A \mid i\rangle^* \tag{12.60}$$

This implies that

$$(AB)^\dagger = B^\dagger A^\dagger \tag{12.61}$$

(do Problem 12.5) In equation (12.36) we have the general result for a vector

$$\boxed{\langle\psi| = |\psi\rangle^\dagger} \tag{12.62}$$

and

$$\boxed{\langle\psi|^\dagger = |\psi\rangle} \tag{12.63}$$

Defining

$$A \mid \psi\rangle \equiv |A\psi\rangle \tag{12.64}$$

we also have

$$\boxed{\langle A^\dagger\phi \mid \psi\rangle = \langle\phi \mid A \mid \psi\rangle = \langle\phi \mid A\psi\rangle} \tag{12.65}$$

and

$$\boxed{\langle A\phi \mid \psi\rangle = \langle\phi \mid A^\dagger \mid \psi\rangle = \langle\phi \mid A^\dagger\psi\rangle} \tag{12.66}$$

Example 12.2 Show that $\langle A^\dagger\phi \mid \psi\rangle = \langle\phi \mid A \mid \psi\rangle$

Solution

$$\begin{aligned}\langle\phi \mid A \mid \psi\rangle &= |\phi\rangle^\dagger A \mid \psi\rangle \\ &= |\phi\rangle^\dagger A^{\dagger\dagger} \mid \psi\rangle \\ &= (A^\dagger \mid \phi\rangle)^\dagger \mid \psi\rangle \\ &\qquad \text{using } (AB)^\dagger = B^\dagger A^\dagger\end{aligned}$$

thus

$$\begin{aligned}\langle\phi \mid A \mid \psi\rangle &= |A^\dagger\phi\rangle^\dagger\ |\psi\rangle \\ &= \langle A^\dagger\phi \mid \psi\rangle\end{aligned}$$

(do Problem 12.6)

12.3.3 Hermitian Operators

An *operator H is Hermitian* if

$$H = H^\dagger$$

We shall now discuss several important properties of Hermitian operators.

Example 12.3 Prove that eigenvalues of Hermitian operators are real.

Solution Let H be a Hermitian operator and let λ be its eigenvalue. Thus

$$\begin{aligned}&H \mid \psi\rangle = \lambda \mid \psi\rangle \\ &\langle\psi \mid H \mid \psi\rangle = \lambda\langle\psi \mid \psi\rangle \\ =\ &\langle\psi \mid H^\dagger \mid \psi\rangle \\ =\ &\langle H\psi \mid \psi\rangle \\ =\ &\lambda^*\ \langle\psi \mid \psi\rangle\end{aligned}$$

Thus

$$\lambda = \lambda^*$$

Example 12.4 Prove that eigenvalues of Hermitian operators belonging to distinct eigenvalues are orthogonal.

Solution Suppose we have two distinct eigenvalues $\lambda \neq \mu$ such that

$$\begin{aligned} H \mid \psi\rangle &= \lambda \mid \psi\rangle \\ \text{and } H \mid \phi\rangle &= \mu \mid \phi\rangle \end{aligned}$$

Thus

$$\begin{aligned} &\langle\phi \mid H \mid \psi\rangle = \lambda \ \langle\phi \mid \psi\rangle \\ = \ &\langle\phi \mid H^\dagger \mid \psi\rangle \\ = \ &\langle H\phi \mid \psi\rangle \\ = \ &\mu^* \ \langle\phi \mid \psi\rangle \end{aligned}$$

but $\lambda = \lambda^*$ and $\mu = \mu^*$. Thus if $\lambda \neq \mu$ we must have

$$\langle\phi \mid \psi\rangle = 0$$

which means $|\phi\rangle$ and $|\psi\rangle$ are orthogonal.

Thus we have the following important properties of Hermitian operators.

1. *Eigenvalues of Hermitian operators are real.*
2. Eigenvectors of Hermitian operators belonging to distinct eigenvalues are orthogonal.
3. Eigenvectors of Hermitian operators *span* the space (i.e. form a complete set).

   Items 2) and 3) can be combined into:
4. *Eigenvectors of Hermitian operators form a CON set.*

(Note: A set of vectors is said to *span* the space if every other vector can be written as a linear combination of this set. For infinite vectors this means they form a *complete set.*)

1) implies that *Hermitian operators correspond to Observables.*

3) implies that the *eigenvectors of Hermitian operators (our observables) form basis vectors.*

12.3.4 Expectation Values and Transition Amplitudes

We previously defined the expectation value of an operator as

$$\langle A \rangle \equiv \int dx \ \psi^*(x) A \psi(x) \tag{12.67}$$

In Dirac notation we write

$$\langle A \rangle = \langle \psi \mid A \mid \psi \rangle \tag{12.68}$$

Example 12.5 Show that these are equivalent.

Solution

$$\begin{aligned} \langle A \rangle &\equiv \langle \psi \mid A \mid \psi \rangle \\ &= \int dx \, dx' \ \langle \psi \mid x \rangle \ \langle x \mid A \mid x' \rangle \ \langle x' \mid \psi \rangle \\ &= \int dx \, dx' \ \psi^*(x) \ \langle x \mid A \mid x' \rangle \ \psi(x') \end{aligned}$$

we now assume A is a *local* operator

$$\text{i.e. } \langle x \mid A \mid x' \rangle \equiv A \ \delta(x - x')$$

$$\Rightarrow \quad \langle A \rangle = \int dx \ \psi^*(x) A \ \psi(x)$$

We can also define a *transition amplitude*

$$\langle \psi \mid A \mid \phi \rangle = \int dx \ \psi^*(x) \ A\phi(x)$$

where A takes the wave function $|\phi\rangle$ to $|\psi\rangle$. This $\langle \psi \mid A \mid \phi \rangle$ is nothing more than a *matrix element.* Thus we see that the expectation value $\langle A \rangle = \langle \psi \mid A \mid \psi \rangle$ is just a *diagonal matrix element.*

12.4 Postulates of Quantum Mechanics (Fancy Version)

In Chapter 4 we discussed the postulates of quantum mechanics in terms of the wave function $\Psi(x,t)$. However, now we see that this is only the component of an abstract vector $|\Psi(t)\rangle$. We shall now re-state the postulates of quantum mechanics using Dirac notation.

1. To each state of a physical system there corresponds a state vector $|\Psi(t)\rangle$.
2. The time development of the state vector is determined by the Schrödinger equation
$$\hat{H} \mid \Psi\rangle = i\hbar\frac{\partial}{\partial t} \mid \Psi\rangle$$
3. (Born Hypothesis) $|\psi|^2 \equiv \langle\psi \mid \psi\rangle$ is the probability density.
4. To every physical observable b there corresponds a Hermitian operator $\hat{B}$ such that $\hat{B} \mid i\rangle = b_i \mid i\rangle$.
5. (Expansion Postulate) $|i\rangle$ form a CON set such that any state vector can be written $|\psi\rangle = \sum\limits_i c_i \mid i\rangle$ (i.e. eigenkets of an observable form *base* kets).
6. (Measurement Postulate) If the state of a system is $|\psi\rangle$ then the probability that a measurement finds the system in state $|\beta\rangle$ is $|\langle\beta \mid \psi\rangle|^2$.
7. (Reduction Postulate) A coherent superposition $|\psi\rangle$ collapses to an eigenstate $|i\rangle$ upon measurement.

12.5 Uncertainty Principle

The proof of the Uncertainty Principle is given in [Griffith, Pg. 109, 1995]. It is better stated as a theorem.

Uncertainty Principle If $[A,B] = iC$

$$\text{then } \sigma_A\sigma_B \geq \frac{1}{2}|\langle C\rangle|$$

where σ_A and σ_B are the uncertainty in A and B (sometimes written ΔA and ΔB) and $\langle C\rangle$ is the expectation value of C.

Example 12.6 Prove the momentum uncertainty principle, namely $\sigma_x\sigma_p \geq \frac{\hbar}{2}$.

Solution

$$\begin{aligned} [x,p] &= i\hbar \\ \therefore\ \ C &= \hbar \\ \Rightarrow\ \ \sigma_x\sigma_p &\geq \frac{1}{2}|\langle\hbar\rangle = \frac{\hbar}{2} \\ \therefore\ \ \sigma_x\sigma_p &\geq \frac{\hbar}{2} \end{aligned}$$

At this point all students should read Section 3.4.3 of [Griffiths, 1995] dealing with the energy-time uncertainty principle. Note especially the physical interpretation on Pg. 115.

Chapter 13

TIME-INDEPENDENT PERTURBATION THEORY, HYDROGEN ATOM, POSITRONIUM, STRUCTURE OF HADRONS

We have been able to solve the Schrödinger equation exactly for a variety of potentials such as the infinite square well, the finite square well, the harmonic oscillator and the Coulomb potentials. However there are many cases in nature where it is not possible to solve the Schrödinger equation exactly such as the Hydrogen atom in an external magnetic field.

We are going to develop some approximation techniques for solving the Schrödinger equation in special situations. A very important case occurs when the total potential is a sum of an exactly solvable potential plus a *weak*, or small, potential. In technical language this weak potential is called a *perturbation*. The mathematical techniques of perturbation theory are among the most widely used in physics. The great successes of the quantum field theory of electromagnetism, called Quantum Electrodynamics, hinged in great part upon the perturbation analysis involved in the so-called *Feynman diagrams*. Such a perturbative framework was possible due to the weakness of the electromagnetic interactions. The same can be said of the weak interactions known as Quantum Flavordynamics. In general however the *strong* interactions between quarks (Quantum Chromodynamics) cannot be analyzed within a perturbative framework (except at very large momentum transfers) and this has held up progress in the theory of strong interactions. For example, it is known that quarks are permanently confined within hadrons, yet the confinement mechanism is still not understood theoretically.

Consider the time-independent Schrödinger equation

$$H \mid n\rangle = E_n \mid n\rangle \tag{13.1}$$

which we wish to solve for the energies E_n and eigenkets $|n\rangle$. Suppose the Hamiltonian H consists of a piece H_0 which is exactly solvable and a small perturbation λV. (We write λV instead of V because we are going to use λ as an expansion parameter.) That is

$$H = H_0 + \lambda V \tag{13.2}$$

where we assume that we know the solution of

$$H_0 \mid n_0\rangle = E_{n_0} \mid n_0\rangle \tag{13.3}$$

Note that the subscript '0' denotes the unperturbed solution. It has nothing to do with the ground state when $n = 0$.

So we *know* the solution to (13.3) but we *want* the solution to (13.1). Let's expand the state ket and energy in a power series

$$|n\rangle = \sum_{i=0}^{\infty} \lambda^i \mid n_i\rangle = |n_0\rangle + \lambda \mid n_1\rangle + \lambda^2 \mid n_2\rangle + \cdots \tag{13.4}$$

and

$$E_n = \sum_{i=0}^{\infty} \lambda^i E_{n_i} = E_{n_0} + \lambda E_{n_1} + \lambda^2 E_{n_2} + \cdots \tag{13.5}$$

where, for example, $\lambda \mid n_1\rangle$ and λE_{n_1} are the first order corrections to the exact unperturbed solutions for the state ket $|n_0\rangle$ and energy E_{n_0}.

Now simply substitute the expansions (13.4) and (13.5) into the Schrödinger equation (13.1) giving

$$(H_0 + \lambda V) \sum_{i=0}^{\infty} \lambda^i \mid n_i\rangle = \sum_{j=0}^{\infty} \lambda^j E_{n_j} \sum_{i=0}^{\infty} \lambda^i \mid n_i\rangle \tag{13.6}$$

or

$$\sum_i \lambda^i H_0 \mid n_i\rangle + \sum_i \lambda^{i+1} V \mid n_i\rangle = \sum_{ij} \lambda^{i+j} E_{n_j} \mid n_i\rangle \tag{13.7}$$

and now we *equate like powers of* λ.

Let's first equate coefficients of λ^0. In the first term of (13.7) this gives $i = 0$. *This does not mean that* $i = 0$ *in the second or third terms because the* i *is just a separate dummy variable in each of the three terms.* The second term would require $i + 1 = 0$ which is impossible for any value of positive–definite i and thus the second term must be absent. The third term $i+j = 0$ can only work for $i = 0$ and $j = 0$. Thus

$$\text{coefficients of } \lambda^0\text{:}\quad H_0 \mid n_0\rangle = E_{n_0} \mid n_0\rangle \tag{13.8}$$

or

$$(H_0 - E_{n_0} \mid n_0\rangle = 0 \tag{13.9}$$

which is just the unperturbed Schrödinger equation (13.3).

Now equate coefficients of λ^1. This gives $i = 1$ in the first term of (13.7). The second term is $i + 1 = 1$ giving $i = 0$ and the third term is $i + j = 1$ which can happen in two ways. Either $i = 0$ and $j = 1$ or $i = 1$ and $j = 0$. Thus

$$\text{coefficients of } \lambda^1\text{:}\; H_0 \mid n_1\rangle + V \mid n_0\rangle = E_{n_1} \mid n_0\rangle + E_{n_0} \mid n_1\rangle \tag{13.10}$$

or

$$(H_0 - E_{n_0} \mid n_1\rangle = (E_{n_1} - V) \mid n_0\rangle \tag{13.11}$$

Equating coefficients of λ^2 gives $i = 2$ in the first term of (13.7) and $i + 1 = 2$ giving $i = 1$ in the second term. The third term $i + j = 2$ can happen in three ways. Either $i = 0$ and $j = 2$ or $i = 1$ and $j = 1$ or $i = 2$ and $j = 0$. Thus

$$\text{coefficients of } \lambda^2\text{:}\; H_0 \mid n_2\rangle + V \mid n_1\rangle = E_{n_2} \mid n_0\rangle + E_{n_1} \mid n_1\rangle + E_{n_0} \mid n_2\rangle \tag{13.12}$$

or

$$(H_0 - E_{n_0}) \mid n_2\rangle = (E_{n_1} - V) \mid n_1\rangle + E_{n_2} \mid n_0\rangle \tag{13.13}$$

Similarly the coefficients of λ^3 give

$$(H_0 - E_{n_0}) \mid n_3\rangle = (E_{n_1} - V) \mid n_2\rangle + E_{n_2} \mid n_1\rangle + E_{n_3} \mid n_0\rangle \tag{13.14}$$

The general pattern is

$$\boxed{\begin{aligned}(H_0 - E_{n_0} \mid n_k\rangle = (E_{n_1} - V) \mid n_{k-1}\rangle + E_{n_2} \mid n_{k-2}\rangle \\ +E_{n_3} \mid n_{k-3}\rangle + \cdots \\ + \cdots E_{n_{k-1}} \mid n_1\rangle + E_{n_k} \mid n_0\rangle\end{aligned}} \tag{13.15}$$

This result is true for both degenerate and non-degenerate perturbation theory.

13.1 Non-degenerate Perturbation Theory

Let's now calculate the energies in perturbation theory.

Look at the zeroth order equation. Multiplying from the left with a bra $\langle n_0|$ gives

$$\langle n_0 \mid H_0 - E_{n_0} \mid n_0\rangle = 0 \tag{13.16}$$

or

$$E_{n_0} = \frac{\langle n_0 \mid H_0 \mid n_0\rangle}{\langle n_0 \mid n_0\rangle} \tag{13.17}$$

and assuming $|n_0\rangle$ is normalized via $\langle n_0 \mid n_0\rangle = 1$ gives

$$E_{n_0} = \langle n_0 \mid H_0 \mid n_0\rangle \tag{13.18}$$

as expected, and is the result that we already would have calculated from our exact unperturbed Schrödinger equation. That is E_{n_0} is *already* known. What interests us is the first order correction E_{n_1} to the unperturbed energy E_{n_0}. To extract E_{n_1} we multiply the first order equation (13.11) on the left again with the bra $\langle n_0|$ giving

$$\langle n_0 \mid H_0 \mid n_1\rangle - E_{n_0}\langle n_0 \mid n_1\rangle = E_{n_1} - \langle n_0 \mid V \mid n_0\rangle \tag{13.19}$$

Now

$$\langle n_0 \mid H_0 = \langle n_0 \mid H_0^\dagger = E_{n_0}\langle n_0| \tag{13.20}$$

because H_0 is Hermitian. Thus the left side of (13.19) is 0. (Note that $|n_0\rangle$ and $|n_1\rangle$ need *not* be orthogonal and thus $\langle n_0 \mid n_1\rangle$ is not 0 in general.) Thus (13.19) gives

$$\boxed{E_{n_1} = \langle n_0 \mid V \mid n_0\rangle \equiv V_{nn}}$$

(13.21)

which Griffiths [Griffiths, 1995] calls the most important result in quantum mechanics! It gives the first order correction to the energy in terms of the unperturbed state kets $|n_0\rangle$ which we already know.

Recall the complete expression for the energy in (13.5), which to first order becomes

$$\begin{aligned} E_n &= E_{n_0} + \lambda E_{n_1} \\ &= \langle n_0 \mid H_0 \mid n_0\rangle + \langle n_0 \mid \lambda V \mid n_0\rangle \end{aligned} \tag{13.22}$$

where λV is the complete perturbation. If you like you can now drop the expansion parameter λ and just write the perturbation as $\mathcal{V}$ in which case we have

$$E_{n_1} = \langle n_0 \mid \mathcal{V} \mid n_0\rangle \tag{13.23}$$

or

$$\begin{aligned} E_n &= E_{n_0} + E_{n_1} \\ &= \langle n_0 \mid H_0 \mid n_0\rangle + \langle n_0 \mid \mathcal{V} \mid n_0\rangle \end{aligned} \tag{13.24}$$

Example Griffiths example pg. 223

Example 14.1 Evaluate the second order expression for the energy.

Solution The second order expression is given in (13.13) and we wish to extract E_{n_2}. As before multiply from the left with $\langle n_0|$ giving (with the left hand side vanishing as before)

$$0 = E_{n_1}\langle n_0 \mid n_1\rangle - \langle n_0 \mid V \mid n_1\rangle + E_{n_2} \tag{13.25}$$

Now $|n_0\rangle$ and $|n_1\rangle$ are not necessarily orthogonal (OG) and we are stuck with the term $\langle n_0 \mid n_1\rangle$. Can we *construct* $|n_1\rangle$ OG to $|n_0\rangle$? Yes. Define

$$|n_1'\rangle \equiv |n_1\rangle + a_1 \mid n_0\rangle \tag{13.26}$$

and evaluate $(H_0 - E_{n_0}) \mid n_1'\rangle$ giving

$$(H_0 - E_{n_0}) \mid n_1'\rangle = (H_0 - E_{n_0}) \mid n_1\rangle + a_1(H_0 - E_{n_0}) \mid n_0\rangle$$

The last term is 0 giving $(H_0 - E_{n_0}) \mid n_1'\rangle = (H_0 - E_{n_0}) \mid n_1\rangle$.

Thus $|n_1'\rangle$ and $|n_1\rangle$ obey the *same equation*. Let's pick

$$a_1 \equiv -\frac{\langle n_0 \mid n_1\rangle}{\langle n_0 \mid n_0\rangle} \tag{13.27}$$

Now let's test the orthogonality of $|n_1'\rangle$ and $|n_0\rangle$.

$$\langle n_0 \mid n_1'\rangle = \langle n_0 \mid n_1\rangle - \frac{\langle n_0 \mid n_1\rangle}{\langle n_0 \mid n_0\rangle}\langle n_0 \mid n_0\rangle = 0$$

showing that $|n_1'\rangle$ is OG to $|n_0\rangle$. Thus from now on let's always take $|n_1\rangle$ as having been *constructed* OG to $|n_0\rangle$. Thus (13.25) becomes

$$E_{n_2} = \langle n_0 \mid V \mid n_1\rangle \tag{13.28}$$

The generalization of (13.21) and (13.28) is

$$\boxed{E_{n_k} = \langle n_0 \mid V \mid n_{k-1}\rangle} \tag{13.29}$$

Wave Functions

We are assuming that we already know the unperturbed kets $|n_0\rangle$ allowing us to evaluate $E_{n_1} = \langle n_0 \mid V \mid n_0\rangle$ but to get the higher corrections E_{n_k} we need $|n_{k-1}\rangle$. We shall now discuss how to evaluate these.

