Phys 3810 (Quantum Mechanics) Notes

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Chapter 1

The Schrödinger Equation and Its Meaning

1.1 The Schrödinger Equation

Classical mechanics is all about finding the trajectory of a particle of mass m when it is subjected to a force $F(\mathbf{r}, t)$. The object is to find the position as a function of time, $\mathbf{r}(t)$. One way or another that's what we did in classical mechanics. We can *not* do this to describe motion at the atomic level because it is essentially impossible to find such a trajectory function. What we *do* find is the **wave function** for the **state** of the particle.

The wave function $\Psi(x, t)$ is *complex*–valued. (For now we will work with one space dimension.)

And without further ado, the wave function is given by the Schrödinger Equation,

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

Essentially, we will spend the rest of this chapter unraveling what it tells us, and the rest of the course finding solutions to it in different cases of physical interest.

1.2 Statistical Meaning of Ψ

The statistical interpretation of Ψ is due to Born and sez that $|\Psi(x, t)|^2$ gives the probability of finding the particle at point x at time t:

$$|\Psi(x, t)|^2 = \text{Probability of finding particle between } x \text{ and } x + dx \text{ at time } t.$$

See the discussion of the text for different attempts to get the meaning of this. Though the search for understanding of QM continues to this day, the consensus is that nature, at its most basic level, *is* probabilistic and we have to accept that fact— and learn how to deal with it.

1.3　Probability

Relations for a *discrete* probability distribution $N(j)$:

$$N = \sum_{j=0}^{\infty} N(j) \qquad P(j) = \frac{N(j)}{N} \qquad \langle f(j) \rangle = \sum_{j=0}^{\infty} f(j) P(j)$$

Standard deviation in j for this distribution is

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

A probability distribution for a continuous variable, $\rho(x)$ satisfies

$$P_{ab} = \int_a^b \rho(x)\, dx \qquad \int_{-\infty}^{\infty} \rho(x)\, dx = 1 \qquad \langle f(x) \rangle = \int_{-\infty}^{\infty} f(x) \rho(x)\, dx$$

and the standard deviation of x is

$$\sigma^2 \equiv \langle (\Delta x) \rangle = \langle x^2 \rangle - \langle x \rangle^2$$

If our wave function $\Psi(x, t)$ is to give a sensible probability distribution it must be **normalized**, that is, it must satisfy

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

An essential idea of QM (shown in a text example) is that of the **probability current**. One can show that with

$$J(x, t) \equiv \frac{i\hbar}{2m} \left(\Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right)$$

then the *rate of change* of the probability of finding the particle between a and b is

$$\frac{dP_{ab}}{dt} = J(a, t) - J(b, t)$$

1.4　Momentum

An **expectation value** of a physical quantity is the average value we get for that quantity if we make repeated measurements of it for particles prepared in the same Ψ. It is

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi(x, t)|^2\, dx$$

The nearest thing to a "velocity" (or rather its expectation value) that we have in QM is to take the time derivative of $\langle x \rangle$. We can then relate this to the momentum, $\langle p \rangle$ by multiplying by m. We find:

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt} = -i\hbar \int \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) dx = \int \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi\, dx$$

and comparing the expectation values of x and p leads us to the associations

$$x \leftrightarrow x \quad \text{(factor)} \qquad p \leftrightarrow \frac{\hbar}{i} \frac{\partial}{\partial x} \quad \text{(operator)}$$

When we want other physical quantities we will build them up from x and p. Then the expectation value of the general physical quantity is

$$\langle Q(x,p) \rangle = \int \Psi^* \, Q\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right) \Psi \, dx$$

As an example of this, the expectation value of the kinetic energy, $T = p^2/2m$ is

$$\langle T \rangle = \frac{-\hbar^2}{2m} \int \Psi^* \frac{\partial^2 \Psi}{\partial x^2} \, dx$$

An interesting result which is as close as we can come to Newton's second law in QM is a case of Ehrenfest's Theorem (shown in one of the problems),

$$\frac{d\langle p \rangle}{dt} = \left\langle -\frac{\partial V}{\partial x} \right\rangle$$

1.5 Uncertainty Principle

While we will do a full derivation of the famous Uncertainty Principle in Chapter 3, we can give a preview of what it will mean when applied to the quantities x and p.

Chapter 2

The Time–Independent Schrödinger Equation

2.1 Introduction

In this chapter we present the **time–independent Schrödinger equation**, the thing people refer to (wrongly) as "the" Schrödinger equation. We will consider the meaning of its solutions in terms the measurement of the energy of a particle and then we will go on to solve practically every one–dimensional problem you will need to solve.

Along the way we will pick up many mathematical techniques and develop our understanding of the wave functions of quantum mechanics.

2.2 Stationary States

We want the find the solution $\Psi(x,t)$ for various physical situations. Even without 3 dimensions we still have a functions of two variables to find.

We will look for solutions that are products of a space function and a time function:

$$\Psi(x,t) = \psi(x)f(t)$$

Putting this form into the (time–dependent) Schrödinger equation, one gets

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

Here the left side depends only on t and the right side depends only on x. It follows that each side must be equal to a constant which call E (for... energy!) The equation for $f(t)$ then gives

$$\frac{df}{dt} = -\frac{iE}{\hbar}f \qquad \Longrightarrow \qquad f(t) = e^{-iEt/\hbar}$$

(where we should have a constant out in front, but that will be handles later in the $\psi(x)$ part) and the x equation gives

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi \tag{2.1}$$

Eq. 2.1 is called the **time-independent Schrödinger equation**. We can't solve it unless the potential function $V(x)$ is specified. But when we do, the solution will be of the form:

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \tag{2.2}$$

Some comments on our separated solution to the Schrödinger equation:

1. We have found **stationary states**, meaning that since the form of the solution gives

$$\Psi(x,t)|^2 = |\psi(x)|^2$$

there is no time dependence to the probability density. This implies that $\langle x \rangle$ is constant and $\langle p \rangle = 0$.

2. The states we find this way are states of definite total energy. The total energy operator, called the **Hamiltonian** is found from the classical expression by

$$H(x,p) = \frac{p^2}{2m} + V(x) \qquad \Longrightarrow \qquad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

so that the time-independent Schrödinger equation is written compactly as

$$\hat{H}\psi = E\psi$$

The expectation value of the total energy operator is

$$\langle H \rangle = \int \psi^* \hat{H}\psi \, dx = E \int |\psi|^2 \, dx = E$$

and one can show that $\sigma_H = 0$. Every measurement of the total energy will return the value E for a particle in this stationary state.

3. The general solution to the time-dependent SE is a linear combination of separable solutions; our solutions of the form given in Eq. 2.2 really give us all we need to solve any problem. The general solution has the form

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iEt/\hbar} \tag{2.3}$$

where the conditions of the problem will give us the coefficients c_n.

2.3   Infinite Square Well ("Box")

We now go on to solve the time–independent SE for "simple" potentials. Yep, simple, right.

We should understand *why* we are solving such problems. In nature particles don't move in the simple potentials that we will consider here. At best, a real-life potential might be close to one that we'll solve, as with the harmonic oscillator. (Then we might say that our simple potential is a "toy model".

But by solving these problems we will get some valuable mathematical experience. Also, since there are very few problems in QM which permit exact solutions, we might be able to use one of these examples as a starting point for a more precise calculation.

The simplest potential is

$$V(x) = \begin{cases} 0, & \text{if } 0 \leq x \leq a \\ \infty, & \text{otherwise} \end{cases}$$

as illustrated in Fig. 2.1 We want to use the TISE to find valid solutions for $\psi(x)$

Outside the well it is clear that the particle can't be found, so we expect to get $\psi = 0$ for $x < 0$ and $x > a$. For the region $0 \geq x \leq a$, with the definition (which we will make often)

$$k = \frac{\sqrt{2mE}}{\hbar}$$
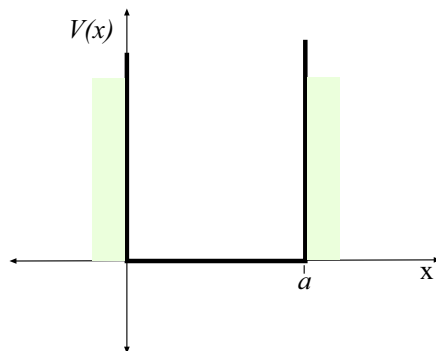
Figure 2.1: Infinite square well, of width a.

(it makes sense, because we fully expect the energy values to be positive) the Schrödinger equation can be written as

$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

which has trig functions as solutions.

The condition that the wave function be continuous (so $\psi(0) = 0$ and $\psi(a) = 0$ leads to a condition on k and gives the solution

$$\psi(x) = A\sin\left(\frac{n\pi x}{a}\right)$$

and energy eigenvalues

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad n = 1, 2, 3, \ldots \tag{2.4}$$

and the normalization condition gives the full solutions

$$\psi(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \tag{2.5}$$

We note:

- The solutions are alternately even and odd about $a/2$

- As we increase in energy (and in n) the successive states have one more node

- The wave functions satisfy

$$\int \psi_m(x)^*\psi_n(x)\,dx = 0 \qquad \text{if} \quad m \neq n$$

and so

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

and we say the ψ_n's are **orthonormal**. (A generalization of the orthonormal basis of our conventional vectors.)

The ψ_n's are **complete**, meaning that *any* function satisfying the boundary conditions can be expressed as a linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi x}{a}\right)$$

We can find the c_n using "Fourier's Trick"; multiply both sides by $\psi_m(x)^*$ and integrate. The result is

$$c_n = \int \psi_n(x)^* f(x)\, dx$$

It follows that the general stationary states of the infinite square well is

$$\Psi(x,t) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi x}{a}\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}$$

where

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \Psi(x,0)\, dx$$

This shows (for this one example at least) that knowing the solutions for the stationary states gives the most general solution to the Schrödinger equation.

The *meaning* of the coefficients in the this expansion for a general state is that $|c_n|^2$ gives the probability that a measurement of the energy of the system gives the value E_n. One often says (loosely) that $|c_n|^2$ is that probability that the system is in the nth state, but as Griffiths notes, the particle *is* in state Ψ.

The c_n's must satisfy

$$\sum_{n=1}^{\infty} |c_n|^2 = 1$$

and one can also show that the expectation value of H for the state Ψ is

$$\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n$$

2.4   The Harmonic Oscillator

The next simplest choice for the potential $V(x)$ is the "spring potential" of elementary classical physics. It is of enormous importance for quantum physics as well, because if a potential function has a minimum somewhere, in the neighborhood of that minimum one can always approximate the potential as a quadratic function having the form $V = \frac{1}{2}kx^2$ (plus a constant, which we can ignore), x being the displacement from the minimum.

Defining ω (the angular frequency of the motion in the classical problem) as

$$\omega = \sqrt{\frac{k}{m}} \qquad \Longrightarrow \qquad V(x) = \tfrac{1}{2}m\omega^2 x^2$$

the TISE for ψ is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \tfrac{1}{2}m\omega^2\psi = E\psi \tag{2.6}$$

which applies for *all* x, though we expect the wave functions to be small (but *not* zero) in the regions where the classical motion is not allowed. The solutions must approach zero as $x \to \pm\infty$ so that they can be normalized.

The differential equation 2.6 can be solved (we'll do it) but it's not especially easy and requires us to think about power series. In fact there are two different ways of solving it. The second way involves the (important) method of "ladder operators" and uses cleaver algebraic tricks as opposed to standard methods of solving DE's. In many courses this special method would be presented later on, but Griffiths sez: Let's do it now! So we'll go though both methods. We'll certainly know a lot about the harmonic oscillator when we're done.

2.4.1 Algebraic Method

Using the momentum operator, the Schrödinger equation for the harmonic oscillator can also be written

$$\frac{1}{2m}[p^2 + (m\omega x)^2]\psi = E\psi$$

We make the definitions of the operators

$$a_\pm \equiv \frac{1}{\sqrt{2\hbar m\omega}}(\mp ip + m\omega x) \tag{2.7}$$

and in a proof which you will find in the book, Griffiths shows that the Hamiltonian can be written in terms of these operators as

$$H = \hbar\omega\left(a_- a_+ - \tfrac{1}{2}\right) = \hbar\omega\left(a_+ a_- + \tfrac{1}{2}\right)$$

Then he shows that if ψ is an eigenstate of H with eigenvalue E, then the states

$$a_+\psi \qquad \text{and} \qquad a_-\psi$$

are also eigenstates of H, and have eigenvalues

$$E + \hbar\omega \qquad \text{and} \qquad E - \hbar\omega$$

respectively. Because of these properties, the operator a_+ is known as a **raising operator** and a_- is known as a **lowering operator**.

