PHYSICS 430

Lecture Notes on Quantum Mechanics

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APOLOGIA

These are my lecture notes for Physics 430 and 431, written a number of years ago. They are still a bit incomplete: Chapters 19 and 20 remain to be written, and Chapter 23 is unfinished. Perhaps this year I will get around to it. It is likely that there are still many misprints scattered here and there in the text, and I will be grateful if these are brought to my attention.

Chapter 1

The Classical State

In the first quarter of this century, it was discovered that the laws of motion formulated by Galileo, Newton, Lagrange, Hamilton, Maxwell, and many others, were inadequate to explain a wide range of phenomena involving electrons, atoms, and light. After a great deal of effort, a new theory (together with a new law of motion) emerged in 1924. That theory is known as **quantum mechanics**, and it is now the basic framework for understanding atomic, nuclear, and subnuclear physics, as well as condensed-matter (or "solid-state") physics. The laws of motion (due to Galileo, Newton,...) which preceded quantum theory are referred to as **classical mechanics**.

Although classical mechanics is now regarded as only an approximation to quantum mechanics, it is still true that much of the structure of the quantum theory is inherited from the classical theory that it replaced. So we begin with a lightning review of classical mechanics, whose formulation begins (but does not end!) with Newton's law $F = ma$.

1.1   Baseball, $F = ma$, and the Principle of Least Action

Take a baseball and throw it straight up in the air. After a fraction of a second, or perhaps a few seconds, the baseball will return to your hand. Denote the height of the baseball, as a function of time, as $x(t)$; this is the **trajectory** of the baseball. If we make a plot of x as a function of t, then any trajectory has the form of a parabola (in a uniform gravitational field, neglecting air resistance), and there are an infinite number of possible trajectories. Which one of these trajectories the baseball actually follows is determined by the momentum of the baseball at the moment it leaves your hand.

However, if we require that the baseball returns to your hand exactly Δt seconds after leaving your hand, then there is only one trajectory that the ball can follow. For a baseball moving in a uniform gravitational field it is a simple exercise to determine

this trajectory exactly, but we would like to develop a method which can be applied to a particle moving in *any* potential field $V(x)$. So let us begin with Newton's law $F = ma$, which is actually a second-order differential equation

$$m\frac{d^2x}{dt^2} = -\frac{dV}{dx} \tag{1.1}$$

It is useful to reexpress this second-order equation as a pair of first-order equations

$$\begin{aligned}
\frac{dx}{dt} &= \frac{p}{m} \\
\frac{dp}{dt} &= -\frac{dV}{dx}
\end{aligned} \tag{1.2}$$

where m is the mass and p is the momentum of the baseball. We want to find the solution of these equations such that $x(t_0) = X_{in}$ and $x(t_0 + \Delta t) = X_f$, where X_{in} and X_f are, respectively, the (initial) height of your hand when the baseball leaves it, and the (final) height of your hand when you catch the ball.[1]

With the advent of the computer, it is often easier to solve equations of motion numerically, rather than struggle to find an analytic solution which may or may not exist (particularly when the equations are non-linear). Although the object of this section is not really to develop numerical methods for solving problems in baseball, we will, for the moment, proceed as though it were. To make the problem suitable for a computer, divide the time interval Δt into N smaller time intervals of duration $\epsilon = \Delta t / N$, and denote, for $n = 0, 1, ..., N$,

$$\begin{aligned}
t_n &\equiv t_0 + n\epsilon \ , \\
x_n &= x(t_n) \ , \quad p_n = p(t_n) \ , \\
\\
x_0 &= X_{in} \ , \qquad x_N = X_f
\end{aligned} \tag{1.3}$$

An approximation to a continuous trajectory $x(t)$ is given by the set of points $\{x_n\}$ connected by straight lines, as shown in Fig. [1.1]. We can likewise approximate derivatives by finite differences, i.e.

$$\begin{aligned}
\left(\frac{dx}{dt}\right)_{t=t_n} &\rightarrow \frac{x(t_{n+1}) - x(t_n)}{\epsilon} = \frac{x_{n+1} - x_n}{\epsilon} \\
\left(\frac{dp}{dt}\right)_{t=t_n} &\rightarrow \frac{p(t_{n+1}) - p(t_n)}{\epsilon} = \frac{p_{n+1} - p_n}{\epsilon} \\
\left(\frac{d^2x}{dt^2}\right)_{t=t_n} &\rightarrow \frac{1}{\epsilon}\left\{\left(\frac{dx}{dt}\right)_{t=t_n} - \left(\frac{dx}{dt}\right)_{t=t_{n-1}}\right\} \\
&\rightarrow \frac{1}{\epsilon}\left\{\frac{(x_{n+1} - x_n)}{\epsilon} - \frac{(x_n - x_{n-1})}{\epsilon}\right\}
\end{aligned} \tag{1.4}$$

---

[1]We will allow these positions to be different, in general, since you might move your hand to another position while the ball is in flight.

and integrals by sums

$$\int_{t_0}^{t_0+\Delta t} dt \ f(t) \to \sum_{n=0}^{N-1} \epsilon f(t_n) \tag{1.5}$$

where $f(t)$ is any function of time. As we know from elementary calculus, the right hand side of (1.4) and (1.5) equals the left hand side in the limit that $\epsilon \to 0$, which is also known as the **continuum limit**.

We can now approximate the laws of motion, by replacing time-derivatives in (1.2) by the corresponding finite differences, and find

$$
\begin{aligned}
x_{n+1} &= x_n + \left(\frac{p_n}{m}\right)\epsilon \\
p_{n+1} &= p_n - \left(\frac{dV(x_n)}{dx_n}\right)\epsilon
\end{aligned}
\tag{1.6}
$$

These are iterative equations. Given position x and momentum p at time $t = t_n$, we can use (1.6) to find the position and momentum at time $t = t_{n+1}$. The finite difference approximation of course introduces a slight error; x_{n+1} and p_{n+1}, computed from x_n and p_n by (1.6) will differ from their exact values by an error of order ϵ^2. This error can be made negligible by taking ϵ sufficiently small.

It is then possible use the computer to find an approximation to the trajectory in one of two ways: (i) the "hit-or-miss" method; and (ii) the method of least action.

- **The Hit-or-Miss Method**

The equations of motion (1.2) require as input both an initial position, in this case $x_0 = X_{in}$, and an initial momentum p_0 which is so far unspecified. The method is to make a guess for the initial momentum $p_0 = P_0$, and then use (1.2) to solve for $x_1, p_1, \ x_2, p_2$, and so on, until x_N, p_N. If $x_N \approx X_f$, then stop; the set $\{x_n\}$ is the (approximate) trajectory. If not, make a different guess $p_0 = P_0'$, and solve again for $\{x_n, p_n\}$. By trial and error, one can eventually converge on an initial choice for p_0 such that $x_N \approx X_f$. For that choice of initial momentum, the corresponding set of points $\{x_n\}$, connected by straight-line segments, gives the approximate trajectory of the baseball. This process is illustrated in Fig. [1.2].

- **The Method of Least Action**

Lets return to the 2nd-order form of Newton's Laws, written in eq. (1.1). Again using (1.4) to replace derivatives by finite differences, the equation $F = ma$ at each time t_n becomes

$$\frac{m}{\epsilon}\left\{\frac{x_{n+1} - x_n}{\epsilon} - \frac{x_n - x_{n-1}}{\epsilon}\right\} = -\frac{dV(x_n)}{dx_n} \tag{1.7}$$

The equations have to be solved for $n = 1, 2, ..., N - 1$, with $x_0 = X_{in}$ and $x_N = X_f$ kept fixed. Now notice that eq. (1.7) can be written as a total derivative

$$\frac{d}{dx_n}\left\{\frac{1}{2}m\frac{(x_{n+1} - x_n)^2}{\epsilon} + \frac{1}{2}m\frac{(x_n - x_{n-1})^2}{\epsilon} - \epsilon V(x_n)\right\} = 0 \tag{1.8}$$

so that $F = ma$ can be interpreted as a condition that a certain function of x_n should be stationary. Let us therefore introduce a very important expression, crucial in both classical and quantum physics, which is known as the **"action"** of the trajectory. The action is a function which depends on all the points $\{x_n\}, \quad n = 0, 1, ..., N$ of the trajectory, and in this case it is

$$S[\{x_i\}] \equiv \sum_{n=0}^{N-1} \left[\frac{1}{2} m \frac{(x_{n+1} - x_n)^2}{\epsilon} - \epsilon V(x_n) \right] \tag{1.9}$$

Then Newton's Law $F = ma$ can be restated as the condition that the action functional $S[\{x_i\}]$ is stationary with respect to variation of any of the x_i (except for the endpoints x_0 and x_N, which are held fixed). In other words

$$
\begin{aligned}
\frac{d}{dx_k} S[\{x_i\}] &= \frac{d}{dx_k} \sum_{n=0}^{N-1} \left[\frac{1}{2} m \frac{(x_{n+1} - x_n)^2}{\epsilon} - \epsilon V(x_n) \right] \\
&= \frac{d}{dx_k} \left\{ \frac{1}{2} m \frac{(x_{k+1} - x_k)^2}{\epsilon} + \frac{1}{2} m \frac{(x_k - x_{k-1})^2}{\epsilon} - \epsilon V(x_k) \right\} \\
&= \epsilon \left\{ -ma(t_k) + F(t_k) \right\} \\
&= 0 \quad \text{for} \ \ k = 1, 2, ..., N-1
\end{aligned}
\tag{1.10}
$$

This set of conditions is known as the **Principle of Least Action**. It is the principle that the action S is stationary at any trajectory $\{x_n\}$ satisfying the equations of motion $F = ma$, eq. (1.7), at every time $\{t_n\}$.

The procedure for solving for the trajectory of a baseball by computer is to program the computer to find the set of points $\{x_n\}$ which minimizes the quantity

$$Q = \sum_k \left(\frac{\partial S}{\partial x_k} \right)^2 \tag{1.11}$$

The minimum is obtained at $Q = 0$, where S is stationary. This set of points, joined by straight-line segments, gives us the approximate trajectory of the baseball.

Problem: Do it on a computer by both methods.

Problem: Dyre's Dilemma[2]

In discussing the motion of the baseball, we have been ignoring a lot of details about baseballs, such as the composition of the interior, the pattern of the stitching, and the brand-name printed on the surface. Instead, the baseball has been treated as though it were essentially a structureless point of mass m. It is necessary to make idealizations like this in physics; the real world is otherwise too complicated to describe. But sometimes an idealization misses something crucial. See if you can find what goes wrong in the following argument, which tries to prove that a rolling wheel (or, for that matter, a rolling baseball) can never come to rest through friction with the ground.

"Proof": As shown in Fig. [1.3], the forward momentum of a wheel in the positive x-direction can only be eliminated by a force applied in the opposite direction. But the only place this force could be applied by friction is the point where the wheel touches the ground. And a force in the negative x-direction, applied at this point, will have the effect of making the wheel spin faster! Therefore, the wheel will never come to rest due to friction. QED.

Is this reasoning correct? Can *you* solve Dyre's Dilemma?

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[2]I owe this exercise to Dr. Jeppe Dyre, Roskilde University, Denmark.

1.2   Euler-Lagrange and Hamilton's Equations

In brief, the Euler-Lagrange equations are the second-order form of the equations of motion (1.1), while Hamilton's equations are the first-order form (1.2). In either form, the equations of motion can be regarded as a consequence of the Principle of Least Action. We will now re-write those equations in a very general way, which can be applied to any mechanical system, including those which are much more complicated than a baseball.

We begin by writing

$$S[\{x_i\}] = \sum_{n=0}^{N-1} \epsilon L[x_n, \dot{x}_n] \tag{1.12}$$

where

$$L[x_n, \dot{x}_n] = \frac{1}{2} m \dot{x}_n^2 - V(x_n) \tag{1.13}$$

and where

$$\dot{x}_n \equiv \frac{x_{n+1} - x_n}{\epsilon} \tag{1.14}$$

$L[x_n, \dot{x}_n]$ is known as the **Lagrangian** function. Then the principle of least action requires that, for each k, $1 \le k \le N-1$,

$$
\begin{aligned}
0 &= \frac{d}{dx_k} S[\{x_i\}] = \sum_{n=0}^{N-1} \epsilon \frac{d}{dx_k} L[x_n, \dot{x}_n] \\
&= \epsilon \frac{\partial}{\partial x_k} L[x_k, \dot{x}_k] + \sum_{n=0}^{N-1} \epsilon \frac{\partial L[x_n, \dot{x}_n]}{\partial \dot{x}_n} \frac{d\dot{x}_n}{dx_k}
\end{aligned} \tag{1.15}
$$

and, since

$$\frac{d\dot{x}_n}{dx_k} = \begin{cases} \frac{1}{\epsilon} & n = k-1 \\ -\frac{1}{\epsilon} & n = k \\ 0 & \text{otherwise} \end{cases} \tag{1.16}$$

this becomes

$$\frac{\partial}{\partial x_k} L[x_k, \dot{x}_k] - \frac{1}{\epsilon} \left\{ \frac{\partial}{\partial \dot{x}_k} L[x_k, \dot{x}_k] - \frac{\partial}{\partial \dot{x}_{k-1}} L[x_{k-1}, \dot{x}_{k-1}] \right\} = 0 \tag{1.17}$$

Recalling that $x_n = x(t_n)$, this last equation can be written

$$\left(\frac{\partial L[x, \dot{x}]}{\partial x} \right)_{t=t_n} - \frac{1}{\epsilon} \left\{ \left(\frac{\partial L[x, \dot{x}]}{\partial \dot{x}} \right)_{t=t_n} - \left(\frac{\partial L[x, \dot{x}]}{\partial \dot{x}} \right)_{t=t_n-\epsilon} \right\} = 0 \tag{1.18}$$

This is the Euler-Lagrange equation for the baseball. It becomes simpler when we take the $\epsilon \to 0$ limit (the "continuum" limit). In that limit, we have

$$\dot{x}_n = \frac{x_{n+1} - x_n}{\epsilon} \quad \to \quad \dot{x}(t) = \frac{dx}{dt}$$

$$S = \sum_{n=1}^{N-1} \epsilon L[x_n, \dot{x}_n] \quad \to \quad S = \int_{t_0}^{t_0+\Delta t} dt\, L[x(t), \dot{x}(t)] \tag{1.19}$$

where the Lagrangian function for the baseball is

$$L[x(t), \dot{x}(t)] = \frac{1}{2} m \dot{x}^2(t) - V[x(t)] \tag{1.20}$$

and the Euler-Lagrange equation, in the continuum limit, becomes

$$\frac{\partial L}{\partial x(t)} - \frac{d}{dt} \frac{\partial L}{\partial \dot{x}(t)} = 0 \tag{1.21}$$

For the Lagrangian of the baseball, eq. (1.20), the relevant partial derivatives are

$$\frac{\partial L}{\partial x(t)} = -\frac{dV[x(t)]}{dx(t)}$$
$$\frac{\partial L}{\partial \dot{x}(t)} = m \dot{x}(t) \tag{1.22}$$

which, when substituted into eq. (1.21) give

$$m \frac{\partial^2 x}{\partial t^2} + \frac{dV}{dx} = 0 \tag{1.23}$$

This is simply Newton's law $F = ma$, in the second-order form of eq. (1.1).

We now want to rewrite the Euler-Lagrange equation in first-order form. Of course, we already know the answer, which is eq. (1.2), but let us "forget" this answer for a moment, in order to introduce a very general method. The reason the Euler-Lagrange equation is second-order in the time derivatives is that $\partial L / \partial \dot{x}$ is first-order in the time derivative. So let us define the **momentum** corresponding to the coordinate x to be

$$p \equiv \frac{\partial L}{\partial \dot{x}} \tag{1.24}$$

This gives p as a function of x and $\dot{x}$, but, alternatively, we can solve for $\dot{x}$ as a function of x and p, i.e.

$$\dot{x} = \dot{x}(x, p) \tag{1.25}$$

Next, we introduce the **Hamiltonian** function

$$H[p, x] = p \dot{x}(x, p) - L[x, \dot{x}(x, p)] \tag{1.26}$$

Since $\dot{x}$ is a function of x and p, H is also a function of x and p.

The reason for introducing the Hamiltonian is that its first derivatives with respect to x and p have a remarkable property; namely, on a trajectory satisfying the Euler-Lagrange equations, the x and p derivatives of H are proportional to the *time*-derivatives of p and x. To see this, first differentiate the Hamiltonian with respect to p,

$$\frac{\partial H}{\partial p} = \dot{x} + p \frac{\partial \dot{x}(x, p)}{\partial p} - \frac{\partial L}{\partial \dot{x}} \frac{\partial \dot{x}(p, x)}{\partial p}$$
$$= \dot{x} \tag{1.27}$$

where we have applied (1.24). Next, differentiating H with respect to x,

$$\begin{aligned} \frac{\partial H}{\partial x} &= p\frac{\partial \dot{x}(x,p)}{\partial x} - \frac{\partial L}{\partial x} - \frac{\partial L}{\partial \dot{x}}\frac{\partial \dot{x}(p,x)}{\partial x} \\ &= -\frac{\partial L}{\partial x} \end{aligned} \tag{1.28}$$

Using the Euler-Lagrange equation (1.21) (and this is where the equations of motion enter), we find

$$\begin{aligned} \frac{\partial H}{\partial x} &= -\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} \\ &= -\frac{dp}{dt} \end{aligned} \tag{1.29}$$

Thus, with the help of the Hamiltonian function, we have rewritten the single 2nd order Euler-Lagrange equation (1.21) as a pair of 1st order differential equations

$$\begin{aligned} \frac{dx}{dt} &= \frac{\partial H}{\partial p} \\ \frac{dp}{dt} &= -\frac{\partial H}{\partial x} \end{aligned} \tag{1.30}$$

which are known as **Hamilton's Equations**.

For a baseball, the Lagrangian is given by eq. (1.20), and therefore the momentum is

$$p = \frac{\partial L}{\partial \dot{x}} = m\dot{x} \tag{1.31}$$

This is inverted to give

$$\dot{x} = \dot{x}(p,x) = \frac{p}{m} \tag{1.32}$$

and the Hamiltonian is

$$\begin{aligned} H &= p\dot{x}(x,p) - L[x,\dot{x}(x,p)] \\ &= p\frac{p}{m} - \left[\frac{1}{2}m(\frac{p}{m})^2 - V(x)\right] \\ &= \frac{p^2}{2m} + V(x) \end{aligned} \tag{1.33}$$

Note that the Hamiltonian for the baseball is simply the kinetic energy plus the potential energy; i.e. the Hamiltonian is an expression for the total energy of the baseball. Substituting H into Hamilton's equations, one finds

$$\begin{aligned} \frac{dx}{dt} &= \frac{\partial}{\partial p}\left[\frac{p^2}{2m} + V(x)\right] = \frac{p}{m} \\ \frac{dp}{dt} &= -\frac{\partial}{\partial x}\left[\frac{p^2}{2m} + V(x)\right] = -\frac{dV}{dx} \end{aligned} \tag{1.34}$$

which is simply the first-order form of Newton's Law (1.2).

1.3 Classical Mechanics in a Nutshell

All the machinery of the Least Action Principle, the Lagrangian Function, and Hamilton's equations, is overkill in the case of a baseball. In that case, we knew the equation of motion from the beginning. But for more involved dynamical systems, involving, say, wheels, springs, levers, and pendulums, all coupled together in some complicated way, the equations of motion are often far from obvious, and what is needed is some systematic way to derive them.

For any mechanical system, the **generalized coordinates** $\{q^i\}$ are a set of variables needed to describe the configuration of the system at a given time. These could be a set of cartesian coordinates of a number of different particles, or the angular displacement of a pendulum, or the displacement of a spring from equilibrium, or all of the above. The dynamics of the system, in terms of these coordinates, is given by a Lagrangian function L, which depends on the generalized coordinates $\{q^i\}$ and their first time-derivatives $\{\dot{q}^i\}$. Normally, in non-relativistic mechanics, we first specify

1. The Lagrangian

$$L[\{q^i \, \dot{q}^i\}] = \text{Kinetic Energy} - \text{Potential Energy} \tag{1.35}$$

One then defines

2. The Action

$$S = \int dt \, L[\{q^i\}, \{\dot{q}^i\}] \tag{1.36}$$

From the Least Action Principle, following a method similar to the one we used for the baseball (see Problem 4), we derive

3. The Euler-Lagrange Equations

$$\frac{\partial L}{\partial q^i} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}^i} = 0 \tag{1.37}$$

These are the 2nd-order equations of motion. To go to 1st-order form, first define

4. The Generalized Momenta

$$p_i \equiv \frac{\partial L}{\partial \dot{q}^i} \tag{1.38}$$

which can be inverted to give the time-derivatives $\dot{q}^i$ of the generalized coordinates in terms of the generalized coordinates and momenta

$$\dot{q}^i = \dot{q}^i[\{q^n, p_n\}] \tag{1.39}$$

Viewing $\dot{q}$ as a function of p and q, one then defines

5. The Hamiltonian

$$H[\{q^i, p_i\}] \equiv \sum_n p_n \dot{q}^n - L[\{q^i, \dot{q}^i\}] \tag{1.40}$$

Usually the Hamiltonian has the form

$$H[p, q] = \text{Kinetic Energy} + \text{Potential Energy} \tag{1.41}$$

Finally, the equations of motion in 1st-order form are given by

6. Hamilton's Equations

$$\begin{aligned}
\dot{q}^i &= \frac{\partial H}{\partial p_i} \\
\dot{p}_i &= -\frac{\partial H}{\partial q^i}
\end{aligned} \tag{1.42}$$

Example: The Plane Pendulum

Our pendulum is a mass m at the end of a weightless rigid rod of length l, which pivots in a plane around the point P. The "generalized coordinate", which specifies the position of the pendulum at any given time, is the angle θ (see Fig. [1.4]).

1. Lagrangian

$$L = \frac{1}{2}ml^2\dot{\theta}^2 - (V_0 - mgl\cos(\theta)) \qquad (1.43)$$

where V_0 is the gravitational potential at the height of point P, which the pendulum reaches at $\theta = \pi/2$. Since V_0 is arbitrary, we will just set it to $V_0 = 0$.

2. The Action

$$S = \int_{t_0}^{t_1} dt \left[\frac{1}{2}ml^2\dot{\theta}^2 + mgl\cos(\theta)\right] \qquad (1.44)$$

3. Euler-Lagrange Equations
   We have

$$\frac{\partial L}{\partial \theta} = -mgl\sin(\theta)$$
$$\frac{\partial L}{\partial \dot{\theta}} = ml^2\dot{\theta} \qquad (1.45)$$

and therefore

$$ml^2\ddot{\theta} + mgl\sin(\theta) = 0 \qquad (1.46)$$

is the Euler-Lagrange form of the equations of motion.

4. The Generalized Momentum

$$p = \frac{\partial L}{\partial \dot{\theta}} = ml^2\dot{\theta} \qquad (1.47)$$

5. The Hamiltonian
   Insert

$$\dot{\theta} = \frac{p}{ml^2} \qquad (1.48)$$

into

$$H = p\dot{\theta} - \left[\frac{1}{2}ml^2\dot{\theta}^2 + mgl\cos(\theta)\right] \qquad (1.49)$$

to get

$$H = \frac{1}{2}\frac{p^2}{ml^2} - mgl\cos(\theta) \qquad (1.50)$$

6. Hamilton's equations

$$\begin{aligned}
\dot{\theta} &= \frac{\partial H}{\partial p} = \frac{p}{ml^2} \\
\dot{p} &= -\frac{\partial H}{\partial \theta} = -mgl\sin(\theta)
\end{aligned} \qquad (1.51)$$

which are easily seen to be equivalent to the Euler-Lagrange equations.

Problem - Two pointlike particles moving in three dimensions have masses m_1 and m_2 respectively, and interact via a potential $V(\vec{x_1} - \vec{x_2})$. Find Hamilton's equations of motion for the particles.

Problem - Suppose, instead of a rigid rod, the mass of the plane pendulum is connected to point P by a weightless spring. The potential energy of the spring is $\frac{1}{2}k(l - l_0)^2$, where l is the length of the spring, and l_0 is its length when not displaced by an external force. Choosing l and θ as the generalized coordinates, find Hamilton's equations.

1.4   The Classical State

Prediction is rather important in physics, since the only reliable test of a scientific theory is the ability, given the state of affairs at present, to predict the future.

Stated rather abstractly, the process of prediction works as follows: By a slight disturbance known as a **measurement**, an object is assigned a mathematical representation which we will call its **physical state**. The laws of motion are mathematical rules by which, given a physical state at a particular time, one can deduce the physical state of the object at some later time. The later physical state is the prediction, which can be checked by a subsequent measurement of the object (see Fig. [1.5]).

From the discussion so far, its easy to see that what is meant in classical physics by the "physical state" of a system is simply its set of generalized coordinates *and* the generalized momenta $\{q^a, p_a\}$. These are supposed to be obtained, at some time t_0, by the measurement process. Given the physical state at some time t, the state at $t + \epsilon$ is obtained by the rule:

$$\begin{aligned}
q^a(t + \epsilon) &= q^a(t) + \epsilon \left(\frac{\partial H}{\partial p_a}\right)_t \\
p_a(t + \epsilon) &= p_a(t) - \epsilon \left(\frac{\partial H}{\partial q^a}\right)_t
\end{aligned} \qquad (1.52)$$

In this way, the physical state at any later time can be obtained (in principle) to an arbitrary degree of accuracy, by making the time-step ϵ sufficiently small (or else, if

possible, by solving the equations of motion exactly). Note that the coordinates $\{q^a\}$ alone are *not* enough to specify the physical state, because they are not sufficient to predict the future. Information about the momenta $\{p_a\}$ is also required.

The space of all possible $\{q^a, p_a\}$ is known as **phase space**. For a single particle moving in three dimensions, there are three components of position and three components of momentum, so the "physical state" is specified by 6 numbers (x, y, z, p_x, p_y, p_z), which can be viewed as a point in 6-dimensional phase space. Likewise, the physical state of a system of N particles consists of 3 coordinates for each particle ($3N$ coordinates in all), and 3 components of momentum for each particle ($3N$ momentum components in all), so the state is given by a set of $6N$ numbers, which can be viewed as a single point in $6N$-dimensional space.

As we will see in the next lectures, classical mechanics fails to predict correctly the behavior of both light and matter at the atomic level, and is replaced by quantum mechanics. But classical and quantum mechanics have a lot in common: they both assign physical states to objects, and these physical states evolve according to 1st-order differential equations. The difference lies mainly in the contrast between a physical state as understood by classical mechanics, the "classical state", and its quantum counterpart, the "quantum state". This difference will be explored in the next few lectures.

Chapter 2

Origins of Quantum Mechanics

Where do correct ideas come from? Do they drop from the sky? No! Are they innate in the mind? No! They come from social practice, and from it alone.
- Mao Tse-Tung

The suggestion that all matter is composed of atoms, and the name "atom" itself, are due to the Greek thinker Democritus, who lived five centuries before Christ. Not until the 19th century, however, did evidence for this hypothesis begin to accumulate, particularly from thermodynamics. The evidence was indirect, but compelling: assuming that gases are composed of atoms, one could derive analytically the equation of state for ideal gases $PV = nRT$, which had been discovered empirically by Boyle and others. In addition, assuming that solids as well as gases are composed of atoms, one could deduce their specific heats, which agreed fairly well with the experimental values at high temperatures . By the early 20th century, improvements in technology and the discovery of radioactivity had enabled physicists to study in some detail the internal structure of atoms, the mass and charge of the electron, and the interaction of atoms with light.

Certain aspects of atomic physics which emerged from these early investigations were puzzling and even paradoxical, in the sense that the observed behavior of electrons, atoms, and light seemed in contradiction to the known laws of mechanics and electromagnetism. These aspects fell roughly into three categories:

1. **The Particle-like Behavior of Light Waves**
Black-body radiation, the photoelectric effect, the Compton effect.

2. **The Puzzling Stability of the Atom**
Why doesn't the electron fall into the nucleus? What is the origin of atomic spectra?

3. **The Wave-like Behavior of Particles**
Electron diffraction.

Quantum mechanics emerged as an attempt to explain these phenomena and, as in the bible, the story begins with light.

2.1   Black-Body Radiation

Isaac Newton believed that light is composed of particles, and he had good reason to think so. All wave motion exibits interference and diffraction effects, which are the signature of any phenomenon involving waves. Newton looked for these effects by passing light through small holes, but no diffraction effects were observed. He concluded that light is a stream of particles.

One of Newton's contemporaries, Christian Huygens, was an advocate of the wave theory of light. Huygens pointed out that the refraction of light could be explained if light moved at different velocities in different media, and that Newton's inability to find diffractive effects could be due simply to the insensitivity of his experiments. Interference effects are most apparent when wavelengths are comparable to, or larger than, the size of the holes. If the wavelength of light were very small compared to the size of the holes used by Newton, interference effects would be very hard to observe.

Huygens turned out to be right. More sensitive optical experiments by Young (1801) and Fresnel demonstrated the interference and diffraction of light, and measurements by Foucault (1850) showed that the speed of light in water was different from the speed of light in air, as required to explain refraction. Then Maxwell, in 1860, by unifying and extending the laws of electricity and magnetism, demonstrated that electric and magnetic fields would be able to propagate through space as waves, traveling with a velocity $v = 1/\sqrt{\mu_0 \epsilon_0}$, which turned out to equal, within experimental error, the known velocity of light. Experimental confirmation of the existence of electromagnetic waves followed shortly after, and by the 1880s the view that light is a wave motion of the electromagnetic field was universally accepted.

It is a little ironic that following this great triumph of the wave theory of light, evidence began to accumulate that light is, after all, a stream of particles (or, at least, light has particle properties which somehow coexist with its wave properties). The first hint of this behavior came from a study of black-body radiation undertaken by Max Planck, which marks the historical beginning of quantum theory.

Any object, at any finite temperature, emits electromagnetic radiation at all possible wavelengths. The emission mechanism is simple: atoms are composed of negatively charged electrons and positively charged nuclei, and upon collision with other atoms these charges oscillate in some way. According to Maxwell's theory, oscillating charges emit (and can also absorb) electromagnetic radiation. So it is no mystery that if we have a metallic box whose sides are kept at some constant temperature T, the interior of the box will be filled with electromagnetic radiation, which is constantly being emitted and reabsorbed by the atoms which compose the sides of the box. There was, however, some mystery in the energy distribution of this radiation as a function of frequency.

The energy density of radiation in the box, as a function of frequency, is easily worked out using the equipartition principle of statistical mechanics. The total energy is

$$
\begin{aligned}
E_{rad} &= \text{ no. of degrees of freedom} \times \frac{1}{2}kT \\
&= 2 \times (\text{no. of standing waves}) \times \frac{1}{2}kT
\end{aligned}
\tag{2.1}
$$

where k is Boltzman's constant and T is the temperature of the box. An electromagnetic field in a box can be thought of as a superposition of an infinite number of standing waves; the "degrees of freedom" are the amplitudes of each distinct standing wave. The factor of 2 comes from the fact that each standing wave can be in one of two possible polarizations.

As we will see in a later lecture, the number of standing waves that can exist in a cubical box of volume V, for frequencies in the interval $[f, f + \Delta f]$, is

$$
N(f)\Delta f = V\frac{4\pi}{c^3}f^2\Delta f
\tag{2.2}
$$

Then the energy of radiation in this range of frequencies will be

$$
\Delta E_{rad} = 2N(f)\Delta f \times \frac{1}{2}kT = \frac{4\pi kTf^2}{c^3}V\Delta f
\tag{2.3}
$$

The energy density per unit frequency $\mathcal{E}(f, T)$ is therefore

$$
\mathcal{E}(f, T) \equiv \frac{\Delta E_{rad}}{V\Delta f} = \frac{4\pi kTf^2}{c^3}
\tag{2.4}
$$

which is known as the Rayleigh-Jeans law.

The Rayleigh-Jeans law can be tested by making a hole in the box, and measuring the intensity of radiation emitted from the box as a function of frequency; this intensity is directly proportional to $\mathcal{E}(f, T)$. Radiation from a small hole in a cavity is known as "black-body radiation", because any radiation falling *into* the hole is not reflected out the hole, but is ultimately absorbed by the walls. The experimental result, compared to the prediction, is shown in Fig. [2.1]. Theory disagrees with experiment at high frequencies. In fact, it is clear that there *had* to be something wrong with theory, because the total energy is predicted to be

$$
\begin{aligned}
E_{rad} &= 2 \times (\text{no. of standing waves}) \times \frac{1}{2}kT \\
&= \infty
\end{aligned}
\tag{2.5}
$$

simply because the range of frequencies is infinite, so there is an infinite number of different standing waves that can be set up in the box. The energy of a box is finite

(otherwise its mass, according to special relativity, would be infinite), so this result cannot possibly be correct.

Planck's contribution to this problem was a masterpiece of what is known in physics as **phenomenology**. The first step of phenomenology is to stare at the data, in this case the experimental curve shown in Fig. [2.1], and try to find some simple analytical expression that fits it. Planck found that

$$\mathcal{E}(f, T) = \frac{8\pi h f^3}{c^3} \frac{1}{e^{hf/kT} - 1} \tag{2.6}$$

would do nicely, if one chose the constant h to be

$$h = 6.626 \times 10^{-34} \text{ J-s} \tag{2.7}$$

The second step is to try to derive the analytical expression for the data, starting from some simple physical assumptions about the system. Planck took aim at the equipartition principle. This principle is only valid if the energy associated with each degree of freedom can take on any value between 0 and ∞, depending on the physical state. In electromagnetism, the energy of a standing wave of a given wavelength is proportional to the square of its amplitude, which can certainly be any number in the range $[0, \infty]$. Planck's suggestion was that, for some unknown reason, the oscillating charges in the walls could only emit or absorb energy in multiples of hf, where f is the frequency of the oscillator. This means that the energy of radiation of frequency f in the box could only have the possible values

$$E_n = nhf \tag{2.8}$$

where n is an integer. This assumption, combined with the rules of statistical mechanics, is enough to deduce the Planck distribution (2.6).

Note the appearance in Planck's formula of the constant h, known as **Planck's constant**. It is one of the three most fundamental constants in physics, sharing the honor with c, the speed of light, and G, Newton's constant. All theoretical predictions of quantum physics, to the extent that they disagree with classical physics, have Planck's constant h appearing somewhere in the expression.

2.2 The Photoelectric Effect

The success of Planck's idea immediately raises the question: why is it that oscillators in the walls can only emit and aborb energies in multiples of hf? The reason for this was supplied by Albert Einstein in 1905, in connection with his explanation of the photoelectric effect.

It was found by Lenard, in 1900, that when light shines on certain metals, the metals emit electrons. This phenomenon is known as the photoelectric effect, and

what is surprising about it is that the energy of the emitted electrons is independent of the intensity of the incident light.

The experimental setup, used to measure the energy of the *most energetic* electrons, is shown in Fig. [2.2]. The electrons are emitted at the photocathode, fall on a collecting plate, and complete a circuit. The resulting current is measured by an ammeter. A battery can be used to put a potential difference V across the gap between the cathode and the plate, which tends to *repel* the electrons back towards the cathode. For an electron to reach the collecting plate, it must have an energy of *at least eV*, where e is the magnitude of the charge of an electron. As the repelling potential is increased, fewer electrons have sufficient energy to reach the plate, and the current measured by the ammeter decreases. Let V_s denote the voltage where the current just vanishes; i.e. V_s is the lowest voltage such that, at any $V > V_s$, the current is zero. This means that the maximum energy of the emitted electrons is just

$$E_{max} = eV_s \tag{2.9}$$

It is found experimentally that E_{max}, contrary to expectation, is independent of the intensity of the light falling on the photocathode. As the intensity increases, for fixed light frequency, the *number* of emitted electrons increases, but E_{max} is constant. On the other hand, when E_{max} is plotted as a function of frequency, the result is as shown in Fig. [2.3]. For frequencies f greater than some minimum $f_0 = E_0/h$, the data for E_{max} vs. f fits a straight line, *whose slope equals Planck's constant!* In other words

$$E_{max} = hf - E_0 \tag{2.10}$$

Einstein's explanation of this formula is quite simple: Light is composed of particles called **photons**. Each photon has an energy

$$E_{photon} = hf \tag{2.11}$$

Suppose that the minimum energy required to free an electron from the photocathode is E_0, and an electron absorbs energy from the light by absorbing a photon. Then the maximum possible energy for an emitted electron is the energy of the absorbed photon, less the minimum energy required to free the electron from the metal, i.e.

$$E_{max} = hf - E_0 \tag{2.12}$$

Raising the intensity of the light simply increases the number of photons hitting the metal per second, which increases the number of emitted electrons per second. But the energy of each electron is dependent only on the energy of the absorbed photon, and this energy depends only on frequency.

Einstein's theory of the photon composition of light immediately explains Planck's condition that the energy of electromagnetic radiation of frequency f, in a box, is restricted to the values

$$E = nhf \tag{2.13}$$

Since there can only be an integer number of photons n at any given frequency, each of energy hf, the energy of the field at that frequency can only be nhf. Planck's restriction on energies is thereby explained in a very natural, appealing way.

Except for one little thing. "Frequency" is a concept which pertains to waves; yet Einstein's suggestion is that light is composed of particles. The notion that the energy of each "particle" is proportional to the frequency of the electromagnetic "wave", which in turn is composed of such "particles", seems like an inconsistent mix of quite different concepts. However, inconsistent or not, evidence in support of the existence of photons continued to accumulate, as in the case of the Compton effect.

2.3   The Compton Effect

Consider an electromagnetic wave incident on an electron at rest. According to classical electromagnetism, the charged electron will begin to oscillate at the frequency of the incident wave, and will therefore radiate further electromagnetic waves at exactly the same frequency as the incident wave. Experiments involving X-rays incident on free electrons show that this is not the case; the X-rays radiated by the electrons are a frequencies lower than that of the incident X-rays. Compton explained this effect in terms of the scattering by electrons of individual photons.

According to special relativity, the relation between energy, momentum, and mass is given by

$$E = \sqrt{p^2c^2 + m^2c^4} \tag{2.14}$$

For particles at rest ($p = 0$), this is just Einstein's celebrated formula $E = mc^2$. For a particle moving at the speed of light, such as a photon, the rest mass $m = 0$; otherwise the momentum would be infinite, since momentum p is related to velocity v via the relativistic expression

$$p = \frac{mv}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{2.15}$$

Then if, for a photon, $m = 0$ and $E = hf$, and given the relation for waves that $v = \lambda f$, we derive a relation between photon momentum and wavelength

$$p = \frac{E}{c} = \frac{hf}{c} = \frac{h}{\lambda} \tag{2.16}$$

where λ is the wavelength of the electromagnetic wave; in this case X-rays.

Now suppose that a photon of the incident X-ray, moving along the z-axis, strikes an electron at rest. The photon is scattered at an angle θ relative to the z-axis, while the electron is scattered at an angle ϕ, as shown in Fig. [2.4]. If $\vec{p}_1$ denotes the momentum of the incident photon, $\vec{p}_2$ denotes the momentum of the scattered photon, and $\vec{p}_e$ is the momentum of the scattered electron, then conservation of momentum tells us that

$$\vec{p}_e = \vec{p}_1 - \vec{p}_2 \tag{2.17}$$

while, from conservation of energy, we have

$$E_1 + mc^2 = E_2 + \sqrt{p_e^2 c^2 + m^2 c^4} \tag{2.18}$$

In this formula E_1 is the energy of the incident photon, and mc^2 is the energy of an electron at rest, while E_2 is the energy of the scattered photon, and $\sqrt{p_e^2 c^2 + m^2 c^4}$ is the energy of the scattered electron. Using the fact that $E = pc$ for photons, we have

$$p_e^2 c^2 + m^2 c^4 = [p_1 c - p_2 c + mc^2]^2 \tag{2.19}$$

Square the momentum conservation equation to find p_e^2

$$\begin{aligned} p_e^2 &= (\vec{p}_1 - \vec{p}_2) \cdot (\vec{p}_1 - \vec{p}_2) \\ &= p_1^2 + p_2^2 - 2p_1 p_2 \cos\theta \end{aligned} \tag{2.20}$$

and insert the expression for p_e^2 into the energy conservation equation (2.19), to find

$$\frac{1}{p_2} - \frac{1}{p_1} = \frac{1}{mc}(1 - \cos\theta) \tag{2.21}$$

Finally, using the relation (2.16), Compton deduced that

$$\lambda_2 - \lambda_1 = \frac{h}{mc}(1 - \cos\theta) \tag{2.22}$$

which, in fact, agrees with experiment.

2.4 The Heisenberg Microscope

The particle-like behavior of light waves has some troubling implications for the concept of a physical state, as understood by classical physics. The classical state of a pointlike particle at any moment in time is given by its position *and* its momentum $(\vec{x}, \vec{p})$, which are supposed to be determined by measurement. Of course, this presupposes that one can measure position and momentum simultaneously, to any required degree of precision. But the relation $p = h/\lambda$ suggests that such simultaneous measurements might not be possible, at least, not if such measurements involve the use of light. Roughly, the reason is this: In order to determine particle position to an accuracy Δx, it is necessary to use light of wavelength $\lambda < \Delta x$. But that means that the photons composing light of such a wavelength carry momentum $p > h/\Delta x$. In order to observe the particle's position, the particle must scatter light. But this means that the scattered photon can impart much of its momentum to the observed particle, changing the momentum of the particle by some undetermined amount of order $\Delta p \approx h/\Delta x$. The product of the two uncertainties is therefore

$$\Delta x \Delta p \approx \Delta x \frac{h}{\Delta x} = h \tag{2.23}$$

This implies that the more accurately we measure the particle's position (Δx very small), the more uncertainty there is in its momentum (Δp very large), and vice versa.

A concrete, although much oversimplified arrangement for measuring particle position is known as "Heisenberg's microscope"; the setup is shown in Fig. [2.5]. The idea is to measure the position of a particle moving along the x-axis with a known momentum p_x, to an accuracy Δx. This is done by shining light on the particle. The particle scatters the incident light, and this scattered light is brought to a focal point by a lens of diameter D. However, the ability of a lens to determine position is limited by the resolution of the lens.

Consider two point sources of light a distance L from the lens, which are separated by an interval Δx. Resolution of these two points requires resolution of an angular separation

$$\phi = \frac{\Delta x}{L} \tag{2.24}$$

On the other hand, according to the Rayleigh criterion, the smallest angular separations which can be resolved by a lens of diameter D is of the order

$$\phi_{min} \approx \frac{\lambda}{D} \tag{2.25}$$

Equating these two angles, we find that the smallest possible separation between two points which can be resolved by the lens is

$$\Delta x \approx \frac{\lambda}{D/L} \approx \frac{\lambda}{\sin\theta} \tag{2.26}$$

If a lens cannot resolve point sources separated by intervals less than Δx, it is also unable to resolve the position of a single point source to an accuracy better than Δx.

Because a lens focuses all light at a certain image point, we cannot determine at exactly what angle the light was scattered, relative to the y-axis. Scattered light will reach the lens at any scattering angle between 0 and θ. But that means that the x-component of the momentum of the scattered photon is uncertain by approximately

$$\Delta p_x \approx p\sin\theta = \frac{h}{\lambda}\sin\theta \tag{2.27}$$

Multiplying (2.24) by (2.27) gives the uncertainty relation

$$\Delta x \Delta p_x \approx h \tag{2.28}$$

as before.

A physical state is supposed to be determined by measurement, but from the relation (2.28) we see that measurements of position and momentum cannot be made simultaneously, to arbitrarily high precision, if light is used to observe the particle position. This is the first hint that something may be wrong with the classical view

of a physical state. Of course, it could be that the relation (2.28) is simply a practical limit on measurement; a particle might have a definite position and momentum despite our inability to measure those quantities simultaneously. But the difficulty could also be much more profound: if a physical state is simply the mathematical representation of the outcome of an accurate measurement process (a view which was advocated in Fig. [1.5] of Lecture 1) and if accurate numbers (x, p) are *never* an outcome of *any* measurement, then perhaps we are mistaken in thinking that a physical state corresponds to definite values of (x, p). In other words, the origin of the uncertainty could be due to trying to fit a square peg (the true physical state, whatever that may be) into a round hole (the set (x, p)). At the very least, if x and p cannot be measured simultaneously, then there is certainly no experimental *proof* that the classical state is the true physical state. This view is obviously a very radical option; for the moment we only raise it as a possibility, and turn to the mystery of the stability of the atom.

2.5 The Bohr Atom

Atoms have radii on the order of 10^{-10} m, and have masses on the order of 10^{-26} kg. In 1911, Ernest Rutherford studied the internal structure of atoms by bombarding gold foil with α-particles from radioactive Cesium. By studying the scattering of the α-particles by the gold atoms (a topic we will turn to at the end of the course), Rutherford found that almost all the mass of the atom is concentrated in a positively charged nucleus, of radius on the order of 10^{-15} m, i.e. 100,000 times smaller than the radius of the atom itself. The nucleus is surrounded by much lighter, negatively charged electrons, which collectively account for less than 1/2000th of the total mass of the atom. Atomic structure was pictured as analogous to the solar system, with the nucleus playing the role of the sun, orbited by much lighter electrons (the "planets"), bound in their orbits by Coulomb attraction to the nucleus.

However, orbital motion is a form of accellerated motion, and electrons are charged particles. According to electromagnetic theory, an accellerating charged particle radiates electromagnetic waves. As electrons move in their orbits, they should be constantly radiating energy in the form of electromagnetic waves, and as the electrons lose energy, they should spiral into the nucleus; a process which would take only a fraction (about 10^{-10}) of a second. By this reasoning, atoms should be about the size of nuclei, but in fact they are roughly 100,000 times larger. So what accounts for the stability of the electron orbits; why don't electrons spiral into the nucleus?

Another mystery of atomic structure was the existence of spectral lines. If a gas is placed in a discharge tube, with a sufficiently large voltage difference maintained at opposite ends of the tube, the gas glows. But, unlike thermal radiation (which occurs due to random collisions among atoms) the light emitted from the discharge tube is not spread diffusely over a broad range of frequencies, but is composed instead of discrete, very definite wavelengths. When such light (in the visible spectrum) is

passed through a prism or diffraction grating, it is split into a relatively small number
of bright lines, known as "spectral lines". It is not hard to understand that an atom,
stimulated by an electric current, might emit light; but why should it only emit that
light at certain definite frequencies? Empirically, spectoscopists had found that each
spectral line of hydrogen could be associated with two integers, m and n, such that
the wavelength λ of the spectral line was given by

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \tag{2.29}$$

where

$$R_H = 109677.576(12) \ \ \text{cm}^{-1} \tag{2.30}$$

is known as "Rydberg's constant" for Hydrogen. This formula works for Hydrogen,
modified forms work for certain other gases, but, at the time, nobody could explain
its success.

In 1913, Niels Bohr discovered that the formula for the spectral lines of Hydrogen
could be derived from one crucial assumption about electron orbits: *the angular
momentum of an electron can only come in multiples of Planck's constant divided by
2π*. In particular, for circular orbits,

$$L = pr = n\frac{h}{2\pi} \tag{2.31}$$

where p is the electron momentum, and r is the radius of the (assumed) circular orbit.
The expression $h/2\pi$ comes up so often in quantum physics that it is given its own
symbol

$$\hbar \equiv \frac{h}{2\pi} \tag{2.32}$$

pronounced **"h-bar"**.

Bohr was led to the assumption (2.31) by the following reasoning: A charged
particle rotating in a circular orbit will emit electromagnetic waves which possess
both energy and angular momentum. Suppose ΔE is the energy of radiation emitted
in a certain time interval Δt. Then according to Maxwell's electrodynamics, the
electromagnetic radiation also contains a certain amount of angular momentum ΔL,
related to ΔE by the formula

$$\Delta E = 2\pi f \Delta L \tag{2.33}$$

where f is the frequency of the radiation. Now, according to Einstein, the smallest
amount of energy emitted is that of one photon, $\Delta E = hf$. Then the smallest amount
of angular momentum that could have been emitted would be

$$\Delta L = \frac{h}{2\pi} \tag{2.34}$$

In the case of the hydrogen atom, this means that the angular momentum of the
electron, upon emitting a photon, must change by exactly this amount. This led

Bohr to guess that, if electron angular momentum can only change by units of $\hbar$, then the total angular momentum of the electron in the Hydrogen atom should be an integer multiple of that amount. This is the condition (2.31). Lets see how it leads to a prediction for atomic spectra.

The electron is assumed to be moving around the nucleus in a circular orbit. Now, for any circular orbit, the centripetal force must equal the attractive force, i.e.

$$\frac{p^2}{mr} = \frac{e^2}{r^2} \tag{2.35}$$

However, Bohr's quantization condition (2.31) implies

$$p_n = \frac{n\hbar}{r} \tag{2.36}$$

where the subscript indicates that each momentum is associated with a particular integer n. Inserting this expression into (2.35) and solving for r, we find

$$r_n = \frac{n^2\hbar^2}{me^2} \tag{2.37}$$

The total energy of the electron, in an orbit of radius r_n, is therefore

$$
\begin{aligned}
E_n &= \frac{p_n^2}{2m} - \frac{e^2}{r_n} \\
&= \frac{n^2\hbar^2}{2mr_n^2} - \frac{e^2}{r_n} \\
&= -\left(\frac{me^4}{2\hbar^2}\right)\frac{1}{n^2}
\end{aligned}
\tag{2.38}
$$

The total energy is negative because the electron is in a bound state; energy must be added to bring the electron energy to zero (i.e. a free electron at rest).

Bohr's idea was that a Hydrogen atom emits a photon when the electron jumps from an energy state E_m, to a lower energy state E_n. The photon energy is the difference of these two energies

$$
\begin{aligned}
E_{photon} &= E_m - E_n \\
hf &= \left(\frac{me^4}{2\hbar^2}\right)\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \\
h\frac{c}{\lambda} &= \left(\frac{me^4}{2\hbar^2}\right)\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \\
\frac{1}{\lambda} &= \left(\frac{me^4}{2ch\hbar^2}\right)\left(\frac{1}{n^2} - \frac{1}{m^2}\right)
\end{aligned}
\tag{2.39}
$$

This final expression not only matches the form of the empirical equation for spectral lines, but an explicit evaluation of the constant factor shows that it is numerically equal to the Rydberg constant

$$R_H = \frac{me^4}{2ch\hbar^2} \tag{2.40}$$

In addition to getting the Hydrogen spectra right, Bohr's quantization condition (2.31) also implies, if it doesn't exactly explain, the stability of the atom. For if Bohr's condition is correct, then there is a minimum radius for the electron orbit, namely

$$r_1 = \frac{\hbar^2}{me^2} = 5.29 \times 10^{-11} \; m \tag{2.41}$$

which is known as the "Bohr radius". The electron can neither spiral nor jump to a radius smaller than this. Therefore, Bohr's theory actually *predicts* the size of the Hydrogen atom, which agrees with empirical estimates based on, e.g., the van der Waals equation of state.[1]

After the success of Bohr's model of the atom, attempts were made to generalize his work to elliptical orbits, to include relativistic effects, and to apply it to multi-electron atoms. The outcome of a great deal of effort was this: sometimes the quantization condition worked, and sometimes it didn't. Nobody understood the range of validity of the quantization condition, nor why classical mechanics should be subject to such a drastic restriction. A good new idea was needed.

2.6   De Broglie Waves

We have already seen that for photons

$$E_{photon} = hf \quad \text{and} \quad p_{photon} = \frac{h}{\lambda} \tag{2.42}$$

Louis de Broglie's very great contribution to physics, in the year 1924, was the suggestion that these relations also hold true for electrons, i.e.

$$E_{electron} = hf \quad \text{and} \quad p_{electron} = \frac{h}{\lambda} \tag{2.43}$$

In the case of light, the conceptual difficulty is with the left-hand side of these equations: how can light waves have particle properties? In the case of electrons, it is the right-hand side of the equations which is difficult to understand: what does one mean by the frequency and wavelength of an electron?

De Broglie had the idea that the wave which is somehow associated with an electron would have to be a standing wave along the electron orbits of the hydrogen

---

[1]Of course, there is a hidden assumption that $n > 0$, i.e. there are no orbits of radius $r = 0$.

atom. Now the condition for a standing wave on, e.g., a circular string, is simply that an integral number of wavelengths fit along the circumference, i.e.

$$n\lambda = 2\pi r \tag{2.44}$$

But then, under the assumption that the wavelength of an electron "wave" is related to its momentum by $p = h/\lambda$, this becomes

$$n\frac{h}{p} = 2\pi r \tag{2.45}$$

or

$$pr = n\hbar \tag{2.46}$$

which is precisely Bohr's quantization condition!

Although deriving the Bohr model is a splendid achievement of de Broglie's assumptions, it is still true that any wave motion should exhibit interference phenomena. By sending light through a pair of slits, Young (in 1801) found the characteristic 2-slit interference pattern of wave motion, thereby confirming the wave-like nature of light. What if one does the same experiment with electrons?

Chapter 3

The Wave-like Behavior of Electrons

Truth is stranger than fiction, but it is because fiction is obliged to stick to possibilities; truth isn't.
- Mark Twain

Matter in the solid state consists of atoms in a regular ("crystalline") array of some kind, and the atomic structure of solids is determined by X-ray diffraction. X-rays, being a form of wave motion, reflect off the atoms in the array, and interfere to form a pattern which can be calculated from the principles of physical optics, given a knowlege of the structure of the array, and the wavelength of the X-rays. The inverse problem, finding the structure of the array given the X-ray interference pattern, is the subject of X-ray crystallography.

In 1927 Davisson and Germer, in an effort to check De Broglie's hypothesis that electrons are associated with wave motion, directed a beam of electrons at the surface of crystalline nickel. The electrons were reflected at various angles, and it was found that the intensity of the reflected electrons, as a function of reflection angle, was identical to the interference pattern that would be formed if the beam were instead composed of X-rays. Assuming that the electron beam was indeed some sort of wave, the wavelength could be determined from the intensity pattern of the reflected electrons. The wavelength λ was found to equal, within experimental error, the de Broglie prediction $\lambda = h/p$, where p is the electron momentum, determined by accellerating the incident beam of electrons across a known potential V. Apart from brilliantly confirming the existence of "de Broglie waves", this is an experiment with extraordinary and profound implications. To discuss these implications, it is useful to consider an experimental setup less complicated than that used by Davisson and Germer, in which the electrons are directed at an inpenetrable barrier containing two, very narrow, slits. First, however, we need an expression for the wavefunction of de Broglie waves.

3.1   Wave Equation for de Broglie Waves

Where there is a wave, there is a wavefunction. The wavefunction $\psi(x,t)$ of a plane wave of frequency f and wavelength λ may be given, e.g., by a sin wave

$$\sin(kx - \omega t) \tag{3.1}$$

where k is the wavenumber

$$k = \frac{2\pi}{\lambda} = \frac{p}{\hbar} \tag{3.2}$$

and ω is the angular frequency

$$\omega = 2\pi f = \frac{E}{\hbar} \tag{3.3}$$

and where we have used the de Broglie relations to express λ and f in terms of electron momentum p and energy E. Then the electron wavefunction could have the form of a sin wave

$$\psi(x,t) = \sin(kx - \omega t) = \sin\left(\frac{px - Et}{\hbar}\right) \tag{3.4}$$

or a cosine

$$\psi(x,t) = \cos(kx - \omega t) = \cos\left(\frac{px - Et}{\hbar}\right) \tag{3.5}$$

or any linear combination of sin and cosine, including the complex function

$$\psi(x,t) = e^{i(px - Et)/\hbar} \tag{3.6}$$

Normally we would rule out a complex wavefunction of the form (3.6), on the grounds that, e.g., the displacement of a vibrating string, or the strength of electric and magnetic fields in a radio wave, or the pressure variation in a sound wave, are strictly real quantitites.

Given the wavefunction, what is the wave equation? Waves on strings, sound waves, and light waves, all satisfy wave equations of the form

$$\frac{\partial^2 \psi}{\partial t^2} = \alpha \frac{\partial^2 \psi}{\partial x^2} \tag{3.7}$$

where $\alpha = 1/v^2$ is a constant. However, if we plug the sin-wave form (3.4) into this expression we find

$$\frac{E^2}{\hbar^2} \sin \frac{px - Et}{\hbar} = \alpha \frac{p^2}{\hbar^2} \sin \frac{px - Et}{\hbar} \tag{3.8}$$

which implies

$$E^2 = \alpha p^2 \tag{3.9}$$

The same result is obtained, of course, for the cosine. This expression for the energy of a non-relativistic particle in terms of its momentum is simply wrong. For a particle of mass m, the correct expression is

$$E = \frac{p^2}{2m} \tag{3.10}$$

In order to recover this expression, we need a wave equation with one time derivative (which brings down one factor of E), and two space derivatives (which bring down a factor of p^2), i.e.

$$\frac{\partial \psi}{\partial t} = \alpha \frac{\partial^2 \psi}{\partial x^2} \tag{3.11}$$

A sin-function will not satisfy this equation, however, since we end up with a cosine on the left-hand side, and a sin on the right-hand side; and vice-versa for the cosine wavefunction. The wavefunction which *does* work is the complex form (3.6), which, when inserted into (3.11) gives

$$\frac{-iE}{\hbar} e^{i(px-Et)/\hbar} = \alpha \frac{-p^2}{\hbar^2} e^{i(px-Et)/\hbar} \tag{3.12}$$

Setting $E = p^2/2m$, we can solve for α to find

$$\frac{\partial \psi}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} \tag{3.13}$$

or, equivalently,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} \tag{3.14}$$

This is the wave equation for de Broglie waves moving in one dimension. The generalization to three dimensions is a wavefunction of the form

$$\psi(\vec{x}, t) = e^{i(\vec{k}\cdot\vec{x}-\omega t)} = e^{i(\vec{p}\cdot\vec{x}-Et)/\hbar} \tag{3.15}$$

which satisfies the wave equation

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi \tag{3.16}$$

It is important to realize that in contrast to waves in classical physics, the amplitude of de Broglie waves is *necessarily* complex.

Problem: Consider a wavefunction of the form

$$\psi(x, t) = A \sin\left(\frac{px - Et}{\hbar}\right) + B \cos\left(\frac{px - Et}{\hbar}\right) \tag{3.17}$$

where A and B are complex numbers. Assuming that this wavefunction solves the wave equation (3.11), show that it *must* be proportional to a complex exponential.

3.2   The Double-Slit Experiment

We consider a beam of electrons which, after accelleration across a potential difference V, aquires a momentum in the x-direction

$$p = \sqrt{2meV} \tag{3.18}$$

The beam is directed at a barrier with two horizontal slits of negligible width, separated by a distance d. Those electrons which pass through the slits eventually fall on a screen, which is lined with detectors (geiger counters or photographic plates), to record the number of electrons falling on the screen, as a function of the vertical distance y along the screen (see Fig. [3.1]).

Let us compute the amplitude of the de Broglie wave at the screen, without concerning ourselves, for the moment, with the connection between the de Broglie wave and the actual motion of the electron. Before encountering the barrier, the de Broglie wave is a plane wave moving in the x-direction, as shown in Fig. [3.2]. On the other side of the barrier, the two slits act as coherent sources of cylindrical waves. To compute the amplitude at a point y on the screen, we simply sum the amplitude of two waves, one originating at slit A, and the other at slit B. The amplitude at point y, of the wave passing through slit A, is

$$\psi_A(y,t) = N \exp[i(kL_{Ay} - \omega t)] = N \exp[i(pL_{Ay} - Et)/\hbar] \tag{3.19}$$

where N is a constant, p is the magnitude of the electron momentum, and L_{Ay} is the distance from slit A to point y on the screen. Similarly, the amplitude of the contribution from slit B is

$$\psi_B(y,t) = N \exp[i(kL_{By} - \omega t)] = N \exp[i(pL_{By} - Et)/\hbar] \tag{3.20}$$

By the superposition principle of wave motion [1] the amplitude of the de Broglie wave at point y is

$$\begin{aligned} \psi(y,t) &= \psi_A(y,t) + \psi_B(y,t) \\ &= 2N \exp[i(pL_{av} - Et)/\hbar] \cos\left(\frac{p\Delta L}{2\hbar}\right) \end{aligned} \tag{3.21}$$

where

$$\begin{aligned} \Delta L &= L_{By} - L_{Ay} \\ L_{av} &= \frac{1}{2}(L_{Ay} + L_{By}) \end{aligned} \tag{3.22}$$

If the distance to the screen is much greater than the separation d of the slits, then ΔL is approximately

$$\Delta L = d \sin\theta \tag{3.23}$$

---

[1]which actually follows from the fact that the wave equation (3.16) is a linear equation.

where θ is the angle, relative to the x-axis, from the center of the barrier to the point y on the screen.

Now the intensity of a wave is proportional to the square of its amplitude. The generalization to complex amplitudes is that the intensity is proportional to the square of the modulus of the amplitude, i.e.

$$I \propto \psi^* \psi \qquad (3.24)$$

The intensity of the de Broglie wave arriving at point y on the screen is therefore

$$I(y) \propto \cos^2\left(\frac{pd\sin\theta}{2\hbar}\right) \qquad (3.25)$$

Finally we can make contact with particle motion, because "intensity" is a concept which applies not only to waves, but also to a beam of particles. Intensity is the energy passing through a surface, per unit area, per unit time. Let

$$N(y) = \text{no. of electrons per unit area per unit time} \qquad (3.26)$$

which reach the screen in the neighborhood of point y. Since each electron has an energy $E = p^2/2m$, it follows that

$$I(y) = N(y)\frac{p^2}{2m} \qquad (3.27)$$

Comparing this expression to (3.24) and (3.25), we have a *prediction* from de Broglie's theory that

$$\begin{aligned} N(y) &\propto \psi^* \psi \\ &\propto \cos^2\left(\frac{pd\sin\theta}{2\hbar}\right) \end{aligned} \qquad (3.28)$$

which can be compared to experiment, simply by counting the number of electrons arriving per second at different regions on the screen. The result of the Davisson-Germer experiment, and other experiments closely analogous to the double-slit experiment, is that de Broglie's prediction is confirmed. Just as photons have particle-like properties, electrons undoubtably have wave-like properties.

Suppose that N_{total} electrons get past the barrier. Lets ask the question: what is the probability that any one of these electrons will pass through a small area ΔA of the screen, centered at point y, in one second? Assuming that the particles move independently, this probability is

$$\text{prob. to cross } \Delta A/\text{sec} = \frac{N(y)\Delta A}{N_{total}} \qquad (3.29)$$

But in order for an electron to pass through a small region of the screen sometime in the interval $t = t_0$ and $t = t_0 + \Delta t$, an electron moving with velocity v must have been located in a small volume

$$\Delta V = \Delta A \times v\Delta t \tag{3.30}$$

in front of the surface ΔA (see Fig. [3.3]). Therefore, the probability that a particle passes the area element ΔA in time Δt, is equal to the probability that the particle, at a given time t_0, is located in a small volume in front of the screen size ΔV, i.e.

$$
\begin{aligned}
\text{prob. to be in } \Delta V \text{ at time } t \;&=\; \text{prob. to cross } \Delta A/\text{sec} \times \Delta t \\
&=\; \frac{N(y)\Delta A}{N_{total}}\Delta t \\
&=\; \frac{1}{vN_{total}}N(y)\Delta V \\
&\propto\; \psi^*(y,t)\psi(y,t)\Delta V
\end{aligned}
\tag{3.31}
$$

We see that the probability for an electron to be in a certain volume ΔV is proportional to the square of the modulus of the de Broglie wave, times the volume element. Now if ψ is a solution of the de Broglie wave equation (3.16), so is $\psi' = \text{const.} \times \psi$; this follows from the linearity of the wave equation. Therefore we can always choose a solution of the wave equation such that the proportionality sign in eq. (3.31) is replaced by an equals sign. With this choice, we arrive at the interpretation of the de Broglie wavefunction proposed by Max Born:

The Born Interpretation

Denote the wavefunction associated with an electron by $\psi(x, y, z, t)$. Then the probability $P_{\Delta V}$ at time t, of finding the elecron inside a small volume ΔV centered at point (x, y, z) is

$$\text{probability } P_{\Delta V}(x, y, z) = \psi^*(x, y, z, t)\psi(x, y, z, t)\Delta V \tag{3.32}$$

If an electron exists, then the total probability that it is *somewhere* in the Universe is 100%. Therefore, a corrollary of the Born interpretation is the **Normalization Condition**

$$\int dx dy dz \, \psi^*(x, y, z, t)\psi(x, y, z, t) = 1 \tag{3.33}$$

which must be satisfied by any wavefunction associated with an electron.