Recall the first order equation (13.11). The $|n_0\rangle$ form a CON set and therefore $|n_1\rangle$ can be expanded in terms of them as

$$|n_1\rangle = \sum_{m\neq n} c_m \mid m_0\rangle + c_n \mid n_0\rangle \tag{13.30}$$

which is substituted into (13.11) giving

$$\sum_{m\neq n} c_m(H_0 - E_{n_0}) \mid m_0\rangle + c_n(H_0 - E_{n_0}) \mid n_0\rangle = (E_{n_1} - V) \mid n_0\rangle \tag{13.31}$$

where the term $(H_0 - E_{n_0}) \mid n_0\rangle = 0$ which is why we wrote the expansion (13.30) with $m \neq n$. Operate on (13.31) with $\langle k_0|$ to give

$$\sum_{m\neq n} c_m \left(\langle k_0 \mid H_0 \mid m_0\rangle - E_{n_0}\langle k_0 \mid m_0\rangle\right) = E_{n_1}\langle k_0 \mid n_0\rangle - \langle k_0 \mid V \mid n_0\rangle \tag{13.32}$$

For $k \neq n$ we have $\langle k_0 \mid n_0\rangle = 0$ and $\langle k_0 \mid m_0\rangle = \delta_{km}$ and $\langle k_0 \mid H_0 \mid m_0\rangle = E_{m_0}\langle k_0 \mid m_0\rangle = E_{m_0}\delta_{km}$ giving

$$c_k(E_{k_0} - E_{n_0}) = -\langle k_0 \mid V \mid n_0\rangle \tag{13.33}$$

or

$$c_k = \frac{\langle k_0 \mid V \mid n_0\rangle}{E_{n_0} - E_{k_0}} \quad (k \neq n) \tag{13.34}$$

which are our expansion coefficients for $k \neq n$.

Example 14.2 Show that $c_n = 0$.

Solution To extract c_n multiply (13.30) by $\langle n_0|$ to give

$$\langle n_0 \mid n_1\rangle = \sum_{m\neq n} c_m \langle n_0 \mid m_0\rangle + c_n$$

Now $\langle n_0 \mid m_0\rangle = 0$ if $m \neq n$ we were able (and did) construct $|n_0\rangle$ OG to $|n_1\rangle$ giving $\langle n_0 \mid n_1\rangle = 0$.

Thus $c_n = 0$.

Thus we could have left off the second term in (13.30) which would not have appeared in (13.31). (However we got zero there anyway.)

Upon substitution of (13.34) and $c_n = 0$ into (13.30) finally gives

$$\boxed{|n_1\rangle = \sum_{m\neq n} \frac{\langle m_0 \mid V \mid n_0\rangle}{E_{n_0} - E_{m_0}} \mid m_0\rangle}$$

(13.35)

for the first order wave function. Therefore the complete expression for the second order energy in (13.28) is

$$\boxed{E_{n_2} = \sum_{m \neq n} \frac{|\langle m_0 \mid V \mid n_0 \rangle|^2}{E_{n_0} - E_{m_0}}} \tag{13.36}$$

where we used $\langle m_0 \mid V \mid n_0 \rangle = \langle n_0 \mid V \mid m_0 \rangle^*$. Equations (13.35) and (13.36) are our final expressions for the corrections to the wave function and energy given completely in terms of unperturbed quantities.

As a practical matter, *perturbation theory usually gives very accurate answers for energies, but poor answers for wave functions* [Griffiths, 1996].

In equations (13.35) and (13.36) we see that the answers will blow up if $E_{n_0} = E_{m_0}$. That is if there is a *degeneracy.* Thus we now consider how to work out perturbation theory for the degenerate case.

13.2 Degenerate Perturbation Theory

In equations (13.35) and (13.36) we see that the expressions diverge if $E_{n_0} = E_{m_0}$, i.e. for degenerate states. (Perhaps even our first order expression $E_{n_1} = \langle n_0 \mid V \mid n_0 \rangle$ is not correct.) Let us therefore re-consider perturbation theory for degenerate states.

However, even though there does not appear to be a problem for the first order energy $E_{n_1} = \langle n_0 \mid V \mid n_0 \rangle$, in fact for degenerate states we really don't know how to evaluate this. For example, suppose we have two-fold degeneracy

$$H_0 \mid m_0 \rangle = E \mid m_0 \rangle \tag{13.37}$$

and

$$H_0 \mid k_0 \rangle = E \mid k_0 \rangle \tag{13.38}$$

then which states are we supposed to use in evaluating E_{n_1} ? Do we use $E_{n_1} = \langle m_0 \mid V \mid m_0 \rangle$ or $\langle k_0 \mid V \mid k_0 \rangle$?

Actually linear combinations are equally valid eigenstates (see below), i.e.

$$H_0(\alpha \mid m_0 \rangle + \beta \mid k_0 \rangle) = E(\alpha \mid m_0 \rangle + \beta \mid k_0 \rangle) \tag{13.39}$$

with the same energy E. Thus should we use the linear combination

$$|n_0\rangle \equiv \alpha \mid m_0\rangle + \beta \mid k_0\rangle \tag{13.40}$$

as the state in E_{n_1} ? If the answer is yes, then what values do we pick for α and β ? Thus even for the first order energy E_{n_1} we must re-consider perturbation theory for degenerate states.

Degenerate perturbation theory is not just some exoteric technique. Degenerate perturbations are among the dramatic features of spectral lines. If a single line represents a degenerate state, then the imposition of an external field can cause the degenerate level to split into two or more levels. Thus the subject of degenerate perturbation theory is very important. Actually *non-degenerate theory is almost useless because very few states are actually non-degenerate.*

13.2.1 Two-fold Degeneracy

Let's consider the case of two-fold degeneracy with

$$H_0 \mid m_0\rangle = E_{m_0} \mid m_0\rangle \tag{13.41}$$

and

$$H_0 \mid k_0\rangle = E_{k_0} \mid k_0\rangle \tag{13.42}$$

with

$$\langle k_0 \mid m_0\rangle = 0 \tag{13.43}$$

and where the degeneracy is specified via

$$E_{m_0} = E_{k_0} \equiv E_0 \tag{13.44}$$

which previously gave a singularity in (13.35) and (13.36).

Now our previous equation (13.15) is valid in both degenerate and non-degenerate perturbation theory. A linear combination of the state $|m_0\rangle$ and $|k_0\rangle$ is *also* a solution to H_0, i.e.

$$H_0(\alpha \mid m_0\rangle + \beta \mid k_0\rangle) = E_0(\alpha \mid m_0\rangle + \beta \mid k_0\rangle) \tag{13.45}$$

because $E_{m_0} = E_{k_0} = E_0$. This can be rewritten as

$$(H_0 - E_{n_0}) \mid n_0\rangle = 0 \tag{13.46}$$

with

$$|n_0\rangle \equiv \alpha \mid m_0\rangle + \beta \mid k_0\rangle \tag{13.47}$$

where (13.46) is just the zero order equation (13.15).

We want to calculate the first order correction to the energy. We use (13.11). In non-degenerate theory we multiplied (13.11) by $\langle n_0|$. Here we shall multiply separately by $\langle m_0|$ and $\langle k_0|$. Thus

$$\langle m_0 \mid H_0 - E_{n_0} \mid n_1\rangle = \langle m_0 \mid E_{n_1} - V \mid n_0\rangle \tag{13.48}$$

Again we can arrange for $\langle m_0 \mid n_1\rangle = 0$. Thus we have

$$\begin{aligned} 0 &= \alpha\langle m_0 \mid E_{n1} - V \mid m_0\rangle + \beta\langle m_0 \mid E_{n_1} - V \mid k_0\rangle \\ &= \alpha(E_{n_1} - V_{mm}) - \beta V_{mk} \end{aligned} \tag{13.49}$$

where

$$V_{mk} \equiv \langle m_0 \mid V \mid k_0\rangle \tag{13.50}$$

Multiplying (13.11) by $\langle k_0|$ gives

$$0 = -\alpha V_{km} + \beta(E_{n_1} - V_{kk}) \tag{13.51}$$

Equations (13.49) and (13.51) can be written in matrix form as

$$\begin{pmatrix} E_{n_1} - V_{mm} & -V_{mk} \\ -V_{km} & E_{n_1} - V_{kk} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0 \tag{13.52}$$

or

$$\begin{pmatrix} V_{mm} & V_{mk} \\ V_{km} & V_{kk} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E_{n_1} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \tag{13.53}$$

which can be solved for E_{n_1} and α and β. Equation (13.52) has solutions if the determinant of the 2×2 matrix is zero. Thus

$$(E_{n_1} - V_{mm})(E_{n_1} - V_{kk}) - V_{km}V_{mk} = 0 \tag{13.54}$$

(The Hamiltonian $H = H_0 + V$ is Hermitian and thus V is also Hermitian implying $V_{mk} = V^\dagger_{mk} = V^*_{km}$. Thus $V_{km}V_{mk} = |V_{km}|^2$).

(13.54) is a quadratic equation in E_{n_1}, namely

$$E^2_{n_1} - (V_{mm} + V_{kk})E_{n_1} + V_{mm}V_{kk} - |V_{km}|^2 = 0 \tag{13.55}$$

which has two solutions

$$\boxed{E_{n_1}^{\pm} = \frac{1}{2}\left[(V_{mm} + V_{kk}) \pm \sqrt{(V_{mm} - V_{kk})^2 + 4 \mid V_{km}\mid^2}\right]} \tag{13.56}$$

which shows that a two-fold degeneracy is "lifted" by a perturbation. Note that all of the matrix elements V_{km} are known in principle because we know $|m_0$ and $|k_0\rangle$ and $V_{km} \equiv \langle k_0 \mid V \mid m_0\rangle$.

13.2.2 Another Approach

Equation (13.56) is the energy equation for the perturbed eigenvalues. The terms V_{mm} and V_{kk} are just like the result (13.21) from non-degenerate theory. In fact suppose $V_{km} = 0$, then (13.56) becomes

$$E_{n_1}^{+} = V_{mm} \tag{13.57}$$

and

$$E_{n_1}^{-} = V_{kk} \tag{13.58}$$

which are *identical to the non-degenerate formula* (13.21). Thus if somehow $V_{km} = 0$ then we can just use our results from non-degenerate theory.

What is the difference between V_{mm} and V_{kk}? Recall that we are only considering *doubly* degenerate theory. $|m\rangle$ and $|k\rangle$ are the *two* degenerate eigenstates that have the same energy, but $|m\rangle$ and $|k\rangle$ are different. See (13.41) and (13.42). Thus V_{mm} and V_{kk} are evaluated by using the two different degenerate states $|m\rangle$ and $|k\rangle$ respectively.

Now how can we get $V_{km} = 0$? There happens to be a handy little theorem to use [Griffiths, 1995, pg. 229].

Theorem Let A be a Hermitian operator that commutes with V. If $|m_0\rangle$ and $|k_0\rangle$ are eigenkets of A with distinct eigenvalues, i.e.

$$A \mid m_0\rangle = \mu \mid m_0\rangle, \;\; A \mid k_0\rangle = \nu \mid k_0\rangle, \;\; \text{and } \mu \neq \nu$$

then $V_{km} = 0$.

Proof By assumption $[A, V] = 0$. Thus

$$\begin{aligned} &\langle m_0 \mid [A, V] \mid k_0\rangle = 0 \\ &= \langle m_0 \mid AV - VA \mid k_0\rangle \\ &= (\mu - \nu)\langle m_0 \mid V \mid k_0\rangle \\ &= (\mu - \nu)V_{mk} \end{aligned}$$

But $\mu \neq \nu$, thus $V_{mk} = 0$.

Thus the following *procedure for degenerate states* is recommended. Look for an Hermitian operator A that commutes with V. Find simultaneous eigenkets of H_0 and A, and call them $|m_0\rangle$ and $|k_0\rangle$ and then use formulas (13.57) and (13.58) to calculate the energies. (If you can't find such an A, you will have to use (13.56). [Griffiths, 1995, pg. 230])

13.2.3 Higher Order Degeneracies

See Section 6.2.2 of [Griffiths, 1995, pg. 231].

We do not have time to cover higher order degeneracies. However note that the *procedure for degenerate states* remains the same as in the case of 2-fold degeneracy, and we can use the formula for non-degenerate states for E_{n_1}.

13.3 Fine Structure of Hydrogen

We would now like to explore the spectrum of the Hydrogen atom in greater detail as an application of perturbation theory. Students are referred to the excellent article by Hänsch, Schawlow and Series ["The Spectrum of Atomic Hydrogen" by T. W. Hänsch, A. L. Schawlow and G. W. Series, *Scientific American*, March 1979, pg. 94]. See also Table 6.1 of Griffiths. [Griffiths, 1996, pg. 237]

The fine structure of Hydrogen consists of two pieces namely the relativistic correction and spin-orbit coupling.

13.3.1 1-Body Relativistic Correction

In wishing to describe the electron relativistically we should really develop the theory of Relativistic Quantum Mechanics or Relativistic Quantum Field Theory which results when Special Relativity and Quantum Mechanics are combined [Weinberg, 1996]. (No one has yet succeeded in combining *General* Relativity with Quantum Mechanics). In quantum field theory the relativistic generalization of the *1-body* Schrödinger equation is called the Klein-Gordon equation for spin-0 particles, or the Dirac equation for spin-$\frac{1}{2}$ particles, or the Rarita-Schwinger equation for spin-$\frac{3}{2}$ particles. (No one has yet solved the 2-body (special) relativistic bound state problem. The equation, called the Bethe-Salpeter equation, can be written down in a very general form but no one can solve it.)

We don't have time to develop the full relativistic theory and instead we shall just use the simplest possible generalization of the Schrödinger equation that we can think of.

Recall the kinetic energy for the (non-relativistic) Schrödinger equation is

$$T = \frac{p^2}{2m} \tag{13.59}$$

where $p = -i\hbar\frac{d}{dx}$ for 1-dimension and $\mathbf{p} = -i\hbar\bigtriangledown$ in 3-dimensions. In the relativistic case recall that

$$E = T + m \tag{13.60}$$

and

$$E^2 = p^2 + m^2 \tag{13.61}$$

giving

$$T = \sqrt{p^2 + m^2} - m \tag{13.62}$$

where we have left off the factors of c (or equivalently used units where $c \equiv 1$). Thus the simplest relativistic generalization of the Schrödinger equation that we can think of is simply to use (13.62), instead of (13.59), as the kinetic energy. The resulting equation is called the *Relativistic Schrödinger equation* or *Thompson equation*. (The reason this is the *simplest* generalization is because more complicated relativistic equations also include relativistic effects in the potential energy V. We shall not study these here.)

The *trouble* with (13.62) is that as an operator it's very weird. Consider the Taylor expansion

$$\begin{aligned} T &= m\sqrt{1 + \left(\frac{p}{m}\right)^2} - m \\ &\approx \frac{p^2}{2m} - \frac{p^4}{8m^3} + \cdots \end{aligned} \tag{13.63}$$

The first term is just the non-relativistic result and the higher terms are relativistic corrections, but it is an infinite series in the *operator* $p = -i\hbar\frac{d}{dx}$. *How* are we *ever* going to solve the differential equation?! Well that's for me to worry about. [J. W. Norbury, K. Maung Maung and D. E. Kahana, Physical Review A, vol. 50, pg. 2075, 3609 (1994)]. In our work now we will only consider the non-relativistic term $\frac{p^2}{2m}$ and the first order relativistic correction defined as

$$V \equiv -\frac{p^4}{8m^3} \tag{13.64}$$

so that the first order correction to the energy, using equation (13.21) or (13.23), is

$$E_{n_1} = \frac{-1}{8m^3}\langle n_0 \mid p^4 \mid n_0\rangle \equiv -\frac{1}{8m^3}\langle p^4\rangle \tag{13.65}$$

In position space this becomes

$$\langle n_0 \mid p^4 \mid n_0\rangle = \int d\mathbf{r}\, d\mathbf{r'}\, \langle n_0 \mid \mathbf{r}\rangle\langle \mathbf{r} \mid p^4 \mid \mathbf{r'}\rangle\langle \mathbf{r'} \mid n_0\rangle \tag{13.66}$$

where

$$\langle n_0 \mid \mathbf{r}\rangle \equiv \psi_n^*(\mathbf{r}) \text{ and } \langle \mathbf{r} \mid p^4 \mid \mathbf{r'}\rangle = \left(-\frac{\hbar^2}{2m}\nabla^2\right)^2 \delta(\mathbf{r}-\mathbf{r'})$$

giving

$$E_{n_1} = -\frac{1}{8m^2}\int d\mathbf{r}\psi_n^*(\mathbf{r})\left(-\frac{\hbar^2}{2m}\nabla^2\right)^2 \psi_n(\mathbf{r}) \equiv -\frac{1}{8m^3}\langle p^4\rangle \tag{13.67}$$

The unperturbed states $|n_0\rangle$ projected into coordinate space are $\langle \mathbf{r} \mid n_0\rangle \equiv \psi_n(\mathbf{r})$ which we found to be

$$\psi_{nlm}(r,\theta,\phi) = \sqrt{(2k)^3\frac{(n-l-1)!}{2n[(n+1)!]^3}}(2kr)^l e^{-kr} L_{n+l}^{2l+1}(2kr)Y_{lm}(\theta,\phi) \tag{13.68}$$

from equation (**??**) where $k \equiv \frac{Z}{na}$ where a is the Bohr radius.

Thus we could obtain E_{n_1} by substituting (13.68) into (13.67), evaluating $\nabla^4\psi_{nlm}(r,\theta,\phi)$ and then performing the resulting integral. There is also an easier way.

We can write

$$\langle p^4\rangle = \langle n_0 \mid p^4 \mid n_0\rangle = \langle n_0 \mid p^2 p^2 \mid n_0\rangle \tag{13.69}$$

Now

$$p^2 \mid n_0\rangle = 2m(E-U) \mid n_0\rangle \tag{13.70}$$

implying

$$\langle n_0 \mid p^{2^\dagger} = \langle n_0 \mid 2m(E-U)^\dagger \tag{13.71}$$

and $p^2 = p^{2^\dagger}$ and $U = U^\dagger$ giving

$$\langle n_0 \mid p^2 = \langle n_0 \mid 2m(E-U) \tag{13.72}$$

so that

$$\langle p^4\rangle = 4m^2\langle n_0 \mid (E-U)^2 \mid n_0\rangle \tag{13.73}$$

or

$$\begin{aligned} E_{n_1} &= \frac{-1}{2m}\langle (E-U)^2\rangle \\ &= \frac{-1}{2m}(E^2 - 2E\langle U\rangle + \langle U^2\rangle) \end{aligned} \tag{13.74}$$

Thus to get E_{n_1}, we only have to calculate $\langle U\rangle$ and $\langle U^2\rangle$. Now $U = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}$ (from equation (9.1) and so what we need are $\langle\frac{1}{r}\rangle$ and $\langle\frac{1}{r^2}\rangle$. The results are

$$\langle\frac{1}{r}\rangle = \frac{Z}{n^2 a} \tag{13.75}$$

where n is the principal quantum number and a is the Bohr radius and [Griffiths, 1995, pg. 238]

$$\langle\frac{1}{r^2}\rangle = \frac{1}{(l+\frac{1}{2})n^3a^2} \tag{13.76}$$

for $Z = 1$.
(do Problem 14.1). Thus we obtain

$$E_{n_1} = -\frac{E_n^2}{2m}\left(\frac{4n}{l+\frac{1}{2}} - 3\right) \tag{13.77}$$

(do Problems 14.2 and 14.3)

But wait a minute ! We used $\langle r|n_0\rangle = \psi_{nlm}(r,\theta,\phi)$. According to the procedure for degenrate states weren't we supposed to find an operator A that commutes with $V = -\frac{p^4}{8m^3}$ and then find simultaneous eigenstates of A and H_0 and use the eiegnstates in $\langle n_0|V|n_0\rangle$? Yes ! An we did ! $V = -\frac{p^4}{8m^3}$ commutes with L^2 and L_z. The states Y_{lm} are simultaneous eigenstates of L^2, L_z and H_0. Thus the states $\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi)$ already are the correct eigenstates to use.