Since the energy of all the states must be positive and so there must be a state ψ_0 for which

$$a_-\psi_0 = 0$$

Now, resurrecting the definition of a_- (which involves a derivative operator thru the momentum operator) we get a much *simpler* DE for the lowest state ψ_0:

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar}x\psi_0$$

for which the normalized solution is

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2} \tag{2.8}$$

The energy of this state is

$$E_0 = \tfrac{1}{2}\hbar\omega$$

so that we can get *all* the states by successively applying the raising operator to this state. The final result is:

$$\psi_n(x) = \frac{1}{\sqrt{n!}}(a_+)^n \psi_0(x) \qquad \text{with} \quad E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega \tag{2.9}$$

Along the way in derivations of these results some important relations were used, which we note down here.

The commutator of two operators A and B is

$$[A, B] \equiv AB - BA$$

and we have the very important commutator,

$$[x, p] = i\hbar$$

The raising and lowering operators relate the individual states by

$$a_+\psi_n = \sqrt{n+1}\,\psi_{n+1} \qquad a_-\psi_n = \sqrt{n}\,\psi_{n-1} \tag{2.10}$$

These relations can be useful when evaluating certain integrals involving the HO wave functions. The integrand may involve x or p operating on a wave function. We can write this in terms of a_+ and a_- operating on the wave function and then use Eq. 2.10 along with orthonormality to do the integrals very easily. An example is found in Example 2.5

2.4.2   Analytic Method

Now go back to original Schrödinger equation for the HO potential and try to get the solutions the conventional hard way. There are reasons for doing this even though we can (in principle) get all the solutions from the results of the last section. First, Eq. 2.9 can be unwieldy to use; secondly the experience in solving this problem will be useful when we solve the more difficult problem of the H atom later on.

Eq. 2.6 can be cleaned up a little by introducing the dimensionless variable

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x \tag{2.11}$$

Then it can be shown that this DE becomes

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi \tag{2.12}$$

where $K = \frac{2E}{\hbar\omega}$.

This still isn't an easy equation. (We've already gotten *one* solution but that doesn't help much.)

We use some inspiration: At large x (large ξ), ξ^2 has got to be much bigger than K, so the DE of 2.12 behaves like

$$\frac{d^2\psi}{d\xi^2} \approx \psi \qquad \text{large } x$$

and for a little figuring, this has the solution

$$\psi(\xi) = Ae^{-\xi^2/2}$$

(there is a solution with positive exponent, but it is not permitted since that function blows up at large x.)

This *suggests* that if we pull off a factor of $e^{-\xi^2/2}$ and define

$$\psi(\xi) \equiv h(\xi)e^{-xi^2/2}$$

then we will get a friendlier equation for $h(\xi)$.

In fact, the equation that we get is

$$\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (K-1)h = 0$$

which looks worse than the original: Science takes a giant leap backwards. At this point we have to set up a power series for $h(\xi)$:

$$h(\xi) = \sum_{j=0}^{\infty} a_j \xi^j$$

Substituting and doing some algebra gives a **recurrence relation** between the coefficients (what we're normally after when use a power series),

$$a_{j+2} = \frac{(2j+1-K)}{(j+1)(j+2)}a_j$$

which in fact *does* determine the solution (before we apply the boundary conditions).

One then realizes that if this power series has an infinite number of terms the solution will be unsuitable for a wave function which must vanish at large ξ. The series must "truncate", and from this it follows that K is specified by

$$2n + 1 - K = 0 \qquad \text{for} \quad n = 1, 2, 3, \ldots$$

and this gives the possible values of the energy,

$$E_n = (n + \tfrac{1}{2})\hbar\omega$$

which is the same answer as before, gotten in a totally different way. We can say that the *reason* that the energy is quantized is that for all the improper values, the wave function found from the Schrödinger equation will behave improperly.

Reassembling the pieces to get the wave functions, we note that from the recursion relation, either

$$a_0 \neq 0, \ a_1 = 0 \qquad \text{or} \qquad a_0 = 0, \ a_1 \neq 0$$

For the first, the wave function is even in x and for the second it is odd in x.

The polynomials $h(\xi)$ are simply related to some well–studied functions in math called the **Hermite polynomials**, of which the first few are

$$H_0 = 1 \qquad H_1 = 2\xi \qquad H_2 = 4\xi^2 - 2 \qquad H_3 = 8\xi^3 - 12\xi$$

and one can show that the normalized wave functions are

$$\psi(\xi) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n\, n!}} H_n(\xi)e^{-\xi^2/2} \tag{2.13}$$

with ξ given by Eq 2.11.

2.5   The Free Particle

Now we turn to a case which might seem even more simple than those we considered: a particle moving freely, that is, $V(x) = 0$ everywhere. In classical mechanics, a particle would move at constant velocity under these conditions.

The TISE for this case is simple:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{2.14}$$

which is a bit more simply written as

$$\frac{d^2\psi}{dx^2} = -k^2\psi \tag{2.15}$$

where $k = \sqrt{2mE}/\hbar$. (This is the same DE as we had for the interior of the box.) There, the solution was written in terms of sin and cos but here we prefer to use complex exponentials. Thus:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

But we have no boundary conditions, so there's no reason to discard either of the terms here.

It helps our understanding to replace the time dependence in this solution. Thus:

$$\Psi(x,t) = Ae^{ik(x-\frac{\hbar k}{2m}t)} + Be^{-ik(x+\frac{\hbar k}{2m}t)}$$

and now from our experience (?) with wave solutions we see that the first term is a (complex) wave moving to the right and the second is a wave moving to the left. The difference between the two terms is the sign associated with k (which was defined as positive) but if we now allow k to be positive or negative we can write down one of the terms for simplicity. So our solution for a wave traveling in *some* direction is

$$\Psi_k(x,t) = Ae^{i(kx-\frac{\hbar k^2}{2m}t)} \qquad \text{with} \quad k = \pm\frac{\sqrt{2mE}}{\hbar} \tag{2.16}$$

Trying to identify the particle "velocity" for this wave gives a small problem. The speed of the quantum wave is the ratio of the t coefficient to the x coefficient, which gives

$$v_{\text{quantum}} = \sqrt{\frac{E}{2m}}$$

whereas from the classical formula $E = \frac{1}{2}mv^2$ we have

$$v_{\text{classical}} = \sqrt{\frac{2E}{m}}$$

The resolution of this "paradox" will be given shortly.

A more serious issue is that the wave function we have cannot be normalized! The solution in 2.16 gives

$$\int_{-\infty}^{\infty} \Psi_k^* \Psi_k \, dx = |A|^2 \int_{-\infty}^{\infty} 1 \, dx = \infty \quad (!)$$

which means that this wave functions cannot describe a true physical state. So there is *no such thing* as a free particle moving with a definite energy. However the solution found here is of enormous use to us *mathematically* so we forge ahead. . .

We *can* get a proper physical state if we sum over solutions of the type in 2.16. Rather, we do an *integral* these functions (over k), weighted by a function we'll call $\phi(k)$:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} \, dk$$

where we put a $1/\sqrt{2\pi}$ in front for later convenience. Such a function can localized in space (and thus normalizeable) but it carries a range eigenvalues k and thus it surely carries a range of "speeds" regardless of the precise meaning of "speed"!

In particular, at $t = 0$ the wavefunction we've constructed is

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx} \, dk$$

and if you had a healthy math background you'd say that $\Psi(x,0)$ is the (inverse) **Fourier transform** of $\psi(k)$. Or, equivalently, $\phi(k)$ is the **Fourier transform** of $\Psi(x,0)$.

The Fourier transform is of great importance in theory of wave and also in QM (which is also all about waves). Is the mathematical means by which we alternate between the coordinate representation of a wave and the frequency representation of a wave. In QM we might say it is the means by which we go from a coordinate representation of a wave function to a momentum representation of a wave function.

A function $F(k)$ and its Fourier transform $f(x)$ are related by "Plancheral's theorem", which is

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) e^{ikx} \, dk \qquad\qquad F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} \, dx \qquad\qquad (2.17)$$

Note the different sign in the exponential in the two transforms.

Of course, these integrals have to *exist* for particular choices of $f(x)$ and $F(k)$; there are lots of juicy mathematical issues. But we push onward...

From this theorem then, we get:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx} \, dx$$

In words, this gives the *momentum* wave function from initial ($t = 0$)value of the *coordinate* wave function $f(x)$.

We see from working a few examples that if $\Psi(x,0)$ is "thin" then the momentum wave function is "broad" and vice-versa. This again brings us close to the content of the Uncertainty Principle, but we return to the question of the velocity of the wave.

We did find that for our wave $\Psi_k(x,t)$, the velocity of its wiggles is given by

$$v_{\text{wave}} = \frac{\hbar|k|}{2m}$$

but these are not wiggles in *probability*, which what is actually measured. The velocity we need to be concerned with is velocity of wiggles in the probability, and this is called the **group velocity**, v_{group}. The velocity of the wave is properly called the **phase velocity**.

As a concrete example one can consider a wave packet, which has the shape of a modulated but *finite* wiggle. The group velocity is the velocity of the modulating "envelope". If the rapid

wiggle comes from a narrow distribution of frequencies centered on ω_0 (with wavenumber k_0) then, whereas the phase velocity of the pure ω_0 wave is

$$v_{\text{phase}} = \left.\frac{\omega}{k}\right|_{k_0} = \frac{\hbar k_0}{2m}$$

one can show that the group velocity is

$$v_{\text{group}} = \left.\frac{d\omega}{dk}\right|_{k_0} = \frac{\hbar k}{m}$$

As v_{group} is what corresponds to the "classical" velocity, then we have

$$v_{\text{group}} = v_{\text{classical}} = 2v_{\text{phase}}$$

thus resolving the confusion.

2.6   The Delta–Function Potential

So far the problems we've solved have had either all localized or **bound states** (square well, harmonic oscillator) or else, like the free particle were unlocalized, or **scattering states**.

These simple cases were not realistic; in the real world a potential will go to *zero* at infinity. Such a potential might give both bound *and* scattering states.

The δ–function potential is the extreme case of a *finite* square well (which we will also solve, shortly). This makes the answer simple at the expense of dealing with some slightly strange mathematics. Recall the properties of the delta function; roughly speaking, one has

$$\delta(x) = \begin{cases} 0 & \text{if } x \neq 0 \\ \infty & \text{if} x = 0 \end{cases}$$

and

$$\int_{-\infty}^{\infty} f(x)\delta(x - a) = f(a) \quad \text{so that} \quad f(x)\delta(x - a) = f(a)\delta(x - a)$$

Delta functions can be made into proper objects when they are treated as "distributions", a generalization of our usual functions. The definition can be extended to three-dimensional integrals.

We consider the potential energy function:

$$V(x) = -\alpha\delta(x)$$

that is, the function is a negative spike of "strength" α. [Watch out; the *units* are subtle here, since α must have units of Energy · Length.]