3.3 Do Electrons Travel Along Trajectories?

The double-slit experiment is arranged in such a way that equal numbers of electrons, per second, pass through slits A and B. This can be checked by closing slit B, counting the total number of electrons per second reaching the screen, and then closing slit A, and counting again. If the counts/sec are equal, then, when both slits are open, the chance that an electron reaching the screen passed through slit A is 50%, with an equal 50% chance that it passed through slit B.

We can determine experimentally the probability $P_A(y)$ that an electron, having passed through slit A, will land on a detector placed at point y on the screen. Close slit B, leaving A open and count the number of particles n_y that land on the detector, and the total number n_T landing anywhere on the screen. Then

$$P_A(y) = \frac{n_y}{n_T} \tag{3.34}$$

In a similar way, by opening slit B and closing slit A, we can determine the probability $P_B(y)$. Then, with both slits open, the probability that an electron that passed through the barrier will land on the detector at y is

$$
\begin{aligned}
P(y) &= (\text{prob. of coming from slit A}) \times P_A(y) \\
&+ (\text{prob. of coming from slit B}) \times P_B(y) \\
&= \frac{1}{2}[P_A(y) + P_B(y)]
\end{aligned} \tag{3.35}
$$

Clearly, if either $P_A(y)$, or $P_B(y)$ (or both) are non-zero, then the probability $P(y)$ is also non-zero.

Now the probabilities $P_A(y)$ and $P_B(y)$ are nearly constant for detectors placed in a sizable region of the screen (see Fig. [3.4]), which is consistent with the fact that the moduli of the de Broglie waves ψ_A and ψ_B are (nearly) constant. Then $P(y)$ should be nearly constant as well.

In fact, $P(y)$ is not constant at all. Instead, it goes like

$$
\begin{aligned}
P(y) \quad &\propto \quad \cos^2\left(\frac{pd\sin\theta}{2\hbar}\right) \\
&\propto \quad \psi^*(y,t)\psi(y,t)
\end{aligned}
\tag{3.36}
$$

In particular there are certain points, satisfying

$$
pd\sin\theta = 2\hbar(n + \frac{1}{2})\pi
\tag{3.37}
$$

where $P(y) = 0$ *even though $P_A(y)$ and $P_B(y)$ are non-zero!* In other words, if one closes slit B, leaving A open, there is a finite chance that the electron will reach such a point. If one closes A and leaves B open, there is a finite chance that the electron will reach that point. But if *both* slits A and B are open, the electron will *never* reach such a point, if the angle from the slits to the point satisfies (3.37). Clearly then, in contrast to (3.35),

$$
\begin{aligned}
P(y) \quad &\neq \quad \text{(prob. of coming from slit A)} \times P_A(y) \\
&+ \quad \text{(prob. of coming from slit B)} \times P_B(y)
\end{aligned}
\tag{3.38}
$$

When a conclusion (eq. (3.35) in this case) turns out to be false, and the reasoning which led to the conclusion is correct, then there must be something wrong with the premises. The premises in this case are that the electrons in the beam travel independently of one another, and that each electron in the beam passed through *either* slit A *or* slit B. More generally, we have assumed that the electron, as a "pointlike particle", follows a trajectory which takes it through one of the two slits on its way to the screen.

It is easy to check whether the interference effect is due to some collective interaction between electrons in the beam. We can use a beam of such low intensity that the electrons go through the barrier one by one. It takes a little longer to accumulate the data needed to compute $P_A(y)$, $P_B(y)$, and $P(y)$, but the results are ultimately the same. So this is not the explanation.

Then perhaps we should stop thinking of the electron as a point-like object, and start thinking of it as *literally* a de Broglie wave? A wave, after all, can pass through both slits; that is the origin of interference. The problem with this idea is that de Broglie waves expand. At slits A and B, the wave is localized just in the narrow region of the open slits, but as the wave propagates towards the screen it expands, typically spanning (in a real electron diffraction experiment) a region on the order of 10 cm across. Then one would detect "parts" of an electron. Assuming a de

Broglie wave which had expanded to several centimeters across was intense enough to trigger even a single geiger counter, then if a set of geiger counters were arranged in a close array, they would all be triggered simultaneously. Likewise, a wave of such dimensions should leave a diffuse glow on a photographic plate, or a thick cylindrical track through a cloud chamber. None of this is ever observed. No matter how big the de Broglie wave of a single electron becomes (as big as a baseball, as big as a house...), only a single "click" of a geiger counter is heard, only a sharp "dot" on a photographic plate is recorded. An electron is not, literally, a wave. As far as can be determined from measurements of electron position, electrons are discrete, point-like objects.

If electrons are pointlike objects, then one could imagine (with the help of a powerful microscope) actually observing the barrier as the electrons reach it, to determine if they go through slit A, or slit B, or somehow through both. If one would perform such an experiment,[2] the result is that each electron is indeed observed to pass either through slit A or slit B (never both), but then the interference pattern is wiped out! Instead, one finds the uniform distribution of eq. (3.35). Thus if an electron is forced (essentially by observation) to go through one or the other of the two slits, the interference effect is lost. Interference is regained only if the electron is *not* constrained to a trajectory which has passed, with certainty, through one or the other slit.

We are left with the uncomfortable conclusion that electrons are pointlike objects which do not follow definite trajectories through space. This sounds like a paradox: how then can electrons get from one point to another? It is actually not a paradox, but it does require a considerable readjustment of our concept of the physical state of electrons (not to mention atoms, molecules, and everything else that makes up the physical Universe). This will be the subject of the next lecture.

---

[2]This is usually presented as a "thought" experiment in most textbooks, but recently a real experiment of this sort has been carried out, with the results described above.

Chapter 4

The Quantum State

We take for granted the idea that every object, at every moment in time, is centered at a definite point in three-dimensional space, and that over a span of time, the location of the object traces a trajectory through that space. We are sure of this because of our long experience, beginning at birth, with the behavior of macroscopic objects, i.e. objects on the scale of a micron or larger, objects which we can *see*, objects which we have the illusion of observing continuously.[1]

It is now time to abandon the view that objects move in trajectories in three-dimensional space, at least in the case of microscopic objects such as electrons, photons, and atoms. This is for two reasons. First, if a particle moves in a trajectory, then it must have a definite position *and* momentum at every moment in time. However, as we have discussed in the case of the Heisenberg microscope, there is no experiment which can verify this. Second, and more importantly, the mere assumption that electrons and photons follow definite trajectories $\vec{x}(t)$ leads to conclusions which disagree with experiment, such as the Davisson-Germer experiment discussed in the last lecture, and many other examples to follow later in the course.

How, then, does an electron get from one point to another, without tracing a path through space? The answer is that the electron *does* follow a path; however, it is not a path in the ordinary three-dimensional space we are used to.

4.1 A New Representation of Motion

Consider a particle moving back and forth, according to the laws of classical physics, in a thin closed pipe of length L. A plot of its trajectory might look like Fig. [4.1]. This is the standard way of representing one-dimensional motion in classical mechanics. To every instant of time t there is a corresponding number $x(t)$, which in this case is the distance from one end of the pipe. Is there any other conceivable representation of motion in one dimension?

---

[1]No observation is truly continuous, because of the discrete, photon composition of light.

   Let us imagine subdividing the length of the pipe into N equal intervals of length $\epsilon = L/N$, as shown in Fig. [4.2]. If the particle is in the first interval, we choose to represent its state not by a *number*, such as x_1, but rather by an N-dimensional *vector*

$$\vec{e}^{\,1} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ . \\ . \\ . \\ 0 \end{bmatrix} \tag{4.1}$$

If the particle is in the second interval, this will be represented by

$$\vec{e}^{\,2} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ . \\ . \\ . \\ 0 \end{bmatrix} \tag{4.2}$$

and so on, down to the N-th interval which is denoted by

$$\vec{e}^{\,N} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ . \\ . \\ . \\ 1 \end{bmatrix} \tag{4.3}$$

The position of the particle is therefore approximated, at any given time, by one of the $\vec{e}^{\,n}$ unit vectors, and as the particle moves from one interval to another, the unit vector "jumps" discontinuously from some $\vec{e}^{\,k}$ to either $\vec{e}^{\,k+1}$ or $\vec{e}^{\,k-1}$, depending on which way the particle is moving. If the number of intervals N is large enough, the particle position can be represented, as a function of time, to arbitrary precision.

   A reasonable objection to this representation of motion is that, in introducing a set of N orthogonal vectors $\{\vec{e}^{\,n}\}$, we have also introduced an N-dimensional space which contains linear combinations of those vectors. What, for example, is the physical meaning of a vector such as

$$\vec{v} \;=\; a\vec{e}^{\,1} + b\vec{e}^{\,2}$$

$$= \begin{bmatrix} a \\ b \\ 0 \\ . \\ . \\ . \\ 0 \end{bmatrix} \tag{4.4}$$

which seems to suggest that the particle could be in intervals 1 and 2 at the same time? In a classical mechanics, a particle is definitely in a single interval at any given time, so only the unit vectors $\vec{e}^{\,n}$ are physically meaningful. The very natural mathematical operation of addition of vectors would therefore have to be regarded, in this representation of classical motion, as physically meaningless.

On the other hand, we have already seen that the de Broglie wavefunction $\psi(x,t)$ gives *probabilistic* information about the location of the electron. Therefore, let us give the following "Born Interpretation" to the N-dimensional vector, whose components ψ_n are allowed to be complex numbers:

$$\vec{\psi} = \psi_1 \vec{e}^{\,1} + \psi_2 \vec{e}^{\,2} + ... + \psi_N \vec{e}^{\,N}$$
$$= \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ . \\ . \\ . \\ \psi_N \end{bmatrix} \tag{4.5}$$

The probability P_n that an electron, in the state represented by the vector $\vec{\psi}$, will be found upon measurement to be in the n-th interval of the tube, is equal to squared modulus

$$P_n = \psi_n^* \psi_n \tag{4.6}$$

Digression

We must pause for a moment to discuss the inner product of vectors with complex components. The **norm** of a vector is defined as square root of the inner product of a vector with itself

$$|v| = \sqrt{\vec{v} \cdot \vec{v}} \tag{4.7}$$

where the inner product is represented as the product of a row vector times a column

vector. If the components of $\vec{v}$ are real numbers, this is given by

$$
\vec{v} \cdot \vec{v} = [v_1, v_2, v_3..., v_N] \begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ . \\ . \\ . \\ v_N \end{bmatrix}
$$

$$
= v_1^2 + v_2^2 + ... + v_N^2 \tag{4.8}
$$

On the other hand, if the components of $\vec{v}$ are complex, this can lead to a negative inner product, and an imaginary norm. In vector algebra the norm of a vector is always real, so the definition of a row vector is modified: its components are the complex conjugate of the corresponding column vector, i.e

$$
\vec{v} \cdot \vec{v} = [v_1^*, v_2^*, v_3^*..., v_N^*] \begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ . \\ . \\ . \\ v_N \end{bmatrix}
$$

$$
= v_1^* v_1 + v_2^* v_2 + ... + v_N^* v_N \tag{4.9}
$$

In vector algebra a vector comes in two forms, rows and columns. However, the notation $\vec{v}$ does not distinguish between row and column vectors, and sometimes this distinction is useful. We therefore introduce the "bra-ket" notation in which a "ket" $|v>$ corresponds to a column vector

$$
|v> \Longleftrightarrow \begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ . \\ . \\ . \\ v_N \end{bmatrix} \tag{4.10}
$$

and a "bra" $<v|$ to the corresponding row vector

$$
<v| \Longleftrightarrow [v_1^*, v_2^*, v_3^*, ..., v_N^*] \tag{4.11}
$$

In this notation, the inner product is

$$
<v|v> = \vec{v} \cdot \vec{v} = v_1^* v_1 + v_2^* v_2 + ... + v_N^* v_N \tag{4.12}
$$

and this is the end of the digression.

Returning to the "Born Interpretation" of the vector $\vec{\psi}$ (or "$|\psi >$"), we see that the total probability for the electron to be found *somewhere* in the tube is

$$
\begin{aligned}
P_{total} &= P_1 + P_2 + ... + P_N \\
&= \psi_1^* \psi_1 + \psi_2^* \psi_2 + ... + \psi_N^* \psi_N \\
&= \vec{\psi} \cdot \vec{\psi} \\
&= < \psi | \psi >
\end{aligned}
\tag{4.13}
$$

From the fact that the probability to find the particle somewhere in the tube is 100%, we can conclude that $|\psi >$ is a unit vector, i.e.

$$
< \psi | \psi >= 1
\tag{4.14}
$$

We can now view electron motion in the following way: The physical state of the electron is represented by unit vectors $|\psi >$ in a complex N-dimensional vector space. Since the tip of a unit vector falls on the surface of sphere of radius $R = 1$, in the N-dimensional space, *the motion of the electron corresponds to a trajectory along the surface of a unit sphere in N-dimensional space.* In this way, an electron can travel smoothly and continuously, with no "jumps", from e.g. the interval 1, represented by vector $\vec{e}^{\,1}$ to the interval 2, represented by $\vec{e}^{\,2}$, as shown in Fig. [4.3]. Of course, in going from interval 1 to interval 2, the electron passes through intermediate states such as (4.4), where the electron cannot be viewed as being either in interval 1 *or* in interval 2. But the electron is always located at a definite point on the surface of the unit-sphere, and it is this surface, rather than the line of length L along the tube, which should be regarded as the arena of electron motion.

To complete this new representation of motion we need to take the limit $\epsilon \to 0$, which sends the number of intervals $N \to \infty$. Then the physical states $|\psi >$ are vectors of unit length in an **infinite** dimensional vector space known as **Hilbert Space**.

4.2   Hilbert Space

Any function $f(x)$ with the property of **square integrability**

$$
\int_{-\infty}^{\infty} dx \; f^*(x) f(x) < \infty
\tag{4.15}
$$

can be regarded as a vector, and a de Broglie wavefunction $\psi(x, t)$ can, in particular, be regarded as a vector of unit length.

Recall that a vector $\vec{v}$ is represented by a set of numbers (the components of the vector) labeled by an index. There is one number, denoted, v_i for each integer value

of the index i in some range $i = 1, 2, ..., N$. But a function f is also a set of numbers labeled by an index. There is one number, denoted $f(x)$, for each real-number value of the index x in the range $-\infty < x < \infty$. The argument of a function, x, is completely analogous to the index i of a vector; the value of the function $f(x)$ corresponds to the component v_i of the vector.

The notation of vector algebra has the advantage that when we want to refer to the vector as whole, and not any particular component of the vector, we can write $\vec{v}$, (or $|v >$ for the column vector in our new "bra-ket" notation). On the other hand, when we denote a function by $f(x)$, it is sometimes unclear whether we are referring to the function as a whole, or just the particular value at the point x. Let us adopt the notation that $|f >$ refers to the entire function, and $f(x)$ just the value ("component") at the argument ("index") x. Then its easy to see that functions behave in every way like vectors with a continuous index. For example, one can add vectors

$$\vec{v} = a\vec{u} + b\vec{w} \tag{4.16}$$

which means, in terms of components

$$v_i = au_i + bw_i \tag{4.17}$$

and one can also add functions

$$|f >= a|g > +b|h > \tag{4.18}$$

which means, in terms of "components"

$$f(x) = ag(x) + bh(x) \tag{4.19}$$

Vectors have inner products with each other

$$< u|v >= \vec{u} \cdot \vec{v} = \sum_{i=1}^{N} u_i^* v_i \tag{4.20}$$

as well as a norm with themselves

$$|v|^2 =< v|v >= \sum_{i=1}^{N} v_i^* v_i \tag{4.21}$$

and so do functions:

$$< g|f >= \int_{-\infty}^{\infty} dx \ g^*(x) f(x) \tag{4.22}$$

and

$$|f|^2 =< f|f >= \int_{-\infty}^{\infty} dx \ f^*(x) f(x) \tag{4.23}$$

If $\{v_i\}$, $i = 1, 2, ..., N$ are the components of the column ("ket") vector $|v >$, then $\{v_i^*\}$ are the components of the corresponding row ("bra") vector $< v|$. Likewise,

$f(x)$, $-\infty < x < \infty$ represent the "components" of $|f>$, and $f^*(x)$ represents the components of the corresponding bra $< f|$.

There is a linear operation called matrix multiplication which turns a vector into another vector

$$\vec{v'} = M\vec{v} \tag{4.24}$$

or

$$|v'> = M|v> \tag{4.25}$$

in our new notation. In terms of components, matrix multiplication is defined as

$$v_i' = \sum_{j=1}^{N} M_{ij} v_j \tag{4.26}$$

and it has the linearity property that

$$M(a|u> +b|v>) = aM|u> +bM|v> \tag{4.27}$$

where a and b are constants. There is a similar linear operation which turns functions into other functions

$$|f'> = O|f> \tag{4.28}$$

having the linearity property

$$O(a|f> +b|g>) = aO|f> +bO|g> \tag{4.29}$$

In terms of "components," this operation is written

$$f'(x) = \int_{-\infty}^{\infty} dy \; O(x,y) f(y) \tag{4.30}$$

where $O(x,y)$ is some function of two variables x and y, in complete analogy to the rule for matrix multiplication (4.26). Finally, the expression in linear algebra

$$
\begin{aligned}
< u|M|v> \;&=\; \vec{u} \cdot M\vec{v} \\
&=\; \sum_{i=1}^{N}\sum_{j=1}^{N} u_i^* M_{ij} v_j
\end{aligned}
\tag{4.31}
$$

corresponds, in the case of functions, to the expression

$$< g|O|f> = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \; g^*(x) O(x,y) f(y) \tag{4.32}$$

A function, therefore, is just a vector with a continuous index. Since there are an infinite number of "components" (one component $f(x)$ for each value of x), the vector is a member of an infinite-dimensional space known as "Hilbert Space." Stated another way: **Hilbert Space is the infinite-dimensional vector space of all square-integrable functions.**

4.3   The Dirac Delta Function

If the linear operation

$$f'(x) = \int_{-\infty}^{\infty} dy \; O(x,y) f(y) \tag{4.33}$$

is analogous to matrix multiplication in ordinary linear algebra, then what choice of $O(x,y)$ corresponds, in particular, to multiplication by the unit matrix?

In linear algebra, multiplication of any vector by the unit matrix I is an operation that takes the vector into itself:

$$|v >= I|v > \tag{4.34}$$

In component form, the unit matrix is known as the **Kronecker Delta** $I_{ij} = \delta_{ij}$, which obviously must have the property that

$$v_i = \sum_i \delta_{ij} v_j \tag{4.35}$$

The Kronecker delta satisfying this equation, for any vector $|v >$ whatever, is given by the diagonal matrix

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \tag{4.36}$$

The corresponding operation for functions

$$|f >= I|f > \tag{4.37}$$

is written in component form

$$f(x) = \int_{-\infty}^{\infty} dy \; \delta(x - y) f(y) \tag{4.38}$$

and the function $\delta(x - y)$ which fulfills this equation, for any function $f(x)$ whatever, is known as the **Dirac Delta function**. It is useful not just in quantum mechanics, but throughout mathematical physics.

The Dirac delta function $\delta(x - y)$ is defined as the limit of a sequence of functions $\delta_L(x - y)$, known as a **delta sequence**, which have the property that

$$f(x) = \lim_{L \to \infty} \int_{-\infty}^{\infty} dy \; \delta_L(x - y) f(y) \tag{4.39}$$

for any function $f(x)$. Two such sequences which can be shown to have this property are

$$\delta_L(x - y) = \sqrt{\frac{L}{\pi}} e^{-L(x-y)^2} \tag{4.40}$$

and

$$\delta_L(x - y) = \int_{-L}^{L} \frac{dk}{2\pi} \; e^{ik(x-y)} \tag{4.41}$$

It is reasonable to ask why one should go to the trouble of introducing sequences. Why not take the $L \to \infty$ limit right away, in eq. (4.40), and define

$$\delta(x - y) = \begin{cases} \infty & \text{if } x = y \\ 0 & \text{if } x \neq y \end{cases} \tag{4.42}$$

in analogy to the Kronecker delta δ_{ij}? The answer is that the Dirac delta function is not, strictly speaking, a function, any more than ∞ is a number, and the integral of the right hand side of (4.42) is ill-defined. If one treats ∞ as an ordinary number, it is easy to produce contradictions, e.g.

$$1 \times \infty = 2 \times \infty \quad \implies \quad 1 = 2 \tag{4.43}$$

Instead, one must think of ∞ as the limit of a sequence of numbers, but which is not itself a number. There are many different sequences which can be used, e.g.

$$1, 2, 3, 4, 5, ...$$
$$\text{or} \quad 2, 4, 6, 8, 10, ...$$
$$\text{or} \quad 1, 4, 9, 16, 25, ... \tag{4.44}$$

all of which have ∞ as their limit. Similarly, there are many different sequences of functions tending to the same limit, which is not a function in the ordinary sense. Such limits are known as "generalized functions," of which the Dirac delta function is one very important example.

Let us check that (4.40) and (4.41) satisfy the defining property (4.39) for delta sequences. For the sequence of gaussians (4.40)

$$\lim_{L \to \infty} \int_{-\infty}^{\infty} dy \sqrt{\frac{L}{\pi}} e^{-L(y-x)^2} f(y)$$

$$= \lim_{L \to \infty} \int_{-\infty}^{\infty} dz \sqrt{\frac{L}{\pi}} e^{-Lz^2} f(x + z)$$

$$= \lim_{L \to \infty} \int_{-\infty}^{\infty} dz \sqrt{\frac{L}{\pi}} e^{-Lz^2} \left[f(x) + \frac{df}{dx} z + \frac{1}{2} \frac{d^2 f}{dx^2} z^2 + ... \right]$$

$$= \lim_{L \to \infty} \sqrt{\frac{L}{\pi}} \left[\sqrt{\frac{\pi}{L}} f(x) + 0 + \frac{1}{4L} \sqrt{\frac{\pi}{L}} \frac{d^2 f}{dx^2} + ... \right]$$

$$= f(x) \tag{4.45}$$

where we have changed variables $z = y - x$, expanded $f(x + z)$ in a Taylor series around the point x, and used the standard formulas of gaussian integration:

$$\int_{-\infty}^{\infty} dz\, e^{-cz^2} = \sqrt{\frac{\pi}{c}}$$

$$\int_{-\infty}^{\infty} dz\, ze^{-cz^2} = 0$$

$$\int_{-\infty}^{\infty} dz\, z^2 e^{-cz^2} = \frac{1}{2c} \sqrt{\frac{\pi}{c}} \tag{4.46}$$

The result (4.45) establishes that the sequence of gaussians (4.40) is a delta sequence:

$$\delta(x - y) = \lim_{L \to \infty} \sqrt{\frac{L}{\pi}} e^{-(x-y)^2/L} \tag{4.47}$$

In a similar way, we can prove that (4.41) is a delta sequence

$$
\lim_{L \to \infty} \int_{-\infty}^{\infty} dy \, f(y) \int_{-L}^{L} \frac{dk}{2\pi} e^{ik(x-y)}
$$
$$
= \lim_{L \to \infty} \int_{-\infty}^{\infty} dy \, f(y) \frac{\sin[L(x - y)]}{\pi(x - y)} \tag{4.48}
$$

Change variables to $z = L(x - y)$, and this becomes

$$
\lim_{L \to \infty} \int_{-\infty}^{\infty} dy \, f(y) \int_{-L}^{L} \frac{dk}{2\pi} e^{ik(x-y)}
$$
$$
= \lim_{L \to \infty} \int_{-\infty}^{\infty} dy \, f(x - \frac{z}{L}) \frac{\sin(z)}{\pi z}
$$
$$
= f(x) \int_{-\infty}^{\infty} dz \, \frac{\sin(z)}{\pi z}
$$
$$
= f(x) \tag{4.49}
$$

which establishes that

$$\delta(x - y) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ik(x-y)} \tag{4.50}$$

A number of useful identities for the Dirac delta function are listed below:

$$
f(x)\delta(x - a) = f(a)\delta(x - a) \tag{4.51}
$$
$$
f(x)\delta[c(x - a)] = f(x)\frac{1}{|c|}\delta(x - a) \tag{4.52}
$$
$$
f(x)\frac{d}{dx}\delta(x - a) = -\frac{df}{dx}\delta(x - a) \tag{4.53}
$$
$$
f(x)\delta[g(x)] = f(x)\left|\frac{dg}{dx}\right|^{-1}\delta(x - x_0) \tag{4.54}
$$

where, in the last line, $g(x)$ is a function with a zero at $g(x_0) = 0$

Since $\delta(x - y)$ is not a function, these identities should *not* be interpreted as meaning: for a given value of x, the number on the right-hand side equals the number on the left-hand side. Instead, they mean that

$$\int_{-\infty}^{\infty} dx \, \text{"left-hand side"} = \int_{-\infty}^{\infty} dx \, \text{"right-hand side"} \tag{4.55}$$

As an example, we prove the third of these identities using the formula for integration by parts:

$$
\begin{aligned}
\int_{-\infty}^{\infty} dx \ f(x)\frac{d}{dx}\delta(x-y) &= \lim_{L\to\infty}\int_{-\infty}^{\infty} dx \ f(x)\frac{d}{dx}\delta_L(x-y) \\
&= \lim_{L\to\infty}\left[f(x)\delta_L(x-y)|_{x=-\infty}^{x=\infty} - \int_{-\infty}^{\infty} dx \ \frac{df}{dx}\delta_L(x-y) \right] \\
&= \lim_{L\to\infty}\int_{-\infty}^{\infty} dx \ \left[-\frac{df}{dx}\delta_L(x-y) \right] \\
&= \int_{-\infty}^{\infty} dx \ \left[-\frac{df}{dx} \right]\delta(x-y) \quad\quad\quad (4.56)
\end{aligned}
$$

where the boundary terms are dropped because $\delta_L(\pm\infty)=0$.

Problem - Prove the other three delta-function identities above, in the sense of eq. (4.55)

4.4 Expectation, Uncertainty, and the Quantum State

In classical mechanics, the physical state of a system is specified by a set of generalized coordinates and momentum $\{q^i, p_i\}$, which is a point in the phase space of the system. In the course of time, the physical state traces a trajectory through the phase space. In the case of a single particle moving in three dimensions, the physical state is denoted $\{\vec{x}, \vec{p}\}$, and the phase space is 6-dimensional. The projection of the trajectory in the 6-dimensional phase space onto the three dimensional subspace spanned by the x, y, and z axes, or in other words, the path $\vec{x}(t)$, is the trajectory which we can actually *see* the particle follow.

In quantum mechanics, the physical state of a pointlike particle, moving in one dimension, is specified at each moment of time by a wavefunction $\psi(x, t)$. At any given time t, this wavefunction is a function only of x, and can be regarded as a vector $|\psi>$ in Hilbert space. Because of the normalization condition imposed by the Born Interpretation

$$
<\psi|\psi> = \int dxdydz \ \psi^*(x, y, z, t)\psi(x, y, z, t) = 1 \quad\quad\quad (4.57)
$$

$|\psi>$ is necessarily a vector of unit length. In the course of time, $|\psi>$ follows a path through Hilbert space. In rough analogy to the motion of unit vectors in finite dimensional spaces, one could imagine that the tip of the unit vector $|\psi>$ traces a path on the surface of a unit sphere, although in this case the space is infinite-dimensional.

A physical state has the property that, given the state at some time t, we can determine the state at a slightly later time $t + \epsilon$. In classical mechanics, the rule is

$$q^a(t + \epsilon) = q^a(t) + \epsilon \left(\frac{\partial H}{\partial p_a} \right)_t$$

$$p_a(t + \epsilon) = p_a(t) - \epsilon \left(\frac{\partial H}{\partial q^a} \right)_t \tag{4.58}$$

The physical state $|\psi>$ in quantum mechanics also has this property. Given the wavefunction $\psi(x, t)$ at any particular time t, the wavefunction at a slightly later time $t + \epsilon$ is determined, for a particle moving freely in one dimension, from the wave equation for de Broglie waves

$$\psi(x, t + \epsilon) = \psi(x, t) + i\epsilon \frac{\hbar}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) \tag{4.59}$$

The Born Interpretation tells us how to use the wavefunction $\psi(x, t)$ to make certain experimental predictions. Unlike the predictions of classical mechanics, however, which specify the outcome of any measurement on a single system with certainty, given the physical state $\{q^i, p_i\}$ of the system, the predictions of quantum mechanics are statistical in nature. The Born Interpretation tells us that the probability to find the particle in a small interval around the point x, of length ΔL, is

$$P_{\Delta L}(x) = \psi^*(x, t)\psi(x, t)\Delta L \tag{4.60}$$

The meaning of this prediction, in practice, is as follows: Suppose we have a very large number of particles N_p which are in identical physical states described by a certain wavefunction $\psi(x, t)$. If we measure the position of all of these particles simultaneously, the number n_x which will be observed to be in the interval ΔL around point x is predicted, according to the Born Interpretation, to be

$$
\begin{aligned}
\frac{n_x}{N_p} &= P_{\Delta L}(x) + O(N_p^{-1/2}) \\
&= \psi^*(x, t)\psi(x, t)\Delta L + O(N_p^{-1/2})
\end{aligned} \tag{4.61}
$$

The term of order $N_p^{-1/2}$ is statistical error, which can be made arbitrarily small by choosing a sufficiently large number of particles N_p.

To understand the origin of the statistical error, consider flipping a coin N times, where N is a very large, even number. Only very rarely does the coin come up heads *exactly* $N/2$ times. Usually the number of heads deviates from $N/2$ by a amount on the order of $\Delta N \sim \sqrt{N}$. The ratio of the deviation ΔN to the total number of coin flips N varies each time one does the full set of N coin flips, but it is generally of order

$$\frac{\Delta N}{N} \sim \frac{1}{\sqrt{N}} \tag{4.62}$$

The deviation of order $N_p^{-1/2}$ in eq. (4.61) has the same origin, and is present in any set of measurements which involve random processes. From now on we will suppose that N_p is so large that this deviation is ignorable.

Instead of simultanously observing a swarm of N_p particles, each of which are in the same state, one could instead perform an experiment in which a single particle is placed in a particular state $\psi(x,t)$, its position is observed, and then the identical experiment is repeated N_p times. If n_x is the number of experiments in which the particle lands in the interval ΔL around point x, then the prediction according to the Born Interpretation is again eq. (4.61). In fact, this is what is actually happening in the electron 2-slit experiment. Electrons can be made to pass one by one through the slits, and the wavefunction of each electron at the location of the screen is identical. The statistical prediction for the number of electrons reaching a particular small region of the screen is then eq. (3.28) of the last lecture.

Let us imagine making a series of experiments on the motion of a particle moving in one dimension, in which the particle is somehow initialized to be in a certain quantum state $|\psi>$, and then the position of the particle is measured. There are two particularly useful numbers which can be predicted by quantum theory, and measured by the series of experiments. One number is the average value $\overline{x}$ of the particle position. Let x_i be the position of the particle in the i-th experiment, and N_E be the total number of experiments. Then the average value of the particle position is defined as

$$\overline{x} \equiv \frac{1}{N_E} \sum_{i=1}^{N_E} x_i \tag{4.63}$$

We can also define the average value of x^2 as

$$\overline{x^2} \equiv \frac{1}{N_E} \sum_{i=1}^{N_E} (x_i)^2 \tag{4.64}$$

The other useful number is the average square deviation δx^2 of the observed positions x_i from their average value $\overline{x}$. The average square deviation is defined as

$$\delta x^2 \equiv \frac{1}{N_E} \sum_{i=1}^{N_E} (x_i - \overline{x})^2 \tag{4.65}$$

or, expanding the quantity in parentheses

$$\begin{aligned}
\delta x^2 &= \frac{1}{N_E} \sum_{i=1}^{N_E} [x_i^2 - 2x_i\overline{x} + \overline{x}^2] \\
&= \overline{x^2} - 2\overline{x}\,\overline{x} + \overline{x}^2 \\
&= \overline{x^2} - \overline{x}^2
\end{aligned} \tag{4.66}$$

The "root-mean-square" deviation δx is just the square-root of δx^2. These two numbers, $\overline{x}$ and δx, can be reported as result of the series of measurements.

The Born Interpretation enables us to predict the values of these two numbers, given the quantum state $|\psi>$. These predicted values come from probability theory. Suppose we make a series of measurements on the quantity Q, which can only take on the possible values $Q_1, Q_2, Q_3..., Q_{n_Q}$; and suppose the corresponding probabilities of finding these values, in any given measurement, is $P_1, P_2, P_3...., P_{n_Q}$. Then the expected average value, or "**Expectation Value**" of Q is defined as

$$< Q >= \sum_{n=1}^{n_Q} Q_n P_n \tag{4.67}$$

where n_Q is the number (which could be infinite) of possible values of the observable Q. This theoretical expectation value should equal (up to statistical error) the average value

$$\overline{Q} = \frac{1}{N_M} \sum_{n=1}^{n_Q} N_n Q_n \tag{4.68}$$

where N_n is the number of measurements that found the value $Q = Q_n$, and N_M is the total number of measurements

$$N_M = \sum_{n=1}^{n_Q} N_n \tag{4.69}$$

(One should be careful not to confuse the index i in eq. (4.63), which labels the experiment, with the index n in eq. (4.67), which labels the possible values the observable Q.) The reason that $< Q >$ and $\overline{Q}$ should equal one another is that the fraction of times that the value $Q = Q_n$ is observed should equal the probability of observing Q_n in any given measurement, i.e.

$$P_n = \frac{N_n}{N_M} \tag{4.70}$$

Inserting this expression for the probability into (4.67), one finds $< Q >= \overline{Q}$.

In the case of a particle moving in one dimension, one of the possible observables is the position x. Since x can take any value in a continous range, the sum in (4.67) is replaced by an integral, and the probability of observing a particle in an infinitesmal interval dx around the point x is

$$P_{dx}(x) = \psi^*(x,t)\psi(x,t)dx \tag{4.71}$$

With these modifications, the formula for expectation values predicts

$$\begin{aligned} < x > \ &= \ \int_{-\infty}^{\infty} x P_{dx}(x) \\ &= \ \int_{-\infty}^{\infty} x\psi^*(x,t)\psi(x,t)dx \end{aligned} \tag{4.72}$$

Likewise, the expectation value for the observable x^2 is

$$< x^2 >= \int_{-\infty}^{\infty} x^2 \psi^*(x,t)\psi(x,t)dx \tag{4.73}$$

and the expectation value of the square deviation is given by

$$\begin{aligned} \Delta x^2 &= < (x- < x >)^2 > \\ &= < (x^2 - 2x < x > + < x >^2) > \\ &= \int_{-\infty}^{\infty} dx \, [x^2 - 2x < x > + < x >^2]\psi^*(x,t)\psi(x,t) \end{aligned} \tag{4.74}$$

Using the fact that $< x >$ is a constant which can be taken outside the integral, and the normalization condition (3.33), we find

$$\begin{aligned} \Delta x^2 &= < x^2 > -2 < x >< x > + < x >^2 \\ &= < x^2 > - < x >^2 \end{aligned} \tag{4.75}$$

as in eq. (4.66). The square root of this quantity, Δx, is referred to as the **Uncertainty** in the position of the particle in the quantum state $|\psi >$.

We see that from the Born interpretation we can extract two numbers from the wavefunction, the expectation value $< x >$ and the Uncertainty Δx, which can be compared to the experimental values of average position $\overline{x}$, and root-mean-square deviation δx respectively. Experimentally, however, there are other observables of a particle which can be measured, such as its momentum and its energy, and values of $\overline{p}$, δp, $\overline{E}$, δE can be determined from experiment. The Born Interpretation does not tell us how to compute these quantities; this will require a further investigation of the dynamics of the quantum state, which is the topic of the next lecture.

Chapter 5

Dynamics of the Quantum State

History is just one damn thing after another.
- Anonymous

The classical motion of a particle is represented by a trajectory in 3-dimensional space, while the quantum-mechanical motion of a particle, according to the last chapter, is supposed to be described by a curve on the unit sphere of an infinite dimensional space. How can classical physics be in any sense an approximation of quantum physics, if the arena of motion is so very different in the two theories?

The answer is this: it is not the physical state of the particle, but rather our observations of its position, that should, in some limit, approximate a classical trajectory. And although the quantum state of a particle doesn't correspond, in general, to a definite point in 3-space, it is still true that the *expectation value* of particle position at time t

$$< x > \equiv \int dx \; x \psi^*(x,t) \psi(x,t) \tag{5.1}$$

traces a trajectory through ordinary space. Given an equation of motion for the quantum state $\psi(x,t)$, it should be possible to derive laws of motion for $< x >$, and compare them with the classical laws of motion for $x(t)$. The simplest possibility is that these two sets of laws look the same. This is known as "Ehrenfest's Principle".

5.1   Ehrenfest's Principle

Let $\{q^a, p_a\}$ be the generalized coordinates and momenta of a mechanical system. Ehrenfest's Principle is the statement that Hamilton's equations of motion are valid as expectation value equations in quantum mechanics:

Ehrenfest's Principle

$$\frac{d}{dt} < q^a > \;=\; < \frac{\partial H}{\partial p_a} >$$
$$\frac{d}{dt} < p_a > \;=\; - < \frac{\partial H}{\partial q^a} > \tag{5.2}$$

In particular, for a particle of mass m moving in a potential $V(x)$ in one dimension,

$$\frac{d}{dt} < x > \;=\; < \frac{p}{m} >$$
$$\frac{d}{dt} < p > \;=\; < -\frac{\partial V}{\partial x} > \tag{5.3}$$

Let us check whether these equations are satisfied by the equation for De Broglie waves in one dimension

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} \tag{5.4}$$

From the first equation of (5.3), we obtain an expression for the expectation value of momentum

$$
\begin{aligned}
< p > \;&=\; m\partial_t < x > \\
&=\; m\partial_t \int dx\ \psi^*(x,t)x\psi(x,t) \\
&=\; m \int dx\ \left\{ \frac{\partial \psi^*}{\partial t} x\psi + \psi^* x \frac{\partial \psi}{\partial t} \right\}
\end{aligned}
\tag{5.5}
$$

Then, applying the equation (5.4) for de Broglie waves

$$< p > \;=\; m\left(\frac{i\hbar}{2m}\right) \int dx \{ -(\frac{\partial^2}{\partial x^2}\psi^*)x\psi + \psi^* x \frac{\partial^2}{\partial x^2}\psi \} \tag{5.6}$$

and using the integration by parts formula[1]

$$\int dx\ (\frac{\partial^2}{\partial x^2}F)G = \int dx\ F\frac{\partial^2}{\partial x^2}G \tag{5.7}$$

this becomes

$$
\begin{aligned}
< p > \;&=\; m\left(\frac{i\hbar}{2m}\right) \int dx\ \psi^*\{ x\frac{\partial^2}{\partial x^2}\psi - \frac{\partial^2}{\partial x^2}(x\psi) \} \\
&=\; m\left(\frac{i\hbar}{2m}\right) \int dx\ \psi^* \left\{ x\frac{\partial^2}{\partial x^2}\psi - \frac{\partial}{\partial x}\left(\psi + x\frac{\partial}{\partial x}\psi \right) \right\} \\
&=\; \int dx\psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi
\end{aligned}
\tag{5.8}
$$

---

[1]We assume that the wave function ψ and its derivatives vanish at $x = \pm\infty$, so there are no boundary terms.

Equation (5.8) should be understood as a prediction, given the quantum state $\psi(x,t)$, for the expectation value of momentum. Next, taking the time-derivative of $<p>$, so as to compare to the second equation of (5.3),

$$
\begin{aligned}
\partial_t <p> &= \partial_t \int dx\ \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi \\
&= \left(\frac{i\hbar}{2m} \right) (-i\hbar) \int dx \{ -(\frac{\partial^2}{\partial x^2}\psi^*)\frac{\partial}{\partial x}\psi + \psi^* \frac{\partial}{\partial x}\frac{\partial^2}{\partial x^2}\psi \} \\
&= \left(\frac{i\hbar}{2m} \right) (-i\hbar) \int dx \psi^* \{ -\frac{\partial^2}{\partial x^2}\frac{\partial}{\partial x}\psi + \frac{\partial}{\partial x}\frac{\partial^2}{\partial x^2}\psi \} \\
&= 0
\end{aligned}
\tag{5.9}
$$

we conclude that $\partial_t <p> = 0$, which agrees with Ehrenfest's principle for the case that the potential $V = 0$.

In the case that $V \neq 0$, the equation for de Broglie waves does not satisfy the second of equations (5.3). So the de Broglie wave equation must be generalized so as to agree with Ehrenfest's principle for *any* potential $V(x)$. This generalized wave equation was found by Schrodinger; it is as central to quantum mechanics as $F = ma$ is to classical mechanics.

5.2 The Schrodinger Wave Equation

The quantum mechanical law of motion found by Schrodinger, describing a particle of mass m moving in one dimension in an arbitrary potential $V(x)$, is known as

The Schrodinger Wave Equation

$$
i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + V(x)\psi
\tag{5.10}
$$

It is easy to verify that this equation does, in fact, satisfy Ehrenfest's principle. Once again, starting with the first of the Ehrenfest equations (5.3),

$$
\begin{aligned}
<p> &= m\partial_t <x> \\
&= m \int dx \left\{ \frac{\partial \psi^*}{\partial t} x\psi + \psi^* x \frac{\partial \psi}{\partial t} \right\}
\end{aligned}
\tag{5.11}
$$

Then rewriting the Schrodinger equation (and its complex conjugate) as

$$\frac{\partial \psi}{\partial t} = \frac{i\hbar}{2m}\frac{\partial^2 \psi}{\partial x^2} - \frac{i}{\hbar}V\psi$$
$$\frac{\partial \psi^*}{\partial t} = -\frac{i\hbar}{2m}\frac{\partial^2 \psi^*}{\partial x^2} + \frac{i}{\hbar}V\psi^* \tag{5.12}$$

and inserting into (5.11), we have

$$
\begin{aligned}
<p> &= m\int dx \left\{ \left(-\frac{i\hbar}{2m}\frac{\partial^2 \psi^*}{\partial x^2} + \frac{i}{\hbar}V\psi^* \right) x\psi \right. \\
&+ \left. \psi^* x \left(\frac{i\hbar}{2m}\frac{\partial^2 \psi}{\partial x^2} - \frac{i}{\hbar}V\psi \right) \right\} \\
&= m\left(\frac{i\hbar}{2m} \right) \int dx \{ -(\frac{\partial^2}{\partial x^2}\psi^*)x\psi + \psi^* x\frac{\partial^2}{\partial x^2}\psi \} \\
&= \int dx \psi^* \left(-i\hbar\frac{\partial}{\partial x} \right) \psi \tag{5.13}
\end{aligned}
$$

which is the same rule for computing $<p>$ as in the previous $V = 0$ case. Then

$$
\begin{aligned}
\partial_t <p> &= -i\hbar\int dx \left[\frac{\partial \psi^*}{\partial t}\frac{\partial \psi}{\partial x} + \psi^*\frac{\partial^2 \psi}{\partial t \partial x} \right] \\
&= -i\hbar\int dx \left[\frac{\partial \psi^*}{\partial t}\frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x}\frac{\partial \psi}{\partial t} \right] \\
&= -i\hbar\int dx \left\{ \left(-\frac{i\hbar}{2m}\frac{\partial^2 \psi^*}{\partial x^2} + \frac{i}{\hbar}V\psi \right)\frac{\partial \psi}{\partial x} \right. \\
&\quad \left. - \frac{\partial \psi^*}{\partial x}\left(\frac{i\hbar}{2m}\frac{\partial^2 \psi}{\partial x^2} - \frac{i}{\hbar}V\psi \right) \right\} \\
&= -\frac{\hbar^2}{2m}\int dx \left[\frac{\partial^2 \psi^*}{\partial x^2}\frac{\partial \psi}{\partial x} + \frac{\partial \psi^*}{\partial x}\frac{\partial^2 \psi}{\partial x^2} \right] \\
&+ \int dx \left[\psi^* V\frac{\partial \psi}{\partial x} + \frac{\partial \psi^*}{\partial x}V\psi \right] \tag{5.14}
\end{aligned}
$$

Again applying integration by parts to the first term of the first integral, and the second term of the second integral, we find

$$
\begin{aligned}
\partial_t <p> &= -\frac{\hbar^2}{2m}\int dx \left[-\frac{\partial \psi^*}{\partial x}\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial \psi^*}{\partial x}\frac{\partial^2 \psi}{\partial x^2} \right] \\
&+ \int dx \left[\psi^* V\frac{\partial \psi}{\partial x} - \psi^*\frac{\partial}{\partial x}(V\psi) \right] \\
&= \int dx \left[\psi^* V\frac{\partial \psi}{\partial x} - \psi^* V\frac{\partial \psi}{\partial x} - \psi^*\frac{\partial V}{\partial x}\psi \right]
\end{aligned}
$$

$$= \int dx \; \psi^* \left(-\frac{\partial V}{\partial x} \right) \psi$$

$$= \; < -\frac{\partial V}{\partial x} > \tag{5.15}$$

exactly as required by Ehrenfest's principle.

We see that Ehrenfest's principle and the Schrodinger equation, taken together, make the following prediction for the expectation value of particle momentum at time t, regardless of the potential $V(x)$

$$< p > = \int dx \; \psi^*(x,t) \; \tilde{p} \; \psi(x,t) \tag{5.16}$$

where $\tilde{p}$ is the differential operator known as the **Momentum Operator**

$$\tilde{p} \equiv -i\hbar \frac{\partial}{\partial x} \tag{5.17}$$

This supplies an important piece of information. The Born interpretation of the wavefunction tells us how to compute the expectation value of of position $< x >$ of a particle, given its wavefunction $\psi(x,t)$. But position is not the only observable of a particle that can be measured; for example, one can also measure a particle's momentum, and the Born interpretation does not tell us how to compute the corresponding expectation value $< p >$. Now we have the rule for finding $< p >$; it is contained in equations (5.16) and (5.17) above.

Eq. (5.17) can be used to express any x-derivative in terms of the momentum operator, and in particular

$$\frac{\partial^2}{\partial x^2} = -\frac{1}{\hbar^2} \tilde{p}^2 \tag{5.18}$$

Then the Schrodinger equation can be written in the compact form

$$i\hbar \partial_t \psi \;\; = \;\; \left(\frac{\tilde{p}^2}{2m} + V \right) \psi$$

$$= \;\; \tilde{H}\psi \tag{5.19}$$

where

$$H[p,q] = \frac{p^2}{2m} + V \tag{5.20}$$

is just the Hamiltonian for a particle of mass m, moving in a potential field V, and $\tilde{H}$ is the **Hamiltonian Operator**

$$\tilde{H} = H[\tilde{p}, x] \tag{5.21}$$

obtained by replacing momentum p by the momentum operator $\tilde{p}$ in the Hamiltonian function.

Finally, we need to check the consistency of the Schrodinger equation with the Born Interpretation. According to the Born Interpretation, at any instant of time t,

$$< \psi | \psi >= \int dx \ \psi^*(x,t) \psi(x,t) = 1 \tag{5.22}$$

for a particle moving in one dimension. Now suppose this normalization condition is true at some time t_0, and and the wavefunction evolves according to the Schrodinger equation. Will this condition also be valid at later times $t > t_0$? To check this, we differentiate $< \psi | \psi >$ with respect to time

$$
\begin{aligned}
\partial_t < \psi | \psi > &= \int dx \ \{ (\partial_t \psi^*) \psi + \psi^* (\partial_t \psi) \} \\
&= \int dx \ \left\{ \left(-\frac{i\hbar}{2m} \partial_x^2 \psi^* + \frac{i}{\hbar} V \psi^* \right) \psi + \psi^* \left(\frac{i\hbar}{2m} \partial_x^2 \psi - \frac{i}{\hbar} V \psi \right) \right\} \\
&= \frac{i\hbar}{2m} \int dx \ \{ -(\partial_x^2 \psi^*) \psi + \psi^* \partial_x^2 \psi \} \\
&= 0
\end{aligned}
\tag{5.23}
$$

where we have once again used the integration by parts formula (5.7). This result means that the norm of the wavefunction is constant in time, which is known as **"Conservation of Probability"**. The inner product $< \psi | \psi >$ is the total probability to find the particle anywhere in space. If the norm is constant, and $< \psi | \psi >= 1$ at some time $t = t_0$, then $< \psi | \psi >= 1$ at any any later time.

The Schrodinger equation for motion in 3-dimensions is a straightforward generalization of the one-dimensional case:

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{-\hbar^2}{2m} \nabla^2 \psi + V(x,y,z) \psi \tag{5.24}$$

In this case, the generalized coordinates are $q^1 = x, \ q^2 = y, \ q^3 = z$, and the first of the Ehrenfest equations (5.2) tells us

$$< p_x >= \int d^3x \ \psi^*(x,y,z,t) \ \tilde{p}_x \ \psi(x,y,z,t)$$

$$< p_y >= \int d^3x \ \psi^*(x,y,z,t) \ \tilde{p}_y \ \psi(x,y,z,t)$$

$$< p_z >= \int d^3x \ \psi^*(x,y,z,t) \ \tilde{p}_z \ \psi(x,y,z,t) \tag{5.25}$$

where

$$
\begin{aligned}
\tilde{p}_x &\equiv -i\hbar \frac{\partial}{\partial x} \\
\tilde{p}_y &\equiv -i\hbar \frac{\partial}{\partial y} \\
\tilde{p}_z &\equiv -i\hbar \frac{\partial}{\partial z}
\end{aligned}
\tag{5.26}
$$

and one can then readily verify the 2nd Ehrenfest equation

$$\partial_t < \vec{p} >=< -\nabla V > \tag{5.27}$$

In terms of the $\tilde{p}$-operators, the Schrodinger equation in 3-dimensions can be written

$$
\begin{aligned}
i\hbar \frac{\partial \psi}{\partial t} &= \left[\frac{1}{2m}(\tilde{p}_x^2 + \tilde{p}_y^2 + \tilde{p}_z^2) + V(x,y,z) \right] \psi \\
&= \tilde{H}\psi
\end{aligned}
\tag{5.28}
$$

Problem: Verify conservation of probability and the Ehrenfest equations in the three-dimensional case.

5.3 The Time-Independent Schrodinger Equation

When the potential $V(x)$ is time-independent we can simplify the Schrodinger equation by the method of separation of variables. Write

$$\psi(x,t) = \phi(x)T(t) \tag{5.29}$$

and substitute into the (one-dimensional) Schrodinger equation:

$$i\hbar\phi(x)\frac{\partial T}{\partial t} = T\tilde{H}\phi \tag{5.30}$$

divide both sides by ϕT

$$i\hbar \frac{1}{T(t)} \frac{\partial}{\partial t} T(t) = \frac{1}{\phi(x)} \tilde{H}\phi(x) \tag{5.31}$$

Since the lhs depends only on t, and the rhs only on x, the only way this equation can be true is if both sides equal a constant, call it E:

$$
\begin{aligned}
i\hbar \frac{1}{T(t)} \frac{\partial}{\partial t} T(t) &= E \\
\frac{1}{\phi(x)} \tilde{H}\phi(x) &= E
\end{aligned}
\tag{5.32}
$$

The first of these two differential equations can be solved immediately:

$$T(t) = e^{-iEt/\hbar} \tag{5.33}$$

while the second equation

$$\tilde{H}\phi = E\phi \tag{5.34}$$

or, more explicitly

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \right] \phi(x) = E\phi(x) \tag{5.35}$$

is known as the **Time-Independent Schrodinger Equation**.

Equation (5.34) is an example of an **Eigenvalue Equation**. This is a linear differential equation in which one has to solve simultaneously for a set of constants, known as the eigenvalues, and a set of corresponding functions known as the eigenfunctions. In the case of the Schrodinger equation, the constant E is called the the "energy eigenvalue," and the function $\phi(x)$ is called the "energy eigenfunction" or "energy eigenstate."

To each energy eigenvalue E there is at least one (and sometimes more than one) energy eigenstate, and to each eigenstate there corresponds a solution

$$\psi(x,t) = \phi(x)e^{-iEt/\hbar} \tag{5.36}$$

of the time-dependent Schrodinger equation. Such solutions are also known as **stationary states** because the time-dependence is contained entirely in an overall phase. This means that the probability to find a particle in the neighborhood of point x, i.e

$$P_\epsilon(x) = \psi^*(x,t)\psi(x,t)\epsilon = \phi^*(x)\phi(x)\epsilon \tag{5.37}$$

is constant in time.

Let $\{\phi_\alpha(x), E_\alpha\}$ denote a complete set of eigenstates and corresponding eigenvalues, in the sense that any other eigenstate which is not in the set can be expressed as a linear combination of those that are. Then the general solution to the time-*dependent* Schrodinger equation is

$$\psi(x,t) = \sum_\alpha c_\alpha \phi_\alpha(x)e^{-iE_\alpha t/\hbar} \tag{5.38}$$

if the energy eigenvalues are a discrete set, or

$$\psi(x,t) = \int d\alpha \, c_\alpha \phi_\alpha(x)e^{-iE_\alpha t/\hbar} \tag{5.39}$$

if the energy eigenvalues span a continuous range, or a combination

$$\psi(x,t) = \sum_\alpha c_\alpha \phi_\alpha(x)e^{-iE_\alpha t/\hbar} + \int d\alpha \, c_\alpha \phi_\alpha(x)e^{-iE_\alpha t/\hbar} \tag{5.40}$$

of sum and integral, if some eigenvalues are discrete and others are found in a continuous range.

Most of the effort in quantum mechanics goes into solving the time-independent Schrodinger equation (5.35). Once a complete set of solutions to that equation is found, the general solution (eq. (5.40)) to the time-dependent problem follows immediately.

5.4 The Free Particle

When the potential $V(x)$ vanishes everywhere, the Schrodinger equation in one dimension reduces to the equation for de Broglie waves

$$i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} \tag{5.41}$$

and this equation was deduced from the wavefunction for plane waves, corresponding to a particle with *definite* momentum p and energy $E_p = p^2/2m$

$$
\begin{aligned}
\psi_p(x,t) &= N\exp[i(px - E_p t)/\hbar] \\
&= N\exp[i(px - \frac{p^2}{2m}t/\hbar] \tag{5.42}
\end{aligned}
$$

The Schrodinger equation (whether $V = 0$ or not) is a linear equation, and any linear equation has the property that, if ψ_{p_1}, ψ_{p_1}, ψ_{p_3}, ... are all solutions of the equation, then so is any linear combination

$$\psi = c_{p_1}\psi_{p_1} + c_{p_2}\psi_{p_2} + c_{p_3}\psi_{p_3} + ... \tag{5.43}$$

In particular,

$$\psi(x,t) = \int_{-\infty}^{\infty}\frac{dp}{2\pi\hbar}f(p)\exp[i(px - \frac{p^2}{2m}t)/\hbar] \tag{5.44}$$

is a linear combination of plane wave solutions (5.42). This means that (5.44) is a solution of the free-particle Schrodinger equation (5.41), for any choice of function $f(p)$ whatsoever.

Problem: Show that the wavefunction in eq. (5.44) is a solution of the free particle Schrodinger equation by substituting (5.44) directly into (5.41).

Equation (5.44) is an example of the general solution (5.39) of a time-dependent Schrodinger equation. The time-independent Schrodinger equation in this case is

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \phi}{\partial x^2} = E\phi \tag{5.45}$$

For each positive eigenvalue $E \in [0, \infty]$ there are two linearly independent solutions

$$\phi_p(x) = e^{ipx/\hbar} \qquad p = \pm\sqrt{2mE} \tag{5.46}$$

such that any other solution for a given E can be expressed as a linear combination

$$\phi(x) = c_1 e^{i\sqrt{2mE}x/\hbar} + c_2 e^{-i\sqrt{2mE}x/\hbar} \tag{5.47}$$

The set of eigenfunctions and corresponding eigenvalues

$$\left\{ \phi_p(x) = e^{ipx/\hbar}, E_p = \frac{p^2}{2m} \right\} \qquad -\infty < p < \infty \tag{5.48}$$

is therefore a complete set of solutions of the time-independent Schrodinger equation. Inserting these solutions into eq. (5.39), we arrive at the general solution (5.44).

It is easy to show that eq. (5.44) is, in fact, the general solution of the free-particle Schrodinger wave equation, in the sense that *any* solution of the free-particle equation can be put into this form. First of all, the wavefunction $\psi(x,t)$ at all times is uniquely determined by the wavefunction at one initial time, say $t=0$, denoted

$$\phi(x) \equiv \psi(x,0) \tag{5.49}$$

This is because the Schrodinger equation is first-order in the time derivative, so that given $\psi(x,t)$ at some time t, the wavefunction is determined an infinitesmal time $t+\epsilon$ later by the rule given in eq. (4.59). Next, for any given $\phi(x)$ we can always find a function $f(p)$ such that

$$\phi(x) = \int_{-\infty}^{\infty} \frac{dp}{2\pi\hbar} \, f(p) e^{ipx/\hbar} \tag{5.50}$$

To determine $f(p)$, multiply both sides of the equation by $\exp[-ip'/\hbar]$, and integrate with respect to x:

$$
\begin{aligned}
\int_{-\infty}^{\infty} dx \, \phi(x) e^{-ip'x/\hbar} &= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} \frac{dp}{2\pi\hbar} \, f(p) e^{i(p-p')x/\hbar} \\
&= \int_{-\infty}^{\infty} \frac{dp}{2\pi\hbar} \, f(p) \int_{-\infty}^{\infty} dx \, \exp[i\frac{p-p'}{\hbar}x] \\
&= \int_{-\infty}^{\infty} \frac{dp}{2\pi\hbar} \, f(p) 2\pi\delta \left(\frac{p-p'}{\hbar} \right) \tag{5.51}
\end{aligned}
$$

where we have used the integral representation of the Dirac delta function (4.50). Using also the identity (4.52):

$$\delta \left(\frac{p-p'}{\hbar} \right) = \hbar\delta(p-p') \tag{5.52}$$

we get

$$\int_{-\infty}^{\infty} dx \, \phi(x) e^{-ip'x/\hbar} = \int_{-\infty}^{\infty} dp \, f(p)\delta(p-p') = f(p') \tag{5.53}$$

The conclusion is that *any* $\phi(x)$ can be expressed in the form (5.50), for $f(p)$ chosen to equal

$$f(p) = \int_{-\infty}^{\infty} dx \, \phi(x) e^{-ipx/\hbar} \tag{5.54}$$

The terminology is that $\phi(x)$ is the **Fourier Transform** of $f(p)$ (eq. (5.50)), and $f(p)$ is the **Inverse Fourier Transform** of $\phi(x)$ (eq. (5.54)).

We now have a prescription, given the wavefunction at any initial time $t = 0$, for finding the wavefunction at any later time: From $\phi(x) = \psi(x, 0)$, compute the inverse Fourier transform $f(p)$ using (5.54), then insert $f(p)$ into the rhs of eq. (5.44). The integral of eq. (5.44) will then give the wavefunction $\psi(x, t)$ at any later time.

5.5   Gaussian Wavepackets

A wavefunction of the form

$$\phi(x) = N\delta_L(x) \tag{5.55}$$

goes to zero, as $L \to \infty$, everywhere except at the point $x = 0$. At the other extreme, a plane wave

$$\phi(x) = Ne^{ip_0 x/\hbar} \tag{5.56}$$

has a constant modulus $|\phi| = N$ at every point along the entire line $-\infty < x < \infty$. A wavefunction which interpolates between these two extreme cases is the "gaussian wavepacket"

$$\phi(x) = Ne^{-x^2/2a^2}e^{ip_0 x/\hbar} \tag{5.57}$$

in which a gaussian damping factor is used to modulate a plane wave. As $a \to 0$, at fixed p_0, this wavefunction is proportional to $\delta_L(x)$ (where $L = 1/2a^2$), while as $a \to \infty$, $\phi(x)$ approaches a plane wave.

Gaussian wavepackets provide a very useful example of how the wavefunction of a free particle evolves in time. Assume that the initial wavefunction $\psi(x, 0)$ has the form of the gaussian wavepacket (5.57), with some fixed value of the constant a. The first task is to **"normalize"** the wavefunction, which means: choose the constant N in (5.57) so that the normalization condition

$$\int dx\ \psi^*(x, t)\psi(x, t) = 1 \tag{5.58}$$

is fulfilled at $t = 0$ (which implies that it will be fulfilled for all t, by conservation of probability). The condition is

$$\begin{aligned}
1 &= \int dx\ \psi^*(x, 0)\psi(x, 0) \\
&= N^2 \int dx\ e^{-x^2/a^2} \\
&= N^2\sqrt{\pi a^2} \tag{5.59}
\end{aligned}$$

Therefore

$$N = \left(\frac{1}{\pi a^2}\right)^{1/4} \tag{5.60}$$

We begin by computing the initial expectation values $< x >_0,\ \ < p >_0$ and the initial uncertainty Δx_0 in position, at time $t = 0$. First

$$
\begin{aligned}
< x >_0 \ &= \ \int dx\ x\phi^*(x)\phi(x) \\
&= \ \left(\frac{1}{\pi a^2}\right)^{1/2} \int_{-\infty}^{\infty} dx\ x e^{-x^2/a^2} \\
&= \ 0
\end{aligned}
\tag{5.61}
$$

and

$$
\begin{aligned}
< p >_0 \ &= \ \int dx\ \phi^*(x)\left(-i\hbar\frac{\partial}{\partial x}\right)\phi(x) \\
&= \ -\frac{i\hbar}{\sqrt{\pi a^2}} \int dx\ \exp\left(-i\frac{p_0 x}{\hbar} - \frac{x^2}{2a^2}\right)\frac{\partial}{\partial x}\exp\left(i\frac{p_0 x}{\hbar} - \frac{x^2}{2a^2}\right) \\
&= \ -i\frac{i\hbar}{\sqrt{\pi a^2}} \int dx\ \left(i\frac{p_0}{\hbar} - \frac{x}{a^2}\right)e^{-x^2/a^2} \\
&= \ p_0
\end{aligned}
\tag{5.62}
$$

These are the relevant expectation values at $t = 0$ of position and momentum. Next, the squared uncertainty is

$$
\begin{aligned}
\Delta x_0^2 \ &= \ < x^2 >_0 - < x >_0^2 = < x^2 >_0 \\
&= \ \int dx\ x^2\phi^*(x)\phi(x) \\
&= \ \left(\frac{1}{\pi a^2}\right)^{1/2} \int_{-\infty}^{\infty} dx\ x^2 e^{-x^2/a^2} \\
&= \ \frac{1}{2}a^2
\end{aligned}
\tag{5.63}
$$

The initial uncertainty in position at time $t = 0$ is therefore

$$
\Delta x_0 = \frac{a}{\sqrt{2}}
\tag{5.64}
$$

To find the time-evolution of the wavefunction, we first compute the inverse Fourier Transform

$$
\begin{aligned}
f(p) \ &= \ \int dx\ \phi(x)e^{-ipx/\hbar} \\
&= \ \left(\frac{1}{\pi a^2}\right)^{1/4} \int dx\ \exp\left[-\frac{x^2}{2a^2} - i\frac{(p - p_0)}{\hbar}x\right]
\end{aligned}
\tag{5.65}
$$

Using the formula for gaussian integration

$$
\int_{-\infty}^{\infty} dz\ e^{-Az^2 - Bz} = \sqrt{\frac{\pi}{A}}e^{B^2/4A}
\tag{5.66}
$$

this becomes

$$f(p) = (4\pi a^2)^{1/4} e^{-a^2(p-p_0)^2/2\hbar^2} \tag{5.67}$$

Then, substituting $f(p)$ into (5.44), we find the wavefunction at any later time t

$$
\begin{aligned}
\psi(x,t) &= (4\pi a^2)^{1/4} \int \frac{dp}{2\pi\hbar} \, e^{-a^2(p-p_0)^2/2\hbar^2} \exp\left[i(px - \frac{p^2}{2m}t)/\hbar\right] \\
&= \frac{(4\pi a^2)^{1/4}}{2\pi\hbar} \int dq \, \exp\left[-\frac{a^2}{2\hbar^2}q^2 + i\frac{q+p_0}{\hbar}x - i\frac{(q+p_0)^2}{2m\hbar}t\right] \\
&= \frac{(4\pi a^2)^{1/4}}{2\pi\hbar} \exp[i(p_0 x - \frac{p_0^2}{2m}t)/\hbar] \\
&\quad \times \int dq \, \exp\left[-\left(\frac{a^2}{2\hbar^2} + \frac{it}{2m\hbar}\right)q^2 + i\left(\frac{x}{\hbar} - \frac{p_0 t}{m\hbar}\right)q\right] \\
&= \frac{(4\pi a^2)^{1/4}}{2\pi\hbar} \left[\frac{\pi}{\frac{a^2}{2\hbar^2} + \frac{it}{2m\hbar}}\right]^{1/2} \exp\left\{-\frac{(x-v_0 t)^2}{2(a^2 + i\hbar t/m)}\right\} e^{i(p_0 x - \frac{p_0^2}{2m}t)/\hbar} \tag{5.68}
\end{aligned}
$$

where

$$v_0 \equiv \frac{p_0}{m} \tag{5.69}$$

Although (5.68) looks like a complicated expression, its modulus is very simple:

$$
\begin{aligned}
|\psi|^2 &= \psi^*(x,t)\psi(x,t) \\
&= \frac{1}{\sqrt{\pi a^2(t)}} \exp\left[-\frac{(x-v_0 t)^2}{a^2(t)}\right] \tag{5.70}
\end{aligned}
$$

where we have defined

$$a(t) \equiv \sqrt{a^2 + \frac{\hbar^2}{m^2 a^2}t^2} \tag{5.71}$$

Note that the modulus of the wavefunction remains a gaussian at all times, but the width $a(t)$ of the gaussian increases, i.e. the wavefunction "spreads out" as time passes.