But for example, a two-fold degeneracy, aren't we supposed to have two different expressions $\langle m_0|V|m_0\rangle$ and $\langle k_0|V|k_0\rangle$ and similarly for higher-fold degeneracies ? Yes ! And we did ! The states $Y_{lm}(\theta,\phi)$ are all different for differnet values of m. Suppose $n = 1$ then we can have $l = 0$ and $l = 1$ which are two degenerate states $|l = 0\rangle$ and $|l = 1\rangle$. Our answer 13.77 is different for different values of l. In other words for two-fold degeneracy $(n = 1, l = 0, 1)$ we had $|m_0\rangle = |l = 0\rangle$ and $|k_0\rangle = |l = 1\rangle$. We just wrote the general state as $|l\rangle$ or Y_{lm}, but it's really a collection of states $|m_0\rangle$ and $|k_0\rangle$. [NNN work out $\langle\frac{1}{r^2}\rangle$ for $Z \neq 1$. Is (13.77) also valid for $Z \neq 1$?]

13.3.2 Two-Body Relativistic Correction

The 2-body (bound state) problem in relativistic quantum mechanics is unsolved! The Schrödinger equation can be solved for 1 and 2 bodies but the relativistic equations, such as Dirac and Klein-Gordon, are 1-body equations. The problem is always how to make U relativistic. Here we shall just consider T.

The non-relativistic kinetic energy is

$$T = T_1 + T_2 = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} \tag{13.78}$$

where $p_1 = -i\hbar\frac{\partial}{\partial x_1}$ and $p_2 = -i\hbar\frac{\partial}{\partial x_2}$ in 1-dimension.

Introducing the reduced mass $\mu \equiv \frac{m_1 m_2}{m_1+m_2}$ and total mass $M \equiv m_1 + m_2$ we found in Chapter 7 that

$$\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2}{\partial x_2^2} = \frac{1}{\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{M}\frac{\partial^2}{\partial X^2} \tag{13.79}$$

where $x \equiv x_1 - x_2$ and $X \equiv \frac{m_1 x_1 + m_2 x_2}{m_1+m_2}$. It was this separation (13.79) that allowed us to solve the 2-body Schrödinger equation in general for all potentials of the form $U(x_1, x_2) \equiv U(x_1 - x_2) \equiv U(x)$. By the way, notice that if we use the center of momentum frame defined by

$$M\dot{X} = 0 = m_1\dot{x}_1 + m_2\dot{x}_2 = p_1 + p_2 \tag{13.80}$$

then

$$p_1 = -p_2 \equiv p \tag{13.81}$$

and then

$$\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \frac{p^2}{2\mu} \tag{13.82}$$

Now the obvious generalization of (13.78) is

$$\begin{aligned} T &= T_1 + T_2 \\ &= \sqrt{p_1^2 + m_1^2} - m_1 + \sqrt{p_2^2 + m_2^2} - m_2 \end{aligned} \tag{13.83}$$

or

$$T \approx \left(\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2}\right) - \left(\frac{p_1^4}{8m_1^3} + \frac{p_2^4}{8m_2^3}\right) + \cdots \tag{13.84}$$

which again reduces to the correct non-relativistic expressions (13.78) or (13.79) or (13.82). When (13.83) is used as the kinetic energy operator, the resulting equation is called the *Relativistic Schrödinger equation* or *Spinless Salpeter equation*. (The Thompson equation is nothing more than the Spinless Salpeter equation with the masses set equal.)

(NNN *Can (13.84) be solved analytically in coordinate space?????)*

13.3.3 Spin-Orbit Coupling

In Section 10.4.1 we have already briefly studied the effect of spin-orbit coupling as an example of the physical effect of spin.

Recall that the spin-orbit effect results because from the point of view of an orbital electron, it sees a positively charged nucleus in orbit around it. (We *want* the electron point of view because we want to calculate its energy.) Thus the electron feels a magnetic field because it is at the center of a current loop. Now the electron has a dipole moment μ due to its inrinsic spin. The interaction energy between a magnetic field $\mathbf{B}$ and a dipole moment was given in (10.61) as

$$U = -\mu \cdot \mathbf{B} \tag{13.85}$$

This will cause a change in the energy levels. The way we calculated this change was *simply* to add U to the Bohr energy levels. This was a good guess, and gave us a qualitative understanding, but we didn't justify this from the point of view of quantum mechanics. The *proper* way to do the calculation is to add (13.85) to the Coulomb potential and solve the new Schrödinger differential equation for the new energy levels. Unfortunately we don't know how to analytically solve this differential equation. Thus we use perturbation theory, with $U = -\mu \cdot \mathbf{B}$ treated as the perturbation (which we called V).

Equation (10.59) can be written

$$\mathbf{B} = \frac{1}{4\pi\epsilon_0}\frac{e}{mc^2r^3}\mathbf{L} \tag{13.86}$$

where $L = mvr$ and $c = \frac{1}{\sqrt{\mu_0\epsilon_0}}$. This gives the magnetic field of the orbiting proton.

We now want the magnetic moment of the spinning electron. Translating equation (**??**) we get

$$\mu = -\frac{e}{2m}\mathbf{S} \tag{13.87}$$

for the *classical* answer. Actually the correct result, from Dirac's relativistic theory is

$$\mu = -\frac{e}{m}\mathbf{S} \tag{13.88}$$

Thus the interaction energy becomes

$$V = -\mu \cdot \mathbf{B} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{m^2c^2r^3}\mathbf{S}\cdot\mathbf{L} \tag{13.89}$$

However there is also a relativistic kinematic correction, known as Thomas precession [Jackson, 1975] which throws in a factor of $\frac{1}{2}$ giving

$$\boxed{V = \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2r^3}\mathbf{S}\cdot\mathbf{L}} \tag{13.90}$$

which is our final expression for the spin-orbit interaction. (Actually if you had been naive and left out the Dirac correction for μ and the Thomas precession, you would still have got the right answer, because they cancel out!)

Now we want to put this expression into our quantum mechanical formula (13.21) for the energy shift. But how are we going to calculate $\langle n_0 \left| \frac{1}{r^3}\mathbf{S}\cdot\mathbf{L}\right| n_0\rangle$? Let's first review a few things about angular momentum.

The full wave function was written in equation (8.6) as $\psi(\mathbf{r}) \equiv \psi(r,\theta,\phi) \equiv R(r)Y(\theta,\phi)$ or $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$. However we also need to include spin which does *not* arise naturally in the Schrödinger equation (it is a relativistic effect). The spin wave function $\chi(s)$ must be tacked on as

$$\langle \mathbf{r} \mid n_0\rangle \equiv \psi(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)\chi(s) \tag{13.91}$$

Recall that the spherical harmonics satisfy

$$\begin{aligned} L^2 Y_{lm} &= l(l+1)\hbar^2 Y_{lm} & (13.92)\\ L_z Y_{lm} &= m\hbar\, Y_{lm} & (13.93) \end{aligned}$$

or

$$\begin{aligned} L^2 \mid lm\rangle &= l(l+1)\hbar^2 \mid lm\rangle & (13.94)\\ L_z \mid lm\rangle &= m\hbar \mid lm\rangle & (13.95) \end{aligned}$$

where the abstract kets $|lm\rangle$ are usually represented as *functions*

$$\langle \theta\phi \mid lm\rangle = Y_{lm}(\theta,\phi) \tag{13.96}$$

The spin angular momentum kets also satisfy

$$\begin{aligned} S^2 \mid sm_s\rangle &= s(s+1)\hbar^2 \mid sm_s\rangle \qquad (13.97)\\ S_z \mid sm_s\rangle &= m_s\hbar \mid sm_s\rangle \qquad (13.98) \end{aligned}$$

where S^2, S_z and $|sm_s\rangle$ are usually represented as matrices.

Now in perturbation theory we want to calculate $E_{n_1} = \langle n_0 \mid V \mid n_0\rangle$ with V given in (13.90). Thus

$$E_{n_1} = \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2}\left[\int r^2 dr\, R^*_{nl}(r)\frac{1}{r^3}R_{nl}(r)\right]\langle lm|\langle sm_s \mid \mathbf{S}\cdot\mathbf{L} \mid sm_s\rangle|lm\rangle \qquad (13.99)$$

Now

$$\int r^2 dr\, R^*_{nl}(r)\frac{1}{r^3}R_{nl}(r) = \frac{1}{(l+\frac{1}{2})(l+1)n^3a^3} \qquad (13.100)$$

(see Griffiths, equation 6.63), but the tricky piece is $\langle\mathbf{L}\cdot\mathbf{S}\rangle$. Recall our *procedure for degenerate states*. In this case we have $V \propto \mathbf{L}\cdot\mathbf{S}$ and we are to look for a Hermitian operator A that commutes with V, i.e. find an A that commutes with $\mathbf{L}\cdot\mathbf{S}$. Let's try a few, say $\mathbf{L}$ and $\mathbf{S}$. Well

$$[\mathbf{L}\cdot\mathbf{S},\mathbf{L}] \neq 0$$

and

$$[\mathbf{L}\cdot\mathbf{S},\mathbf{S}] \neq 0$$

However

$$[\mathbf{L}\cdot\mathbf{S},\mathbf{J}] = [\mathbf{L}\cdot\mathbf{S},L^2] = [\mathbf{L}\cdot\mathbf{S},S^2] = [\mathbf{L}\cdot\mathbf{S},J^2] = 0$$

(do Problem 14.4)
and so *any* of $\mathbf{J}$, L^2, S^2 or J^2 will do for the operator A. Now the *procedure for degenerate states* is to find simultaneous eigenkets of H_0 and A and use them to calculate the expectation value of V. Such eigenkets are $|jm\rangle$, $|lm\rangle$ or $|sm\rangle$. Which to choose? $\langle lm \mid \mathbf{L}{\cdot}\mathbf{S} \mid lm\rangle$ or $\langle sm \mid \mathbf{L}{\cdot}\mathbf{S} \mid sm\rangle$ is complicated. It's easier to write

$$\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2) \qquad (13.101)$$

which comes from

$$J^2 = (\mathbf{L}+\mathbf{S})\cdot(\mathbf{L}+\mathbf{S}) = L^2 + S^2 + 2\mathbf{L}\cdot\mathbf{S} \qquad (13.102)$$

To calculate $\langle \mathbf{L}\cdot\mathbf{S}\rangle$ we choose what is convenient, namely

$$\begin{aligned}\langle \mathbf{L}\cdot\mathbf{S}\rangle &= \frac{1}{2}[\langle jm \mid J^2 \mid jm\rangle - \langle lm|\langle sm_s \mid L^2 \mid sm_s\rangle|lm\rangle \\ &\qquad -\langle lm|\rangle sm_s \mid S^2 \mid sm_s\rangle|lm\rangle] \\ &= \frac{1}{2}[\langle jm \mid J^2 \mid jm\rangle - \langle lm \mid L^2 \mid lm\rangle - \langle sm \mid S^2 \mid sm\rangle] \\ &= \frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)] \qquad (13.103)\end{aligned}$$

giving

$$E_{n_1} = \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2}\frac{\frac{1}{2}\hbar^2[j(j+1)-l(l+1)-s(s+1)]}{l(l+\frac{1}{2})(l+1)n^3a^3} \qquad (13.104)$$

or

$$E_{n_1} = \frac{nE_{n_0}^2}{mc^2}\left[\frac{j(j+1)-l(l+1)-\frac{3}{4}}{l(1+\frac{1}{2})(l+1)}\right] \qquad (13.105)$$

(do Problem 14.5)

The *fine-structure* correction consists of *both* the relativistic correction (13.77) and the spin-orbit correction (13.105). Adding them gives

$$E_{n_1} = \frac{E_n^2}{2mc^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right) \qquad (13.106)$$

to give the grand result for the energy levels of hydrogen including fine structure as

$$\boxed{E_{n_j} = -\frac{13.6\text{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]} \qquad (13.107)$$

This is known as the fine-structure formula. (do Problem 14.6) Note the presence of the famous fine structure constant

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137} \qquad (13.108)$$

13.4 Zeeman effect

reference: D.J. Griffiths, “Quantum Mechanics”, section 6.4

13.5 Stark effect

reference: D.J. Griffiths, “Quantum Mechanics”

13.6 Hyperfine splitting

reference: D.J. Griffiths, “Quantum Mechanics”, section 6.5

reference: D.J. Griffiths, “Introduction to Elementary Particles”, section 5.5

13.7 Lamb shift

reference: D.J. Griffiths, “Introduction to Elementary Particles”, section 5.4

13.8 Positronium and Muonium

reference: D.J. Griffiths, “Introduction to Elementary Particles”, section 5.6

13.9 Quark Model of Hadrons

reference: D.J. Griffiths, “Introduction to Elementary Particles”, sections 5.7 - 5.10

Chapter 14

VARIATIONAL PRINCIPLE, HELIUM ATOM, MOLECULES

14.1 Variational Principle

14.2 Helium Atom

14.3 Molecules

Chapter 15

WKB APPROXIMATION, NUCLEAR ALPHA DECAY

(Note: these notes closely follow [Griffiths, 1995])

For most of the arbitrary potentials that we can think up, the Schrödinger equation cannot be solved analytically. However for certain *types* of potential, there are certain approximation methods that work well. We have already explored perturbation theory which is good if we know the answer to a certain potential which is perturbed.

The Wentzel, Kramers, Brillouin (WKB) approximation is good for calculating *energies* and *tunnelling probabilities* through potentials which *vary slowly*. If a potential varies slowly then for small changes in position it can be considered as a finite square well or finite square barrier, and we can thus use our previous solutions. The difference will be however, that the potential is not truly flat but varies. Thus we expect that our previous solutions are valid except that the *amplitude* and *wavelength* will change as the potential changes.

15.1 Generalized Wave Functions

Recall the time-independent Schrödinger equation for 1-body in 1-dimension for a constant potential $U = U_0$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U_0\psi = E\psi \tag{15.1}$$

Recall our discussion in Section 6.3, where we write this as

$$\psi'' + \frac{2m(E-U_0)}{\hbar^2}\psi = 0 \quad \text{for } E > U_0 \tag{15.2}$$

or

$$\psi'' - \frac{2m(U_0-E)}{\hbar^2}\psi = 0 \quad \text{for } E < U_0 \tag{15.3}$$

The region $E > U$ is sometimes called the "classical" region [Griffiths, 1995, pg. 275] because $E < U$ is not allowed classically. Defining

$$k \equiv \frac{\sqrt{2m(E-U_0)}}{\hbar} \tag{15.4}$$

and

$$\kappa \equiv \frac{\sqrt{2m(U_0-E)}}{\hbar} \tag{15.5}$$

which are both *real* for $E > U_0$ and $E < U_0$ respectively. Thus the Schrödinger equation is

$$\psi'' + k^2\psi = 0 \tag{15.6}$$

or

$$\psi'' - \kappa^2\psi = 0 \tag{15.7}$$

with solutions

$$\psi(x) = A\,e^{ikx} + B\,e^{-ikx} \tag{15.8}$$

or

$$\psi(x) = C\,e^{\kappa x} + C\,e^{-\kappa x} \tag{15.9}$$

(Of course (15.8) can also be written $E\cos kx + F\sin kx$, etc.) These wave functions (15.8) and (15.9) are only the *correct solutions for a constant potential* $U = U_0$. If $U = U(x)$ they are not correct! However if U is *slowly varying* then over small distances it does approximate a constant potential. The *answers* for a slowly varying potential are

$$\boxed{\psi(x) \approx \frac{A}{\sqrt{k}}e^{i\int k\,dx} + \frac{B}{\sqrt{k}}e^{-i\int k\,dx}} \tag{15.10}$$

and

$$\boxed{\psi(x) \approx \frac{C}{\sqrt{k}} e^{\int \kappa \, dx} + \frac{D}{\sqrt{\kappa}} e^{\int \kappa \, dx}}$$

(15.11)

where now $k \equiv k(x)$ and $\kappa = \kappa(x)$ are both functions of x because $U = U(x)$. I call these the generalized wave functions because they are obviously generalizations of (15.8) and (15.9) which we had for the constant potential $U = U_0$. The generalized wave functions have *variable amplitude* and *variable wavelength* whereas these are constant for (15.8) and (15.9). The variable wavelength are the $k(x)$ and $\kappa(x)$ terms in the exponential. Recall $p = \hbar k = \frac{h}{\lambda}$.

Let's now see how to derive the generalized wave functions. In general *any* (complex) wave function can be expressed in terms of an amplitude and phase via

$$\psi(x) \equiv A(x) e^{i\phi(x)} \tag{15.12}$$

This assumption is *not* an approximation, but rather, is *exact*. Let's find $A(x)$ and $\phi(x)$ by substituting into the Schrödinger equation. For definiteness, use the first of the two Schrödinger equations, namely (15.6). Substitution yields

$$A'' + 2iA'\phi' + iA\phi'' - A\phi'^2 + Ak^2 = 0 \tag{15.13}$$

and equating the Real and Imaginery parts gives

$$A'' + A(k^2 - \phi'^2) = 0 \tag{15.14}$$

and

$$A\phi'' + 2A'\phi' = 0 \tag{15.15}$$

which are *exact* equations relating the amplitude and phase of the general wave function (15.12). The second equation can be solved in general by writing it as

$$(A^2\phi')' = 0 \tag{15.16}$$

yielding

$$A^2\phi' = C^2, \quad \text{or} \;\; A = \frac{C}{\sqrt{\phi'}} \tag{15.17}$$

where C is a constant. We don't use $A = \pm\frac{C}{\sqrt{\phi'}}$, because A being an amplitude, will give the same results for all observables whether we use $+$ or $-$. The first equation (15.14) cannot be solved in general. (If it could we would have a general solution of the Schrödinger equation!) The WKB approximation consists of setting A'' to zero

$$\text{WKB approximation: } A'' \approx 0 \tag{15.18}$$

This makes good sense. If the potential is slowly varying over x then the strength or amplitude of the wave function will only vary slowly.

Thus we can solve (15.14) in general as

$$\phi' = \pm k \tag{15.19}$$

giving

$$A = \frac{C}{\sqrt{k}} \tag{15.20}$$

and the general solution of the first order ODE is

$$\phi(x) = \pm \int k(x)dx \tag{15.21}$$

Thus the generalized wave function (15.12) is written, in the WKB approximation, as

$$\psi(x) \approx \frac{C}{\sqrt{k}} e^{\pm i \int k(x)dx} \tag{15.22}$$

The general solution is a linear combination

$$\psi(x) = \frac{A}{\sqrt{k}} e^{i \int k(x)dx} + \frac{B}{\sqrt{k}} e^{-i \int k(x)dx}$$

in agreement with (15.10). Equation (15.11) can be solved in a similar manner. (do Problem 15.1)

Example 15.1 Derive the quantization condition

$$\phi(a) = \int_0^a k(x)dx = n\pi \tag{15.23}$$

for a potential well with infinite vertical walls.

Solution (All students should first go back and review the infinite square well potential.)

The well is shown in Fig. 8.2 of Griffiths [1995]. It is specified as

$$\begin{aligned} U(x) &= \text{an arbitrary function if } 0 < x < a \\ &= \infty \text{ at } x = 0 \text{ and } x = a. \end{aligned}$$

Clearly we only consider the classical region $E > U$ with the solution (15.10), which we write as

$$\psi(x) = \frac{1}{\sqrt{k}}(A \sin\phi + B \cos\phi) \tag{15.24}$$

with $\phi(x) \equiv \int\limits_0^x k(x')dx'$ which implies $\phi(0) = 0$.