We will want to solve for *all* the quantum states, both for $E < 0$ and $E > 0$. But how to solve the DE when we have such a strange function as $\delta(x)$ present? It's not as scary as it seems; we just need to break up the problem and use one special trick. First, define

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

which is OK because E is negative. With this definition, the TISE for all x *except* $x = 0$ becomes

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi$$

for which the general solution has the form

$$\psi(x) = Ae^{-\kappa x} + Be^{+\kappa x}$$

but to keep the function from blowing up for $x \to \pm\infty$ we have to choose the terms with the right behavior. This leads to

$$\psi(x) = \begin{cases} Be^{\kappa x} & x < 0 \\ Fe^{-\kappa x} & x > 0 \end{cases}$$

Now we don't have a DE right *at* $x = 0$, but we can solve for B and F (and the energy!) using boundary conditions an normalization. First, $\psi(x)$ must be continuous at $x = 0$. This give $F = B$, and we can write the wave function simply as

$$\psi(x) = Be^{-\kappa|x|}$$

The other condition one might think of applying is the continuity of $d\psi/dx$ everywhere, but in fact here it does *not* need to be continuous because of the behavior of V at $x = 0$. The trick we use is to *integrate* the respective terms of the Schrödinger equation from $x = -\epsilon$ to $x = +\epsilon$:

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

where we let $\epsilon \to 0$. After a few steps (for example, the right side gives zero) one finds

$$\left.\frac{d\psi}{dx}\right|_{0^+} - \left.\frac{d\psi}{dx}\right|_{0^-} = \frac{2m\alpha B}{\hbar^2}$$

Here the left side is the difference in slopes of ψ between the right side of the origin and the left side. A little more work gives us the value of the energy:

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

Finally we can get B from normalization of ψ. One can show:

$$B = \frac{\sqrt{m\alpha}}{\hbar}$$

There is just *one* bound state for this potential. (The finite square wells which we'll solve later will in general have one or more.)

Now we solve for the scattering states $(E > 0)$. Again with the definition $k = \sqrt{2mE}/\hbar$ the Schrödinger equation is

$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

which has solutions which can be expressed as trig functions or complex exponentials. We choose the latter, getting

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

and for now we can't rule out either term for the limit $x \to \infty$. (And note that again, these are non-normalizable states so that some care is needed.) We will write:

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Fe^{ikx} + Ge^{-ikx} & x > 0 \end{cases}$$

We have to solve for these coefficients, but we *don't* need to solve for the energy because any positive value is permissible.

Continuity of ψ gives

$$A + B = F + G$$

If we do the same trick as before and integrate the Schrödinger equation over a small interval around the origin, one can show

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta) \qquad \text{where} \quad \beta = \frac{m\alpha}{\hbar^2 k}$$

but this is only two equations to find the four unknowns, A, B, F and G. The condition of normalization for localized states does not help us here. We actually have to make a choice of coefficients depending on the "experiment" we are considering.

We have seen that the term with e^{+ikx} corresponds to a wave traveling to the right; e^{-ikx} gives a wave traveling to the left. We choose to consider particles (a whole lot of them, in fact) which are incident *from the left*. They interact with the potential and afterward have probabilities of continuing to travel to the right or to bounce back and travel to the left. But with with choice there are no particles with $x > 0$ which are traveling to the left; particles are only incoming from the left side. This means that $G = 0$ in our solution, but the other coefficients are not zero. Then the matching conditions give

$$B = \frac{i\beta}{1 - i\beta}A \qquad \text{and} \qquad F = \frac{1}{1 - i\beta}A$$

Now a further bit of interpretation for this result. The incoming wave represents the motion of a *single particle*. (Though experimental setups send a "beam" of particles toward a target, the incoming wave here does *not* represent more than one particle!) Certainly in the elementary sense of the word, A is the amplitude of the incoming wave, B is the amplitude of the reflected wave and F is the amplitude of the transmitted wave.

If we take these values to also be *quantum mechanical* amplitudes for the different processes, then squaring them should give probabilities and we can take ratios to get the relative probability of reflection or transmission. Thus the relative probability for reflection is

$$R \equiv \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2}$$

and the relative probability for transmission is

$$T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2}$$

also called the **reflection and transmission coefficients**. These give $R + T = 1$, as they should. Substituting for β gives the results

$$R = \frac{1}{1 + (2\hbar^2 E/m\alpha^2)} \qquad T = \frac{1}{1 + (m\alpha^2/2\hbar^2 E)}$$

(These results can be made for rigorous if one wants; the point is that we must be very careful about how we handle non-normalizable states and what the solutions *mean*.

One can also solve the problem of the *positive* delta-function potential, i.e. a delta-function *barrier*. There are no bound states for that potential, but an incident wave will have a probability

of passing through this barrier, in fact the same as for the well, since R and T just depend on α^2. So the particle has a probability of passing through an *infinitely high* (though very thin) barrier. In classical motion, a particle cannot get through a barrier if its energy is less than the maximum potential "height" of that barrier. The phenomenon of quantum motion through barriers where it is forbidden classically is known as **tunneling**.

2.7 Finite Square Well

Now consider the finite square well potential

$$V(x) = \begin{cases} -V_0 & \text{for } -a < x < a \\ 0 & \text{for } |x| > a \end{cases} \tag{2.18}$$

where V_0 is a positive constant.

Again we expect to get both bound and scattering states. This problem requires more algebra to solve it than the delta-function potential, but the math is not hard.

First, look for bound states, for which $E < 0$. As before, define

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

Outside the well, where $V = 0$, the TISE can be written as

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi$$

which has exponential solutions. Choosing the ones with the proper behavior as $x \to \pm\infty$ gives

$$\psi(x) = \begin{cases} Be^{\kappa x} & x < -a \\ Fe^{-\kappa x} & x > a \end{cases}$$

In the region $-a < x < a$, with $V = -V_0$, the TISE is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_0\psi = E\psi$$

Then if we define

$$\ell \equiv \frac{\sqrt{2m(E + V_0)}}{\hbar}$$

it can be written

$$\frac{d^2\psi}{dx^2} = -\ell^2\psi$$

and this is a simple DE. Here we *do* want to use trig fuctions and the solution is

$$\psi(x) = C\sin(\ell x) + D\cos(\ell x) \qquad \text{for} \quad -a < x < a$$

and now we have 5 (!) unknowns to solve for: B, F, C, D and the energy E (buried inside κ). We will find them though the boundary conditions, normalization and *symmetry*.

First, symmetry (an important tool in quantum mechanics). Certainly, the *potential* is symmetric for $x \leftrightarrow -x$. Are the *solutions* symmetric in some way? One can show that for a symmetric potential one can (at least) *choose* the solutions to be either symmetric or anti-symmetric, that is:

$$\psi(-x) = \begin{cases} \psi(x) & \text{symmetric} \\ -\psi(x) & \text{anti-symmetric} \end{cases}$$

In one could have gotten this fact from the boundary conditions, but this is useful to understand and it does save some work.

The condition of symmetry gives $B = \pm F$.

We will now explicitly look for *symmetric* solutions for the finite square well. (The well *will* have such a solution. It *may* have an anti-symmetric solution; that case is dealt with in one of the Problems.)

So then we have $B = F$ and it also gives $C = 0$ since $\sin(\ell x)$ is an odd function. Our solution is now

$$\psi(x) = \begin{cases} Fe^{+\kappa x} & x < a \\ D\cos(\ell x) & -a < x < a \\ Fe^{-\kappa x} & x > a \end{cases}$$

Applying continuity of the wave function *and its derivative* at $x = a$ gives

$$Fe^{-\kappa a} = D\cos(\ell a) \qquad -\kappa Fe^{-\kappa a} = \ell D\sin(\ell a)$$

(Note: For this problem, the potential $V(x)$ makes a finite jump but otherwise is *not* pathological at the boundary. We are thus also required to make $\psi(x)$ *smooth* there, so the derivative is continuous.)

One can then show that with the definitions

$$z \equiv \ell a \qquad z_0 \equiv \frac{a}{\hbar}\sqrt{2mV_0}$$

we have the condition

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1} \tag{2.19}$$

And from this transcendental[1] equation we can get z and then the value of E. A useful strategy is to plot both sides of 2.19 together and note where the curves intersect (see text). Of course, computers can give a numerical solution.

We see that even a "simple" problem can require some messy math for a solution! Such is life.

We can consider limiting cases of the potential to check these results:

• A wide, deep well[2]: In this case z_0 is big. One can see graphically that there are many crossings for the left and right sides of 2.19, always occuring just below $z_n \equiv n\pi/2$. For these solutions, one can show

$$E + V_0 \approx \frac{n^2\pi^2\hbar^2}{2m(2a)^2} \qquad \text{where } n \text{ is odd}.$$

that is to say, these are the energies of the states measured *from the bottom of the well*. This agrees with our previous box result. But here we miss half the solutions because we've only considered symmetric states. (See Prob 2.29 for the rest.)

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[1] Meaning that it's mathematically messy, not that you're going to meditate on it.
[2] *Deep... and wide..., deeeeep and wide...*

• Shallow, narrow well: Then z_0 is small. There is still one intersection of the curves (plots of left and right sides of 2.19) so there is always *one* (symmetric) bound state.

As for solving for all the coefficients, we can get them from normalization of the wave function. That's uninteresting, so we move on to do the scattering states.

Now consider $E > 0$. For the regions where $V = 0$, we have, with k defined as $k \equiv \sqrt{2mE}/\hbar$,

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

for $x < -a$, since we we want a solution with both an incident wave and a reflected wave, as when we did the delta-function potential.

In the well, with

$$\ell \equiv \frac{\sqrt{2m(E + V_0)}}{\hbar}$$

the solution is

$$\psi(x) = C\sin(\ell x) + D\cos(\ell x)$$

and for $x > a$ we want a solution with *only* a right-going (transmitted) wave:

$$\psi(x) = Fe^{ikx}$$

Solving: We an take $E > 0$ as *given* and find relations between the coefficients from the boundary conditions. The conditions are the ψ and $\frac{d\psi}{dx}$ are continuous at both $x = -a$ and at $x = a$. Here the algebra starts to be a little challenging (and it involves complex numbers), but one can show:

$$B = i\frac{\sin(2\ell a)}{2kl}(\ell^2 - k^2)F \qquad \text{and} \qquad F = \frac{e^{-2ika}A}{\cos(2\ell a) - i\frac{(k^2+\ell^2)}{2k\ell}\sin(2\ell a)}$$

and we will just calculate the transmission coefficient, $T = |F|^2/|A|^2$. In fact due to the messy algebra, it's easier to present T^{-1}, and for that we find:

$$T = 1 + \frac{V_0^2}{4E(E + V_0)}\sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E + V_0)}\right) \tag{2.20}$$

Of course, $T = 1$ if $V_0 = 0$ but also $T = 1$ if the sin in 2.20 gives zero. That occurs when

$$\frac{2a}{\hbar}\sqrt{2m(E_n + V_0)} = n\pi$$

for any integer n, E_n being the energies of these perfectly–transmitted waves. And this occurs when

$$E_n + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}$$

which in fact are the energies of the infinite square well. Interestingly, this resonance–type effect can actually be observed in (forward) electron scattering on atoms.

2.7.1   Square Barrier

Now consider the finite square *barrier*, given by the potential

$$V(x) = \begin{cases} +V_0 & \text{for } -a < x < a \\ 0 & \text{for } |x| > a \end{cases} \tag{2.21}$$

(again with $V_0 > 0$) has a similar solution. Since the potential has its lowest value at infinity there are *no* bound states and we only have scattering states. Griffiths decides to let this be a homework problem, but the result is important enough that we should at least discuss it

The solutions divide into three cases: $E < V_0$, $E = V - 0$ and $E > V_0$. For the first one, with the usual definitions $k = \sqrt{2mE}/\hbar$ and $\kappa = \sqrt{2m(V_0 - E)}/\hbar$ the solutions is

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < -a \\ Ce^{\kappa x} + De^{-\kappa x} & -a < x < a \\ Fe^{ikx} & x > a \end{cases} \tag{2.22}$$

where as the previous case of the scattering state of the square well, we have made the "experimental" boundary condition of an incoming wave on the left and no incoming wave on the right (but outgoing waves on both sides).

The most interesting result is the answer for the trasmission coefficient; with a lot of algebra, one can show that

$$T^{-1} = \left|\frac{A}{F}\right|^2 = 1 + \frac{V_0^2}{4E(V_0 - E)}\sinh^2\left(\frac{2a}{\hbar}\sqrt{2m(V_0 - E)}\right) \tag{2.23}$$

For this case (total energy less than that of the potential barrier height) the particle would never get across the barrier according to classical mechanics. (for a classical particle coming in from the left, $x = -a$ would be a "turning point"). But according to our interpretation of the scattering wave function and the coefficient T, in quantum mechanics the particle has a non-zero chance of getting through the barrier and this phenomenon is generally known as **tunneling**.