We can then calculate $< x >$ and Δx at any time $t > 0$:

$$
\begin{aligned}
< x > &= \frac{1}{\sqrt{\pi a^2(t)}} \int dx \, x \exp\left[-\frac{(x-v_0 t)^2}{a^2(t)}\right] \\
&= \frac{1}{\sqrt{\pi a^2(t)}} \int dx' \, (x' + v_0 t) \exp\left[-\frac{x'^2}{a^2(t)}\right] \\
&= v_0 t \tag{5.72}
\end{aligned}
$$

and also

$$\Delta x^2 = < (x - < x >)^2 > = < (x - v_0 t)^2 >$$

$$
\begin{aligned}
&= \frac{1}{\sqrt{\pi a^2(t)}} \int dx \ (x - v_0 t)^2 \exp\left[-\frac{(x - v_0 t)^2}{a^2(t)} \right] \\
&= \frac{1}{\sqrt{\pi a^2(t)}} \int dx' \ x'^2 \exp\left[-\frac{x'^2}{a^2(t)} \right] \\
&= \frac{1}{2} a^2(t)
\end{aligned}
\tag{5.73}
$$

so that

$$
\Delta x = \frac{a(t)}{\sqrt{2}} = \frac{1}{\sqrt{2}} \sqrt{a^2 + \frac{\hbar^2}{m^2 a^2} t^2}
\tag{5.74}
$$

To compute $<p>$, we make use again of the representation (5.44)

$$
\begin{aligned}
<p> &= \int dx \ \psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x} \right) \psi(x,t) \\
&= \int dx \left\{ \int \frac{dp_1}{2\pi\hbar} \ f(p_1) e^{i(p_1 x - E_{p_1} t)/\hbar} \right\}^* \left(-i\hbar \frac{\partial}{\partial x} \right) \int \frac{dp_2}{2\pi\hbar} \ f(p_2) e^{i(p_2 x - E_{p_2} t)/\hbar} \\
&= \int \frac{dp_1}{2\pi\hbar} \ f^*(p_1) e^{iE_{p_1} t/\hbar} \int \frac{dp_2}{2\pi\hbar} \ p_2 f(p_2) e^{-iE_{p_2} t/\hbar} \int dx \ e^{i(p_2 - p_1)x/\hbar} \\
&= \int \frac{dp_1}{2\pi\hbar} \ f^*(p_1) e^{iE_{p_1} t/\hbar} \int \frac{dp_2}{2\pi\hbar} \ p_2 f(p_2) e^{-iE_{p_2} t/\hbar} 2\pi\hbar \delta(p_1 - p_2) \\
&= \int \frac{dp}{2\pi\hbar} p f^*(p) f(p)
\end{aligned}
\tag{5.75}
$$

Note that the time-dependence has vanished completely from this equation. It follows that

$$
<p> = <p>_0 = p_0
\tag{5.76}
$$

and the expectation values of position and momentum together obey

$$
\begin{aligned}
<x>_t &= <x>_0 + \frac{<p>_0}{m} t \\
<p>_t &= p_0
\end{aligned}
\tag{5.77}
$$

With the "$<>$" signs removed, these are the equations of a classical trajectory in phase space for a free particle of mass m.

On the other hand, the positional uncertainty Δx of the quantum state, which is proportional to the width $a(t)$ of the gaussian, increases in time; this is known as the "spreading of the wavepacket". As noted in Lecture 3, one of the reasons that the electron cannot be regarded as being *literally* a wave is that its wavefunction expands to macroscopic size quite rapidly, and it is quite certain that electrons are not macroscopic objects. Let us consider the time t_{2a} that it takes a free particle wavefunction to double in size $(a(t) = 2a(0))$:

$$
t_{2a} = \sqrt{3} \frac{ma^2}{\hbar}
\tag{5.78}
$$

and the time it takes to expand to some very much larger size $a(t) = A >> a$

$$t_A = \frac{maA}{\hbar} \tag{5.79}$$

As an example, choose the initial spread of the wavepacket to be on the order of the diameter of atomic hydrogen

$$a = 10^{-10} \text{ m} \tag{5.80}$$

and A to be a macroscopic distance, e.g.

$$A = 10 \text{ cm} \tag{5.81}$$

Begin by considering an electron, which has a mass $m_e = 9.11 \times 10^{-31}$ kg; and $\hbar = 1.05 \times 10^{-34}$ J-s. Then the time required for the wavefunction to expand from $a = 10^{-10}$ m to 2×10^{-10}m is

$$t_{2a} = \sqrt{3}\frac{m_e a^2}{\hbar} = 1.5 \times 10^{-16} \text{ s} \tag{5.82}$$

Likewise, the time required for the wavefunction to spread to $A = 10$ cm is

$$t_A = \frac{m_e aA}{\hbar} = 8.7 \times 10^{-6} \text{ s} \tag{5.83}$$

If the energy of the electron is $E = 10$ electron volts (eV), then the velocity is

$$v = \sqrt{2E/m} = 1.87 \times 10^6 \text{ m/s} \tag{5.84}$$

Therefore, for the wavefunction of a 10 eV electron to expand from an atomic diameter to a width of 10 cm, the electron need only travel

$$d = vt_A = 16.3 \text{ m} \tag{5.85}$$

Compare these figures for an electron with the corresponding results for an object the mass of a baseball, say $m_B = .25$ kg. Supposing the width of the wavefunction is also initially $a = 10^{-10}$ m, the corresponding numbers are

$$\begin{aligned} t_{2a} &= 4.1 \times 10^{14} \text{ s} = 1.3 \text{ million years} \\ t_A &= 2.4 \times 10^{23} \text{ s} = 1.8 \times 10^{17} \text{ years} \end{aligned} \tag{5.86}$$

In other words, for all practical purposes, the wavefunction of an object of macroscopic mass doesn't expand at all.

5.6   Group Velocity and Phase Velocity

We have seen that the expectation value of position $< x >$ moves at a velocity $v =< p > /m$. This is a consequence of Ehrenfest's principle for a free particle. On the other hand, the velocity v_{phase} of any plane wave is given by the usual formula

$$v_{phase} = \lambda f \tag{5.87}$$

so that for a De Broglie wave of a definite momentum p

$$
\begin{aligned}
v_{phase} &= \frac{h}{p}\frac{E_p}{h} \\
&= \frac{E_p}{p} = \frac{p^2/2m}{p} \\
&= \frac{p}{2m}
\end{aligned}
\tag{5.88}
$$

which is half the velocity that one might expect, since a classical particle with momentum p moves at a velocity p/m. There is no contradiction, however. The velocity $v_{phase} = \lambda f$ of a plane wave is known as the **"phase velocity"** of the wave; it refers to the speed at which a point of given phase on the wave (a crest or a trough, say), propagates through space. However, that is not necessarily the same speed at which the energy carried by a group of waves travels through space. That velocity is known as the **"group velocity"**.

Consider a wave which is a superposition of two plane waves of frequencies f_1, f_2, and wavelengths λ_1, λ_2, respectively, and which have the same amplitude A. We will assume that the difference between frequencies Δf is much smaller than the average frequency $\overline{f}$, i.e.

$$\Delta f << \overline{f} \quad \text{and} \quad \Delta \lambda << \overline{\lambda} \tag{5.89}$$

By the superposition principle of wave motion

$$
\begin{aligned}
\psi(x,t) &= \psi_1(x,t) + \psi_2(x,t) \\
&= A\left[e^{i(k_1 x - \omega_1 t)} + e^{i(k_2 x - \omega_2 t)} \right] \\
&= 2A e^{i(\overline{k}x - \overline{\omega}t)} \cos[\frac{1}{2}i(\Delta k x - \Delta \omega t)]
\end{aligned}
\tag{5.90}
$$

which is the product of two waves, one of which is moving with the velocity

$$v_{phase} = \frac{\overline{\omega}}{\overline{k}} \tag{5.91}$$

and the other moving with velocity

$$v_{group} = \frac{\Delta \omega}{\Delta k} \tag{5.92}$$

The corresponding exponentials can be expanded into sines and cosines, the product of two cosines is shown in Fig. [5.2]. The "packets" of waves move collectively with the group velocity v_{group}; the crest of a wave within each packet travels at the phase velocity v_{phase}.

Now let us consider a general wavepacket of the form

$$\psi(x,t) = \int dk \ f(k)e^{i(kx-\omega(k)t)} \tag{5.93}$$

For a free particle in quantum mechanics, the wavenumber and angular frequency are related to momentum and energy

$$k = \frac{p}{\hbar} \quad \text{and} \quad \omega = \frac{E_p}{\hbar} \tag{5.94}$$

Suppose, as in the case of the gaussian wavepacket (eq. (5.67)), that $f(k)$ is peaked around a particular value k_0. In that case, we can make a Taylor expansion of $\omega(k)$ around $k = k_0$:

$$\omega(k) = \omega_0 + \left(\frac{d\omega}{dk}\right)_{k_0} (k - k_0) + O[(k - k_0)^2] \tag{5.95}$$

Inserting this exansion into (5.93), and dropping terms of order $(k - k_0)^2$ and higher, we get

$$
\begin{aligned}
\psi(x,t) &\approx \int dk \ f(k) \exp\left[i\left(k_0 x + (k - k_0)x - \omega_0 t - \frac{d\omega}{dk}(k - k_0)t\right)\right] \\
&\approx e^{i(k_0 x - \omega_0 t)} \int dk f(k) \exp\left[i(k - k_0)(x - v_{group}t)\right] \\
&\approx e^{i(k_0 x - \omega_0 t)} F[x - v_{group}t] \tag{5.96}
\end{aligned}
$$

where

$$v_{group} = \left(\frac{d\omega}{dk}\right)_{k=k_0} \tag{5.97}$$

This is again a product of two waveforms; a plane wave moving with velocity

$$v_{phase} = \frac{\omega_0}{k_0} \tag{5.98}$$

and a wavepulse $F[x - v_{group}t]$ moving with velocity v_{group} of equation (5.97). The product is indicated schematically in Fig. [5.3]. It is clear that the wavepacket propagates collectively at the velocity of the pulse, v_{group} rather than the velocity of a crest v_{phase}.[2]

---

[2]According to (5.96) the wavepacket propagates without changing its shape, which is not quite true, as we have seen in the case of the gaussian wavepacket. The "spreading" of the wavepacket is due to terms of order $(k - k_0)^2$, which were dropped in eq. (5.96).

In the case of a free particle, we have

$$
\begin{aligned}
v_{group} &= \left(\frac{d\omega}{dk}\right)_{k=k_0} \\
&= \left(\frac{d(E_p/\hbar)}{d(p/\hbar)}\right)_{p=<p>} \\
&= \left(\frac{dE_p}{dp}\right)_{p=<p>} \\
&= \frac{<p>}{m}
\end{aligned}
\tag{5.99}
$$

which is the standard relation between velocity and momentum. The conclusion is that, although the phase velocity of a de Broglie wave is half the classical velocity, a packet of de Broglie waves travels collectively at exactly the classical velocity.

5.7   The Particle in a Closed Tube

Finally we return to the example of Lecture 4, in which a particle is moving in a closed tube of length L; collisions between the particle and the ends of the tube are assumed to be elastic. Since the potential barrier against leaving the tube is, for all practical purposes, infinite, the particle is moving in an infinite potential well

$$
V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & \text{otherwise} \end{cases}
\tag{5.100}
$$

The problem is to solve the time-independent Schrodinger equation (5.35) in this potential.

In the interval $x \in [0, L]$, the time-independent Schrodinger equation is the same as that for a free particle

$$
-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi = E\phi
\tag{5.101}
$$

and has the same solutions for $E > 0$, namely any linear combination

$$
\phi(x) = c_1 e^{ipx/\hbar} + c_2 e^{-ipx/\hbar} \qquad \text{where} \quad p = \sqrt{2mE}
\tag{5.102}
$$

On the other hand, in the regions $x < 0$ and $x > L$, we have

$$
\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \infty\right]\phi = E\phi
\tag{5.103}
$$

The only possible solution of this equation, for finite E, is

$$
\phi(x) = 0 \qquad x < 0 \ \text{ or } \ x > L
\tag{5.104}
$$

which simply means that the probability of finding the particle outside the tube is zero.

The solution of a differential equation must be a continuous function. Continuity of the wavefunction at the points $x = 0$ and $x = L$ gives two boundary conditions

$$\begin{aligned} 0 = \phi(0) &= c_1 + c_2 \\ 0 = \phi(L) &= c_1 e^{ipL/\hbar} + c_2 e^{-ipL/\hbar} \end{aligned} \tag{5.105}$$

The first condition gives $c_2 = -c_1$, and then the second condition becomes

$$2ic_1 \sin\left[\frac{pL}{\hbar}\right] = 0 \tag{5.106}$$

The second equation can be recognized as the condition for a standing wave in an interval of length L, i.e.

$$\sin(kL) = 0 \tag{5.107}$$

which is satisfied for wavenumbers

$$k = \frac{n\pi}{L} \tag{5.108}$$

or, in terms of wavelengths $\lambda = 2\pi/k$,

$$L = n\frac{\lambda}{2} \tag{5.109}$$

In the case of a particle in a tube, the wavenumber k is the same as for de Broglie waves

$$k = \frac{2\pi}{\lambda} = \frac{p}{\hbar} \tag{5.110}$$

and the standing wave requirement $\sin(kL) = 0$ implies

$$\begin{aligned} \frac{pL}{\hbar} &= n\pi \\ \Rightarrow \quad p_n &= n\frac{\pi\hbar}{L} \end{aligned} \tag{5.111}$$

where a subscript n has been added to indicate that each $p = \sqrt{2mE}$ is associated with a positive integer $n = 1, 2, 3, \ldots$. The energy eigenstates are therefore

$$\phi_n(x) = \begin{cases} N \sin\left[\frac{n\pi}{L}x\right] & 0 \le x \le L \\ 0 & \text{otherwise} \end{cases} \tag{5.112}$$

where $N = 2ic_1$, each with a corresponding eigenvalue

$$E_n = \frac{p_n^2}{2m} = n^2\frac{\pi^2\hbar^2}{2mL^2} \tag{5.113}$$

It is useful to normalize $\phi_n(x)$, so that the solution to the time-dependent Schrodinger equation

$$\psi_n(x,t) = \phi_n(x)e^{-iE_nt/\hbar} \tag{5.114}$$

is a physical state. The normalization condition is

$$
\begin{aligned}
1 &= \int_{-\infty}^{\infty} dx\ \psi_n^*(x,t)\psi_n(x,t) \\
&= |N|^2 \int_0^L dx\ \sin^2\left[\frac{n\pi x}{L}\right] \\
&= |N|^2 \frac{L}{2} \tag{5.115}
\end{aligned}
$$

This determines the normalization constant

$$N = \sqrt{\frac{2}{L}} \tag{5.116}$$

so that

$$\left\{\phi_n(x) = \sqrt{\frac{2}{L}}\sin[\frac{n\pi x}{L}], \quad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}\right\}, \quad n = 1,2,3,... \tag{5.117}$$

is the complete set of energy eigenvalues and energy eigenfunctions (in the interval $[0, L]$). Then the general solution of the time-dependent Schrodinger equation, according to eq. (5.38) is

$$
\begin{aligned}
\psi(x,t) &= \sum_{n=1}^{\infty} a_n\phi_n(x)e^{-iE_nt/\hbar} \\
&= \sqrt{\frac{2}{L}}\sum_{n=1}^{\infty} a_n \sin[\frac{n\pi x}{L}]e^{-iE_nt/\hbar} \tag{5.118}
\end{aligned}
$$

Now suppose that the wavefunction $\psi(x,t)$ is specified at an initial time $t = 0$. How do we find the wavefunction at any later time $t > 0$, using eq. (5.118)? The problem is to find the set of constants $\{a_n\}$ given $\psi(x,0)$.

The method for finding the a_n , for the particle in a tube, is closely analogous to solving for $f(p)$ for the free particle in eq. (5.44), given $\psi(x,0)$. Begin with

$$\psi(x,0) = \sum_{n=1}^{\infty} a_n\phi_n(x) \tag{5.119}$$

and multiply both sides of the equation by $\phi_k^*(x)$[3]

$$\phi_k^*(x)\psi(x,0) = \sum_{n=1}^{\infty} a_n\phi_k^*(x)\phi_n(x) \tag{5.120}$$

---

[3]Since ϕ_n is a real function, complex conjugation does nothing. It is indicated here because in general, when the energy eigenstates are complex, this operation is necessary.

Integrate over x

$$\int_0^L dx \; \phi_k^*(x)\psi(x,0) = \sum_{n=1}^{\infty} a_n \int_0^L dx \; \phi_k^*(x)\phi_n(x) \tag{5.121}$$

and use the **orthogonality relation**

$$
\begin{aligned}
< \phi_k | \phi_n > \;\; &= \;\; \int_{-\infty}^{\infty} dx \; \phi_k^*(x)\phi_n(x) \\
&= \;\; \frac{2}{L} \int_0^L dx \; \sin[k\frac{\pi x}{L}] \sin[n\frac{\pi x}{L}] \\
&= \;\; \delta_{kn} \tag{5.122}
\end{aligned}
$$

where δ_{ij} is the Kronecker delta introduced in Lecture 4.

Eq. (5.122) is refered to as orthogonality because it is the expression, for vectors in Hilbert space, which corresponds to the orthogonality relation for unit vectors $\vec{e}^{\,i}$ in an N-dimensional vector space

$$\vec{e}^{\,i} \cdot \vec{e}^{\,j} = \delta_{ij} \tag{5.123}$$

In a later lecture we will see that the set of energy eigenstates $\{|\phi_n >\}$ can (and should) be viewed as a set of orthonormal basis vectors in Hilbert space.

Applying the orthogonality relation, eq. (5.121) becomes

$$
\begin{aligned}
\int_0^L dx \; \phi_k^*(x)\psi(x,0) \;\; &= \;\; \sum_{n=1}^{\infty} a_n \delta_{kn} \\
&= \;\; a_k \tag{5.124}
\end{aligned}
$$

This gives us the complete prescription for finding the physical state of the particle at any time $t > 0$, given the state at an initial time $t = 0$. One has to compute the set of coefficients

$$
\begin{aligned}
a_n \;\; &= \;\; < \phi_n | \psi(t=0) > \\
&= \;\; \int_0^L dx \; \phi_n^*(x)\psi(x,0) \tag{5.125}
\end{aligned}
$$

and substitute these into eq. (5.118) to get the wavefunction $\psi(x,t)$.

The expectation values of position and momentum, as a function of time, can also be expressed in terms of the coefficients a_n. For the position

$$
\begin{aligned}
< x > \;\; &= \;\; \int dx \psi^*(x,t) x \psi(x,t) \\
&= \;\; \int dx \left\{ \sum_{i=1}^{\infty} a_i \phi_i(x) e^{-iE_i t/\hbar} \right\}^* x \sum_{j=1}^{\infty} a_j \phi_j(x) e^{-iE_j t/\hbar} \\
&= \;\; \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} a_i^* a_j e^{i(E_i-E_j)t/\hbar} X_{ij} \tag{5.126}
\end{aligned}
$$

where we have defined

$$
\begin{aligned}
X_{mn} &\equiv \int_0^L \phi_m^*(x) x \phi_n(x) \\
&= \frac{2}{L} \int_0^L dx \ x \sin[m\frac{\pi x}{L}] \sin[n\frac{\pi x}{L}] \\
&= \begin{cases} \frac{1}{2}L & m = n \\ 0 & m - n \text{ even} \\ \frac{2L}{\pi^2}[(m+n)^{-2} - (m-n)^{-2}] & m - n \text{ odd} \end{cases}
\end{aligned} \tag{5.127}
$$

Similarly, for momentum

$$
\begin{aligned}
<p> &= \int dx \psi^*(x,t) \tilde{p} \psi(x,t) \\
&= \int dx \left\{ \sum_{i=1}^{\infty} a_i \phi_i(x) e^{-iE_i t/\hbar} \right\}^* \left(-i\hbar \frac{\partial}{\partial x} \right) \sum_{j=1}^{\infty} a_j \phi_j(x) e^{-iE_j t/\hbar} \\
&= \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} a_i^* a_j e^{i(E_i - E_j)t/\hbar} P_{ij}
\end{aligned} \tag{5.128}
$$

where

$$
\begin{aligned}
P_{mn} &\equiv \int_0^L \phi_m^*(x) \left(-i\hbar \frac{\partial}{\partial x} \right) \phi_n(x) \\
&= -i\hbar \frac{2\pi n}{L^2} \int_0^L dx \ \sin[m\frac{\pi x}{L}] \cos[n\frac{\pi x}{L}] \\
&= \begin{cases} -\frac{i\hbar}{L} \frac{4mn}{m^2 - n^2} & m - n \text{ odd} \\ 0 & m - n \text{ even} \end{cases}
\end{aligned} \tag{5.129}
$$

Example: The Step Function Wavepacket

As an example of the use of these formulas, suppose that a particle is initially in the physical state

$$
\begin{aligned}
\psi(x,0) &= \frac{1}{\sqrt{2a}} \begin{cases} e^{ip_0 x/\hbar} & x_0 - a < x < x_0 + a \\ 0 & \text{otherwise} \end{cases} \\
&= \Theta[a^2 - (x - x_0)^2] e^{ip_0 x/\hbar}
\end{aligned} \tag{5.130}
$$

where $\Theta(x)$ is the step function

$$
\Theta(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases} \tag{5.131}
$$

Problem: Show that this state is normalized, and that the position and expectation values at time $t = 0$ are

$$
<x> = x_0 \qquad <p> = p_0 \tag{5.132}
$$

The real part of $\psi(x,0)$ is sketched in Fig. [5.4]. Then the coefficients a_n are easily calculated:

$$
\begin{aligned}
a_n &= \sqrt{\frac{2}{L}} \int_{x_0-a}^{x_0+a} dx \; e^{ipx/\hbar} \sin[\frac{n\pi x}{L}] \\
&= \sqrt{\frac{2}{L}} \left[\frac{\exp i\left[\frac{p}{\hbar} - \frac{n\pi}{L}\right]x_0}{\frac{p}{\hbar} - \frac{n\pi}{L}} \cos\left[\frac{p}{\hbar} - \frac{n\pi}{L}\right]a \right. \\
&\quad \left. - \frac{\exp i\left[\frac{p}{\hbar} + \frac{n\pi}{L}\right]x_0}{\frac{p}{\hbar} + \frac{n\pi}{L}} \cos\left[\frac{p}{\hbar} + \frac{n\pi}{L}\right]a \right]
\end{aligned}
\tag{5.133}
$$

Now collecting formulas:

$$
\begin{aligned}
\psi(x,t) &= \sqrt{\frac{2}{L}} \sum_{n=1}^{\infty} a_n \sin[\frac{n\pi x}{L}] e^{-iE_n t/\hbar} \\
<x> &= \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} a_i^* a_j e^{i(E_i-E_j)t/\hbar} X_{ij} \\
<p> &= \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} a_i^* a_j e^{i(E_i-E_j)t/\hbar} P_{ij} \\
E_n &= n^2 \frac{\pi^2\hbar^2}{2mL^2}
\end{aligned}
\tag{5.134}
$$

From this set of equations we can calculate $\psi(x,t)$, $<x>$, $<p>$ at any time t to any desired accuracy, by keeping a sufficiently large number of terms in the sums.

Now lets plug in some numbers. Suppose the particle is an electron, p_0 is the momentum corresponding to an energy of 10 eV,

$$
p_0 = 1.7 \times 10^{-24} \text{ kg-m/s}
\tag{5.135}
$$

and also choose

$$
\begin{aligned}
a &= 10^{-8} \text{ m} \\
L &= 10^{-7} \text{ m}
\end{aligned}
\tag{5.136}
$$

The corresponding wavefunction, calculated at various instants, is shown in Fig. [5.5]. The expectation values of position and momentum are plotted as a function of time in Fig. [5.6]. These should be compared to the corresponding figures for $x(t)$ and $p(t)$ for a *classical* pointlike electron of momentum p_0, initially located at the point x_0. Note that the wavefunction for the electron "bounces" from one end of the wall to the other while slowly spreading out. The expectation values of position and momentum, as expected, closely parallel the classical behavior.

Chapter 6

Energy and Uncertainty

We have seen that for a gaussian wavepacket

$$\phi(x) = \frac{1}{(\pi a^2)^{1/4}} e^{-(x-x_0)^2/2a^2} e^{ip_0 x/\hbar} \tag{6.1}$$

the uncertainty in position is $\Delta x = a/\sqrt{2}$, which means that this uncertainty vanishes as $a \to 0$. In this limit, $\phi^* \phi$ approaches a Dirac delta function, and all the probability $P_{dx}(x)$ is concentrated at the point $x = x_0$. If a particle is in such a quantum state when its position is measured, it is *certain* to be found at the point $x = x_0$; this quantum state is known as an **Eigenstate of Position**.

On the other hand, as $a \to \infty$, the gaussian wavepacket (6.1) approaches a plane wave. According to de Broglie, the plane wave represents a particle moving with a *definite* momentum p_0, therefore the uncertainty in momentum should be $\Delta p = 0$ in that limit. If the particle is in a plane wave state when its momentum is measured, it is *certain* to be found to have momentum $p = p_0$; this quantum state is known as an **Eigenstate of Momentum**.

Because the eigenstates of position and momentum are very different, it is impossible for a particle to be in a physical state in which *both* its position *and* its momentum are certain; i.e. $\Delta x = \Delta p = 0$. A simple consequence is that no measurement can determine, precisely and simultaneously, the position and momentum of a particle. If such measurements were possible, they would leave the particle in a physical state having $\Delta x = \Delta p = 0$, and no such quantum state exists. A more quantitative expression of this limitation on measurements is known as the **Heisenberg Uncertainty Principle**. To derive it, we need to be able to compute Δp for an arbitrary physical state.

6.1   The Expectation Value of p^n

According to the Born Interpretation, the expectation value of any function $F(x)$ of position is given by

$$
\begin{aligned}
< F(x) > &= \int F(x) P_{dx}(x) \\
&= \int dx\, F(x) \psi^*(x,t) \psi(x,t)
\end{aligned}
\tag{6.2}
$$

while from Ehrenfest's Principle, one finds that the expectation value of momentum is

$$
<p> = \int dx\, \psi^*(x) \left(-i\hbar \frac{\partial}{\partial x} \right) \psi(x,t)
\tag{6.3}
$$

But we would also like to know how to compute the expectation value of energy

$$
\begin{aligned}
< E > = < H > &= < \frac{p^2}{2m} + V(x) > \\
&= \frac{1}{2m} <p^2> + <V(x)>
\end{aligned}
\tag{6.4}
$$

as well as the uncertainty in momentum

$$
\Delta p^2 = <p^2> - <p>^2
\tag{6.5}
$$

and to evaluate either of these quantities, it is necessary to evaluate $<p^2>$. What is needed is a probability distribution for momentum, $P_{dp}(p)$, analogous to $P_{dx}(x)$, giving the probability that the particle momentum will be found within a small range of momenta around p. This distribution can be deduced from the rule for computing $<p>$, and the inverse Fourier transform representation (5.50).

At a given time t_0, the wavefunction is a function of x only, which we denote, again, by

$$
\phi(x) \equiv \psi(x, t_0)
\tag{6.6}
$$

and expectation value of momentum at that instant is given by

$$
<p> = \int dx \phi^*(x) \left(-i\hbar \frac{\partial}{\partial x} \right) \phi(x)
\tag{6.7}
$$

Expressing $\phi(x)$ in terms of its inverse Fourier transform, eq. (5.50), and proceeding as in eq. (5.75)

$$
\begin{aligned}
<p> &= \int dx\, \phi^*(x) \left(-i\hbar \frac{\partial}{\partial x} \right) \phi(x) \\
&= \int dx \left\{ \int \frac{dp_1}{2\pi\hbar}\, f(p_1) e^{ip_1 x/\hbar} \right\}^* \left(-i\hbar \frac{\partial}{\partial x} \right) \int \frac{dp_2}{2\pi\hbar}\, f(p_2) e^{ip_2 x/\hbar} \\
&= \int \frac{dp_1}{2\pi\hbar}\, f^*(p_1) \int \frac{dp_2}{2\pi\hbar}\, p_2 f(p_2) \int dx\, e^{i(p_2 - p_1)x/\hbar} \\
&= \int \frac{dp_1}{2\pi\hbar}\, f^*(p_1) \int \frac{dp_2}{2\pi\hbar}\, p_2 f(p_2) 2\pi\hbar \delta(p_1 - p_2)
\end{aligned}
\tag{6.8}
$$

Then, using the delta function to eliminate one of the p-integrations, we find

$$< p > = \int dp \, p \frac{f^*(p)f(p)}{2\pi\hbar} \tag{6.9}$$

Comparison of this expression to the corresponding expression for position

$$< x > = \int x P_{dx}(x) \tag{6.10}$$

shows that the probability $P_{dp}(p)$ to find the particle momentum in an infinitesmal range dp around momentum p is

$$P_{dp}(p) = \frac{f^*(p)f(p)}{2\pi\hbar} dp \tag{6.11}$$

Then the expectation value $< G(p) >$ of any function of momentum is given by

$$< G(p) > = \int \frac{dp}{2\pi\hbar} \, G(p) f^*(p) f(p) \tag{6.12}$$

and in particular

$$< p^n > = \int \frac{dp}{2\pi\hbar} \, p^n f^*(p) f(p) \tag{6.13}$$

It is useful to express $< p^n >$ directly in terms of the wavefunction $\phi(x)$, rather than its Fourier transform. Using eq. (5.54) to reexpress $f(p)$ in terms of $\phi(x)$, and inserting this expression into (6.13), we have

$$
\begin{aligned}
< p^n > \ &= \ \int \frac{dp}{2\pi\hbar} p^n \left\{ \int dx_1 \, \phi(x_1) e^{-ipx_1/\hbar} \right\}^* \int dx_2 \, \phi(x_2) e^{-ipx_2/\hbar} \\
&= \ \int dx_1 \, \phi^*(x_1) \int dx_2 \, \phi(x_2) \int \frac{dp}{2\pi\hbar} p^n e^{i(x_1-x_2)p/\hbar} \\
&= \ \int dx_1 \, \phi^*(x_1) \int dx_2 \, \phi(x_2) \left(i\hbar \frac{\partial}{\partial x_2} \right)^n \int \frac{dp}{2\pi\hbar} e^{i(x_1-x_2)p/\hbar} \\
&= \ \int dx_1 \, \phi^*(x_1) \int dx_2 \, \phi(x_2) \left(i\hbar \frac{\partial}{\partial x_2} \right)^n \delta(x_1 - x_2) \tag{6.14}
\end{aligned}
$$

Integrating by parts n times with respect to x_2, this becomes

$$
\begin{aligned}
< p^n > \ &= \ \int dx_1 \int dx_2 \phi^*(x_1) \delta(x_1 - x_2) \left(-i\hbar \frac{\partial}{\partial x_2} \right)^n \phi(x_2) \\
&= \ \int dx \phi^*(x) \left(-i\hbar \frac{\partial}{\partial x} \right)^n \phi(x) \tag{6.15}
\end{aligned}
$$

The conclusion is that the expectation value $< p^n >$ at any time t is just

$$< p^n > = \int dx \, \psi^*(x,t) \, \tilde{p}^n \, \psi(x,t) \tag{6.16}$$

where $\tilde{p}$ is the momentum operator

$$\tilde{p} = -i\hbar \frac{\partial}{\partial x} \tag{6.17}$$

introduced in the last lecture.

6.2   The Heisenberg Uncertainty Principle

Let us use (6.16) to compute the momentum uncertainty Δp for the gaussian wavepacket

$$\phi(x) = \frac{1}{(\pi a^2)^{1/4}} e^{-x^2/2a^2} e^{ip_0 x/\hbar} \tag{6.18}$$

which we already know has a momentum expectation value

$$< p >= p_0 \tag{6.19}$$

and a position uncertainty

$$\Delta x = \frac{a}{\sqrt{2}} \tag{6.20}$$

The squared momentum uncertainty is

$$
\begin{aligned}
\Delta p^2 &= \ <p^2> - <p>^2 = <p^2> - p_0^2 \\
&= \ -\hbar^2 \int dx\, \phi^*(x) \frac{\partial^2}{\partial x^2} \phi(x) \ - \ p_0^2 \\
&= \ -\frac{\hbar^2}{\sqrt{\pi a^2}} \int dx \exp\left(-i\frac{p_0 x}{\hbar} - \frac{x^2}{2a^2}\right) \\
&\quad \times \left[(i\frac{p_0}{\hbar} - \frac{x}{a^2})^2 - \frac{1}{a^2}\right] \exp\left(i\frac{p_0 x}{\hbar} - \frac{x^2}{2a^2}\right) \ - \ p_0^2 \\
&= \ \frac{\hbar^2}{2a^2} \tag{6.21}
\end{aligned}
$$

or

$$\Delta p = \frac{\hbar}{\sqrt{2}a} \tag{6.22}$$

Multiplying Δx and Δp, the product of uncertainties is simply

$$\Delta x \Delta p = \frac{\hbar}{2} \tag{6.23}$$

We will show in the next chapter (the section on the generalized Uncertainty Principle) that $\hbar/2$ is the smallest value for the product of $\Delta x \Delta p$ that can be obtained for *any* wavefunction; wavefunctions which differ from the gaussian wavepacket have products greater than $\hbar/2$. Therefore, *for any physical state, the product of position and momentum uncertainties obeys the inequality*

$$\Delta x \Delta p \geq \frac{\hbar}{2} \tag{6.24}$$

A corollary of this fact is

The Heisenberg Uncertainty Principle

It is impossible, by any measurement process, to simultaneously determine the position and momentum of a particle to an accuracy greater than

$$\Delta x \Delta p = \frac{\hbar}{2} \tag{6.25}$$

If in fact we could determine the position and momentum to an accuracy greater than (6.25), then the particle would be left in a physical state with $\Delta x \Delta p < \hbar/2$. But according to eq. (6.24) there are no such physical states. Therefore, measurements of that kind are impossible.

The Uncertainty Principle is an unavoidable consequence of quantum theory, and if one could design a measurement process which would be more accurate than the bound (6.25), then quantum theory would be wrong. We have already discussed one attempt to measure x and p simultaneously, in the example of the Heisenberg microscope. In that case it was found that the photon composition of light, combined with the Rayleigh criterion of resolution, results in $\Delta x \Delta p \approx \hbar$, which is in agreement with the Uncertainty Principle. There have been other ingenious proposals for measurements which would violate the Uncertainty Principle, especially due to Albert Einstein in his discussions with Niels Bohr.[1] A careful study of these proposals always reveals a flaw. In much the same way that the existence of perpetual motion machines is ruled out by the Second Law of Thermodynamics, the existence of an apparatus which would give a precise determination of position and momentum is in conflict with the nature of physical states in quantum mechanics.

However, the example of Heisenberg's microscope often leads to a misunderstanding that the Uncertainty Principle is simply saying that "the observation disturbs what is being observed." It is true that an observation usually changes the physical state of the observed system. But it is not true that this is full content of the Uncertainty principle. If position-momentum uncertainty were only a matter of light disturbing the observed particle, then we would be free to imagine that a particle really has a definite position and definite momentum at every moment in time, but that the physical properties of light prevent their accurate simultaneous determination. This interpretation is wrong, because if a particle had a definite position and momentum at every moment of time, then the particle would follow a definite trajectory. We have already seen that the assumption that particles follow trajectories is inconsistent with electron interference. The Heisenberg principle is best understood, not as a slogan "the observation disturbs what is observed," but rather as a consequence of the nature of physical states in quantum mechanics, which cannot be simultaneously eigenstates of position and momentum. The fact that uncertainties

---

[1]c.f. Niels Bohr, "Discussions with Einstein," in *Atomic Physics and Human Knowledge*, available on loan in my office.

in position and momentum exist independent of any "disturbance" of the system by observation, and that these uncertainties have important physical consequences, is very well illustrated by the stability of the Hydrogen atom.

• Why the Hydrogen Atom is Stable

Suppose the wavefunction of an electron is concentrated, more or less uniformly, in a sphere of radius R around the nucleus, and falls rapidly to zero outside this sphere. The precise form of the wavefunction is not so important, because we only want to make a very rough estimate of the electron energy, whose expectation value is given by

$$
\begin{aligned}
< H > \ &= \ < \text{Kinetic Energy} > + < \text{Potential Energy} > \\
&= \ < \frac{p^2}{2m} > + < -\frac{e^2}{r} > \\
&= \ \int d^3x \ \psi^*(x,y,z,t)(-\frac{\hbar^2}{2m}\nabla^2)\psi(x,y,z,t) \\
&+ \ \int d^3x \ \psi^*(x,y,z,t)(-\frac{e^2}{r})\psi(x,y,z,t) \quad (6.26)
\end{aligned}
$$

First of all we can estimate the expectation value of the potential energy, which is roughly

$$
< V > \sim -\frac{e^2}{R} \quad (6.27)
$$

Next, the uncertainty in the particle position is

$$
\Delta x \approx \Delta y \approx \Delta z \sim R \quad (6.28)
$$

which implies, by the Uncertainty Principle,

$$
\Delta p_x \approx \Delta p_y \approx \Delta p_z \sim \frac{\hbar}{2R} \quad (6.29)
$$

and the expectation value of kinetic energy is therefore on the order

$$
\begin{aligned}
< KE > \ &= \ \frac{1}{2m} < p_x^2 + p_y^2 + p_z^2 > \\
&= \ \frac{1}{2m}(\Delta p_x^2 + \Delta p_y^2 + \Delta p_z^2) \\
&\sim \ \frac{3\hbar^2}{8mR^2} \quad (6.30)
\end{aligned}
$$

The expectation value of the total energy is then

$$
< H > = \frac{3\hbar^2}{8mR^2} - \frac{e^2}{R} \quad (6.31)
$$

The total energy is minimized for $d < H > /dR = 0$, and this minimum is obtained at

$$R = \frac{3\hbar^2}{4me^2} \tag{6.32}$$

which is not very far off the Bohr radius

$$r_1 = \frac{\hbar^2}{me^2} \tag{6.33}$$

We can now understand why the electron doesn't fall into the nucleus. The potential energy is minimized by an electron localized at $r = 0$. However, the more localized an electron wavefunction is, the smaller Δx is, and the smaller Δx is, the greater is the uncertainty in Δp. But the greater the value of Δp, the greater is the expectation value of kinetic energy

$$< \frac{p^2}{2m} > \sim \frac{\hbar^2}{2m\Delta x^2} \tag{6.34}$$

and at some point this (positive) kinetic energy overwhelms the (negative) Coulomb potential, which goes like $-e^2/\Delta x$. This is why the minimum electron energy in the Hydrogen atom is obtained by a wavefunction of some finite extent, on the order of the Bohr radius.

The application of the Uncertainty principle to the Hydrogen atom shows that there is much more to this principle than simply the fact that an observation disturbs an observed object. There are very many hydrogen atoms in the universe; very few of them are under observation. If Δp were due to a disturbance by observation, then there would be nothing to prevent an unobserved electron from falling into the nucleus. Nevertheless, all hydrogen atoms, observed or not, have a stable ground state, and this is due to the fact that there is no physical state in which an electron is both localized, and at rest.

Problem: Compute the expectation value of the kinetic and potential energy from eq. (6.26), using the gaussian wavepacket in three dimensions

$$\phi(x, y, z) = N \exp[-(x^2 + y^2 + z^2)/2R^2] \tag{6.35}$$

(apply the normalization condition to determine N). In computing the expectation value of the potential energy, the formula for spherical coordinates

$$\int dx dy dz \ f(r) = 4\pi \int dr \ r^2 f(r) \tag{6.36}$$

may be useful. Find the value of R which minimizes $< H >$, and compare this value to the Bohr radius. Also compare numerically the minimum value of $< H >$ to the ground state energy E_1 of the Bohr atom.

6.3   The Energy of Energy Eigenstates

We have seen that the expectation value of energy is given by

$$< E >= \int dx \; \psi^*(x,t)\tilde{H}\psi(x,t) \tag{6.37}$$

but of course a series of experiments can give much more information about the energy distribution than just $< E >$. According to Bohr's model of the Hydrogen atom, an orbiting electron can be found to have only certain definite energies

$$E_n = -\left(\frac{me^4}{2\hbar^2}\right)\frac{1}{n^2} \tag{6.38}$$

and there must be some truth to this idea, because it explains atomic spectra so well. We would like to use the Schrodinger equation to compute which energies are possible for an orbiting electron or for any other system, and the probabilities of finding these energies in a measurement process.

A first sign that the energies of bound states may be discrete comes from the particle in a tube, where it was found that the energy eigenvalues are

$$E_n = n^2\frac{\pi^2\hbar^2}{2mL^2} \tag{6.39}$$

The question is: In what way are the energy eigenvalues of the time-independent Schrodinger equation related to the energies that might actually be found in a particular measurement? We now show, using eq. (6.37), and the orthogonality property (see below) of the energy eigenstates

$$< \phi_n|\phi_m >= 0 \quad \text{if} \quad E_n \neq E_m \tag{6.40}$$

that the set of energy eigenvalues coincides with the set of energies that can be found by measurement, and also show how to compute the probability associated with each energy.

For simplicity, assume that the eigenvalues are discrete and non-degenerate, which means that no two eigenvalues are equal. To prove the orthogonality property (6.40), begin by considering the quantity

$$H_{mn} = \int dx \; \phi_m^*(x) \; \tilde{H} \; \phi_n(x) \tag{6.41}$$

From the time-independent Schrodinger equation

$$\tilde{H}\phi_k(x) = E_k\phi_k(x) \tag{6.42}$$

this becomes

$$\begin{aligned} H_{mn} &= E_n \int dx \; \phi_m^*(x)\phi_n(x) \\ &= E_n < \phi_m|\phi_n > \end{aligned} \tag{6.43}$$

On the other hand, using the integration by parts formula (5.7),

$$
\begin{aligned}
H_{mn} &= \int dx \left\{ -\frac{\hbar^2}{2m} \phi_m^* \frac{\partial^2 \phi_n}{\partial x^2} + V(x) \phi_m^* \phi_n \right\} \\
&= \int dx \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2 \phi_m^*}{\partial x^2} \phi_n + V(x) \phi_m^* \phi_n \right\} \\
&= \int dx \, (\tilde{H} \phi_m)^* \phi_n \\
&= E_m^* < \phi_m | \phi_n >
\end{aligned}
\tag{6.44}
$$

Comparing (6.43) and (6.44),

$$
E_n < \phi_m | \phi_n > = E_m^* < \phi_m | \phi_n >
\tag{6.45}
$$

For the case $n = m$, this equation implies

$$
E_n = E_n^*
\tag{6.46}
$$

i.e. the energy eigenvalues are real, while for $n \neq m$

$$
(E_n - E_m) < \phi_m | \phi_n > = 0
\tag{6.47}
$$

When the eigenvalues are non-degenerate, it means that

$$
n \neq m \implies E_n \neq E_m
\tag{6.48}
$$

and therefore

$$
< \phi_m | \phi_n > = 0 \qquad (n \neq m)
\tag{6.49}
$$

Choosing the eigenstates ϕ_n to satisfy the normalization condition

$$
< \phi_n | \phi_n > = 1
\tag{6.50}
$$

establishes the relation

$$
< \phi_m | \phi_n > = \delta_{mn}
\tag{6.51}
$$

which we have already seen to be true (eq. (5.122)) in the case of the particle in a tube.

According to eq. (5.38), the general solution to the time-dependent Schrodinger equation can be expressed in terms of the energy eigenstates as

$$
\psi(x, t) = \sum_n a_n \phi_n e^{-iE_n t/\hbar}
\tag{6.52}
$$

Then the energy expectation value is

$$
\begin{aligned}
< E > &= \int dx \left[\sum_n a_m \phi_m e^{-iE_m t/\hbar} \right]^* \tilde{H} \sum_n a_n \phi_n e^{-iE_n t/\hbar} \\
&= \sum_m \sum_n a_m^* a_n e^{-i(E_n - E_m)t/\hbar} E_n < \phi_m | \phi_n > \\
&= \sum_n E_n a_n^* a_n
\end{aligned}
\tag{6.53}
$$

Now recall the expression (4.67), from probability theory, for the expectation value of any quantity Q

$$< Q >= \sum_n Q_n P(Q_n) \tag{6.54}$$

where $\{Q_n\}$ are the set of possible values of the quantity, and $P(Q_n)$ is the probability that the value Q_n will be found by measurement. Comparing (6.53) to (6.54), we find that:

I. The set of energies that can be found by measurement is the set of energy eigenvalues $\{E_n\}$ of the time independent Schrodinger equation; and

II. The probability that a state $\psi(x,t)$ will be found to have an energy E_n is given by the squared modulus of coefficients

$$P(E_n) = |a_n|^2 \tag{6.55}$$

To compute a_n in terms of the wavefunction $\psi(x,t)$, we multiply both sides of (6.52) by $\phi_m^*(x)$, and integrate over x, and use the orthogonality property (6.51)

$$
\begin{aligned}
\int dx \, \phi_m^*(x)\psi(x,t) &= \int dx \, \phi_m^*(x) \sum_n a_n \phi_n e^{-iE_n t/\hbar} \\
< \phi_m|\psi > &= \sum_n a_n e^{-iE_n t/\hbar} < \phi_m|\phi_n > \\
&= \sum_n a_n e^{-iE_n t/\hbar} \delta_{mn} \\
&= a_m e^{-iE_m t/\hbar}
\end{aligned} \tag{6.56}
$$

So we see that

$$a_n(t) \equiv a_n e^{-iE_n t/\hbar} =< \phi_n|\psi > \tag{6.57}$$

and the probability for finding the energy E_n, when the system is in the physical state $|\psi >$, is given by

$$P(E_n) = | < \phi_n|\psi > |^2 \tag{6.58}$$

In particular, for the particle in a tube, the lowest possible energy for the particle is the lowest eigenvalue

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2} \tag{6.59}$$

and the corresponding eigenstate

$$\phi_1(x) = \sqrt{\frac{2}{L}} \sin(\frac{\pi x}{L}) \tag{6.60}$$

is known as the **"ground state."** In general, the ground state is the lowest energy state of a quantum system (in quantum field theory, it is also known as the "vacuum

state"). Energy eigenstates of higher energies are known as **"excited states."** The fact that the ground state energy of the particle in the tube E_1 is greater than zero is another example of the Uncertainty Principle at work. Since the the particle is confined in a region of length L, it means that $\Delta x \leq L$, and therefore

$$\Delta p > \frac{\hbar}{2L} \tag{6.61}$$

Assuming $< p >= 0$, this would give a lower bound to the energy of roughly

$$E \approx \frac{(\Delta p)^2}{2m} > \frac{\hbar^2}{8mL^2} \tag{6.62}$$

and this lower bound is in fact smaller, by some numerical factors, than the true ground state energy E_1 given in (6.59), in agreement with the Uncertainty Principle. Note that the dependence on $\hbar, m, L$ of the lower bound is the same as that of E_1. Again, it is not a question of "the observation disturbing the observed." There is simply no physical state of a particle in a tube which has an energy lower than E_1.

Energy eigenstates are stationary states, in the sense that the time-dependence of the wavefunction is entirely contained in an overall phase factor

$$\psi_\alpha(x,t) = \phi_\alpha(x)e^{-iE_\alpha t/\hbar} \tag{6.63}$$

and this phase cancels out when computing expectation values of any function of x and p, e.g.

$$
\begin{aligned}
< x > \ &= \ \int dx \ \psi_\alpha^*(x,t) \ x \ \psi_\alpha(x,t) \\
&= \ \int dx \ \phi_\alpha^*(x) \ x \ \phi_\alpha(x) \\
< p > \ &= \ \int dx \ \psi_\alpha^*(x,t) \ \tilde{p} \ \psi_\alpha(x,t) \\
&= \ \int dx \ \phi_\alpha^*(x) \ \tilde{p} \ \phi_\alpha(x)
\end{aligned}
\tag{6.64}
$$

Therefore

$$
\begin{aligned}
\partial_t < x > \ &= \ 0 \\
< -\frac{\partial V}{\partial x} > \ &= \ 0
\end{aligned}
\tag{6.65}
$$

where the second equation follows from $\partial_t < p >= 0$, and Ehrenfest's Principle. Note that these equations are similar to the corresponding expressions for a stationary state in classical mechanics: the particle is static, so

$$\partial_t x = 0 \tag{6.66}$$

and it remains static because the force on the particle vanishes, i.e.

$$F = -\frac{\partial V}{\partial x} = 0 \tag{6.67}$$

On the other hand, in classical mechanics the kinetic energy of a stationary state is zero. This is not the case in quantum mechanics. For the example of the particle in a tube, the expectation value of momentum vanishes in an energy eigenstate

$$
\begin{aligned}
< p >_n & = \int_0^L dx \, \phi_n^*(x) \, \tilde{p} \, \phi_n(x) \\
& = \frac{2}{L} \int_0^L dx \, \sin(\frac{n\pi x}{L}) \left(-i\hbar \frac{\partial}{\partial x}\right) \sin(\frac{n\pi x}{L}) \\
& = 0
\end{aligned}
\tag{6.68}
$$

However, as required by the Uncertainty Principle, the uncertainty in momentum is *not* zero:

$$
\begin{aligned}
(\Delta p_n)^2 & = \int_0^L dx \phi_n^*(x) \, (\tilde{p} - <p>_n)^2 \, \phi_n(x) \\
& = \frac{2}{L} \int_0^L dx \, \sin(\frac{n\pi x}{L}) \left(-i\hbar \frac{\partial}{\partial x}\right)^2 \sin(\frac{n\pi x}{L}) \\
& = \frac{n^2 \hbar^2 \pi^2}{L^2}
\end{aligned}
\tag{6.69}
$$

The energy eigenvalues (in this example) are simply given by the kinetic energy which is due to this uncertainty

$$E_n = \frac{(\Delta p_n)^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \tag{6.70}$$

There is no adequate classical picture, either in terms of a particle following a trajectory (in which case $< x >$ changes in time), or of a particle at rest (in which case the kinetic energy vanishes), of the energy eigenstates. These are best pictured as standing waves, which, at a more fundamental level, represent the components of vectors in Hilbert space. Nevertheless, when standing waves of different energies are superimposed, it is possible to produce a wavepacket which, as we have seen in the last lecture, roughly follows a classical trajectory according to Ehrenfest's Principle. This is an important point to keep in mind: Dynamics, non-stationarity, change of any sort in quantum mechanics, implies an uncertainty in the value of energy. If the value of the energy is certain, the system is in an energy eigenstate, and if the system is in an energy eigenstate, the system is stationary.

Chapter 7

Operators and Observations

Is this a dagger I see before me, the handle toward my hand? Come, let me clutch thee! I have thee not, and yet I see thee still. Art thou not, fatal vision, as sensible to feeling as to sight? Or art thou but a dagger of the mind, a false creation, proceeding from the heat-oppressed brain?
- Shakespeare, *Macbeth*

   The mathematical core of quantum mechanics is linear algebra in an infinite number of dimensions. Almost every manipulation in quantum theory can be intepreted as an operation involving inner products and/or matrix multiplication. This is for three reasons. First, as we have seen in Lecture 4, physical states in quantum mechanics are represented by wavefunctions, and any function can be regarded as a vector with a continuous index. Second, the dynamical equation of quantum mechanics, i.e. the Schrodinger equation, is a linear differential equation. As we will see, linear differential operators can be interpreted as infinite-dimensional matrices. Finally, the predictions of quantum mechanics, namely, the probabilities of observing such-and-such an event, are in fact determined by the inner products of vectors in Hilbert Space. This lecture will be devoted to these mathematical aspects of quantum theory.

7.1   Probabilities From Inner Products

We have so far learned how to use the quantum state $|\psi>$ to calculate the expectation value of any function of position, any function of momentum, or any sum of such functions, such as energy. In particular

$$< x > \ = \ \int dx \ \psi^*(x,t) \ \tilde{x} \ \psi(x,t)$$

$$< p > \ = \ \int dx \ \psi^*(x,t) \ \tilde{p} \ \psi(x,t)$$

$$< H > \;\; = \;\; \int dx \; \psi^*(x,t) \; \tilde{H} \; \psi(x,t) \tag{7.1}$$

where

$$\begin{aligned}
\tilde{x}\psi(x,t) &\equiv x\psi(x,t) \\
\tilde{p}\psi(x,t) &\equiv -i\hbar\frac{\partial}{\partial x}\psi(x,t) \\
\tilde{H}\psi(x,t) &\equiv \left\{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right\}\psi(x,t)
\end{aligned} \tag{7.2}$$

The probabilities for finding a particle near a certain position x_0, or momentum p_0, or at a certain energy E_n, are given by

$$\begin{aligned}
P_{dx}(x_0) &= |\psi(x_0)|^2 dx \\
P_{dp}(p_0) &= |\frac{1}{\sqrt{2\pi\hbar}}f(p_0)|^2 dp \\
P(E_n) &= |a_n|^2
\end{aligned} \tag{7.3}$$

where

$$\begin{aligned}
a_n &= < \phi_n|\psi > \\
f(p_0) &= \int dx \; \phi(x)e^{-ip_0 x/\hbar}
\end{aligned} \tag{7.4}$$

A probability is a number, a quantum state $|\psi >$ is a vector. Numbers can be obtained from vectors by taking inner products. The probability $P(E_n)$ is clearly the square modulus of an inner product, and in fact the other two probabilities can also be expressed in that way. Define

$$\begin{aligned}
\phi_{x_0}(x) &\equiv \delta(x - x_0) \\
\phi_{p_0}(x) &\equiv \frac{1}{\sqrt{2\pi\hbar}}e^{ip_0 x/\hbar}
\end{aligned} \tag{7.5}$$

Then we may write

$$\begin{aligned}
\psi(x_0) &= \int dx \; \delta(x - x_0)\psi(x) \\
&= < \phi_{x_0}|\psi >
\end{aligned} \tag{7.6}$$

and also

$$\begin{aligned}
\frac{1}{\sqrt{2\pi\hbar}}f(p) &= \int dx \; \left[\frac{1}{\sqrt{2\pi\hbar}}e^{ip_0 x/\hbar}\right]^* \psi(x,t) \\
&= < \phi_{p_0}|\psi >
\end{aligned} \tag{7.7}$$

In terms of ϕ_{x_0}, ϕ_{p_0}, ϕ_n, the probabilities can be rewritten as follows:

$$
\begin{aligned}
P_{dx}(x_0) &= |<\phi_{x_0}|\psi>|^2 dx \\
P_{dp}(p_0) &= |<\phi_{p_0}|\psi>|^2 dp \\
P(E_n) &= |<\phi_n|\psi>|^2
\end{aligned}
\tag{7.8}
$$

The (generalized) functions ϕ_{x_0}, ϕ_{p_0}, ϕ_n all share two things in common. First, they all satisfy **Eigenvalue Equations**:

$$
\begin{aligned}
\tilde{x}\phi_{x_0}(x) &= x_0\phi_{x_0}(x) \\
\tilde{p}\phi_{p_0}(x) &= p_0\phi_{p_0}(x) \\
\tilde{H}\phi_n(x) &= E_n\phi_n(x)
\end{aligned}
\tag{7.9}
$$

The functions ϕ_{x_0}, ϕ_{p_0}, ϕ_n are known as "**Eigenfunctions**" or "**Eigenstates**" (the terms are synonymous), of the operators $\tilde{x}$, $\tilde{p}$, $\tilde{H}$ respectively, and the corresponding numbers x_0, p_0, E_n are known as "**Eigenvalues**". Secondly, the inner products of these eigenstates are either delta-functions or Kronecker deltas, depending on whether the eigenvalues belong to a continuous range ($x_0, p_0 \in [-\infty, \infty]$), or a discrete set ($E_n \in \{E_k\}$):

$$
\begin{aligned}
<\phi_{x_1}|\phi_{x_2}> &= \int dx\, \delta(x-x_1)\delta(x-x_2) \\
&= \delta(x_1-x_2) \\
<\phi_{p_1}|\phi_{p_2}> &= \int dx\, \frac{1}{2\pi\hbar}e^{i(p_2-p_1)x/\hbar} \\
&= \delta(p_1-p_2) \\
<\phi_n|\phi_m> &= \delta_{nm}
\end{aligned}
\tag{7.10}
$$

The relationship that exists between observables x, p, H and operators $\tilde{x}, \tilde{p}, \tilde{H}$, and between probabilites and inner products, generalizes to all other observable quantities of a system.

7.2 Operators and Observables

An **Observable** is any property of a system that can be measured; e.g. position, momentum, energy, angular momentum, magnetic moment, and so on. In classical mechanics, all observables are functions of the generalized coordinates and momenta $\{q^a, p_a\}$, so a knowledge of the physical state implies a knowledge of all possible observables of the system.

An **Operator** is a rule for changing functions into other functions. Given any function $|\psi>$ as input, an operator specifies a unique function $|\psi'>$ as output. Symbolically,

$$
|\psi'> = O|\psi> \quad \text{or} \quad |O\psi>
\tag{7.11}
$$

or, in "component" notation

$$\psi'(x) = \tilde{O}\psi(x) \tag{7.12}$$

A **linear operator** has the property that, for any two functions $|\psi_1 >$ and $\psi_2 >$, and any two constants a and b,

$$O\{a|\phi_1 > +b|\psi_2 >\} = aO|\psi_1 > +bO|\psi_2 > \tag{7.13}$$

Examples of linear operators are multiplication by a constant

$$\tilde{O}\psi(x) = c\psi(x) \tag{7.14}$$

or multiplication by a fixed function $F(x)$,

$$\tilde{O}\psi(x) = F(x)\psi(x) \tag{7.15}$$

or differentiation

$$\tilde{O}\psi(x) = \frac{\partial}{\partial x}\psi(x) \tag{7.16}$$

A non-linear operation could be, e.g., taking a square root

$$\tilde{O}\psi(x) = \sqrt{\psi(x)} \tag{7.17}$$

In Lecture 4 it was noted that any linear operator O has a **matrix representation** $O(x, y)$ such that eq. (7.11) can be written, in component form,

$$\psi'(x) = \int dy \, O(x, y)\psi(y) \tag{7.18}$$

in analogy to matrix multiplication

$$\begin{aligned} \vec{v}' &= M\vec{v} \\ v'_i &= \sum_{i=1}^{N} M_{ij}v_j \end{aligned} \tag{7.19}$$

Given a linear operation $\tilde{O}$, we can always obtain a corresponding matrix representation $O(x, y)$ by using the Dirac delta function

$$\begin{aligned} \tilde{O}\psi(x) &= \tilde{O}\int dy \, \delta(x - y)\psi(y) \\ &= \int dy \, \left[\tilde{O}\delta(x - y)\right]\psi(y) \end{aligned} \tag{7.20}$$

so that

$$O(x, y) = \tilde{O}\delta(x - y) \tag{7.21}$$

An important subset of linear operators are the Hermitian operators. An **Hermitian operator** is a linear operator with the property that

$$< \psi|O|\psi > \ = \ \int dxdy \ \psi^*(x)O(x,y)\psi(y)$$
$$= \ \text{a real number, for any } \psi(x) \text{ whatever} \qquad (7.22)$$

The Relation Between Operators and Observables:

In quantum mechanics, to every observable O there exists a corresponding hermitian operator $\tilde{O}$. Knowledge of the physical state $\psi(x,t)$ at some time t implies a knowledge of the expectation value of every observable, according to the rule

$$< O > \ = \ < \psi|O|\psi >$$
$$= \ \int dx \int dy \ \psi^*(x)O(x,y)\psi(y)$$
$$= \ \int dx \ \psi^*(x) \ \tilde{O} \ \psi(x) \qquad (7.23)$$

This is a principle of quantum mechanics which simply generalizes the examples we have already seen.

$\underline{O = \text{position}}$

$$< x > \ = \ < \psi|x|\psi >$$
$$\tilde{x}\psi(x) \ = \ x\psi(x)$$
$$X(x,y) \ = \ x\delta(x-y) \qquad (7.24)$$

$\underline{O = \text{momentum}}$

$$< p > \ = \ < \psi|p|\psi >$$
$$\tilde{p}\psi(x) \ = \ -i\hbar\frac{\partial}{\partial x}\psi(x)$$
$$P(x,y) \ = \ -i\hbar\frac{\partial}{\partial x}\delta(x-y) \qquad (7.25)$$

$\underline{O = \text{energy}}$

$$
\begin{aligned}
E &= <\psi|H|\psi> \\
\tilde{H}\psi(x) &= \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) \\
H(x,y) &= \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\delta(x-y)
\end{aligned}
\tag{7.26}
$$

Note that

$$
\tilde{H} = H[\tilde{p},x] = \frac{\tilde{p}^2}{2m} + V(x) \tag{7.27}
$$

so that, as noted in Lecture 5, the operator corresponding to the Hamiltonian function is obtained by replacing the momentum p by the momentum operator $\tilde{p}$.

The reason that an observable must correspond to an *Hermitian* operator is that expectation values are real numbers. The reality condition (7.22) requires, for an Hermitian operator,

$$
\begin{aligned}
<\psi|O|\psi> &= <\psi|O|\psi>^* \\
\int dxdy\, \psi^*(x)O(x,y)\psi(y) &= \int dxdy\, \psi(x)O^*(x,y)\psi^*(y) \\
&= \int dxdy\, \psi^*(y)O^*(x,y)\psi(x) \\
&= \int dxdy\, \psi^*(x)O^*(y,x)\psi(y) \\
&= \int dxdy\, \psi^*(x)O^\dagger(x,y)\psi(y) \\
&= <\psi|O^\dagger|\psi>
\end{aligned}
\tag{7.28}
$$

where we renamed variables $x \rightarrow y$ and $y \rightarrow x$ in the second to last line. The operator $\tilde{O}^\dagger$ is known as the **Hermitian Conjugate** of the operator $\tilde{O}$. It is pronounced **"O-dagger,"** and has matrix elements

$$
O^\dagger(x,y) = O^*(y,x) \tag{7.29}
$$

An operator is Hermitian iff

$$
\tilde{O}\psi(x) = \tilde{O}^\dagger\psi(x) \tag{7.30}
$$

or, in matrix representation

$$
\int dy\, O(x,y)\psi(y) = \int dy\, O^*(y,x)\psi(y) \tag{7.31}
$$

for any physical state $|\psi>$.