The boundary conditions, as usual, are

$$\psi(0) = \psi(a) = 0$$

$\psi(0) = 0$ implies $B = 0$ or $\psi(x) = \frac{A}{\sqrt{k}} \sin\phi(x)$. Then $\psi(a) = 0$ gives $\sin\phi(a) = 0$ implying $\phi(a) = \pm n\pi$ where $n = 1, 2, 3 \cdots$. As with the infinite square well we drop the $-$ sign to give

$$\phi(a) = \int_0^a k(x)dx = n\pi$$

Example 15.2 Show how the above quantization condition gives the exact result for the square well potential. Why is the result exact?

Solution We have

$$k(x) \equiv \frac{\sqrt{2m[E - U(x)]}}{\hbar}$$

For $U(x) = 0 =$ constant we have

$$k(x) = \text{constant } = \frac{\sqrt{2mE}}{\hbar}$$

which upon substitution into (15.23) gives

$$E_n = n^2 \frac{\pi^2\hbar^2}{2ma^2}$$

in agreement with our previous result for the infinite square well in (3.14).

The reason why we get the exact result is because $A(x)$ does not change as a function of x, and so the WKB approximation $A'' \approx 0$ is actually exact.

15.2 Finite Potential Barrier

Before reading this section, *please* go back and review Section 6.4 where the finite potential barrier was first introduced.

In Section 6.4 we studied the finite potential barrier with a *flat* top. Now we will consider a bumpy top or a top represented by some arbitrary function. (Compare to the infinite well with a bumpy bottom in Example 15.1.) The potential barrier with a flat top is shown in Fig. 6.2. A bumpy top is shown in Fig. 15.1. Regions I and III are identical in Figs. 6.2 and 15.1 and thus the solutions in those regions are the same, regardless of the shape of the top of the potential. Thus from Section 6.4 we still have

$$\begin{aligned} \psi_I(x) &= A\,e^{ikx} + B\,e^{-ikx} \\ &\equiv \psi_i + \psi_R \end{aligned} \tag{15.25}$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \tag{15.26}$$

and ψ_i and ψ_R are the incident and reflected waves respectively. Also we still have

$$\psi_{III}(x) = C\,e^{ikx} \tag{15.27}$$

for the transmitted wave.

We would like to study *tunnelling* and so we consider the case $E < U(x)$ where the energy of the incident particle is smaller than the potential barrier (non-classical region). For the flat top barrier we previously had $\psi_{II}(x) = D\,e^{\kappa x} + F\,e^{-\kappa x}$ where $\kappa \equiv \frac{\sqrt{2m(U_0-E)}}{\hbar}$. However we now consider a bumpy top described by the potential $U(x)$ and so in region II let's use the WKB approximately, namely,

$$\psi_{II}(x) \approx \frac{D}{\sqrt{\kappa}} e^{\int \kappa\, dx} + \frac{F}{\sqrt{\kappa}} e^{-\int \kappa\, dx} \tag{15.28}$$

with

$$\kappa(x) \equiv \frac{\sqrt{2m[U(x)-E]}}{\hbar} \tag{15.29}$$

From our previous experience we know that F is always bigger than D, so that the dominant effect inside the well is one of exponential decay. Thus let's set

$$D \approx 0 \tag{15.30}$$

which will be accurate for *high or wide barriers, which is equivalent to the tunnelling probability being small.* Thus

$$\psi_{II}(x) \approx \frac{F}{\sqrt{\kappa}} e^{-\int \kappa \, dx} \tag{15.31}$$

Now the tunnelling probability is $T \equiv \left|\frac{C}{A}\right|^2$ but instead of getting $\frac{D}{A}$ from (15.27) and (15.25) let's use the WKB wave function (15.31). Because we must have $\psi_I(-a) = \psi_{II}(-a)$ and $\psi_{II}(a) = \psi_{III}(a)$ then

$$\left|\frac{C}{A}\right| = e^{-\int_{-a}^{a} \kappa \, dx} \tag{15.32}$$

giving

$$T \approx e^{-2\gamma} \text{ with } \gamma \equiv \int_{-a}^{a} \kappa \, dx \tag{15.33}$$

with $\kappa(x)$ given in (15.29) where $U(x) > E$.

15.3 Gamow's Theory of Alpha Decay

As an application of the WKB approximation let us consider Gamow's theory of alpha decay. (Gamow is pronounced Gamof.) Alpha decay is the phenomenon whereby nuclei spontaneously emit alpha particles (i.e. Helium nuclei).

The force between two nucleons is very attractive and very short range. A good *model* of the force is shown in Fig. 15.2C representing an attractive finite potential well. The radius of the well is about 1 fm, corresponding to the range of the nuclear force. Realistic nuclei are made of both neutrons and protons and therefore the protons experience a repulsive Coulomb force in addition to the attractive nuclear force. The combination of these two is shown in Fig. 15.2D.

Consider the nucleus ^{238}U, which is known to undergo alpha decay. Prior to alpha decay, Gamow considered the alpha particle to be rattling around inside the ^{238}U nucleus, or to be rattling around inside the potential well of Fig. 15.2D. In this picture notice that the Coulomb potential represents a *barrier* that the alpha particle must climb over, or tunnel through, in order to escape. This is perhaps a little counter-intuitive as one would think that the charge on the alpha particle would *help* rather than hinder its escape, but such is not the case. (It's perhaps easier to think of Fig. 15.2D in terms of scattering, whereby an incident alpha particle encounters a repulsive barrier, but if it has sufficient energy it overcomes the barrier and gets captured by the nuclear force.) Also we will be considering zero orbital angular momentum $l = 0$. For $l \neq 0$ there is also an angular momentum barrier in addition to the Coulomb barrier.

We are going to use the theory we developed in the previous section for the finite potential barrier. You may object that Fig. 15.1 looks nothing like Fig. 15.2D, but in fact they are similar if one considers that we want to calculate the tunnelling probability for the alpha particle to go from being trapped at $r = r_1$ to escaping to $r = r_2$ where r_2 can be as large as you like. (Also we developed our previous theory for 1-dimension and here we are applying it to 3-dimensions, but that's OK because the radial Schrödinger equation is an effective 1-dimension equation in the variable r.)

The Coulomb potential between an alpha particle of charge $+2e$ and a nucleus of charge $+Ze$ is

$$U(r) = +\frac{1}{4\pi\epsilon_0}\frac{2Ze^2}{r} \equiv \frac{c}{r} \tag{15.34}$$

where

$$C \equiv \frac{2Ze^2}{4\pi\epsilon_0} \tag{15.35}$$

Thus (15.33) with $\kappa = \frac{\sqrt{2m[U(r)-E]}}{\hbar}$, (15.33) becomes

$$\gamma = \frac{1}{\hbar}\int_{r_1}^{r_2} \sqrt{2m\left(\frac{c}{r} - E\right)} \tag{15.36}$$

what is E? It is the energy of the particle at position r_2, i.e. the energy of the escaped particle. Note if we had set $r_2 = \infty$ we would get $\gamma = \infty$, which is a common disease of the Coulomb potential. Gamow's *model* is that the particle has the energy E before it escapes. See Fig. 15.2D. Thus

$$E = \frac{1}{4\pi\epsilon_0}\frac{2Ze^2}{r_2} \tag{15.37}$$

We obtain

$$\gamma \approx K_1 \frac{Z}{\sqrt{E}} - K_2\sqrt{Zr_1} \tag{15.38}$$

with

$$K_1 = \left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{\pi\sqrt{2m}}{\hbar} = 1.980\,\mathrm{MeV}^{1/2} \tag{15.39}$$

and

$$K_2 = \left(\frac{e^2}{4\pi\epsilon_0}\right)^{1/2}\frac{4\sqrt{m}}{\hbar} = 1.485\,fm^{-1/2} \tag{15.40}$$

The above 3 equations are derived in [Griffiths, 1995]. Make *certain* you can do the derivation yourself.

We want to know the lifetime τ or half-life $\tau_{1/2}$ of the decaying nucleus. They are related via

$$\tau = \frac{\tau_{1/2}}{\ln 2} = \frac{\tau_{1/2}}{0.693} \tag{15.41}$$

In the Gamow *model* of the alpha particle rattling around before emission then the time between collisions with the wall, or potential barrier would be $\frac{2r_1}{v}$ where v is the speed of the particle. Thus the lifetime would be

$$\tau = \text{time between collisions} \times \text{probability of escape}$$

or

$$\tau = \frac{2r_1}{v}e^{-2\gamma} \tag{15.42}$$

where v can be estimated from the energy.
(do Problems 15.2–15.5)

Chapter 16

TIME-DEPENDENT PERTURBATION THEORY, LASERS

In 1-dimension the time-dependent Schrödinger equation (1.22) is

$$\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}+U\right)\Psi(x,t)=i\hbar\frac{\partial}{\partial t}\Psi(x,t) \tag{16.1}$$

and in 3-dimensions the equation (8.1) is

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2+U\right)\Psi(\mathbf{r},t)=i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) \tag{16.2}$$

In *general* we have

$$U=U(\mathbf{r},t) \tag{16.3}$$

That is the potential energy can be a function of both position and time. *If the potential is not a function of time $U \neq U(t)$ then we were able to use separation of variable to solve the Schrödinger equation* (16.1) or (16.2). This was discussed extensively in Chapter 2. We found

$$\Psi(x,t)=\psi(x)e^{\frac{-i}{\hbar}Et} \text{ for } U\neq U(t) \tag{16.4}$$

This very simple time dependence meant that $|\Psi|^2 \equiv \Psi^*\Psi$ was constant in time. That is Ψ was a stationary state. All expectation values were also stationary. *All of our studies up to now have been concerned with time-independent potentials* $U \neq U(t)$. Thus we spent a lot of time calculating the energy levels of square wells, the harmonic oscillator, the Coulomb potential and even perturbed states, but there was *never* the possibility that a system could jump from one energy level to another because of time-independence. If an atom was in a certain energy level it was stuck there forever.

The spectra of atoms is due to time-dependent transitions between states. If we are to understand how light is emitted and absorbed by atoms we better start thinking about non-stationary states or time-dependent Hamiltonians. Thus we are back to the very difficult problem of solving the *partial differential* Schrödinger equation, (16.1) or (16.2), for a general potential $U = U(\mathbf{r}, t)$. *This time separation of variables won't work*, and the partial differential Schrödinger equation *cannot* be solved for *general* $U(\mathbf{r}, t)$.

Thus we can either specialize to certain forms of $U(\mathbf{r}, t)$ *or* we can develop an approximation scheme known as time-dependent perturbation theory.

16.1 Equivalent Schrödinger Equation

As with time-independent perturbation theory we write the Hamiltonian H in terms of an unperturbed piece H_0 and a perturbation $V(t)$ as in

$$H = H_0 + V(t) \tag{16.5}$$

analogous to (13.2), (except we are not going to use an expansion parameter λ here). H_0 is the time-*independent* Hamiltonian (with $V(t) = 0$),

$$H_0 = \frac{p^2}{2m} + U(\mathbf{r}) \tag{16.6}$$

for which we assume we know the full solution to the time-independent Schrödinger equation

$$H_0 \mid n\rangle = E_n \mid n\rangle \tag{16.7}$$

analogous to (13.3). The problem we want to solve is

$$H \mid \Psi(t)\rangle = i\hbar \frac{\partial}{\partial t} \mid \Psi(t)\rangle \tag{16.8}$$

where

$$\langle \mathbf{r} \mid \Psi(t)\rangle \equiv \Psi(\mathbf{r}, t) \tag{16.9}$$

Recall the following results from Section 2.3. We can *always* write the general solution $\Psi(\mathbf{r},t)$ in terms of a complete set

$$\Psi(\mathbf{r},t)=\sum_n c_n\Psi_n(\mathbf{r},t) \tag{16.10}$$

For the case $U\neq U(t)$ this was a linear combination of separable solutions

$$\Psi(\mathbf{r},t)=\sum_n c_n\Psi_n(\mathbf{r},t)=\sum_n c_n\psi_n(\mathbf{r})e^{-i\omega_n t} \tag{16.11}$$

or

$$|\Psi(t)\rangle=\sum_n c_n\mid n(t)\rangle=\sum_n c_n\mid n\rangle e^{-i\omega_n t} \tag{16.12}$$

where

$$|n(t)\rangle\equiv|n\rangle e^{-i\omega_n t} \tag{16.13}$$

and

$$\omega_n\equiv\frac{E_n}{\hbar} \tag{16.14}$$

We also wrote (16.11) using

$$c_n'(t)\equiv c_n e^{-i\omega_n t} \tag{16.15}$$

as

$$\Psi(\mathbf{r},t)=\sum_n c_n\Psi_n(\mathbf{r},t)=\sum_n c_n'(t)\psi_n(\mathbf{r}) \tag{16.16}$$

or

$$|\Psi(t)\rangle=\sum_n c_n\mid n(t)\rangle=\sum_n c_n'(t)\mid n\rangle \tag{16.17}$$

both of which *look* more like an expansion in terms of the complete set $\{\psi_n(\mathbf{r})\}$ or $\{|n\rangle\}$.

For the time-dependent case $U=U(t)$ we write our complete set expansion as

$$\Psi(\mathbf{r},t)\equiv\sum_n c_n(t)\psi_n(\mathbf{r})e^{-i\omega_n t} \tag{16.18}$$

or

$$\begin{aligned}|\Psi(t)\rangle &= \sum_n c_n(t)\mid n\rangle e^{-i\omega_n t} && (16.19)\\ &= c_a(t)\mid a\rangle e^{-i\omega_a t}+c_b(t)\mid b\rangle e^{-i\omega_n t} && (16.20)\\ &\ \text{(for 2–level system)}\end{aligned}$$

which contains *both* $c_n(t)$ *and* $e^{-i\omega_n t}$ whereas above for $U \neq U(t)$we only had one or the other. Here $c_n(t)$ contains an *arbitrary* time dependence whereas $c'_n(t)$ above only had the oscillatory time dependence $c'_n(t) \equiv c_n e^{-i\omega_n t}$.

Equations (16.18) or (16.19) are *general* expansions for *any* wave functions valid for *arbitrary* $U(\mathbf{r}, t)$. If we know $c_n(t)$ we know $\Psi(t)$. Thus let's substitute (16.18) or (16.19) into the Schrödinger equation and get an *equivalent* equation for $c_n(t)$, which we will solve for $c_n(t)$, put back into (16.18) and then have $\Psi(t)$.

Subsituting (16.19) into (16.8) gives

$$H_0 \sum_n c_n(t) e^{-i\omega_n t} \mid n\rangle + V(t) \sum_n c_n(t) e^{-i\omega_n t} \mid n\rangle \tag{16.21}$$

$$= i\hbar \sum_n \dot{c}_n(t) e^{-i\omega_n t} \mid n\rangle + \sum_n c_n(t) E_n e^{-i\omega_n t} \mid n\rangle \tag{16.22}$$

where $\dot{c}_n \equiv \frac{dc_n}{dt}$.

To extract c_n we do the usual thing of multiplying by $\langle m|$ to give

$$\sum_n c_n(t) e^{-i\omega_n t} \langle m \mid H_0 \mid n\rangle + \sum_n c_n(t) e^{-i\omega_n t} \langle m \mid V \mid n\rangle$$

$$= i\hbar\, \dot{c}_m e^{-i\omega_m t} + c_m E_m e^{-i\omega_m t} \tag{16.23}$$

where $\langle m \mid n\rangle = \delta_{mn}$ has killed the sums on the right hand side. Now $\langle m \mid H_0 \mid n\rangle = E_m \delta_{mn}$. Thus the first term on the left cancels the second term on the right to give

$$\dot{c}_m(t) = \frac{-i}{\hbar} \sum_n V_{mn}(t) e^{i\omega_{mn} t} c_n(t) \tag{16.24}$$

where

$$V_{mn}(t) \equiv \langle m \mid V(t) \mid n\rangle \tag{16.25}$$

and

$$\omega_{mn} \equiv \omega_m - \omega_n. \tag{16.26}$$

Let's condense things a bit. Define

$$v_{mn}(t) \equiv V_{mn}(t) e^{i\omega_{mn} t} \tag{16.27}$$

and because $\omega_{mm} \equiv 0$ this implies

$$v_{mm}(t) = V_{mm}(t) \tag{16.28}$$

Thus

$$\boxed{\dot{c}_m(t) = \frac{-i}{\hbar} v_{mn}(t) c_n(t)} \tag{16.29}$$

where we have used the Einstein summation convention for the repeated index n, i.e. $v_{mn}(t)c_n(t) \equiv \sum_n v_{mn}(t)c_n(t)$.

Equation (16.29) is the fundamental equation of time-dependent perturbation theory, and it is completely equivalent to the Schrödinger equation. All we have to do is solve (16.29) for $c_m(t)$ and then we have the complete wave function $\Psi(\mathbf{r}, t)$. Thus I call equation (16.29) the *equivalent Schrödinger equation.*

So far we have made *no approximations*!

Actually (16.29) consists of a whole collection of simultaneous or coupled equations. For example, for a 2-level system [Griffiths, 1995], equation (16.29) becomes

$$\begin{aligned} \dot{c}_a(t) &= \frac{-i}{\hbar}(v_{aa}c_a + v_{ab}c_b) \\ \dot{c}_b(t) &= \frac{-i}{\hbar}(v_{ba}c_a + v_{bb}c_b) \end{aligned} \tag{16.30}$$

or in matrix form

$$\begin{pmatrix} \dot{c}_b \\ \dot{c}_b \end{pmatrix} = \frac{-i}{\hbar} \begin{pmatrix} v_{aa} & v_{ab} \\ v_{ba} & v_{bb} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} \tag{16.31}$$

The general equivalent Schrödinger equation in matrix form is then

$$\boxed{\begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \\ \dot{c}_3 \\ \vdots \end{pmatrix} = \frac{-i}{\hbar} \begin{pmatrix} v_{11} & v_{12} & v_{13} & \cdots \\ v_{21} & v_{22} & v_{23} & \cdots \\ v_{31} & v_{32} & v_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \\ \end{pmatrix}} \tag{16.32}$$

again recalling that, for example $v_{11} = V_{11}(t)$ and $v_{21} = V_{21}(t)e^{i\omega_{21}t}$. Equation (16.32) is entirely the same as (16.29) and involves no approximations. Thus (16.32) is also entirely equivalent to the Schrödinger equation.