The case $E = V_0$ needs to be covered for mathematical completeness. Here, the solution to the Schrödinger equation is

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < -a \\ C + Dx & -a < x < a \\ Fe^{ikx} & x > a \end{cases} \tag{2.24}$$

leading to

$$T^{-1}1 + \frac{2mE}{\hbar^2}a^2$$

The last case, $E > V_0$ has the same solution as that of the square *well* considered above, but with V_0 replaced with $-V_0$. This gives

$$T^{-1} = \left|\frac{A}{F}\right|^2 = 1 + \frac{V_0^2}{4E(E - V_0)}\sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E - V_0)}\right) \tag{2.25}$$

In this case, motion through the barrier is also possible for a classical particle of energy E.

Chapter 3

Formalism

3.1 Introduction

We've now covered the basics of the *meaning* of the wave functions and gotten tons o' practice by solving the 1-D Schrödinger equation for a good assortment of potentials. What's left?

Well, the obvious things: We need to solve problems in three dimensions, we need to deal with multi-particle systems and also learn about **spin**, a dynamical quantity which occurs in the quantum world. And more mathematical methods.

But we also need a firmer grounding in the fundamentals of quantum theory. This is because we will encounter other important dynamical quantities (possibly abstract, like spin) and we need to know how to work with their operators and associated quantum states. We need to know how to deal with *any* "observable" in QM beyond the ones we've seen: x and p.

3.2 Hilbert Space

Quantum Mechanics is, as we've seen, based on wave functions and operators. The wave functions are treated much like abstract vectors, (as we saw from considering linear combinations of them) and the operators are also *linear* operators which makes of think of matrices. This leads us to the branch of mathematics known as **Linear Algebra**. ("The natural language of quantum mechanics", as Griffiths sez.)

Alas, most of us don't haven't learned linear algebra so well when we get to QM. (Were it not for QM it might be totally neglected in our math–phys education.) In any case, it is necessary to learn some of it.

Griffiths has a big, important appendix giving a "refresher" course in linear algebra.

First, we have vectors in an N–dimensional space, represented by an N-tuple of (complex) components:

$$\text{Vector} \quad |\alpha\rangle \quad \implies \quad \mathbf{a} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix}$$

Two vectors have an **inner product** (also called a **scalar product**),

$$\langle \alpha | \beta \rangle = a_1^* b_1 + a_2^* b_2 + \cdots a_N^* b_N \ .$$

Note the complex conjugation of the components for the first vector. The inner product is not commutative; switch the order and the result is complex–conjugated.

Vectors are transformed by **linear operators** i.e. they are linear transformations. These transformations are *represented* by matrices. When we transform vector $|\alpha\rangle$ to vector $|\beta\rangle$ by means of the transformation $\mathcal{T}$ (represented by matrix $\mathbf{T}$), we have:

$$|\beta\rangle = \mathcal{T}|\alpha\rangle \qquad \Longrightarrow \qquad \mathbf{b} = \mathsf{T}\mathbf{a} = \begin{pmatrix} t_{11} & t_{12} & \cdots & t_{1N} \\ t_{21} & t_{22} & \cdot & t_{2N} \\ \vdots & \vdots & \vdots & \vdots \\ t_{N1} & \cdots & \cdots & t_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix}$$

As written here, $|\alpha\rangle$ and $|\beta\rangle$ denote the *abstract* vectors and $\mathcal{T}$ the abstract operator, while $\mathbf{a}$ and $\mathbf{b}$ and T give their **representations** for a particular basis.

In linear algebra, one studies the types of matrices which can arise in linear transformations and the operations we perform with and *on* these matrices. In some of this work, we study how we can change between different bases, giving different representations.

The "vectors" in QM *are* the wave functions. The ones we've seen are functions of x (could it be otherwise?) so these are vectors with an infinite number of components (that is, the values at each point, of which there are an infinite number). So things get very abstract here!

What we need to do to adapt the normal language of linear algebra to that of the new vectors is change from the *discrete* index of regular vectors to the *continuous* index of functions. In doing this, sums go over to integrals.

Actually, later on when we encounter spin (more generally, angular momentum), we will go back to the familiar finite-dimensional vector space.

A vector (wave function) that we encounter in QM must be normalizeable, so that we can demand $\int \Psi^* \Psi dx = 1$. So we will deal with a special class of functions, those for which

$$\int |f(x)|^2 \, dx < \infty$$

We very loosely refer to these functions as our "vectors" in a **Hilbert space** and hope that no mathematicians are listening to our sloppy definitions.

These vectors (functions) will have an inner product defined as

$$\langle f|g \rangle = \int_a^b f(x)^* g(x) \, dx$$

(where a and b are limits appropriate for the vector space) which *must* exist for functions in this space. Note,

$$\langle f|g \rangle = \langle g|f \rangle^*$$

so the inner product is *not* commutative.

A function f is normalized if $\langle f|f \rangle = 1$. A set of basis functions in the space is **orthonormal** if

$$\langle f_m|f_n \rangle = \delta_{mn}$$

A set of set of functions f_n in the space is **complete** if any other function $f(x)$ in the space can be expressed as a linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n f_n(x)$$

If the set of functions here is orthonormal, then the c_n's can be found by "Fourier's trick",

$$c_n = \langle f_n | f \rangle$$

3.3 Observables

We use a similar notation for the expectation value of an observable $Q(x, p)$:

$$\langle Q \rangle = \int \Psi^* \hat{Q} \Psi \, dx = \langle \Psi | \hat{Q} \Psi \rangle \, .$$

$\hat{Q}$ will always be a linear operator.

Since $\langle Q \rangle$ is the average of many *measurements*, it must be real: $\langle Q \rangle = \langle Q \rangle^*$. This implies

$$\langle \Psi | \hat{Q} \Psi \rangle = \langle | \hat{Q} \Psi \rangle^* = \langle \hat{Q} \Psi | \Psi \rangle$$

for any function Ψ in the space. So operators corresponding to observables *must* have the property

$$\langle f | \hat{Q} f \rangle = \langle \hat{Q} f | f \rangle$$

for all $f(x)$. Such an operator is said to be **Hermitian**. So a Hermitian operator can be applied to the second *or* first member of an inner product with the same result.

The operator $\hat{x} = x$ clearly is Hermitian since it simply multiplies. One can show that the momentum operator $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$ is Hermitian; but note, the derivative operator $\frac{\partial}{\partial x}$ by itself is *not* Hermitian.

3.4 Determinate States

Measuring the value of the observable Q on an ensemble of particles all prepared in the same state in general does *not* give the same value every time; generally we can only get the expectation value $\langle Q \rangle$. Quantum mechanics is this sense **indeterminate**.

But could we prepare a state such that it did give the same value for Q each time? Such a state would be a **determinate state** for the observable Q. Actually, we've seen this already, as stationary states are determinate states for the Hamiltonian.

For such a state — if the measurement of Q each time gives the value q— the standard deviation of Q would be zero. One can then show that for this state Ψ,

$$\hat{Q} \Psi = q \Psi$$

This is an **eigenvalue equation** for the operator $\hat{Q}$; Ψ is an eigenfunction of $\hat{Q}$, with corresponding **eigenvalue** q.

We note that an eigenvalue is a *number*. An eigenfunction can be multiplied by a number and it will still be an eigenfunction (with the same eigenvalue). An eigenfunction *can't* be zero (otherwise it wouldn't be a legal vector for our states) but an *eigenvalue* can certainly be zero.

Sometimes several *independent* eigenfunctions will have the same eigenvalue. In such a case we say the eigenfunctions are **degenerate**.

In the TISE we had $\hat{H} \psi = E \psi$; E is the eigenvalue of the $\hat{H}$ operator. (And the full wave function, $\Psi(x, t) = \psi(x) e^{-iIt/\hbar}$ is *still* an eigenfunction of $\hat{H}$.)

3.5   Eigenfunctions of Hermitian Operators

We thus have reason to care about the general problem of eigenfunctions of Hermitian operators. That is because the QM operators corresponding to observables must be Hermitian, and because the determinate state for an observable must be an eigenstate of the corresponding operator.

Eigenfunctions and eigenvalues fall into two classes:

• The spectrum is **discrete**: Eigenvalues are separated from one another, though there may be an infinite number of them. In this case, the eigenfunctions are in our Hilbert space, as they are normalizeable.

• The spectrum is **continuous**: Eigenvalues *fill out* an entire range of the real numbers. In this case, the eigenfunctions are *not* normalizeable, though a linear combination of them could be... but then this linear combination is not itself an eigen function! We saw this in the case of the free particle.

In some problems there is both a discrete spectrum *and* a continuous spectrum, as in the case of the finite square well. Now some more depth on these two cases, and some theorems.

3.5.1   Discrete Spectrum

Here we get normalizeable eigenfunctions. They satisfy two conditions; one can show that

1. The eigenvalues are real.

2. Eigenfunctions belonging to *different* eigenvalues are orthongonal.

We saw that the eigenfunctions of the infinite square well and the harmonic oscillator were orthogonal. But it is a general property.

Alas, if the there are degenerate (that is, they have the same eigenvalue) the second theorem does not apply. But in this case we can *construct* orthogonal eigenfunctions from the ones that we find. (If necessary, one can use the "Gram–Schmidt" process from Linear Algebra; in practice we won't need to do this.)

So actually, in all cases we will have a set of mutually orthogonal eigenfunctions.

The eigenfunctions of an observable operator are also **complete**, that is, any other function in the Hilbert space can be expressed as a linear combination of them. (We also say that they **span** the space.) This property will later on prove to be extremely useful when we have to construct *approximate* solutions to the Schrödinger equation.

3.5.2   Continuous Spectrum

Here the eigenfunctions are not normalizeable. There are problems with this case because the inner product of two functions may not even exist (in the conventional sense). But we can get the above properties for the discrete spectrum to hold in a more *abstract* sense. The theory can be made more rigorous, but we will deal with a few examples:

The eigenfunctions of the momentum operator (with eigenvalue p) satisfy

$$\frac{\hbar}{i}\frac{d}{dx}f_p(x) = pf_p(x)$$

This gives

$$f_p(x) = Ae^{ipx/\hbar}$$

which is *not* square–integrable for *any* value of p, even a complex one. So there are no eigenfunctions of the momentum operator in the *proper* Hilbert space.

However, if we restrict ourselves to *real* eigen values p (which is what we would expect) then we find that the inner product of two such functions is

$$\langle f_{p'}|f\rangle = \int_{-\infty}^{\infty} f_{p'}(x)^* f_p(x)\, dx = |A|^2 \int_{-\infty}^{\infty} e^{i(p'-p)x/\hbar}$$

But what is this? One can show:

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iqx/\hbar}\, dx = \delta(q)$$

(this is an exercise elsewhere in the text) and then

$$\langle f_{p'}|f_p\rangle = |A|^2 2\pi\hbar\delta(p - p')$$

If we choose

$$A = \frac{1}{\sqrt{2\pi\hbar}} \qquad \text{then} \qquad f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \quad \text{so} \quad \langle f_{p'}|f_p\rangle = \delta(p - p')$$

which looks a lot like "real" orthogonality, where we get a *Kronecker* delta for the inner product. Here, it's a delta *function*. Griffiths calls this state of affairs **Dirac orthonormality**.

The momentum eigenfunctions are also complete as long as we use an integral in place of the sum to forma linear combinations of basis functions. Consider an arbitrary *square–integrable* function $f(x)$. It can be written in the form

$$f(x) = \int_{-\infty}^{\infty} c(p)\, f_p(x)\, dp = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} c(p) e^{ipx/\hbar}\, dp$$

We can get the coefficient $c(p)$ with the *continuum* version of "Fourier's trick":

$$\langle f_{p'}|f\rangle = \int_{-\infty}^{\infty} c(p)\langle f_{p'}|f_p\langle = \int_{-\infty}^{\infty} c(p)\delta(p - p')\, dp = c(p')$$

This is essentially what occurred in a previous discussion where we inverted a Fourier transform via "Plancheral's theorem".

The eigenfunctions of momentum are (complex) sinusoidal functions, with wavelength $\lambda = 2\pi\hbar/p$, which is the old De Broglie formula, using $h = 2\pi\hbar$. But the use of momentum here is more subtle than what De Broglie hypothesized since there is no possible quantum motion with a *definite* value of the momentum.

Thus we have dealt with the eigenfunctions of p. They are not in the *true* Hilbert space of quantum states but our ability to use them puts them... in the *suburbs* of the Hilbert space.