This hermiticity relation is quite restrictive; for example, it is not even satisfied by the simple operation of differentiation:

$$\tilde{O}\psi(x) = \frac{\partial}{\partial x}\psi(x) \tag{7.32}$$

In that case

$$O(x, y) = \frac{\partial}{\partial x}\delta(x - y) \tag{7.33}$$

so that

$$O^\dagger(x, y) = \frac{\partial}{\partial y}\delta(y - x) \tag{7.34}$$

and therefore

$$
\begin{aligned}
\tilde{O}^\dagger\psi(x) &= \int dy O^\dagger(x, y)\psi(y) \\
&= \int dy \left[\frac{\partial}{\partial y}\delta(y - x)\right]\psi(y) \\
&= \int dy\, \delta(x - y)\left[-\frac{\partial\psi}{\partial y}\right] \\
&= -\frac{\partial}{\partial x}\psi(x) \\
&= -\tilde{O}\psi(x)
\end{aligned}
\tag{7.35}
$$

Since $\tilde{O}$ is not hermitian in this case, it is possible for $<\psi|O|\psi>$ to be imaginary. In fact, for the gausian wavepacket (6.1)

$$
\begin{aligned}
<\phi|O\phi> &= \frac{1}{\sqrt{\pi a^2}}\int dx\, \exp[-\frac{x^2}{2a^2} - i\frac{p_0 x}{\hbar}]\frac{\partial}{\partial x}\exp[-\frac{x^2}{2a^2} + i\frac{p_0 x}{\hbar}] \\
&= i\frac{p_0}{\hbar}
\end{aligned}
\tag{7.36}
$$

So the derivative operator cannot correspond to a physical observable, because it would lead to imaginary expectation values.

The operators of the three examples above, corresponding to the observables of position, momentum, and energy, had therefore better be Hermitian. Lets check this.

Hermiticity of the Position Operator

From the matrix representation

$$X(x, y) = x\delta(x - y) \tag{7.37}$$

we have, from the properties of delta functions,

$$
\begin{aligned}
X^\dagger(x, y) &= X^*(y, x) \\
&= y\delta(y - x) \\
&= x\delta(x - y) \\
&= X(x, y)
\end{aligned}
\tag{7.38}
$$

Therefore the position operator is Hermitian, and $< x >$ is always real.

Hermiticity of the Momentum Operator

The matrix representation of the momentum operator is

$$
\begin{aligned}
P(x,y) &= \tilde{p}\delta(x-y) \\
&= -i\hbar\frac{\partial}{\partial x}\delta(x-y)
\end{aligned}
\tag{7.39}
$$

Then hermitian conjugate of the momentum operator has matrix elements

$$
\begin{aligned}
P^\dagger(x,y) &= P^*(y,x) \\
&= i\hbar\frac{\partial}{\partial y}\delta(x-y)
\end{aligned}
\tag{7.40}
$$

and we have

$$
\begin{aligned}
\tilde{p}^\dagger\psi(x) &= \int dy\, P^\dagger(x,y)\psi(y) \\
&= \int dy\,\left[i\hbar\frac{\partial}{\partial y}\delta(x-y)\right]\psi(y) \\
&= \int dy\,\delta(x-y)\left[-i\hbar\frac{\partial}{\partial y}\right]\psi(y) \\
&= -i\hbar\frac{\partial}{\partial x}\psi(x) \\
&= \tilde{p}\psi(x)
\end{aligned}
\tag{7.41}
$$

Therefore the momentum operator is Hermitian, and $< p >$ is always real.

Hermiticity of the Hamiltonian Operator

In this case

$$
\begin{aligned}
\tilde{H}^\dagger\psi(x) &= \int dy\,\left[\left\{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}+V(y)\right\}\delta(x-y)\right]\psi(y) \\
&= -\frac{\hbar^2}{2m}\int dy\,\psi(y)\frac{\partial^2}{\partial y^2}\delta(x-y)\ +\ \int dy\,V(y)\delta(x-y)\psi(y) \\
&= \frac{\hbar^2}{2m}\int dy\,\frac{\partial\psi}{\partial y}\frac{\partial}{\partial y}\delta(x-y)\ +\ V(x)\psi(x) \\
&= -\frac{\hbar^2}{2m}\int dy\,\frac{\partial^2\psi}{\partial y^2}\delta(x-y)\ +\ V(x)\psi(x) \\
&= \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\psi(x) \\
&= \tilde{H}\psi(x)
\end{aligned}
\tag{7.42}
$$

where we have integrated twice by parts. This establishes the hermiticity of the Hamiltonian.

The Hermitian conjugate $\tilde{O}^\dagger$ of any linear operator $\tilde{O}$, hermitian or not, has the following important property:

$$< \psi_1|O|\psi_2 >=< O^\dagger\psi_1|\psi_2 > \tag{7.43}$$

for any $|\psi_1 >$ and $|\psi_2 >$. This is because

$$
\begin{aligned}
< \psi_1|O|\psi_2 > &= \int dx \int dy \, \psi_1^*(x)O(x,y)\psi_2(y) \\
&= \int dy \left[\int dx \, O(x,y)\psi_1^*(x)\right]\psi_2(y) \\
&= \int dy \left[\int dx \, O^*(x,y)\psi_1(x)\right]^* \psi_2(y) \\
&= \int dy \left[\int dx \, O^\dagger(y,x)\psi_1(x)\right]^* \psi_2(y) \\
&= < O^\dagger\psi_1|\psi_2 >
\end{aligned}
\tag{7.44}
$$

In particular, for an Hermitian operator

$$< \psi_1|O|\psi_2 >=< O\psi_1|\psi_2 > \tag{7.45}$$

Exercise: Show that the Hermitian conjugate of a product of linear operators A, B, C, D is given by

$$(ABCD)^\dagger = D^\dagger C^\dagger B^\dagger A^\dagger \tag{7.46}$$

7.3   Eigenstates As States of Zero Uncertainty

What does a measurement *do*?

A measurement apparatus is designed to determine the value of some observable O, and by doing so it must leave the system in a physical state in which the value of that observable is a definite number. But that means that the system is left in a state for which the uncertainty ΔO of the observable vanishes, at least at the instant the measurement is performed. If, for example, the position of a particle is measured precisely, then the particle is *known* to be at that position the instant the measurement is performed; the physical state must resemble a Dirac delta function. Likewise, if the momentum of a particle is measured, the particle is *known* to have that momentum, and the physical state must resemble a plane wave. In general, whatever the state of the system may be just before the measurement, the outcome of a measurement is a state of "zero-uncertainty" $\Delta O = 0$ in the observable O. Exactly *how* a measurement apparatus accomplishes this feat is a question which will not concern us now, but will be taken up later in the course.

From the fact that every observable $O = x, p, E, ...$ is associated with an Hermitian operator $\tilde{O} = \tilde{x}, \tilde{p}, \tilde{H}, ...$, we see that a zero-uncertainty state $\phi(x)$ must have the property

$$(\Delta O)^2 = <\phi|(O- <O>)^2|\phi> = 0 \tag{7.47}$$

Denote the expectation value $<O>$ by λ, and define

$$\tilde{D} \equiv \tilde{O} - \lambda \tag{7.48}$$

Since $\tilde{O}$ is Hermitian, and multiplication by a constant λ is an Hermitian operation, the operator $\tilde{D}$ is also Hermitian. Then, using the hermiticity of $\tilde{D}$

$$\begin{aligned}
(\Delta O)^2 &= <\phi|(D)^2|\phi> \\
&= <\phi|D|D\phi>] \\
&= <\phi|D|\phi'> \\
&= <D\phi|\phi'> \\
&= <\phi'|\phi'> \\
&= \int dx\ \phi'^*(x)\phi'(x)
\end{aligned} \tag{7.49}$$

where we have defined

$$\phi'(x) \equiv \tilde{D}\phi(x) \tag{7.50}$$

Now putting together

$$\begin{aligned}
\Delta O &= 0 \\
(\Delta O)^2 &= \int dx\ \phi'^*(x)\phi'(x) \\
\phi'^*(x)\phi'(x) &\geq 0 \qquad \text{for all } x
\end{aligned} \tag{7.51}$$

we must conclude that

$$\begin{aligned}
0 &= \phi'(x) \\
&= \tilde{D}\phi(x) \\
&= [\tilde{O} - \lambda]\phi(x)
\end{aligned} \tag{7.52}$$

or, in other words, for a zero-uncertainty state

$$\tilde{O}\phi(x) = \lambda\phi(x) \tag{7.53}$$

This an eigenvalue equation, of the form already seen for position, momentum and energy in equation (7.9). Therefore:

I) Any state with vanishing uncertainty in the observable O is an eigenstate of the corresponding Hermitian operator $\tilde{O}$.

A measurement process therefore has the property that, whatever the physical state of the object may be at the time just prior to the measurement, the system is left in one of the eigenstates of $\tilde{O}$ at a time just after the measurement.

We can go further. Given that the expectation value of the observable $< O >$ in the eigenstate ϕ is the eigenvalue λ, and given that the uncertainty $\Delta O = 0$ vanishes, it follows that a measurement of O could only result in the value $O =< O >= \lambda$. Any measurement that was different from the mean value would imply a non-zero uncertainty. But since the result of a measurement is to leave the system in such a zero-uncertainty state, it follows that

II) A measurement of the observable O can only result in a value which is equal to one of the eigenvalues of the corresponding operator $\tilde{O}$.

In general there are many solutions $\phi(x), \lambda$ to the eigenvalue equation (7.53), so it is useful to denote a set of linearly independent solutions as $\{\phi_\alpha(x), \lambda_\alpha\}$, with different solutions distinguished by the value of the subscript α. The eigenvalue equation is written

$$\tilde{O}\phi_\alpha = \lambda_\alpha \phi_\alpha \tag{7.54}$$

with ϕ_α the eigenstate and λ_α the corresponding eigenvalue. If all the eigenvalues are different, the eigenvalues are said to be **non-degenerate**. If there are n linearly-independent eigenstates $\phi_{\alpha_1}, \phi_{\alpha_2}, ..., \phi_{\alpha_n}$ whose eigenvalues are the same, i.e. $\lambda_{\alpha_1} = \lambda_{\alpha_2} = ... = \lambda_{\alpha_n}$, then the eigenvalue is said to be **n-fold degenerate**. For example, the energy eigenvalues of a free particle are two-fold degenergate, because for each eigenvalue E there are two linearly independent eigenstates, e.g.

$$e^{i\sqrt{2mE}/\hbar} \quad \text{and} \quad e^{-i\sqrt{2mE}/\hbar} \tag{7.55}$$

which satisfy

$$\tilde{H}\phi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi = E\phi \tag{7.56}$$

<u>Theorem H1</u>

The eigenvalues of an Hermitian operator are real.

Proof: This follows directly from the definition of an Hermitian operator

$$< \psi|O|\psi > \quad \text{is real} \tag{7.57}$$

Choose ψ to be an eigenstate ϕ_α

$$< \phi_\alpha|O|\phi_\alpha >= \lambda_a < \phi_\alpha|\phi_\alpha > \tag{7.58}$$

Since the inner product of any vector with itself is a real number, it follows that the lhs is real if and only if λ_α is real.

Theorem H2

If two eigenstates of an Hermitian operator correspond to different eigenvalues, then the two eigenstates are orthogonal.

Proof: Suppose $\phi_{\alpha'}$ and $\phi_{\alpha''}$ are eigenstates of an Hermitian operator $\tilde{O}$, and $\lambda_{\alpha'} \neq \lambda_{\alpha''}$. From eq. (7.45), we have

$$
\begin{aligned}
< \phi_{\alpha'} |O| \phi_{\alpha''} > &= < O\phi_{\alpha'} | \phi_{\alpha''} > \\
< \phi_{\alpha'} |\lambda_{\alpha''}| \phi_{\alpha''} > &= < \lambda_{\alpha'}\phi_{\alpha'} | \phi_{\alpha''} > \\
\lambda_{a''} < \phi_{\alpha'} | \phi_{\alpha''} > &= \lambda_{\alpha'}^{*} < \phi_{\alpha'} | \phi_{\alpha''} > \\
\lambda_{a''} < \phi_{\alpha'} | \phi_{\alpha''} > &= \lambda_{a'} < \phi_{\alpha'} | \phi_{\alpha''} >
\end{aligned}
\tag{7.59}
$$

Given that the eigenvalues are different, the only way this equation can hold true is that

$$
< \phi_{\alpha'} | \phi_{\alpha''} > = 0 \tag{7.60}
$$

Theorem H3

For any square-integrable function $\psi(x)$ and any Hermitian operator $\tilde{O}$, the function ψ can always be expressed as some linear combination of the eigenstates of $\tilde{O}$

$$
\psi(x) = \sum_{\alpha} c_{\alpha} \phi_{\alpha}(x) \tag{7.61}
$$

where the sum is replaced by an integral if the eigenvalues span a continuous range.
(We will not try to prove this here.)

With the help of these theorems, we are ready to say something about physics:

The Generalized Born Interpretation (I)

Suppose that an observable O corresponds to a Hermitian operator $\tilde{O}$ whose eigenvalues are discrete and non-degenerate, and whose eigenstates are normalized to

$$
< \phi_{\alpha'} | \phi_{\alpha''} > = \delta_{\alpha'\alpha''} \tag{7.62}
$$

Denote the quantum state of the system at the time of measurement by $|\psi>$. Then:

(I) The outcome of any measurement of the observable will be one of the eigenvalues $\{\lambda_{\alpha}\}$.

(II) The probability $P(\lambda_\alpha)$ that any given eigenvalue will be the result of the measurement is

$$P(\lambda_a) = |<\phi_\alpha|\psi>|^2 \tag{7.63}$$

The argument for eq. (7.63) is identical to the reasoning of Lecture 6 concerning energy eigenvalues. This time, we will carry the argument through in bra-ket notation. The expectation value is given by

$$<O> = <\psi|O|\psi> \tag{7.64}$$

From Theorem H3

$$|\psi> = \sum_\alpha c_\alpha |\phi_\alpha> \tag{7.65}$$

To determine the coefficients c_α, multiply both sides of eq. (7.65) by $<\phi_\beta|$

$$<\phi_\beta|\psi> = \sum_\alpha c_\alpha <\phi_\beta|\phi_\alpha> \tag{7.66}$$

Using Theorem H2

$$<\phi_\beta|\psi> = \sum_\alpha c_\alpha \delta_{\alpha\beta} \tag{7.67}$$

therefore

$$c_\beta = <\phi_\beta|\psi> \tag{7.68}$$

The bra vector $<\psi|$ corresponding to the ket $|\psi>$ is

$$<\psi| = \sum_\alpha c_\alpha^* <\phi_\alpha| \tag{7.69}$$

Substituting these expressions into the expectation value

$$
\begin{aligned}
<O> &= \left[\sum_\alpha c_\alpha^* <\phi_\alpha|\right] O \left[\sum_\beta c_\beta |\phi_\beta>\right] \\
&= \sum_\alpha \sum_\beta c_\alpha^* c_\beta <\phi_\alpha|O|\phi_\beta> \\
&= \sum_\alpha \sum_\beta c_\alpha^* c_\beta <\phi_\alpha|\lambda_\alpha|\phi_\beta> \\
&= \sum_\alpha \sum_\beta \lambda_\alpha c_\alpha^* c_\beta <\phi_\alpha|\phi_\beta> \\
&= \sum_\alpha \sum_\beta \lambda_\alpha c_\alpha^* c_\beta \delta_{\alpha\beta} \\
&= \sum_\alpha \lambda_\alpha c_\alpha^* c_\alpha \\
&= \sum_\alpha \lambda_\alpha |<\phi_\alpha|\psi>|^2 \tag{7.70}
\end{aligned}
$$

Finally, compare this expression for $< O >$ against the expression for an expectation value from probability theory

$$< O >= \sum_{\alpha} O_{\alpha} P[O_{\alpha}] \tag{7.71}$$

where $\{O_{\alpha}\}$ are the possible values that the observable can have. We have already shown, in the beginning of this section, that the only values which can be found by a measurement are the eigenvalues of $\tilde{O}$, i.e.

$$\{O_{\alpha}\} = \{\lambda_{\alpha}\} \tag{7.72}$$

then the probability is uniquely determined to be

$$P(\lambda_a) = |< \phi_{\alpha}|\psi >|^2 \tag{7.73}$$

and this establishes the Generalized Born Interpretation.

Exercise: Write equations (7.64) through (7.73) in component notation (i.e. in terms of functions and integrals over functions).

Let us record and review the solutions to the eigenvalue equations seen thus far:

Eigenstates of Position

For

$$\tilde{x} = x \tag{7.74}$$

the eigenvalue equation is

$$x\phi_{x_0}(x) = x_0\phi_{x_0}(x) \tag{7.75}$$

which has solutions

$$\{\text{eigenstates}\ \ \phi_{x_0}(x) = \delta(x - x_0), \ \ \text{eigenvalues}\ \ x_0 \in [-\infty, \infty]\} \tag{7.76}$$

with inner products

$$< \phi_{x_1}|\phi_{x_2} >= \delta(x_1 - x_2) \tag{7.77}$$

As a consequence of theorem H3, any arbitrary function $\psi(x)$ can be written as a superposition of these eigenstates:

$$\begin{aligned} \psi(x) &= \int dx_0 \ c_{x_0}\phi_{x_0}(x) \\ &= \int dx_0 \ c_{x_0}\delta(x - x_0) \end{aligned} \tag{7.78}$$

which is seen to be satisfied by choosing

$$c_{x_0} = \psi(x_0) \tag{7.79}$$

Eigenstates of Momentum

For

$$\tilde{p} = -i\hbar \frac{\partial}{\partial x} \tag{7.80}$$

the eigenvalue equation is

$$-i\hbar \frac{\partial}{\partial x} \phi_{p_0}(x) = p_0 \phi_{p_0}(x) \tag{7.81}$$

which has solutions

$$\left\{ \text{eigenstates} \ \ \phi_{p_0}(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ip_0 x/\hbar}, \ \ \text{eigenvalues} \ \ p_0 \in [-\infty, \infty] \right\} \tag{7.82}$$

with inner products

$$< \phi_{p_1} | \phi_{p_2} > = \delta(p_1 - p_2) \tag{7.83}$$

As a consequence of theorem H3, any arbitrary function $\psi(x)$ can be written as a superposition of these eigenstates:

$$\psi(x) = \int dp_0 \ c_{p_0} \phi_{p_0}(x) \tag{7.84}$$

The coefficient function c_{p_0} is obtained by multiplying both sides of this equation by $\phi_{p_1}^*(x)$, and integrating over x

$$
\begin{aligned}
\int dx \ \phi_{p_1}^*(x)\psi(x) &= \int dx \int dp_0 \ c_{p_0} \phi_{p_1}^*(x)\phi_{p_0}(x) \\
\frac{1}{\sqrt{2\pi\hbar}} \int dx \ \psi(x) e^{-ip_1 x/\hbar} &= \int \frac{dp_0}{2\pi\hbar} c_{p_0} \int dx \ e^{i(p_0 - p_1)x/\hbar} \\
&= \int dp \ c_{p_0} \delta(p_1 - p_2) \tag{7.85}
\end{aligned}
$$

or

$$c_p = \frac{1}{\sqrt{2\pi\hbar}} \int dx \ \psi(x) e^{-ip_1 x/\hbar} \tag{7.86}$$

Eigenstates of Energy: The Particle in a Tube

The Hamiltonian operator is

$$\tilde{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \tag{7.87}$$

where $V(x)$ for the particle in a tube was given in eq. (5.100). The eigenvalue equation is the time-independent Schrodinger equation

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \phi_n(x) = E_n \phi_n(x) \tag{7.88}$$

which has solutions

$$\left\{ \text{eigenstates} \ \ \phi_n(x) = \sqrt{\frac{2}{L}} \sin[\frac{n\pi x}{L}], \ \ \text{eigenvalues} \ \ E_n = n^2 \frac{\hbar^2 \pi^2}{2mL^2},, \ \ n = 1, 2, 3, ... \right\}$$
(7.89)

The eigenstates have inner products

$$< \phi_n | \phi_m > = \delta_{nm}$$
(7.90)

Once again, theorem H3 insists that any arbitrary function $\psi(x)$ can be written as a linear combination[1]

$$
\begin{aligned}
\psi(x) &= \sum_{n=1}^{\infty} c_n \phi_n(x) \\
&= \sqrt{\frac{2}{L}} \sum_{n=1}^{\infty} c_n \sin[\frac{n\pi x}{L}]
\end{aligned}
$$
(7.91)

This is a Fourier series, and it is well known that any function in the interval $[0, L]$ can be expressed in this form. The coefficients c_n are obtained in the same way as before, i.e. by multiplying both sides by ϕ_m^* and integrating over x:

$$
\begin{aligned}
|\psi> &= \sum_{n=1}^{\infty} c_n \phi_n(x) \\
< \phi_m | \psi> &= \sum_{n=1}^{\infty} c_n < \phi_m | \phi_n > \\
&= \sum_{n=1}^{\infty} c_n \delta_{nm}
\end{aligned}
$$
(7.92)

and we find

$$
\begin{aligned}
c_m &= < \phi_m | \psi> \\
&= \sqrt{\frac{2}{L}} \int_0^L dx \ \sin[\frac{m\pi x}{L}] \psi(x)
\end{aligned}
$$
(7.93)

7.4   The Generalized Uncertainty Principle

Suppose we want to devise a measurement apparatus that will measure two observables A and B simultanously. From the discussion of previous sections, it is clear

---

[1]We exclude pathological cases for which $< E >= \infty$, such as wavefunctions which are non-zero in the regions $x < 0$ or $x > L$.

that the result of such a measurement will be to leave the system in a state of zero uncertainty in both observables, i.e. $\Delta A = \Delta B = 0$, and that means that the physical state would have to be an eigenstate of both both $\tilde{A}$ and $\tilde{B}$. Now, it may or may not be true that such physical states exist, in general, for all possible eigenvalues of $\tilde{A}$ and $\tilde{B}$. If not, then it is not possible to measure the observables A and B simultanously. For example, in the case of position x and momentum p, there are no physical states which are eigenstates of both $\tilde{x}$ and $\tilde{p}$; this is why it is impossible to measure both x and p simultaneously and precisely.

There is a simple test for whether or not two observables can be measured simultaneously, which requires the concept of the commutator. The **Commutator** of two operators is defined to be

$$[\tilde{A}, \tilde{B}] \equiv \tilde{A}\tilde{B} - \tilde{B}\tilde{A} \tag{7.94}$$

If $[\tilde{A}, \tilde{B}] = 0$, the two operators are said to commute. Commutators are computed by letting them act on an arbitrary function. For example:

$$[\tilde{x}, \tilde{x}^2]f(x) = (xx^2 - x^2 x)f(x) = 0 \tag{7.95}$$

therefore $\tilde{x}$ and $\tilde{x}^2$ commute, i.e.

$$[\tilde{x}, \tilde{x}^2] = 0 \tag{7.96}$$

Similarly

$$
\begin{aligned}
[\tilde{x}, \tilde{p}_y]f(x, y, z) &= \left[x(-i\hbar\frac{\partial}{\partial y}) - (-i\hbar\frac{\partial}{\partial y})x\right]f(x) \\
&= -i\hbar\left[(x\frac{\partial f}{\partial y} - x\frac{\partial f}{\partial y}\right] \\
&= 0
\end{aligned}
\tag{7.97}
$$

which means that $\tilde{x}$ and $\tilde{p}_y$ commute,

$$[\tilde{x}, \tilde{p}_y] = 0 \tag{7.98}$$

However,

$$
\begin{aligned}
[\tilde{x}, \tilde{p}]f(x) &= \left[x(-i\hbar\frac{\partial}{\partial x}) - (-i\hbar\frac{\partial}{\partial x})x\right]f(x) \\
&= -i\hbar\left(x\frac{\partial f}{\partial x} - \frac{\partial}{\partial x}(xf)\right) \\
&= -i\hbar\left(x\frac{\partial f}{\partial x} - x\frac{\partial f}{\partial x} - f\right) \\
&= i\hbar f
\end{aligned}
\tag{7.99}
$$

From this we can conclude that the operators corresponding to position along the x-axis, and momentum in the x-direction, do *not* commute, and that

$$[\tilde{x}, \tilde{p}] = i\hbar \tag{7.100}$$

Problem: Compute the commutators: $[\tilde{H}, \tilde{x}]$, $[\tilde{H}, \tilde{p}]$, $[\tilde{p}^2, \tilde{x}^2]$.

The condition that two observables can be measured simultaneously is then stated by:

The Commutator Theorem

Two observables A and B are simultaneously measureable (have the same set of eigenstates) if and only their corresponding operators commute, i.e. $[\tilde{A}, \tilde{B}] = 0$.

The fact that position and momentum are not simultaneously observable is a special case of this theorem. For simplicity, we will prove theorem only in the case that the eigenvalues of $\tilde{A}$ and $\tilde{B}$ are discrete and non-degenerate.

Let us begin with the "if" part of the theorem: $[\tilde{A}, \tilde{B}] = 0$ implies that eigenstates of $\tilde{A}$ are eigenstates of $\tilde{B}$ and vice versa. Now $[\tilde{A}, \tilde{B}] = 0$ means that

$$\tilde{A}\tilde{B}f(x) = \tilde{B}\tilde{A}f(x) \tag{7.101}$$

and let ϕ_a be any eigenstate of $\tilde{A}$, i.e.

$$\tilde{A}\phi_a = a\phi_a \tag{7.102}$$

Then

$$\begin{aligned} \tilde{A}\tilde{B}\phi_a(x) &= \tilde{B}\tilde{A}\phi_a(x) \\ &= a\tilde{B}\phi_a(x) \end{aligned} \tag{7.103}$$

Now if we define

$$\phi'_a = \tilde{B}\phi_a \tag{7.104}$$

then eq. (7.103) becomes

$$\tilde{A}\phi'_a = a\phi'_a \tag{7.105}$$

which means that ϕ'_a is an eigenstate of $\tilde{A}$ with eigenvalue a. But since the eigenvalues of $\tilde{A}$ are non-degenerate, it can only be that ϕ'_a is proportional to ϕ_a, i.e.

$$\phi'_a(x) = b\phi_a(x) \tag{7.106}$$

where b is some constant. In that case, from the definition of ϕ',

$$\tilde{B}\phi_a(x) = b\phi_a(x) \tag{7.107}$$

This proves that every eigenstate of $\tilde{A}$ is an eigenstate of $\tilde{B}$. Such states are zero-uncertainty states of both A and B, so simultaneous measurement is possible.

Next we prove the "only if" part of the commutator theorem. Suppose the outcome of a measurement is that $A = a$ and $B = b$. Since the eigenvalues of $\tilde{A}$ are non-degenerate, the resulting physical state is ϕ_a, where

$$\tilde{A}\phi_a = a\phi_a \tag{7.108}$$

However, this must also be a zero-uncertainty state for B, and therefore

$$\tilde{B}\phi_a = b\phi_a \tag{7.109}$$

It follows that

$$\begin{aligned} AB|\phi_a> &= bA|\phi_a> \\ &= ba|\phi_a> \end{aligned} \tag{7.110}$$

while

$$\begin{aligned} BA|\phi_a> &= aB|\phi_a> \\ &= ab|\phi_a> \end{aligned} \tag{7.111}$$

therefore

$$\begin{aligned} [A,B]|\phi_a> &= (AB-BA)|\phi_a> \\ &= (ba-ab)|\phi_a> \\ &= 0 \end{aligned} \tag{7.112}$$

Now, according to theorem H3, any square-integrable function can be represented as a linear combination of eigenstates of $\tilde{A}$, i.e.

$$|f> = \sum_a c_a|\phi_a> \tag{7.113}$$

and this means that

$$\begin{aligned} [\tilde{A},\tilde{B}]|f> &= \sum_a c_a[\tilde{A},\tilde{B}]|\phi_a> \\ &= 0 \end{aligned} \tag{7.114}$$

If the operator $[\tilde{A},\tilde{B}]$ acting on any function $f(x)$ gives 0, then the operator itself is zero

$$[\tilde{A},\tilde{B}] = 0 \tag{7.115}$$

which proves the "only if" portion of theorem.

The proof above extends trivially to continuous non-degenerate eigenvalues, simply replacing a discrete index by a continuous index, and sums by integrals. The commutator theorem is also true if the eigenvalues are degenerate, but those complications will be postponed to a later lecture.

There is a generalization of the Heisenberg Uncertainty Principle to the case of any two observables which cannot be simultaneously measured:

The Generalized Uncertainty Principle

The uncertainties ΔA and ΔB of any two observables in any physical state $|\psi >$ satisfy the inequality

$$\Delta A \Delta B \geq \frac{1}{2}| < \psi|[A, B]|\psi > | \tag{7.116}$$

Proof: Begin with the expressions for uncertainty

$$
\begin{aligned}
(\Delta A)^2 &= < \psi|(\tilde{A}- < A >)^2|\psi > \\
(\Delta B)^2 &= < \psi|(\tilde{B}- < B >)^2|\psi >
\end{aligned}
\tag{7.117}
$$

and define the Hermitian operators

$$\tilde{D}_A \equiv A- < A > \quad \text{and} \quad \tilde{D}_B = B- < B > \tag{7.118}$$

and also

$$|\psi_1 >= D_A|\psi > \quad \text{and} \quad |\psi_2 >= D_B|\psi > \tag{7.119}$$

Then

$$
\begin{aligned}
(\Delta A)^2 &= < \psi|D_A D_A|\psi > \\
&= < \psi|D_A|\psi_1 > \\
&= < D_A\psi|\psi_1 > \quad \text{(hermiticity)} \\
&= < \psi_1|\psi_1 >
\end{aligned}
\tag{7.120}
$$

Similarly,

$$(\Delta B)^2 =< \psi_2|\psi_2 > \tag{7.121}$$

Now, making use of the Cauchy-Schwarz inequality for vectors (see problem below)

$$|u||v| \geq | < u|v > | \tag{7.122}$$

and squaring both sides, we have

$$
\begin{aligned}
|<\psi_1|\psi_1>||<\psi_2|\psi_2>| &\geq |<\psi_1|\psi_2>|^2 \\
(\Delta A)^2(\Delta B)^2 &\geq \frac{1}{2}\left[|<\psi_1|\psi_2>|^2 + |<\psi_2|\psi_1>|^2\right] \\
&\geq \frac{1}{2}\left[|<D_A\psi|D_B\psi>|^2 + |<D_B\psi|D_A\psi>|^2\right] \\
&\geq \frac{1}{2}\left[|<\psi|D_AD_B\psi>|^2 + |<\psi|D_BD_A\psi>|^2\right]
\end{aligned}
$$
$$(7.123)$$

Next write

$$
\begin{aligned}
D_AD_B &= F+G \\
D_BD_A &= F-G
\end{aligned}
$$
$$(7.124)$$

where

$$
\begin{aligned}
F &= \frac{1}{2}(D_AD_B + D_BD_A) \\
G &= \frac{1}{2}[D_A, D_B] = \frac{1}{2}[A, B]
\end{aligned}
$$
$$(7.125)$$

Substituting these expressions into (7.123) we get

$$
\begin{aligned}
(\Delta A)^2(\Delta B)^2 &\geq \frac{1}{2}[(<F> + <G>)(<F> + <G>)^* \\
&\quad + (<F> - <G>)(<F> - <G>)^*] \\
&\geq |<F>|^2 + |<G>|^2 \\
&\geq |<G>|^2 \\
&\geq \frac{1}{4}|<\psi|[A, B]|\psi>|^2
\end{aligned}
$$
$$(7.126)$$

Taking the square root of both sides establishes the generalized Uncertainty Principle. In particular, the Heisenberg Uncertainty principle follows by choosing $A = x$ and $B = p$, in which case

$$
\begin{aligned}
\Delta x \Delta p &\geq \frac{1}{2}|<\psi|i\hbar|\psi>| \\
&\geq \frac{\hbar}{2}
\end{aligned}
$$
$$(7.127)$$

as seen in Lecture 6.

Problem: By minimizing the norm of the vector

$$|u> + q|v>$$
$$(7.128)$$

with respect to q, prove the Cauchy-Schwarz inequality

$$|u||v| \geq |<u|v>|$$
$$(7.129)$$

7.5   The Time-Energy Uncertainty Relation

It was noted, at the end of the last lecture, that change of any kind in a quantum-mechanical system implies an uncertainty in the energy of that system. We would like to quantify this remark: How long does it take for a physical state to change substantially, and how is that length of time related to the energy uncertainty?

Of course, it is necessary to define what is meant by a "substantial" change in the state. Consider position, momentum, or any other observable Q. At a given moment, Q has a certain expectation value $< Q >$, and an uncertainty ΔQ. As time passes, $< Q >$ usually changes in some way. We will say that $< Q >$ has changed "substantially" when it has increased or decreased by an amount equal to the uncertainty ΔQ of the observable. The relation between the time Δt required for such a change, and the energy uncertainty ΔE, is expressed in the form of an inequality known as

The Time-Energy Uncertainty Relation

Let Q be any observable, and let Δt be the time required for the expectation value $< Q >$ to change by an amount equal to its uncertainty ΔQ. Then

$$\Delta t \Delta E \geq \frac{\hbar}{2} \tag{7.130}$$

where ΔE is the uncertainty in the energy of the system.

To prove this statement, let us begin with an expression for the rate of change of the observable

$$
\begin{aligned}
\frac{d}{dt} < Q > &= \frac{d}{dt} \int dx \, \psi^*(x,t) \, \tilde{Q} \, \psi(x,t) \\
&= \int dx \left[\frac{d\psi^*}{dt} \tilde{Q}\psi + \psi^* \tilde{Q} \frac{d\psi}{dt} \right] \\
&= \int dx \left[(\frac{1}{i\hbar}\tilde{H}\psi)^* \tilde{Q}\psi + \psi^* \tilde{Q}(\frac{1}{i\hbar}\tilde{H}\psi \right] \\
&= \frac{1}{i\hbar}[- < H\psi|Q|\psi > + < \psi|Q|H\psi >] \\
&= \frac{1}{i\hbar}[- < \psi|HQ|\psi > + < \psi|QH|\psi >] \\
&= < \psi|\frac{1}{i\hbar}[Q,H]|\psi > \tag{7.131}
\end{aligned}
$$

Then the time Δt required for $< Q >$ to change by an amount equal to its uncertainty ΔQ satisfies

$$\left| \frac{d < Q >}{dt} \right| \Delta t = \Delta Q$$

$$\frac{1}{\hbar}| < \psi|[Q, H]|\psi > |\Delta t \;\; = \;\; \Delta Q \tag{7.132}$$

We now apply the generalized uncertainty principle, eq. (7.116) with $A = Q$ and $B = H$ (note that $\Delta H \equiv \Delta E$)

$$\frac{1}{\hbar}(\Delta Q \Delta E)\Delta t \geq \frac{1}{\hbar}\left(\frac{1}{2}| < \psi|[Q, H]|\psi > |\right)\Delta t = \frac{1}{2}\Delta Q \tag{7.133}$$

or, dividing by ΔQ on both sides

$$\Delta E \Delta t \geq \frac{\hbar}{2} \tag{7.134}$$

which proves the energy-time uncertainty relation, for *any* observable Q.

   As an example of this uncertainty relation, consider the time required for a free particle to move a distance equal to its uncertainty in position Δx; i.e. for $< x >$ to change by Δx. The wavepacket is moving with a group velocity

$$v_g = \frac{< p >}{m} \tag{7.135}$$

so the time it takes for the packet to move a distance equal to the uncertainty in position is

$$\Delta t = \frac{\Delta x}{v_g} = \frac{m \Delta x}{< p >} \tag{7.136}$$

On the other hand, the uncertainty in energy is related to the uncertainty in momentum via

$$\Delta E = \Delta\left(\frac{p^2}{2m}\right) = \frac{< p > \Delta p}{m} \tag{7.137}$$

Then

$$\begin{aligned}
\Delta t \Delta E \;\; &= \;\; \frac{m \Delta x}{< p >}\frac{< p > \Delta p}{m} \\
&= \;\; \Delta x \Delta p \\
&\geq \;\; \frac{\hbar}{2} \tag{7.138}
\end{aligned}$$

as predicted by the time-energy uncertainty relation.

Chapter 8

Rectangular Potentials

Most of the effort in solving quantum-mechanical problems goes into solving the time-independent Schrodinger equation (243). Given a complete set of solutions to the time-independent equation, the general solution (248) of the time-dependent equation follows immediately.

We have already seen that in the case of a free particle, the energy eigenvalues could take on any value in the range $[0, \infty]$, while in the case of a particle trapped in a tube, the energies could take on only certain discrete values. This distinction between the energies of bound and unbound particles is very general, and in fact the solutions to any time-independent Schrodinger equation, with any potential $V(x)$, are always of two kinds: (i) bound states, which have discrete energy eigenvalues, $E_1, E_2, E_3, ...$; and (ii) unbound or "scattering" states, which have energies in a continuous range $E \in [E_{low}, \infty]$. So we begin this lecture with an explanation of why the energies of bound states are always discrete, and also why the unbound states, which are energy eigenstates and therefore stationary, have something to do with the scattering of particles by a potential, which is of course a dynamic process.

8.1   A Qualitative Sketch of Energy Eigenstates

Consider a particle of total energy E in the potential shown in Fig. [8.1]. In classical physics, if $E < V_{max}$, the particle could never be found in the regions where $V(x) > E$, because that would imply that the kinetic energy $KE = E - V$ was negative. Such intervals are referred to as the **"classically forbidden"** regions; intervals where $E > V(x)$ are the **"classically allowed"** regions. A particle in region II could never get out; it would be a bound state trapped by the potential, forever bouncing between points x_2 and x_3. On the other hand, a particle in region I or III could never enter region II, but would bounce off the potential wall at points x_1 and x_4, respectively.

In quantum mechanics the physical state is governed by the Schrodinger equation, and generally there is no reason that the wavefunction must be exactly zero in regions where $E < V(x)$. This means that there is usually a finite probability to find a par-

ticle in the classically forbidden regions, and this fact gives rise to some remarkable phenomena which are inconceivable at the classical level. Nevertheless, the wavefunction does behave quite differently in the classically allowed and the classically forbidden regions, as one might expect, since classical behavior is an approximation to quantum mechanics, and should become exact in the $\hbar \to 0$ limit.

The time-independent Schrodinger equation is a 2nd order differential equation

$$\frac{d^2\phi}{dx^2} = -\frac{2m}{\hbar^2}(E - V)\phi \tag{8.1}$$

In general, the first derivative of a function $f' = df/dx$ is the slope of $f(x)$, the second derivative $f'' = d^2f/dx^2$ is the curvature. If $f'' > 0$ at point x, then $f(x)$ is concave upwards at that point; similarly, if $f'' < 0$, then $f(x)$ is concave downwards. From eq. (8.1), we can see that:

<u>$E > V$</u> Classically Allowed Region

$$\begin{array}{ll} \phi > 0 & \phi(x) \text{ concave downwards} \\ \phi < 0 & \phi(x) \text{ concave upwards} \end{array} \tag{8.2}$$

Since the wavefunction tends to curve downwards when ϕ is positive, and upward when ϕ is negative, the result is an oscillating wavefunction in the classically allowed regions, as shown in Fig. [8.2].

<u>$E < V$</u> Classically Forbidden Region

$$\begin{array}{ll} \phi > 0 & \phi(x) \text{ concave upwards} \\ \phi < 0 & \phi(x) \text{ concave downwards} \end{array} \tag{8.3}$$

In the classically forbidden regions, oscillatory behavior is impossible, and the wavefunction tends to either grow or decay exponentially, as shown in Fig. [8.3]

We can use this qualitative information to sketch a rough picture of what an energy eigenstate in the potential shown in Fig. [8.1] must look like. Let us begin with $E > V_{max}$. In that case, there are no classically forbidden regions, and the function oscillates everywhere. The curvature, and therefore the rate of oscillation, depends on the ratio

$$\frac{\phi''}{\phi} = -\frac{\hbar^2}{2m}(E - V) \tag{8.4}$$

so that the greater $E - V$ is, the faster the wavefunction oscillates. The general behavior is shown in Fig. [8.4]; an energy eigenstate will look something like this for *any* energy $E > V_{max}$.

Now suppose the energy is in the range $E \in [0, V_{max}]$. Then there will be classically forbidden regions, and in these regions the wavefunction will grow or decay exponentially. In the classically allowed regions, the wavefunction oscillates as shown in Fig. [8.5].

Finally, suppose that $E < 0$. Then, except for a finite interval where $V(x) < 0$ and $E > V$, the entire real line is a classically forbidden region. Typical solutions of the time-independent Schrodinger equation would blow up exponentially as $x \to \pm\infty$. Such wavefunctions are physically meaningless; they say that the particle is infinitely more probable to be found at the "point" $x = \pm\infty$ than anywhere else, but infinity, as we know, is not a point. Wavefunctions of this kind are called **non-normalizable** and do not belong to the Hilbert space of physical states. Non-normalizable solutions of the time-independent Schrodinger equation are simply thrown away in quantum mechanics. Although such wavefunctions satisfy the equation of interest, they do not correspond to physical states.

Almost all solutions with $E < 0$ are therefore excluded, but not quite all. It is still consistent with the behaviour (8.3) for the wavefunction to decay exponentially to zero as $x \to \pm\infty$, as shown in Fig. [8.6]. In wavefunctions of this sort, the probability of finding the particle outside region II drops exponentially with distance, so it is reasonable to say that the particle is trapped by the potential well, or in other words that the particle is in a "bound state." However, it is only possible to have the wavefunction decay to zero in regions I *and* III only for certain very special values of the energy eigenvalue E, for reasons which will now be explained.

Suppose the value of the wavefunction $\phi(x)$ and its first derivative $\phi'(x)$ are specified at some point $x = a$. Since the time-independent Schrodinger equation is a 2nd-order equation, this is enough information to solve the equation and find the wavefunction everywhere in space. Now for almost all choices of first derivative ϕ' at $x = a$, the wavefunction will eventually diverge to $\phi \to \pm\infty$ as $x \to \infty$, as shown in Fig. [8.7]. For $\phi'(a) > c$, the wavefunction diverges to $+\infty$, while for $\phi'(a) < c$, the wavefunction diverges to $-\infty$, where c is some constant. However, precisely at $\phi'(a) = c$, it is possible for the wavefunction to decay smoothly to zero as $x \to \infty$, as we would expect for a bound state. Even so, we do not yet have a physical state, because in general the wavefunction will be divergent as $x \to -\infty$. But there is one more parameter that can be varied, namely, the energy eigenvalue E. So imagine varying E, always choosing $\phi'(a)$ so that $\phi(x) \to 0$ as $x \to \infty$. As E varies, the point b in Fig. [8.7] where the wavefunction starts to blow up can be moved further and further to the left. Eventually, for one special value of E, we get $b \to -\infty$, and the wavefunction decays smoothly to zero both in region I and region III, as shown in Fig. [8.6]. Only for such an energy does the wavefunction represent a physical bound state. Changing the energy slightly results in an unacceptable, exponentially divergent solution.

In general there is more than one value of E, sometimes an infinite number of values, which are associated with bound state solutions. But since an infinitesmal

change in any of those eigenvalues results in a non-physical state, the bound state energies always form a discrete set.

Finally, it should be noted that it is not always the case that $V(x) \to 0$ as $x \to \pm\infty$. Suppose, e.g., that $V(x) \to V_\infty > 0$ as $x \to \pm\infty$. In that case, unbound states would have energies in the range $E \in [V_\infty, \infty]$, while the bound state energies would be a discrete set with values $E < V_\infty$.

8.2 Unbound States and Quantum Scattering

Consider a particle which is moving in a tube closed at one end. The corresponding potential is

$$V(x) = \begin{cases} 0 & x < 0 \\ \infty & x \geq 0 \end{cases} \tag{8.5}$$

Initially, before the particle encounters the end of the tube, its state is represented by some wavepacket indicated in Fig. [8.8a], with a momentum expectation value $< p >= p_0$. After bouncing off the end of the tube, the "scattered" wavepacket will be moving in the opposite direction with $< p >= -p_0$, as shown in Fig. [8.8c]. At some intermediate time, the wavepacket is in contact with the end of the tube. Since the wavepacket is finite in extent, there is going to be some delay from the time that the front of the wavepacket reflects off the end of the tube, to the time that the back of the wavepacket reflects off the end. During this time interval, part of the wavepacket which reflected off the end of the tube overlaps with the rest of the incoming wavepacket, which has not yet encountered the end of the tube (Fig. [8.8b]).

Now if the wavepacket is of some finite extent Δx, then by the Uncertainty Principle $\Delta p \sim \hbar/\Delta x$. Imagine preparing the initial wavepacket with a very small uncertainty Δp. As $\Delta p \to 0$, then $\Delta x \to \infty$, and the time (and space) interval in which the incoming and reflected waves overlap becomes very large. The limiting case, with $\Delta x = \infty$, is shown in Fig. [8.9]. In this case, the incoming "wavepacket" at any instant of time is an infinite plane wave

$$\phi_{inc}(x) = Ae^{ip_0x/\hbar} \tag{8.6}$$

while the reflected wavepacket is also an infinite plane wave of the opposite momentum

$$\phi_{ref}(x) = Be^{-ip_0x/\hbar} \tag{8.7}$$

These plane waves overlap over the entire half-line $x \in [-\infty, 0]$, so the total wavefunction is the superposition of the incoming and reflected waves

$$\begin{aligned} \phi(x) &= \phi_{inc}(x) + \phi_{ref}(x) \\ &= Ae^{ip_0x/\hbar} + Be^{-ip_0x/\hbar} \end{aligned} \tag{8.8}$$

Because $\phi(x) = 0$ for $x > 0$ and because the wavefunction is continuous at $x = 0$, we must have

$$\phi(x) = 0 \quad \Rightarrow \quad A = -B \tag{8.9}$$

or

$$\phi(x) = N \sin[p_0 x / \hbar] \tag{8.10}$$

The state (8.10) is a stationary state. Substituting (8.10) into the time-independent Schrodinger equation, the corresponding energy eigenvalue is found to be

$$E = \frac{p_0^2}{2m} \tag{8.11}$$

Despite the stationarity, this energy eigenstate is obviously just the limit of a non-stationary situation, in which an incoming wavepacket is scattered backwards by an infinite potential. During the (long) interval in which the incoming wavepacket (with Δp very small) reflects from the end of the tube, the wavefunction near the end of the tube looks very much like the energy eigenstate (8.10). In fact, in the $\Delta p \to 0$ limit, we can easily identify the part of the eigenstate that corresponds to the incoming wavepacket (ϕ_{inc}) and the part which corresponds to the scattered wavepacket (ϕ_{ref}). This is a general feature of unbound states: an *unbound* stationary state can be viewed as the limit of a dynamical situation, in which an incoming wavepacket of a very precise momentum is scattered by a potential. Part of the unbound state is identified as the incoming wave, other parts represent the scattered waves.

As a second example, consider a particle wavepacket incident on the potential well of Fig. [8.1]. The incoming wavepacket is shown in Fig. [8.10a]. Upon encountering the potential, the wavepacket splits into a reflected wavepacket, moving backwards towards $x = -\infty$, and a transmitted wavepacket which has passed through the well and is moving on towards $x = +\infty$, as shown in Fig. [8.10c].[1] At some intermediate time, the incoming and reflected wavepackets overlap, and as we take $\Delta p \to 0$ for the incoming wave, the incoming and reflected waves overlap over a very large region. . The limiting case is shown in Fig. [8.5]. This is again a stationary state, but the wave to the left of the potential well is a superposition of incoming and reflected waves

$$\begin{aligned} \phi_{left}(x) &= \phi_{inc}(x) + \phi_{ref}(x) \\ &= Ae^{ip_0 x / \hbar} + Be^{-ip_0 x / \hbar} \end{aligned} \tag{8.12}$$

while the wavefunction to the right of the potential well is the outgoing transmitted wave

$$\begin{aligned} \phi_{right}(x) &= \phi_{trans}(x) \\ &= Ce^{ip_0 x / \hbar} \end{aligned} \tag{8.13}$$

---

[1]Incidentally, this is another reason why a particle in quantum mechanics cannot be taken *literally* as a wave. Although the wavepacket splits into reflected and transmitted packets, the particle itself does not split: there is some probability that the particle would be found to reflect, and some probability that the particle is transmitted, but the particle itself never splits into a reflected particle and a transmitted particle.

In any real scattering experiment, of course, there is always some finite uncertainty in the momentum of the incoming particle, the wavepacket is always finite in extent, and that means that eventually the incident wave is completely replaced by the scattered waves. Nevertheless, to compute the quantities of interest in a scattering experiment, it is convenient to consider the $\Delta p = 0$ limit, and work with stationary states in which the incoming and reflected waves always overlap. The "quantities of interest" in a scattering experiment are the ratio of intensities of the incident and scattered waves, because such ratios can be directly related to observable quantities.

In connection with the 2-slit experiment discussed in Lecture 3, we learned that if we have a beam of n_p particles of average velocity $v = <p>/m$, with the wavefunction of each particle represented at some time t by $\phi(x)$, then the intensity of the beam at point x at time t is given by

$$
\begin{aligned}
I &= n_p v \phi^*(x) \phi(x) \\
&= \text{average no. of particles} \\
&\quad \text{passing point } x \text{ per unit time}
\end{aligned}
\tag{8.14}
$$

The goal of scattering theory is to find the intensity of the scattered beam as compared to the intensity of the incoming beam. In the simple case of an incoming particle of momentum p_0 approaching the end of a tube,

$$
\begin{aligned}
I_{inc} &= \frac{p_0}{m} \phi^*_{inc}(x) \phi_{inc}(x) = \frac{p_0}{m} |A|^2 \\
I_{ref} &= \frac{p_0}{m} \phi^*_{ref}(x) \phi_{ref}(x) = \frac{p_0}{m} |B|^2
\end{aligned}
\tag{8.15}
$$

and, since $A = -B$,

$$
I_{ref} = I_{inc}
\tag{8.16}
$$

Physically, this means that if the flux of incoming particles past some point x_0 is, say, 1000 particles per second, then the flux of reflected particles past that point is also 1000 particles per second; i.e. every incident particle is reflected, no particles are transmitted past the infinite potential barrier at $x = 0$. In the second example shown in Fig. [8.10] we have, in addition to I_{inc} and I_{ref}, an intensity for the transmitted wave, representing particles which have gone through the potential barrier

$$
I_{trans} = \frac{p_0}{m} \phi^*_{trans}(x) \phi_{trans}(x) = \frac{p_0}{m} |C|^2
\tag{8.17}
$$

The quantities we need to calculate, which can then be compared with experiment, are the **Reflection Coefficient**

$$
\begin{aligned}
R &= \frac{I_{ref}}{I_{inc}} = \frac{|B|^2}{|A|^2} \\
&= \frac{\text{no. of particles/sec reflected}}{\text{no. of particles/sec incident}}
\end{aligned}
\tag{8.18}
$$

and the **Transmission Coefficient**

$$
\begin{aligned}
T &= \frac{I_{trans}}{I_{inc}} = \frac{|C|^2}{|A|^2} \\
&= \frac{\text{no. of particles/sec transmitted}}{\text{no. of particles/sec incident}}
\end{aligned}
\tag{8.19}
$$

Of course, the ratios B/A and C/A can only be obtained by actually solving the time-independent Schrodinger equation, which we will do, in this lecture, for simple rectangular potentials.

8.3   The Step Potential

Consider a particle moving in a potential which rises suddenly from $V(x) = 0$, at $x < 0$, to $V(x) = V$, at $x \geq 0$, as shown in Fig. [8.11]. If $E > V$ then the entire real line is a classically allowed region; an particle moving to the right will pass the potential barrier and continue moving to the right. On the other hand, if $E < V$, the half-line $x > 0$ is a classically forbidden region; an incoming particle will be reflected at $x = 0$ and move away to the left. We will consider these two cases separately:

Energies $E > V$

The Schrodinger equation in region I $(x < 0)$ is the equation for a free particle

$$
-\frac{\hbar^2}{2m}\frac{\partial^2 \phi_1}{\partial x^2} = E\phi_1
\tag{8.20}
$$

with the usual free particle solution

$$
\phi_1(x) = Ae^{ip_1 x/\hbar} + Be^{-ip_1 x/\hbar} \quad \text{where} \quad p_1 = \sqrt{2mE}
\tag{8.21}
$$

In region II $(x > 0)$ the equation is

$$
-\frac{\hbar^2}{2m}\frac{\partial^2 \phi_2}{\partial x^2} = (E - V)\phi_2
\tag{8.22}
$$

with the solution

$$
\phi_2(x) = Ce^{ip_2 x/\hbar} + De^{-ip_2 x/\hbar} \quad \text{where} \quad p_2 = \sqrt{2m(E - V)}
\tag{8.23}
$$

The scattering region is at $x = 0$, this is where $\partial V/\partial x \neq 0$. The part of the wavefunction that represents a (very long) wavepacket moving towards the scattering region is

$$
\phi_{inc}(x) = \begin{cases} Ae^{ip_1 x/\hbar} & x < 0 \\ De^{-ip_2 x/\hbar} & x > 0 \end{cases}
\tag{8.24}
$$

The choice of A and D is a choice of the initial state. If $D = 0$ then the particle is initially approaching the potential step from the left; if $A = 0$ the particle is approaching from the right. If both A and D are non-zero, then the initial wavepacket is split into two pieces, one approaching from the left and one approaching from the right. It is possible to have a initial wavepacket which is discontinuous in this way, but it is uncommon. The standard experimental setup would be to have a particle source located to one side or the other of the scattering region. We will suppose that the particles are coming in from the left, and set $D = 0$. In that case the remaining pieces of the wavefunction have the interpretation as transmitted and reflected waves

$$
\begin{aligned}
\phi_{ref}(x) &= B e^{-ip_1 x/\hbar} \quad (x < 0) \\
\phi_{trans}(x) &= C e^{ip_2 x/\hbar} \quad (x > 0)
\end{aligned}
\tag{8.25}
$$

To determine the reflection and transmission coefficients, we need B and C in terms of A.

The solution of the Schrodinger equation must be a continuous function, and its first derivative must also be continuous. If this were not true, the second derivative would be infinite, which violates the Schrodinger equation if the energy and potential are finite. [2] Imposing continuity of the wavefunction ϕ and its first derivative ϕ' at $x = 0$ give the conditions

$$
\begin{aligned}
\phi_1(0) = \phi_2(0) &\implies A + B = C \\
\phi_1'(0) = \phi_2'(0) &\implies p_1(A - B) = p_2 C
\end{aligned}
\tag{8.26}
$$

These two equations allow us to solve for B and C in terms of A:

$$
\begin{aligned}
B &= \frac{p_1 - p_2}{p_1 + p_2} A \\
C &= \frac{2p_1}{p_1 + p_2} A
\end{aligned}
\tag{8.27}
$$

The resulting wavefunction is sketched in Fig. [8.12].

Recall that intensity is proportional to the (group) velocity, $I = v\phi^*\phi$, and in this case the velocity of the transmitted wave $v_2 = p_2/m$ is different from the velocity of the incident and reflected waves $v_1 = p_1/m$. The transmission coefficient is therefore

$$
\begin{aligned}
T &= \frac{v_2 |C|^2}{v_1 |A|^2} \\
&= \frac{p_2}{p_1} \frac{4p_1^2}{(p_2 + p_1)^2}
\end{aligned}
\tag{8.28}
$$

---

[2] An exception is if the potential becomes infinite at some point, as in the case of a particle in a tube. In such situations, the slope of the wavefunction can be discontinuous.

while the reflection coefficient is

$$R = \frac{v_1|B|^2}{v_1|A|^2}$$

$$= \frac{(p_2 - p_1)^2}{(p_2 + p_1)^2} \tag{8.29}$$

Notice that

$$R + T = 1 \tag{8.30}$$

which has the interpretation that

$$\text{no. of particles reflected/sec} \quad + \quad \text{no. of particles transmitted/sec}$$
$$= \quad \text{no. of particles incident/sec} \tag{8.31}$$

and is a consequence of the conservation of probability by the Schrodinger equation.

It should also be noted that $R \neq 0$, in general. This is in sharp contrast to classical physics, where *no* particles of energy $E > V$ would be reflected.

Question: Why is (8.31) a consequence of conservation of probability?

Energies $E < V$

In this case, the solutions (8.21) in region I and (8.23) in region II are the same as before, however

$$p_2 = \sqrt{2m(E - V)} = iq_2 \tag{8.32}$$

is an imaginary number. The solution ϕ_2 in the classically forbidden region is then

$$\phi_2(x) = Ce^{-q_2 x/\hbar} + De^{q_2 x/\hbar} \quad \text{where} \quad q_2 = \sqrt{2m(V - E)} \tag{8.33}$$

Like any solution in the classically forbidden region, ϕ_2 is, in general, a combination of exponentially growing and exponentially decaying functions. Solutions with $D \neq 0$ are non-normalizable, however, and do not correspond to physical states. So we need only consider solutions with $D = 0$.

Once again applying continuity of the wavefunction and its first derivative, we have

$$\phi_1(0) = \phi_2(0) \implies A + B = C$$
$$\phi_1'(0) = \phi_2'(0) \implies ip_1(A - B) = -q_2 C \tag{8.34}$$

Solving for B and C,

$$B = \frac{p_1 - iq_2}{p_1 + iq_2}A$$
$$C = \frac{2p_1}{p_1 + iq_2}A \tag{8.35}$$

But in this case

$$R = \frac{|B|^2}{|A|^2} = 1 \tag{8.36}$$

which means that all incident particles are reflected; no particles are transmitted towards $x \to +\infty$, as in the classical case. The resulting wavefunction is shown in Fig. [8.13]. *Unlike* the classical case, however, there is a finite probability to find the particle at any finite distance $x > 0$

$$P_{\Delta x}(x > 0) = |C|^2 e^{-2q_2 x/\hbar} \Delta x \tag{8.37}$$

Once again, there is no way of interpreting this result in classical terms. Classically, force is proportional to the derivative of the potential, so there is only a force on the particle at $x = 0$. There is nothing to prevent a particle at $x > 0$ to continue moving to the left. Quantum mechanically, although there is a finite probability to find the particle at $x > 0$, that probability decreases exponentially with x, and any particle of energy $E < V$ is ultimately reflected.

8.4   The Finite Square Well: Bound States

An attractive potential which is finite at infinity normally has a discrete (finite or infinite) number of bound states, and an infinite number of unbound states with energies in the range $[E_{min}, \infty]$. The simplest example is the finite square well potential[3]

$$V(x) = \begin{cases} 0 & x < -a \\ -V_0 & -a \le x \le a \\ 0 & x > a \end{cases} \tag{8.38}$$

shown in Fig. [8.14].

For particle energies $E > 0$ the entire real line is classically allowed; these are the unbound states. For $E < 0$ regions I and II are classically forbidden, and the wavefunction of a physical state must fall exponentially to zero as $x \to \pm\infty$. These are the bound states.

---

[3]It is conventional to call it a "square" well although the shape may just as well be rectangular. The potential for a particle in a tube is known as the "infinite square well."

<u>Bound States $E < 0$</u>

We begin with a discussion of the bound states. In Regions I and III the Schrodinger equation is the same as a free particle equation, and the solution is

$$
\begin{aligned}
\phi_I(x) &= a_1 e^{i\sqrt{2mE}x/\hbar} + a_2 e^{-i\sqrt{2mE}x/\hbar} \\
\phi_{III}(x) &= b_1 e^{i\sqrt{2mE}x/\hbar} + b_2 e^{-i\sqrt{2mE}x/\hbar}
\end{aligned}
\tag{8.39}
$$

However, since $E < 0$, the square-root is imaginary. Writing $E = -\mathcal{E}$, we have

$$
\begin{aligned}
\phi_I(x) &= a_1 e^{-\sqrt{2m\mathcal{E}}x/\hbar} + a_2 e^{\sqrt{2m\mathcal{E}}x/\hbar} \\
\phi_{III}(x) &= b_1 e^{-\sqrt{2m\mathcal{E}}x/\hbar} + b_2 e^{\sqrt{2m\mathcal{E}}x/\hbar}
\end{aligned}
\tag{8.40}
$$

If ψ is a physical state, we must set $a_2 = b_1 = 0$; otherwise the wavefunction blows up exponentially as $x \to \pm\infty$ and the state is non-normalizable. Then

$$
\begin{aligned}
\phi_I(x) &= A e^{-\sqrt{2m\mathcal{E}}x/\hbar} \\
\phi_{III}(x) &= B e^{\sqrt{2m\mathcal{E}}x/\hbar}
\end{aligned}
\tag{8.41}
$$

Now suppose we choose A to be a real number. Then $\phi(x)$ must be real everywhere. The reason is that the Schrodinger equation is a linear equation with real coefficients, so writing

$$
\phi(x) = \phi^R(x) + i\phi^I(x)
\tag{8.42}
$$

its easy to see that ϕ^R and ϕ^I must *both* satisfy the Schrodinger equation

$$
\tilde{H}\phi^R = E\phi^R \qquad \tilde{H}\phi^I = E\phi^I.
\tag{8.43}
$$

Setting A to be a real number means that $\phi^I = 0$ for $x > a$, which means it is zero everywhere, because the Schrodinger equation says that $\phi''(x) \propto \phi(x)$. The conclusion is that $\phi(x)$ is real everywhere; in particular, the constant B is also a real number.

Let $\phi(x)$ be a solution of the time-independent Schrodinger equation with energy E_n. We can show that

$$
\varphi(x) = \phi(-x)
\tag{8.44}
$$

is also an eigenstate of $\tilde{H}$, with the same energy. Start with the time-independent Schrodinger equation

$$
-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x) + V(x)\phi(x) = E\phi(x)
\tag{8.45}
$$

make the change of variables $x \to -x$

$$
\begin{aligned}
-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(-x) + V(-x)\phi(-x) &= E\phi(-x) \\
-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\varphi(x) + V(x)\varphi(x) &= E\varphi(x)
\end{aligned}
\tag{8.46}
$$

This proves that $\varphi(x)$ is also a solution. The crucial fact used in (8.46) was the symmetry of $V(x)$ around $x = 0$

$$V(x) = V(-x) \tag{8.47}$$

Without this symmetry, $\varphi(x) = \phi(-x)$ would not be a solution of the Schrodinger equation.

If E_n is degenerate, then $\phi(x)$ and $\varphi(x)$ could be two different states. On the other hand, if E_n is non-degenerate, then the two functions must be proportional to one another:

$$\varphi(x) = c\phi(x) \tag{8.48}$$

where c is a real-valued constant, since ϕ and φ are both real-valued. Finally, the normalization condition requires

$$\int dx \, \varphi^2 = c^2 \int dx \, \phi^2 = 1 \tag{8.49}$$

which means, since ϕ is normalized, that $c = \pm 1$. We conclude that if E_n is non-degenerate there are two possibilities:

1. "Even Parity"

$$\phi(-x) = +\phi(x) \tag{8.50}$$

2. "Odd Parity"

$$\phi(-x) = -\phi(x) \tag{8.51}$$

Assuming that the energy eigenvalues are non-degenerate, the algebra simplifies a lot. In region II, the Schrodinger equation is of the form

$$\frac{d^2\phi_{II}}{dx^2} = -\frac{2m}{\hbar^2}(V_0 - \mathcal{E})\phi_{II} \tag{8.52}$$

with solutions

$$\phi_{II} = c_1 e^{i\sqrt{2m(V_0-\mathcal{E})}x/\hbar} + c_2 e^{-i\sqrt{2m(V_0-\mathcal{E})}x/\hbar} \tag{8.53}$$

However, since ϕ_{II} must be a real function, we expand the exponentials in a combination of sin and cosine

$$\phi_{II} = C_E \cos\left[\sqrt{2m(V_0 - \mathcal{E})}x/\hbar\right] + C_O \sin\left[\sqrt{2m(V_0 - \mathcal{E})}x/\hbar\right] \tag{8.54}$$

We have seen that the non-degenerate solutions have to be either even or odd parity. For even parity, $C_O = 0$, while for odd parity $C_E = 0$. We deal with these cases separately.