16.2 Dyson Equation

If $V(t)$ is *small* then the equivalent Schrödinger equation (16.29) can be *iterated*. Integrating both sides gives

$$\int_{t_0}^{t} \frac{dc_m(t_1)}{dt_1} dt_1 = c_m(t) - c_m(t_0) = \frac{-i}{\hbar} \int_{t_0}^{t} dt_1 v_{mn}(t_1) c_n(t_1) \tag{16.33}$$

At $t = t_0$, the system is in state $|i\rangle$ and $c_m(t_0) = \delta_{mi}$. Thus

$$c_m(t) = \delta_{mi} + \left(\frac{-i}{\hbar}\right) \int_{t_0}^{t} dt_1 v_{mn}(t_1) c_n(t_1) \tag{16.34}$$

The idea of *iteration* is as follows. For the $c_n(t_1)$ appearing on the right hand side just write it as a *replica* of (16.34), namely

$$c_n(t_1) = \delta_{ni} + \left(\frac{-i}{\hbar}\right) \int_{t_0}^{t_1} dt_2 v_{nk}(t_2) c_k(t_2) \tag{16.35}$$

where $\sum\limits_k$ is implied for the repeated index k. Substitute the replica back into (16.34) to give

$$\begin{aligned} c_m(t) = \delta_{mi} \quad &+ \quad \left(\frac{-i}{\hbar}\right) \int_{t_0}^{t} dt_1 v_{mn}(t_1) \Big[\delta_{ni} \\ &+ \quad \left(\frac{-i}{\hbar}\right) \int_{t_0}^{t_1} dt_2 v_{nk}(t_2) c_k(t_2) \Big] \\ = \delta_{mi} \quad &+ \quad \left(\frac{-i}{\hbar}\right) \int_{t_0}^{t} dt_1 v_{mi}(t_1) \\ &+ \quad \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 v_{mn}(t_1) v_{nk}(t_2) c_k(t_2) \end{aligned} \tag{16.36}$$

where we have used $v_{mn}(t_1)\delta_{ni} \equiv \sum\limits_n v_{nm}(t_1)\delta_{ni} = v_{mi}(t_1)$. Do the same again. Make a replica of (16.34) but now for $c_k(t_2)$ and substitute. Continuing this procedure the final result is

$$\begin{aligned} c_m(t) = 1 \quad &+ \quad \left(\frac{-i}{\hbar}\right) \int_{t_0}^{t} dt_1 v_{mi}(t_1) \\ &+ \quad \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 v_{mn}(t_1) v_{ni}(t_2) \\ &+ \quad \left(\frac{-i}{\hbar}\right)^3 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 v_{mn}(t_1) v_{nk}(t_2) v_{ki}(t_3) \\ &\qquad\qquad + \cdots \end{aligned} \tag{16.37}$$

or

$$c_m(t) = 1 + \sum_{j=1}^{\infty} \left(\frac{-i}{\hbar}\right)^j \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{j-1}} dt_j v_{mn}(t_1) v_{nk}(t_2) \cdots v_{ki}(t_j) \tag{16.38}$$

This is called the Dyson equation for $c_m(t)$. (Actually what is usually called the Dyson equation is for a thing called the time evolution operator, but it looks the same as our equations.) We shall often only use the result to *first* order which is

$$\boxed{c_m(t) = \delta_{mi} + \left(\frac{-i}{\hbar}\right) \int_{t_0}^{t} dt_1 v_{mi}(t_1)} \tag{16.39}$$

called the Strong Incompletely Coupled Approximation (SICA).

16.3 Constant Perturbation

[NNN constant perturbation was assumed in *all* my NASA papers and also is discussed in Merzbacher and Schiff (Pg. 197)].

The simplest perturbation to treat is a *constant* perturbation. Yikes! you say. Isn't that supposed to be the subject of *time-independent* perturbation theory that we already discussed? Nope. When we talk about a *constant* perturbation in *time-dependent* perturbation theory what we mean is a potential turned *on* at time t_0 remaining constant, and then being turned off at time t. Thus our time integral looks like

$$\begin{aligned} \int_{-\infty}^{\infty} V_{ki}(t')dt' &= \int_{-\infty}^{t_0} O\, dt' + \int_{t_0}^{t} V_{kn}\, dt' + \int_{t}^{\infty} O\, dt' \\ &= V_{kn} \int_{t_0}^{t} dt' \end{aligned} \tag{16.40}$$

(Of course there are other things inside the integrals, but I have left them out for now.) V_{kn} can be taken outside of the second integral because it is constant over the time interval $t_0 \to t$, whereas it's obviously *not* constant over the entire time interval $-\infty \to +\infty$. Thus overall we still do have a time dependent interaction. See [Schiff, 1955, 2nd ed., pg. 197; Griffiths, 1995, problems 9.28 9.14, see part c, pg. 320].

Let's analyze the first order equation (16.39) which is

$$\begin{aligned} c_m(t) &= \delta_{mi} + \left(\frac{-i}{\hbar}\right) \int_{t_0}^{t} dt_1 \, V_{mi} \, e^{i\omega_{mi} t_1} \\ &= \delta_{mi} + \left(\frac{-i}{\hbar}\right) V_{mi} \int_{t_0}^{t} dt_1 \, e^{i\omega_{mi} t_1} \\ &= \delta_{mi} - \frac{V_{mi}}{\hbar\omega_{mi}} \left(e^{i\omega_{mi} t} - e^{i\omega_{mi} t_0}\right) \end{aligned} \tag{16.41}$$

Now let's take $t_0 = 0$ and $m \neq i$, giving $\delta_{mi} = 0$. Thus

$$c_m(t) = V_{mi} \frac{1 - e^{i\omega_{mi} t}}{\hbar\omega_{mi}} \tag{16.42}$$

giving

$$P_{i\to m}(t) \equiv |c_m(t)|^2 = \frac{2}{\hbar^2} |V_{mi}|^2 \frac{1 - \cos\omega_{mi} t}{\omega_{mi}^2} \tag{16.43}$$

which is the *transition probability for a constant perturbation.* Now $P_{i\to m}(t)$ represents the transition probability between the *two states* $|i\rangle$ and $|m\rangle$. For a *two-state system* the *total probability* $P(t)$ is just

$$P(t) = P_{i\to m}(t) \tag{16.44}$$

The *transition rate* is defined as

$$w \equiv \frac{dP(t)}{dt} \tag{16.45}$$

which has units of second^{-1} and is therefore a *rate.* From (16.43) we get

$$\boxed{w = \frac{2}{\hbar^2} |V_{mi}|^2 \frac{\sin\omega_{mi} t}{\omega_{mi}}} \tag{16.46}$$

which is the *transition rate for a two-level system under a constant perturbation.* The amazing thing is that it is a function of time which oscillates sinusoidally. (See discussion in Griffiths, Pg. 304 of "flopping" frequency. His discussion is for a harmonic perturbation, which we discuss next, but the discussion is also relevant here.)

(do Problem 16.4)

Now $P_{i\to m}(t)$ represents the transition probability between two states $|i\rangle$ and $|m\rangle$. But $|i\rangle$ can undergo a transition to a whole set of possible *final* states $|k\rangle$. Thus the total probability $P(t)$ is the sum of these,

$$P(t) = \sum_k P_k(t) \tag{16.47}$$

where

$$P_k(t) \equiv P_{i\to k}(t) \equiv |c_k(t)|^2 \tag{16.48}$$

If the energies are closely spaced or continuous, we replaced $\sum\limits_k$ by an integral

$$P(t) = \int_0^\infty \rho(E_k) dE_k P_k(t) \tag{16.49}$$

where $\rho(E_k)$ is called the *density of states.* It's just the number of energy levels per energy interval dE_k. Thus $\rho(E_k)dE_k$ is just the *number* of levels in interval dE_k. Often we will assume a *constant* density of states ρ which just then comes outside the integral.

Note that formulas (16.47) and (16.49) involved *addition of probabilities.* See Griffiths, Pg. 310 footnote. From (16.43) we get, assuming constant ρ, and with $dE_k = \hbar d\omega_k$

$$P(t) = \frac{2}{\hbar}|V_{ki}|^2 \rho \int_0^\infty d\omega_k \frac{1-\cos\omega_{ki}t}{\omega_{ki}^2} \tag{16.50}$$

We want to change variables using $d\omega_k = d\omega_{ki}$. However it is important to realize that

$$\int_0^\infty d\omega_k = \int_{-\infty}^\infty d\omega_{ki} \tag{16.51}$$

because ω_k varies from 0 to ∞ but so *also* does ω_i. Thus when $\omega_k = 0$ and $\omega_i = \infty$ then $\omega_{ki} = -\infty$ and when $\omega_k = \infty$ and $\omega_i = 0$ then $\omega_{ki} = +\infty$. Thus

$$P(t) = \frac{2}{\hbar}|V_{ki}|^2 \rho \int_{-\infty}^\infty d\omega_{ki} \frac{1-\cos\omega_{ki}t}{\omega_{ki}^2} \tag{16.52}$$

because the integrand is an even function. Using [Spiegel, 1968, Pg. 96]

$$\int_0^\infty \frac{1-\cos px}{x^2} dx = \frac{\pi p}{2} \tag{16.53}$$

which, due to the integrand being even implies $\int\limits_{-\infty}^{\infty} \frac{1-\cos px}{x^2} dx = \pi p$, giving

$$P(t) = \frac{2\pi}{\hbar}|V_{ki}|^2 \rho t \tag{16.54}$$

from which we use $w \equiv \frac{dP}{dt}$ to obtain

$$\boxed{w = \frac{2\pi}{\hbar}|V_{ki}|^2\rho(E_k)} \tag{16.55}$$

which is the *transition rate for a multi-level system under a constant perturbation.* This is the famous *Fermi Golden Rule Number 2 for a constant perturbation.*

Footnote: Sometimes you might see an alternative derivation as follows. [NASA TP-2363, Pg. 4]

$$\begin{aligned} w &\equiv \lim_{t\to\infty}\frac{dP(t)}{dt} \\ &= \lim_{t\to\infty}\frac{2}{\hbar}|V_{ki}|^2\rho\int_0^\infty d\omega_k\frac{\sin\omega_{ki}t}{\omega_{ki}} \end{aligned}$$

Using the representation of the delta function [Merzbacher, 2nd ed., 1970, pg. 84]

$$\delta(x) = \frac{1}{\pi}\lim_{\theta\to\infty}\frac{\sin x\theta}{x}$$

giving

$$w = \frac{2}{\hbar}|V_{ki}|^2\rho\int_{-\infty}^{\infty} d\omega_{ki}\pi\delta(\omega_{ki}) = \frac{2\pi}{\hbar}|V_{ki}|^2\rho$$

It represents a *constant rate* of transition [Merzbacher, 2nd ed., 1970, pg. 479, equation (18.107)].

16.4 Harmonic Perturbation

Plane electromagnetic (EM) waves consist of harmonically varying (i.e. sinusoidally varying) electric and magnetic fields. We can learn a great deal about the structure of atoms, nuclei and particles by exciting them with EM radiation (photons) and studying the decay products. This is the reason as to why we are interested in perturbations.

Let's write the perturbation as

$$V(t) = \mathcal{V}\cos\omega t \tag{16.56}$$

which, upon substitution into the first order amplitude (16.39), yields

$$\begin{aligned} c_m(t) &= \delta_{mi} + \left(\frac{-i}{\hbar}\right) \mathcal{V}_{mi} \int_{t_0}^{t} dt_1 \frac{e^{i\omega t_1} + e^{-i\omega t_1}}{2} e^{i\omega_{mi} t_1} \\ &= \delta_{mi} + \left(\frac{-i}{\hbar}\right) \mathcal{V}_{mi} \left[\frac{e^{i(\omega_{mi}+\omega)t} - e^{i(\omega_{mi}+\omega)t_0}}{2i(\omega_{mi}+\omega)} \right. \\ &\qquad \left. + \frac{e^{i(\omega_{mi}-\omega)t} - e^{i(\omega_{mi}-\omega)t_0}}{2i(\omega_{mi}-\omega)} \right] \end{aligned} \tag{16.57}$$

which is identical to (16.41) if $\omega \equiv 0$, because (16.56) just becomes $V(t) = V$.

Again let's take $t_0 = 0$ and $m \neq i$, giving $\delta_{mi} = 0$. Thus

$$c_m(t) = \mathcal{V}_{mi} \left[\frac{1 - e^{i(\omega_{mi}+\omega)t}}{2\hbar(\omega_{mi}+\omega)} + \frac{1 - e^{i(\omega_{mi}-\omega)t}}{2\hbar(\omega_{mi}-\omega)} \right] \tag{16.58}$$

which is identical to (16.42) if $\omega \equiv 0$. When we work out $|c_m(t)|^2$ it's a big mess. When $\omega \approx \omega_{mi}$ the second term dominates so let's just consider

$$c_m(t) \approx \mathcal{V}_{mi} \frac{1 - e^{i(\omega_{mi}-\omega)t}}{2\hbar(\omega_{mi}-\omega)} \tag{16.59}$$

giving

$$P_{i \to m}(t) \equiv |c_m(t)|^2 \approx |\mathcal{V}_{mi}|^2 \frac{\sin^2\left(\frac{\omega_{mi}-\omega}{2}\right)t}{\hbar^2(\omega_{mi}-\omega)^2} \tag{16.60}$$

(do Problem 16.1)

This is the transition probability for a *two-state system* under a harmonic perturbation. Again using (16.44) and (16.45) gives

$$\boxed{w = \frac{1}{2\hbar^2} |\mathcal{V}_{mi}|^2 \frac{\sin(\omega_{mi}-\omega)t}{\omega_{mi}-\omega}} \tag{16.61}$$

which is the *transition rate for a two-level system under a harmonic perturbation*, which like (16.46) also oscillates in time.

For a multi-level system, using the same constant density ρ as before, we have from (16.60)

$$P(t) = \frac{1}{\hbar} |\mathcal{V}_{ki}|^2 \rho \int_0^\infty d\omega_k \frac{\sin^2\left(\frac{\omega_{ki}-\omega}{2}\right)t}{(\omega_{ki}-\omega)^2} \tag{16.62}$$

and changing the variable to $x \equiv \frac{\omega_{ki}-\omega}{2}$ the integral becomes

$$\int_0^\infty d\omega_k = \int_{-\infty}^\infty dx \tag{16.63}$$

as before giving

$$P(t) = \frac{1}{\hbar}|\mathcal{V}_{ki}|^2 \rho \frac{1}{2} \int_{-\infty}^\infty dx \frac{\sin^2 xt}{x^2} \tag{16.64}$$

Using [Spiegel, 1968, pg. 96]

$$\int_0^\infty \frac{\sin^2 px}{x^2} dx = \frac{\pi p}{2} \tag{16.65}$$

which, due to the integrand being even implies $\int\limits_{-\infty}^{\infty} \frac{\sin^2 px}{x^2} dx = \pi p$, giving

$$P(t) = \frac{\pi}{2\hbar}|\mathcal{V}_{ki}|^2 \rho t \tag{16.66}$$

from which we use $w \equiv \frac{dP}{dt}$ to obtain

$$\boxed{w = \frac{\pi}{2\hbar}|\mathcal{V}_{ki}|^2 \rho(E_k)} \tag{16.67}$$

which is the *transition rate for a multi-level system under a harmonic perturbation*, or the *Fermi Golden Rule Number 2 for a harmonic perturbation*,

Footnote: Sometimes you might again see an alternative derivation as follows [NASA TP-2363, pg. 4]

$$\begin{aligned} w &\equiv \lim_{t\to\infty} \frac{dP(t)}{dt} \\ &= \lim_{t\to\infty} \frac{1}{2\hbar}|V_{ki}|^2 \rho \int_0^\infty d\omega_k \frac{\sin(\omega_{ki}-\omega)t}{\omega_{ki}-\omega} \end{aligned}$$

and using

$$\lim_{t\to\infty} \frac{\sin(\omega_{ki}-\omega)t}{\omega_{ki}-\omega} = \pi\delta(\omega_{ki}-\omega) = \pi\delta(\omega_k - \omega_i - \omega)$$

giving

$$w = \frac{1}{2\hbar}|V_{ki}|^2 \rho \int_{-\infty}^\infty d(\omega_{ki}-\omega)\pi\delta(\omega_{ki}-\omega) = \frac{\pi}{2\hbar}|V_{ki}|^2 \rho$$

and which again represents a constant rate of transition. (If you want (16.56) to look the same as (16.55) just rewrite (16.56) as $V(t) = 2\mathcal{V}\cos\omega t$.)

16.5 Photon Absorption

Electromagnetic (EM) waves, or photons, consist of mutually orthogonal electric and magnetic oscillating fields. The electrons in atoms respond primarily to the electric field because of their charge. If we ignore the spatial variation of the EM fields then [Griffiths, 1995, pg. 306]

$$\mathbf{E} = E_0 \cos t\omega t\, \hat{k} \tag{16.68}$$

where we have assumed the field $\mathbf{E}$ points in the $\hat{k}$ direction, and [Griffiths, equation 9.32]

$$V(t) = -eE_0 z \cos\omega t \tag{16.69}$$

Compare this to (16.56). Thus

$$\mathcal{V}_{mi} = -\mathcal{P}E_0 \tag{16.70}$$

where the z component of the electric dipole moment is

$$\mathcal{P} \equiv e\langle m \mid z \mid i\rangle \tag{16.71}$$

giving from (16.61)

$$w = \frac{1}{2\hbar^2}|\mathcal{P}|^2 E_0^2 \frac{\sin(\omega_{mi} - \omega)t}{\omega_{mi} - \omega} \tag{16.72}$$

Here we have in mind that an atomic electron is excited by a single incident photon polarized in the $\hat{k}$ direction.

All students should read pages 307-309 of [Griffiths, 1995] for an excellent discussion of absorption and stimulated emission and spontaneous emission. These topics are very important in the study of lasers. Note especially that the *rate of absorption is the same as the rate of stimulated emission* (just swap indices).

16.5.1 Radiation Bath

Suppose that instead of excitation by a single photon, the atom is placed in a radiation bath. Even though we are still considering only a two-level system (see Fig. 9.4, Griffiths, pg. 307), there will be a large distribution of incident photon energies entirely analogous to our previous distribution of continuous final states. Thus we use a density of states formalism to describe the distribution of *incident* photons.

We introduce a density of *initial* states $\rho(E)$ analogous to (16.49) as

$$P(t) = \int_0^\infty \rho(E)dE\, P_k(t) \tag{16.73}$$

Again assuming a harmonic perturbation $V(t) \equiv \mathcal{V}\cos\omega t$ one obtains

$$\boxed{w = \frac{\pi}{2\hbar}|\mathcal{V}_{ki}|^2\rho(E)} \tag{16.74}$$

which is the *transition rate for a radiation bath initial state under a harmonic perturbation* and is again the *Fermi Golden Rule Number 2*, with the density of *initial* states in the radiation bath described by $\rho(E)$. (do Problem 16.2)

In the above expression for photons we again have $\mathcal{V}_{ki} = -\mathcal{P}E_0$ as in (16.70). However the initial radiation bath is not really characterized by an electric field E_0 but rather by the energy density (this time energy per unit volume)

$$u = \frac{1}{2}\epsilon_0 E_0^2 \tag{16.75}$$

to give

$$|\mathcal{V}_{ki}|^2 = |\mathcal{P}|^2\frac{2u}{\epsilon_0} \tag{16.76}$$

giving

$$w = \frac{\pi}{\epsilon_0\hbar}|\mathcal{P}|^2 u\rho(E) \tag{16.77}$$

(Note: in comparing this with equation (9.43) of Griffiths, realize that $\rho(\omega_0)$ used by Griffiths is actually the energy per unit frequency *per unit volume.* This is related to my $\rho(E)$ via $\frac{\rho(\omega_0)}{\hbar} = u\rho(E)$.)

Using the electric dipole moment, analogous to (16.71) as

$$\mathbf{P} \equiv e\langle m \mid \mathbf{r} \mid i\rangle \tag{16.78}$$

and averaging over all polarizations [Griffiths, pg. 311] gives a factor of 1/3, i.e.

$$\boxed{w = \frac{\pi}{3\epsilon_0\hbar}|\mathbf{P}|^2 u\rho(E)} \tag{16.79}$$

(The averaging works like this; consider $\mathbf{r}^2 = x^2 + y^2 + z^2$ but now suppose $x^2 = y^2 = z^2$ giving $\mathbf{r}^2 = 3z^2$ and thus $z^2 = \frac{1}{3}\mathbf{r}^2$.)

16.6 Photon Emission

Energy levels can decay by either stimulated emission or *spontaneous emission.* This is discussed nicely by [Griffiths, 1995]. The transition rates for these processes are called the Einstein A and B coefficients. [Eisberg and Resnick, pg. 428].

The stimulated emission rate is $B\rho$ [Griffiths, 1995, pg. 312] where

$$\boxed{B = \frac{\pi}{3\epsilon_0 \hbar^2} |\mathbf{P}|^2} \tag{16.80}$$

and the spontaneous emission rate is

$$\boxed{A = \frac{\omega^3}{3\pi\epsilon_0 \hbar c^3} |\mathbf{P}|^2} \tag{16.81}$$

Students should study the derivation of these formulas in [Griffiths, 1995, pg. 311-312].