And thus we have given the eigenfunctions of momentum and energy; later we'll deal with eigenfunctions of other dynamical quantities, such as angular momentuym and spin.

But we've overlooked something; what about the most basic operator of all, the coordinate x? As an operator, it is simply multiplicative, but what are *its* eigenfunctions and eigenvalues? The answer is so simple it's actually a bit confusing.

The eigenfunction of the operator x having eigenvalue y is

$$g_y(x) = \delta(x - y), \quad \text{which satisfies} \quad \langle g_{y'}|g_y\rangle = \delta(y - y')$$

which again is a Dirac delta rather than a Kronecker delta so that these eigenfunctions use *Dirac* orthonormality and so are not proper. As with the momentum eigenfunctions, these are complete.

3.6   General Statistical Interpretation

The wave function $\Psi(x,t)$ was introduced in Chapter 1 as something we would use to find the probabilty of a measurement of coordinate, x. We will now discuss the general theory of probabilities of measurement of any dynamical quantity. Actually, these are the *postulates* of QM; we haven't derived them. But up to now we have gotten some experience in the mathematics needed to know what they are talking about!

If you measure the quantity $Q(x,p)$ of a particle in the state $\Psi(x,t)$ you will get *one of the eigenvalues* of the hermitian operator $\hat{Q}(x, \frac{\hbar}{i}\frac{d}{dx})$.

If the spectrum of $\hat{Q}$ is discrete, the probability of getting eigenvalue q_n is $|c_n|^2$, where

$$c_n = \langle f_n | \Psi \rangle$$

If the spectrum of $\hat{Q}$ is continuous, the probability of the eigenvalue z to be in the range dz is $|c(z)|^2 \, dz$, where

$$c(z) = \langle f_z | \Psi \rangle$$

Upon measurement of Q, the wave function collapses to the corresponding eigenstate.

3.7   The Uncertainty Principle

We've already seen examined (but not proven) a special case; we found that

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

for any state satisfying the Schrödinger equation.

For any two observables A and B, with the commutator of their operators given by

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

one can show that for any quantum state ψ,

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \left\langle [\hat{A}, \hat{B}] \right\rangle \right)^2 \tag{3.1}$$

This is the **generalized uncertainty principle**.

With $\hat{A} = x$ and $\hat{B} = \hat{p} = \frac{\hbar}{i}\frac{d}{dx}$, using $[\hat{x}, \hat{p}] = i\hbar$, Eq. 3.1 gives

$$\sigma_x^2 \sigma_p^2 \geq \left(\frac{\hbar}{2} \right)^2 \qquad \Longrightarrow \qquad \sigma_x \sigma_p \geq \frac{\hbar}{2}$$

3.7.1   Minimum Uncertainty Wavepacket

In a couple of the problems we have already encountered a quantum state which gave the *minimum* uncertainty product. They were gaussian wavepackets, but can we show that this must be the case?

Griffiths shows that if we demand that uncertainty product give $\frac{\hbar}{2}$ then we can produce a differential equation for ψ:

$$\left(\frac{\hbar}{i}\frac{d}{dx} - \langle p \rangle \right) \psi = ia(x - \langle x \rangle)\psi$$

for some constant a. This has the solution

$$\psi(x) = Ae^{-a(x-\langle x \rangle)^2/2\hbar}e^{i\langle p \rangle x/\hbar}$$

which as in our examples is a gaussian wavepacket.

3.8 Energy–Time Uncertainty

One can show:

$$\frac{d}{dt}\langle Q \rangle = \frac{i}{\hbar}\left\langle [\hat{H}, \hat{Q}]\right\rangle + \left\langle \frac{\partial \hat{Q}}{dt}\right\rangle \tag{3.2}$$

Rant on the abuse of this relation too long to be included in the notes. Perhaps next year.

3.9 Dirac Notation

We can now express the general quantum theory, taking the things far beyond our initial simplistic view of the quantum state.

We work in analogy with finding the components of the vector $\mathbf{A}$. To get them take the dot product of $\mathbf{A}$ with the different unit vectors:

$$A_x = \hat{\mathbf{i}} \cdot \mathbf{A} \qquad A_y = \hat{\mathbf{j}} \cdot \mathbf{A}$$

But if we consider a coordinate system where the axes are rotated (call it the (x', y') system) then the components are given by

$$A'_x = \hat{\mathbf{i}}' \cdot \mathbf{A} \qquad A'_y = \hat{\mathbf{j}}' \cdot \mathbf{A}$$

The idea here is that the vector $\mathbf{A}$ exists independent of our choice of coordinates, but to *express* that vectors we must find its components using a particular choice of coordinates, and then those components are found by taking a dot product with the basis vectors.

Chapter 4

The Schrödinger Equation in Three Dimensions

There is lots left to do: We need to know how solve for quantum motion in three dimension; adding two more dimensions brings in more features to our quantum states.

4.1 Schrödinger Equation in Three Dimensions

First, we need to be clear about how the make our Schrödinger equation applicable to three dimensions.

As the classical energy is now

$$\tfrac{1}{2}mv^2 + V(\mathbf{r}) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(\mathbf{r}) \ ,$$

we make the replacements

$$p_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x} \ , \qquad p_y \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial y} \ , \qquad p_z \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial z}$$

which can be summarized as

$$\mathbf{p} \quad \rightarrow \quad \frac{\hbar}{i}\nabla$$

We note that V is a function of all three coordinates. Making these replacements in our old equation $i\hbar\frac{\partial\Psi}{\partial t} = H\Psi$, (with now Ψ being $\Psi(\mathbf{r},t)$), we find

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\psi$$

where ∇^2 is the laplacian,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The meaning of $\Psi(\mathbf{r},t)$ is just as it was before; the probability of finding the particle at $\mathbf{r}$ within $d^3r = dx\,dy\,dz$ (at time t) is

$$|\Psi(\mathbf{r},t)|^2\,dx\,dy\,dz$$

If the potential is independent of time there will be a complete set of of stationary eigenstates

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-iE_n t/\hbar}$$

where the $\psi(\mathbf{r})$'s satisfy the TISE

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

Then the general solution is

$$\Psi(\mathbf{r}, t) = \sum_n c_n\psi_n(\mathbf{r})e^{-iE_nt/\hbar}$$

All of this is fine if the problem can be (easily) expressed in Cartesian coordinates; a few problems have easy solution in terms of (x, y, z). An example is the isotropic harmonic oscillator, which has the potential $V(\mathbf{r}) = \frac{1}{2}kr^2$, but which can be expressed as

$$V(\mathbf{r}) = \frac{1}{2}k(x^2 + y^2 + z^2)$$

But more often the potential depends on the distance r from the origin in a way such that Cartesian coordinates are not easy to work with. Then one is forced to use spherical coordinates.

4.2   Spherical Coordinates; Separation of Variables

We will assume $V(r)$ is function of r only. We recall from our other fine coursework that the laplacian can be expressed in spherical coordinates as

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

so that the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + V(r)\psi = E\psi$$

Gak! How can we ever solve this?

The same way as always. Assume a solution with *separated variables*:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Recall what we do with this: Substitute into the differential equation, then divide through by RY. We get an equation where one side depends only on r and the other only on (θ, ϕ). One can then show that each side of that equation must be equal to a constant.

Now, that constant could be anything, we have a good reason to write it as $\ell(\ell + 1)$. We will find that ℓ must be an integer, but for now with no loss in generality, we use that form and then the separated equations are

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = \ell(\ell + 1)$$

$$\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2Y}{\partial\phi^2}\right\} = -\ell(\ell + 1)$$

which still looks pretty grim, but the separation has made things easier (and the first is an ordinary differential equation). Eventually we want to solve this for a particular choice of $V(r)$, but we note that the angular equation doesn't depend on that choice.

4.3   The Angular Equation

Rearranging, we have

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} = -\ell(\ell+1)\sin^2\theta Y$$

This equation might look familiar! It also occurs in E & M when we solve the Laplace equation in spherical coordinates *except* that we now include a ϕ dependence which is not considered in our E & M book! (The problems didn't need it.) Here in QM we *must* consider the ϕ dependence of the wave function.

As this is still a differential equation in two coordinates, we do a further separation of variables and write

$$Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$$

Again we substitute, split up the equation and set both sides equal to the same constant which this time we call m^2 (again, for good reasons to be seen later). The resulting separated equations are

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + \ell(\ell+1)\sin^2\theta = m^2$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$$

The first one is still pretty messy, but the second one is easy!

The solution for Φ is

$$\frac{d^2\Phi}{d\phi^2} = -m^2 \qquad \Longrightarrow \qquad \Phi(\phi) = e^{im\phi}$$

where we "absorb" the constant in all the other factors and we deal with the possibilities $e^{\pm im\phi}$ by letting m be positive or negative. We chose the complex form here because it is easier to work with; wave functions don't have to be real!

We do require that the wave function have *one* value at each point in space so Φ must have the same value if we incrase ϕ by 2π. One can show that this implies

$$m = 0,\ \pm 1,\ \pm 2,\ldots$$

Using this, we go back to the Θ equation which we now write as

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + [\ell(\ell+1)\sin^2\theta - m^2]\Theta = 0 \tag{4.1}$$

We won't even attempt to "derive" the solution to this. It's enough to present them and give their properties. The solution to 4.1 is

$$\Theta(\theta) = AP_\ell^m(\cos\theta)$$

where P_ℓ^m is the **associated Legendre function**, defined by

$$P_\ell^m(x) = (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|}P_\ell(x)$$

and where m can take on the $2\ell+1$ values

$$m = -\ell,\ -\ell+1,\ \ldots,\ \ell$$

and the $P_\ell(x)$ are the familiar (?) Legendre polynomials, which in fact are given by the Rodrigues formula,

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \left(\frac{d}{dx} \right)^\ell (x^2 - 1)^\ell$$

of which the first few are

$$P_0(x) = 1 \qquad P_1(x) = x \qquad P_2(x) = \tfrac{1}{2}(3x^2 - 1)$$

Note that $P_\ell^m(x)$ is in general *not* a polynomial; e.g. for $\ell = 2$,

$$P_2^0(x) = \tfrac{1}{2}(3x^2 - 1) \qquad P_2^1(x) = 3x\sqrt{1 - x^2} \qquad P_2^2(x) = 3(1 - x^2)$$

and by the definitions we are using,

$$P_\ell^{-m} = P_\ell^m \qquad \text{and} \qquad P_\ell^0 = P_\ell$$

but conventions differ amongst the reference books!

While the P_ℓ^m's look messy if we substitute $x = \cos\theta$ and $\sqrt{1 - x^2} = \sin\theta$ then we have

$$P_0^0 = 1 \qquad\qquad P_1^0 = \cos\theta \qquad P_1^1 = \sin\theta$$

$$P_2^0 = \tfrac{1}{3}(3\cos^2\theta - 1) \qquad P_2^1 = 3\sin\theta\cos\theta \qquad P_2^2 = 3\sin^2\theta$$

Polar plots of these functions remind one of the orbitals from basic chemistry... for good reason, as we'll see eventually.

We should note that since the θ equation was second order there should be *two* solutions here. The others, called $Q_\ell(x)$ blow up at $\theta = 0$ and $\theta = \pi$ so they're not permitted.

Now we put $\Theta(\theta)$ and $\Phi(\phi)$ together to get the full angular wave function, which we will call $Y(\theta, \phi)$. We need to choose how the product $\Theta\Phi$ is normalized. Of course we still have to find $R(r)$, but when we do the normalization condition on the whole wave function will be

$$\int |\psi|^2 \, d^3r = \int_0^\infty |R|^2 r^2 \, dr \int_0^{2\pi} \int_0^\pi |Y|^2 \sin\theta \, d\theta \, d\phi = 1$$

and for later convenience we will choose things so that the separate factors are normalized:

$$\int_0^\infty |R|^2 r^2 \, dr = 1 \qquad \text{and} \qquad \int_0^{2\pi} \int_0^\pi |Y|^2 \sin\theta \, d\theta \, d\phi = 1$$

The following formula will do the job:

$$Y_\ell^m(\theta, \phi) = \epsilon \sqrt{\frac{(2\ell + 1)}{4\pi} \frac{(\ell - |m|)!}{(\ell + |m|)!}} \, e^{im\phi} \, P_\ell^m(\cos\theta) \qquad \text{where} \quad \epsilon = \begin{cases} (-1)^m & m \geq 0 \\ 1 & m \leq 0 \end{cases} \qquad (4.2)$$

The Y_ℓ^m's are called the **spherical harmonics**, and they are of enormous importance in theoretical physics. Note, different references may use different phases from Eq. 4.2.