Even Parity Bound States

The requirement that $\phi(x) = \phi(-x)$ also implies that $A = B$. So we have altogether

$$
\begin{aligned}
\phi_I(x) &= A e^{-\sqrt{2m\mathcal{E}}x/\hbar} \\
\phi_{II}(x) &= C_E \cos\left[\sqrt{2m(V_0 - \mathcal{E})}x/\hbar\right] \\
\phi_{III}(x) &= A e^{\sqrt{2m\mathcal{E}}x/\hbar}
\end{aligned}
\tag{8.55}
$$

The continuity of the wavefunction at $x = \pm a$ requires

$$
A e^{-\sqrt{2m\mathcal{E}}a/\hbar} = C_E \cos\left[\sqrt{2m(V_0 - \mathcal{E})}a/\hbar\right]
\tag{8.56}
$$

while the continuity of the first derivative at $x = \pm a$ gives

$$
\sqrt{2m\mathcal{E}}\, A e^{-\sqrt{2m\mathcal{E}}a/\hbar} = \sqrt{2m(V_0 - \mathcal{E})}\, C_E \sin\left[\sqrt{2m(V_0 - \mathcal{E})}a/\hbar\right]
\tag{8.57}
$$

Dividing equation (8.57) by equation (8.56) results in a transcendental equation for $\mathcal{E} = -E$

$$
\sqrt{\mathcal{E}} = \sqrt{V_0 - \mathcal{E}}\, \tan\left[\sqrt{2m(V_0 - \mathcal{E})}a/\hbar\right]
\tag{8.58}
$$

which determines the energy eigenvalues.

This transcendental equation can be solved graphically, by plotting the left and right hand sides of the equation to find the points at which the two curves intersect. The result is shown in Fig. [8.15]. We learn from the figure that the solutions, denoted by $\mathcal{E}_n$, with n an odd integer, are all at $\mathcal{E} < V_0$. This is because for $\mathcal{E} > V_0$ the tangent in eq. (8.58) becomes a hyperbolic tangent, so the rhs diverges to $-\infty$ as $x \to \infty$, never again intersecting $\sqrt{\mathcal{E}}$. Each solution $\mathcal{E}_n$ is located between points where the tangent equals 0; these "nodes" occur at

$$
\mathcal{E} = V_0 - (k\pi)^2 \frac{\hbar^2}{2ma^2} \qquad (k = 0, 1, 2, ...)
\tag{8.59}
$$

and since $\mathcal{E} > 0$, this means that the number K of even-parity energy eigenvalues is the largest number such that

$$
[(K-1)\pi]^2 \frac{\hbar^2}{2ma^2} \leq V_0
\tag{8.60}
$$

Thus there are a finite number - and no less than one! - of even-parity bound states. The number K of such bound states increases as the well becomes deeper (larger V_0), and wider (larger a).

Odd Parity Bound States

This time, the requirement that $\phi(-x) = -\phi(x)$ implies that $B = -A$, and $C_E = 0$. The wavefunction has the form

$$
\begin{aligned}
\phi_I(x) &= Ae^{-\sqrt{2m\mathcal{E}}x/\hbar} \\
\phi_{II}(x) &= C_O \sin\left[\sqrt{2m(V_0 - \mathcal{E})}x/\hbar\right] \\
\phi_{III}(x) &= -Ae^{\sqrt{2m\mathcal{E}}x/\hbar}
\end{aligned}
\tag{8.61}
$$

From continuity of the wavefunction at $x = \pm a$ we have

$$
Ae^{-\sqrt{2m\mathcal{E}}a/\hbar} = C_O \sin\left[\sqrt{2m(V_0 - \mathcal{E})}a/\hbar\right]
\tag{8.62}
$$

and from continuity of the first derivative at $x = \pm a$

$$
-\sqrt{2m\mathcal{E}}\,Ae^{-\sqrt{2m\mathcal{E}}a/\hbar} = \sqrt{2m(V_0 - \mathcal{E})}C_O \cos\left[\sqrt{2m(V_0 - \mathcal{E})}a/\hbar\right]
\tag{8.63}
$$

Dividing eq. (8.63) by eq. (8.62) gives us the transcendental equation for the energies of odd parity bound states

$$
\begin{aligned}
\sqrt{\mathcal{E}} &= -\sqrt{V_0 - \mathcal{E}}\,\mathrm{ctn}\left[\sqrt{2m(V_0 - \mathcal{E})}a/\hbar\right] \\
&= \sqrt{V_0 - \mathcal{E}}\,\tan\left[\sqrt{2m(V_0 - \mathcal{E})}\frac{a}{\hbar} + \frac{\pi}{2}\right]
\end{aligned}
\tag{8.64}
$$

which can be solved graphically, as shown in Fig. [8.16]. Once again, there are as many roots as there are nodes of the tangent; this time the nodes are located at

$$
\mathcal{E} = V_0 - [(k + \frac{1}{2})\pi]^2 \frac{\hbar^2}{2ma^2} \qquad (k = 0, 1, 2, ...)
\tag{8.65}
$$

and the number of odd parity nodes is the largest integer M such that

$$
[(K - \frac{1}{2})\pi]^2 \frac{\hbar^2}{2ma^2} < V_0
\tag{8.66}
$$

Note that for

$$
V_0 < \left(\frac{\pi}{2}\right)^2 \frac{\hbar^2}{2ma^2}
\tag{8.67}
$$

there are no odd-parity bound states.

To sum up, we have found that for a finite square well

1. The number of bound state energies is finite, and there is at least one bound state;

2. The number of bound states increases with the width and depth of the well;

3. The energies are non-degenerate;

4. Each energy eigenstate is either even parity or odd parity, and this is a consequence of the symmetry of the potential $V(x) = V(-x)$, and the fact that the energies are non-degenerate.

5. Although the particle is bound to the well, the wavefunction of the particle may be non-negligible far outside the well, where (in classical physics) there are no forces at all acting on the particle.

Scattering States $E > 0$

For $E > 0$, the solution of the time-independent Schrodinger equation in all three regions is

$$\begin{aligned}
\phi_{III}(x) &= Ae^{i\sqrt{2mE}x/\hbar} + Be^{-i\sqrt{2mE}x/\hbar} \\
\phi_{II}(x) &= Ce^{i\sqrt{2m(E+V_0)}x/\hbar} + De^{-i\sqrt{2m(E+V_0)}x/\hbar} \\
\phi_{I}(x) &= Ee^{i\sqrt{2mE}x/\hbar} + Fe^{-i\sqrt{2mE}x/\hbar}
\end{aligned} \tag{8.68}$$

As explained in the introduction, the wavefunction in regions I and III can be thought of as a superposition of incoming and outgoing wavepackets, in the limit that the uncertainty in momentum of the wavepackets goes to zero. The momentum is either $p = \sqrt{2mE}$, in which case the packet is moving from left to right, or $p = -\sqrt{2mE}$, in which case the packet is moving from right to left. Therefore, we can interpret the components of ϕ_{III} and ϕ_I as representing:

$Ae^{i\sqrt{2mE}x/\hbar}$ an incoming wavepacket from the left

$Be^{-i\sqrt{2mE}x/\hbar}$ an outgoing wavepacket to the left

$Ee^{i\sqrt{2mE}x/\hbar}$ an outgoing wavepacket to the right

$Fe^{-i\sqrt{2mE}x/\hbar}$ an incoming wavepacket from the right

Now suppose we are interested in an experimental situation in which a particle of a fairly precise momentum is sent towards the potential well from the left. In that case there is no incoming wavepacket from the right, so we can set $F = 0$. The incoming wavepacket eventually reaches the potential well. Some of the incoming wavepacket is reflected towards the left; some is transmitted towards the right. So we now have

$$\begin{aligned}
\phi_{III}(x) &= Ae^{i\sqrt{2mE}x/\hbar} + Be^{-i\sqrt{2mE}x/\hbar} \\
\phi_{II}(x) &= Ce^{i\sqrt{2m(E+V_0)}x/\hbar} + De^{-i\sqrt{2m(E+V_0)}x/\hbar} \\
\phi_{I}(x) &= Ee^{i\sqrt{2mE}x/\hbar}
\end{aligned} \tag{8.69}$$

where

$$Ae^{i\sqrt{2mE}x/\hbar} \quad \text{represents the incoming wavepacket}$$

$$Be^{-i\sqrt{2mE}x/\hbar} \quad \text{represents the reflected wavepacket}$$

$$Ee^{i\sqrt{2mE}x/\hbar} \quad \text{represents the transmitted wavepacket}$$

The reflection and transmission coefficients will therefore be

$$R = \frac{BB^*}{AA^*} \qquad T = \frac{EE^*}{AA^*} \tag{8.70}$$

so the problem is to compute B and E in terms of A.

We should pause to note that $\phi(x) \neq \pm\phi(-x)$. The reason is that in this case the energy is degenerate; a particle approaching the potential from the left can have exactly the same energy as a particle approaching the well from the right. In this situation, an energy eigenstate does not *necessarily* have the property that $\phi(x) = \pm\phi(-x)$; although $\varphi(x) = \phi(-x)$ is an energy eigenstate, it is not necessarily equivalent to $\phi(x)$ if the energy is degenerate. For the wavefunction $\phi(x)$ of eq. (8.69), which represents a particle approaching the well from the left and then scattering, $\varphi(x)$ represents a particle approaching the potential from the *right*, and then scattering.

Denote

$$k = \frac{\sqrt{2mE}}{\hbar} \quad \text{and} \quad q = \frac{\sqrt{2m(E+V_0)}}{\hbar} \tag{8.71}$$

so that

$$\begin{aligned}
\phi_{III}(x) &= Ae^{ikx} + Be^{-ikx} \\
\phi_{II}(x) &= Ce^{iqx} + De^{-iqx} \\
\phi_{I}(x) &= Ee^{ikx}
\end{aligned} \tag{8.72}$$

Imposing continuity of the wavefunction and its first derivative at $x = a$ give us

$$\begin{aligned}
\underline{\phi_I(a) = \phi_{II}(a)} &\implies Ee^{ika} = Ce^{iqa} + De^{-iqa} \\
\underline{\phi_I'(a) = \phi_{II}'(a)} &\implies kEe^{ika} = q(Ce^{iqa} - De^{-iqa})
\end{aligned} \tag{8.73}$$

The corresponding continuity conditions at $x = -a$ are

$$\begin{aligned}
\underline{\phi_{III}(-a) = \phi_{II}(-a)} &\implies Ae^{-ika} + Be^{ika} = Ce^{-iqa} + De^{iqa} \\
\underline{\phi_{III}'(-a) = \phi_{II}'(-a)} &\implies k(Ae^{-ika} - Be^{ika}) = q(Ce^{-iqa} - De^{iqa})
\end{aligned} \tag{8.74}$$

We first solve eq. (8.73) for C and D in terms of E:

$$\begin{aligned}
C &= \frac{1}{2}\left(1 + \frac{k}{q}\right)Ee^{i(k-q)a} \\
D &= \frac{1}{2}\left(1 - \frac{k}{q}\right)Ee^{i(k+q)a}
\end{aligned} \tag{8.75}$$

substitute into (8.74)

$$Ae^{-ika} + Be^{ika} = \left[\frac{1}{2}(1 + \frac{k}{q})e^{i(k-2q)a} + \frac{1}{2}(1 - \frac{k}{q})e^{i(k+2q)a}\right] E$$

$$k(Ae^{-ika} - Be^{ika}) = q\left[\frac{1}{2}(1 + \frac{k}{q})e^{i(k-2q)a} - \frac{1}{2}(1 - \frac{k}{q})e^{i(k+2q)a}\right] E \quad (8.76)$$

Solving for E in terms of A, we find

$$2kAe^{-ika} = \left[(k+q)\frac{1}{2}(1 + \frac{k}{q})e^{i(k-2q)a} + (k-q)\frac{1}{2}(1 - \frac{k}{q})e^{i(k+2q)a}\right] E$$

$$= \left[(k + \frac{k^2}{2q} + \frac{q}{2})e^{i(k-2q)a} + (k - \frac{k^2}{2q} - \frac{q}{2})e^{i(k+2q)a}\right] E \quad (8.77)$$

so that

$$\frac{E}{A} = \frac{2e^{-ika}}{(1 + \frac{k}{2q} + \frac{q}{2k})e^{i(k-2q)a} + (1 - \frac{k}{2q} - \frac{q}{2k})e^{i(k+2q)a}}$$

$$= \frac{e^{-2ika}}{\cos(2qa) + \frac{1}{2}(\frac{k}{2q} + \frac{q}{2k})(e^{-2iqa} - e^{2iqa})}$$

$$= \frac{e^{-2ika}}{\cos(2qa) - \frac{i}{2}(\frac{k}{q} + \frac{q}{k})\sin(2qa)} \quad (8.78)$$

In a similar way, one can solve for B in terms of A

$$\frac{B}{A} = \frac{\frac{1}{2}ie^{-2ika}(\frac{q}{k} - \frac{k}{q})\sin(2qa)}{\cos(2qa) - \frac{1}{2}i(\frac{q}{k} + \frac{k}{q})\sin(2qa)} \quad (8.79)$$

From these ratios, we obtain the transmission and reflection coefficients

$$T = \left|\frac{E}{A}\right|^2 = \frac{1}{\cos^2(2qa) + \frac{1}{4}(\frac{k}{q} + \frac{q}{k})^2\sin^2(2qa)}$$

$$R = \left|\frac{B}{A}\right|^2 = \frac{\frac{1}{4}(\frac{q}{k} - \frac{k}{q})^2\sin^2(2qa)}{\cos^2(2qa) + \frac{1}{4}(\frac{k}{q} + \frac{q}{k})^2\sin^2(2qa)} \quad (8.80)$$

and it is easy to check that

$$R + T = 1 \quad (8.81)$$

as required by conservation of probability.

Now notice that something interesting happens when the energy E of the incoming particle is such that

$$2qa = 2\sqrt{2m(E + V_0)}\frac{a}{\hbar} = n\pi \quad (8.82)$$

In this case

$$T = 1 \quad \text{and} \quad R = 0 \tag{8.83}$$

i.e. there is no reflection at all. A particle of this energy is certain to be transmitted past the potential well. The condition (8.82) has a simple interpretation in terms of de Broglie wavelengths. The momentum of the particle inside the well is

$$P = \sqrt{2m(E - V)} = \sqrt{2m(E + V_0)} \tag{8.84}$$

so the condition (8.82) is

$$\begin{aligned}
2a\frac{P}{\hbar} &= n\pi \\
2a\frac{P}{h}2\pi &= n\pi \\
2a &= n\frac{\lambda}{2}
\end{aligned} \tag{8.85}$$

where we use the de Broglie relation $p = h/\lambda$. Since the width of the potential well is $2a$, it means that there is no reflection whenever the width of the well is exactly an integer number of half-wavelengths across, which is also the condition for a standing wave on an interval of length $2a$.

There is a related phenomenon in atomic physics known as the Ramsauer effect, in which low energy electrons are scattered by a thin film of some material. At certain well-defined energies, the scattering of the electrons is minimized. In this case, an atom can be viewed as an attractive potential well for the electrons. Since an atom is electrically neutral, the potential is zero until the incoming electrons move past the electrons orbiting the nucleus. As the electron approaches closer to the nucleus, there is of course an attractive force, since the nucleus is positive. The analysis of the scattering is more complicated than for the finite square well, the motion is in three dimensions rather than one dimension, and the potential well is not rectangular. Nevertheless, the solid is nearly "transparent" for incoming electrons of certain definite energies; an effect which is closely analogous to the finite square well case.

8.5 Tunnelling

Next we consider a repulsive square well potential

$$V(x) = \begin{cases} 0 & x < -a \\ V_0 & -a \leq x \leq a \\ 0 & x > a \end{cases} \tag{8.86}$$

Since this potential differs from the attractive square well of the last section only by the sign in front of V_0, there is no need to repeat the algebra of the last section. We

can simply take the formulas for the scattering state of the attractive well, replace V_0 everywhere by $-V_0$, and these will be the corresponding formulas for the repulsive well. Then again denote

$$k = \frac{\sqrt{2mE}}{\hbar} \quad \text{and} \quad q = \frac{\sqrt{2m(E - V_0)}}{\hbar} \tag{8.87}$$

so that

$$\begin{aligned} \phi_{III}(x) &= Ae^{ikx} + Be^{-ikx} \\ \phi_{II}(x) &= Ce^{iqx} + De^{-iqx} \\ \phi_{I}(x) &= Ee^{ikx} \end{aligned} \tag{8.88}$$

Classically, if $E > V_0$, the incoming particle will travel through the well and continue moving to the right. If $E < V_0$ the incoming particle is reflected at $x = -a$, and travels back to the left.

In quantum mechanics, if $E > V_0$, the situation is qualitatively much like the case for the attractive potential: some of the incoming wave is reflected, and some is transmitted. It is worth noting that no matter how large E is compared to V_0, there is always some finite probability that the particle is reflected. Quantum-mechanically, if a bullet is fired at a fixed target of tissue paper, there is always some (exceedingly small) probability that the bullet will bounce off the paper.

If $E < V_0$, then the quantity

$$q = \frac{\sqrt{2m(E - V_0)}}{\hbar} \tag{8.89}$$

is imaginary. Substituting

$$q = iQ \quad \text{and} \quad \sin(2qa) = -i\sinh(2Qa) \tag{8.90}$$

into equation (8.80) gives us

$$\begin{aligned} T &= \frac{1}{\cosh^2(2Qa) + \frac{1}{4}(\frac{k}{Q} + \frac{Q}{k})^2\sinh^2(2Qa)} \\ R &= \frac{\frac{1}{4}(\frac{Q}{k} - \frac{k}{Q})^2\sinh^2(2Qa)}{\cosh^2(2Qa) + \frac{1}{4}(\frac{k}{Q} + \frac{Q}{k})^2\sinh^2(2Qa)} \end{aligned} \tag{8.91}$$

If the width of the well is large enough, so that

$$2a >> \frac{1}{Q} = \frac{\hbar}{\sqrt{2m(V_0 - E)}} \tag{8.92}$$

then

$$\sinh^2(2Qa) \approx \cosh^2(2Qa) \approx \frac{1}{4}e^{2Qa} \tag{8.93}$$

and the transmission coefficient is approximately

$$T \approx e^{-4Qa} = \exp[-4\sqrt{2m(V_0 - E)}a/\hbar] \tag{8.94}$$

The situation is sketched in Figure [8.17]. Most of the incoming wave is reflected. In the classically forbidden region, the wavefunction decays exponentially. However, since the width of the classically forbidden region is finite, the wavefunction at the other end of the barrier is finite, and so there exists a transmitted wave. This means that no matter how high the barrier V_0 is compared to the energy E of the incoming particle, there is always some finite probability for the particles to penetrate through the barrier.

Quantum-mechanically, a soap bubble heading for a brick wall has a finite, although exceedingly small, probability of being found on the other side of the brick wall.

The fact that a particle can penetrate a potential barrier whose height exceeds the energy of the particle is known as "**Tunnelling**". It has important applications throughout modern physics, e.g. in the study of semiconductors, and of radioactive decay.

Chapter 9

The Harmonic Oscillator

There are only a very few potentials for which the Schrodinger equation can be solved analytically. The most important of these is the potential

$$V(x) = \frac{1}{2}k(x - x_0)^2 \tag{9.1}$$

of the harmonic oscillator, because so many of the systems encountered in nuclear physics, condensed matter physics, and elementary particle physics can be treated, to a first approximation, as a set of coupled harmonic oscillators.

There are several reasons why the harmonic oscillator potential shows up so often. First of all, *any* finite potential looks like a harmonic oscillator potential in the neighborhood of its minimum. Suppose the minimum of a potential is at the point $x = x_0$. Expand the potential in a Taylor series around x_0

$$V(x) = V(x_0) + \left(\frac{dV}{dx}\right)_{x=x_0}(x - x_0) + \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_{x=x_0}(x - x_0)^2 + ... \tag{9.2}$$

Because $V(x)$ is a minimum at x_0, the first derivative of the potential vanishes there, so

$$V(x) = V(x_0) + \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_{x=x_0}(x - x_0)^2 + ... \tag{9.3}$$

For small displacements, this is just a harmonic oscillator.

Secondly, any time the classical equations of motion are linear, it means that we are dealing with a harmonic oscillator, or a set of coupled harmonic oscillators. Newton's law of motion $F = ma$ is generally non-linear, since $F(x)$ is usually a non-linear function of x. However, if F depends linearly on x, it follows that the potential depends quadratically on x, which implies a harmonic oscillator. Now it so happens that any non-dispersive wave equation, e.g.

$$\frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} = \frac{\partial^2 y}{\partial x^2} \tag{9.4}$$

is a linear equation of motion. This equation might describe a transverse wave on a string, or a sound wave in a solid, or an electromagnetic plane wave, propagating in the x-direction. Any system that satisfies a wave equation of this form can be thought of as an infinite set of harmonic oscillators. To see this, we define the Fourier transform $Y(q, t)$ of the wavefunction $y(x, t)$ at any time t as

$$Y(q, t) = \int_{-\infty}^{\infty} dx \, y(x, t) e^{iqx} \tag{9.5}$$

with the inverse transform

$$y(x, t) = \int_{-\infty}^{\infty} \frac{dq}{2\pi} \, Y(q, t) e^{-iqx} \tag{9.6}$$

The functions $y(x, t)$ and $Y(q, t)$ contain the same amount of information about the wave at time t, since one function can be obtained from the other. Now multiply both sides of (9.4) by e^{iqx}, integrate over x, and then integrate by parts:

$$
\begin{aligned}
\int dx \, \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2} e^{iqx} &= \int dx \, \frac{\partial^2 y}{\partial x^2} e^{iqx} \\
\frac{\partial^2}{\partial t^2} \int dx \, \frac{1}{v^2} y(x, t) e^{iqx} &= \int dx \, y(x, t) \frac{\partial^2}{\partial x^2} e^{iqx} \\
\frac{1}{v^2} \frac{\partial^2}{\partial t^2} \int dx \, y(x, t) e^{iqx} &= -q^2 \int dx \, y(x, t) e^{iqx} \\
\frac{1}{v^2} \frac{\partial^2}{\partial t^2} Y(q, t) &= -q^2 Y(q, t) \tag{9.7}
\end{aligned}
$$

But this is simply the equation of motion of a harmonic oscillator

$$\text{accelleration} \quad \left(\frac{\partial^2 Y}{\partial t^2} \right) \propto - \text{ displacement} \quad (Y) \tag{9.8}$$

We conclude that the wave equation (9.4) is secretly an infinite number of harmonic oscillator equations; one equation for each wavenumber q.

Wave equations show up everywhere in classical physics. Waves propagate in solids, liquids, gases, and plasmas; they propagate in the electromagnetic field, and even (according to Einstein's theory of general relativity) in the gravitational field. All of these systems can therefore be regarded, at some level of approximation, as sets of harmonic oscillators. This is why the harmonic oscillator potential is the most important problem to solve in quantum physics. Fortunately, it is a problem with a simple and elegant solution.

9.1   Raising and Lowering Operators

Let a and b be any two real numbers, and define

$$c = a + ib \tag{9.9}$$

Then there is a simple identity

$$a^2 + b^2 = c^*c \tag{9.10}$$

Lets find the corresponding identity for operators. Instead of two real numbers, consider two Hermitian operators A and B, which, of course, have only real eigenvalues. Define the non-Hermitian operator

$$C = A + iB \tag{9.11}$$

whose hermitian conjugate is

$$C^\dagger = A - iB \tag{9.12}$$

Then the sum of squares of A and B satisfies the identity

$$A^2 + B^2 = C^\dagger C - i[A, B] \tag{9.13}$$

and the commutator of C with $C^\dagger$ is

$$\left[C, C^\dagger \right] = -2i[A, B] \tag{9.14}$$

These relations are easy to check (exercise!), keeping in mind that operators A and B do not necessarily commute. Now, the Hamiltonian operator can be written as a sum of squares of Hermitian operators

$$\tilde{H} = \left(\frac{\tilde{p}}{\sqrt{2m}} \right)^2 + (\sqrt{V(x)})^2 \tag{9.15}$$

so, writing

$$
\begin{aligned}
A &= \sqrt{V} \\
B &= \frac{\tilde{p}}{\sqrt{2m}} \\
C &= \sqrt{V} + i\frac{\tilde{p}}{\sqrt{2m}}
\end{aligned}
\tag{9.16}
$$

we have

$$\tilde{H} = C^\dagger C - i\sqrt{\frac{1}{2m}}[\sqrt{V}, \tilde{p}] \tag{9.17}$$

and

$$\left[C, C^\dagger \right] = -2i\sqrt{\frac{1}{2m}}[\sqrt{V}, \tilde{p}] \tag{9.18}$$

This is not a particularly useful way to express $\tilde{H}$ in most situations; generally the commutator $[\sqrt{V}, \tilde{p}]$ is just another complicated operator. In the case of the harmonic

oscillator, however, this commutator is very simple:

$$
\begin{aligned}
[A, B] &= \sqrt{\frac{1}{2m}} \left[\sqrt{\frac{1}{2}kx^2}, \tilde{p} \right] \\
&= \sqrt{\frac{k}{4m}} [x, p] \\
&= i\hbar \sqrt{\frac{k}{4m}}
\end{aligned}
\tag{9.19}
$$

In classical physics, the resonant angular frequency of a harmonic oscillator of mass m and spring constant k is

$$
\omega = \sqrt{\frac{k}{m}} \tag{9.20}
$$

so

$$
[A, B] = i\frac{1}{2}\hbar\omega \tag{9.21}
$$

Therefore

$$
\tilde{H} = C^\dagger C + \frac{1}{2}\hbar\omega \tag{9.22}
$$

and

$$
\left[C, C^\dagger \right] = \hbar\omega \tag{9.23}
$$

We now define the **Lowering Operator**

$$
\begin{aligned}
a &= \sqrt{\frac{1}{\hbar\omega}}C \\
&= \sqrt{\frac{1}{\hbar\omega}} \left(\sqrt{\frac{k}{2}}x + i\frac{\tilde{p}}{\sqrt{2m}} \right) \\
&= \frac{1}{\sqrt{2\hbar}} \left(\sqrt{m\omega}x + i\frac{\tilde{p}}{\sqrt{m\omega}} \right)
\end{aligned}
\tag{9.24}
$$

and its Hermitian conjugate known as the **Raising Operator**

$$
\begin{aligned}
a^\dagger &= \sqrt{\frac{1}{\hbar\omega}}C^\dagger \\
&= \frac{1}{\sqrt{2\hbar}} \left(\sqrt{m\omega}x - i\frac{\tilde{p}}{\sqrt{m\omega}} \right)
\end{aligned}
\tag{9.25}
$$

The commutator of these two operators follows from $[C, C^\dagger] = \hbar\omega$,

$$
\left[a, a^\dagger \right] = 1 \tag{9.26}
$$

In terms of the raising and lowering operators, we have

$$
\begin{aligned}
\tilde{H} &= \hbar\omega(a^\dagger a + \frac{1}{2}) \\
x &= \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger) \\
p &= \frac{1}{i}\sqrt{\frac{m\omega\hbar}{2}}(a - a^\dagger)
\end{aligned}
\tag{9.27}
$$

The reason for calling a the "lowering" operator is that it has the amazing property of taking an eigenstate of $\tilde{H}$ into another eigenstate, with a lower energy. Suppose φ_n is some particular eigenstate, with

$$
\tilde{H}\varphi_n = E_n\varphi_n
\tag{9.28}
$$

Define

$$
\phi' = a\varphi_n
\tag{9.29}
$$

then

$$
\begin{aligned}
\tilde{H}\phi' &= \hbar\omega(a^\dagger a + \frac{1}{2})a\varphi_n \\
&= \hbar\omega(a^\dagger a a + \frac{1}{2}a)\varphi_n
\end{aligned}
\tag{9.30}
$$

The commutation relation (9.26) implies

$$
a^\dagger a = aa^\dagger - 1
\tag{9.31}
$$

so that

$$
\begin{aligned}
\tilde{H}\phi' &= \hbar\omega[(aa^\dagger - 1)a + \frac{1}{2}a]\varphi_n \\
&= a[\hbar\omega(a^\dagger a + \frac{1}{2}) - \hbar\omega]\varphi_n \\
&= a[\tilde{H} - \hbar\omega]\varphi_n \\
&= (E_n - \hbar\omega)a\varphi_n \\
&= (E_n - \hbar\omega)\phi'
\end{aligned}
\tag{9.32}
$$

which proves that $a\phi_n$ is an energy eigenstate with eigenvalue $E = E_n - \hbar\omega$. The operator $a^\dagger$ is termed the "raising operator" for similar reasons. Let

$$
\phi" = a^\dagger\varphi_n
\tag{9.33}
$$

Then

$$
\begin{aligned}
\tilde{H}\phi" &= \hbar\omega(a^\dagger a + \frac{1}{2})a^\dagger\varphi_n \\
&= \hbar\omega(a^\dagger a a^\dagger + \frac{1}{2}a^\dagger)\varphi_n
\end{aligned}
\tag{9.34}
$$

The commutation relation (9.26) also says that

$$aa^\dagger = a^\dagger a + 1 \tag{9.35}$$

so

$$
\begin{aligned}
\tilde{H}\phi" &= \hbar\omega[a^\dagger(a^\dagger a + 1) + \frac{1}{2}a^\dagger]\varphi_n \\
&= a^\dagger[\hbar\omega(a^\dagger a + \frac{1}{2}) + \hbar\omega]\varphi_n \\
&= a^\dagger[\tilde{H} + \hbar\omega]\varphi_n \\
&= (E_n + \hbar\omega)a^\dagger\varphi_n \\
&= (E_n + \hbar\omega)\phi"
\end{aligned}
\tag{9.36}
$$

and therefore $\phi" = a^\dagger\varphi_n$ *is an energy eigenstate with eigenvalue* $E = E_n + \hbar\omega$.

Next we use the fact that the harmonic oscillator, like the hydrogen atom, has a lowest energy state (or "ground" state). That there must be a lowest energy state is clear from the uncertainty principle, but we can also see it from the fact that

$$
\begin{aligned}
< p^2 > &= < \psi|p^2|\psi > = < p\psi|p\psi > &\geq 0 \\
< x^2 > &= < \psi|x^2|\psi > = < x\psi|x\psi > &\geq 0
\end{aligned}
\tag{9.37}
$$

where we have used the hermiticity of x and p, and also the fact that the norm of any non-zero vector is greater than zero. Then

$$< H >= \frac{1}{2m} < p^2 > + \frac{1}{2}k < x^2 > \ \geq \ 0 \tag{9.38}$$

This proves that a ground state exists, with an energy greater than or equal to zero. However, the existence of a ground state seems to contradict the fact that, by operating on the ground state with the lowering operator a, we get a state with still lower energy. Denote the ground state by φ_0, the ground-state energy by E_0, and let $\varphi' = a\varphi_0$. Then, according to eq. (9.32)

$$\tilde{H}(a\varphi_0) = (E_0 - \hbar\omega)(a\varphi_0) \tag{9.39}$$

This equation is satisfied if $\varphi' = a\varphi_0$ is an eigenstate of $\tilde{H}$ with energy $E_0 - \hbar\omega$, which means that φ_0 is not the ground state, *or* if

$$a\varphi_0 = 0 \tag{9.40}$$

Since we have proved that a ground state exists, then the lowering operator must "annihilate" the ground state; i.e. bring it to 0, as shown in (9.40). Equation (9.40) is a first-order differential equation for the ground state:

$$\left(\sqrt{m\omega}x + \hbar\frac{1}{\sqrt{m\omega}}\frac{\partial}{\partial x} \right)\varphi_0 = 0 \tag{9.41}$$

which has the unique solution

$$\varphi_0 = N e^{-m\omega x^2/2\hbar} \tag{9.42}$$

The constant N is determined from the normalization condition

$$
\begin{aligned}
1 &= N^2 \int_{-\infty}^{\infty} dx\, e^{-m\omega x^2/\hbar} \\
&= N^2 \sqrt{\frac{\pi\hbar}{m\omega}}
\end{aligned}
\tag{9.43}
$$

so the ground-state eigenfunction is

$$\varphi_0 = \left[\frac{m\omega}{\pi\hbar}\right]^{1/4} e^{-m\omega x^2/2\hbar} \tag{9.44}$$

The corresponding ground-state energy E_0 is

$$
\begin{aligned}
\tilde{H}\varphi_0 &= \hbar\omega\left(a^\dagger a + \frac{1}{2}\right)\varphi_0 \\
&= \frac{1}{2}\hbar\omega\varphi_0 \\
\Longrightarrow\ E_0 &= \frac{1}{2}\hbar\omega
\end{aligned}
\tag{9.45}
$$

The state with the next-to-lowest energy is obtained by operating with the raising operator $a^\dagger$ on the ground state:

$$\varphi_1 = c_1 a^\dagger \varphi_0 \tag{9.46}$$

where c_1 is a normalization constant. Since the raising operator raises the energy by $\hbar\omega$, the energy of this state is

$$
\begin{aligned}
E_1 &= E_0 + \hbar\omega \\
&= \hbar\omega\left(1 + \frac{1}{2}\right)
\end{aligned}
\tag{9.47}
$$

The state with the next higher energy is

$$
\begin{aligned}
\varphi_2 &\propto a^\dagger \varphi_1 \\
&= c_2 (a^\dagger)^2 \varphi_0
\end{aligned}
\tag{9.48}
$$

with energy

$$
\begin{aligned}
E_2 &= E_1 + \hbar\omega \\
&= \hbar\omega\left(2 + \frac{1}{2}\right)
\end{aligned}
\tag{9.49}
$$

Proceeding in this way, we find an infinite set of eigenstates of the form

$$\begin{aligned}
\varphi_n &= c_n (a^\dagger)^n \varphi_0 \qquad n = 0, 1, 2, 3, ... \\
E_n &= \hbar\omega(n + \frac{1}{2})
\end{aligned} \tag{9.50}$$

Now, how do we know that this is all the eigenstates that there are? Suppose, for example, that there were an eigenstate φ' with an energy in between E_0 and E_1. If that were the case, the applying the lowering operator to the state would either annihilate the state, or else give an eigenstate with an energy lower than the ground state. Since the ground state exists, and is φ_0 by definition, it means that $a\varphi' = 0$. But the only solution to this equation is $\varphi' = \varphi_0$. Therefore, there is no state with energy between E_0 and E_1. So suppose instead there were a state φ'' with energy between E_n and E_{n+1}. Applying the lowering operator to φ'' lowers the energy by integer multiples of $\hbar\omega$, until we reach a state φ' with an energy between E_0 and E_1. But we have just seen that there is no such state. This means that there is no state with energy between E_n and E_{n+1}. So the only possible energies are those shown in (9.50).

Still, how do we know that these energies are non-degenerate? Suppose, e.g., there was a state $\varphi_1' \neq \varphi_1$ with energy E_1. Applying the lowering operator, we would get a second ground state φ_0' with energy E_0. But then, since there is no energy lower than the ground-state energy,

$$a\varphi_0' = 0 \implies \varphi_0' = \varphi_0 \tag{9.51}$$

which implies, since

$$\varphi_0' \propto a\varphi_1' \tag{9.52}$$

that $\varphi_1' = \varphi_1$. This argument is easily generalized to any energy E_n, and the conclusion is that there is only one eigenstate for each energy eigenvalue.

Next, we need to find the normalization constants c_n in (9.50). This is done iteratively. Begin from

$$c_0 = 1 \tag{9.53}$$

and impose the normalization condition

$$\begin{aligned}
1 &= < \varphi_n | \varphi_n > \\
&= c_n^2 < (a^\dagger)^n \varphi_0 | (a^\dagger)^n \varphi_0 > \\
&= c_n^2 < a^\dagger (a^\dagger)^{n-1} \varphi_0 | (a^\dagger)^n \varphi_0 > \\
&= c_n^2 < (a^\dagger)^{n-1} \varphi_0 | a(a^\dagger)^n | \varphi_0 >
\end{aligned} \tag{9.54}$$

The idea is to commute the a operator to the right, past the $a^\dagger$ operators, until it finally operates on, and annhilates, the ground state φ_0. We have

$$a(a^\dagger)^n = (aa^\dagger)(a^\dagger)^{n-1}$$

$$
\begin{aligned}
&= (a^\dagger a + 1)(a^\dagger)^{n-1} \\
&= a^\dagger a (a^\dagger)^{n-1} + (a^\dagger)^{n-1} \\
&= a^\dagger (a^\dagger a + 1)(a^\dagger)^{n-2} + (a^\dagger)^{n-1} \\
&= (a^\dagger)^2 (a^\dagger a + 1)(a^\dagger)^{n-3} + 2(a^\dagger)^{n-1} \\
&= (a^\dagger)^3 (a^\dagger a + 1)(a^\dagger)^{n-4} + 3(a^\dagger)^{n-1} \\
&\quad . \\
&\quad . \\
&\quad . \\
&= (a^\dagger)^n a + n(a^\dagger)^{n-1}
\end{aligned}
\tag{9.55}
$$

Equation (9.54) becomes

$$
1 = c_n^2 < (a^\dagger)^{n-1}\varphi_0 | [(a^\dagger)^n a + n(a^\dagger)^{n-1}] | \varphi_0 >
\tag{9.56}
$$

Using $a|\varphi_0 >= 0$,

$$
\begin{aligned}
1 &= n c_n^2 < (a^\dagger)^{n-1}\varphi_0 | (a^\dagger)^{n-1} | \varphi_0 > \\
&= n \frac{c_n^2}{c_{n-1}^2} < \varphi_{n-1} | \varphi_{n-1} > \\
&= n \frac{c_n^2}{c_{n-1}^2}
\end{aligned}
\tag{9.57}
$$

so that

$$
c_n = \frac{c_{n-1}}{\sqrt{n}}
\tag{9.58}
$$

Using this equation, and $c_0 = 1$, we get

$$
\begin{aligned}
c_1 &= 1 \\
c_2 &= \frac{1}{\sqrt{2 \cdot 1}} \\
c_3 &= \frac{1}{\sqrt{3 \cdot 2 \cdot 1}}
\end{aligned}
\tag{9.59}
$$

or, in general

$$
c_n = \frac{1}{\sqrt{n!}}
\tag{9.60}
$$

We now have the general solution for the energy eigenstates of the harmonic oscillator:

$$
\begin{aligned}
\varphi_n(x) &= \frac{1}{\sqrt{n!}}(a^\dagger)^n \varphi_0(x) \\
&= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{n!}} \left[\frac{1}{\sqrt{2}}(\sqrt{\frac{m\omega}{\hbar}}x - \sqrt{\frac{\hbar}{m\omega}}\frac{\partial}{\partial x})\right]^n e^{-m\omega x^2/2\hbar}
\end{aligned}
\tag{9.61}
$$

Rescaling x

$$y = \sqrt{\frac{m\omega}{\hbar}} x \tag{9.62}$$

The general solution becomes

$$
\begin{aligned}
\varphi(x) &= \frac{1}{\sqrt{n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left(\frac{1}{\sqrt{2}}\right)^n \left(y - \frac{\partial}{\partial y}\right)^n e^{-y^2/2} \\
&= \frac{1}{\sqrt{n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left(\frac{1}{\sqrt{2}}\right)^n \mathcal{H}_n(y) e^{-y^2/2} \tag{9.63}
\end{aligned}
$$

with corresponding eigenvalues

$$E_n = \hbar\omega(n + \frac{1}{2}) \tag{9.64}$$

The functions $\mathcal{H}_n(y)$ are known as **Hermite Polynomials**. Operating n times on the ground state with the raising operator $a^\dagger$ results in a function which is just the ground state multiplied by an n-th order polynomial in the variable $y = \sqrt{m\omega/\hbar}x$. These are the Hermite polynomials. The first several Hermite polynomials are:

$$
\begin{aligned}
\mathcal{H}_0(y) &= 1 \\
\mathcal{H}_1(y) &= 2y \\
\mathcal{H}_2(y) &= 4y^2 - 2 \\
\mathcal{H}_3(y) &= 8y^3 - 12y \tag{9.65}
\end{aligned}
$$

By applying eq. (9.63), the Hermite polynomials, and the eigenstates $\varphi_n(x)$, can be determined to any order desired.

9.2   Algebra and Expectation Values

One of the most remarkable properties of the quantum harmonic oscillator is that many calculations involving expectation values can be done algebraically, without ever using the explicit form of the eigenstates $\varphi_n(x)$. The reasons for this are, first, that the x and p operators are linear combinations of the raising and lowering operators (eq. (9.27)); and second, that the raising and lowering operators have a simple algebraic action on the eigenstates.

Consider the raising operator acting on the state φ_n. Using eq. (9.61) we have

$$
\begin{aligned}
a^\dagger |\varphi_n> &= \frac{1}{\sqrt{n!}} (a^\dagger)^{n+1} |\varphi_0> \\
&= \sqrt{(n+1)} \frac{1}{\sqrt{(n+1)!}} (a^\dagger)^{n+1} |\varphi_{n+1}> \\
&= \sqrt{n+1} |\varphi_{n+1}> \tag{9.66}
\end{aligned}
$$

and we can also derive a similar equation for $a\varphi_n$:

$$
\begin{aligned}
a|\varphi_n> &= \frac{1}{\sqrt{n!}}a(a^\dagger)^n|\varphi_0> \\
&= \frac{1}{\sqrt{n!}}[(a^\dagger)^n a + n(a^\dagger)^{n-1}]|\varphi_0> \\
&= n\frac{1}{\sqrt{n!}}(a^\dagger)^{n-1}|\varphi_0> \\
&= \sqrt{n}\frac{1}{\sqrt{(n-1)!}}(a^\dagger)^{n-1}|\varphi_0> \\
&= \sqrt{n}|\varphi_{n-1}>
\end{aligned}
\tag{9.67}
$$

In summary:

$$
\begin{aligned}
a|\varphi_n> &= \sqrt{n}|\varphi_{n-1}> \\
a^\dagger|\varphi_n> &= \sqrt{n+1}|\varphi_{n+1}> \\
x &= \sqrt{\frac{\hbar}{2m\omega}}(a+a^\dagger) \\
p &= \frac{1}{i}\sqrt{\frac{m\omega\hbar}{2}}(a-a^\dagger)
\end{aligned}
\tag{9.68}
$$

As an example of the use of these relations, let us compute the position uncertainty Δx in the n-th energy eigenstate. As usual

$$
(\Delta x)^2 = <x^2> - <x>^2
\tag{9.69}
$$

Now

$$
\begin{aligned}
\sqrt{\frac{2m\omega}{\hbar}}<x> &= <\varphi_n|(a+a^\dagger)|\varphi_n> \\
&= \sqrt{n}<\varphi_n|\varphi_{n-1}> + \sqrt{n+1}<\varphi_n|\varphi_{n+1}> \\
&= 0
\end{aligned}
\tag{9.70}
$$

Next, applying successively the relations (9.68)

$$
\begin{aligned}
\frac{2m\omega}{\hbar}<x^2> &= <\varphi_n|(a+a^\dagger)(a+a^\dagger)|\varphi_n> \\
&= <\varphi_n|(aa + aa^\dagger + a^\dagger a + a^\dagger a^\dagger)|\varphi_n> \\
&= <\varphi_n|aa|\varphi_n> + <\varphi_n|aa^\dagger|\varphi_n> + <\varphi_n|a^\dagger a|\varphi_n> + <\varphi_n|a^\dagger a^\dagger|\varphi_n> \\
&= \sqrt{n}<\varphi_n|a|\varphi_{n-1}> + \sqrt{n+1}<\varphi_n|a|\varphi_{n+1}>
\end{aligned}
$$

$$+\sqrt{n} < \varphi_n|a^\dagger|\varphi_{n-1} > +\sqrt{n+1} < \varphi_n|a^\dagger|\varphi_{n+1} >$$

$$= \sqrt{n(n-1)} < \varphi_n|\varphi_{n-2} > +(n+1) < \varphi_n|\varphi_n >$$

$$+n < \varphi_n|\varphi_n > +\sqrt{(n+1)(n+2)} < \varphi_n|\varphi_{n+2} >$$

$$= 0 + (n+1) + n + 0$$

$$= 2n + 1 \tag{9.71}$$

so the position uncertainty is

$$\Delta x = \sqrt{\frac{\hbar}{2m\omega}(2n+1)} \tag{9.72}$$

Notice that the explicit form of the wavefunction $\varphi_n(x)$ was not needed to compute Δx; the calculation is completely algebraic, and required only the relations (9.68). It is easy to see that any expression of the form

$$< \phi_m|F[x,p]|\phi_n > \tag{9.73}$$

where $F[x,p]$ is any polynomial in the x and p operators, can also be computed algebraically by the same method.

Chapter 10

Symmetry and Degeneracy

We live in a world which is almost, but not quite, symmetric. The Earth is round, nearly, and moves in an orbit around the Sun which is circular, almost. Our galaxy looks roughly like a spiral. Human beings and most animals have a left-right symmetry; the left-hand side looks the same as the right-hand side, more or less. Starfish have a pentagonal symmetry, table salt has a cubic symmetry, and in general Nature abounds in geometrical shapes of various kinds.

The symmetry which is apparent in large structures (animals, planets, galaxies...) is even more evident at the very small scales that are the domain of quantum physics. Symmetries appear in the arrangement of atoms in solids, in the arrangement of electrons in atoms, and in the structure of the nucleus. Symmetry principles are especially important for understanding the variety and behavior of the elementary particles, out of which all larger structures are built.

The mathematical expression of a geometrical symmetry is an invariance under some transformation of coordinates. Let us consider some examples which will be important:

- **Reflection Symmetry**   A stick-figure sketch is shown in Fig. [10.1]. Suppose we assign to every point on the sketch a set of coordinates (x, y) in the coordinate system shown, and then suppose that every point on the sketch is moved to another point

$$(x, y) \rightarrow (x', y') \tag{10.1}$$

according to the rule

$$x' = x + a \qquad y' = y + b \tag{10.2}$$

where a and b are constants. This is an example of a transformation of coordinates, known as a **Translation**. Under this transformation, the whole figure is moved to somewhere else in the plane, as shown in Fig. [10.2]. This is *not* an invariance of the sketch, since the transformed sketch can be distinguished, by its new position, from the original sketch. So we say that the translations (10.2) are *not* a symmetry of the

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figure. On the other hand, suppose every point (x', y') on the original sketch were moved to a new point (x', y') according to the rule

$$x' = -x \qquad y' = y \tag{10.3}$$

This transformation replaces the right-hand side of the figure by the left-hand side, and vice-versa. The transformed stick figure is indistinguishable from the original figure, and it is therefore said to be symmetric under **left-right reflection**.

- **Periodicity (Symmetry under Finite Translations)** Consider next the sin-wave shown in Fig. [10.3]. In general, if we transform every point $(x, y) \rightarrow (x', y')$ according to the rule (10.2), the figure will end up in a different place, and thus be distinguishable from the untransformed figure. However, if we make the transformation

$$x' = x + 2\pi n \qquad y' = y \tag{10.4}$$

where n is an integer, then the new figure is the same as the old, due to the periodicity of sin-waves. These special translations are therefore a symmetry of periodic functions, such as sin and cosine.

- **Rotation Symmetry** As a final example, consider the points on a circle of radius R. Each point on the circle can be assigned polar coordinates (r, θ), where $r = R$ and $0 \le \theta < 2\pi$. A circle is obviously symmetric under arbitary rotations

$$r' = r \qquad \theta' = \theta + \delta\theta \tag{10.5}$$

where $\delta\theta$ is any constant angle.

Symmetries are important in quantum mechanics whenever the Hamiltonian is invariant under some coordinate transformation:

$$
\begin{aligned}
x' &= f(x) \\
\frac{\partial}{\partial x'} &= \left(\frac{\partial f}{\partial x}\right)^{-1} \frac{\partial}{\partial x}
\end{aligned}
\tag{10.6}
$$

where the word "invariant" means that

$$\tilde{H}[-i\hbar\frac{\partial}{\partial x'}, x'] = \tilde{H}[-i\hbar\frac{\partial}{\partial x}, x] \tag{10.7}$$

Suppose $\phi_\alpha(x)$ is an eigenstate of $\tilde{H}$

$$\tilde{H}[-i\hbar\frac{\partial}{\partial x}, x]\phi_\alpha(x) = E_\alpha\phi_\alpha(x) \tag{10.8}$$

If we relabel the coordinates $x \to x'$,

$$\tilde{H}[-i\hbar \frac{\partial}{\partial x'}, x']\phi_\alpha(x') = E_\alpha \phi_\alpha(x') \tag{10.9}$$

and then use the invariance of the Hamiltonian under $x' = f(x)$, we find

$$\tilde{H}[-i\hbar \frac{\partial}{\partial x}, x]\phi_\alpha(f(x)) = E_\alpha \phi_\alpha(f(x)) \tag{10.10}$$

which proves that the transformed wavefunction

$$\phi'(x) = \phi_\alpha(f(x)) \tag{10.11}$$

is also an energy eigenstate, with energy E_α.

The reason that the symmetries of the Hamiltonian are important is that they are invariably associated with conservation laws; i.e. the expectation value of some observable Q (different from the energy) is constant in time

$$\frac{d}{dt} < Q >= 0 \tag{10.12}$$

For example, symmetry of the Hamiltonian with respect to arbitrary translations (10.2) is associated with the conservation of momentum; and symmetry of the Hamiltonian with respect to rotations by an arbitrary angle (10.5) is associated with the conservation of angular momentum. It is always possible to choose the set of energy eigenstates $\{\phi_\alpha\}$ to be eigenstates not only of the Hamiltonian, but also of some subset of the conserved observables, and the values of these observables can be used to distinguish between different energy eigenstates which may have the same energy eigenvalue. This lecture will be devoted to some examples of symmetric Hamiltonians, and their corresponding conservation laws.

10.1 The Free Particle, and Momentum Conservation

The free particle Hamiltonian in one dimension is invariant under arbitrary translations

$$x' = x + a \tag{10.13}$$

because $V(x') = V(x) = 0$ everywhere, and because

$$\frac{\partial}{\partial x'} = \frac{\partial}{\partial x} \tag{10.14}$$

Let us define a linear operator T, which acts on functions by transforming the coordinate

$$TF(x) = F(x') = F(x + a) \tag{10.15}$$

Then

$$
\begin{aligned}
T\tilde{H}[\frac{\partial}{\partial x}, x]\psi(x) &= \tilde{H}[\frac{\partial}{\partial x'}, x']\psi(x') \\
&= \tilde{H}[\frac{\partial}{\partial x}, x]\psi(x') \\
&= \tilde{H}[\frac{\partial}{\partial x}, x]T\psi(x)
\end{aligned}
\tag{10.16}
$$

From this equation, we see that the operator T commutes with the the Hamilitonian operator

$$
[T, \tilde{H}] = 0 \tag{10.17}
$$

Now notice that

$$
\begin{aligned}
TF(x) &= F(x + a) \\
&= F(x) + \frac{\partial F}{\partial x}a + \frac{1}{2}\frac{\partial^2 F}{\partial x^2}a^2 + ... \\
&= \sum_{n=0}^{\infty} \frac{a^n}{n!}\frac{\partial^n}{\partial x^n}F(x) \\
&= \exp\left[a\frac{\partial}{\partial x}\right]F(x) \\
&= \exp[ia\tilde{p}/\hbar]F(x)
\end{aligned}
\tag{10.18}
$$

which means that T is the exponential of the momentum operator. Since T commutes with $\tilde{H}$ for any displacement a, it follows that the momentum operator p also commutes with H

$$
[\tilde{p}, \tilde{H}] = 0 \tag{10.19}
$$

This is easy to check for the free particle Hamiltonian, since $\tilde{H} = \tilde{p}^2/2m$, and $\tilde{p}$ commutes with $\tilde{p}^2$.

In Lecture 8, we found an equation of motion for expectation values

$$
\frac{d}{dt} < Q > = \frac{i}{\hbar} < [Q, H] > \tag{10.20}
$$

It follows that *if an Hermitian operator commutes with the Hamiltonian, the corresponding observable is conserved:*

$$
\frac{d}{dt} < Q > = 0 \tag{10.21}
$$

In the special case of the free particle, we therefore have conservation of momentum

$$
\frac{d}{dt} < p > = 0 \tag{10.22}
$$

We have already noted that the energies of the free particle are 2-fold degenerate; i.e. for each energy E there are two linearly independent states with the same energy, and any linear combination of those two states

$$\psi(x) = a e^{i\sqrt{2mE}x/\hbar} + b e^{-i\sqrt{2mE}x/\hbar} \tag{10.23}$$

is also an eigenstate with energy E. However, since $\tilde{p}$ commutes with $\tilde{H}$, it follows from the commutator theorem that energy E and momentum p are simultaneously observable. This means that we can choose the complete set of energy eigenstates $\{\phi_\alpha\}$ to be eigenstates of $\tilde{H}$ *and* $\tilde{p}$, which is

$$\left\{ \phi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}; \quad E_p = \frac{p^2}{2m}; \quad p \in [-\infty, \infty] \right\} \tag{10.24}$$

Each value of the momentum p singles out one and only one energy eigenstate $\phi_p(x)$, whereas an energy eigenvalue, by itself, is not enough to specify the state uniquely.

10.2 Parity

The free particle potential

$$V(x) = 0 \tag{10.25}$$

the harmonic oscillator potential

$$V(x) = \frac{1}{2}kx^2 \tag{10.26}$$

and the finite square well potential

$$V(x) = \begin{cases} 0 & x < -a \\ -V_0 & -a \le x \le a \\ 0 & x > a \end{cases} \tag{10.27}$$

are all invariant under the **Parity** transformation

$$x' = -x \tag{10.28}$$

which is a left-right reflection of the x-axis. The kinetic energy term of the Hamiltonian is also invariant under this transformation, since

$$
\begin{aligned}
-\frac{\hbar^2}{2m} \frac{\partial}{\partial x'} \frac{\partial}{\partial x'} &= -\frac{\hbar^2}{2m} \left(-\frac{\partial}{\partial x} \right) \left(-\frac{\partial}{\partial x} \right) \\
&= -\frac{\hbar^2}{2m} \frac{\partial}{\partial x} \frac{\partial}{\partial x}
\end{aligned}
\tag{10.29}
$$

therefore the Hamiltonians of the free particle, the Harmonic oscillator, and the finite square well are invariant under the Parity transformation. Define the Parity operator as the linear operator which has the property

$$PF(x) = F(-x) \tag{10.30}$$

Once again, we see that

$$
\begin{aligned}
P\tilde{H}[\partial_x, x]\psi(x) &= \tilde{H}[-\partial_x, -x]\psi(-x) \\
&= \tilde{H}[\partial_x, x]\psi(-x) \\
&= \tilde{H}[\partial_x, x]P\psi(x)
\end{aligned}
\tag{10.31}
$$

so the Parity operator commutes with the Hamiltonian

$$[P, \tilde{H}] = 0 \tag{10.32}$$

and is conserved

$$\frac{d}{dt} < P >= 0 \tag{10.33}$$

It is easy to show that Parity is an Hermitian operator (exercise). Suppose ϕ_β is an eigenstate of the Parity operator with eigenvalue β

$$P\phi_\beta(x) = \beta\phi_\beta \tag{10.34}$$

Then

$$PP\phi_\beta(x) = \beta P\phi_\beta(x) = \beta^2\phi_\beta(x) \tag{10.35}$$

On the other hand,

$$PP\phi_\beta(x) = P\phi_\beta(-x) = \phi_\beta(x) \tag{10.36}$$

Comparing the last two equations, we see that

$$\beta^2 = 1 \implies \beta = \pm 1 \tag{10.37}$$

Eigenstates with $\beta = +1$ are known as "even-parity" eigenstates, denoted $\phi_+(x)$, and have the property

$$\phi_+(-x) = +\phi_+(x) \tag{10.38}$$

while eigenstates with $\beta = -1$ are known as "odd-parity" eigenstates, denoted $\phi_-(x)$, with the property

$$\phi_-(-x) = -\phi_-(x) \tag{10.39}$$

By the Commutator Theorem, the Hamiltonian operator and the Parity operator have a common set of eigenstates. We have already seen in Lecture 9 that every energy eigenstate of the finite square well was either an even parity state, or an odd parity state. The same is true for the energy eigenstates of the Harmonic oscillator. The harmonic oscillator ground state $\phi_0(x)$ is a gaussian function which is invariant

under $x \to -x$; it is therefore an even-parity eigenstate. The raising operator, on the other hand transforms as

$$a^\dagger(-x, -\partial_x) = -a^\dagger(x, \partial_x) \tag{10.40}$$

Using the general form for the harmonic oscillator eigenstates

$$\phi_n(x) = \frac{1}{\sqrt{n!}} (a^\dagger)^n \phi_0(x) \tag{10.41}$$

it is clear that

$$P\phi_n(x) = \phi_n(-x) = (-1)^n \phi_n(x) \tag{10.42}$$

and the energy eigenstates are even-parity for n even, and odd-parity for n odd.

Finally, the free particle Hamiltonian is invariant under Parity, so there must be a complete set of energy eigenstates which are also eigenstates of the parity operator. Note that the eigenstates of momentum are *not* eigenstates of parity

$$Pe^{ipx/\hbar} = e^{-ipx/\hbar} \neq \pm e^{ipx/\hbar} \tag{10.43}$$

On the other hand, an energy eigenstate does not have to be a momentum eigenstate. As we have seen, an eigenstate of energy E has the general form

$$\phi_E(x) = ae^{ipx/\hbar} + be^{-ipx/\hbar} \qquad p = \sqrt{2mE} \tag{10.44}$$

If $\phi_E(x)$ is an even-parity eigenstate, it requires that $a = b$, or

$$\phi_{E+}(x) = A \cos[\frac{px}{\hbar}] \tag{10.45}$$

while if $\phi_E(x)$ is an odd-parity eigenstate, it means that $a = -b$, or

$$\phi_{E-}(x) = B \sin[\frac{px}{\hbar}] \tag{10.46}$$

So a complete set of energy eigenstates is given by the set

$$\{\phi_{E+}(x), \ \phi_{E-}(x), \ E \in [0, \infty]\} \tag{10.47}$$

This is complete because *any* energy eigenstate of the form (10.44) can be expressed as a linear combination of ϕ_{E+} and ϕ_{E-}. Note that specifying the energy E, and the parity ± 1, determines the energy eigenstate uniquely.

It may seem odd that an eigenstate of momentum is not an eigenstate of parity (and vice versa). After all, both are associated with coordinate transformations which are symmetries of the free particle Hamiltonian. However, the order of these transformations is important. Suppose we have a particle at point x. If we first make a translation $x' = x + a$, and then a tranformation $x'' = -x'$, the particle winds up at coordinates $x'' = -x - a$. On the other hand, if we make these transformations in

reverse order, first $x' = -x$ and then $x'' = x' + a$, the particle ends up at $x'' = -x + a$, which is a different point. It is not surprising, then, that the momentum operator $\tilde{p}$ and the Parity operator P don't commute:

$$\begin{aligned} P\tilde{p}f(x) &= (-\tilde{p})f(-x) \\ &= -\tilde{p}Pf(x) \\ &\neq \tilde{p}Pf(x) \end{aligned} \tag{10.48}$$

Since

$$[P, \tilde{p}] \neq 0 \tag{10.49}$$

it follows that P and $\tilde{p}$ cannot have the same set of eigenstates. There are two lessons to be learned from this:

1. When the order of symmetry transformations is important, then the operators associated with those transformations do not commute.

2. When two (or more) operators commute with the Hamiltonian, but not with each other, there are always degenerate energy eigenvalues.

10.3   The Particle in a Square

As a second example of the two principles stated above, we consider a two-dimensional problem: a particle moving freely inside a square of length L, whose lower left-hand corner is located at the point $x = 0$, $y = 0$. The symmetries of a square include: reflection of the x-axis around the point $x = L/2$:

$$x' = L - x \tag{10.50}$$

reflection of the y-axis around $y = L/2$

$$y' = L - y \tag{10.51}$$

and the interchange of coordinates

$$x' = y \qquad y' = x \tag{10.52}$$

which is equivalent to a reflection around the line $x = y$.

The Hamiltonian for a particle of mass m moving in the square is

$$\tilde{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + V(x, y) \tag{10.53}$$

where

$$V(x, y) = v(x) + v(y)$$
$$v(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{otherwise} \end{cases} \tag{10.54}$$

The variables in the Hamiltonian are separable:

$$\tilde{H} = \tilde{H}_x + \tilde{H}_y$$
$$\tilde{H}_x = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + v(x)$$
$$\tilde{H}_y = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + v(y) \tag{10.55}$$

so the method of separation of variables

$$\phi(x, y) = \psi(x)\varphi(y) \tag{10.56}$$

can be applied to solve the time-independent Schrodinger equation

$$\tilde{H}\phi = E\phi \tag{10.57}$$

We get

$$\varphi(y)\tilde{H}_x\psi(x) + \psi(x)\tilde{H}_y\varphi(y) = E\psi(x)\varphi(y) \tag{10.58}$$

and dividing by $\phi(x, y)$ on both sides

$$\frac{\tilde{H}_x\psi(x)}{\psi(x)} + \frac{\tilde{H}_y\varphi(y)}{\varphi(y)} = E \tag{10.59}$$

Since the first ratio is only a function of x, and the second is only a function of y, the only way that the sum of the two ratios can be a constant, for all values of x and y, is if each ratio is a constant, i.e.

$$\tilde{H}_x\psi_n(x) = E_n\psi_n(x)$$
$$\tilde{H}_y\varphi_m(y) = E_m\varphi_m(y) \tag{10.60}$$

In this way the two-dimensional equation has been reduced to two one-dimensional equations, each of which is identical to the Schrodinger equation for a particle in a tube, and which have the same solutions:

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin[\frac{n\pi x}{L}] \qquad E_n = n^2\frac{\hbar^2\pi^2}{2mL^2}$$
$$\varphi_m(y) = \sqrt{\frac{2}{L}}\sin[\frac{m\pi y}{L}] \qquad E_m = m^2\frac{\hbar^2\pi^2}{2mL^2} \tag{10.61}$$

A complete set of energy eigenstates is then

$$\left\{ \phi_{nm}(x,y) = \frac{2}{L} \sin[\frac{n\pi x}{L}] \sin[\frac{m\pi y}{L}], \quad E_{nm} = (n^2 + m^2)\frac{\hbar^2 \pi^2}{2mL^2} \right\} \qquad (10.62)$$

The energies E_{nm} are two-fold degenerate for $n \neq m$, since

$$E_{nm} = E_{mn} \qquad (10.63)$$

Since the Hamiltonian $\tilde{H}$ is invariant under reflections of the x-axis around the point $x = L/2$, and reflections of the y-axis around $y = L/2$, we define the corresponding operators

$$\begin{aligned} R_x f(x,y) &= f(L-x,y) \\ R_y f(x,y) &= f(x,L-y) \end{aligned} \qquad (10.64)$$

It is easy to see that R_x and R_y commute,

$$\begin{aligned} R_x R_y f(x,y) &= R_y R_x f(x,y) \\ &= f(L-x,L-y)) \\ &\Longrightarrow [R_x, R_y] = 0 \end{aligned} \qquad (10.65)$$

and that the energy eigenstates of eq. (10.62) are eigenstates of both R_x and R_y, with eigenvalues ± 1, since

$$\sin\left[\frac{n\pi(L-x)}{L}\right] = \left\{ \begin{array}{ll} 1 & n \text{ odd} \\ -1 & n \text{ even} \end{array} \right. \times \sin[\frac{n\pi x}{L}] \qquad (10.66)$$

However, the Hamiltonian $\tilde{H}$ is also invariant under an interchange of the x and y coordinates

$$\mathcal{I}f(x,y) = f(y,x) \qquad (10.67)$$

and this operator does *not* commute with R_x and R_y:

$$\begin{aligned} \mathcal{I}R_x f(x,y) &= f(y,L-x) \\ R_x \mathcal{I}f(x,y) &= f(L-y,x) \end{aligned} \qquad (10.68)$$

The eigenvalues of $\mathcal{I}$ are determined by the same reasoning as in the case of parity. Suppose ϕ_β is an eigenstate of $\mathcal{I}$ with eigenvalue β. Then

$$\mathcal{I}\mathcal{I}\phi_\beta(x,y) = \mathcal{I}\phi_\beta(y,x) = \phi_\beta(x,y) \qquad (10.69)$$

but also

$$\mathcal{I}\mathcal{I}\phi_\beta(x,y) = \beta\mathcal{I}\phi_\beta(x,y) = \beta^2\phi_\beta(x,y) \qquad (10.70)$$

Therefore

$$\beta^2 = 1 \implies \beta = \pm 1 \tag{10.71}$$

Because $\phi_{nm}(x, y)$ and $\phi_{mn}(x, y)$ have the same energy, so does any linear combination

$$\Phi(x, y) = a\phi_{nm}(x, y) + b\phi_{mn}(x, y) \tag{10.72}$$

Requiring Φ to be an eigenstate of $\mathcal{I}$ with eigenvalue $\beta = 1$ means that $\phi(x, y) = \phi(y, x)$, or

$$a \sin[\frac{n\pi y}{L}] \sin[\frac{m\pi x}{L}] + b \sin[\frac{m\pi y}{L}] \sin[\frac{n\pi x}{L}]$$
$$= a \sin[\frac{n\pi x}{L}] \sin[\frac{m\pi y}{L}] + b \sin[\frac{m\pi x}{L}] \sin[\frac{n\pi y}{L}] \tag{10.73}$$

which is satisfied for $a = b$. Likewise, for Φ an eigenstate of $\mathcal{I}$ with eigenvalue $\beta = -1$, which means that $\phi(x, y) = -\phi(y, x)$ we need $a = -b$. Finally, the complete set of energy eigenstates which are also eigenstates of the $x - y$ interchange operator $\mathcal{I}$ are

$$\left\{ \begin{array}{l} \Phi_{nm+} = \frac{1}{\sqrt{2}}[\phi_{nm}(x, y) + \phi_{nm}(y, x)] \\ \Phi_{nm-} = \frac{1}{\sqrt{2}}[\phi_{nm}(x, y) - \phi_{nm}(y, x)] \end{array} \right\} \tag{10.74}$$

Once again, we see that there are symmetry operations which do not commute with one another, and that the energy eigenvalues are degenerate. The choice of a complete set of energy eigenstates, (10.62) or (10.74), is determined by requiring that the energy eigenstates, in addition to being eigenstates of the Hamiltonian, are also eigenstates of one of the symmetry operators.