The *lifetime* of an excited state is just [Griffiths, 1995, pg. 313]

$$\boxed{\tau = \frac{1}{A}} \tag{16.82}$$

16.7 Selection Rules

To get the lifetime of a state we always need to calculate $\mathbf{P} \equiv q\langle]\psi_b \mid \mathbf{r} \mid \psi_a\rangle$. Specifically for Hydrogen atom wave functions this is

$$\mathcal{P} = -e\langle n'l'm' \mid \mathbf{r} \mid nlm\rangle \tag{16.83}$$

Such a calculation is done in Problem 16.6. There we found that a lot of these matrix elements are zero. It would be very helpful if we had a quick way of knowing this rather than always having to grind through integrals.

There are two famous *selection rules* for photon emission. These are

$$\boxed{\Delta m = \pm 1, 0} \tag{16.84}$$

and

$$\boxed{\Delta l = \pm 1} \tag{16.85}$$

Transitions will not occur unless these are satisfied. They are very clearly derived on pages 315-318 of [Griffiths, 1995]. All students should fully understand these derivations and include them in their booklet write-ups.

16.8 Lasers

Chapter 17

SCATTERING, NUCLEAR REACTIONS

17.1 Cross Section

Experiments carried out at particle accelerators have had a dramatic effect on our understanding of the ultimate structure of matter. In *principle* the experiment is simple. Fire a beam of particles at a target and watch what comes out! In reality the phrase "watch what comes out" means *count* particles of a certain type at a variety of energies and at a variety of angles. Usually an experimentalist converts this "count" into a quantity called a *cross section.*

The actual count rate N (in units of sec^{-1} is just the luminosity of the beam $\mathcal{L}$ ($\text{cm}^{-2}\text{sec}^{-1}$) times the reaction cross section σ (cm^2),

$$N = \mathcal{L}\sigma \tag{17.1}$$

Thus to measure a cross section the experimentalist just divides the count rate by the beam luminosity.

When measuring a *total* cross section σ, the experimentalist doesn't measure either the energy or the angle of the outgoing particle. She just measuress the total number of counts. However one might be interested in how many particles are emitted as a function of angle. This is the *angular distribution* or *angular differential cross section* $\frac{d\sigma}{d\Omega}$. Or one instead might be interested in the number of particles as a function of energy. This is called the *spectral distribution* or *energy differential cross section* $\frac{d\sigma}{dE}$. One might be interested in both variables or the *doubly differential cross section* $\frac{d^2\sigma}{dEd\Omega}$.

These are all related to the total cross section via

$$\sigma = \int \frac{d\sigma}{dE}dE = \int \frac{d\sigma}{d\Omega}d\Omega = \int \frac{d^2\sigma}{dEd\Omega}dEd\Omega \tag{17.2}$$

For example $\frac{d\sigma}{dE}$ is actually a *function* that one would measure and perhaps plot. The integral of that function is the total cross section.

17.2 Scattering Amplitude

Quantum mechanics is a theory of waves. The incident beam in our particle accelerator can be considered as a collection of plane waves Ae^{ikz} moving in the z direction (the beam direction), as shown in Fig. 17.1. When the plane wave scatters it turns into an outgoing spherical wave $\frac{e^{ikr}}{r}$ modified by a distortion factor called a *scattering amplitude* $f(\theta)$.

Example 17.1 Justify the use of $\psi = Ae^{ikz}$ for an incident beam of particles.

Solution The asymptotic region is that region where $U = 0$. Thus the Schrödinger equation, *for* $l = 0$, is

$$\nabla^2\psi + k^2\psi = 0$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar}$$

In 1-dimension (the z direction) the Schrödinger equation is

$$\frac{d^2\psi}{dz^2} + k^2\psi = 0$$

which has solution

$$\psi = Ae^{ikx}$$

for an incident beam in the z direction.

Let's discuss the outgoing spherical wave in more detail. When the experimentalist detects an outgoing scattered particle, the detector is in what we call the asymptotic region where $U = 0$ and $r \to \infty$. We found previously that for a constant potential $U = U_0$ the general solution to the Schrödinger equation for arbitrary l was given in (8.70) as

$$\begin{aligned} u_l(r) &= Ar\, j_l(kr) + Br\, n_l(kr) \\ &= Cr\, h_l^{(1)}(kr) + Dr\, h_l^{(2)}(kr) \end{aligned} \tag{17.3}$$

where $k \equiv \frac{\sqrt{2m(E-U_0)}}{\hbar}$. (For our detector in the asymptotic region we have $U_0 = 0$.) In problem 17.1 it is shown that

$$R_l(r \to \infty) = C(-i)^{l+1}\frac{e^{ikr}}{kr} \tag{17.4}$$

with $R(r) \equiv \frac{u(r)}{r}$. By the way we shall often need the asymptotic expressions for these functions, namely

$$j_l(x \to \infty) \to \frac{\sin(x - l\pi/2)}{x} \tag{17.5}$$

and

$$n_l(x \to \infty) \to -\frac{\cos(x - l\pi/2)}{x} \tag{17.6}$$

(do Problem 17.1)

In problem 17.1 we see that $h_l^{(2)}(kr)$ corresponds to an *incoming* spherical wave and therefore we must have $D = 0$ because the scattered wave will be outgoing. Thus the incident plus scattered wave, from (17.3), is

$$\psi(r, \theta, \phi) = A\left[e^{ikz} + \sum_{lm} c_{lm} h_l^{(1)}(kr) Y_{lm}(\theta, \phi)\right] \tag{17.7}$$

where we have used $R(r) \equiv \frac{u(r)}{r}$. In the asymptotic region this is

$$\psi(r_\infty, \theta, \phi) = A\left[e^{ikz} + \sum_{lm} c_{lm}(-i)^{l+1}\frac{e^{ikr}}{kr} Y_{lm}(\theta, \phi)\right] \tag{17.8}$$

or

$$\psi(r_\infty, \theta, \phi) \equiv A\left[e^{ikz} + f(\theta, \phi)\frac{e^{ikr}}{r}\right] \tag{17.9}$$

where we have defined the *scattering amplitude* as

$$f(\theta, \phi) \equiv \frac{1}{k}\sum_{lm} c_{lm}(-i)^{l+1} Y_{lm}(\theta, \phi) \tag{17.10}$$

Equation (17.9) is very intuitive. It says that the scattering process consists of an incident plane wave e^{ikz} and an outgoing scattered spherical wave $\frac{e^{ikr}}{r}$. The *advantage* of writing it in terms of the scattering amplitude is because it is directly related to the angular differential cross section [Griffiths, 1995]

$$\frac{d\sigma}{d\Omega} = |f(\theta, \phi)|^2 \tag{17.11}$$

Thus our formula for the angular distribution is

$$\frac{d\sigma}{d\Omega} = \frac{1}{k^2} \sum_{lm} \sum_{l'm'} i^{l-l'} c^*_{lm} c_{l'm'} Y^*_{lm} Y_{l'm'} \tag{17.12}$$

We integrate this to get the total cross section

$$\sigma = \frac{1}{k^2} \sum_{lm} \sum_{l'm'} i^{l-l'} c^*_{lm} c_{l'm'} \int Y^*_{lm} Y_{l'm'} d\Omega \tag{17.13}$$

but

$$\int Y^*_{lm} Y_{l'm'} d\Omega = \delta_{ll'} \delta_{mm'} \tag{17.14}$$

giving

$$\sigma = \frac{1}{k^2} \sum_{lm} |c_{lm}|^2 \tag{17.15}$$

But all these equations are overkill! I don't know of any potential which is not azimuthally symmetric. If azimuthal symmetry holds then our answers won't depend on ϕ or m. We could leave our equations as they stand and simply grind out our answers and always discover independence of ϕ and m in our answers. But it's better to simply things and build in the symmetry from the start. *Azimuthal symmetry is simply achieved by setting* $m = 0$.

From equation (**??**) we had

$$Y_{lm}(\theta, \phi) = \epsilon \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_{lm}(\cos\theta) \tag{17.16}$$

where $P_{lm}(\cos\theta)$ are the *Associated Legendre functions*, which are related to the *Legendre polynomials* $P_l(\cos\theta)$ by

$$P_l(\cos\theta) \equiv P_{lo}(\cos\theta) \tag{17.17}$$

Thus

$$Y_{lo}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta) \tag{17.18}$$

where $\epsilon = 1$ for $m = 0$. The wave functions (17.7) and (17.8) become

$$\psi(r,\theta) = A\left[e^{ikz} + \sum_l \sqrt{\frac{2l+1}{4\pi}} c_l h_l^{(1)}(kr) P_l(\cos\theta)\right] \tag{17.19}$$

and

$$\psi(r_\infty,\theta) = A\left[e^{ikz} + \sum_l \sqrt{\frac{2l+1}{4\pi}} c_l (-i)^{l+1} \frac{e^{ikr}}{kr} P_l(\cos\theta)\right] \tag{17.20}$$

and the scattering amplitude (17.10) is

$$f(\theta) = \frac{1}{k}\sum_l (-i)^{l+1} c_l \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta) \tag{17.21}$$

which is called the *partial wave expansion* of the scattering amplitude. Obviously the angular distribution is now written as

$$\boxed{\frac{d\sigma}{d\Omega} = |f(\theta)|^2} \tag{17.22}$$

and

$$\boxed{\sigma = \frac{1}{k^2}\sum_l |c_l|^2} \tag{17.23}$$

17.2.1 Calculation of c_l

(This section closely follows [Griffiths, 1995])

How then do we calculate c_l? Answer: by matching boundary conditions (as usual). We match the wave function in the exterior, asymptotic region to the wave function in the interior region near the potential.

It is often useful to write the incident plane wave in spherical coordinates, just as we did for the outgoing spherical wave. We use Rayleigh's formula

$$e^{ikz} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos\theta) \tag{17.24}$$

and put it into (17.3)

$$\psi(r,\theta) = A \sum_{l=0}^{\infty} \left[i^l (2l+1) j_l(kr) + \sqrt{\frac{2l+1}{4\pi}} c_l h_l^{(1)}(kr) \right] P_l(\cos\theta) \tag{17.25}$$

Example 17.2 Calculate the total cross section for scattering from a hard sphere. (This is the example in [Griffiths, 1995, pg. 361]).

Solution A hard sphere is defined as

$$\begin{aligned} U(r) &= \infty \text{ for } r \leq a \text{ (interior region I)} \\ &= 0 \text{ for } r > a \text{ (exterior region II)} \end{aligned}$$

The wave function in the interior region is

$$\psi_I(r,\theta) = 0$$

because the incident beam cannot penetrate. The exterior wave function is given (always) by (17.25) as

$$\psi_{II}(r,\theta) = A \sum_l \left[i^l (2l+1) j_l(kr) + \sqrt{\frac{2l+1}{4\pi}} c_l h_l^{(1)}(kr) \right] P_l(\cos\theta)$$

We match these wave functions at the boundary

$$\psi_I(a,\theta) = \psi_{II}(a,\theta)$$

to give

$$\sum_l \left[i^l (2l+1) j_l(ka) + \sqrt{\frac{2l+1}{4\pi}} c_l h_l^{(1)}(ka) \right] P_l(\cos\theta) = 0$$

from which we obtain

$$c_l = -i^l \sqrt{4\pi(2l+1)} \frac{j_l(ka)}{h_l^{(1)}(ka)}$$

(do Problem 17.2) giving

$$\sigma = \frac{4\pi}{k^2} \sum_l (2l+1) \left| \frac{j_l(ka)}{h_l^{(1)}(ka)} \right|^2$$

which is our final answer. In the low energy limit, $ka \ll 1$, this reduces to [Griffiths, 1995, pg. 362]

$$\sigma \approx 4\pi a^2$$

17.3 Phase Shift

Rather than calculating the coefficients c_l, the theory of scattering is often formulated in terms of a more physically intuitive quantity called the phase shift δ_l. The idea is that the scattering potential causes a change in phase of the incident wave. Remarkably, the scattering amplitude and cross section can be expressed entirely in terms of the phase shift.

Some good references for this section are

"Quantum Mechanics" by D. B. Beard and G. B. Beard
(QC174.1.B37) (1970)
"Quantum Mechanics" by G. L. Trigg (QC174.1.T7) (1964)
"Quantum Mechanics" by L. I. Schiff (QC174.1.S34) (1955)
"Principles of Quantum Mechanics" by H. C. Ohanion (1990)

Recall the solution to the Schrödinger equation for constant $U(r) = U_0$ when $l = 0$ is written in several ways

$$\begin{aligned} u(r) &= A\cos kr + B\sin kr \\ &= A\sin(kr+\delta) \\ &= A[cos\delta \sin kr + \sin\delta\cos kr] \\ &= A\,e^{ikr} + B\,e^{-ikr} \end{aligned} \tag{17.26}$$

where in the third line we used $\sin(A+B) = \sin A \cos B + \cos A \sin B$. Here δ is the phase shift and simply serves as an arbitrary constant instead of B. Now for arbitrary l we wrote equation (8.70) as

$$\begin{aligned} u_l(r) &= Ar\, j_l(kr) + Br\, n_l(kr) \\ &= Cr\, h_l^{(1)}(kr) + Dr\, h_l^{(2)}(kr) \end{aligned} \qquad (17.27)$$

Now j_l is a "generalized" sine and n_l is a "generalized" cosine, so in analogy with (17.26) we write

$$u_l(r) \equiv Ar\left[\cos\delta_l\, j_l(kr) - \sin\delta_l\, n_l(kr)\right] \qquad (17.28)$$

where we pute a minus sign in front of $\sin\delta_l$ because $n_l(kr) \to -\cos kr$. [Schiff, 1955, pg. 86 (3rd ed.); Arfken, 1985, pg. 627 (3rd ed.)]. Using the asymptotic expressions (17.5) and (17.6) we get

$$\begin{aligned} u_l(r\to\infty) &\to \frac{Ar}{kr}\left[\cos\delta_l \sin\left(kr - \frac{l\pi}{2}\right) + \sin\delta_l \cos\left(kr - \frac{l\pi}{2}\right)\right] \\ &= \frac{A}{k}\sin\left(kr - \frac{l\pi}{2} + \delta_l\right) \end{aligned} \qquad (17.29)$$

The relation between the scattering amplitude and phase shift is

$$\boxed{\begin{aligned} f(\theta) &= \tfrac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)(e^{2i\delta_l}-1)P_l(\cos\theta) \\ &= \tfrac{1}{k}\sum_{l=0}^{\infty}(2l+1)e^{i\delta_l}\sin\delta_l P_l(\cos\theta) \end{aligned}} \qquad (17.30)$$

(do Problem 17.3) and the cross section is easily calculated as

$$\boxed{\sigma = \frac{4\pi}{k^2}\sum_l (2l+1)\sin^2\delta_l} \qquad (17.31)$$

(do Problem 17.4) From this result one can prove the famous Optical Theorem

$$\boxed{\sigma = \frac{4\pi}{k}\mathrm{Im}\, f(0)}$$

(17.32)

where Im $f(0)$ denotes the imaginary part of the forward scattering amplitude $f(\theta = 0)$. (do Problem 17.5)

(The example of hard sphere scattering is worked out, using phase shift, in [“An Introduction to Quantum Physics” by G. Sposito, 1970, QC174.1.S68])

(do Problem 17.6)

17.4 Integral Scattering Theory

17.4.1 Lippman-Schwinger Equation

Defining

$$H_0 \equiv -\frac{\hbar^2}{2m}\nabla^2 \tag{17.33}$$

the abstract Schrödinger equation is

$$(E - H_0) \mid \psi\rangle = U \mid \psi\rangle \tag{17.34}$$

or

$$(\nabla^2 + k^2)\psi = \frac{2m}{\hbar^2}U\psi \tag{17.35}$$

with

$$k \equiv \frac{\sqrt{2mE}}{\hbar}$$

The Schrödinger equation can be solved with Green function techniques. Writing

$$(\nabla^2 + k^2)G(\mathbf{r}) \equiv \delta^3(\mathbf{r}) \tag{17.36}$$

the general solution of the Schrödinger equation is

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) + \frac{2m}{\hbar^2}\int d^3\mathbf{r}'\, G(\mathbf{r} - \mathbf{r}')U(\mathbf{r}')\psi(\mathbf{r}') \tag{17.37}$$

where $G(\mathbf{r} - \mathbf{r}')$ is called a Green’s function, and $\phi(\mathbf{r})$ is the solution to the *free* Schrödinger equation (with $U = 0$).

In abstract notation this may be written

$$|\psi\rangle = |\phi\rangle + UG \mid \psi\rangle \tag{17.38}$$

or just

$$\boxed{\psi = \phi + UG\psi} \tag{17.39}$$

Equations (17.37) or (17.39) are just the *integral form of the Schrödinger equation* and is often called the *Lippman-Schwinger equation.* It may be iterated as

$$\psi = \phi + UG\phi + UGUG\phi + UGUGUG\phi + \cdots \tag{17.40}$$

which is called the *Born series.* The first *Born approximation* is just

$$\psi \approx \phi + UG\phi \tag{17.41}$$

Equation (17.40) is reminiscent of the series representing Feynman diagrams and G is often called the *propagator.* (Read [Griffiths, 1995, pg. 372])

Example 17.4 Show that (17.37) satisfies the Schrödinger equation.

Solution $\phi(\mathbf{r})$ satisfies the free Schrödinger equation,

$$(\nabla^2 + k^2)\phi = 0$$

$$\begin{aligned}
\Rightarrow (\nabla^2 + k^2)\phi(\mathbf{r}) &= (\nabla^2 + k^2)\phi(\mathbf{r}) \\
&\quad + \frac{2m}{\hbar^2}\int d^3\mathbf{r}'[(\nabla^2 + k^2)G(\mathbf{r} - \mathbf{r}')]U(\mathbf{r}')\psi(\mathbf{r}') \\
&= O + \frac{2m}{\hbar^2}\int d^3\mathbf{r}'\, \delta^3(\mathbf{r} - \mathbf{r}')U(\mathbf{r}')\psi(\mathbf{r}') \\
&= \frac{2m}{\hbar^2}U(\mathbf{r})\psi(\mathbf{r})
\end{aligned}$$

We solve (17.36) for G, plug into (17.37), and we have a general (*iterative*!) solution for the Schrödinger equation. Problem 17.7 verifies that

$$G(\mathbf{r}) = -\frac{e^{ikr}}{4\pi r} \tag{17.42}$$

(do Problem 17.7). Thus

$$\boxed{\psi(\mathbf{r}) = \phi(\mathbf{r}) - \frac{m}{2\pi\hbar^2}\int d^3\mathbf{r}'\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}U(\mathbf{r}')\psi(\mathbf{r}')} \tag{17.43}$$

17.4.2 Scattering Amplitude

The Lippman-Schwinger equation (17.43) is a general equation. Let's now apply it to scattering. Obviously

$$\phi(\mathbf{r}) = Ae^{ikz} \tag{17.44}$$

represents the incident beam of particles and the second term in (17.43) must be $f(\theta)\frac{e^{ikr}}{r}$, allowing us to extract the scattering amplitude and calculate the cross section.