The spherical harmonics are mutually orthonormal:

$$\int_0^{2\pi} \int_0^\pi Y_\ell^m(\theta, \phi)^* \, Y_{\ell'}^{m'}(\theta, \phi) \sin\theta \, d\theta \, d\phi = \delta_{\ell\ell'} \delta_{mm'}$$

The first few are:

$$Y_0^0 = \sqrt{\frac{1}{4\pi}} \qquad Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \qquad Y_2^{\pm 1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi} \qquad \text{etc.}$$

Note, Y_0^0 is *not* equal to 1.

We will have more to say about the angular function $Y(\theta, \phi)$ and its relation to the *angular momentum* of a particle later on. For now, we return to the equation for the radial function $R(r)$.

4.4   The Radial Equation

The Schrödinger equation for a particular radial potential $V(r)$ gives the radial equation:

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E]R = \ell(\ell+1)R$$

And how do we solve *this*??

A useful trick is to define a sort of reduced radial wave function $u(r)$

$$u(r) \equiv rR(r)$$

We then get

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu \tag{4.3}$$

We can note that 4.3 has the same form as a one-dimensional Schrödinger equation except that the potential is replaced by the **effective potential**

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$$

and where the extra term is called the **centrifugal** term. (We have seen some similar in classical mechanics for the central force problem!) The terms acts like a potential which pushes the particle outward, just like the corresponding pseudo-force in classical mechanics.

Note that with this definition of $u(r)$, the normalization condition on the radial function is $\int_0^\infty |u|\,dr = 1$.

That all we can do with the radial function until we make a specific choice for the potential $V(r)$, i.e. the physical problem we want to solve!

4.5   Example: Spherical "Box"

As an example leading to more complicated H atom, Griffiths considers the case of the potential

$$V(r) = \begin{cases} 0 & r < a \\ \infty & r > a \end{cases}$$

which might call a spherical infinite well, or something.

Outside the well, we must have $\psi = 0$. Inside the well, the radial equation is

$$\frac{d^2u}{dr^2} = \left[\frac{\ell(\ell+1)}{r^2} - k^2\right]u \qquad \text{where} \quad k = \frac{\sqrt{2mE}}{\hbar}$$

We want to solve this DE; one of the boundary conditions is that $u(a) = 0$ in order for the wave function ψ to be continuous. (Being a pathological potential as usual we do not demand $\frac{d\psi}{dr} = 0$.)

The $\ell = 0$ case is easy:

$$\frac{d^2u}{dr^2} = -k^2u \qquad \Longrightarrow \qquad u(r) = A\sin(kr) + B\cos(kr)$$

Recalling that the actual radial function is $R = \frac{u}{r}$ and that the cosine term would blow up at $r = 0$, we must have $B = 0$, then the boundary condition at $r = a$ gives $\sin(ka) = 0$ or $ka = n\pi$ and then

$$E_{n,\ell=0} = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad n = 1, 2, 3, \ldots$$

and the complete solution, after normalizing, is

$$\psi_n(\mathbf{r}) = \frac{1}{\sqrt{2\pi a}}\frac{\sin(n\pi r/a)}{r}$$

But what about arbitrary ℓ for this problem? That solution introduces some new functions often seen in mathematical physics which we will just *give* here. For the general case, the general solution for u is a linear combination of **spherical Bessel functions**,

$$u(r) = Arj_\ell(kr) + Brn_\ell(kr)$$

where $j_\ell(x)$ is the spherical Bessel function of order ℓ and $n_\ell(x)$ is the spherical Neumann function of order ℓ, defined as

$$j_\ell(x) = (-x)^\ell\left(\frac{1}{x}\frac{d}{dx}\right)^\ell\frac{\sin x}{x} \qquad\qquad n_\ell(x) = -(-x)^\ell\left(\frac{1}{x}\frac{d}{dx}\right)^\ell\frac{\cos x}{x}$$

The first few are

$$j_0(x) = \frac{\sin x}{x} \qquad n_0(x) = -\frac{\cos x}{x} \qquad j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x} \ .$$

See the text or standard reference books!

We find that the $n_\ell(x)$'s blow up at the origin so they are not permitted. So the B coefficient must be zero and the radial wave function is

$$R(r) = Aj_\ell(kr)$$

The permitted values of the energy E come from the boundary condition at $r = a$. The radial wave function must be continuous at $r = a$ and since it is zero outside the well, we must have

$$R(a) = Aj_\ell(ka) = 0$$

so that ka is a zero (root) of the function $j_\ell(x)$. This function has many roots, so that if we let $\beta_{n\ell}$ be the nth root of $j_\ell(x)$ then

$$k = \frac{\beta_{n\ell}}{a} \qquad \text{which gives} \qquad E_{n\ell} = \frac{\hbar^2}{2ma^2}\beta_{n\ell}^2$$

as the nth energy level of the states of angular index ℓ.

With this, the complete wave function is

$$\psi_{n\ell m} = A_{n\ell} j_\ell(\beta_{n\ell} r/a) Y_\ell^m(\theta, \phi)$$

where $A_{n\ell}$ will be determined by normalization.

We note that each energy level actually has $2\ell + 1$ states because for each ℓ there are $2\ell + 1$ possible values of m, and the energy is the same for each.

4.6 The H Atom!

4.6.1 Introduction

At last we are ready to solve the first (and last) problem which is an "exact" rendering of something in the physical world. With a positive charge $+e$ nailed down to the origin, a point charge $-e$ and mass $m = m_{\text{e}}$ moves around in three dimensions, with the potential energy given by

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

It should be stated that what we will do here for the H atom is *not* exact in that there is *lots* that is not put into our solution: Motion of the proton, special relativity, the dependence of the interaction on the spins of the particles and the correct quantum treatment of the electromagnetic interaction. But apart from that, we will have put in *most* of the physics for a real physical problem.

We should recall that Bohr solved this system using a simple model which is *instructive* but which we now know is basically incorrect. He assumed that the electron executes a circular orbit constrained so that its angular momentum is an integral multiple of $\hbar$. He was able to show that the permitted energies of the system are given by

$$E_n = \frac{(-13.6 \text{ eV})}{n^2} \qquad n = 1, 2, 3, \ldots$$

which, with relations for photon energy and wavelength: $E = \hbar\omega = hf$ and $\lambda f = c$ gave the observed spectra for hydrogen atoms, in particular the visible Balmer lines.

In the years from 1912 to 1925, people tried to extend Bohr's simple theory to more complex system, largely without success. With the advent of quantum mechanics it was realized that the approach to atomic motion using specific trajectories is fundamentally wrong.

4.6.2 The Radial Equation and Asymptotic Behavior

As the angular part of the wave function has already been found, it remains only (?) to solve the radial equation for the Coulomb potential. With $u(r) = eR(r)$, it is

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} \right] u = Eu \qquad (4.4)$$

Our problem is to find the allowed functions $u(r)$, which will give the allowed energies (the eigenfunctions and eigenvalues). Clearly, we will require that $u(r) \to 0$ as $r \to \infty$.

This is certainly the hardest DE to be solved (analytically) in this entire course. But as it is also the most important we will want to *work out* its solution, using tricks similar to those used in the analytic solution for the harmonic oscillator.

Though there are indeed scattering solutions for the Coulomb problem (the solution of which is a notorious sticky point in the theory of scattering) we are definitely dealing with *bound state* solutions here, so we can assume $E < 0$. We will make the definitions

$$\kappa = \frac{\sqrt{-2mE}}{\hbar} \qquad \rho = \kappa r \qquad \text{and} \qquad \rho_0 = \frac{me^2}{2\pi\epsilon_0 \hbar \kappa}$$

The reduced radii ρ and ρ_0 are dimensionless, allowing us to focus on the math with physical constants flying around. Substituting into 4.4 gives

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u \tag{4.5}$$

which is (superficially) simpler than 4.4 but is *still* a nasty differential equation.

At this point we recall our strategy for solving the HO differential equation. We looked at the behavior of the DE (and thus its solutions) at large distance. As we might have expected, it turned out to be some kind of exponential decay which we then factored out of the solution; we then solved for the remaining part.

For a radial function we actually have *two* extremes one at large distance and another at $r \to 0$ (that is, very small r).

For large ρ (large r), the radial equation and its solution becomes

$$\frac{d^2u}{d\rho^2} = u \qquad \implies \qquad u(\rho) = Ae^{-\rho} + Be^{\rho}$$

for which only the $e^{-\rho}$ term is possible. As $\rho \to 0$ we get

$$\frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u \qquad \implies \qquad u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}$$

for which we can keep only the $\rho^{\ell+1}$ for proper behavior at small ρ.

Now the idea is to pull the factors for these limiting solutions and solve for what's left. Define:

$$u(\rho)\rho^{\ell+1}e^{-\rho}v(\rho) \tag{4.6}$$

and now solve for $v(\rho)$. One might hope that the equation for it is *simpler* but that isn't really the case. Looking ahead, there is a restriction on $v(\rho)$ in that it can't be such that $u(\rho)$ blows up at large ρ. From 4.6, $v(\rho)$ can't "overpower" the factor $e^{-\rho}$.

Substitution gives

$$\rho\frac{d^2v}{d\rho^2} + 2(\ell + 1 - \rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell + 1]v = 0 \tag{4.7}$$

The *only* thing we can do now is to write a (power) series expansion for $v(\rho)$,

$$v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j$$

and try to solve for the c_j's. Substitution of the series solution gives the recurrence relation

$$c_{j+1} = \left[\frac{2(j + \ell + 1) - \rho_0}{(j + 1)(j + 2\ell + 2)}\right] c_j$$

which will give all of the c_j's if we have the first one. But ρ_0 remains unknown because we don't have a value for the energy E. What fixes this value?

It is the condition mentioned above that $v(\rho)$ can't overpower the factor $e^{-\rho}$. One can show that unless the series for $v(\rho)$ stops ("truncates") at some term, the series will give a function like $e^{2\rho}$, which we can't allow. So there has to be a maximal index $j_{\max}$ for which we get

$$c_{j_{\max}+1} = 0 \qquad \Longrightarrow \qquad 2(j_{\max} + \ell + 1) - \rho_0 = 0$$

If we define $n \equiv j_{\max} + \ell + 1$, then $\rho_0 = 2n$ and we can derive a condition on the energy E:

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}$$

which then gives

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} \equiv \frac{E_1}{n^2} \qquad \text{for} \quad n = 1, 2, 3, \dots \tag{4.8}$$

In 4.8, n has those values because $j_{\max}$ and ℓ can possibly be zero.

We can scrape up everything and write down the wave functions, remembering that ρ was defined using κ:

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{n} \equiv \frac{1}{an} \qquad \text{where} \qquad a \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m}$$

and a is the Bohr radius, namely the radius of the smallest orbit of the simple Bohr model.

The wave function for the state with the three quantum numbers (n, ℓ, m) is

$$\psi_{n,\ell,m}(\mathbf{r}) = R_{n\ell}(r)Y_\ell^m(\theta, \phi)$$

where

$$R_{n\ell}(r) = \frac{1}{r}\rho^{\ell+1}e^{-\rho}\,v(\rho)$$

and $v(\rho)$ is a polynomial of degree $j_{\max} = n - \ell - 1$ in ρ with the recursion relation

$$c_{j+1} = \frac{2(j + \ell + 1 - n)}{(j + 1)(j + 2\ell + 2)}c_j$$

4.6.3   The States of the H atom

The ground state has $n = 1$ and gives $E_1 = -13.6$ eV, so the **binding energy** of H in the ground state is 13.6 eV.

The ground state wave function is

$$\psi_{100}(r, \theta, \phi) = R_{10}(r)\,Y_0^0(\theta, \phi) = \frac{1}{\sqrt{\pi a^3}}e^{-r/a} \tag{4.9}$$

For $n = 2$, the energy is

$$E_2 = \frac{-13.6 \text{ eV}}{4} = -3.4 \text{ eV}$$

(i.e. the energy of the **first excited state**) and we can have $\ell = 0$ $\ell = 1$ for this case, the latter having the possibilities $m = -1, 0, +1$. (All 4 states have $n = 2$.)