10.4 The Quantum Corral

The "quantum corral" refers to a particle moving in the interior of a circle. The potential, in polar coordinates, is given by

$$V(r) = \left\{ \begin{array}{ll} 0 & r < R \\ \infty & r > R \end{array} \right. \tag{10.75}$$

which, since it depends only on the radial coordinate, is obviously invariant under arbitrary rotations

$$r' = r \qquad \theta' = \theta + \delta'\theta \tag{10.76}$$

Polar coordinates are related to cartesian coordinates by

$$x = r \cos\theta \qquad y = r \sin\theta \tag{10.77}$$

and the Laplacian operator ∇^2, in two dimensions, is given in polar coordinates by

$$
\begin{aligned}
\nabla^2 &\equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \\
&= \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}
\end{aligned}
\tag{10.78}
$$

Under an arbitrary rotation of the form (10.76), $\partial/\partial\theta' = \partial/\partial\theta$, so the Laplacian is invariant. It follows that the Hamiltonian for a particle moving inside a circle

$$
\tilde{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}\right) + V(r)
\tag{10.79}
$$

is invariant under rotations.

As in the previous examples, we introduce a rotation operator $\mathcal{R}_{\delta\theta}$ defined by

$$
\mathcal{R}_{\delta\theta} f(r,\theta) = f(r, \theta + \delta\theta)
\tag{10.80}
$$

and, proceeding as in the case of the translation operator

$$
\begin{aligned}
f(r, \theta + \delta\theta) &= f(r,\theta) + \frac{\partial f}{\partial \theta}\delta\theta + \frac{1}{2}\frac{\partial^2 f}{\partial \theta^2} + \dots \\
&= \exp[\delta\theta\frac{\partial}{\partial \theta}]f(r,\theta)
\end{aligned}
\tag{10.81}
$$

so that

$$
\mathcal{R}_{\delta\theta} = \exp[\delta\theta\frac{\partial}{\partial \theta}]
\tag{10.82}
$$

Since the Hamiltonian is invariant under rotations

$$
[\mathcal{R}_{\delta\theta}, \tilde{H}] = 0
\tag{10.83}
$$

it follows from (10.82) that

$$
[\frac{\partial}{\partial \theta}, \tilde{H}] = 0
\tag{10.84}
$$

Now, in cartesian coordinates

$$
\begin{aligned}
\frac{\partial}{\partial \theta} &= \frac{\partial x}{\partial \theta}\frac{\partial}{\partial x} + \frac{\partial y}{\partial \theta}\frac{\partial}{\partial y} \\
&= -r\sin\theta\frac{\partial}{\partial x} + r\cos\theta\frac{\partial}{\partial y} \\
&= x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \\
&= \frac{1}{-i\hbar}(x\tilde{p}_y - y\tilde{p}_x)
\end{aligned}
\tag{10.85}
$$

In three dimensions, angular momentum around the z-axis is given by

$$L_z = xp_y - yp_x \tag{10.86}$$

In two dimensions, this is the only possible component of angular momentum. The corresponding operator is $L_z = x\tilde{p}_y - y\tilde{p}_x$, and we see that the rotation operator is just the exponentiated angular momentum operator

$$\mathcal{R}_{\delta\theta} = e^{i\delta\theta L_z/\hbar} \tag{10.87}$$

and L_z commutes with the Hamiltonian

$$[L_z, \tilde{H}] = 0 \tag{10.88}$$

It follows that

$$\frac{d}{dt} < L_z > = 0 \tag{10.89}$$

In other words, symmetry of the potential with respect to rotations around some axis implies the Conservation of Angular Momentum around that axis.

By the Commutator Theorem, the operators L_z and $\tilde{H}$ have a common set of eigenstates. Since

$$L_z = -i\hbar\frac{\partial}{\partial\theta} \tag{10.90}$$

the Hamiltonian operator contains the angular momentum operator

$$\tilde{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{1}{\hbar^2 r^2}L_z^2\right) + V(r) \tag{10.91}$$

so we begin by solving for the eigenstates of angular momentum

$$\begin{aligned} L_z\phi(r,\theta) &= \alpha\phi(r,\theta) \\ -i\hbar\frac{\partial}{\partial\theta}\phi(r,\theta) &= \alpha\phi(r,\theta) \end{aligned} \tag{10.92}$$

which is similar to the momentum eigenvalue equation, and has a similar solution

$$\phi(r,\theta) = \varphi(r)e^{i\alpha\theta/\hbar} \tag{10.93}$$

There is one difference, however, between the eigenstates of momentum and angular momentum. Whereas the position $x + a$ is different from position x, for any non-zero constant a, the angle $\theta + 2\pi$ is identical to θ. This imposes an additional constraint

$$\phi(r,\theta + 2\pi) = \phi(r,\theta) \tag{10.94}$$

on the wavefunction of any physical state. In particular, for the angular momentum eigenstates (10.93), the constraint can only be satisfied if the eigenvalues α of angular momentum take on only discrete values

$$\alpha = n\hbar, \qquad n = 0, \pm 1, \pm 2, \pm 3, ... \tag{10.95}$$

and these are the only values which could result from an accurate measurement. In short, *the values of angular momentum are "quantized" in units of $\hbar$*. Essentially, it is a consequence of the wavelike properties of matter, combined with the 2π-periodicity of angles. Denote an eigenstate of angular momentum by

$$\phi_n(r, \theta) = \varphi_n(r)e^{in\theta} \tag{10.96}$$

and substitute into the time-independent Schrodinger equation,

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{1}{\hbar^2 r^2}L_z^2\right) + V(r)\right]\phi_n = E_n\phi_n \tag{10.97}$$

Using the fact that

$$L_z\phi_n = n\hbar\phi_n \tag{10.98}$$

the Schrodinger equation becomes

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{n^2}{r^2}\right) + V(r)\right]\varphi_n(r) = E_n\varphi_n(r) \tag{10.99}$$

As in the case of the infinite square well, the wavefunction must be zero where $V(r) = \infty$, i.e.

$$\varphi(r) = 0 \quad \text{when} \quad r \geq R \tag{10.100}$$

Inside the circle, at $r \leq R$, the Schrodinger equation is

$$\left[\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + (\frac{2mE}{\hbar^2} - \frac{n^2}{r^2})\right]\varphi_n(r) = 0 \tag{10.101}$$

Define

$$\begin{aligned} k^2 &= \frac{2mE}{\hbar^2} \\ \rho &= kr \end{aligned} \tag{10.102}$$

In terms of the rescaled radial coordinate ρ, the time-independent equation becomes

$$\left[\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial}{\partial \rho} + (1 - \frac{n^2}{\rho^2})\right]\varphi_n = 0 \tag{10.103}$$

This is one of the standard differential equations of mathematical physics, known as *Bessel's Equation*. The solutions are the Bessel Functions, denoted $J_n(\rho)$, and Neumann Functions, $N_n(\rho)$. The Neumann functions are infinite, and therefore non-differentiable wrt x and y, at $r = 0$. So Neumann functions do not correspond to physical states, and can be discarded. We are therefore left with solutions

$$\varphi_n(r) = J_n(kr) \quad \text{with energy} \quad E = \frac{\hbar^2 k^2}{2m} \tag{10.104}$$

This is a bound state solution, since the particle is bound by the potential inside a circle, and we know that the energies of bound states are discrete. In this case, the possible energies are determined by the condition that

$$\phi_n(R, \theta) = 0 \implies \varphi_n(R) = 0 \implies J_n(kR) = 0 \tag{10.105}$$

Bessel functions are oscillating functions (wavefunctions in classically allowed regions oscillate), so the constant k must be chosen such that kR is a "zero" of the Bessel function J_n. Denote

$$J_n(x_{nj}) = 0 \tag{10.106}$$

where $\{x_{n1}, x_{n2}, x_{n3}, ...\}$ are the zeros of the n-th Bessel function. In particular

$$
\begin{aligned}
x_{0j} &= 2.405, \ 5.520, \ 8.654, ... \\
x_{1j} &= 3.832, \ 7.016, \ 10.173, ...
\end{aligned}
\tag{10.107}
$$

and the possible energies must therefore satisfy

$$kR = x_{nj} \qquad E_{nj} = \frac{\hbar^2 k^2}{2m} \tag{10.108}$$

Finally, the complete set of energy eigenstates and eigenvalues are

$$\left\{ \phi_{nj} = J_n(\frac{x_{nj}}{R} r) e^{in\theta}, \quad E_{nj} = \frac{\hbar^2 x_{nj}^2}{2mR^2}, \quad L_z = n\hbar \right\} \tag{10.109}$$

Note that the energy eigenvalues are degenerate, $E_{nj} = E_{(-n)j}$. This means that there must be at least two operators which commute with the Hamiltonian, but not with each other. In this case, an operator which commutes which $\tilde{H}$, but not with L_z, is the reflection operator

$$P_\theta f(r, \theta) = f(r, -\theta) \tag{10.110}$$

corresponding to the reflection symmetry $\theta' = -\theta$.

Very recent advances in technology, specifically, the invention of the scanning tunnelling microscope, and the development of techniques for manipulating matter at the atomic scale, have made it possible to actually trap electrons in a circle, and measure the square modulus of the wavefunction. The result, shown in Fig. [10.4], is breath-taking. The peaks arranged in a circle show the electron clouds of iron atoms, which are used to form the "corral". The circular ripples inside the "corral" show the wavefunction (modulus squared) of the trapped electrons. In the photograph, the electrons are in an energy eigenstate, and the wavefunction (modulus squared) is proportional to the square of a Bessel function.

10.5 Complete Sets of Observables

To summarize the lessons of this lecture:

1. *If two (or more) hermitian operators commute with the Hamiltonian, but not with each other, then the energy eigenvalues of the Hamiltonian must be degenerate.*

Reason: if H commutes with A and B, then H and A share a common set of eigenstates, and H and B share a common set of eigenstates. But if A doesn't commute with B, these two sets of eigenstates must be different. However, if the eigenvalues of H were non-degenerate, then there is only one possible choice of energy eigenstates. Since there are (at least) two different sets of energy eigenstates, the energy eigenvalues must be degenerate.

Example: The free particle Hamiltonian commutes with momentum p and parity P, but $[p, P] \neq 0$. The common set of eigenstates of H and p is

$$\left\{ e^{i\sqrt{2mE}x/\hbar}, \quad e^{-i\sqrt{2mE}x/\hbar}, \quad E \in [0, \infty] \right\} \tag{10.111}$$

and the common set of eigenvalues of H and P is

$$\left\{ \cos[\sqrt{2mE}x/\hbar], \quad \sin[\sqrt{2mE}x/\hbar], \quad E \in [0, \infty] \right\} \tag{10.112}$$

Each of these sets is a **Complete Set of States**, in the sense that any energy eigenstate can be written as a linear combination of the eigenstates of either set. Then, by theorem H3, *any* wavefunction $\phi(x)$ can be written as a sum of eigenstates of either set.

2. *Symmetries of the Hamiltonian imply conservation laws.*

Reason: Symmetry under coordinate transformations can be associated with operators which produce those transformations; these operators commute with any Hamiltonian which is invariant under the given transformation. Operators which commute with the Hamiltonian are conserved, according to eq. (10.20).

Examples: Symmetry of the free-particle Hamiltonian under translations implies conservation of momentum; symmetry of the Hamiltonian under rotations, e.g. for a particle bound inside a circle, implies conservation of angular momentum.

3. *As a general rule, symmetry operations do not commute. Therefore, as a consequence of item 1, the more symmetric the Hamiltonian, the greater is the degeneracy in its energy eigenvalues.*

Example: It will be seen in the next lecture that the energy degeneracy of a spherically symmetric Hamiltonian in three dimensions is greater than the energy degeneracy of a rotationally invariant Hamiltonian in two dimensions.

Items 1 and 3 actually hold true not just for the Hamiltonian, but for all operators. If A commutes with B and C, but B and C don't commute with each other, then the eigenvalues of A are degenerate. The more symmetries an operator has, the greater is the degeneracy in its eigenvalues.

Suppose the operators A, B, C commute, and that the set of eigenstates of A which are also eigenstates of B and C is unique. Then the set $\{A, B, C\}$ is known as a **Complete Set of Observables**. Measurement of a complete set of observables is sufficient to uniquely determine the quantum state (which must be an eigenstate of all operators in the set). Examples:

a. Momentum p is a complete set of observables. In fact, *any* operator with non-degenerate eigenvalues is a complete set.

b. Energy E is a complete set, for the Harmonic Oscillator and Square Well potentials.

c. Energy E and parity P is a complete set, for the free particle.

d. Energy E and reflection R_x is a complete set for the particle in a square. So is E and the observable corresponding to x-y interchange $\mathcal{I}$.

e. Energy E and angular momentum L_z is a complete set for the "quantum corral".

Chapter 11

Angular Momentum

When the potential energy in three dimensions depends only on the radial coordinate, the potential is said to be "spherically symmetric", and the Hamiltonian is invariant under arbitrary rotations; in particular, the Hamiltonian is invariant under rotations around the x, y, and z-axes. In the last lecture we found that for rotations around the origin in the $x - y$ plane, the rotation operator is

$$R_z(\delta\theta) = e^{iL_z\delta\theta/\hbar} \tag{11.1}$$

There is nothing special about the z-axis; rotations around the x and y-axes must have the corresponding forms

$$\begin{aligned} R_x(\delta\theta) &= e^{iL_x\delta\theta/\hbar} \\ R_y(\delta\theta) &= e^{iL_y\delta\theta/\hbar} \end{aligned} \tag{11.2}$$

In the case of rotations around different axes, the order of rotations is important. For example, consider a particle at a point on the z-axis, shown in Fig. [11.1], and imagine doing first a rotation by 90° around the z-axis, and then a rotation by 90^0 along the x-axis. The first rotation, around the z-axis, leaves the particle where it is. The second rotation, around the x-axis, brings the particle to a final position along the y-axis. Now reverse the order of coordinate transformations: A rotation around the x-axis brings the particle to a point to the y-axis, and the subsequent rotation around the z-axis brings the particle to a point on the x-axis. Thus the two transformations, performed in different orders, result in different final positions for the particle.

It follows that, although we expect the angular momentum operators to commute with a symmetric Hamiltonian, we do *not* expect the L_x, L_y, L_z operators to commute with each other. The energy eigenvalues will therefore be degenerate, angular momentum is conserved, and the angular momentum operators can be used to select among different complete sets of energy eigenstates. In this lecture, we will learn how to construct eigenstates of angular momentum, which is a necessary step towards solving the Schrodinger equation for spherically symmetric potentials

11.1   The Angular Momentum Commutators

Angular momentum in classical physics is defined as

$$\vec{L} = \vec{r} \times \vec{p} \tag{11.3}$$

or, in components,

$$
\begin{aligned}
L_x &= yp_z - zp_y \\
L_y &= zp_x - xp_z \\
L_z &= xp_y - yp_x
\end{aligned}
\tag{11.4}
$$

The corresponding quantum-mechanical operators are obtained by replacing p with $\tilde{p}$, i.e.

$$
\begin{aligned}
\tilde{L}_x &= y\tilde{p}_z - z\tilde{p}_y = -i\hbar \left\{ y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right\} \\
\tilde{L}_y &= z\tilde{p}_x - x\tilde{p}_z = -i\hbar \left\{ z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right\} \\
\tilde{L}_z &= x\tilde{p}_y - y\tilde{p}_z = -i\hbar \left\{ x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right\}
\end{aligned}
\tag{11.5}
$$

Spherical coordinates are related to cartesian coordinates by

$$
\begin{aligned}
z &= r\cos\theta \\
x &= r\sin\theta\cos\phi \\
y &= r\sin\theta\sin\phi
\end{aligned}
\tag{11.6}
$$

and a spherically symmetric potential, also known as a **central potential**, is a function which is independent of the angular coordinates θ, ϕ, i.e.

$$V(r, \theta, \phi) = V(r) \tag{11.7}$$

We have already deduced that the Hamiltonian should commute with the angular momentum operators, simply because the Hamiltonian of a particle in a central potential is invariant under a rotation of coordinates, and the operators which generate rotations are the exponential of the angular momentum operators. These commutators can of course be checked directly, e.g in the case of the z-component of angular momentum we have

$$
\begin{aligned}
[\tilde{L}_z, \tilde{H}] &= [\tilde{L}_z, \frac{1}{2m}\tilde{p}^2 + V(r)] \\
&= \frac{1}{2m}[\tilde{L}_z, \tilde{p}^2] + [L_z, V(r)]
\end{aligned}
\tag{11.8}
$$

where

$$
\begin{aligned}
[\tilde{L}_z, V(r)] &= x[p_y, V(r)] - y[p_x, V(r)] \\
&= -i\hbar \left(x\frac{\partial V}{\partial y} - y\frac{\partial V}{\partial x} \right) \\
&= -i\hbar \left(x\frac{\partial V}{\partial r}\frac{\partial r}{\partial y} - y\frac{\partial V}{\partial r}\frac{\partial r}{\partial x} \right) \\
&= -i\hbar \left(x\frac{\partial V}{\partial r}\frac{y}{r} - y\frac{\partial V}{\partial r}\frac{x}{r} \right) \\
&= 0
\end{aligned}
\tag{11.9}
$$

and

$$
\begin{aligned}
[\tilde{L}_z, \tilde{p}^2] &= [(x\tilde{p}_y - y\tilde{p}_x), \tilde{p}_x^2 + \tilde{p}_y^2 + \tilde{p}_z^2] \\
&= [x\tilde{p}_y, \tilde{p}_x^2] - [y\tilde{p}_x, \tilde{p}_y^2] \\
&= \tilde{p}_y[x, \tilde{p}_x^2] - \tilde{p}_x[y, \tilde{p}_y^2] \\
&= -2i\hbar\tilde{p}_y\tilde{p}_x + 2i\hbar\tilde{p}_x\tilde{p}_y \\
&= 0
\end{aligned}
\tag{11.10}
$$

This proves that

$$
[\tilde{L}_z, \tilde{H}] = 0
\tag{11.11}
$$

Similar steps show that

$$
[\tilde{L}_x, \tilde{H}] = [\tilde{L}_y, \tilde{H}] = 0
\tag{11.12}
$$

which means that *in a central potential, angular momentum is conserved.*

However, since the order of rotations around the x, y, and z-axes are important, the operators $\tilde{L}_x$, $\tilde{L}_y$, $\tilde{L}_z$ cannot commute among themselves. For example,

$$
\begin{aligned}
[\tilde{L}_x, \tilde{L}_y] &= [(y\tilde{p}_z - z\tilde{p}_y), (z\tilde{p}_x - x\tilde{p}_z)] \\
&= [y\tilde{p}_z, z\tilde{p}_x] + [z\tilde{p}_y, x\tilde{p}_z] \\
&= y\tilde{p}_x[\tilde{p}_z, z] + x\tilde{p}_y[z, \tilde{p}_z] \\
&= i\hbar(-y\tilde{p}_x + x\tilde{p}_y) \\
&= i\hbar\tilde{L}_z
\end{aligned}
\tag{11.13}
$$

Altogether,

$$
\begin{aligned}
[\tilde{L}_x, \tilde{L}_y] &= i\hbar\tilde{L}_z \\
\left[\tilde{L}_y, \tilde{L}_z\right] &= i\hbar\tilde{L}_x \\
\left[\tilde{L}_z, \tilde{L}_x\right] &= i\hbar\tilde{L}_y
\end{aligned}
\tag{11.14}
$$

These angular momentum commutators are the fundamental equations that will be applied in this lecture. They will be used to determine both the eigenvalues and the

eigenstates of angular momentum, by an algebraic methods which closely resembles the treatment of the harmonic oscillator.

The fact that the angular momentum operators commute with the Hamiltonian, but not with each other, means that the energy eigenvalues of the Hamiltonian are degenerate. It also means that all three components of angular momentum cannot be measured simultaneously, which tells us that there does not exist any physical state in which the direction of angular momentum is definite. However, despite the fact that the *direction* of angular momentum is indefinite, there do exist states in which the *magnitude* of angular momentum is definite; these are eigenstates of the squared angular momentum operator

$$\tilde{L}^2 = \tilde{L}_x^2 + \tilde{L}_y^2 + \tilde{L}_z^2 \tag{11.15}$$

Each of the components of angular momentum commutes with $\tilde{L}^2$. For example,

$$\begin{aligned}
[\tilde{L}_z, \tilde{L}^2] &= [\tilde{L}_z, \tilde{L}_x^2 + \tilde{L}_y^2 + \tilde{L}_z^2] \\
&= [\tilde{L}_z, \tilde{L}_x^2] + [\tilde{L}_z, \tilde{L}_y^2]
\end{aligned} \tag{11.16}$$

We evaluate the first commutator with the help of the relations in eq. (11.14)

$$\begin{aligned}
[\tilde{L}_z, \tilde{L}_x^2] &= \tilde{L}_z \tilde{L}_x \tilde{L}_x - \tilde{L}_x \tilde{L}_x \tilde{L}_z \\
&= (\tilde{L}_x \tilde{L}_z + [\tilde{L}_z, \tilde{L}_x]) \tilde{L}_x - \tilde{L}_x^2 \tilde{L}_z \\
&= \tilde{L}_x \tilde{L}_z \tilde{L}_x + i\hbar \tilde{L}_y \tilde{L}_x - \tilde{L}_x^2 \tilde{L}_z \\
&= \tilde{L}_x (\tilde{L}_x \tilde{L}_z + [\tilde{L}_z, \tilde{L}_x]) + i\hbar \tilde{L}_y \tilde{L}_x - \tilde{L}_x^2 \tilde{L}_z \\
&= i\hbar (\tilde{L}_x \tilde{L}_y + \tilde{L}_y \tilde{L}_x)
\end{aligned} \tag{11.17}$$

The second commutator gives a similar result:

$$\begin{aligned}
[\tilde{L}_z, \tilde{L}_y^2] &= \tilde{L}_z \tilde{L}_y \tilde{L}_y - \tilde{L}_y \tilde{L}_y \tilde{L}_z \\
&= (\tilde{L}_y \tilde{L}_z + [\tilde{L}_z, \tilde{L}_y]) \tilde{L}_y - \tilde{L}_y^2 \tilde{L}_z \\
&= \tilde{L}_y \tilde{L}_z \tilde{L}_y - i\hbar \tilde{L}_x \tilde{L}_y - \tilde{L}_x^2 \tilde{L}_z \\
&= \tilde{L}_y (\tilde{L}_y \tilde{L}_z + [\tilde{L}_z, \tilde{L}_y]) - i\hbar \tilde{L}_x \tilde{L}_y - \tilde{L}_y^2 \tilde{L}_z \\
&= -i\hbar (\tilde{L}_y \tilde{L}_x + \tilde{L}_x \tilde{L}_y) \\
&= -[\tilde{L}_z, \tilde{L}_x^2]
\end{aligned} \tag{11.18}$$

Adding the two commutators together gives zero, and therefore $\tilde{L}_z$ commutes with $\tilde{L}^2$. The same result is obtained for the other components of angular momentum:

$$[\tilde{L}_x, \tilde{L}^2] = [\tilde{L}_y, \tilde{L}^2] = [\tilde{L}_z, \tilde{L}^2] = 0 \tag{11.19}$$

11.2 The Eigenvalues of Angular Momentum

The energy eigenvalues of $\tilde{H}$, for a particle in a central potential, are degenerate, since $\tilde{H}$ commutes with the components of angular momentum, which do not commute with each other. The same can be said for the eigenvalues of $\tilde{L}^2$. These eigenvalues must be degenerate, because $\tilde{L}^2$ also commutes with $\tilde{L}_x$, $\tilde{L}_y$, $\tilde{L}_z$, which do commute with each other. By the commutator theorem $\tilde{L}^2$ and $\tilde{L}_x$ have a common set of eigenstates; so do $\tilde{L}^2$ and $\tilde{L}_x$, and also $\tilde{L}^2$ and $\tilde{L}_z$. But, again by the commutator theorem, these must be *different* sets of eigenstates.

Denote the eigenstates of $\tilde{L}^2$ and, say, L_z, as φ_{ab}. Angular momentum has units of action, i.e. energy×time, which is the same units as Planck's constant $\hbar$. So we may as well write the eigenvalues of angular momentum in units of $\hbar$ where

$$
\begin{aligned}
\tilde{L}^2 \varphi_{ab} &= a^2 \hbar^2 \varphi_{ab} \\
\tilde{L}_z \varphi_{ab} &= b\hbar \varphi_{ab}
\end{aligned}
\tag{11.20}
$$

where a and b are dimensionless numbers. The eigenvalues of $\tilde{L}_z$ may be positive or negative, but the eigenvalues of $\tilde{L}^2$ are necessarily positive, because $\tilde{L}^2$ is a sum of squares of Hermitian operators. Therefore,

$$
\begin{aligned}
<\varphi_{ab}|\tilde{L}^2 \varphi_{ab}> &= <\varphi_{ab}|\tilde{L}_x^2|\varphi_{ab}> + <\varphi_{ab}|L_y^2|\varphi_{ab}> + <\varphi_{ab}|L_z^2|\varphi_{ab}> \\
a^2 \hbar^2 <\varphi_{ab}|\varphi_{ab}> &= <\varphi_{ab}|\tilde{L}_x^2|\varphi_{ab}> + <\varphi_{ab}|\tilde{L}_y^2|\varphi_{ab}> + \hbar^2 b^2 <\varphi_{ab}|\varphi_{ab}> \\
a^2 \hbar^2 &= <\tilde{L}_x \varphi_{ab}|\tilde{L}_x \varphi_{ab}> + <\tilde{L}_y \varphi_{ab}|\tilde{L}_y \varphi_{ab}> + \hbar^2 b^2 \\
a^2 \hbar^2 &= \hbar^2 b^2 + |\tilde{L}_x \varphi_{ab}|^2 + |\tilde{L}_y \varphi_{ab}|^2
\end{aligned}
\tag{11.21}
$$

which establishes that the eigenvalues of $\tilde{L}^2$ are positive semi-definite, and also that

$$
-a \le b \le a
\tag{11.22}
$$

The fact that $\tilde{L}^2$ is a sum of squares of Hermitian operators, which commute in a simple way among themselves (eq. (11.14)), suggests trying the same trick that we used for the Harmonic oscillator. Applying eq. (9.13) of Lecture 9, we have

$$
\begin{aligned}
\tilde{L}^2 &= (\tilde{L}_x^2 + \tilde{L}_y^2) + \tilde{L}_z^2 \\
&= (\tilde{L}_+ \tilde{L}_- + i[\tilde{L}_x, \tilde{L}_y]) + \tilde{L}_z^2 \\
&= \tilde{L}_+ \tilde{L}_- - \hbar L_z + \tilde{L}_z^2
\end{aligned}
\tag{11.23}
$$

where

$$
\begin{aligned}
\tilde{L}_+ &\equiv \tilde{L}_x + i\tilde{L}_y \\
\tilde{L}_- &\equiv \tilde{L}_x - i\tilde{L}_y
\end{aligned}
\tag{11.24}
$$

$\tilde{L}_-$ is the Hermitian conjugate of $\tilde{L}_+$. Equivalently, since

$$
[\tilde{L}_+, \tilde{L}_-] = -2i[\tilde{L}_x, \tilde{L}_y] = 2\hbar \tilde{L}_z
\tag{11.25}
$$

we have

$$
\begin{aligned}
\tilde{L}^2 &= \tilde{L}_+\tilde{L}_- - \hbar\tilde{L}_z + \tilde{L}_z^2 \\
&= \tilde{L}_-\tilde{L}_+ + [\tilde{L}_+, \tilde{L}_-] - \hbar\tilde{L}_z + \tilde{L}_z^2 \\
&= \tilde{L}_-\tilde{L}_+ + \hbar\tilde{L}_z + \tilde{L}_z^2
\end{aligned}
\tag{11.26}
$$

Finally, we need the commutators of $\tilde{L}_z$ with $\tilde{L}_\pm$:

$$
\begin{aligned}
[\tilde{L}_z, \tilde{L}_+] &= [\tilde{L}_z, \tilde{L}_x] + i[\tilde{L}_z, \tilde{L}_y] \\
&= i\hbar\tilde{L}_y + i(-i\hbar\tilde{L}_x) \\
&= \hbar\tilde{L}_+
\end{aligned}
\tag{11.27}
$$

and likewise

$$
[\tilde{L}_z, \tilde{L}_-] = -\hbar\tilde{L}_-
\tag{11.28}
$$

In summary, the commutators of (11.14) in terms of $\tilde{L}_x$, $\tilde{L}_y$, $\tilde{L}_z$ can be replaced by commutators involving $\tilde{L}_\pm, \tilde{L}_z$, and $\tilde{L}^2$ can also be expressed in terms of $\tilde{L}_\pm$, $\tilde{L}_z$:

$$
\begin{aligned}
[\tilde{L}_+, \tilde{L}_-] &= 2\hbar\tilde{L}_z \\
\left[\tilde{L}_z, \tilde{L}_\pm\right] &= \pm\hbar\tilde{L}_\pm \\
\tilde{L}^2 &= \tilde{L}_+\tilde{L}_- + \tilde{L}_z^2 - \hbar\tilde{L}_z \\
&= \tilde{L}_-\tilde{L}_+ + \tilde{L}_z^2 + \hbar\tilde{L}_z
\end{aligned}
\tag{11.29}
$$

The point of introducing the $\tilde{L}_\pm$ operators is that they act on eigenstates of $\tilde{L}_z$ just like the raising and lowering operators a and $a^\dagger$ act on eigenstates of the harmonic oscillator Hamiltonian. Let

$$
\varphi' = L_+\varphi_{ab}
\tag{11.30}
$$

Then

$$
\begin{aligned}
L_z\varphi' &= L_zL_+\varphi_{ab} \\
&= (L_+L_z + \hbar L_+)\varphi_{ab} \\
&= (\hbar b + \hbar)L_+\varphi_{ab} \\
&= \hbar(b+1)\varphi'
\end{aligned}
\tag{11.31}
$$

and we see that $\varphi' = L_+\varphi_{ab}$ is also an eigenstate of L_z, with the eigenvalue $\hbar(b+1)$. The raising operator has therefore raised the eigenvalue of L_z by the amount $\hbar$. The "raised" eigenstate φ is also an eigenstate of L^2, with the same eigenvalue as φ_{ab}:

$$
\begin{aligned}
\tilde{L}^2\varphi' &= \tilde{L}^2\tilde{L}_+\varphi_{ab} \\
&= \tilde{L}_+\tilde{L}^2\varphi_{ab} \\
&= \hbar^2 a^2\tilde{L}_+\varphi_{ab} \\
&= \hbar^2 a^2\varphi'
\end{aligned}
\tag{11.32}
$$

Therefore,

$$\tilde{L}_+ \varphi_{ab} = C_{ab}^+ \varphi_{a,b+1} \tag{11.33}$$

where C_{ab}^+ is a constant. This establishes the fact that L_+ is a raising operator, analogous to the $a^\dagger$ operator used in solving the harmonic oscillator. In a similar way, we can show that L_- is a lowering operator. Define

$$\varphi" = \tilde{L}_- \varphi_{ab} \tag{11.34}$$

Then

$$
\begin{aligned}
\tilde{L}_z \varphi" &= \tilde{L}_z \tilde{L}_- \varphi_{ab} \\
&= (\tilde{L}_- \tilde{L}_z - \hbar L_-) \varphi_{ab} \\
&= (\hbar b - \hbar) \tilde{L}_- \varphi_{ab} \\
&= \hbar(b-1) \varphi"
\end{aligned}
\tag{11.35}
$$

so that $\varphi" = \tilde{L}_- \varphi_{ab}$ is also an eigenstate of $\tilde{L}_z$, with the eigenvalue $\hbar(b-1)$. It is also an eigenstate of $\tilde{L}^2$:

$$
\begin{aligned}
\tilde{L}^2 \varphi" &= \tilde{L}^2 \tilde{L}_- \varphi_{ab} \\
&= \tilde{L}_- \tilde{L}^2 \varphi_{ab} \\
&= \hbar^2 a^2 \tilde{L}_- \varphi_{ab} \\
&= \hbar^2 a^2 \varphi"
\end{aligned}
\tag{11.36}
$$

Therefore $\tilde{L}_-$ is a lowering operator

$$\tilde{L}_- \varphi_{ab} = C_{ab}^- \varphi_{a,b-1} \tag{11.37}$$

where C_{ab}^- is a constant.

In the case of the Harmonic oscillator, we deduced from the fact that $< E > \geq 0$ that there must be a state of lowest energy φ_0, and therefore a lowest energy eigenvalue E_0. Since the lowering operator a cannot produce a state of lower energy than E_0, it must annihilate the ground state

$$a\varphi_0 = 0 \tag{11.38}$$

The argument for angular momentum is quite similar. We have already found that the eigenvalues of $\tilde{L}_z$ have both a lower *and* and upper bound, for fixed $\hbar^2 a^2$, since

$$-a \leq b \leq a \tag{11.39}$$

So let us denoted the minimum value of b as b_{min} and the maximum value as b_{max}, where $|b_{min}|, |b_{max}| \leq a$. The corresponding eigenstates must have the property that

$$
\begin{aligned}
\tilde{L}_+ \varphi_{ab_{max}} &= 0 \\
\tilde{L}_- \varphi_{ab_{min}} &= 0
\end{aligned}
\tag{11.40}
$$

Now, we must be able to reach the highest state $\varphi_{ab_{max}}$ by acting successively on $\varphi_{ab_{min}}$ with the raising operator

$$\varphi_{ab_{max}} \propto (\tilde{L}_+)^n \varphi_{ab_{min}} \tag{11.41}$$

which implies, since the raising operator raises b to $b + 1$, that

$$b_{max} = b_{min} + n \qquad n = \text{ a positive integer or } 0 \tag{11.42}$$

or, equivalently,

$$
\begin{aligned}
b_{max} &= b_{av} + \frac{n}{2} \\
b_{min} &= b_{av} - \frac{n}{2} \\
b_{av} &= \frac{1}{2}(b_{max} + b_{min})
\end{aligned}
\tag{11.43}
$$

Next, using the expressions for $\tilde{L}^2$ in (11.29)

$$
\begin{aligned}
\tilde{L}^2 \varphi_{ab_{max}} &= (\tilde{L}_- \tilde{L}_+ + \tilde{L}_z^2 + \hbar \tilde{L}_z)\varphi_{ab_{max}} \\
\hbar^2 a^2 \varphi_{ab_{max}} &= \hbar^2 b_{max}(b_{max} + 1)\varphi_{ab_{max}}
\end{aligned}
\tag{11.44}
$$

so that

$$
\begin{aligned}
a^2 &= b_{max}(b_{max} + 1) \\
&= (b_{av} + \frac{1}{2}n)(b_{av} + \frac{1}{2}n + 1)
\end{aligned}
\tag{11.45}
$$

Likewise,

$$
\begin{aligned}
\tilde{L}^2 \varphi_{ab_{min}} &= (\tilde{L}_+ \tilde{L}_- + \tilde{L}_z^2 - \hbar \tilde{L}_z)\varphi_{ab_{min}} \\
\hbar^2 a^2 \varphi_{ab_{min}} &= \hbar^2 b_{min}(b_{min} - 1)\varphi_{ab_{min}}
\end{aligned}
\tag{11.46}
$$

so that

$$
\begin{aligned}
a^2 &= b_{min}(b_{min} - 1) \\
&= (b_{av} - \frac{1}{2}n)(b_{av} - \frac{1}{2}n - 1) \\
&= (-b_{av} + \frac{1}{2}n)(-b_{av} + \frac{1}{2}n + 1)
\end{aligned}
\tag{11.47}
$$

Equating the right-hand sides of (11.45) and (11.47)

$$(b_{av} + \frac{1}{2}n)(b_{av} + \frac{1}{2}n + 1) = (-b_{av} + \frac{1}{2}n)(-b_{av} + \frac{1}{2}n + 1) \tag{11.48}$$

which implies that:

$$
\begin{aligned}
b_{av} &= 0 \\
b_{max} &= \frac{n}{2} \\
b_{min} &= -\frac{n}{2} \\
a^2 &= \frac{n}{2}\left(\frac{n}{2}+1\right)
\end{aligned}
\tag{11.49}
$$

It is customary to use the notation

$$
\begin{aligned}
l &\equiv \frac{n}{2} \\
m &\equiv b
\end{aligned}
\tag{11.50}
$$

and to relabel eigenstates φ_{ab} as φ_{lm}. In this notation, the eigenvalues of angular momentum are

$$
\begin{aligned}
\tilde{L}^2 \varphi_{lm} &= l(l+1)\hbar^2 \varphi_{lm} \\
\tilde{L}_z \varphi_{lm} &= m\hbar\varphi_{lm} \\
l &= 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, 3, ... \\
m &= -l, -l+1, -l+2, ..., l-3, l-2, l-1, l
\end{aligned}
\tag{11.51}
$$

Note that, as predicted, the eigenvalues of $\tilde{L}^2$ are degenerate: to each eigenvalue $L^2 = l(l+1)\hbar^2$ there are $2l+1$ linearly independent eigenstates φ_{lm}, for values of m in the range $-l \le m \le l$, as in (11.51). In other words, each L^2 eigenvalue is $2l+1$-fold degenerate.

11.3 The Angular Momentum Cones

It is time to pause and interpret the remarkable result, eq. (11.51), of the last section. What we have found is that angular momentum is "quantized", in the sense that a measurement of the magnitude of angular momentum will only find one of the discrete set of values

$$
|L| = \sqrt{l(l+1)}\hbar, \qquad l = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, 3, ...
\tag{11.52}
$$

and a measurement of the component of angular momentum along a certain axis, e.g. the z-axis, would only find one of the possible values

$$
L_z = m\hbar \qquad m \in \{-l, -l+1, -l+2, ...l-2, l-1, l\}
\tag{11.53}
$$

These eigenvalues have been deduced without solving the Schrodinger equation, or any other differential equation. They were obtained from the commutation relations (11.14) and a bit of clever algebra, nothing more.

Confirmation of these results comes from Nature. All elementary particles, for example, have an intrinsic spin angular momentum. The magnitude of this spin angular momentum depends on the type of elementary particle, but it is *always* one of the values (11.52). The π-meson has spin 0, corresponding to $l = 0$. Electrons, protons, neutrons, and quarks have "spin $\frac{1}{2}$", i.e. their total spin angular momentum has a magnitude

$$|S| = \sqrt{\frac{3}{4}}\hbar \tag{11.54}$$

corresponding to $l = \frac{1}{2}$. The ρ and ω mesons have "spin 1", i.e.

$$|S| = \sqrt{2}\hbar \tag{11.55}$$

corresponding to $l = 1$. The Δ-hyperon has "spin $\frac{3}{2}$" ($l = \frac{3}{2}$), and so on. The component of spin angular momentum along a particular axis can also be measured experimentally for those particles which have a magnetic moment. The component of magnetic moment along a given axis is proportional to the spin angular momentum along that axis. Experimentally, the values of the component S_z along, e.g., the z-axis, obey the relation (11.53). There are, however, some important differences between intrinsic spin angular momentum (whose magnitude can never change for a given type of particle) and orbital angular momentum, which can change by discrete amounts. We will reserve further discussion of spin angular momentum for later in the course.

Apart from the fact that both the total magnitude $|L|$ and component L_z come in discrete amounts (11.51), angular momentum in quantum mechanics differs from angular momentum in classical mechanics in several ways. Of these, the most striking is the fact that the angular momentum in the z-direction (or in any other direction) is always smaller than the magnitude of total (non-zero) angular momentum. $L_z = l\hbar$ is the largest possible value for L_z, and

$$l\hbar < \sqrt{l(l+1)}\hbar \tag{11.56}$$

which means that the angular momentum can never be completely aligned in a particular direction. In fact, if the angular momentum *did* point in a definite direction, then all components L_x, L_y, L_z would be definite. But these components cannot be simultaneously definite, because the corresponding operators don't commute. These means that there is no physical state in which the angular momentum points in a particular direction.

In classical physics, we visualize angular momentum $\vec{L}$ as a vector. In quantum physics, it is better to visualize the angular momentum associated with a given eigenstate φ_{lm} as a cone. In an eigenstate the magnitude of angular momentum $|L|$ and the z-component L_z are fixed,

$$|L| = \sqrt{l(l+1)}\hbar \qquad L_z = m\hbar \tag{11.57}$$

while values of L_x and L_y are indefinite; although their squared expectation values must satisy

$$< L_x^2 > + < L_y^2 > + < L_z^2 > = < L^2 > \tag{11.58}$$

We can picture the angular momentum associated with φ_{lm} as the cone of all vectors $\vec{L}$ satisfying (11.57). The cones for $l = 2$, $m = -2, -1, 0, 1, 2$, are shown in Fig. [11.2].

In classical mechanics it is easy to add two or more angular momenta; it is just a matter of vector addition. In quantum mechanics, as one might imagine, the process is more complicated. For example, suppose one has two electrons which are each in angular momentum eigenstates, and we ask: "what is the total angular momentum of the system?" (How does one go about adding "cones" of angular momentum?) We will learn the quantum-mechanical rules for addition of angular momentum in the second semester of this course.

Problem: Show that in a φ_{lm} eigenstate, that

$$< L_x > = < L_y > = 0 \tag{11.59}$$

and that

$$< L_x^2 > = < L_y^2 > = \frac{1}{2}\hbar^2 \left[l(l+1) - m^2 \right] \tag{11.60}$$

From this information, verify the generalized uncertainty principle (eq. (7.116)) for $\Delta L_x \Delta L_y$.

11.4 Eigenfunctions of Angular Momentum

In the case of the harmonic oscillator, we found the ground state wavefunction by solving the first-order differential equation

$$a\varphi_0(x) = 0 \tag{11.61}$$

and then all other eigenstates can be obtained by applying the raising operator $a^\dagger$. In the case of angular momentum, the strategy is very similar. For a given l, we first solve the first-order differential equations

$$\begin{aligned}
L_+\varphi_{ll}(x, y, z) &= 0 \\
L_z\varphi_{ll}(x, y, z) &= l\hbar\varphi_{ll}
\end{aligned} \tag{11.62}$$

and then obtain all other φ_{lm} wavefunctions in the multiplet by applying successively the lowering operator L_-.

It is much easier to solve these differential equations in spherical coordinates r, θ, ϕ

$$\begin{aligned}
z &= r\cos\theta \\
x &= r\sin\theta\cos\phi \\
y &= r\sin\theta\sin\phi
\end{aligned} \tag{11.63}$$

because in spherical coordinates, the r variable drops out of the angular momentum operators:

$$\tilde{L}_x = i\hbar \left(\sin\phi \frac{\partial}{\partial\theta} + \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right)$$

$$\tilde{L}_y = i\hbar \left(-\cos\phi \frac{\partial}{\partial\theta} + \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right)$$

$$\tilde{L}_z = -i\hbar \frac{\partial}{\partial\phi}$$

$$\tilde{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \qquad (11.64)$$

and therefore any eigenstate of angular momentum has the form

$$\varphi_{lm}(x,y,z) = f(r)Y_{lm}(\theta,\phi) \qquad (11.65)$$

where

$$\tilde{L}^2 Y_{lm}(\theta,\phi) = l(l+1)\hbar^2 Y_{lm}(\theta,\phi)$$

$$\tilde{L}_z Y_{lm}(\theta,\phi) = m\hbar Y_{lm}(\theta,\phi) \qquad (11.66)$$

and where $f(r)$ is any function such that the normalization condition

$$1 = \int dxdydz \ \phi^*(x,y,z\phi(x,y,z)$$

$$= \int_0^\infty dr \ r^2 \int_0^\pi d\theta \ \sin\theta \int_0^{2\pi} d\phi \ f^*(r)f(r)Y_{lm}^*(\theta,\phi)Y_{lm}(\theta,\phi) \qquad (11.67)$$

is satisfied. It is conventional to normalize the Y_{lm} such that the integral over angles is also equal to one:

$$\int_0^\pi d\theta \ \sin\theta \int_0^{2\pi} d\phi \ Y_{lm}^*(\theta,\phi)Y_{lm}(\theta,\phi) = 1 \qquad (11.68)$$

With this normalization, the $Y_{lm}(\theta,\phi)$ are known as **"Spherical Harmonics"**.

In spherical coordinates, the raising and lowering operators are

$$\tilde{L}_+ = \tilde{L}_x + i\tilde{L}_y$$

$$= \hbar e^{i\phi} \left(\frac{\partial}{\partial\theta} + i\cot\theta \frac{\partial}{\partial\phi} \right)$$

$$\tilde{L}_- = \tilde{L}_x - i\tilde{L}_y$$

$$= -\hbar e^{-i\phi} \left(\frac{\partial}{\partial\theta} - i\cot\theta \frac{\partial}{\partial\phi} \right) \qquad (11.69)$$

and we solve the first-order differential equations

$$\tilde{L}_+ Y_{ll} = 0 \qquad \tilde{L}_z Y_{ll} = l\hbar Y_{lm} \tag{11.70}$$

by the method of separation of variables

$$Y_{lm}(\theta, \phi) = A(\theta)B(\phi) \tag{11.71}$$

The L_z eigenvalue equation (for any m) becomes

$$-i\hbar \frac{dB}{d\phi} = m\hbar B \tag{11.72}$$

which has the solution

$$B(\phi) = e^{im\phi} \tag{11.73}$$

As was pointed out in the case of the "quantum corral", discussed in the last lecture, the angle $\phi = 0$ is the same as the angle $\phi = 2\pi$, so the wavefunctions must satisfy the periodicity condition

$$Y_{lm}(\theta, \phi + 2\pi) = Y_{lm}(\theta, \phi) \tag{11.74}$$

But this means, since $B(\phi) = e^{im\phi}$, that m must be restricted to the integer values

$$m = 0, \pm 1, \pm 2, \pm 3, ..., \pm n, ... \tag{11.75}$$

As a result, since $-l \leq m \leq l$, the possible values for l are

$$l = 0, 1, 2, 3, ..., n, ... \tag{11.76}$$

So, although we have found algebraically that m could have both integer *and* half-integer values

$$m = 0, \pm \frac{1}{2}, \pm 1, \pm \frac{3}{2}, ..., \pm n/2, ... \tag{11.77}$$

it turns out that the periodicity condition has ruled out the half-integer possibilities for orbital angular momentum. As we will see next semester, the half-integer values are still possible for intrinsic spin angular momentum, where the requirement of angular periodicity of the wavefunction does not apply.

So far we have

$$Y_{lm}(\theta, \phi) = A(\theta)e^{im\phi} \tag{11.78}$$

and in particular

$$Y_{ll}(\theta, \phi) = A(\theta)e^{il\phi} \tag{11.79}$$

Applying the raising operator to this state, we must have

$$\begin{aligned}
0 &= \tilde{L}_+ Y_{ll} \\
&= \hbar e^{i\phi} \left(i\cot\theta \frac{\partial}{\partial \phi} + \frac{\partial}{\partial \theta} \right) A(\theta)e^{il\phi} \\
&= \hbar e^{i(l+1)\phi} \left(-l\cot\theta + \frac{\partial}{\partial \theta} \right) A(\theta) \tag{11.80}
\end{aligned}$$

or

$$\frac{d}{d\theta}A(\theta) = l\cot\theta A(\theta) \tag{11.81}$$

which is solved by

$$A(\theta) = \text{const.} \times \sin^l \theta \tag{11.82}$$

Then

$$Y_{ll}(\theta, \phi) = N \sin^l \theta e^{il\phi} \tag{11.83}$$

where N is a normalization constant, which is determined from the normalization condition

$$\begin{aligned}
1 &= \int_0^\pi d\theta \, \sin\theta \int_0^{2\pi} d\phi \, Y_{ll}^* Y_{ll} \\
&= 2\pi N^2 \int_0^\pi d\theta \, \sin^{(2l+1)} \theta \\
&= \frac{2\pi^{3/2} l!}{\Gamma(l + \frac{3}{2})} N^2
\end{aligned} \tag{11.84}$$

where the Γ-function is a special function with the properties

$$\Gamma(x + 1) = x\Gamma(x) \qquad \Gamma(\frac{1}{2}) = \sqrt{\pi} \tag{11.85}$$

Of course, the normalization condition only determines N, even assuming N is real, up to an overall sign. The convention is to choose this sign to be $(-1)^l$, so that finally

$$Y_{ll}(\theta, \phi) = (-1)^l \left[\frac{\Gamma(l + \frac{3}{2})}{2\pi^{3/2} l!} \right]^{1/2} \sin^l \theta e^{il\phi} \tag{11.86}$$

From here we can get the other Y_{lm} using the lowering operator

$$\tilde{L}_- Y_{l,m}(\theta, \phi) = C_{lm}^- Y_{l,m-1}(\theta, \phi) \tag{11.87}$$

given the constants C_{lm}^-. Corresponding constants C_{lm}^+ are defined from

$$\tilde{L}_+ Y_{l,m}(\theta, \phi) = C_{lm}^+ Y_{l,m+1}(\theta, \phi) \tag{11.88}$$

To get the C_{lm}^- constants, we again resort to some clever algebra. We have

$$\begin{aligned}
\tilde{L}_- \tilde{L}_+ &= \tilde{L}^2 - \tilde{L}_z^2 - \hbar \tilde{L}_z \\
\tilde{L}_+ \tilde{L}_- &= \tilde{L}^2 - \tilde{L}_z^2 + \hbar \tilde{L}_z
\end{aligned} \tag{11.89}$$

Then

$$\begin{aligned}
< \varphi_{lm} | \tilde{L}_- \tilde{L}_+ | \varphi_{lm} > &= < \varphi_{lm} | (\tilde{L}^2 - \tilde{L}_z^2 - \hbar \tilde{L}_z) | \varphi_{lm} > \\
< \tilde{L}_+ \varphi_{lm} | \tilde{L}_+ \varphi_{lm} > &= \hbar^2 [l(l+1) - m^2 - m] < \varphi_{lm} | \varphi_{lm} > \\
(C_{lm}^+)^* C_{lm}^+ &= \hbar^2 (l - m)(l + m + 1)
\end{aligned} \tag{11.90}$$

so that

$$C_{lm}^+ = \hbar\sqrt{(l-m)(l+m+1)}e^{i\omega} \tag{11.91}$$

Likewise

$$
\begin{aligned}
<\varphi_{lm}|\tilde{L}_+\tilde{L}_-|\varphi_{lm}> &=& <\varphi_{lm}|(\tilde{L}^2 - \tilde{L}_z^2 + \hbar\tilde{L}_z)|\varphi_{lm}> \\
<\tilde{L}_-\varphi_{lm}|\tilde{L}_-\varphi_{lm}> &=& \hbar^2[l(l+1) - m^2 + m) <\varphi_{lm}|\varphi_{lm}> \\
(C_{lm}^-)^*C_{lm}^- &=& \hbar^2(l+m)(l-m+1)
\end{aligned}
\tag{11.92}
$$

so that

$$C_{lm}^- = \hbar\sqrt{(l+m)(l-m+1)}e^{i\omega} \tag{11.93}$$

where ω is an arbitrary phase. This can always be absorbed into a rescaling of the wavefunction; i.e. $\varphi_{lm} \rightarrow e^{i\omega}\varphi_{lm}$, which does not affect the physical state at all. So we can always choose the C_{lm}^- to be real. It is not hard to show that

$$C_{lm}^- = (C_{l,m-1}^+)^* \tag{11.94}$$

Exercise: Prove this relation.

Therefore, if the C^- coefficients are real, then the C^+ coefficients are also real, and we have

$$
\begin{aligned}
C_{lm}^- &= \hbar\sqrt{(l+m)(l-m+1)} \\
C_{lm}^+ &= \hbar\sqrt{(l-m)(l+m+1)}
\end{aligned}
\tag{11.95}
$$

and we can now compute all the Y_{lm} using

$$
\begin{aligned}
Y_{ll}(\theta,\phi) &=& (-1)^l \left[\frac{\Gamma(l+\frac{3}{2})}{2\pi^{3/2}l!}\right]^{1/2} \sin^l\theta e^{il\phi} \\
\tilde{L}_-Y_{lm} &=& \hbar\sqrt{(l+m)(l-m+1)}Y_{l,m-1} \\
\tilde{L}_+Y_{lm} &=& \hbar\sqrt{(l-m)(l+m+1)}Y_{l,m+1}
\end{aligned}
\tag{11.96}
$$

Since the Y_{ll} was normalized to 1 in equation (11.84), all of the Y_{lm} obtained by applying the lowering operator will also be normalized to 1. Also, since $\tilde{L}^2$ and $\tilde{L}_z$ are Hermitian operators, spherical harmonics corresponding to different values of l and/or m will be orthogonal:

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \, Y_{lm}^*(\theta,\phi)Y_{l'm'}(\theta,\phi) = \delta_{ll'}\delta_{mm'} \tag{11.97}$$

Example: the $l=1$ multiplet

As an example of the procedure, let us compute the $l = 1$ multiplet of spherical harmonics, i.e. Y_{11}, Y_{10}, $Y_{1,-1}$. We begin with

$$
\begin{aligned}
Y_{11} &= (-1) \left[\frac{\Gamma(\frac{5}{2})}{2\pi^{3/2}} \right]^{1/2} \sin\theta e^{i\phi} \\
&= -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi}
\end{aligned}
\tag{11.98}
$$

then

$$
\begin{aligned}
L_- Y_{11} &= -\sqrt{\frac{3}{8\pi}} \hbar e^{-i\phi} \left(i\cot\theta \frac{\partial}{\partial\phi} - \frac{\partial}{\partial\theta} \right) \sin\theta e^{i\phi} \\
\hbar\sqrt{2} Y_{10} &= \sqrt{\frac{3}{8\pi}} \hbar(\cot\theta \sin\theta + \cos\theta) \\
Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos\theta
\end{aligned}
\tag{11.99}
$$

And applying the lowering operator again

$$
\begin{aligned}
\tilde{L}_- Y_{10} &= \sqrt{\frac{3}{4\pi}} \hbar e^{-i\phi} \left(i\cot\theta \frac{\partial}{\partial\phi} - \frac{\partial}{\partial\theta} \right) \cos\theta \\
\hbar\sqrt{2} Y_{1,-1} &= \sqrt{\frac{3}{4\pi}} \hbar e^{-i\phi} \sin\theta \\
Y_{1,-1} &= \sqrt{\frac{3}{8\pi}} e^{-i\phi} \sin\theta
\end{aligned}
\tag{11.100}
$$

It is easy to check that applying the lowering operator one more time annihilates the state

$$
\tilde{L}_- Y_{1,-1} = 0
\tag{11.101}
$$

as it should. In fact, in constructing the spherical harmonics, we could start with the solution of the differential equation

$$
\tilde{L}_- Y_{l,-l} = 0
\tag{11.102}
$$

and obtain the rest of the Y_{lm} by using the raising operator $\tilde{L}_+$.

Problem: Obtain the $l = 1$ multiplet by solving (11.102), and then applying the raising operator.

Of course, one rarely has to go to the trouble of computing the spherical harmonics, since they are listed in many books. The first few, including the $l = 1$ multiplet we

have just computed, are

$$
\begin{aligned}
Y_{00} &= \sqrt{\frac{1}{4\pi}} \\
Y_{11} &= -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi} \\
Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos \theta \\
Y_{1,-1} &= \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi} \\
Y_{22} &= \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\phi} \\
Y_{21} &= -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi} \\
Y_{20} &= \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) \\
Y_{2,-1} &= \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{-i\phi} \\
Y_{2,-2} &= \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{-2i\phi}
\end{aligned} \tag{11.103}
$$

There is a nice graphical way of representing the spherical harmonics. The modulus of the spherical harmonics $|Y_{lm}|$ is a function only of θ, and is independent of ϕ. So, in polar coordinates (r, θ) where θ is the angle away from the z-axis, we plot the function

$$
r(\theta) = |Y_{lm}(\theta, \phi)| \tag{11.104}
$$

The resulting diagrams are shown in Fig. [11.3].

• **The Rigid Rotator** As a first application of the spherical harmonics, let us consider a rigid rod with moment of inertia I, which pivots freely around one fixed end at $r = 0$. Since the length of the rod is fixed, the generalized coordinates are the angular position of the rod (θ, ϕ). The classical Hamiltonian describing the dynamics of this simple system is

$$
H = \frac{1}{2I} L^2 \tag{11.105}
$$

where $\vec{L}$ is the angular momentum. The corresponding Schrodinger equation is then simply

$$
\tilde{H} \varphi_{lm}(\theta, \phi) = \frac{1}{2I} \tilde{L}^2 \varphi_{lm}(\theta, \phi) = E_{lm} \varphi_{lm}(\theta \phi) \tag{11.106}
$$

and the energy eigenstates are angular momentum eigenstates

$$\varphi_{lm}(\theta, \phi) = Y_{lm}(\theta, \phi) \qquad E_{lm} = \frac{1}{2I} l(l+1)\hbar^2 \tag{11.107}$$

We note that the energy eigenvalues are degenerate, as expected

$$E_{lm} = E_{lm'} \qquad -l \le m, m' \le l \tag{11.108}$$

11.5   The Radial Equation for Central Potentials

It has already been noted that the angular momentum operators involve only θ and ϕ, so an eigenstate of $\tilde{L}^2$ and L_z has the general form

$$\varphi = f(r)Y_{lm}(\theta, \phi) \tag{11.109}$$

where $f(r)$ is an arbitrary function of r. For central potentials $V(r, \theta, \phi) = V(r)$, the Hamiltonian commutes with the angular momentum operators, so by the commutator theorem $\tilde{H}, \tilde{L}^2, \tilde{L}_z$ have a common set of eigenstates of the form (11.109). However, if φ is an eigenstate of H, then the radial function $f(r)$ is no longer arbitrary, but is determined from an ordinary differential equation in the variable r known as the **"Radial Equation"**.

Let us begin with the classical Hamiltonian

$$H = \frac{\vec{p} \cdot \vec{p}}{2m} + V(r) \tag{11.110}$$

The momentum vector $\vec{p}$, in spherical coordinates, can be expressed as a sum of two vectors, one of which $(\vec{p}_r)$ is parallel to the radial direction, and the other $(\vec{p}_\perp)$ perpendicular to the radial direction, i.e.

$$
\begin{aligned}
\vec{p} &= \vec{p}_r + \vec{p}_\perp \\
\vec{p}_r &\equiv p\cos(\theta_{rp})\hat{e}_r = \frac{1}{r^2}(\vec{r} \cdot \vec{p})\vec{r} \\
|\vec{p}_\perp| &\equiv p\sin(\theta_{rp}) = \frac{|\vec{r} \times \vec{p}|}{r} \\
&= \frac{|\vec{L}|}{r}
\end{aligned}
\tag{11.111}
$$

so that

$$H = \frac{1}{2m}\left[p_r^2 + \frac{L^2}{r^2} \right] + V(r) \tag{11.112}$$

where

$$p_r = |\vec{p}_r| = \frac{\vec{r} \cdot \vec{p}}{r} \tag{11.113}$$

Upon quantization, r, $\vec{p}$ and $\vec{L}$ become operators,

$$
\begin{aligned}
\tilde{r}F(r,\theta,\phi) &= rF(r,\theta,\phi) \\
\tilde{\vec{p}}F(r,\theta,\phi) &= -i\hbar\nabla F(r,\theta,\phi) \\
\tilde{\vec{L}}F(r,\theta,\phi) &= -i\hbar\vec{r}\times\nabla F(r,\theta,\phi)
\end{aligned} \tag{11.114}
$$

and we define the operator corresponding to p_r as

$$
\tilde{p}_r = \frac{1}{2}\left(\frac{\vec{r}}{r}\cdot\tilde{\vec{p}}+\tilde{\vec{p}}\cdot\frac{\vec{r}}{r}\right) \tag{11.115}
$$

This ordering of r and $\tilde{p}$ is chosen so that $\tilde{p}_r$ is an Hermitian operator. If we had simply substituted $\vec{p}\to\tilde{\vec{p}}$ in (11.113), then $\tilde{p}_r$ would not be Hermitian, and neither would the Hamiltonian, which involves $\tilde{p}_r^2$. In terms of differential operators

$$
\begin{aligned}
\tilde{p}_r F &= -\frac{1}{2}i\hbar\left[\frac{1}{r}\vec{r}\cdot\nabla+\nabla\cdot\frac{\vec{r}}{r}\right]F \\
&= -\frac{1}{2}i\hbar\left[\frac{\partial}{\partial r}+\frac{\vec{r}}{r}\cdot\nabla+\frac{1}{r}(\nabla\cdot\vec{r})+\vec{r}\cdot(\nabla\frac{1}{r})\right]F \\
&= -\frac{1}{2}i\hbar\left[2\frac{\partial}{\partial r}+\frac{3}{r}-\frac{1}{r}\right]F \\
&= -i\hbar\left[\frac{\partial}{\partial r}+\frac{1}{r}\right]F \\
&= -i\hbar\frac{1}{r}\frac{\partial}{\partial r}rF
\end{aligned} \tag{11.116}
$$

so that

$$
\tilde{p}_r = -i\hbar\frac{1}{r}\frac{\partial}{\partial r}r \tag{11.117}
$$

In terms of this operator, the Schrodinger equation

$$
\tilde{H}\varphi(r,\theta,\phi)=E\varphi(r,\theta,\phi) \tag{11.118}
$$

is

$$
\left[\frac{1}{2m}\left(\tilde{p}_r^2+\frac{1}{r^2}\tilde{L}^2\right)+V(r)\right]\varphi(r,\theta,\phi)=E\varphi(r,\theta,\phi) \tag{11.119}
$$

or, explicitly

$$
\left[-\frac{\hbar^2}{2m}\left((\frac{1}{r}\frac{\partial^2}{\partial r^2}r)+\frac{1}{r^2}(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2})\right)+V(r)\right]\varphi=E\varphi \tag{11.120}
$$

This equation could be obtained more quickly by starting from

$$
\left[-\frac{\hbar^2}{2m}\nabla^2+V(r)\right]\varphi=E\varphi \tag{11.121}
$$

and then just expressing ∇^2 in spherical coordinates

$$\nabla^2 = (\frac{1}{r}\frac{\partial^2}{\partial r^2}r) + \frac{1}{r^2}(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}) \qquad (11.122)$$

Comparing ∇^2 to eq. (11.64), we see that it contains the operator $\tilde{L}^2$, although the reason for this is not so clear. The appearance of the angular momentum operator, on the other hand, is quite obvious from eq. (11.112).