The coordinate system is shown in Fig. 17.2. The coordinate $\mathbf{r}'$ gives the location of the potential $U(\mathbf{r}')$ or scatttering region. The coordinate $\mathbf{r}$ is the location of the detector, and $\mathbf{r} - \mathbf{r}'$ is the displacement between the "target" and detector. In a typical scattering experiment we have $\mathbf{r} \gg \mathbf{r}'$. To see this put the origin inside the scattering region. Then $\mathbf{r}'$ just gives the region of the scattering center, and we put our detector far away so that $\mathbf{r} \gg \mathbf{r}'$. In that case

$$\begin{aligned} |\mathbf{r} - \mathbf{r}'| &= \sqrt{|\mathbf{r} - \mathbf{r}'|^2} = \sqrt{r^2 - 2\mathbf{r}\cdot\mathbf{r}' + \mathbf{r}'^2} \\ &= r\sqrt{1 - \frac{2\mathbf{r}\cdot\mathbf{r}'}{r^2} + \left(\frac{r'}{r}\right)^2} \approx r\sqrt{1 - \frac{2\mathbf{r}\cdot\mathbf{r}'}{r^2}} \\ &\approx r - \hat{e}_r \cdot \mathbf{r}' \end{aligned} \tag{17.45}$$

Choose

$$\mathbf{k} \equiv k\hat{e}_r \tag{17.46}$$

giving

$$|\mathbf{r} - \mathbf{r}'| \approx r - \mathbf{k}\cdot\mathbf{r}' \tag{17.47}$$

Thus [Griffiths, 1994, pg. 367]

$$\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \approx \frac{e^{ikr}}{r} e^{-i\mathbf{k}\cdot\mathbf{r}'} \tag{17.48}$$

giving

$$\psi(\mathbf{r}) = Ae^{ikz} - \frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int d^3\mathbf{r}'\, e^{-i\mathbf{k}\cdot\mathbf{r}'} U(\mathbf{r}')\psi(\mathbf{r}') \tag{17.49}$$

and thus

$$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2 A}\int d^3\mathbf{r}'\, e^{-i\mathbf{k}\cdot\mathbf{r}'} U(\mathbf{r}')\psi(\mathbf{r}') \tag{17.50}$$

which is an *exact* expression for the scattering amplitude.

17.4.3 Born Approximation

The (first) Born approximation simply replaces ψ with ϕ to give

$$f(\theta, \phi) \approx -\frac{m}{2\pi\hbar^2} \int d^3\mathbf{r}'\, e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}'} U(\mathbf{r}') \tag{17.51}$$

where $\mathbf{k}$ points in the incident direction and $\mathbf{k}'$ in the scattered direction. See Figure 11.10 of [Griffiths, 1995, pg. 368]. The *momentum transfer* is defined as

$$\mathbf{q} \equiv \mathbf{k}' - \mathbf{k} \tag{17.52}$$

At *low energy* $q \approx 0$ and

$$f(\theta, \phi) \approx -\frac{m}{2\pi\hbar^2} \int d^3\mathbf{r}\, U(\mathbf{r}) \tag{17.53}$$

Now assume a spherically symmetric potential $U(\mathbf{r}) \equiv U(r)$, then

$$(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}' = \mathbf{q} \cdot \mathbf{r}' \equiv qr' \cos\theta' \tag{17.54}$$

giving (17.51) as

$$f(\theta) \approx -\frac{m}{2\pi\hbar^2} 2\pi \int r'^2 dr' \sin\theta'\, d\theta'\, e^{iqr'\cos\theta'} U(r') \tag{17.55}$$

Using [Griffiths, 1995, equation 11.49, pg. 364]

$$\int_0^\pi \sin\theta\, d\theta\, e^{isr\cos\theta} = \frac{2\sin sr}{sr} \tag{17.56}$$

gives

$$f(\theta) \approx -\frac{2m}{\hbar^2 q} \int_0^\infty r\, dr \sin(qr) U(r) \tag{17.57}$$

and

$$q = 2k \sin\frac{\theta}{2} \tag{17.58}$$

Example 17.4 Calculate the scattering amplitude and differential cross section for scattering from the Yukawa potential

$$U(r) = C\frac{e^{-\mu r}}{r} \tag{17.59}$$

Solution

$$f(\theta) \approx -\frac{2m}{\hbar^2 q} C \int_0^\infty dr \sin(qr)\, e^{-\mu r}$$

$$\text{and} \quad \int_0^\infty dr \sin(qr)\, e^{-\mu r} = \frac{q}{\mu^2 + q^2}$$

giving

$$f(\theta) = -\frac{2mC}{\hbar^2} \frac{1}{\mu^2 + q^2} \tag{17.60}$$

and

$$\frac{d\sigma}{d\Omega} = \frac{4m^2 C^2}{\hbar^4} \frac{1}{(\mu^2 + q^2)^2} \tag{17.61}$$

(do Problem 17.8)

Example 17.5 Derive the Rutherford scattering cross section from quantum mechanics.

Solution The Coulomb potential energy is

$$U(r) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} \tag{17.62}$$

Thus in the previous example $C = \frac{1}{4\pi\epsilon_0} q_1 q_2$ and $\mu = 0$ giving

$$\begin{aligned} f(\theta) &\approx -\frac{2m}{\hbar^2 q} \left(\frac{1}{4\pi\epsilon_0} q_1 q_2 \right) \frac{1}{q} \\ &= \frac{m q_1 q_2}{2\pi\epsilon_0 \hbar^2} \frac{1}{q^2} \end{aligned}$$

Using $q = 2k \sin\theta/2 = 2\frac{\sqrt{2mE}}{\hbar} \sin\theta/2$ gives

$$f(\theta) \approx \frac{q_1 q_2}{16\pi\epsilon_0} \frac{1}{E \sin^2 \theta/2} \tag{17.63}$$

or

$$\boxed{\frac{d\sigma}{d\Omega} = \left(\frac{q_1 q_2}{16\pi\epsilon_0}\right)^2 \frac{1}{E^2 \sin^4 \theta/2}} \tag{17.64}$$

which is the famous Rutherford scattering formula with the characteristic $\frac{1}{\sin^4 \theta/2}$ dependence. The *same* result occurs in classical mechanics. All students should know how to derive this result classically.

17.5 Nuclear Reactions

Chapter 18

SOLIDS AND QUANTUM STATISTICS

18.1 Solids

18.2 Quantum Statistics

Chapter 19

SUPERCONDUCTIVITY

Chapter 20

ELEMENTARY PARTICLES

Chapter 21

chapter 1 problems

21.1 Problems

1.1 Suppose 10 students go out and measure the length of a fence and the following values (in meters) are obtained: 3.6, 3.7, 3.5, 3.7, 3.6, 3.7, 3.4, 3.5, 3.7, 3.3. A) Pick a random student. What is the probability that she made a measurement of 3.6 m? B) Calculate the expectation value (i.e. average or mean) using each formula of (1.2), (1.5), (1.8).

1.2 Using the example of problem 1.1, calculate the variance using both equations (1.15) and (1.16).

1.3 Griffiths Problem 1.6.

Hints: Some useful integrals are [Spiegel, 1968, pg.98]
$\int_0^\infty e^{-ax^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$
$\int_0^\infty x^m e^{-ax^2}dx = \frac{\Gamma[(m+1)/2]}{2a^{(m+1)/2}}$
Also note $\Gamma(3/2) = \frac{\sqrt{\pi}}{2}$
Properties of the Γ function are listed in [Spiegel, 1968, pg.101]

1.4 Calculate $\frac{d\langle x\rangle}{dt}$ and show that it is the same as the velocity expectation value $\langle v\rangle$ calculated in Example 1.6.1.

1.5 Griffiths Problem 1.12.

21.2 Answers

1.1 A) 0.2 B) 3.57

1.2 0.0181

1.3 Griffiths Problem 1.6. A) $A = \sqrt{\frac{\lambda}{\pi}}$ B) $\langle x \rangle = a$, $\langle x^2 \rangle = a^2 + \frac{1}{2\lambda}$, $\sigma = \frac{1}{\sqrt{2\lambda}}$

21.3 Solutions

1.1

Let $N(x)$ be the number of times a measurement of x is made. Thus

$$\begin{aligned} N(3.7) &= 4 \\ N(3.6) &= 2 \\ N(3.5) &= 2 \\ N(3.4) &= 1 \\ N(3.3) &= 1 \end{aligned}$$

total number of measurements $N = 10$
A) Probability of 3.6 is $\frac{2}{10} = \frac{1}{5} = 0.2$
B)

$$\begin{aligned} \overline{x} &= \frac{1}{N}\sum x \\ &= \frac{1}{10}(3.7 + 3.7 + 3.7 + 3.7 + 3.6 + 3.6 \\ &\quad + 3.5 + 3.5 + 3.4 + 3.3) \\ &= 3.57 \end{aligned}$$

$$\begin{aligned} \langle x\rangle \equiv \overline{x} &= \frac{1}{N}\sum_x xN(x) \\ &= \frac{1}{10}[(3.7 \times 4) + (3.6 \times 2) + (3.5 \times 2) \\ &\quad + (3.4 \times 1) + (3.3 \times 1)] \\ &= 3 \end{aligned}$$

finally

$$\begin{aligned} \langle x\rangle = \overline{x} &= \sum_x xP(x) \\ &= \left(3.7 \times \frac{4}{10}\right) + \left(3.6 \times \frac{2}{10}\right) + \left(3.5 \times \frac{2}{10}\right) \\ &\quad + \left(3.4 \times \frac{1}{10}\right) + \left(3.3 \times \frac{1}{10}\right) \\ &= 3 \end{aligned}$$

1.2

We found the average $\langle j \rangle = 3.57$. (I will round it off later.) The squared distances are

$$\begin{aligned}(\Delta 3.7)^2 &= (3.7-3.57)^2 = 0.0169,\ (\Delta 3.6)^2 = 0.0009,\\ (\Delta 3.5)^2 &= 0.0049,\ (\Delta 3.4)^2 = 0.0289,\ (\Delta 3.3)^2 = 0.0729\end{aligned}$$

The average squared distance, using (1.15) is

$$\begin{aligned}\sigma^2 &= \left(0.0169 \times \frac{4}{10}\right) + \left(0.009 \times \frac{2}{10}\right) + \left(0.0049 \times \frac{2}{10}\right)\\ &\quad + \left(0.0289 \times \frac{1}{10}\right) + \left(0.0729 \times \frac{1}{10}\right)\\ &= 0.0181\end{aligned}$$

Using the second equation (1.16) we have

$$\begin{aligned}\langle j \rangle^2 &= 3.57^2 = 12.7449 \qquad \text{and}\\ \langle j^2 \rangle &= \sum j^2 P(j)\\ &= \left(3.7^2 \times \frac{4}{10}\right) + \left(3.6^2 \times \frac{2}{10}\right) + \left(3.5^2 \times \frac{2}{10}\right)\\ &\quad + \left(3.4^2 \times \frac{1}{10}\right) + \left(3.3^2 \times \frac{1}{10}\right)\\ &= \left(13.69 \times \frac{4}{10}\right) + \left(12.96 \times \frac{2}{10}\right) + \left(12.25 \times \frac{2}{10}\right)\\ &\quad + \left(11.56 \times \frac{1}{10}\right) + \left(10.89 \times \frac{1}{10}\right)\\ &= 12.763\end{aligned}$$

Thus $\sigma^2 = \langle j^2 \rangle - \langle j \rangle^2 = 12.763 - 12.7449 = 0.0181$ in agreement with above.

1.3 Griffith's Problem 1.6

A)

$$\begin{aligned}
& \int_{-\infty}^{\infty} \rho(x)dx = 1 && \rho(x) = Ae^{-\lambda(x-a)^2} \\
= \;& A\int_{-\infty}^{\infty} e^{-\lambda(x-a)^2} dx && \text{let } u = x-a, \quad \frac{du}{dx} = 1, \quad du = dx \\
= \;& A\int_{-\infty}^{\infty} e^{-\lambda u^2} du && e^{-\lambda u^2} \text{ is an even function} \\
= \;& 2A\int_{0}^{\infty} e^{-\lambda u^2} du && \\
= \;& 2A\frac{1}{2}\sqrt{\frac{\pi}{\lambda}} \qquad \text{integral found Pg. 98 of [Spiegel 1968]} && \\
= \;& A\sqrt{\frac{\pi}{\lambda}} && \\
& \text{therefore } \; A = \sqrt{\frac{\lambda}{\pi}} &&
\end{aligned}$$

B)

$$\begin{aligned}
\langle x\rangle &= \int_{-\infty}^{\infty} x\rho(x)dx = A\int_{-\infty}^{\infty} xe^{-\lambda(x-a)^2} dx \\
&= A\int_{-\infty}^{\infty} (u+a)e^{-\lambda u^2} du \\
&= A\left[\int_{-\infty}^{\infty} \underbrace{ue^{-\lambda u^2}}_{\text{odd function}} \; du + a \underbrace{\int_{-\infty}^{\infty} e^{-\lambda u^2} du}_{=\sqrt{\frac{\pi}{\lambda}} \text{ from above}}\right] \\
&= A\left[0 + a\sqrt{\frac{\pi}{\lambda}}\right] = a
\end{aligned}$$

$$\begin{aligned}
\langle x^2\rangle &= \int_{-\infty}^{\infty} x^2\rho(x)dx = A\int_{-\infty}^{\infty} x^2 e^{-\lambda(x-a)^2}dx \\
&= A\int_{-\infty}^{\infty}(u+a)^2 e^{-\lambda u^2}du \\
&= A\left[\int_{-\infty}^{\infty} u^2 e^{-\lambda u^2}du + 2a\int_{-\infty}^{\infty} u e^{-\lambda u^2}du + a^2\int_{-\infty}^{\infty} e^{-\lambda u^2}du\right] \\
&\equiv A[I+J+K]
\end{aligned}$$

now $J=0$ because integrand is an odd function,

$$\text{and} \qquad K = a^2\sqrt{\frac{\pi}{\lambda}}$$

to evaluate I use Pg. 98 of [Spiegel 1968]

$$\begin{aligned}
\int_0^{\infty} x^m e^{-ax^2}dx &= \frac{\Gamma[(m+1)/2]}{2a^{(m+1)/2}} \\
\text{therefore} \int_0^{\infty} x^2 e^{-ax^2}dx &= \frac{\Gamma(3/2)}{2a^{3/2}} = \frac{\sqrt{\pi}/2}{2a^{3/2}} = \frac{\sqrt{\pi}}{4a^{3/2}}
\end{aligned}$$

(See Pg. 101 of [Spiegel 1968])

Now the integrand of I is an even function

therefore $I = \int_{-\infty}^{\infty} u^2 e^{-\lambda u^2}du = 2\int_0^{\infty} u^2 e^{-\lambda u^2}du = 2\frac{\sqrt{\pi}}{4\lambda^{3/2}} = \frac{\sqrt{\pi}}{2\lambda^{3/2}}$

$$\begin{aligned}
\text{Thus } \langle x^2\rangle &= A\left[\frac{\sqrt{\pi}}{2\lambda^{3/2}} + O + a^2\sqrt{\frac{\pi}{\lambda}}\right] \\
&= \sqrt{\frac{\lambda}{\pi}}\left[\frac{1}{2\lambda}\sqrt{\frac{\pi}{\lambda}} + a^2\sqrt{\frac{\pi}{\lambda}}\right] = \frac{1}{2\lambda} + a^2
\end{aligned}$$

C)

Thus
it makes <u>sense</u>
that $\langle x\rangle = a$!

1.4 (See Griffiths Pg. 15)

$$\begin{aligned}
\frac{d\langle x\rangle}{dt} &= \frac{d}{dt}\int \Psi^* x \Psi dx \\
&= \int \frac{\partial}{\partial t}(\Psi^* x \Psi) dx \\
&= \int \left(\frac{\partial \Psi^*}{\partial t} x\Psi + \Psi^* x \frac{\partial \Psi}{\partial t}\right) dx
\end{aligned}$$

and according to the Schrödinger equation

$$\begin{aligned}
\frac{\partial \Psi}{\partial t} &= \frac{1}{i\hbar}\left[-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + U\Psi\right] = \frac{i\hbar}{2m}\frac{\partial^2\Psi}{\partial x^2} - \frac{i}{\hbar}U\Psi \\
\frac{\partial \Psi^*}{\partial t} &= -\frac{i\hbar}{2m}\frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar}U\Psi^* \quad (\text{assuming U} = \text{U}^*) \\
\text{therefore } \frac{d\langle x\rangle}{dt} &= \frac{i\hbar}{2m}\int\left(-\frac{\partial^2\Psi^*}{\partial x^2}x\Psi + \Psi^* x \frac{\partial^2 \Psi}{\partial x^2}\right) dx \\
&= -\frac{i\hbar}{2m}\int x \frac{\partial}{\partial x}\left(\frac{\partial \Psi^*}{\partial x}\Psi - \Psi^*\frac{\partial \Psi}{\partial x}\right) dx \\
&= -\frac{i\hbar}{2m}\left\{\left[x\left(\frac{\partial \Psi^*}{\partial x}\Psi - \Psi^*\frac{\partial\Psi}{\partial x}\right)\right]_{-\infty}^{\infty} - \int\left(\frac{\partial \Psi^*}{\partial x}\Psi - \Psi^*\frac{\partial \Psi}{\partial x}\right) dx\right\}
\end{aligned}$$

from integration by parts

but $\Psi(\infty) = 0$ therefore boundary term $\to 0$

$$\begin{aligned}
\frac{d\langle x\rangle}{dt} &= -\frac{i\hbar}{2m}\int\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)dx \\
&\quad \text{integrate by parts again on the } \underline{\text{first}} \text{ term} \\
&= -\frac{i\hbar}{m}\int\Psi^*\frac{\partial\Psi}{\partial x}dx \\
&\equiv \frac{\langle p\rangle}{m} \\
&= \langle v\rangle \qquad \text{in Example 1.6.1}
\end{aligned}$$

therefore *must* have $\hat{p} = -i\hbar\frac{\partial}{\partial x}$ (and *not* $\hat{p} = +i\hbar\frac{\partial}{\partial x}$).