The $\ell = 0$ and $\ell = 1$ cases give two different truncates series, hence two different radial functions. When we find and normalize them such that $\int_0^\infty |R| r^2 \, dr = 1$, they are

$$R_{20}(r) = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2}\frac{r}{a}\right) e^{-r/2a} \qquad\qquad R_{21}(r)\frac{1}{\sqrt{24}} a^{-3/2}\frac{r}{a} e^{-r/2a}$$

For arbitrary n, ℓ can have the values

$$\ell = 0, 1, 2, \ldots n - 1$$

and for each ℓ there are $2\ell + 1$ possible values for m. Thus the *degeneracy* of energy level E_n is

$$d(n) = \sum_{\ell=0}^{n-1}(2\ell + 1) = n^2$$

The polynomials we get for the radial function for each (n, ℓ) are in fact known to old–timey mathematicians. They even have a name; they are called the associated Laguerre polynomials $L_{n_1}^{n_2}(x)$:

$$v(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho) \qquad \text{where} \qquad L_{q-p}^{p} \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$$

and the $L_q(x)$ are the (regular) Laguerre polynomials,

$$L_q(x) = e^x \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)$$

The radial function still needs to be normalized, though. When we do this and put everything together, the big result for the H atom wave function for the state given by (n, ℓ, m) is:

$$\psi(\mathbf{r}) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]}} \, e^{-r/(na)} \left(\frac{2r}{na}\right)^\ell \left[L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na}\right)\right] Y_\ell^m(\theta, \phi) \qquad (4.10)$$

which is probably the most messiest thing we'll ever produce in this course, but we note again that this is an "exact" answer for a realistic system and those are rare in quantum mechanics.

We note again that the full wave function depends on the numbers (n, ℓ, m) while the radial function depends on both n and ℓ. The energy E depends only on n.

The H atom wave functions are orthonormal:

$$\int \psi_{n',\ell',m'}^* \, \psi_{n\ell m} \, r^2 \sin\theta \, dr \, d\theta \, d\phi = \delta_{n'n}\delta_{\ell'\ell}\delta_{m'm}$$

For states with different energy eigenvalues, this *has* to be the case, but the wave functions were chosen so that *all* are mutually orthonormal.

There are various ways to visualize these solutions; one can make shaded density plots of $|\psi|^2$ and plot surfaces of constant $|\psi|^2$. Note that if we are ignoring the factor of the angular function and considering a *radial* probability distribution we need to plot $r^2|R(r)|^2$ because *that* is the function which is a normalized probability distribution.

4.6.4   The H atom spectrum

It's worth pointing out that *using the only physics of basic QM*, if a particle is in one of stationary states of the H atom found above, it *stays* in that state! Of course from basic modern physics we know that the electron can make transitions to other states and in doing so emits or absorbs a photon of a characteristic energy, but that process involves some ideas that (for the time being) we have to clumsily attach to the present picture.

The missing physics is the interaction of the electron with the electromagnetic field, and such a treatment must include the possibly of the creation and destruction of photons (if not also electrons). With such physics one could calculate the *times* involved in these transitions. We'll have to come back to that later.

With that in mind, having derived the possible energies E_n, we know that when the electron makes a transition from state n_i to the state n_f there is emitted a photon whose energy (given by $E = \hbar\omega = hf$, with $\lambda f = c$) is

$$E_\gamma = -\Delta E = E_i - E_f = (-13.6 \text{ eV}) \left(\frac{1}{n_1^2} - \frac{1}{n_f^2} \right)$$

This can expressed in a form which gives the photon wavelength,

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_f^2} \right) \qquad \text{where} \qquad R = \frac{m}{4\pi c\hbar^3} \left(\frac{c^2}{4\pi\epsilon_0} \right)^2 = 1.097 \times 10^7 \text{ m}^{-1}$$

With $n_f = 1$ we get the **Lyman series** of spectral "lines"; for $n_f = 2$ we have the **Balmer series**, for $n_f = 3$ the **Paschen series**, and so on[1].

One can literally see the photons from the Balmer series by electrically exciting a tube of hydrogen gas. In such a tube the hydrogen *molecules* have been dissociated with the resulting photons coming from the electron motion in the isolated atoms.

We also note that these series (the first few at least) are of enormous importance in astronomy.

4.7   Angular Momentum

With motion in three dimensions we can consider a new dynamical quantity that had no meaning in 1-D, and that is **angular momentum**.

We recall the importance of angular momentum in classical mechanics: It has the definition $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ and the total angular momentum of a system is conserved if there is no net external torque.

Angular momentum is important in quantum systems which have rotational symmetry of some sort, and that's a lot of them.

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \qquad \Longrightarrow \qquad L_x = yp_z - zp_y$$

where we make the replacement $p_x \to \frac{\hbar}{i} \frac{\partial}{\partial x}$. We also define

$$L_{\text{op}}^2 = L_x^2 + L_y^2 + L_z^2$$

---

[1] In order, the first six series are named Lyman, Balmer, Paschen, Brackett, Pfund, Humphreys. Few people are impressed by this kind of knowledge.

We would like to find the eigenfunctions and eigenvalues of the various L operators. The first order of business is to find the commutation relations between them to see how many of them are compatible (as discussed in Chap. 3). One can show:

$$[L_x, L_y] = i\hbar L_z \qquad [L_y, L_z] = i\hbar L_x \qquad [L_z, L_x] = i\hbar L_y$$

This shows that the three components of the **L** operator are —it not compatible and we can only get eigenfunctions of *one* of them for the stationary states. However,

$$[L^2, L_x] = 0 \qquad [L^2, L_y] = 0 \qquad [L^2, L_z] = 0$$

so that L^2 is compatible with any one component; so we can (possibly) find simultaneous eigen-functions of both L^2 and L_z.

Now we recall that for the solution of the QM harmonic oscillator there were two approaches: one using just the operator language (algebraic) and the other using a normal differential equation (analytic). We will use the same kinds of approaches here.

4.7.1   Algebraic Approach to Angular Momentum

Define what we later justify as "ladder operators":

$$L_\pm \equiv L_x \pm iL_y \tag{4.11}$$

First off, one can show the following: Suppose f is an eigenfunction of of L^2 with eigenvalue λ and is also an eigenfunction of L_z with eigenvalue μ. Then:

- $L_\pm f$ is also an eigenfunction of L^2 with eigenvalue λ.

- $L_\pm f$ is also an eigenfunction of L_z with eigenvalue $\mu \pm \hbar$.

This property justifies the names "ladder operator"; we note that its application changes L_z eigenvalues *within the same L^2 eigenvalue.*

One can show that the eigenvalues of L^2 are

$$\lambda = \hbar^2 \ell(\ell + 1)$$

and the eigenvalues of L_z are $m\hbar$, where m goes from $-\ell$ to ℓ in integer steps. Thus we denote the eigenfunctions by f_ℓ^m, with

$$L^2 f_\ell^m = \hbar^2 \ell(\ell + 1) \qquad L_z f_\ell^m = \hbar m f_\ell^m$$

The number ℓ can be any integer of "half-integer", that is,

$$\ell = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \dots$$

And we will see that even though the integers apply to the spatial motion of the electron in the H atom, the half-integer values also have a role in physics!

4.7.2   Analytic Approach to Angular Momentum

By making operators out of the classical expression $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, we can show that the *operator* for $\mathbf{L}$ is:

$$\mathbf{L} = \frac{\hbar}{i} \left(\hat{\boldsymbol{\phi}} \frac{\partial}{\partial \theta} - \hat{\boldsymbol{\theta}} \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right)$$

and the the L_z and ladder operators are

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \qquad L_{\pm} = \pm \hbar e^{\pm i\phi} \left(\frac{\partial}{\partial \theta} \pm i \cot \theta \frac{\partial}{\partial \phi} \right)$$

and the L^2 operator is

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

As this is the same as the operator in the angular (azimuthal) equation, we conclude that the spherical harmonics are the eigenfunctions of L^2 and L_z.

4.7.3   Spin

$$[S_x, S_y] = i\hbar S_z \qquad [S_y, S_z] = i\hbar S_x \qquad [S_z, S_x] = i\hbar S_y \tag{4.12}$$

$$S^2 |s\ m\rangle = \hbar^2 s(s+1)|s\ m\rangle \qquad S_z|s\ m\rangle = \hbar m|s\ m\rangle \qquad S_{\pm}|s\ m\rangle = \hbar \sqrt{s(s+1) - m(m \pm 1)}\, |s\ m\rangle$$

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_- \quad \text{where} \quad \chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\mathsf{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \mathsf{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\mathsf{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \mathsf{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \mathsf{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\chi_+^{(x)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \chi_-^{(x)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

4.7.4   Electron in a Magnetic Field

Here we consider the behavior of an isolated electron in a magnetic field. Of course real electrons will interact with their immediate environment as well as any external magnetic field and we do consider the behavior of an atomic electron in an external magnetic field but here we will ignore the spatial motion of the electron so that its behavior is just given by its Pauli spinor χ.

The electron will interact with a field $\mathbf{B}$ because it has a magnetic moment $\boldsymbol{\mu}$. Just as the magnetic moment of the electron is intrinsic, so is the magnetic moment; it does *not* arise as a

result of the spatial motion of some charge density. However we might think that the two quantities are *related* even proportional to one another. And is indeed the case; if the spin angular momentum is **S**, then the magnetic dipole moment is given by

$$\boldsymbol{\mu} = \gamma \mathbf{S} \tag{4.13}$$

where γ, a constant called the **gyromagnetic ratio** is a constant to be determined by some deeper theory of electrons, but that is not our concern now; in facct it is very close to $-e/m_{\mathrm{e}}$, but we will leave it as γ.

Eq. 4.13 is a relation between the quantum mechanical *operators* for $\boldsymbol{\mu}$ and **S**.

The Hamiltonian (energy operator) of the magnetic dipole is the same as the classical expression;

$$H = -\boldsymbol{\mu} \cdot \mathbf{B} \tag{4.14}$$

and the two relations combined give

$$H = -\gamma \mathbf{B} \cdot \mathbf{S} \tag{4.15}$$

Larmor Precession

For an electron in a uniform field $\mathbf{B} = B_0 \hat{\mathbf{z}}$ the Hamiltonian operator is (expressed in matrix form... it operates on Pauli spinors!):

$$\mathsf{H} = -\gamma B_0 \mathsf{S}_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4.16}$$

$$\chi(t) = a\chi_+ e^{-iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar} = \begin{pmatrix} ae^{-iE_+ t/\hbar} \\ be^{-iE_- t/\hbar} \end{pmatrix}$$

4.7.5   Combining Angular Momenta; The C–G Coefficients

It is quite often the case in quantum problems that we must consider angular momenta of individual particles and relate them to the *total angular momentum of the quantum system.*

We will first consider a system with two spin angular momenta, from the operators $\mathbf{S}^{(1)}$ and $\mathbf{S}^{(2)}$, with $S_1 = \frac{1}{2}$ and $S_2 = \frac{1}{2}$. The states are for short denoted by

$$\uparrow\uparrow, \quad \uparrow\downarrow, \quad \downarrow\uparrow, \quad \downarrow\downarrow$$

We want to find the eigenstates of the operator

$$\mathbf{S} \equiv \mathbf{S}^{(1)} + \mathbf{S}^{(2)} \tag{4.17}$$

that is, the total (spin) angular momentum. We find that the operators $\mathbf{S}^2$ and S_z have eigenstates given by the quantum numbers s and m, denoted by

$$|s\,m\rangle \quad \text{with} \quad s = 1,\, m = -1, 0, 1 \quad \text{and} \quad s = 0,\, m = 0$$

and the relation between the two sets of states is found to be

$$\begin{aligned}
|1\,1\rangle &= \uparrow\uparrow \\
|1\,0\rangle &= \tfrac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\
|1\,-1\rangle &= \downarrow\downarrow
\end{aligned}$$

These states are collectively called the **triplet** state with $s = 1$ and the orthogonal state is

$$|0\ 0\rangle = \tfrac{1}{\sqrt{2}}(\uparrow\downarrow \ - \ \downarrow\uparrow) \tag{4.18}$$

called the **singlet** state, with $s = 0$.