Having found the eigenstates of angular momentum, we write

$$\varphi(r,\theta,\phi) = R_{klm}(r)Y_{lm}(\theta,\phi) \qquad (11.123)$$

where the index k is introduced to distinguish between states of different energy, which have the eigenvalues of L^2 and L_z. Substitute into the Schrodinger equation

$$\left[\frac{1}{2m}\tilde{p}_r^2 + \frac{1}{2mr^2}\tilde{L}^2 + V(r)\right] R_{klm}(r)Y_{lm}(\theta,\phi) = E_{klm}R_{klm}(r)Y_{lm}(\theta,\phi)$$

$$Y_{lm}\left[\frac{1}{2m}\tilde{p}_r^2 + \frac{\hbar^2}{2mr^2}l(l+1) + V(r)\right] R_{klm}(r) = E_{klm}R_{klm}(r)Y_{lm}(\theta,\phi) \qquad (11.124)$$

Cancelling Y_{lm} on both sides of the equation, we note that neither the potential nor the differential operator depend on m, so we can write that $R_{klm} = R_{kl}$ and $E_{klm} = E_{kl}$. We then have an equation which involves only the radial coordinate

$$\frac{1}{2m}\left[\tilde{p}_r^2 + \frac{\hbar^2 l(l+1)}{r^2}\right] R_{kl}(r) + V(r)R_{kl}(r) = E_{kl}R_{kl}(r) \qquad (11.125)$$

which, using

$$\begin{aligned}\tilde{p}_r^2 &= -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}r \\ &= -\hbar^2\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right] \end{aligned} \qquad (11.126)$$

becomes

$$\frac{d^2 R_{kl}}{dr^2} + \frac{2}{r}\frac{dR_{kl}}{dr} + \left[\frac{2m}{\hbar^2}\{E_{kl} - V(r)\} - \frac{l(l+1)}{r^2}\right] R_{kl}(r) = 0 \qquad (11.127)$$

This is the radial equation for energy eigenstates in a spherical potential.

• **The Free Particle**   The simplest possible central potential is $V(r) = 0$. If we write

$$E = \frac{\hbar^2 k^2}{2m} \tag{11.128}$$

Then the radial equation is

$$\frac{d^2 R_{kl}}{dr^2} + \frac{2}{r}\frac{dR_{kl}}{dr} + \left[k^2 - \frac{l(l+1)}{r^2}\right] R_{kl}(r) = 0 \tag{11.129}$$

Rescaling the r coordinate,

$$u = kr \tag{11.130}$$

this becomes

$$\left[\frac{d^2}{du^2} + \frac{2}{u}\frac{d}{du} + \left(1 - \frac{l(l+1)}{u^2}\right)\right] R_{kl}(r) = 0 \tag{11.131}$$

Writing

$$R_{kl}(r) = W_l(u) \tag{11.132}$$

we have a second-order differential equation

$$\frac{d^2 W_l}{du^2} + \frac{2}{u}\frac{dW_l}{du} + \left(1 - \frac{l(l+1)}{u^2}\right) W_l = 0 \tag{11.133}$$

which is known as the **Spherical Bessel Equation**. Solutions of this equation, which are finite and differentiable at $r = 0$ are the **spherical Bessel functions** $W_l(u) = j_l(u)$, the first few of which are listed below:

$$
\begin{aligned}
j_0(u) &= \frac{\sin(u)}{u} \\
j_1(u) &= \frac{\sin(u)}{u^2} - \frac{\cos(u)}{u} \\
j_2(u) &= \left(\frac{3}{u^3} - \frac{1}{u}\right)\sin(u) - \frac{3}{u^2}\cos(u)
\end{aligned} \tag{11.134}
$$

Putting everything together, the eigenstates of energy and angular momentum

$$\{\tilde{H},\ \tilde{L}^2, \tilde{L}_z\} \tag{11.135}$$

for $V = 0$ are

$$\varphi_{klm}(r, \theta, \phi) = j_l(kr)Y_{lm}(\theta, \phi) \tag{11.136}$$

with eigenvalues

$$E_k = \frac{\hbar^2 k^2}{2m} \qquad L^2 = l(l+1)\hbar^2 \qquad L_z = m\hbar \tag{11.137}$$

Since there is one and only one eigenstate corresponding to a given set of eigenvalues of $\{\tilde{H},\ \tilde{L}^2, \tilde{L}_z\}$, it follows that $E,\ L^2,\ L_z$ is a complete set of observables.

For the free particle in one dimension, we found that E, P was a complete set of observables, where P is parity, and also that p is a complete set of observables, where p is momentum. Similarly, in three dimensions, the three components of momentum $\{p_x, p_y, p_z\}$ are a complete set of observables, because there is one and only one eigenstate of $\{\tilde{p}_x, \tilde{p}_y, \tilde{p}_z\}$ with a given set of eigenvalues

$$
\begin{aligned}
-i\hbar\frac{\partial}{\partial x}\psi_p(x,y,z) &= p_x\psi_p(x,y,z) \\
-i\hbar\frac{\partial}{\partial y}\psi_p(x,y,z) &= p_y\psi_p(x,y,z) \\
-i\hbar\frac{\partial}{\partial z}\psi_p(x,y,z) &= p_z\psi_p(x,y,z)
\end{aligned}
\tag{11.138}
$$

namely

$$
\psi_p(x,y,z) = N\exp[i(p_x x + p_y y + p_z z)/\hbar]
\tag{11.139}
$$

This wavefunction is *also* an eigenstate of the Hamiltonian

$$
\tilde{H}\psi_p = -\frac{\hbar^2}{2m}\nabla^2\psi_p = E_p\psi_p
\tag{11.140}
$$

with energy

$$
E_p = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)
\tag{11.141}
$$

The Hamiltonian of a free particle is invariant under translations

$$
\vec{r} \rightarrow \vec{r} + \vec{a}
\tag{11.142}
$$

and also under rotations of the coordinates. The energy eigenstates $\{\psi_p\}$ are eigenstates of the Hamiltonian and the translation operator

$$
T = e^{i\vec{a}\cdot\vec{\tilde{p}}}
\tag{11.143}
$$

while the energy eigenstates $\{j_l(kr)Y_{lm}(\theta,\phi)\}$ are eigenstates of the Hamiltonian and the rotation operator along the z-axis

$$
R = e^{i\delta\phi\tilde{L}_z}
\tag{11.144}
$$

as well as the total angular momentum operator $\tilde{L}^2$.

Chapter 12

The Hydrogen Atom

Historically, the first application of the Schrodinger equation (by Schrodinger himself) was to the Hydrogen atom, and the result for the frequency of the Hydrogen spectral lines was the same as that obtained by Bohr.[1] In this lecture we will retrace Schrodinger's steps in solving the Schrodinger equation for the Hydrogen atom. Unlike the case of the harmonic oscillator, and case of angular momentum, the raising-lowering operator trick doesn't apply here. Nevertheless, we will see that the energy eigenvalues of the Hamiltonian are again determined, ultimately, by algebra.

The Hydrogen atom is a simple system: a light electron bound to a heavy proton. The proton is so much heavier than the electron (about 2000 times heavier) that we may regard its position as fixed, at the center of a system of spherical coordinates. The potential energy between the electron and proton is given, in suitable units, by the Coulomb expression

$$V(r) = -\frac{e^2}{r} \tag{12.1}$$

Since this potential is spherically symmetric, we know from the preceding lecture that the Hamiltonian will commute with the angular momentum operators, and therefore that energy eigenstates may also be chosen to be eigenstates of L^2 and L_z, i.e.

$$\phi_E(r, \theta, \phi) = R_{kl}(r)Y_{lm}(\theta, \phi) \tag{12.2}$$

The time-independent Schrodinger equation is

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} \right] \phi_E(r, \theta, \phi) = E\phi_E(r, \theta, \phi) \tag{12.3}$$

or

$$\left[\frac{1}{2m}(\tilde{p}_r^2 + \frac{1}{r^2}\tilde{L}^2) - \frac{e^2}{r} \right] R_{kl}(r)Y_{lm}(\theta, \phi) = ER_{kl}Y_{lm} \tag{12.4}$$

---

[1]The difference is that Bohr's rather ad hoc quantization condition ($mvr = n\hbar$) was successful only for Hydrogen and a few other simple atoms. In contrast, the Schrodinger equation is a law of motion, as fundamental as $F = ma$ (which it replaces).

which reduces, as shown in the previous lecture, to the "radial equation" for $R_{kl}(r)$

$$\frac{d^2 R_{kl}}{dr^2} + \frac{2}{r}\frac{dR_{kl}}{dr} + \left[\frac{2m}{\hbar^2}\{E_{kl} + \frac{e^2}{r}\} - \frac{l(l+1)}{r^2}\right] R_{kl}(r) = 0 \qquad (12.5)$$

or

$$\left[\frac{1}{r}\frac{d^2}{dr^2}r - \frac{l(l+1)}{r^2} + \frac{2me^2}{\hbar^2}\frac{1}{r} + \frac{2mE}{\hbar^2}\right] R(r) = 0 \qquad (12.6)$$

We are interested in the spectrum of atomic hydrogen, so this means we would like to solve for the bound states, i.e. those states for which $E < 0$. From now on, we take $E = -|E| < 0$. Multiply the above equation by r on the left, and define

$$u(r) = rR(r) \qquad (12.7)$$

so that

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2me^2}{\hbar^2}\frac{1}{r} - \frac{2m|E|}{\hbar^2}\right] u(r) = 0 \qquad (12.8)$$

This equation involves two constants, namely

$$\frac{2mE}{\hbar^2} \quad \text{and} \quad \frac{2me^2}{\hbar^2} \qquad (12.9)$$

which we can reduce to one constant by rescaling r. Define

$$k^2 = \frac{2m|E|}{\hbar^2} \quad \text{and} \quad r = \frac{\rho}{2k} \qquad (12.10)$$

Substitute into (12.8), and we find

$$\frac{d^2 u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right) u = 0 \qquad (12.11)$$

where we have defined

$$\lambda = \frac{me^2}{k\hbar^2} = \frac{1}{ka_0} \qquad (12.12)$$

(a_0 is the Bohr radius $\hbar^2/me^2$). The problem is reduced to finding values λ and functions $u(\rho)$ which satisfy (12.11).

The strategy for solving (12.11) is to first solve the equation in the asymptotic limits $\rho \to \infty$ and $\rho \to 0$. With the solutions for very large and very small ρ in hand, we then look for a solution which interpolates between these two regions.

Begin with $\rho \to \infty$. Then terms proportional to $1/\rho^2$ and $1/\rho$ can be dropped, and the equation becomes

$$\frac{d^2 u}{d\rho^2} - \frac{u}{4} = 0 \qquad (12.13)$$

which has the general solution

$$u(\rho) = Ae^{-\rho/2} + Be^{\rho/2} \tag{12.14}$$

The second term, proportional to the constant B, is non-normalizable, therefore $B = 0$ for physical states. Hence, we find that

$$u(\rho) \to Ae^{-\rho/2} \quad \text{as} \quad \rho \to \infty \tag{12.15}$$

Next, consider the $\rho \to 0$ regime. Then terms proportional to a constant, or $1/\rho$, are negligible compared to the term proportional to $1/\rho^2$, so the radial equation is approximately

$$\frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u = 0 \tag{12.16}$$

which, one can easily check, is solved by

$$u(\rho) = C\rho^{l+1} + D\rho^{-l} \tag{12.17}$$

For any value $l > 0$ the wavefunction (proportional to u/r) is non-normalizable for $D \neq 0$, and even at $l = 0$ the ratio u/r is non-differentiable at $r = 0$ if $D \neq 0$. So we will set $D = 0$ also.

Since we now know that $u(\rho) \sim e^{-\rho/2}$ at large ρ, and $u(\rho) \sim \rho^{l+1}$ at small ρ, we can guess that the exact solution might have the form

$$u(\rho) = e^{-\rho/2}\rho^{l+1}F(\rho) \tag{12.18}$$

where $F(\rho)$ is some unknown function, which goes to a constant as $\rho \to 0$, and grows slower than an exponential as $\rho \to \infty$. This kind of educated guess regarding the form of the solution of an equation is called an "**ansatz**". Substituting (12.18) in (12.11) gives an equation for $F(\rho)$

$$\left[\rho\frac{d^2}{d\rho^2} + (2l + 2 - \rho)\frac{d}{d\rho} - (l + 1 - \lambda)\right]F(\rho) = 0 \tag{12.19}$$

The next step is to write $F(\rho)$ as a power series

$$F(\rho) = \sum_{j=0}^{\infty} c_j\rho^j \tag{12.20}$$

and insert into (12.19) to get

$$\rho\sum_j c_j j(j-1)\rho^{j-2} + \sum_j (2l + 2 - \rho)c_j j\rho^{j-1} - \sum_j (l + 1 - \lambda)c_j\rho^j = 0$$

$$\sum_j \{c_j j(j-1) + c_j j(2l + 2)\}\rho^{j-1} - \sum_j \{c_j j + c_j(l + 1 - \lambda)\}\rho^j = 0 \tag{12.21}$$

Since this equation has to be true for *every* value of ρ, it follows that the coefficient of each power of ρ must vanish. The coefficient in front of ρ^j is

$$c_{j+1}(j+1)j + c_{j+1}(2l+2)(j+1) - c_j j - c_j(l+1-\lambda) = 0 \tag{12.22}$$

or

$$c_{j+1}(j+1)(2l+2+j) - c_j(l+1+j-\lambda) = 0 \tag{12.23}$$

This equation allows us to compute the coefficients $\{c_j\}$ iteratively:

$$c_{j+1} = \frac{j+l+1-\lambda}{(j+1)(j+2l+2)}c_j \tag{12.24}$$

However, we have also required that $F(r)$ grow more slowly than an exponential, in order that $u(\rho) \sim \exp[-\rho/2]$ as $\rho \to \infty$. It turns out that this can only be true for very special values of the constant λ. Recall that the asympotic behavior of a solution of the Schrodinger equation can be *either* $\exp[+\rho/2]$ *or* $\exp[-\rho/2]$. Suppose it turns out that $F(\rho) \sim \exp(\rho)$ as $\rho \to \infty$. Then we would end up with the non-normalizable solution for $u(r)$. In fact, for almost all values of λ, this is exactly what happens. According to (12.24), at large index j

$$c_{j+1} \approx \frac{c_j}{j+1} \tag{12.25}$$

which implies

$$c_j \approx \frac{\text{const.}}{j!} \tag{12.26}$$

This means that at large ρ, where the power series in ρ is dominated by the terms at large index j,

$$\begin{aligned} F(\rho) &= \sum_j c_j \rho^j \\ &\approx \text{const.} \times \sum_j \frac{1}{j!}\rho^j \\ &\approx \text{const.} \times e^\rho \end{aligned} \tag{12.27}$$

in which case

$$u(\rho) \approx \rho^{l+1} e^{\rho/2} \tag{12.28}$$

which is non-normalizable. So, even though we started with an ansatz (12.18) which seemed to incorporate the asymptotic behavior we want, the equation for F ends up generating, for almost any choice of λ, the asympotic behavior that we don't want. This situation is already familiar from the discussion in Lecture 8. Typically, solutions of the Schrodinger equation for $E < 0$ are non-normalizable for almost all values of E. Only at a discrete set of bound-state energies is it possible to have the wavefunction fall to zero asymptotically.

For the hydrogen atom, the only way to have a normalizable solution is if one of the c_j coefficients vanishes, i.e. for some $j = j_s$, we have $c_{j_s+1} = 0$. Then, from eq. (12.24),

$$c_j = 0 \quad \text{for all} \quad j > j_s \tag{12.29}$$

and

$$
\begin{aligned}
F(\rho) &= \sum_{j=0}^{j_s} c_j \rho^j \\
&\sim c_{j_s} \rho^{j_s} \quad \text{as} \quad \rho \to \infty
\end{aligned}
\tag{12.30}
$$

Since $F(\rho)$ is a polynomial, $R(r) = u(\rho)/r$ will be normalizable.

From eq. (12.24), we see that the condition for c_{j_s+1} to vanish, given $c_{j_s} \neq 0$, is that

$$\lambda = n = j_s + l + 1 \tag{12.31}$$

where n is an integer. Therefore, the bound-state energies of the Hydrogen atom are deduced from the condition that

$$\lambda = \frac{1}{ka_0} = n \tag{12.32}$$

The integer n is known as the "**principal quantum number**." Using

$$k = \frac{\sqrt{2m|E|}}{\hbar} \quad \text{and} \quad a_0 = \frac{\hbar^2}{me^2} \tag{12.33}$$

the bound-state energies, labeled by the integer n, are

$$E_n = -\frac{me^4}{2n^2\hbar^2} \tag{12.34}$$

This is the same result as that obtained by Niels Bohr; it is in agreement with the experimental result (eq. 2.29 and 2.30 of Chapter 2) for the Hydrogen spectrum.

We can now write

$$\rho = 2kr = \frac{2r}{na_0} \tag{12.35}$$

Putting everything together, the energy eigenstates are

$$
\begin{aligned}
\varphi_{nlm}(r,\theta,\phi) &= N_{nl} R_{nl}(r) Y_{lm}(\theta,\phi) \\
&= N_{nl} \frac{u_{nl}(2r/na_0)}{r} Y_{lm}(\theta,\phi) \\
\rho &= \frac{2r}{na_0} \\
u_{nl}(\rho) &= \rho^{l+1} e^{-\rho/2} F_{nl}(\rho)
\end{aligned}
$$

$$
\begin{aligned}
F_{nl}(\rho) &= \sum_{j=0}^{n-l-1} c_j \rho^j \\
c_{j+1} &= \frac{j+l+1-\lambda}{(j+1)(j+2l+2)} c_j \\
c_0 &= 1
\end{aligned}
\tag{12.36}
$$

with the normalization constants N_{nl} determined from the normalization condition

$$
\begin{aligned}
1 &= \int_0^\infty dr\, r^2 \int_0^\pi d\theta \sin(\theta) \int d\phi\, \varphi_{nlm}^*(r,\theta,\phi)\varphi_{nlm}(r,\theta,\phi) \\
&= N_{nl}^2 \int_0^\infty dr\, r^2 R_{nl}^2(r) \\
&= N_{nl}^2 \int_0^\infty dr\, u_{nl}^2(2r/na_0)
\end{aligned}
\tag{12.37}
$$

and corresponding to an energy eigenvalue

$$
E_n = -\frac{me^4}{2n^2\hbar^2}
\tag{12.38}
$$

The choice $c_0 = 1$ is arbitrary. A different choice would simply lead to a different normalization constant, and the wavefunction would end up exactly the same.

It is clear that the energy eigenvalues are degenerate. To specify a unique eigenstate $\varphi_{nlm}(r,\theta,\phi)$, it is necessary to specify three integers: n, l, m. On the other hand, the energy eigenvalue E_n depends only on one of those integers. To determine the degree of degeneracy, i.e. the number of linearly independent eigenstates with the same energy E_n, we observe that the maximum index j_s of the (non-zero) c_j coefficients satisfies

$$
j_s = n - l - 1 \geq 0
\tag{12.39}
$$

and therefore

$$
l = 0, 1, 2, ..., n-1
\tag{12.40}
$$

Also, there are $2l + 1$ values of m,

$$
m = -l, -l+1, ..., l-1, l
\tag{12.41}
$$

corresponding to a given value of l. Therefore, the total number of l, m combinations that can exist for a given integer n are

$$
\begin{aligned}
\text{degeneracy of } E_n &= \sum_{l=0}^{n-1}(2l+1) \\
&= \left(2\sum_{l=0}^{n-1} l\right) + n \\
&= n^2
\end{aligned}
\tag{12.42}
$$

In atomic physics, the integer values of the l quantum number are assigned letters, namely:

$$
\begin{aligned}
l &= 0 \quad \text{S} \\
l &= 1 \quad \text{P} \\
l &= 2 \quad \text{D} \\
l &= 3 \quad \text{F}
\end{aligned}
\tag{12.43}
$$

Beyond $l = 3$, the assignment is alphabetical, i.e. $l = 3, 4, 5, 6...$ correspond to "F,G,H,I..." respectively (the reasons for these letter assignments go back to the history of spectroscopy, and need not concern us here.)[2] Thus the $\{nlm\} = \{100\}$ state is referred to as the "1S" state; the $\{nlm\} = \{21m\}$ states are referred to as the "2P" states, and so on, as indicated in Fig. [12.1].

We now use the formulas in eq. (12.36) to calculate the $1S$ and $2S$ wavefunctions explicitly.

- **The 1S Ground State**   Since $j_s = n - l - 1 \geq 0$, the smallest possible value for n is $n = 1$, which implies that $l = m = 0$. This is the lowest energy state, or "ground state" of the hydrogen atom; it is the state where the binding energy is greatest. According to (12.36) we have

$$
\begin{aligned}
\varphi_{100} &= N \frac{u_{10}(2r/a_0)}{r} Y_{00} \\
&= \frac{N}{\sqrt{4\pi}} \frac{u_{10}(2r/a_0)}{r}
\end{aligned}
\tag{12.44}
$$

where

$$
\begin{aligned}
u_{10}(\rho) &= e^{-\rho/2} \rho F_{10}(\rho) \\
&= e^{-\rho/2} \rho \sum_{j=0}^{1-0-1} c_j \rho^j \\
&= e^{-\rho/2} \rho
\end{aligned}
\tag{12.45}
$$

Therefore

$$
\varphi_{100} = \frac{N}{\sqrt{4\pi}} \frac{2}{a_0} e^{-r/a_0}
\tag{12.46}
$$

---

[2] "S" stands for the "sharp" series of spectral lines, "P" stands for the "principal" series, "D" for "diffuse" and "F" for "fundamental."

We must normalize the wavefunction to determine N:

$$
\begin{aligned}
1 &= \int r^2 dr d\Omega |\varphi_{100}|^2 \\
&= N^2 \int dr r^2 u_{10}(2r/a_0)^2 \\
&= N^2 \left(\frac{2}{a_0}\right)^2 \int_0^\infty dr \ r^2 e^{-2r/a_0} \\
&= N^2 a_0
\end{aligned}
\tag{12.47}
$$

So, finally, the ground-state wavefunction is

$$
\varphi_{100}(r,\theta,\phi) = \frac{2}{\sqrt{4\pi a_0^3}} e^{-r/a_0}
\tag{12.48}
$$

• **The 2S Excited State**   The $n = 2$ states are known as the "first excited" states, since they correspond to the lowest energy excitation above the ground state. The $l = 0$ state is always referred to as the S-state; so the $\{nlm\} = \{200\}$ is known as the 2S state, in spectroscopic notation. Again, using eq. (12.36)

$$
\begin{aligned}
\phi_{200}(r,\theta,\phi) &= N \frac{u_{20}(r/a_0)}{r} Y_{00} \\
u_{200}(\rho) &= e^{-\rho/2} \rho F_{20}(\rho) \\
&= e^{-\rho/2} \rho \sum_{j=0}^{2-0-1} c_j \rho^j \\
&= e^{-\rho/2} \rho (c_0 + c_1 \rho) \\
c_1 &= \frac{0 + l + 1 - n}{(0+1)(0+2l+2)} c_0 \\
&= -\frac{1}{2}
\end{aligned}
\tag{12.49}
$$

so that

$$
\begin{aligned}
\phi_{200} &= \frac{N}{\sqrt{4\pi}}(1 - \frac{1}{2}\rho)\frac{\rho}{r} e^{-\rho/2} \\
&= \frac{N}{a_0\sqrt{4\pi}}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}
\end{aligned}
\tag{12.50}
$$

normalization gives $N = (2a_0)^{-1/2}$, and therefore

$$\varphi_{200} = \frac{1}{\sqrt{8\pi a_0^3}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \tag{12.51}$$

In general, the wavefunction for principal quantum number has the form

$$\varphi_{nlm} = (\text{polynomial in } r \text{ of order} \leq \text{n-1}) \times e^{-r/na_0} Y_{lm}(\theta, \phi) \tag{12.52}$$

A polynomial can go through zero, so in general the probability distribution in the radial direction has "bumps", whose positions depend on both n and l. In particular, if we are only interested in the probability of finding an electron between radii r_1 and r_2, then

$$\begin{aligned}
\text{prob}(r_1 < r < r_2) &= \int_{r_1}^{r_2} dr r^2 \int d\Omega \; \varphi_{nlm}^* \varphi_{nlm} \\
&= \int_{r_1}^{r_2} dr \; r^2 R_{nl}^2(r) \\
&= \int_{r_1}^{r_2} dr \; P(r) \tag{12.53}
\end{aligned}$$

where we define the radial probability density

$$\begin{aligned}
P(r) &= r^2 R_{nl}^2(r) \\
&= ((\text{2n-th order polynomial in } r) \times e^{-2r/na_0} \tag{12.54}
\end{aligned}$$

A sketch of $P(r)$ vs. r is shown in Fig. [12.2], for a number of low-lying energy eigenstates.

12.1 The Scale of the World

We know that the volume of a gram of water is one cubic centimeter. Why isn't the volume instead one cubic kilometer, or one cubic parsec?

If you burn a log in a fireplace, enough energy is released to warm the room. If you burn instead a stick of dynamite, the energy released will destroy the room, and probably the rest of the house. But neither the log nor the dynamite will release enough energy to flatten a city, or vaporize the planet. Why not?

Quantum mechanics answers these questions, given as input the masses of the electron and proton, and the electron charge. In fact, the solution of the Hydrogen atom provides us with rough, order-of-magnitude estimates for the volume of a mole of solid anything, and the energy released by burning a mole of anything. This is

because the volume of a solid depends mainly on the number of atoms, and the size of each atom. The energy released in a chemical reaction also depends on the number of molecules participating in the reaction, and the energy released by each molecule. The number of molecules in a mole is known as Avogadro's number, which is

$$
\begin{aligned}
N_A &= 6.02 \times 10^{23} \\
&\approx \frac{1 \text{ gram}}{m_{proton} \text{ in grams}}
\end{aligned}
\tag{12.55}
$$

The proton mass gives slightly the wrong value, due to the proton-neutron mass difference. Anyway, N_A tells us approximately how many protons or neutrons there are in a gram, or how many molecules in a mole (= (no. of protons+neutrons per molecule) $\times$ one gram). Quantum mechanics then predicts, in principle, the *volume* of each molecule, and the energy released in any given chemical reaction.

Of course, using quantum mechanics to find the precise volume of any given molecule is a formidable task. But we can use the solution of the hydrogen atom to make order-of-magnitude estimates. The volume of any given molecule is certainly larger than that of the hydrogen atom, but usually not by much more than one or two powers of 10. Likewise, the energy released in a chemical reaction is typically less than the hydrogen atom binding energy, but this is still a rough order-of-magnitude estimate. If we are satisfied with accuracy within a couple of orders of magnitude, then we can answer the two questions posed above:

1. What is the volume of a mole of (solid or liquid) anything?

2. How much energy is released by burning a mole of anything?

Start with the first question. We will imagine that all molecules fit inside a cube of length equal to the diameter of the Hydrogen atom in its ground state. This gives us a volume

$$
v \sim (2a_0)^3
\tag{12.56}
$$

where a_0 is the Bohr radius

$$
a_0 = \frac{\hbar^2}{me^2} = 5 \times 10^{-9} \text{ cm}
\tag{12.57}
$$

so that

$$
v \sim 10^{-24} \text{cm}^3
\tag{12.58}
$$

Then the volume of a mole is

$$
V_{mole} = N_A v \sim 0.6 \text{ cm}^3
\tag{12.59}
$$

which is at least the right order of magnitude. The volume of a mole of anything is a few cubic centimeters, not cubic kilometers or cubic parsecs.

To estimate the energy released by burning a mole of anything, assume that the energy released per molecule is of the order of magnitude of the binding energy of an electron in the Hydrogen atom ground state. This is surely not very accurate, but again, we are not going to worry about a few powers of ten. The binding energy is

$$|E_1| = \frac{me^4}{2\hbar^2} \approx 2 \times 10^{-18} \text{ J} \tag{12.60}$$

Then burning a mole of anything would release an energy E on the order

$$E \sim N_A |E_1| \sim 1200 \text{ kJ} \tag{12.61}$$

which is sufficient to turn half a kilogram of water, at 100 C and 1 atm pressure, completely into steam. Released in a short time this would make a good bang, but its certainly not enough energy to flatten a city.

In this way, we can use quantum mechanics to estimate the "scale of the world;" i.e. volume per gram, energy released in chemical reactions, and so on. In fact, with a bit more work, its possible to go on and estimate the order-of-magnitude size of animals and mountains![3] As explained in Lecture 6, the size and binding energy of the Hydrogen atom is ultimately due to an interplay between the attractive Coulomb potential and a kinetic energy coming from the Uncertainty principle. It is this interplay that sets the scale of the world. Of course, the argument is a little incomplete: it required as input the masses of the electron and proton, as well as the electron charge.[4] Where do *these* numbers come from? It is the religious belief of most physicists (including your professor) that all such numbers will one day be derived from an ultimate "Theory of Everything," whose cornerstone will be the principles of quantum mechanics.[5]

---

[3]There is a beautiful essay by V. Weisskopf on this subject.

[4]Nowadays, its possible to calculate the mass of the proton from the theory of the strong interactions (QCD), but this still requires input of a dimensionful constant known as "QCD Λ."

[5]An excellent non-technical discussion is found in S. Weinberg's recent book, entitled *Dreams of a Final Theory*.

Chapter 13

Electron Spin

Lets go back, for a moment, to the classical picture of the Hydrogen atom, with an electron moving in a circular orbit around the proton. A charge moving in a circle constitutes a current loop, and, according to the usual laws of electromagnetism a current loop is associated with a magnetic moment according to the rule

$$\mu = \frac{1}{c} I A \tag{13.1}$$

where μ is the magnetic moment, I is the current, and A is the area enclosed by the circular orbit. The current is the charge per unit length of loop, times the velocity, so in this case, for a circular orbit of radius r

$$
\begin{aligned}
I &= -\frac{e}{2\pi r} v \\
v &= \frac{p}{M} = \frac{L}{Mr} \\
A &= \pi r^2
\end{aligned}
\tag{13.2}
$$

Putting it all together, and noting that as vector quantities both $\vec{\mu}$ and $\vec{L}$ are normal to the loop, we get

$$\vec{\mu} = -\frac{e}{2Mc} \vec{L} \tag{13.3}$$

(note that the radius r drops out of the expression). Finally, in an external magnetic field $\vec{B}$, the interaction energy between the magnetic dipole and the field is given by

$$
\begin{aligned}
E_{mag} &= -\vec{B} \cdot \vec{\mu} \\
&= \frac{e}{2Mc} \vec{B} \cdot \vec{L}
\end{aligned}
\tag{13.4}
$$

Suppose then that a hydrogen atom is sitting in an external constant magnetic field, directed along the z-axis. In that case, the Hamiltonian relevant for the motion of the electron is

$$H = H_0 + \frac{e}{2Mc} B_z L_z \tag{13.5}$$

where H_0 is the Hydrogen atom Hamiltonian in the absence of an external field

$$H_0 = \frac{p^2}{2M} - \frac{e^2}{r} \tag{13.6}$$

Going over to quantum theory, H_0 and L_z become operators which, as it happens, commute with each other: an eigenstate φ_{nlm} of H_0 is also an eigenstate of L_z

$$L_z \varphi_{nlm} = m\hbar \varphi_{nlm} \tag{13.7}$$

Therefore, an eigenstate of H_0 is an eigenstate of the total Hamiltonian

$$H\varphi_{nlm} = \left(E_n^0 + mB_z \frac{e\hbar}{2Mc} \right) \varphi_{nlm} \tag{13.8}$$

with energy eigenvalues

$$E_{nlm} = E_n^0 + mB_z \frac{e\hbar}{2Mc} \tag{13.9}$$

where E_n^0 are the energy eigenvalues of the electron when there is no external field.

This means that if we insert a collection of hydrogen atoms between the poles of a strong magnet, then spectral lines corresponding to transitions between principal quantum numbers n_1 and n_2 should split into many spectral lines, corresponding to transitions between states with different values of the L_z quantum numbers m_1 and m_2. There are certain **selection rules** governing which transitions are possible; these rules will be derived in a later chapter. This splitting of spectral lines in an external magnetic field is known as the (strong-field) **Zeeman effect**.

The only trouble is that when the experiment is actually done, an analysis of the spectral lines reveals that in fact there are *twice* as many energy levels as one would expect, for each pair of quantum numbers n and l. Instead of the $2l + 1$ levels one would expect (because there are $2l + 1$ values of m for each l), there are *two* sets of $2l + 1$ levels, with energies

$$\begin{aligned} E_{nlm}^+ &\approx E_n^0 + (m+1)B_z \frac{e\hbar}{2Mc} \\ E_{nlm}^- &\approx E_n^0 + (m-1)B_z \frac{e\hbar}{2Mc} \end{aligned} \tag{13.10}$$

What can possibly account for this extra splitting?

The most natural explanation is that, in addition to the magnetic moment due to its orbital angular momentum, an electron also has an intrinsic magnetic moment, associated with an intrinsic spin angular momentum. Classically, after all, any spinning charge aquires a magnetic moment in the direction of the spin angular momentum. So let us suppose that the intrinsic magnetic moment of the electron is

$$\vec{\mu_e} = -\frac{eg}{2Mc}\vec{S} \tag{13.11}$$

where g is some constant, known as the **gyromagnetic ratio**. In quantum theory S must be a Hermitian operator, and we assume that it satisfies the same commutation relations as orbital angular momentum

$$
\begin{aligned}
[S_x, S_y] &= i\hbar S_z \\
[S_y, S_z] &= i\hbar S_x \\
[S_z, S_x] &= i\hbar S_y
\end{aligned}
$$
(13.12)

From these commutation relations alone, we know from the discussion in Lecture 11 that the possible eigenvalues of S^2 and S_z are

$$
\begin{aligned}
S^2 &= s(s+1)\hbar^2 \qquad s = 0, \frac{1}{2}, 1, \frac{3}{2}, ... \\
S_z &= s_z\hbar \qquad\qquad -s \le s_z \le s
\end{aligned}
$$
(13.13)

Taking the electron magnetic moment into account, the total Hamiltonian is then

$$
\begin{aligned}
H &= H_0 + \frac{e}{2Mc}B_z L_z - (\mu_e)_z B_z \\
H &= H_0 + \frac{e}{2Mc}B_z(L_z + gS_z)
\end{aligned}
$$
(13.14)

The electron spin is independent of the electron position and momentum, therefore we may assume that

$$
[H_0, S_z] = [L_z, S_z] = 0
$$
(13.15)

and this means that operators H_0, L_z, S_z have a common set of eigenstates, which we denote $|nlms_z>$. Then

$$
\begin{aligned}
H|nlms_z> &= E_{nms_z}|nlms_z> \\
E_{nms_z} &= E_n^0 + \frac{e\hbar}{2Mc}B_z(m + gs_z)
\end{aligned}
$$
(13.16)

Comparison to (13.10) shows that we get agreement if the electron has an intrinsic spin

$$
s = \frac{1}{2} \quad \Rightarrow \quad s_z = \pm\frac{1}{2}
$$
(13.17)

and gyromagnetic ratio

$$
g \approx 2
$$
(13.18)

so that E^+ corresponds to $s_z = \frac{1}{2}$, and E^- to $s_z = -\frac{1}{2}$.

An independent check of the double-valued character of the electron magnetic moment is provided by the **Stern-Gerlach Experiment**, in which a beam of electrons is sent through a (non-uniform) magnetic field, oriented (mainly) in the z-direction, as shown in Fig. [13.1]. Classically, the force exerted on a dipole μ in a non-uniform magnetic field is

$$
\vec{F} = \nabla(\mu \cdot B)
$$
(13.19)

so the z-component of the force is

$$
\begin{aligned}
F_z &= \frac{\partial B_z}{\partial z}\mu_z \\
&= \frac{eg}{2Mc}\frac{\partial B_z}{\partial z}S_z
\end{aligned}
\tag{13.20}
$$

A measurement of the deflection of the electron beam is therefore going to be a measurement of the z-component of electron spin. If $s = \frac{1}{2}$, then there are only two possibilities: $s_z = \pm\frac{1}{2}$, and the force is oriented either up or down along the z-axis, with equal magnitude. Each electron should be deflected along one of only two trajectories, as shown in Fig. [13.1]. This is, in fact what is found experimentally. The Stern-Gerlach apparatus is therefore a way of measuring the component of electron spin along a given axis, for any given electron. If deflected upwards, the electron is in an $S_z = +\frac{1}{2}\hbar$ (or **"spin up"**) eigenstate. If the electron is deflected downwards, it is in an $S_z = -\frac{1}{2}\hbar$ (or **"spin down"**) eigenstate.

As already mentioned, any spinning charged object has a magnetic moment, according to the laws of classical electromagnetism. Should we then think of the electron as being *literally* a spinning ball of charge? There are two main problems with such a picture. First, if we imagine that the electron is composed of some substance with a constant charge-to-mass ratio of e/M, then, generalizing only slightly the reasoning that applies to a current loop, the electron should have a magnetic moment

$$
\vec{\mu} = \frac{e}{2Mc}\vec{S}
\tag{13.21}
$$

instead of what is actually found, which is about twice that value

$$
\vec{\mu} = \frac{e}{2Mc}g\vec{S}
\tag{13.22}
$$

with gyromagnetic ratio $g \approx 2$. The second reason is simply the fact that, in this picture, the electron spin angular momentum is just the orbital angular momentum of electron "substance." But, as we have already seen, orbital angular momentum can only have values $l = 0, 1, 2, ...$; in particular, $l = \frac{1}{2}$ is ruled out. So the picture of an electron as a spinning volume of charged "electron stuff" cannot easily account for the origin of the electron magnetic moment.

13.1 Spin Wavefunctions

The next question is how to write the wavefunction of an eigenstate of spin angular momentum. If the electron were a spinning ball of charge, then it would be natural to represent the spin wavefunction by spherical harmonics $Y_{ss_z}(\theta', \phi')$, where $\partial_t\theta'$ is the classical angular velocity of the spinning ball. As we have seen, the "ball of charge"

picture is inadequate, and in any case there are no spherical harmonics with $s = \frac{1}{2}$. So...what to do?

For the moment lets forget all about the x, y, z-degrees of freedom of the particle, and concentrate just on the spin. Now, although we don't have spherical harmonics for $s = 1/2$, we can still represent the eigenstates of S^2 and S_z by two orthonormal ket vectors

$$|s = \frac{1}{2}, s_z = \frac{1}{2}> \quad \text{and} \quad |s = \frac{1}{2}, s_z = -\frac{1}{2}> \qquad (13.23)$$

where

$$
\begin{aligned}
S^2|\frac{1}{2}\frac{1}{2}> &= \frac{3}{4}\hbar^2|\frac{1}{2}\frac{1}{2}> \\
S_z|\frac{1}{2}\frac{1}{2}> &= \frac{1}{2}\hbar|\frac{1}{2}\frac{1}{2}> \\
S^2|\frac{1}{2} - \frac{1}{2}> &= \frac{3}{4}\hbar^2|\frac{1}{2} - \frac{1}{2}> \\
S_z|\frac{1}{2} - \frac{1}{2}> &= -\frac{1}{2}\hbar|\frac{1}{2} - \frac{1}{2}>
\end{aligned}
\qquad (13.24)
$$

Then (if we disregard position dependence) *any* $s = \frac{1}{2}$ state can be represented as a superposition

$$|\psi >= a|\frac{1}{2}\frac{1}{2}> + b|\frac{1}{2} - \frac{1}{2}> \qquad (13.25)$$

Now this looks exactly like the way we would represent a vector in a two-dimensional space. So before going on, its worth recalling a few facts of vector algebra.

Let $\vec{e}_1$ and $\vec{e}_2$ be two orthonormal vectors (i.e. orthogonal unit vectors) in a two dimensional space. For example, $\vec{e}_1$ and $\vec{e}_2$ could be unit vectors along the x and y axes, respectively. Orthonormality means that

$$
\begin{aligned}
\vec{e}_1 \cdot \vec{e}_1 &= 1 \\
\vec{e}_2 \cdot \vec{e}_2 &= 1 \\
\vec{e}_1 \cdot \vec{e}_2 &= 0
\end{aligned}
\qquad (13.26)
$$

If we have a set of D orthonormal vectors in a D-dimensional space, those vectors are known as a *basis* for the vector space, and any vector can be expressed a linear combination of those basis vectors. In the case we are considering, $D = 2$, any vector can be written in the form

$$\vec{v} = a\vec{e}_1 + b\vec{e}_2 \qquad (13.27)$$

It is useful and traditional to represent a (ket) vector in a finite dimensional space as a column of numbers, i.e.

$$\vec{v} \leftrightarrow \left[\begin{array}{c} a \\ b \end{array} \right] \qquad (13.28)$$

This is the column vector representation of the vector $\vec{v}$, in the *basis* $\{\vec{e}_1, \ \vec{e}_2\}$. You will notice that the components of the column vector are inner products of the ket vector $\vec{v}$ with the bra vectors $\{\vec{e}_1, \ \vec{e}_2\}$, i.e.

$$
\begin{aligned}
a &= \vec{e}_1 \cdot \vec{v} = < e_1 | v > \\
b &= \vec{e}_2 \cdot \vec{v} = < e_2 | v >
\end{aligned}
\tag{13.29}
$$

We can choose $\vec{v} = \vec{e}_1$ or $\vec{e}_2$, and find the values of a and b for the basis vectors. Its easy to see that the corresponding column vectors are

$$
\vec{e}_1 \leftrightarrow \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad \vec{e}_2 \leftrightarrow \begin{bmatrix} 0 \\ 1 \end{bmatrix}
\tag{13.30}
$$

In Lecture 3 we discussed the notion of a linear operator: its simply a rule for changing any vector $\vec{v}$ into another vector $\vec{v}'$

$$
\vec{v}' = M\vec{v}
\tag{13.31}
$$

such that, for any two vectors,

$$
M(a\vec{u} + b\vec{v}) = aM\vec{u} + bM\vec{v}
\tag{13.32}
$$

The **matrix element** m_{ij} of a linear operator M in the basis $\{\vec{e}_k\}$ is given by the inner product

$$
M_{ij} = \vec{e}_i \cdot M\vec{e}_j
\tag{13.33}
$$

or, in bra-ket notation

$$
M_{ij} = < e_i | M | e_j >
\tag{13.34}
$$

Suppose we are given the matrix elements of some linear operator M in a certain basis. Then its easy to see that the components

$$
v_i' = < e_i | v' >
\tag{13.35}
$$

of the transformed vector $|v'> = M|v>$, in terms of the components

$$
v_i = < e_i | v >
\tag{13.36}
$$

of the original vector are given by the usual rule of matrix multiplication

$$
\begin{aligned}
v_i' &= < e_i | v' > \\
&= < e_i | M | v > \\
&= < e_i | M \sum_j v_j | e_j > \\
&= \sum_j < e_i | M | e_j > v_j \\
&= \sum_j M_{ij} v_j
\end{aligned}
\tag{13.37}
$$

In column vector notation, this is written

$$\begin{bmatrix} v_1' \\ v_2' \end{bmatrix} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} \tag{13.38}$$

After this brief excursion in vector algebra, lets return to the problem of electron spin. The idea is that we can express the spin wavefunction as a column vector of 2 components, known as a **spinor**, and express the spin operators as 2×2 matrices. To begin with, the basis vectors are chosen to be the two eigenstates of S^2, S_z for $s = \frac{1}{2}$,

$$|e_1> = |\frac{1}{2}\frac{1}{2}> \qquad |e_2> = |\frac{1}{2} - \frac{1}{2}> \tag{13.39}$$

In this basis, the eigenstates themselves can be written as the column vectors (spinors)

$$|\frac{1}{2}\frac{1}{2}> \leftrightarrow \chi_+ \equiv \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad |\frac{1}{2} - \frac{1}{2}> \leftrightarrow \chi_- \equiv \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{13.40}$$

and *any* spin-$\frac{1}{2}$ state can be written as a superposition, in ket notation

$$|\psi> = \psi_+|e_1> + \psi_-|e_2> \tag{13.41}$$

or, in column vector notation,

$$|\psi> \leftrightarrow \begin{bmatrix} \psi_+ \\ \psi_- \end{bmatrix} \tag{13.42}$$

Now we can figure out what the spin operators S^2, S_x, S_y, S_z look like as matrices, using the relationships that were proved, in Lecture 11, for *any* operators satisfying the angular momentum commutation relations (13.12). Writing equations (330) and (373) from Lecture 11 in ket-notation, we have

$$\begin{aligned} S^2|ss_z> &= s(s+1)\hbar^2|ss_z> \\ S_z|ss_z> &= s_z\hbar|ss_z> \\ S_-|ss_z> &= \sqrt{(s+s_z)(s-s_z+1)}\hbar|s, s_z - 1> \\ S_+|ss_z> &= \sqrt{(s-s_z)(s+s_z+1)}\hbar|s, s_z + 1> \\ S_x &= \frac{1}{2}(S_+ + S_-) \\ S_y &= \frac{1}{2i}(S_+ - S_-) \end{aligned} \tag{13.43}$$

where we have just used the symbol S instead of L, s instead of l, and s_z instead of m. For the electron, $s = \frac{1}{2}$ and $s_z = \frac{1}{2}, -\frac{1}{2}$. From these relations, we easily get all the matrix elements, e.g.

$$(S_x)_{12} = <e_1|S_x|e_2>$$

$$
\begin{aligned}
&= \ < \frac{1}{2}\frac{1}{2}|S_x|\frac{1}{2}-\frac{1}{2} > \\
&= \ \frac{1}{2}\left[< \frac{1}{2}\frac{1}{2}|S_+|\frac{1}{2}-\frac{1}{2} > + < \frac{1}{2}\frac{1}{2}|S_-|\frac{1}{2}-\frac{1}{2} > \right] \\
&= \ \frac{1}{2}\left[< \frac{1}{2}\frac{1}{2}|\hbar|\frac{1}{2}\frac{1}{2} > +0 \right] \\
&= \ \frac{1}{2}\hbar
\end{aligned}
\tag{13.44}
$$

After computing all the needed components, the matrix form of the spin operators, for spin $s = \frac{1}{2}$, are

$$
\begin{aligned}
S^2 &= \ \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad
S_z = \frac{1}{2}\hbar \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \\
S_x &= \ \frac{1}{2}\hbar \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\
S_y &= \ \frac{1}{2}\hbar \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}
\end{aligned}
\tag{13.45}
$$

It is useful to extract a common factor of $\frac{\hbar}{2}$, and to write

$$
S_x = \frac{\hbar}{2}\sigma_x \qquad S_y = \frac{\hbar}{2}\sigma_y \qquad S_z = \frac{\hbar}{2}\sigma_z
\tag{13.46}
$$

where the matrices

$$
\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad
\sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad
\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}
\tag{13.47}
$$

are known as the **Pauli Spin Matrices**.

Exercise: Consider a particle with spin $s = 1$. Find the matrix representation of S^2, S_x, S_y, S_z in the basis of eigenstates of S^2, S_z, denoted
$|ss_z> = |11>, |10>, |1-1>$

Next we must take account of the spatial degrees of freedom. Suppose the wavefunction ψ is an eigenstate of momenta *and* an eigenstate of S_z, with eigenvalue $s_z = \frac{1}{2}\hbar$ ("spin up"). Then we require, as usual,

$$
\begin{aligned}
-i\hbar\partial_x\psi &= \ p_x\psi \\
-i\hbar\partial_y\psi &= \ p_y\psi \\
-i\hbar\partial_z\psi &= \ p_z\psi
\end{aligned}
\tag{13.48}
$$

and, in addition,

$$S_z \psi = \frac{1}{2}\hbar\psi \qquad (13.49)$$

where S_z is the matrix shown in (13.45). Its easy to see that the solution is

$$\psi_{p+} = e^{i\vec{p}\cdot\vec{x}/\hbar} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad (13.50)$$

Similarly, an eigenstate of momentum and S_z with $s_z = -\frac{1}{2}$ ("spin down") will be

$$\psi_{p-} = e^{i\vec{p}\cdot\vec{x}/\hbar} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \qquad (13.51)$$

According to our general rules, the (normalized) superposition of two physical states is also a physical state, so in general an electron wavefunction must have the form

$$\begin{aligned}
\psi &= \int d^3p \, [f_+(p)\psi_{p+} + f_-(p)\psi_{p-}] \\
&= \int d^3p \begin{bmatrix} f_+(p)e^{i\vec{p}\cdot\vec{x}} \\ f_-(p)e^{i\vec{p}\cdot\vec{x}} \end{bmatrix} \\
&= \begin{bmatrix} \psi_+(x) \\ \psi_-(x) \end{bmatrix} \qquad (13.52)
\end{aligned}$$

where $\psi_+(x)$ and $\psi_-(x)$ are any two square-integrable functions satisfying a normalization condition

$$\begin{aligned}
<\psi|\psi> &= \sum_{i=+,-} \int d^3x \, \psi_i^*(\vec{x})\psi_i(\vec{x}) \\
&= \int d^3x \, [|\psi_+(\vec{x})|^2 + |\psi_-(\vec{x})|^2] \\
&= 1 \qquad (13.53)
\end{aligned}$$

The interpretation of the two terms in the spinor wavefunction, $\psi_{+/-}(x)$, is easy to see from a computation of the S_z expectation value

$$\begin{aligned}
<S_z> &= <\psi|S_z|\psi> \\
&= \int dxdydz \, [\psi_+^*, \psi_-^*]\frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} \psi_+ \\ \psi_- \end{bmatrix} \\
&= \int dxdydz \left(+\frac{1}{2}\hbar|\psi_+|^2 + (-\frac{1}{2}\hbar)|\psi_-|^2\right) \\
&= (\frac{1}{2}\hbar)\text{Prob(spin up)} + (-\frac{1}{2}\hbar)\text{Prob(spin down)} \qquad (13.54)
\end{aligned}$$

where "spin up" and "spin down" refer to the two possibilities of finding $s_z = \frac{1}{2}$ and $s_z = -\frac{1}{2}$. Comparing the last two lines

$$
\begin{aligned}
\text{Prob(spin up)} &= \int dx\,dy\,dz\; |\psi_+|^2 \\
\text{Prob(spin down)} &= \int dx\,dy\,dz\; |\psi_-|^2
\end{aligned}
\tag{13.55}
$$

Although ψ_+ and ψ_- are, in general, independent functions, there are many important cases where the spatial and spin parts of the wavefunction factorize, i.e.

$$
\psi = \psi(x) \begin{bmatrix} a \\ b \end{bmatrix}
\tag{13.56}
$$

An example we have just seen are the eigenstates of momenta and S_z shown in eq. (13.50) and (13.51). Another example is the set of eigenstates of H, L^2, L_z, S^2, S_z, where H is the Hydrogen atom Hamiltonian. The "spin-up" eigenstates are

$$
\varphi(r, \theta, \phi)\chi_+ = R_{nl}(r)Y_{lm}(\theta, \phi) \begin{bmatrix} 1 \\ 0 \end{bmatrix}
\tag{13.57}
$$

while the "spin-down" eigenstates are

$$
\varphi(r, \theta, \phi)\chi_- = R_{nl}(r)Y_{lm}(\theta, \phi) \begin{bmatrix} 0 \\ 1 \end{bmatrix}
\tag{13.58}
$$

In ket notation, the states are labeled by their quantum numbers:

$$
\{|nlm s s_z >\} \quad \text{where} \quad s = \frac{1}{2}, \; s_z = \pm\frac{1}{2}
\tag{13.59}
$$

We can get some practice in the use of spinor notation and spin matrices, by studying the precession of electron spin in an external magnetic field.

● **Electron Precession**

Suppose an electron is in a state where $p \approx 0$, so the electron spinor, while it can depend on time, does not depend on space, i.e.

$$
\psi(t) = \begin{bmatrix} \psi_+(t) \\ \psi_-(t) \end{bmatrix}
\tag{13.60}
$$

In addition, suppose that there is an external, constant magnetic field, of magnitude B, in the z-direction. The Hamiltonian is then

$$
\begin{aligned}
H &= \frac{p^2}{2M} - \vec{\mu} \cdot \vec{B} \\
&\approx \frac{e\hbar B g}{4Mc}\sigma_z \\
&\approx \frac{1}{2}\hbar\Omega\sigma_z
\end{aligned}
\tag{13.61}
$$

where

$$\Omega = \frac{eB}{Mc} \tag{13.62}$$

Ω is known as the "cyclotron frequency." The eigenstates of this Hamiltonian are then simply $\chi_{\pm}$, because H is proportional to σ_z, and $\chi_{\pm}$ are the eigenstates of σ_z:

$$
\begin{aligned}
H\chi_{+} &= E_{+}\chi_{+} \quad \text{where} \quad E_{+} = \frac{1}{2}\hbar\Omega \\
H\chi_{-} &= E_{-}\chi_{-} \quad \text{where} \quad E_{-} = -\frac{1}{2}\hbar\Omega
\end{aligned} \tag{13.63}
$$

Eigenstates of the Hamiltonian are stationary states; an electron in such a state will remain in that eigenstate indefinitely. But suppose instead that the electron spin is initially in an eigenstate of S_x or S_y. What we now show is that the electron spin will then tend to precess around the z-axis.

First, some notation. Define "spin-up" states and "spin-down" states in the x, y, and z-directions to be the $\pm\frac{1}{2}\hbar$ eigenstates of S_x, S_y, S_z respectively:

$$
\begin{aligned}
S_x\alpha_x &= \frac{1}{2}\hbar\alpha_x & S_x\beta_x &= -\frac{1}{2}\hbar\beta_x \\
S_y\alpha_y &= \frac{1}{2}\hbar\alpha_y & S_y\beta_y &= -\frac{1}{2}\hbar\beta_y \\
S_z\alpha_z &= \frac{1}{2}\hbar\alpha_z & S_z\beta_z &= -\frac{1}{2}\hbar\beta_z
\end{aligned} \tag{13.64}
$$

We know already that

$$\alpha_z = \chi_{+} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \text{and} \quad \beta_z = \chi_{-} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{13.65}$$

Finding the eigenstates α_y, β_y requires finding the eigenstates of the Pauli matrix σ_y. It is instructive do this in detail.

The first thing to do is to find the eigenvalues of σ_y. The eigenvalue equation is

$$\sigma_y \vec{u} = \lambda \vec{u} \tag{13.66}$$

and the eigenvalues are determined by solving the **secular equation**

$$\det[\sigma_y - \lambda I] = 0 \tag{13.67}$$

where I is the unit matrix. For the Pauli matrix σ_y, this is

$$\det \begin{bmatrix} -\lambda & i \\ -i & -\lambda \end{bmatrix} = \lambda^2 - 1 = 0 \tag{13.68}$$

so the eigenvalues are

$$\lambda_1 = +1 \quad \lambda_2 = -1 \tag{13.69}$$

Note that (i) σ_y is an Hermitian matrix; and (ii) the eigenvalues are both real. As we found last semester, the eigenvalues of any hermitian operator are real, and eigenstates corresponding to different eigenvalues are orthogonal. So far, we have verified the reality of the eigenvalues. Now we solve for the two corresponding eigenstates, denoted

$$\alpha_y = \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \quad \text{for eigenvalue} \quad \lambda = 1 \tag{13.70}$$

and

$$\beta_y = \begin{bmatrix} b_1 \\ b_2 \end{bmatrix} \quad \text{for eigenvalue} \quad \lambda = -1 \tag{13.71}$$

Start by solving for

$$\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} a_1 \\ a_2 \end{bmatrix}$$

$$\begin{bmatrix} -ia_2 \\ ia_1 \end{bmatrix} = \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \tag{13.72}$$

which has the solution

$$a_2 = ia_1 \quad \text{or} \quad \alpha_y = \begin{bmatrix} a_1 \\ ia_1 \end{bmatrix} \tag{13.73}$$

Finally, we determine a_1 by normalization

$$\begin{aligned} 1 &= \alpha_y \cdot \alpha_y = |a_1|^2 + |ia_1|^2 = 2|a_1|^2 \\ &\implies a_1 = \frac{1}{\sqrt{2}} \end{aligned} \tag{13.74}$$

so

$$\lambda_1 = +1 \qquad \alpha_y = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix} \tag{13.75}$$

The procedure for $\lambda_2 = -1$ is identical:

$$\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \end{bmatrix} = - \begin{bmatrix} b_1 \\ b_2 \end{bmatrix}$$

$$\begin{bmatrix} -ib_2 \\ ib_1 \end{bmatrix} = \begin{bmatrix} -b_1 \\ -b_2 \end{bmatrix} \tag{13.76}$$

And this time $b_2 = -ib_1$. Normalizing to determine b_1, we find

$$\lambda_2 = -1 \qquad \beta_y = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix} \tag{13.77}$$

Note that the inner product

$$\alpha_y \cdot \beta_y = \frac{1}{2}[1, -i] \begin{bmatrix} 1 \\ -i \end{bmatrix} = 1 + (-i)^2 = 0 \tag{13.78}$$

vanishes, so α_y and β_y are orthogonal, as expected.

By similar means we can find the eigenstates of σ_x, with the result:

$$\begin{aligned} \alpha_x &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} & \beta_x &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix} \\ \alpha_y &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix} & \beta_y &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix} \\ \chi_+ = \alpha_z &= \begin{bmatrix} 1 \\ 0 \end{bmatrix} & \chi_- = \beta_z &= \begin{bmatrix} 0 \\ 1 \end{bmatrix} \end{aligned} \tag{13.79}$$

Exercise: Obtain the eigenstates α_x and β_x of S_x by the same means used for obtaining the eigenstates of S_y.

To analyze the variation with time of the electron magnetic moment in an external magnetic field, we use the time-dependent Schrodinger equation with Hamiltonian (13.61)

$$i\hbar \partial_t \psi = \frac{1}{2} \hbar \Omega \sigma_z \psi \tag{13.80}$$

or, in matrix form,

$$\begin{bmatrix} \partial_t \psi_+ \\ \partial_t \psi_- \end{bmatrix} = -i \frac{1}{2} \Omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \psi_+ \\ \psi_- \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} i \Omega \psi_+ \\ \frac{1}{2} i \Omega \psi_- \end{bmatrix} \tag{13.81}$$

These are two independent first-order differential equations, one for ψ_+ and one for ψ_-, and the general solution is easily seen to be

$$\psi(t) = \begin{bmatrix} a e^{-i\Omega t/2} \\ b e^{i\Omega t/2} \end{bmatrix} \tag{13.82}$$

where a and b are constants

Suppose that at time $t = 0$ the electron is in a "spin-up" state in the x-direction. This means that the constants a and b are determined to be

$$a = b = \frac{1}{\sqrt{2}} \tag{13.83}$$

Let $T = 2\pi/\Omega$ be the period corresponding to an angular frequency Ω. Then, from the solution above, we see that the wavefunction for the electron spin "precesses" around the z-axis:

$$
\begin{aligned}
\psi(0) &= \alpha_x \quad \text{(assumption)} \\
\psi(\frac{T}{4}) &= \frac{1}{\sqrt{2}} \begin{bmatrix} e^{-i\pi/4} \\ e^{i\pi/4} \end{bmatrix} = e^{-i\pi/4}\alpha_y \\
\psi(\frac{T}{2}) &= \frac{1}{\sqrt{2}} \begin{bmatrix} e^{-i\pi/2} \\ e^{i\pi/2} \end{bmatrix} = e^{-i\pi/2}\beta_x \\
\psi(\frac{3T}{4}) &= \frac{1}{\sqrt{2}} \begin{bmatrix} e^{-3i\pi/4} \\ e^{3i\pi/4} \end{bmatrix} = e^{-3i\pi/4}\beta_y \\
\psi(T) &= \frac{1}{\sqrt{2}} \begin{bmatrix} e^{-i\pi} \\ e^{i\pi} \end{bmatrix} = e^{-i\pi}\alpha_x
\end{aligned} \tag{13.84}
$$

Thus the spin direction of the electron precesses around the z-axis with a precession frequency $f = \Omega/2\pi$. The fact that a spin 1/2 particle precesses in the presence of an external magnetic field is of considerable practical importance for the Nuclear Magnetic Resonance Imaging technique in medicine, which takes advantage of the precession of atomic nuclei of spin 1/2.

- **Spin-Orbit Coupling**

Even when there is no external magnetic field, the frequencies of the spectral lines of the Hydrogen atom are not *exactly* as predicted by Bohr. Certain lines of the spectrum, when observed using a high-resolution spectrometer, are found to actually be two closely spaced spectral lines; this phenomenon is known as atomic fine structure. Historically, it was an attempt to explain this fine structure of spectral lines in the alkali elements that led Goudsmit and Uhlenbeck, in 1925, to propose the existence of electron spin.

To understand the Goudsmit-Uhlenbeck reasoning, consider an elecron moving with velocity $\vec{v}$ across a static electric field, such as the Coulomb field due to an atomic nucleus. According to theory of special relativity, the electromagnetic field as it appears in the rest frame of the electron is no longer entirely electric, but also contains a magnetic component

$$
\begin{aligned}
\vec{B} &= -\frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}\frac{\vec{v}}{c} \times \vec{E} \\
&\approx -\frac{1}{Mc}\vec{p} \times \vec{E}
\end{aligned} \tag{13.85}
$$

Given that the electron has a magnetic moment $\vec{\mu}$, there should be an interaction energy due to the electron magnetic moment, in the rest frame of the electron

$$
H' = -\vec{\mu} \cdot \vec{B} \tag{13.86}
$$

However, we really want the interaction energy in the rest frame of the laboratory, which is also (approximately) the rest frame of the proton. In transforming this energy back to the proton rest frame there is a slight subtlety: the electron is not moving with a uniform velocity $\vec{v}$, but is rather in *accellerated* motion as it circles around the proton. To take this accelleration carefully into account would take us too far afield, but suffice it to say that the interaction energy H' above is modified by a factor of $\frac{1}{2}$, called the Thomas precession factor[1]

$$
\begin{aligned}
H' &= -\frac{1}{2}\vec{\mu} \cdot \vec{B} \\
&= -\frac{\vec{\mu}}{2Mc} \cdot (\vec{E} \times \vec{p}) \\
&= -\frac{e}{2Mc}\vec{\mu} \cdot \left(\frac{\vec{r}}{r^3} \times \vec{p} \right) \\
&= -\frac{e}{2Mc}\frac{1}{r^3}\vec{L} \cdot \vec{\mu}
\end{aligned}
\tag{13.87}
$$

Using

$$
\begin{aligned}
\vec{\mu} &= -\frac{eg}{2Mc}\vec{S} \\
&\approx -\frac{e}{Mc}\vec{S}
\end{aligned}
\tag{13.88}
$$

we get

$$
H' = \frac{e^2}{2M^2c^2}\frac{1}{r^3}\vec{L} \cdot \vec{S}
\tag{13.89}
$$

This expression is known as the "spin-orbit" coupling, because it involves a coupling of the electron spin angular momentum with the electron orbital angular momentum. The full Hydrogen atom Hamiltonian should contain this spin-dependent term.

Now the spin-orbit term involves all the x, y, z components of angular momentum, and we know that there is no physical state which is an eigenstate of all of these terms simultaneously. However, let us define the *total* electron angular momentum

$$
\vec{J} = \vec{L} + \vec{S}
\tag{13.90}
$$

Then

$$
J^2 = L^2 + 2\vec{L} \cdot \vec{S} + S^2
\tag{13.91}
$$

or

$$
\vec{L} \cdot \vec{S} = \frac{1}{2}(J^2 - L^2 - S^2)
\tag{13.92}
$$

The total Hamiltonian is then

$$
H = H_0 + \frac{e^2}{4M^2c^2}\frac{1}{r^3}(J^2 - L^2 - S^2)
\tag{13.93}
$$

---

[1]A derivation can be found in, e.g., Jackson's *Electrodynamics*.

Now

$$[J^2, L^2] = [J^2, S^2] = 0 \tag{13.94}$$

since L^2 and S^2 commute with all the components of $\vec{J} = \vec{L} + \vec{S}$, and therefore

$$[H, J^2] = [H, L^2] = [H, S^2] = 0 \tag{13.95}$$

Recall that in solving for the eigenstates of H_0, we had to first find the eigenstates of L^2. For similar reasons, to find the eigenstates of H, we need first to find the eigenstates of J^2, L^2, and S^2. Finding the eigenstates of *total* angular momentum J^2, given the eigenstates

$$Y_{lm}\chi_{\pm} \tag{13.96}$$

of orbital (L^2, L_z) and spin (S^2, S_z) angular momentum is carried out by a systematic procedure known as the **Addition of Angular Momentum**, which is our next order of business.