1.5 (Griffiths 1.12)

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

$$\frac{d}{dt}\langle p\rangle = -i\hbar\left[\int_{-\infty}^{\infty}\frac{\partial\Psi^*}{\partial t}\frac{\partial\Psi}{\partial x}dx + \Psi^*\frac{\partial}{\partial x}\frac{\partial\Psi}{\partial t}dx\right]$$

use the Schrödinger equation

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} &+ U(x)\Psi = i\hbar\frac{\partial}{\partial t}\Psi \\
-\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2} &+ U(x)\Psi^* = -i\hbar\frac{\partial}{\partial t}\Psi^* \\
&\quad \text{assuming } U = U^* \text{ (real)}
\end{aligned}$$

$$\begin{aligned}
\Rightarrow \frac{d\langle p\rangle}{dt} &= \int_{-\infty}^{\infty}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2} + U\Psi^*\right)\frac{\partial\Psi}{\partial x}dx \\
&\quad - \int_{-\infty}^{\infty}\Psi^*\frac{\partial}{\partial x}\left(-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + U\Psi\right)dx \\
&= -\frac{\hbar^2}{2m}\left[\int_{-\infty}^{\infty}\frac{\partial^2\Psi^*}{\partial x^2}\frac{\partial\Psi}{\partial x}dx - \int_{-\infty}^{\infty}\Psi^*\frac{\partial^3\Psi}{\partial x^3}dx\right] \\
&\quad + \int_{-\infty}^{\infty}\left(U\Psi^*\frac{\partial\Psi}{\partial x} - \Psi^*\frac{\partial U}{\partial x}\Psi - \Psi^*U\frac{\partial\Psi}{\partial x}\right)dx \\
&= -\frac{\hbar^2}{2m}(I_1 - I_2) - \int_{-\infty}^{\infty}\Psi^*\frac{\partial U}{\partial x}\Psi\,dx \\
&= -\frac{\hbar^2}{2m}(I_1 - I_2) - \langle\frac{\partial U}{\partial x}\rangle
\end{aligned}$$

$$\text{where} \qquad I_1 \equiv \int_{-\infty}^{\infty} \frac{\partial^2 \Psi^*}{\partial x^2} \frac{\partial \Psi}{\partial x} dx \quad I_2 \equiv \int_{-\infty}^{\infty} \Psi^* \frac{\partial^3 \Psi}{\partial x^2} dx$$

$$\therefore \qquad \text{need to show } I_1 = I_2 \text{ then will have } \frac{d\langle p \rangle}{dt} = -\langle \frac{\partial U}{\partial x} \rangle$$

recall integration by parts formula $\int_a^b f\,dg = [fg]_a^b - \int_a^b g\,df$

$$\begin{aligned}
I_2 &\equiv \int_{-\infty}^{\infty} \Psi^* \frac{\partial^3 \Psi}{\partial x^3} dx = \int_{-\infty}^{\infty} \Psi^* \frac{\partial}{\partial x} \left(\frac{\partial^2 \Psi}{\partial x^2} \right) dx \\
&= \int_{-\infty}^{\infty} \Psi^* \partial \left(\frac{\partial^2 \Psi}{\partial x^2} \right) \\
&= \underbrace{\left[\Psi^* \frac{\partial^2 \Psi}{\partial x^2} \right]_{-\infty}^{\infty}}_{= 0 \text{ because } \Psi^*(\infty) = \Psi^*(-\infty) = 0} - \int_{-\infty}^{\infty} \frac{\partial^2 \Psi}{\partial x^2} \partial \Psi^* \text{ using integration by parts} \\
&= -\int_{-\infty}^{\infty} \frac{\partial^2 \Psi}{\partial x^2} \frac{\partial \Psi^*}{\partial x} dx \\
I_1 &\equiv \int_{-\infty}^{\infty} \frac{\partial^2 \Psi^*}{\partial x^2} \frac{\partial \Psi}{\partial x} dx = \int_{-\infty}^{\infty} \frac{\partial \Psi}{\partial x} \frac{\partial}{\partial x} \left(\frac{\partial \Psi^*}{\partial x} \right) dx \\
&= \int_{-\infty}^{\infty} \frac{\partial \Psi}{\partial x} \partial \left(\frac{\partial \Psi^*}{\partial x} \right) \\
&= \underbrace{\left[\frac{\partial \Psi}{\partial x} \frac{\partial \Psi^*}{\partial x} \right]_{-\infty}^{\infty}}_{= 0 \text{ because must also have } \frac{\partial \Psi}{\partial x}(\infty) = \frac{\partial \Psi}{\partial x}(-\infty) = 0} - \int_{-\infty}^{\infty} \frac{\partial \Psi^*}{\partial x} \partial \left(\frac{\partial \Psi}{\partial x} \right)
\end{aligned}$$

$$\text{if slope } \frac{\partial \Psi}{\partial x} \neq 0 \text{ when } \Psi(\infty) = 0 \text{ would have}$$

$$\begin{aligned}
&= -\int_{-\infty}^{\infty} \frac{\partial \Psi^*}{\partial x} \frac{\partial}{\partial x} \left(\frac{\partial \Psi}{\partial x} \right) dx \\
&= -\int_{-\infty}^{\infty} \frac{\partial \Psi^*}{\partial x} \frac{\partial^2 \Psi}{\partial x^2} dx \\
&\therefore I_1 = I_2 \qquad \text{QED}
\end{aligned}$$

Chapter 22

chapter 2 problems

22.1 Problems

2.1 Griffiths, Problem 2.19.

2.2 Refer to Example 2.1.1. Determine the constants for the other 3 forms of the solution using the boundary condition (i.e. determine B, C, F, δ, G, γ from boundary conditions). Show that *all* solutions give $x(t) = A\sin\omega t$.

2.3 Check that the solution given in Example 2.1.2 really does satisfy the differential equation. That is substitute $x(t) = E\cos(\omega t + \delta) + \frac{A}{\omega^2 - \alpha^2}\cos\alpha t$ and check that $\ddot{x} + \omega^2 x = A\cos\alpha t$ is satisfied.

2.4 Solve equation (2.11).

2.5 Prove that $c_n = \langle \psi_n \mid f \rangle$ (Equation (2.36)).

22.2 Answers

2.1

$$\begin{array}{llll} C = A + B, & D = i(A - B) & \text{for} & C\cos kx + D\sin kx \\ A = \frac{F}{2}e^{i\alpha}, & B = \frac{F}{2}e^{-i\alpha} & \text{for} & F\cos(kx + \alpha) \\ A = \frac{G}{2i}e^{i\beta}, & B = -\frac{G}{2i}e^{-i\beta} & \text{for} & G\sin(kx + \beta) \end{array}$$

2.2

$$\begin{array}{ll} B = \frac{A}{2i} & C = -\frac{A}{2i} \\ \delta = \frac{\pi}{2} & F = -A \\ \gamma = \pi & G = A \end{array}$$

2.3 $f(t) = Ae^{-\frac{i}{\hbar}Et}$ (equation (2.12)

22.3 Solutions

2.1 Griffiths Problem 2.19

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

$$\begin{aligned}
& Ae^{ikx} + Be^{-ikx} = A(\cos kx + i\sin kx) + B(\cos kx - i\sin kx) \\
= \;& (A+B)\cos kx + i(A-B)\sin kx \\
\equiv \;& C\cos kx + D\sin kx \Rightarrow C = A+B \qquad D = i(A-B)
\end{aligned}$$

Note if D is real then $D^* = D$ i.e.

$$\begin{gathered}
-i(A^* - B^*) = i(A-B) \\
-A^* + B^* = A - B \\
\text{satisfied if } A = B^* \quad (\Rightarrow A^* = B)
\end{gathered}$$

Thus even though D *looks* complex, it actually can be real.

$$\begin{aligned}
F\cos(kx+\alpha) &= F\frac{e^{i(kx+\alpha)} + e^{-i(kx+\alpha)}}{2} \qquad \text{using } \cos\theta = \frac{e^{i\theta}+e^{-i\theta}}{2} \\
&= \left(\frac{F}{2}e^{i\alpha}\right)e^{ikx} + \left(\frac{F}{2}e^{-i\alpha}\right)e^{-ikx} \\
&\equiv Ae^{ikx} + Be^{-ikx} \Rightarrow A = \frac{F}{2}e^{i\alpha} \quad B = \frac{F}{2}e^{-i\alpha}
\end{aligned}$$

$$\begin{aligned}
G\sin(kx+\beta) &= G\frac{e^{i(kx+\beta)} - e^{-i(kx+\beta)}}{2i} \qquad \text{using } \sin\theta = \frac{e^{i\theta}-e^{-i\theta}}{2i} \\
&= \left(\frac{G}{2i}e^{i\beta}\right)e^{ikx} + \left(-\frac{G}{2i}e^{i\beta}\right)e^{-ikx} \\
&\equiv Ae^{ikx} + Be^{-ikx} \Rightarrow A = \frac{G}{2i}e^{i\beta} \quad B = \frac{-G}{2i}e^{-i\beta}
\end{aligned}$$

2.2 Boundary conditions $x(0) = 0$, $x(T/4) = A$

i) $x(t) = Be^{i\omega t} + Ce^{-i\omega t}$

$x(0) = 0 = B + C$ therefore $C = -B$

$$\begin{aligned}
\text{therefore } x(t) &= B(e^{i\omega t} - e^{-i\omega t}) \\
&= 2iB \sin \omega t \\
x(T/4) &= A = 2iB \sin \frac{2\pi}{T}\frac{T}{4} = 2iB \sin \frac{\pi}{2} = 2iB \\
\text{therefore } B &= \frac{A}{2i} \qquad C = -\frac{A}{2i} \\
\text{therefore } x(t) &= \frac{A}{2i}(e^{i\omega t} - e^{-i\omega t}) = A \sin \omega t
\end{aligned}$$

ii) $x(t) = F \cos(\omega t + \delta)$

$x(0) = 0 = F \cos \delta$

Therefore either $F = 0$ or $\cos \delta = 0 \Rightarrow \delta = \frac{\pi}{2}$

($F = 0$ means $x = 0$ always and we don't have anything. Thus we take the second solution $\delta = \frac{\pi}{2}$)

$$\begin{aligned}
\text{therefore } x(t) &= F \cos\left(\omega t + \frac{\pi}{2}\right) = -F \sin \omega t \\
x(T/4) &= A = -F \sin \frac{2\pi}{T}\frac{T}{4} = -F \sin \frac{\pi}{2} = -F \\
\text{therefore } \delta &= \frac{\pi}{2} \qquad F = -A \\
\text{therefore } x(t) &= -A \cos\left(\omega t + \frac{\pi}{2}\right) = -A(-\sin \omega t) = A \sin \omega t
\end{aligned}$$

iii)

$$\begin{aligned}
x(t) &= G \sin(\omega t + \gamma) \\
x(0) &= 0 = G \sin \gamma \Rightarrow \gamma = \pi \\
\text{therefore } x(t) &= G \sin(\omega t + \pi) = G \sin \omega t \\
x(T/4) &= A = G \sin \frac{\pi}{2} = G \\
\text{therefore } & \quad \gamma = \pi \qquad G = A \\
\text{therefore } x(t) &= A \sin(\omega t + \pi) = A \sin \omega t
\end{aligned}$$

2.3

$$\begin{aligned}
x(t) &= E\cos(\omega t+\delta)+\frac{A}{\omega^2-\alpha^2}\cos\alpha t\\
\dot{x} &= -E\omega\sin(\omega t+\delta)-\frac{A\alpha}{\omega^2-\alpha^2}\sin\alpha t\\
\ddot{x} &= -E\omega^2\cos(\omega t+\delta)-\frac{A\alpha^2}{\omega^2-\alpha^2}\cos\alpha t
\end{aligned}$$

left hand side:

$$\begin{aligned}
\ddot{x}+\omega^2 x &= -E\omega^2\cos(\omega t+\delta)-\frac{A\alpha^2}{\omega^2-\alpha^2}\cos\alpha t\\
&\quad +E\omega^2\cos(\omega t+\delta)+\frac{A\omega^2}{\omega^2-\alpha^2}\cos\alpha t\\
&= (-\alpha^2+\omega^2)\frac{A}{\omega^2-\alpha^2}\cos\alpha t\\
&= A\cos\alpha t\\
&= \text{right hand side}
\end{aligned}$$

QED

2.4

$$\begin{aligned}
\frac{1}{f}\frac{df}{dt} &= -\frac{i}{\hbar}E\\
\int\frac{1}{f}\frac{df}{dt}dt &= -\frac{i}{\hbar}E\int dt+C' \qquad C'=\text{constant}\\
\ln f &= -\frac{i}{\hbar}Et+C'\\
f(t) &= e^{-\frac{i}{\hbar}Et+C'}=e^{C'}e^{-\frac{i}{\hbar}Et}\equiv Ce^{-\frac{i}{\hbar}Et}
\end{aligned}$$

2.5

$$\begin{aligned}
\langle \psi_n \mid f \rangle &\equiv \int \psi_n^*(x) f(x) dx \\
&= \int \psi_n^*(x) \sum_m c_m \psi_m(x) dx \\
&= \sum_m c_m \int \psi_n^*(x) \psi_m(x) dx \\
&= \sum_m c_m \delta_{mn} \qquad \text{from (2.32)} \\
&= c_n
\end{aligned}$$

QED

Chapter 23

chapter 3 problems

23.1 Problems

3.1 Consider the infinite 1-dimensional box. If the particle is an electron, how wide would the box have to be to approximate classical behavior?

(Hint: Classical behavior will pertain if the energy levels are "closely spaced" or if E_1 is close to zero. The latter condition is easier to quantify, but close to zero compared to what? The only "natural" energy side is the rest mass of the electron. Thus let's just say that classical behavior pertains if $E_1 = \frac{m_e c^2}{100}$.)

3.2 For the infinite 1-dimensional box, show that the same energy levels and wave functions as obtained in (3.14) and (3.19) also arise if the other solution $y(x) = Ae^{(\alpha+i\beta)x} + Be^{(\alpha-i\beta)x}$ is used from Theorem 1.

23.2 Answers

3.1 $a \approx 10,000\ \text{fm}\ = 10^{-11}\ \text{m}$ (*approximately*)

23.3 Solutions

3.1

$$E_1 = \frac{\pi^2\hbar^2}{2ma^2} = \frac{m_e c^2}{100}$$

Now rest mass of electron is $m_e c^2 = 0.511$ MeV and $\hbar c = 197$ MeV fm where a fermi is fm $\equiv 10^{-15} m$. (1 fm $\approx$ size of proton)

$$\frac{\pi^2(\hbar c)^2}{2m_e c^2 a^2} = \frac{m_e c^2}{100}$$

Therefore

$$\begin{aligned}
a^2 &= 100\frac{\pi^2(\hbar c)^2}{2(m_e c^2)^2} \\
&= 100\frac{n^2 \times 197^2 \text{ MeV}^2 \text{ fm}^2}{2 \times 0.511^2 \text{ MeV}^2} \\
&= 73,343,292 \text{ fm}^2 \\
a &= 8,564 \text{ fm} \\
a &\approx 10,000 \text{ fm } = 10^{-11} m \qquad (\textit{approximately})
\end{aligned}$$

3.2 Boundary conditions $\psi(x=0) = \psi(x=a) = 0$. The solution to the auxilliary equation is given in the text (3.4) as $r = \pm ik$. Thus $\alpha = 0$ and $\beta = k$ where $r \equiv \alpha \pm i\beta$. Thus $r_1 = +ik$ and $r_2 = -ik$ which are distinct roots. The solution is $\psi(x) = Ae^{r_1 x} + Be^{r_2 x}$. The other solution from Theorem 1 is

$$\begin{aligned}
\psi(x) &= Ae^{(\alpha+i\beta)} + Be^{(\alpha-i\beta)x} \\
&= Ae^{ikx} + Be^{-ikx} \\
\psi(x=0) = 0 &= A + B \quad \text{therefore} \quad B = -A \\
\text{therefore } \psi(x) &= A(e^{ikx} - e^{-ikx}) = 2iA \sin kx \\
\psi(x=a) = 0 &= 2iA \sin ka \\
\text{therefore } ka &= 0, \ \pm\pi, \ \pm 2\pi
\end{aligned}$$

and using same reasoning as in text we get

$$k = \frac{n\pi}{a} \qquad n = 1, 2, 3 \cdots$$

$$\begin{aligned} \text{giving} \qquad E_n^2 &= \frac{\hbar^2 k^2}{2m} = n^2 \frac{\pi^2 \hbar^2}{2ma^2} \\ \text{or} \qquad E_n &= \frac{n\pi\hbar}{\sqrt{2m}a} \end{aligned}$$

The wave function normalization follows (3.17) and (3.18). From the above we have

$$\begin{aligned} \psi(x) &= A(e^{ikx} - e^{-ikx}) \qquad \text{(see Solution to Problem 2.2)} \\ &= 2iA \sin kx = 2iA \sin \frac{n\pi}{a} x \end{aligned}$$

Now

$$-4A^2 \int_0^a \sin^2 \frac{n\pi}{a} x \, dx = 1$$

The integral is done in the text (see equation (3.19)) giving $-4A^2 \frac{a}{2} = 1$. Thus $A = i\frac{1}{2}\sqrt{\frac{2}{a}}$

Thus

$$\begin{aligned} \psi(x) &= 2iA \sin \frac{n\pi}{a} x \\ &= 2i \, i\frac{1}{2}\sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x \\ &= -\sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x \end{aligned}$$

which is the same as (3.19) except for an irrelevant minus sign.

Chapter 24

chapter 4 problems

24.1 Problems

4.1 Show that the expectation value of the Hamiltonian or Energy operator is real (i.e. show that $\langle\hat{E}\rangle$ is real where $\hat{E} = i\hbar\frac{\partial}{\partial t}$).

4.2 Find the eigenfunctions of the momentum operator assuming that $\hat{P}\phi = p\phi$ where p is the momentum.

4.3 Griffiths Problem 2.8.

4.4 Griffiths Problem 2.9.

4.5 Griffiths Problem 2.10.

24.2 Answers

4.2 Griffiths Problem 2.8.

A)

$$A = \sqrt{\frac{30}{a^5}}$$

B)

$$\begin{aligned} \langle x\rangle &= \frac{a}{2} \\ \langle p\rangle &= 0 \\ \langle H\rangle &= \frac{5\hbar^2}{ma^2} \end{aligned}$$

4.4 Griffiths Problem 2.9.

$$\begin{aligned} c_i &= 0.99928 \\ c_2 &= 0 \\ c_3 &= 0.03701 \end{aligned}$$

24.3 Solutions

4.1 In Section 2.3.3 we saw that the expectation value of the Hamiltonian was just the total energy, i.e. $\langle H\rangle = E$.

Instead of using $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U$ let's instead note that $\hat{H}\Psi = i\hbar\frac{\partial}{\partial t}\Psi$ and use $\hat{H} = i\hbar\frac{\partial}{\partial t}$. Thus

$$\begin{aligned}\langle\hat{H}\rangle &= i\hbar\int_{-\infty}^{\infty}\Psi^*\frac{\partial}{\partial t}\Psi\,dx\\ \langle\hat{H}\rangle^* &= -i\hbar\int_{-\infty}^{\infty}\Psi\frac{\partial}{\partial t}\Psi^*\,dx\end{aligned}$$

From the Schrödinger equation

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

we have

$$\langle\hat{H}\rangle = -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\Psi^*\frac{\partial^2\Psi}{\partial x^2}dx + \int_{-\infty}^{\infty}\Psi^* U\Psi\,dx$$

and

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

assuming

$$U = U^*$$

we have

$$\begin{aligned}\langle\hat{H}\rangle^* &= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\Psi\frac{\partial^2\Psi^*}{\partial x^2}dx + \int_{-\infty}^{\infty}\Psi U\Psi^*\,dx\\ \Rightarrow\ \langle\hat{H}\rangle - \langle\hat{H}\rangle^* &= -\frac{\hbar^2}{2m}\left\{\int_{-\infty}^{\infty}\Psi^*\frac{\partial^2\Psi}{\partial x^2}dx - \int_{-\infty}^{\infty}\Psi\frac{\partial^2\Psi^*}{\partial x^2}dx\right\}\end{aligned}$$

The second integral is evaluated using integration by parts. Define

$$\begin{aligned}I &\equiv \int_{-\infty}^{\infty}\Psi\frac{\partial^2\Psi^*}{\partial x^2}dx\\ &= \int_{-\infty}^{\infty}\Psi\frac{\partial}{\partial x}\left(\frac{\partial\Psi^*}{\partial x}\right)dx\\ &= \int_{-\infty}^{\infty}\Psi d\left(\frac{\partial\Psi^*}{\partial x}\right)\end{aligned}$$

$$\begin{aligned}
&= \left[\Psi\frac{\partial\Psi^*}{\partial x}\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\frac{\partial\Psi^*}{\partial x}d\Psi \\
&= 0 - \int_{-\infty}^{\infty}\frac{\partial\Psi^*}{\partial x}\frac{\partial\Psi}{\partial x}dx \\
&= -\int_{-\infty}^{\infty}\frac{\partial\Psi}{\partial x}\frac{\partial\Psi^*}{\partial x}dx = -\int_{-\infty}^{\infty}\frac{\partial\Psi}{\partial x}d\Psi^* \\
&= -\left[\frac{\partial\Psi}{\partial x}\Psi^*\right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty}\Psi^* d\left(\frac{\partial\Psi}{\partial x}\right) \\
&= 0 + \int_{-\infty}^{\infty}\Psi^*\frac{\partial}{\partial x}\left(\frac{\partial\Psi}{\partial x}\right)dx \\
&= \int_{-\infty}^{\infty}\Psi^*\frac{d^2\Psi}{dx^2}dx
\end{aligned}$$

Thus

$$\begin{aligned}
\langle\hat{H}\rangle &- \langle\hat{H}\rangle^* = 0 \\
\langle\hat{H}\rangle &= \langle\hat{H}\rangle^*
\end{aligned}$$

Thus the expectation value of the Hamiltonian operator is real.

4.2

$$\begin{aligned}
&\hat{P}\phi = p\phi \\
&\hat{P} \equiv -i\hbar\frac{\partial}{\partial x} \\
&-i\hbar\frac{\partial\phi}{\partial x} = p\phi \\
&\int\frac{1}{\phi}\frac{\partial\phi}{\partial x}dx = \frac{p}{-i\hbar}\int dx \\
&\ln\phi = \frac{i}{\hbar}px \\
&\phi = \phi_0 e^{\frac{i}{\hbar}px}
\end{aligned}$$

which are the *momentum eigenfunctions.*

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