The steps which give the above result can be generalized (through a technical study of the theory of angular momentum) to where states from individual spins s_1 and s_2 combine to give eigenstates of total spin, s and its z component, m. The possibilities for s are

$$s = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \dots, |s_1 - s_2| \tag{4.19}$$

If we are given a state of total spin $|s\ m\rangle$, it can be written as a linear combination of the composite states $|s_1\ m_1\rangle\,|s_2\ m_2\rangle$. For a given s_1 and s_2, the and the relation has the form

$$|s\ m\rangle = \sum_{m_1 + m_2 = m} C^{s_1\ s_2\ s}_{m_1\ m_2\ m} |s_1\ m_1\rangle\,|s_2\ m_2\rangle \tag{4.20}$$

Note, the only composite states which contribute are those where the z-components add to give m.

The constants $C^{s_1\ s_2\ s}_{m_1\ m_2\ m}$ in 4.20 are called **Clebsch–Gordan coefficients**, and they can be gotten from a table obtainable from the Particle Data website. All of them have the form of a square root of some rational number.

Chapter 5

Multi-Particle Systems

There remains one fundamental principle of QM we haven't covered. That is the way to treat multi-particle system.

5.1   The Schrödinger Equation for Two or More Particles

The extension of the Schrödinger to two or more particles is not *conceptually* difficult. Now the wave function (state) ψ becomes a function of the coordinates of the two particles (and time): $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$. and the meaning of the wave function is that it gives a probability density for two particles to be found at certain points; thus the probability for particle 1 to be within $d^3\mathbf{r}_1$ of $\mathbf{r}_1$ and for particle 2 to be within $d^3\mathbf{r}_2$ of $\mathbf{r}_2$ at time t is

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 \, d^3\mathbf{r}_1 \, d^3\mathbf{r}_2$$

and the wave function is normalized such that

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 \, d^3\mathbf{r}_1 \, d^3\mathbf{r}_2 = 1$$

The Hamiltonian operator now has a kinetic energy operator for each particle, and the potential is a function of both coordinates:

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t) \tag{5.1}$$

For time-independent potentials we can obtain a complete set of solutions of the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2)e^{-iEt/\hbar}$$

for which $\psi(\mathbf{r}_1, \mathbf{r}_2)$ satisfies the time–independent Schrödinger equation:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\,\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\,\psi + V(\mathbf{r}_1, \mathbf{r}_2)\,\psi = E\psi \tag{5.2}$$

where E is the total energy of the system.

5.1.1   Central Forces; Relative and CM Coordinates

In one of the more important exercises of the book (Prob 5.1) you can show that if we have a two–particle system and the interaction potential only depends on the relative position vector $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$ then with the definitions

$$\mathbf{R} \equiv \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \qquad \mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2 \qquad M \equiv m_1 + m_2 \qquad \mu \equiv \frac{m_1 m_2}{m_1 + m_2} \qquad (5.3)$$

the two–particle time-independent Schrödinger equation becomes

$$-\frac{\hbar^2}{2M}\nabla_R^2 \psi - \frac{\hbar^2}{2\mu}\nabla_r^2 \psi + V(\mathbf{r})\psi = E\psi \qquad (5.4)$$

which we note (from the terms which depend only on $\mathbf{R}$ or $\mathbf{r}$) is a separable equation; that is, if we assume a wave function of the form

$$\psi(\mathbf{R}, \mathbf{r}) = \psi_R(\mathbf{R})\psi_r(\mathbf{r})$$

then we will get two separate differential equations in the variables $\mathbf{R}$ and $\mathbf{r}$. The DE for $\psi_r(\mathbf{r})$ looks just like our old single–particle Schrödinger equation but with the reduced mass μ in place of the particle mass m.

   The DE for the center of mass location $\mathbf{R}$ is just that of a free particle of mass M; thus is has our usual (but badly–behave) plane-wave solutions.

   From this we can see that there was a *small* error in our solution for the hydrogen atom; in the formulae for the energy levels we had the electron mass m_e where we should have had the reduced mass of the electron–proton system, but the difference is small.

5.2   Bosons and Fermions

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm\psi(\mathbf{r}_2, \mathbf{r}_1)$$

5.3   Atoms

Having achieved victory over the H atom (for the time being) we would like to go on and —now that we can handle multi-particle systems— solve for the atoms in the periodic table. Then, molecules and crystals and DNA and...

   Whoa, hold on there, Clyde. This is going to be hard. First, consider the Hamiltonian for the next–simplest atom, helium, which is cnosists of a (very small) nucleus of charge $+2e$ with two electrons "orbiting" it. As we'll see, the Hamiltonian for this system is

$$H = \left\{ -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m_2}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \qquad (5.5)$$

which differs from a sum of two Hamiltonians of the hydrogen type by the last term, which gives the repulsion between the two electrons. In this case we definitely can *not* separate the DE into simpler equations and it remains a DE in 6 coordinates!

But the other atoms are even worse. The simplest Hamiltonian one could write down for an atom of atomic number Z (and thus with Z electrons) is:

$$H = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m_1}\nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{Ze^2}{r_j} \right\} + \frac{1}{2}\left(\frac{1}{4\pi\epsilon_0}\right)\sum_{j\neq k}^{Z}\frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|} \tag{5.6}$$

which is utterly unsolvable without making some approximations. And that indeed is the big question when we do *real* calculations for *real* physical systems: What approximations can we make that will get us close to the answer and for which we are *able* to do the calculation?

5.3.1   Helium Atom

Returning now to the helium atom: We treat the nucleus as being "nailed down"; in this case there is no simple way to use anything like "center of mass" and "relative" coordinates but we can be fairly confident that this is a small correction[1].

The Hamiltonian for the helium atom is the one given in Eq. 5.5, with terms for the kinetic energies of the two electrons, their attraction to the nucleus, and the last term, which gives their mutual repulsion.

Now the absolute worst plausible guess for the wave function for the ground state of this system would be to take two ground state hydrogen wave functions for the two coordinates and then multiply:

$$\psi_0(\mathbf{r_1}, \mathbf{r_2}) = \psi_{100}(\mathbf{r_1})\psi_{100}(\mathbf{r_2}) = \frac{8}{\pi a^3}e^{-2(r_1+r_2)/a}$$

Don't worry about the fact that this function is *symmetric* for exchange of the particle labels; we would combine this with a *spin* wave function which is anti-symmetric in the spin coordinates and thus a total wave function which is anti-symmetric overall. Since there is no spin dependence in the simple Hamiltonian, nothing is changed.

One can show that if we *ignore* the electron–electron repulsion term in H then this state is an eigenstate with energy

$$E = 4(E_{100} + E_{100}) = 8E_1 = -109 \text{ eV}$$

(The 4 comes from the nuclear charge squared.) This disagrees big time with the experimental value, $E_{\text{expt}} = -78.975$ eV, which only serves to tell us that the e-e repulsion is significant. (It adds a significant *positive* contribution to the energy.)

One is forced to get *approximate* solutions for the helium atom, and all the other atoms for that matter. These methods will be covered in chapters 6 and 7.

5.3.2   Bigger Atoms

In the treatment of atoms given in elementary chemistry courses one is taught that we can under-stand the periodic table by placing the electrons for the various elements in sequence into a set of orbitals. The orbitals are labeled by the quantum numbers (n, l, m) and are like those of the H atom except that for each n the orbitals with different l's now differ in energy.

With such a scheme one can predict the important properties of chemical bonds and why the noble gases are so noble.

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[1]For precision work, though one would need to have a way of treating the motion of the nucleus. Such prescriptions exist and are complicated.

5.4   Free Electron Gas

Major results from this section:

The **Fermi momentum** and **Fermi energy**, in terms or the number density of electrons in the system is

$$k_F = (3\rho\pi^2)^{1/3} \qquad E_F = \frac{\hbar^2}{2m}(3\rho\pi^2)^{2/3} \tag{5.7}$$

Total energy of the system is

$$E_{\text{tot}} = \frac{\hbar^2(3\pi^2Nq)^{5/3}}{10\pi^2m}V^{-2/3} \tag{5.8}$$

The pressure which results *solely* from the quantum mechanical requirement for the antisymmetrization of electron wave functions is

$$P = \frac{(3\pi^2)^{2/3}\hbar^2}{5m}\rho^{5/3} \tag{5.9}$$

This is sometimes called the **degeneracy pressure**.

5.4.1   Application to Compact Stellar Objects

An important application of the results for the (non-interacting) gas of fermions is that of understanding the properties of **white dwarfs** and **neutron stars**. These are done in Griffiths' Problems 5.35 and 5.36, whose results I considered essential material for this course.

The white dwarf star consists of nuclei with nearly equal numbers of protons and neutrons (e.g. He and C nuclei) enough electrons to make things neutral. To a good approximation one can ignore the interactions of the charged particles and focus on the kinetic energy of the quantum gas of electrons. This energy increases as one makes the system more compact, as given by the expression for the degeneracy pressure. In addition to the electron kinetic energy, there is a gravitational attraction off all the particle in the star, holding the star together. The star will attain a size such that the total energy is minimized and one can show that for stars having the mass of the sun, the radius is about that of the earth. This fact was deduced from observations of the white dwarf companion of Sirius, and at the time the mass density of such an object was quite surprising.

One should be concerned that the motion of the electrons is not relativistic, because that would mean that our calculation is invalid, but for the case of a star of the sun's mass the electron energies are only slightly relativistic. If we assume that the motion of *all* the electrons is *highly* relativistic, we can show (in our crude calculation) that this happens when the star's mass is about 1.7 times the mass of the sun. (The more precise value as found by Chandrasekhar is closer to 1.4 solar masses.) At this value the star undergoes a further collapse so that the electrons combine with the protons to form neutrons, and the star becomes a much smaller ball of neutrons, again held together by gravity.

For a neutron star, one can neglect the neutron–neutron (strong force) interaction and just treat them as a gas of fermions. When we do this and again minimize the total energy of the star, we find that the equilibrium radius is about 12 km, that is, the size of a city. In this case we are safer in neglecting relativity, but for good calculations, the n-n forces are significant.

5.5   Periodic Potential

A fundamental problem in applying QM to the motion of electrons moving in a crystalline solid is that of a periodic potential. To show the effects of a periodic potential in the simplest way, we

will solve the problem of one-dimensional motion in a "Dirac comb" potential, one where the is a delta–function spike at points on the x axis separated by a distance a.

Though the potential is periodic, the wavefunctions need not be. One can show that we can solve solve for energy eigenstates which have the property

$$\psi(x + a) = e^{iKa}\psi(x) \tag{5.10}$$

a fact known as **Bloch's theorem**.

Bloch's theorem assumes that the crystal has no edges which is not true in reality; a common way to deal with this is to impose **periodic boundary conditions** on the wave functions,

$$\psi(x + Na) = \psi(x) \tag{5.11}$$

This choice leads to a condition on K,

$$K = \frac{2\pi n}{Na} \qquad (n = 0, \pm 1 \pm 2, \ldots)$$

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja) \tag{5.12}$$

After working through the math of the Schrödinger equation, the continuity conditions (rendered a little tricky from the singular nature of the potential) leads to the condition

$$\cos(Ka) = \cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka) \tag{5.13}$$

With the definitions

$$z \equiv ka \qquad \text{and} \qquad \beta \equiv \frac{m\alpha a}{\hbar^2}$$

the right side of Eq. 5.13 can be written as

$$f(z) \equiv \cos(z) + \beta\frac{\sin(z)}{z} \tag{5.14}$$

and Eq. 5.13 is $\cos(Ka) = f(z)$ which tells us that if $f(z)$ goes outside the range $(-1, +1)$ there is no solution for the energy E. We can see this more clearly by plotting $f(z)$ vs z and seeing that for some z's (that is, some k's, some E's) is gives illegal values for $\cos(Ka) = f(z)$. Thus there are intervals in E which are physically forbidden and so we have energy **bands** and energy **band gaps**.

Then in a simple model of the behavior of the electrons we can fill up the states (indexed by K). When a band is completely filled it will require a large amount of energy to boost an electron to the next higher state; this feature explains why there electrical **insulators** and **conductors**.