Chapter 14

The Addition of Angular Momentum

"*Consider the lilies of the field, how they grow. They toil not, neither do they spin...*"
    The Book of Mathew

In the previous chapter we found that there was a contribution to the Hydrogen atom Hamiltonian proportional to the operator

$$L \cdot S = \frac{1}{2}(J^2 - L^2 - S^2) \tag{14.1}$$

In order to find eigenstates of $L \cdot S$, we need to find eigenstates of L^2, S^2, and the total angular momentum J^2. Now, first of all, the usual eigenstates of L^2, L_z, S^2, S_z that we wrote down in the last Lecture, namely

$$\varphi(r, \theta, \phi)\chi_+ = R_{nl}(r)Y_{lm}(\theta, \phi) \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \text{and} \quad \varphi(r, \theta, \phi)\chi_- = R_{nl}(r)Y_{lm}(\theta, \phi) \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{14.2}$$

are (mostly) *not* eigenstates of $L \cdot S$. This is because $L \cdot S = L_x S_x + L_y S_y + L_z S_z$, and while the wavefunctions above are eigenstates of L_z and S_z, they are (mostly) not eigenstates of L_x, L_y and S_x, S_y. Because these wavefunctions are not eigenstates of $L \cdot S$, they are not eigenstates of the total angular momentum J^2, either.

Defining $J_x = L_x + S_x$ etc., and using the fact that the orbital angular momentum operators commute with the spin angular momentum operators (they act on different degrees of freedom), its easy to see that the components of total angular momentum satisfy the now-familiar commutation relations

$$\begin{aligned} [J_x, J_y] &= i\hbar J_z \\ [J_y, J_z] &= i\hbar J_x \\ [J_z, J_x] &= i\hbar J_y \end{aligned} \tag{14.3}$$

So this means that $J_z = L_z + S_z$ must commute with J^2. What we want to do is to construct eigenstates of J^2, J_z, L^2, S^2, denoted $|jj_z ls >$, as linear combinations of the eigenstates of L^2, L_z, S^2, S_z denoted by $|lmss_z >$, whose corresponding eigenfunctions are shown in (14.2). In other words, we want to find the set of **Clebsch-Gordon coefficients** $C_{jj_z ls}^{lmss_z}$ such that

$$|jj_z ls >= \sum_{s_z, m=j_z-s_z} C_{jj_z ls}^{lmss_z} |lmss_z > \tag{14.4}$$

or, in wavefunction notation

$$\Phi_{jj_z} = \sum_{s_z, m=j_z-s_z} C_{jj_z ls}^{lmss_z} Y_{lm}\chi_{s_z} \tag{14.5}$$

(In the case of the Hydrogen atom, $s = \frac{1}{2}$. But the technique we are going to use will work for any value of s.)

The trick is to notice that one of the $|lmss_z >$ states, known as the **"highest weight state"**, is also an eigenstate of J^2. Suppose we ask which state is the eigenstate with the highest eigenvalue of J_z. Now $J_z = L_z + S_z$, and any eigenstate of L_z, S_z is also an eigenstate of J_z, although it is usually not an eigenstate of J^2. The eigenstate with the highest eigenvalue of J_z has to be the state with the highest eigenvalue of L_z and S_z, and there is only one such state

$$\text{"highest weight state"} = Y_{ll}\chi_+ \tag{14.6}$$

which has $j_z = l + \frac{1}{2}$. Now if the highest j_z is $l + \frac{1}{2}$, then this must also be the highest possible value of j that can be constructed from the $Y_{lm}\chi_{s_z}$. But there is only one state with $j_z = l + s$, so this must also be the eigenstate of the operator J^2 with $j = l + s$. So we conclude that

$$\Phi_{jj} = Y_{ll}\chi_+ \qquad (j = l + s) \tag{14.7}$$

(By exactly the same reasoning, there is also a lowest weight state

$$\Phi_{j,-j} = Y_{l,-l}\chi_- \qquad (j = l + s) \tag{14.8}$$

with $j_z = -(l + s)$.)

Exercise: Using

$$
\begin{aligned}
J^2 &= L^2 + S^2 + 2L \cdot S \\
J_z &= L_z + S_z
\end{aligned}
\tag{14.9}
$$

and expressing L_x, L_y, S_x, S_y in terms of ladder operators, show explicitly that the highest weight state is an eigenstate of J^2, i.e.

$$
\begin{aligned}
J^2 Y_{ll}\chi_+ &= j_{max}(j_{max} + 1)\hbar^2 Y_{ll}\chi_+ \quad \text{where} \quad j_{max} = l + \frac{1}{2} \\
J_z Y_{ll}\chi_+ &= j_{max}\hbar Y_{ll}\chi_+
\end{aligned}
\tag{14.10}
$$

From this one eigenstate of J^2 (the highest weight state), it is simple to construct all the other eigenstates of J^2 and J_z, by successively applying the ladder operator

$$J_- = L_- + S_- \tag{14.11}$$

and the relations

$$
\begin{aligned}
J_-|jj_z> &= \sqrt{j(j+1) - j_z(j_z - 1)}\hbar|j, j_z - 1 > \\
L_-|lm> &= \sqrt{l(l+1) - m(m-1)}\hbar|l, m - 1 > \\
S_-|ss_z> &= \sqrt{s(s+1) - s_z(s_z - 1)}\hbar|s, s_z - 1 >
\end{aligned}
\tag{14.12}
$$

To see how it works, lets pick a particular example to work out, with $l = 1$. In this case, the highest weight state is

$$\Phi_{\frac{3}{2}\frac{3}{2}} = Y_{11}\chi_+ \tag{14.13}$$

Now apply the J_- operator on both sides of this equation, and use eq. (14.12)

$$
\begin{aligned}
J_-\Phi_{\frac{3}{2}\frac{3}{2}} &= (L_- + S_-)Y_{11}\chi_+ \\
\hbar\sqrt{\frac{3}{2}(\frac{3}{2}+1) - \frac{3}{2}(\frac{3}{2}-1)}\Phi_{\frac{3}{2}\frac{1}{2}} &= (L_-Y_{11})\chi_+ + Y_{11}(S_-\chi_+) \\
\hbar\sqrt{3}\Phi_{\frac{3}{2}\frac{1}{2}} &= \hbar\left(\sqrt{1(1+1) - 0}Y_{10}\chi_+ + Y_{11}\cdot\sqrt{\frac{1}{2}(\frac{1}{2}+1) - \frac{1}{2}(\frac{1}{2}-1)}\chi_-\right) \\
&= \hbar\left(\sqrt{2}Y_{10}\chi_+ + Y_{11}\chi_-\right)
\end{aligned}
\tag{14.14}
$$

Dividing both sides by $\sqrt{3}\hbar$, we have found the eigenstate of J^2, J_z with $j = \frac{3}{2}$ and $j_z = \frac{1}{2}$

$$\Phi_{\frac{3}{2}\frac{1}{2}} = \sqrt{\frac{2}{3}}Y_{10}\chi_+ + \sqrt{\frac{1}{3}}Y_{11}\chi_- \tag{14.15}$$

To get the state with $j_z = -\frac{1}{2}$, we just apply J_- again, to both sides of (14.15)

$$
\begin{aligned}
J_-\Phi_{\frac{3}{2}\frac{1}{2}} &= (L_- + S_-)\left(\sqrt{\frac{2}{3}}Y_{10}\chi_+ + \sqrt{\frac{1}{3}}Y_{11}\chi_-\right) \\
\hbar\sqrt{\frac{3}{2}(\frac{3}{2}+1) - \frac{1}{2}(\frac{1}{2}-1)}\Phi_{\frac{3}{2}-\frac{1}{2}} &= \hbar\sqrt{\frac{1}{3}}\left(\sqrt{2}(L_-Y_{10})\chi_+ + (L_-Y_{11})\chi_- \right. \\
&\quad \left. +\sqrt{2}Y_{10}(S_-\chi_+) + Y_{11}(S_-\chi_-)\right) \\
2\hbar\Phi_{\frac{3}{2}-\frac{1}{2}} &= \hbar\sqrt{\frac{1}{3}}\left(2Y_{1-1}\chi_+ + \sqrt{2}Y_{10}\chi_- \right. \\
&\quad \left. +\sqrt{2}Y_{10}\chi_- + 0\right)
\end{aligned}
\tag{14.16}
$$

and we get

$$\Phi_{\frac{3}{2}-\frac{1}{2}} = \sqrt{\frac{2}{3}}Y_{10}\chi_- + \sqrt{\frac{1}{3}}Y_{1-1}\chi_+ \tag{14.17}$$

The remaining state with $j = \frac{3}{2}$ has to be the lowest weight state (14.8). But just as a check of the algebra, we obtain it by applying the ladder operator one more time

$$
\begin{aligned}
J_-\Phi_{\frac{3}{2}-\frac{1}{2}} &= (L_- + S_-)\left(\sqrt{\frac{2}{3}}Y_{10}\chi_- + \sqrt{\frac{1}{3}}Y_{1-1}\chi_+\right) \\
\hbar\sqrt{3}\Phi_{\frac{3}{2}-\frac{3}{2}} &= \hbar\sqrt{\frac{1}{3}}\left(\sqrt{2}(L_-Y_{10})\chi_- + (L_-Y_{1-1})\chi_+ + \sqrt{2}Y_{10}(S_-\chi_-) + Y_{1-1}(S_-\chi_+)\right) \\
&= \hbar\sqrt{\frac{1}{3}}\left(2Y_{1-1}\chi_- + 0 + 0 + Y_{1-1}\chi_-\right) \\
&= \hbar\sqrt{3}Y_{1-1}\chi_- \tag{14.18}
\end{aligned}
$$

and therefore

$$\Phi_{\frac{3}{2}-\frac{3}{2}} = Y_{1-1}\chi_- \tag{14.19}$$

as it should.

But is this all the eigenstates of J^2, J_z that we can form from the $l = 1$, $s = \frac{1}{2}$ states? So far we have constructed *four* orthonormal states

$$\{\Phi_{\frac{3}{2}j_z}, \ j_z = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}\} \tag{14.20}$$

which are eigenstates of J^2, J_z, out of *six* orthonormal states

$$
\begin{matrix}
Y_{11}\chi_+ & Y_{10}\chi_+ & Y_{1-1}\chi_+ \\
Y_{11}\chi_- & Y_{10}\chi_- & Y_{1-1}\chi_-
\end{matrix} \tag{14.21}
$$

So out of these six states, we ought to be able to build two more states which are orthogonal to the four $\{\Phi_{\frac{3}{2}j_z}\}$. Now these extra two states can't have $j = 3/2$, because we have already constructed all of those states, and they can't be $j > 3/2$, basically because a state with $j_z > \frac{3}{2}$ isn't available. So lets try to find states with $j = 1/2$. There are exactly two such states

$$\Phi_{\frac{1}{2}\frac{1}{2}} \quad \text{and} \quad \Phi_{\frac{1}{2}-\frac{1}{2}} \tag{14.22}$$

so this would bring the total to six. But how do we get them? The trick is to first find $\Phi_{\frac{1}{2}\frac{1}{2}}$ from the fact that it has to be orthogonal to $\Phi_{\frac{3}{2}\frac{1}{2}}$, and also normalized. Then we can use the ladder operator to get the other state.

We begin from the fact that $\Phi_{\frac{1}{2}\frac{1}{2}}$ is an eigenstate of J_z, with $j_z = \frac{1}{2}$. There are two states in the set of six (14.21) which have this value of j_z, namely

$$Y_{11}\chi_- \quad \text{and} \quad Y_{10}\chi_+ \tag{14.23}$$

but these are not eigenstates of J^2. So we look for a linear combination

$$\Phi_{\frac{1}{2}\frac{1}{2}} = aY_{11}\chi_- + bY_{10}\chi_+ \tag{14.24}$$

which has the orthonormality properties

$$
\begin{aligned}
< \Phi_{\frac{3}{2}\frac{1}{2}}|\Phi_{\frac{1}{2}\frac{1}{2}} > &= 0 \\
< \Phi_{\frac{1}{2}\frac{1}{2}}|\Phi_{\frac{1}{2}\frac{1}{2}} > &= 1
\end{aligned}
\tag{14.25}
$$

Substituting (14.15) and (14.24) into the first equation or (14.25)

$$
\begin{aligned}
0 &= \left[\sqrt{\frac{1}{3}} < Y_{11}\chi_-| + \sqrt{\frac{2}{3}} < Y_{10}\chi_+|\right] [a|Y_{11}\chi_- > +b|Y_{10}\chi_+ >] \\
&= \sqrt{\frac{1}{3}}[a + \sqrt{2}b]
\end{aligned}
\tag{14.26}
$$

Therefore

$$\Phi_{\frac{1}{2}\frac{1}{2}} = a\left[Y_{11}\chi_- - \sqrt{\frac{1}{2}}Y_{10}\chi_+\right] \tag{14.27}$$

Impose the normalization condition on this state

$$
\begin{aligned}
1 &= a^2\left[< Y_{11}\chi_-| - \sqrt{\frac{1}{2}} < Y_{10}\chi_+|\right]\left[|Y_{11}\chi_- > -\sqrt{\frac{1}{2}}|Y_{10}\chi_+ >\right] \\
&= a^2(1 + \frac{1}{2}) \quad \Rightarrow \quad a = \sqrt{\frac{2}{3}}
\end{aligned}
\tag{14.28}
$$

So

$$\Phi_{\frac{1}{2}\frac{1}{2}} = \sqrt{\frac{2}{3}}Y_{11}\chi_- - \sqrt{\frac{1}{3}}Y_{10}\chi_+ \tag{14.29}$$

The last thing to do is to apply the ladder operator to both sides of this equation to get the last of the six states

$$
\begin{aligned}
J_-\Phi_{\frac{1}{2}\frac{1}{2}} &= (L_- + S_-)\left(\sqrt{\frac{2}{3}}Y_{11}\chi_- - \sqrt{\frac{1}{3}}Y_{10}\chi_+\right) \\
\hbar\Phi_{\frac{1}{2}-\frac{1}{2}} &= \sqrt{\frac{2}{3}}(L_-Y_{11}\chi_- - \sqrt{\frac{1}{3}}(L_-Y_{10})\chi_+ + \sqrt{\frac{2}{3}}Y_{11}(S_-\chi_-) - \sqrt{\frac{1}{3}}Y_{10}(S_-\chi_+) \\
&= \frac{\hbar}{\sqrt{3}}\left[2Y_{10}\chi_- \sqrt{2}Y_{1-1}\chi_+ + 0 - Y_{10}\chi_-\right]
\end{aligned}
\tag{14.30}
$$

and finally

$$\Phi_{\frac{1}{2}-\frac{1}{2}} = \sqrt{\frac{1}{3}}Y_{10}\chi_- - \sqrt{\frac{2}{3}}Y_{1-1}\chi_+ \tag{14.31}$$

The set of all six eigenstates of J^2, J_z that can be formed from the six states $Y_{1m}\chi_\pm$, together with the operation used to construct each, are displayed in Fig. [14.1]. But there is nothing special about $l = 1$, of course, and the procedure shown above works for arbitrary l, as shown in Fig. [14-2]. Note that, since $-l \le m \le l$ there are $(2l + 1)$ value for m, and 2 possible values of $s_z = \pm\frac{1}{2}$. This means there are $2(2l + 1)$ orthogonal $Y_{lm}\chi_\pm$ states for each fixed $l, s = \frac{1}{2}$. From these, one constructs a set of eigenstates of J^2 with $j_{max} = l + \frac{1}{2}$, and $j_{min} = l - \frac{1}{2}$. The total number of J^2 eigenstates is the same as the number of $Y_{lm}\chi_\pm$ states , i.e.

$$
\begin{aligned}
N &= (2j_{max} + 1) + (2j_{min} + 1) \\
&= (2(l + \frac{1}{2}) + 1) + (2(l - \frac{1}{2}) + 1) \\
&= 2(2l + 1)
\end{aligned} \tag{14.32}
$$

Now lets go back to the Hydrogen atom. Let H_0 be the Hydrogen atom Hamiltonian without the spin-orbit contribution, i.e.

$$
H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} \tag{14.33}
$$

Including electron spin, the eigenstates of H_0, L^2, L_z, S^2, S_z are the set of states

$$
\begin{aligned}
\{|nlmss_z>\} &\Leftrightarrow \{R_{nl}(r)Y_{lm}(\theta, \phi)\chi_{s_z}, \quad n = 1, 2, ...; \quad l = 0, 1.., n - 1; \\
&m = -l, ..., l, \quad s_z = \frac{1}{2}, -\frac{1}{2}\}
\end{aligned} \tag{14.34}
$$

What has been done in this chapter is to show how to construct eigenstates of H_0, J^2, J_z, L^2, S^2

$$
\begin{aligned}
\{|njj_zls>\} &\Leftrightarrow \{R_{nl}(r)\Phi_{jj_z}, \quad n = 1, 2, ...; \quad l = 0, 1, .., n - 1, \\
&j = l + \frac{1}{2}, l - \frac{1}{2}; \quad j_z = -j, ..., j\}
\end{aligned} \tag{14.35}
$$

Now, taking into account the spin-orbit term, the Hamiltonian of the Hydrogen atom is really

$$
H = H_0 + H' \tag{14.36}
$$

where

$$
H' = \frac{e^2}{4M^2c^2}\frac{1}{r^3}(J^2 - L^2 - S^2) \tag{14.37}
$$

Since H still commutes with L^2, S^2, J^2, J_z, the eigenfunctions of H will still have the form

$$
R'_{nlj}(r)\Phi_{jj_z} \tag{14.38}
$$

but now $R'(r)$ will be a little different from $R_{nl}(r)$, and also the new energy eigenvalues E'_{njl} will be a little different from the Bohr energies E_n. Since spin-orbit coupling is

a small effect, there is a powerful method known as time-independent perturbation theory which allows one to "sneak up" on the eigenstates and eigenvalues of H, given the eigenstates and eigenvalues of H_0. This method will be presented in all its glory in Lecture 17, but let us borrow, ahead of time, one of the results, which is that, if $|njj_zls>$ is an eigenstate of H_0, the energy eigenvalue of H is approximately

$$E'_{njj_zls} \approx E_n + <njj_zls|H'|njj_zls> \tag{14.39}$$

Then the spin-orbit coupling introduces a correction to the atomic energies which can be calculated:

$$
\begin{aligned}
\Delta E &= <njj_zls|H'|njjzls> \\
&= \frac{e^2}{4M^2c^2} \int dr\ r^2 R_{nl}(r) \frac{1}{r^3} R_{nl}(r) < \Phi_{jj_z}|(J^2 - L^2 - S^2)|\Phi_{jj_z}> \\
&= \frac{e^2}{4M^2c^2} \int dr\ r^2 R_{nl}(r) \frac{1}{r^3} R_{nl}(r) \times [j(j+1) - l(l+1) - \frac{1}{2}(\frac{1}{2}+1)]\hbar^2 \\
&= [j(j+1) - l(l+1) - \frac{1}{2}(\frac{1}{2}+1)]\hbar^2 \frac{e^2}{M^2c^2a_0^3n^3l(l+1)(2l+1)} \tag{14.40}
\end{aligned}
$$

where a_0 is the Bohr radius. For a given l, we have seen that the j quantum number can have one of two values, $j = l + \frac{1}{2}$ or $j = l - \frac{1}{2}$, in which case

$$j(j+1) - l(l+1) - \frac{3}{4} = \begin{cases} l & \text{for}\ \ j = l + \frac{1}{2} \\ -(l+1) & \text{for}\ \ j = l - \frac{1}{2} \end{cases} \tag{14.41}$$

Using also the expression for the Bohr energy

$$E_n = -\frac{Me^4}{2\hbar^2n^2} \tag{14.42}$$

and defining the "**Fine Structure Constant**"

$$\alpha \equiv \frac{e^2}{\hbar c} \approx \frac{1}{137} \tag{14.43}$$

the final result for the energies E' of atomic orbits is

$$
\begin{aligned}
E'_{n,j=l+\frac{1}{2}} &= E_n + \frac{1}{(2l+1)(l+1)}|E_n|\frac{\alpha^2}{n} \\
E'_{n,j=l-\frac{1}{2}} &= E_n - \frac{1}{(2l+1)l}|E_n|\frac{\alpha^2}{n} \tag{14.44}
\end{aligned}
$$

The fact that the electron energy levels now depend (slightly) on l and $j = l \pm \frac{1}{2}$, in addition to the principal quantum number n, causes a small splitting of the atomic spectral lines associated with transitions between the various electron states. The

splitting is very small; we can see that the correction to atomic energies is on the order of the square of the fine structure constant, α^2, which is less than one part in $10,000$.

At this point, you may feel a little let down. Did we go to all the trouble of learning how to add angular momenta, just to compute a tiny, arcane splitting of hydrogen atom spectral lines? The answer, of course, is no. The technique for adding angular momentum is one of the most important tools there is in atomic, molecular, nuclear, particle, and condensed matter physics, and the reason is simple: Things are made of other things, and those other things spin. Atoms, for example, consist of electrons and a nucleus. Like the electron, atomic nuclei also spin. So the possible spin angular momenta of a given atom is determined by adding the total angular momentum of the electron ($J = L + S$) to the spin angular momentum of the nucleus. Nuclei are made of protons and neutrons, each of which have spin $\frac{1}{2}$. The energy levels of nuclei depend on the total spin of the nuclei, and this requires adding the spins of the protons and neutrons, together with their orbital angular momentum in the nucleus. Likewise, protons and neutrons (and many other short-lived particles) are composed of three quarks. Each quark has spin $\frac{1}{2}$. To determine which combination of three quarks would give spin $\frac{1}{2}$ protons and neutrons, and which would lead to higher spin objects like hyperons, its necessary to be able to add the spin angular momenta of the quarks. In short, its important to learn how to add angular momentum, because all physical objects are composed of spinning particles. Viewed at the atomic level *everything* spins, including the lilies of the field.

14.1　The General Method

Consider a composite system consisting of two subsystems, and suppose each subsystem has a certain angular momentum. It could be that the system is an atom, one subsystem is all the electrons, and the other subsystem is the nucleus. Or perhaps the system is a deuterium nucleus, consisting of one proton, or one neutron. Or maybe the system is a pi meson, consisting of one quark, and one antiquark. Depending on the particular case, the angular momentum of each subsystem might be the orbital angular momentum of the subsystem, the spin of the subsystem, or maybe the total (spin plus orbital) angular momentum of the subsystem. The point is, adding angular momentum is an algebraic technique, and it really doesn't matter whether we are adding spin to spin, orbital to orbital, orbital to spin, etc. We will just denote the angular momentum of one system by J_1, and the angular momentum of the other system by J_2, with the understanding that these can be any type of angular momentum.

It is assumed that we know the eigenstates of $J_1^2, J_{1z}, J_2^2, J_{2z}$, which we denote

$$\{\psi^1_{j_1 m_1} \psi^2_{j_2 m_2}\} \tag{14.45}$$

or, in ket notation

$$\{|j_1, m_1, j_2, m_2 >\} \tag{14.46}$$

with eigenvalues

$$
\begin{aligned}
J_1^2 \psi_{j_1 m_1}^1 \psi_{j_2 m_2}^2 &= j_1(j_1 + 1)\hbar^2 \psi_{j_1 m_1}^1 \psi_{j_2 m_2}^2 \\
J_{1z} \psi_{j_1 m_1}^1 \psi_{j_2 m_2}^2 &= m_1 \hbar \psi_{j_1 m_1}^1 \psi_{j_2 m_2}^2 \\
J_2^2 \psi_{j_1 m_1}^1 \psi_{j_2 m_2}^2 &= j_2(j_2 + 1)\hbar^2 \psi_{j_1 m_1}^1 \psi_{j_2 m_2}^2 \\
J_{2z} \psi_{j_1 m_1}^1 \psi_{j_2 m_2}^2 &= m_2 \hbar \psi_{j_1 m_1}^1 \psi_{j_2 m_2}^2
\end{aligned}
\tag{14.47}
$$

If, for example, J_1 and J_2 were both orbital angular momenta, then

$$\psi_{j_1 m_1}^1 \psi_{j_2 m_2}^2 = Y_{j_1 m_1}(\theta_1, \phi_1) Y_{j_2 m_2}(\theta_2, \phi_2) \tag{14.48}$$

Denote the sum of the two angular momenta by

$$\vec{J} = \vec{J_1} + \vec{J_2} \tag{14.49}$$

Given the eigenstates of $J_1^2, J_{1z}, J_2^2, J_{2z}$, we want to find the eigenstates of Φ_{jm} of the total angular momentum J^2, J_z, J_1^2, J_2^2.

Once again, the idea is to start from the highest-weight state, namely

$$\Phi_{jj} = \phi_{j_1 j_1}^1 \phi_{j_2 j_2}^2 \qquad (j = j_1 + j_2) \tag{14.50}$$

and get all the other states with $j = j_1 + j_2$ by applying the ladder operators. Then we construct states with the next lowest value of angular momentum, $j = j_1 + j_2 - 1$, and then states with $j = j_1 + j_2 - 2$, and so on. The first question is: where does this procedure end? If $j = j_1 + j_2$ is the highest possible value of total angular momentum, what is the lowest possible value?

This question can be answered by counting states. For a given j_1 and j_2 there are a total of $2j_1 + 1$ possible values of m_1, and $2j_2 + 1$ possible values of m_2, so the total number of orthonormal states $\psi_{j_1 m_1}^1 \psi_{j_2 m_2}^2$ is

$$N = (2j_1 + 1)(2j_2 + 1) \tag{14.51}$$

Denote by j_{min} the lowest possible value of total angular momentum that can be constructed from states of given j_1 and j_2. Then the total number of eigenstates of total angular momentum will be

$$N' = \sum_{j=j_{min}}^{j_1+j_2} (2j + 1) \tag{14.52}$$

and j_{min} is determined from the requiring $N = N'$. The solution to this condition is that

$$j_{min} = |j_1 - j_2| \tag{14.53}$$

which we now quickly verify. Suppose, e.g., that $j_1 > j_2$, so that $j_{min} = j_1 - j_2$. Then

$$
\begin{aligned}
N' &= \sum_{j=j_1-j_2}^{j_1+j_2} (2j+1) \\
&= \sum_{j=1}^{j_1+j_2} (2j+1) - \sum_{j=1}^{j_1-j_2-1} (2j+1) \\
&= 2\sum_{j=1}^{j_1+j_2} j - 2\sum_{j=1}^{j_1-j_2-1} j + (2j_2+1) \tag{14.54}
\end{aligned}
$$

and using the fact that

$$
\sum_{l=1}^{L} l = \frac{L(L+1)}{2} \tag{14.55}
$$

we find

$$
\begin{aligned}
N' &= (j_1+j_2)(j_1+j_2+1) - (j_1-j_2)(j_1-j_2-1) + (2j_2+1) \\
&= (2j_1+1)(2j_2+1) \\
&= N \tag{14.56}
\end{aligned}
$$

The procedure for finding all the states is shown in Fig. [14.3]. Starting from the highest weight state, eq. (14.50), we apply J_- to the left-hand side and $J_{1-} + J_{2-}$ to the right-hand side to get $\Phi_{j,j-1}$. Proceeding in this way, one finds all the states with $j_{max} = j_1 + j_2$. Next, the state with $j = m = j_{max} - 1$ must have the form

$$
\Phi_{j_{max}-1,j_{max}-1} = a\phi^1_{j_1 j_1}\phi^2_{j_2,j_2-1} + b\phi^1_{j_1,j_1-1}\phi^2_{j_2,j_2} \tag{14.57}
$$

because these are the only states with $j_z = j_{max} - 1$. The two constants a and b are determined by orthogonality

$$
< \Phi_{j_{max},j_{max}-1}|\Phi_{j_{max}-1,j_{max}-1} >= 0 \tag{14.58}
$$

and normalization

$$
< \Phi_{j_{max}-1,j_{max}-1}|\Phi_{j_{max}-1,j_{max}-1} >= 1 \tag{14.59}
$$

Having determined a and b, apply J_- to the left hand side, and $J_{1-} + J_{2-}$ to the right hand side, to find $\Phi_{j_{max}-1,j_{max}-2}$, and continue applying the ladder operator successively to find all states with $j_{max} - 1$. Then determine the three constants a, b, c in the state

$$
\Phi_{j_{max}-2,j_{max}-2} = a\phi^1_{j_1 j_1}\phi^2_{j_2,j_2-2} + b\phi^1_{j_1,j_1-1}\phi^2_{j_2,j_2-1} + c\phi^1_{j_1 j_1-2}\phi^2_{j_2,j_2} \tag{14.60}
$$

from the two orthogonality conditions

$$
\begin{aligned}
< \Phi_{j_{max},j_{max}-2}|\Phi_{j_{max}-2,j_{max}-2} > &= 0 \\
< \Phi_{j_{max}-1,j_{max}-2}|\Phi_{j_{max}-2,j_{max}-2} > &= 0 \tag{14.61}
\end{aligned}
$$

and the normalization condition

$$< \Phi_{j_{max}-2,j_{max}-2} | \Phi_{j_{max}-2,j_{max}-2} >= 1 \tag{14.62}$$

Ladder operators are applied again, and the whole procedure is continued until all of the states with total angular momentum $j = |j_1 - j_2|$ have been found. At that point, stop.

An important application of this procedure is the addition of the spin angular momentum of two spin $\frac{1}{2}$ particles; a case that turns up again and again in atomic, nuclear, and particle physics. In this case, there are four eigenstates of $S_1^2, S_{1z}, S_2^2, S_{2z}$, denoted

$$\chi_\pm^1 \chi_\pm^2 \tag{14.63}$$

We want to find all possible eigenstates of S^2, S_z, S_1^2, S_2^2. In this case

$$s_{max} = \frac{1}{2} + \frac{1}{2} = 1 \qquad s_{min} = |\frac{1}{2} - \frac{1}{2}| = 0 \tag{14.64}$$

The highest weight state is

$$\Phi_{11} = \chi_+^1 \chi_+^2 \tag{14.65}$$

Applying the ladder operators

$$
\begin{aligned}
S_- \Phi_{11} &= (S_{1-} + S_{2-}) \chi_+^1 \chi_+^2 \\
\sqrt{2}\hbar \Phi_{10} &= (S_{1-}\chi_+^1)\chi_+^2 + \chi_+^1 (S_{2-}\chi_+^2) \\
&= \hbar [\chi_-^1 \chi_+^2 + \chi_+^1 \chi_2^+]
\end{aligned}
\tag{14.66}
$$

to find

$$\Phi_{10} = \frac{1}{\sqrt{2}} [\chi_+^1 \chi_-^2 + \chi_-^1 \chi_+^2] \tag{14.67}$$

Again apply the ladder operators

$$
\begin{aligned}
S_- \Phi_{10} &= \frac{1}{\sqrt{2}} (S_{1-} + S_{2-})[\chi_+^1 \chi_-^2 + \chi_-^1 \chi_+^2] \\
\hbar\sqrt{2}\Phi_{1-1} &= \frac{1}{\sqrt{2}} [(S_{1-}\chi_+^1)\chi_-^2 + (S_{1-}\chi_-^1)\chi_+^2 + \chi_+^1 (S_{2-}\chi_-^2) + \chi_-^1 (S_{2-}\chi_+^2)] \\
&= \frac{\hbar}{\sqrt{2}} [\chi_-^1 \chi_-^2 + 0 + 0 + \chi_-^1 \chi_-^2]
\end{aligned}
\tag{14.68}
$$

which gives, as it should, the lowest weight state

$$\Phi_{1-1} = \chi_-^1 \chi_-^2 \tag{14.69}$$

There are three states with $j = 1$, which are known as the **triplet spin states**. The one remaining state at $j = 0$ is known, for obvious reasons, as the **singlet spin state**. The singlet state

$$\Phi_{00} = a\chi_+^1 \chi_-^2 + b\chi_-^1 \chi_+^2 \tag{14.70}$$

is determined by the orthogonality and normalization conditions

$$
\begin{aligned}
< \Phi_{10}|\Phi_{00} > &= 0 \\
< \Phi_{00}|\Phi_{00} > &= 1
\end{aligned}
\tag{14.71}
$$

From the orthogonality condition

$$
\begin{aligned}
0 &= \frac{1}{\sqrt{2}}[< \chi_+^1\chi_-^2|+ < \chi_-^1\chi_+^2|][a|\chi_+^1\chi_-^2 > +b|\chi_-^1\chi_+^2 >] \\
&= \frac{1}{\sqrt{2}}(a+b)
\end{aligned}
\tag{14.72}
$$

which tells us that $b = -a$. Substituting into the normalization condition

$$
\begin{aligned}
1 &= a^2[< \chi_+^1\chi_-^2|- < \chi_-^1\chi_+^2|][|\chi_+^1\chi_-^2 > -|\chi_-^1\chi_+^2 >] \\
&= 2a^2 \quad \Leftarrow \quad a = \frac{1}{\sqrt{2}}
\end{aligned}
\tag{14.73}
$$

we find that the spin singlet state is

$$
\Phi_{00} = \frac{1}{\sqrt{2}}[\chi_+^1\chi_-^2 - \chi_-^1\chi_+^2]
\tag{14.74}
$$

The triplet and singlet states, and procedure for finding them, is shown in Fig. [14.4].

One of the many applications of addition of spin $\frac{1}{2}$ angular momentum is to the so-called "hyperfine splitting" of the hydrogen atom ground state; this has important consequences for (of all things!) radio astronomy. Now the ground state of the hydrogen atom has zero orbital angular momentum, so there is no $L \cdot S$ splitting of the energy level. However, the proton, like the electron, is a spin $\frac{1}{2}$ particle, and, like the electron, it has a certain magnetic moment

$$
\mu_p = \frac{g_p e}{2m_p} S_p
\tag{14.75}
$$

where, experimentally, $g_p = 5.59$. For the electron, the corresponding "g-factor" is very close to $g_e = 2$, and the electron magnetic moment is

$$
\mu_e = -\frac{e}{m_e} S_e
\tag{14.76}
$$

Now, according to classical electrodynamics, the magnetic field due to a magnetic dipole at position $\vec{r}$ is given by

$$
\vec{B} = \frac{\mu_0}{4\pi r^3}[3(\vec{\mu} \cdot \vec{e}_r)\vec{e}_r - \vec{\mu}] + \frac{2\mu_0}{3}\vec{\mu}\delta^3(r)
\tag{14.77}
$$

So the contribution to the Hamiltonian for the electron, due to the interaction of the electron magnetic dipole moment with the magnetic field due to the proton dipole moment is

$$H' = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \frac{3(S_p \cdot e_r)(S_e \cdot e_r) - S_p \cdot S_e}{r^3} + \frac{\mu_0 g_p e^2}{3 m_p m_e} S_p \cdot S_e \delta^3(r) \qquad (14.78)$$

The S_p operators in H' act on the spin degrees of freedom of the proton. Therefore we have to enlarge, a little bit, our expression for the hyrogen wavefunction, to include these extra quantized degrees of freedom. The ground state wavefunction(s), which are eigenstates of $H_0, S_e^2, S_{ez}, S_p^2, S_{pz}$, are the four states

$$R_{n0}(r) Y_{00}(\theta, \phi) \chi_\pm^e \chi_\pm^p \qquad (14.79)$$

where $\chi_\pm^e$ refers to the spin state of the electron, and $\chi_\pm^p$ refers to the spin state of the proton. We can also, following the procedure above, reorganize these four states into four other states, which are eigenstates of $H_0, S^2, S_z, S_e^2, S_p^2$, where $\vec{S} = \vec{S}_e + \vec{S}_p$, i.e.

$$\psi_{s=1,s_z}^{triplet} = R_{n0}(r) Y_{00}(\theta, \phi) \begin{cases} \chi_+^e \chi_+^p & (s_z = 1) \\ \frac{1}{\sqrt{2}}(\chi_+^e \chi_-^p + \chi_-^e \chi_+^p) & (s_z = 0) \\ \chi_-^e \chi_-^p & (s_z = -1) \end{cases}$$

$$\psi_{s=0,s_z=0}^{singlet} = R_{n0}(r) Y_{00}(\theta, \phi) \frac{1}{\sqrt{2}}(\chi_+^e \chi_-^p - \chi_-^e \chi_+^p) \qquad (14.80)$$

Then, once again making use of a result (to be shown) from first order perturbation theory

$$\begin{aligned} \Delta E_{1s_z}^{triplet} &= <\psi_{ss_z}^{triplet}|H'|\psi_{ss_z}^{triplet}> \\ \Delta E^{singlet} &= <\psi^{singlet}|H'|\psi^{singlet}> \end{aligned} \qquad (14.81)$$

The expectation values above involve an integration over angles θ, ϕ. The Y_{00} spherical harmonic has no angular dependence, but the first term in H' does have such dependence. When the integral over solid angle is carried out, the first term in H' averages to zero. The integration over r, θ, ϕ for the second term is very easily carried out, since it involves a delta function, and we find

$$\begin{aligned} \Delta E &= \frac{\mu_0 g_p e^2}{3 m_e m_p} <\psi|\delta^3(r) S_p \cdot S_e|\psi> \\ &= \frac{\mu_0 g_p e^2}{3 m_e m_p} <\psi|\delta^3(r) \frac{1}{2}(S^2 - S_p^2 - S_e^2)|\psi> \\ &= \frac{\mu_0 g_p e^2}{3 m_e m_p} \frac{1}{2} \hbar^2 [s(s+1) - \frac{3}{4} - \frac{3}{4}) <\psi|\delta^3(r)|\psi> \\ &= \frac{\mu_0 g_p e^2 \hbar^2}{3 m_e m_p} |\psi(r=0)|^2 \frac{1}{2}[s(s+1) - \frac{3}{2}] \end{aligned} \qquad (14.82)$$

Then, using the fact that for the Hydrogen atom ground state

$$|\psi(r=0)|^2 = \frac{1}{\pi a_0^3} \tag{14.83}$$

with Bohr radius $a_0 = \hbar^2/me^2$, we get

$$\Delta E = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a_0^4} \begin{cases} \frac{1}{4} & (triplet) \\ -\frac{3}{4} & (singlet) \end{cases} \tag{14.84}$$

It is then possible for the electron-proton system to make a transition from the higher energy triplet state, to the lower energy singlet state, emitting a photon, whose energy is the difference in energies between the triplet/singlet states. According to De Broglie relation, the frequency of this emitted photon will be

$$\begin{aligned} f &= \frac{\Delta E_{triplet} - \Delta E_{singlet}}{h} \\ &= \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 a^4 h} \\ &= 1420 \text{ MHz} \end{aligned} \tag{14.85}$$

with a corresponding wavelength of 21 cm.

Atomic hydrogen is the most common element found in interstellar space, and transitions back and forth between the triplet and singlet states (separated by only about 6 millionths of an electron volt), occur very easily. For that reason, the 21 cm spectral line due to transitions between the hydrogen triplet and singlet states, is one of the most dominant features of the interstellar radio spectrum.

Chapter 15

Identical Particles

I wouldn't belong to any club that would have ME as a member!
- Groucho Marx

   In ordinary experience, no two objects are *exactly* identical. "Identical" twins are similar, rather than identical; "identical" ping-pong balls can be always be distinguished (at least under a microscope) by some small difference in size, shape or surface markings.

   It's different with elementary particles. As far as we can tell, there are no scratches, marks, or personality traits that would distinguish one electron from another electron, or one proton from another. When we speak of identical particles in quantum physics, we mean the particles are *identical*, not just very very similar. The fact that there are objects in the world which seem to be exactly identical leads to a very interesting (almost metaphysical!) question of principle regarding physical states.

   To start out, imagine that we have two identical spin-0 particles. The position of one particle is denoted by x_1, and that of the other particle by x_2. Consider the state where particle 1 is at the point a, and particle 2 is at the point b, so the state would be [1]

$$\psi(x_1, x_2) = \delta(x_1 - a)\delta(x_2 - b) \tag{15.1}$$

Now suppose someone comes along and interchanges the two particles (Fig. [15.1]). The particles would then be in a different physical state

$$\begin{aligned} \psi'(x_1, x_2) &= \delta(x_1 - b)\delta(x_2 - a) \\ &= \psi(x_2, x_1) \end{aligned} \tag{15.2}$$

However...if the particles are *exactly* identical, then there is no way of ever distinguishing between the states $\psi(x_1, x_2)$, and $\psi'(x_1, x_2)$. A measurement could only determine

---

[1]Strictly speaking, a delta function is not a physical state, because it isn't normalized to one. So, to be more rigorous, just replace the delta functions by gaussians which are narrowly peaked around points a and b. This doesn't affect the argument at all.

that one particle was found at point a, and one particle was found at point b. The particles themselves don't carry labels telling which is particle 1, and which is particle 2. But if there are different physical states which are experimentally indistiguishable, then the difference between them amounts to a kind of "hidden" information, which is not accessible to human knowledge.

Now, there is really no obvious reason, a priori, that wavefunctions *can't* carry hidden information. Perhaps this information is really there, but only accessible to the Lord and His Angels. In a similar vein, the example of the Heisenberg microscope in Lecture 2 suggested that there is no experimental way to measure position and momentum simultaneously to arbitrary precision. That doesn't logically imply that a particle *can't* have a definite position and momentum, at any given time, but we found in fact that there are no physical states with this property. Therefore, let us tentatively take the point of view that physical states do not contain any experimentally inaccessible information, and see where it leads. We have two particles, with particle 1 at position x_1 and particle 2 at position x_2. Now interchange the particles, as in Fig. [15.1], moving particle 2 to position x_1, and particle 1 to position x_2. Mathematically, this means relabeling $x_1 \rightarrow x_2$ and $x_2 \rightarrow x_1$; i.e. it is an interchange of particle coordinates. Quantum mechanically, if the two-particle state is denoted $\psi(x_1, x_2)$, the interchange of coordinates brings us to a new state which depends on the variables x_1 and x_2 in a different way, namely

$$\psi'(x_1, x_2) = \psi(x_2, x_1) \tag{15.3}$$

which is experimentally indistinguishable from the old state. Now we will make the following

Interchange Hypothesis:

Interchanging the positions of two identical particles does not change the physical state.

This hypothesis imposes a very strong constraint on physical states. Its interesting to first see what it would imply in classical physics. The classical state of a system of two identical particles, according to the discussion in the first chapter, is given by a point in the 12-dimensional phase space

$$\{\vec{x}_1, \vec{p}_1, \vec{x}_2, \vec{p}_2\} \tag{15.4}$$

In classical physics, an interchange should involve interchanging the position *and* momentum of each particle. Such an interchange would lead, in general, to a different (although experimentally indistinguishable) point in phase space

$$\{\vec{x}_2, \vec{p}_2, \vec{x}_1, \vec{p}_1\} \tag{15.5}$$

The only physical states which are left unchanged by an interchange of coordinates and momenta, would be those special points in phase space for which

$$\vec{x}_1 = \vec{x}_2 \qquad \vec{p}_1 = \vec{p}_2 \tag{15.6}$$

This constraint would imply, e.g., that all electrons in the universe are located at the same point, and are moving with the same velocity!

Clearly, the Interchange Hypothesis is too much to ask of classical physics. Quantum physics, however, is a little more tolerant, due the superposition principle. Although neither state (15.1) nor state (15.2) satisfies the Interchange hypothesis, a superposition of the two states

$$\Psi_S(x_1, x_2) = \delta(x_1 - a)\delta(x_2 - b) + \delta(x_1 - b)\delta(x_2 - a) \tag{15.7}$$

clearly does (the "S" stand for "symmetric"). Unlike the classical states satisfying the Interchange Hypthesis, the quantum state $\Psi_S(x_1, x_2)$ allows one to find two identical particles at two different places, while being symmetric in the positions x_1 and x_2.

However, there is one other state that be constructed from states (15.1) and (15.2) which *also* satisfies the Interchange Hypothesis, namely

$$\Psi_A(x_1, x_2) = \delta(x_1 - a)\delta(x_2 - b) - \delta(x_1 - b)\delta(x_2 - a) \tag{15.8}$$

(the "A" stands for "antisymmetric"). In this case, the change in coordinates gives a change in sign

$$\Psi_A(x_2, x_1) = -\Psi_A(x_1, x_2) \tag{15.9}$$

It is important to understand, at this point, that two wavefunctions that differ only by an overall sign, or in general, two wavefunctions that differ only by an overall phase, i.e.

$$\psi \quad \text{and} \quad e^{i\delta}\psi \tag{15.10}$$

correspond to the same physical state, because the constant $e^{i\delta}$ factor drops out of all expectation values and probabilities. In particular, Ψ_A and $-\Psi_A$ correspond to the same physical state. So in general, we are looking for 2-particle wavefunctions which satisfy

$$\psi(x_2, x_1) = e^{i\delta}\psi(x_1, x_2) \tag{15.11}$$

What possible values can there be, in eq. (15.11), for the phase $e^{i\delta}$?

Lets define an **exchange operator** that operates on wavefunctions by interchanging the coordinates, and, if the particle has spin, also the spin indices, i.e.

$$P_E\psi(z_1, z_2) = \psi(z_2, z_1) \tag{15.12}$$

where

$$z_i \equiv \{\vec{x}_i, s_{iz}\} \tag{15.13}$$

and s_z is the spin index, if the particles have an intrinisic spin. Then the states satisfying the Interchange Hypothesis would satisfy

$$P_E \psi(z_1, z_2) = e^{i\delta} \psi(z_1, z_2) \tag{15.14}$$

Its easy to see that P_E is an Hermitian operator (why?), and eq. (15.14) is an eigenvalue equation. Then, by same logic we used to deduce the eigenstates of parity, we apply eq. (15.12) twice to get

$$\begin{aligned} P_E P_E \psi(z_1, z_2) &= P_E \psi(z_2, z_1) \\ &= \psi(z_1, z_2) \end{aligned} \tag{15.15}$$

Then apply eq. (15.14) twice, to find

$$\begin{aligned} P_E P_E \psi(z_1, z_2) &= \epsilon^{i\delta} P_E \psi(z_1, z_2) \\ &= \left(\epsilon^{i\delta}\right)^2 \psi(z_1, z_2) \end{aligned} \tag{15.16}$$

Comparing (15.15) and (15.16), we deduce that the only possible eigenvalues are

$$e^{i\delta} = \pm 1 \tag{15.17}$$

Therefore, the only 2-particle physical states which satisfy the Interchange Hypothesis are the **symmetric states** $\psi_S(z_1, z_2)$, with the property

$$\psi_S(z_1, z_2) = +\psi(z_2, z_1) \tag{15.18}$$

and the **antisymmetric states** $\psi_A(z_1, z_2)$

$$\psi_A(z_1, z_2) = -\psi_A(z_2, z_1) \tag{15.19}$$

All of this easily generalizes to systems containing any number of identical particles. Suppose there are N such particles, and the corresponding wavefunction is denoted $\psi(z_1, z_2, ..., z_N)$. Denote by P_E^{ij} the operator which exchanges the i-th position and spin with the j-th position and spin, i.e.

$$P_E^{ij} \psi(z_1, z_2, .., z_i, .., z_j, ..., z_N) = \psi(z_1, z_2, .., z_j, .., z_i, ..., z_N) \tag{15.20}$$

Then the states which are allowed by the Interchange hypothesis are the symmetric states, satisfying

$$\psi_S(z_1, z_2, .., z_i, .., z_j, ..., z_N) = +\psi_S(z_1, z_2, .., z_j, .., z_i, ..., z_N) \tag{15.21}$$

and the antisymmetric states, satisfying

$$\psi_A(z_1, z_2, .., z_i, .., z_j, ..., z_N) = -\psi_A(z_1, z_2, .., z_j, .., z_i, ..., z_N) \tag{15.22}$$

for any choice of i, j with $i \neq j$.

So far, all this reasoning has been very hypothetical. *If* quantum states carry no experimentally inaccessible "hidden information," *then* the wavefunctions must be either symmetric or antisymmetric with respect to an interchange of positions and spins. Now comes an absolutely astounding fact, known as

The Spin Statistics Theorem

Systems of identical particles with integer spin $s = 0, 1, 2...$ are described by wavefunctions that are **symmetric** *under the interchange of particle coordinates and spin. Systems of identical particles with half-integer spin $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}...$ are described by wavefunctions that are* **antisymmetric** *under the interchange of particle coordinates and spin.*

Particles with integer spin are known as **Bosons**. Examples are pi-mesons (spin zero), photons (spin 1), and gravitons (spin 2). Particles with half-integer spin are known as **Fermions**. Examples include electrons, protons, and neutrinos (spin 1/2), the Omega hyperon (spin 3/2), and the (hypothetical) gravitino (spin 3/2) predicted by a theory known as supergravity.

The Spin-Statistics Theorem is called a theorem because it can be proven from a handful of axioms (causality, locality, Lorentz invariance...) in the context of a relativistic extension of quantum mechanics known as quantum field theory. We will touch briefly on quantum field theory at the very end of the semester, but the proof of the Spin-Statistics Theorem is not easy, and is simply beyond the scope of the course. Let us just note here that its implications have been tested, experimentally, in many ways. The most important consequence for atomic physics is known as

The Pauli Exclusion Principle

No two electrons can be in exactly the same quantum state.

This is the fact which makes chemistry possible, and leads to the remarkable repetition of chemical properties among the elements which is summarized in the Periodic Table. But in order to understand the Exclusion Principle, and how it follows from the Spin-Statistics Theorem, its useful to first look at some simple examples of 2-electron wavefunctions.

15.1   Two-Electron States

Suppose we have two spin-zero identical particles (such as pions) which are prepared in such a way that one particle has momentum p_a, and the other particle has momentum p_b. What is the wavefunction of the system?

Were it not for the spin statistics theorem, the wavefunction could be (up to a normalization constant)

$$\psi(x_1, x_2) = e^{ip_a \cdot x_1/\hbar} e^{ip_b \cdot x_2/\hbar} \qquad \text{or} \qquad e^{ip_a \cdot x_2/\hbar} e^{ip_b \cdot x_1/\hbar} \tag{15.23}$$

or any linear combination

$$\psi(x_1, x_2) = A e^{ip_a \cdot x_1/\hbar} e^{ip_b \cdot x_2/\hbar} + B e^{ip_a \cdot x_2/\hbar} e^{ip_b \cdot x_1/\hbar} \tag{15.24}$$

However, the spin-statistics theorm tells us that the only possible combination is the one which is symmetric with respect to the interchange of coordinate labels $1 \leftrightarrow 2$. Thus there is only one possible state in this case

$$\psi_S(x_1, x_2) = e^{ip_a \cdot x_1/\hbar} e^{ip_b \cdot x_2/\hbar} + e^{ip_a \cdot x_2/\hbar} e^{ip_b \cdot x_1/\hbar} \tag{15.25}$$

Next suppose there are two electrons, one with momentum p_a, the other with momentum p_b. This time, we also have to say something about the spin states. First, suppose the particle with momentum p_a has spin up, and the particle with momentum p_b has spin down. Again, without knowing the spin-statistics theorem, the states could be

$$\psi = e^{ip_a \cdot x_1/\hbar} \chi_+^1 e^{ip_b \cdot x_2/\hbar} \chi_-^2 \qquad \text{or} \qquad e^{ip_a \cdot x_2/\hbar} \chi_+^2 e^{ip_b \cdot x_1/\hbar} \chi_-^1 \tag{15.26}$$

or any linear combination (χ_+^1 means "particle 1 has spin up, etc.). But the spin-statistics theorem tells us that, up to a normalization constant, only the antisymmetric combination

$$\psi_A = e^{ip_a \cdot x_1/\hbar} \chi_+^1 e^{ip_b \cdot x_2/\hbar} \chi_-^2 - e^{ip_a \cdot x_2/\hbar} \chi_+^2 e^{ip_b \cdot x_1/\hbar} \chi_-^1 \tag{15.27}$$

will occur in nature.

The 2-electron state (15.27) is not an eigenstate of the total electron spin

$$S^2 = (S_1 + S_2)^2 = S_1^2 + S_2^2 + 2 S_1 \cdot S_2 \tag{15.28}$$

because $\chi_+^1 \chi_-^2$ is not an eigenstate of $S_1 \cdot S_2$. But we saw, in the last chapter, that it is possible to combine the spin angular momentum of two spin $\frac{1}{2}$ particles into eigenstates of total spin $s = 0$ and $s = 1$. What is then the wavefunction if one particle has momentum p_a, the other p_b, and the total spin angular momentum is $s = 1$?

Lets begin with the spin part of the wavefunction. In the last chapter, it was found that spin $\frac{1}{2}$ combinations that give $s = 1$ are

$$
\begin{aligned}
\Phi_{11}^S &= \chi_+^1 \chi_+^2 \\
\Phi_{10}^S &= \frac{1}{\sqrt{2}}[\chi_+^1 \chi_-^2 + \chi_-^1 \chi_+^2] \\
\Phi_{1-1}^S &= \chi_-^1 \chi_-^2
\end{aligned}
\tag{15.29}
$$

The superscript "S" has been added to draw attention to the fact that these states are symmetric with respect to the interchange $1 \leftrightarrow 2$. But the spin-statistics theorem only says that the *total* wavefunction, including the spin and the spatial parts, must change sign under the $1 \leftrightarrow 2$ interchange. So if the spin part is symmetric, the spatial part must be antisymmetric, i.e.

$$
e^{ip_a \cdot x_1/\hbar} e^{ip_b \cdot x_2/\hbar} - e^{ip_a \cdot x_2/\hbar} e^{ip_b \cdot x_1/\hbar}
\tag{15.30}
$$

and the possible wavefunctions for $s = 1$ are

$$
\psi^{triplet} = (e^{ip_a \cdot x_1/\hbar} e^{ip_b \cdot x_2/\hbar} - e^{ip_a \cdot x_2/\hbar} e^{ip_b \cdot x_1/\hbar}) \begin{cases} \Phi_{11}^S = & \chi_+^1 \chi_+^2 \\ \Phi_{10}^S = & \frac{1}{\sqrt{2}}[\chi_+^1 \chi_-^2 + \chi_-^1 \chi_+^2] \\ \Phi_{1-1}^S = & \chi_-^1 \chi_-^2 \end{cases}
\tag{15.31}
$$

The other possibility is $s = 0$. In this case, the spin wavefunction is

$$
\Phi_{00}^A = \frac{1}{\sqrt{2}}[\chi_+^1 \chi_-^2 - \chi_-^1 \chi_+^2]
\tag{15.32}
$$

Since this part of the wavefunction is antisymmetric under the $1 \leftrightarrow 2$ interchange, the spatial part must be symmetric, and therefore

$$
\begin{aligned}
\psi^{singlet} &= (e^{ip_a \cdot x_1/\hbar} e^{ip_b \cdot x_2/\hbar} + e^{ip_a \cdot x_2/\hbar} e^{ip_b \cdot x_1/\hbar}) \Phi_{00}^A \\
&= (e^{ip_a \cdot x_1/\hbar} e^{ip_b \cdot x_2/\hbar} + e^{ip_a \cdot x_2/\hbar} e^{ip_b \cdot x_1/\hbar}) \times \frac{1}{\sqrt{2}}[\chi_+^1 \chi_-^2 - \chi_-^1 \chi_+^2]
\end{aligned}
\tag{15.33}
$$

Finally, lets ask if its possible to prepare 2 electrons in a state where both electrons have the same momentum $p_a = p_b = p$, and both particles have the same spin, e.g. both are spin up. Its not hard to see that the only wavefunction which would describe such a system is

$$
\psi = e^{ip \cdot x_1/\hbar} e^{ip \cdot x_2/\hbar} \chi_+^1 \chi_+^2
\tag{15.34}
$$

But this is a symmetric state, therefore, it cannot exist in nature! Two electrons can never be prepared in a state, or found to be in a state, with the same momenta and the same spin. Such a state, incidentally, is an $s = 1$ state, and one can see from eq. (15.32) that the $s = 1$ states vanish for $p_a = p_b$. This is a first example of the **Pauli Exclusion Principle**.

The Exclusion Principle itself is derived from the Spin-Statistics Theorm by the following argument: Any state of N electrons is a superposition of products of N 1-particle states, with each 1-particle state of the form

$$\psi_a(x_i) = \left[\begin{array}{c} \psi_{a+}(x_i) \\ \psi_{a-}(x_i) \end{array} \right] \tag{15.35}$$

For example, for the Hydrogen atom the index a could be $a = (nlmss_z)$, so that, e.g.

$$\psi_{nlmss_z}(x_i) = R_{nl}(r_i)Y_{lm}(\theta_i, \phi_i)\chi^i_{s_z} \tag{15.36}$$

Now suppose we try to prepare a state in which one electron is in state a, a second is in state b, a third in state c, and so on. Because of the spin-statistics theorm, such a state must be antisymmetric under the interchange of any two indices $i \leftrightarrow j$. Then the only possibility is

$$\Psi = \sum_{n_a=1}^{N} \sum_{n_b=1}^{N} \dots \sum_{n_z=1}^{N} D_{n_a n_b \dots n_z} \psi_a(x_{n_a})\psi_b(x_{n_b})\dots\psi_z(x_{n_z}) \tag{15.37}$$

where $D_{n_a n_b \dots n_z}$ is antisymmetric under interchange of any two indices, i.e.

$$D_{n_a n_b n_c \dots n_z} = -D_{n_b n_a n_c \dots n_z} \tag{15.38}$$

But suppose that any two states are the same, e.g. $a = b$. Then for any term in the sum, e.g.

$$D_{ijk\dots}\psi_a(x_i)\psi_a(x_j)\psi_c(x_k)\dots. \tag{15.39}$$

there is an equal term in the sum, of the opposite sign, i.e.

$$D_{jik\dots}\psi_a(x_j)\psi_a(x_i)\psi_c(x_k)\dots \tag{15.40}$$

where opposite sign of this term is due to the antisymmetry property (15.38), and so the two contributions (15.39) and (15.40) cancel. This means that if any two 1-electron states are the same, the N-particle wavefunction is zero. There is zero probability to find two electrons in the same quantum state. This is the Pauli Exclusion Principle, whose consequences for atomic physics are profound.

15.2   The Helium Atom

Before talking about atoms in general, let's discuss one in particular: Helium. This is obviously the next step up in complexity from Hydrogen and, since it has two electrons rather than one, is a good place to apply our knowlege of 2-electron wavefunctions. The Hamiltonian for the system is

$$\begin{aligned} H &= \left\{ \frac{p_1^2}{2m} - \frac{2e^2}{r_1} \right\} + \left\{ \frac{p_2^2}{2m} - \frac{2e^2}{r_2} \right\} + \frac{e^2}{r_{12}} \\ &= H_0(1) + H_0(2) + V' \end{aligned} \tag{15.41}$$

where r_1 (r_2) is the distance of electron 1 (electron 2) to the nucleus, and r_{12} is the distance between the two electrons. We have neglected all other terms in the Hamiltonian that involve spin; nevertheless, due to the spin-statistics theorem, electron spin turns out to be very important in determining the possible electron states.

The first thing to do is neglect V' also, and construct eigenstates of

$$H_0(12) = H_0(1) + H_0(2) \tag{15.42}$$

This is easy because the variables are separable, and the solutions of

$$H_0\Psi(x_1, x_2) = E\Psi(x_1, x_2) \tag{15.43}$$

are just

$$\begin{aligned}
\Psi_{nlm,n'l'm'} &= \phi_{nlm}(r_1, \theta_1, \phi_1)\phi_{n'l'm'}(r_2, \theta_2, \phi_2) \\
E_{nlm,n'l'm'} &= E_n + E_{n'}
\end{aligned} \tag{15.44}$$

where the $\phi_{nlm}(r, \theta, \phi)$ and E_n are just the Hydrogen atom wavefunctions, with the one modification that the charge e^2 in those expressions are replaced by $2e^2$, since the Helium nucleus has two protons. Of course, if the quantum numbers (nlm) and $(n'l'm')$ are different, then any linear combination

$$\Psi = A\phi_{nlm}(r_1, \theta_1, \phi_1)\phi_{n'l'm'}(r_2, \theta_2, \phi_2) + B\phi_{nlm}(r_2, \theta_2, \phi_2)\phi_{n'l'm'}(r_1, \theta_1, \phi_1) \tag{15.45}$$

is also an eigenstate of $H_0(12)$, with energy $E_n + E_{n'}$. In particular, we can form normalized, symmetric and antisymmetric combinations

$$\begin{aligned}
\Psi^S_{nlm,n'm'l'} &= \frac{1}{\sqrt{2}}[\phi_{nlm}(r_1, \theta_1, \phi_1)\phi_{n'l'm'}(r_2, \theta_2, \phi_2) + \phi_{nlm}(r_2, \theta_2, \phi_2)\phi_{n'l'm'}(r_1, \theta_1, \phi_1)] \\
\Psi^A_{nlm,n;l'm'} &= \frac{1}{\sqrt{2}}[\phi_{nlm}(r_1, \theta_1, \phi_1)\phi_{n'l'm'}(r_2, \theta_2, \phi_2) - \phi_{nlm}(r_2, \theta_2, \phi_2)\phi_{n'l'm'}(r_1, \theta_1, \phi_1)]
\end{aligned} \tag{15.46}$$

So far we have only written down the spatial part of the energy eigenstates, and ignored the spin part. But H commutes with the total spin operators S^2, S_z, so we should be able to construct energy eigenstates which are also total spin eigenstates. The only possibilities for total spin is $s = 1$, which has a triplet of symmetric spin wavefunctions, and $s = 0$, which has a single antisymmetric spin wavefunction. To satisy spin-statistics, $s = 1$ must go with an antisymmetric spatial wavefunction, and $s = 0$ with a symmetric spatial wavefunction, so all in all

$$\begin{aligned}
\Psi^{triplet}_{nlm,n'l'm'} &= \frac{1}{\sqrt{2}}[\phi_{nlm}(r_1, \theta_1, \phi_1)\phi_{n'l'm'}(r_2, \theta_2, \phi_2) \\
&\quad -\phi_{nlm}(r_2, \theta_2, \phi_2)\phi_{n'l'm'}(r_1, \theta_1, \phi_1)] \begin{cases} \Phi_{11} \\ \Phi_{10} \\ \Phi_{1-1} \end{cases} \\
\Psi^{singlet}_{nlm,n'l'm'} &= \frac{1}{\sqrt{2}}[\phi_{nlm}(r_1, \theta_1, \phi_1)\phi_{n'l'm'}(r_2, \theta_2, \phi_2) \\
&\quad +\phi_{nlm}(r_2, \theta_2, \phi_2)\phi_{n'l'm'}(r_1, \theta_1, \phi_1)]\Phi_{00}
\end{aligned} \tag{15.47}$$

if (nlm) and $(n'm'l')$ are different, and

$$\Psi^{singlet}_{nlm,nlm} = \phi_{nlm}(r_1, \theta_1, \phi_1)\phi_{nlm}(r_2, \theta_2, \phi_2)\Phi_{00} \tag{15.48}$$

if (nlm) and $(n'm'l')$ are the same. Note that in the ground state

$$\Psi^{singlet}_{100,100} = \phi_{100}(1)\phi_{100}(2) \times \frac{1}{\sqrt{2}}[\chi^1_+\chi^2_- - \chi^1_-\chi^2_+] \tag{15.49}$$

the electrons are in spin up/spin down combinations. It is impossible to put two spin up electrons (or two spin down electrons) into the Helium ground state; this is another illustration of the exclusion principle.

Now lets consider the case where one electron is in the (100) state, and the other electron is in the (nlm) state. The $s = 0$ singlet combination is known as **Parahelium**, and the $s = 1$ triplet combination is known as **Orthohelium**. Neglecting the electrostatic repulsive potential V' between the two electrons, Orthohelium and Parahelium are degenerate in energy.

In order to see how the electron repulsion removes the degeneracy between Ortho- and Parahelium, we will treat V' as though it were a small perturbing potential, and use the formula

$$\Delta E = <\Psi|V'|\Psi> \tag{15.50}$$

which is valid if V' is a small correction to the rest of the Hamiltonian. Actually, in this case V' is not so small; it is the same order of magnitude in strength as the attractive potential of the electrons to the nucleus. But we will go ahead and use eq. (15.50) anyway, trusting that it will produce results that are at least qualitatively, if not quantitatively, correct. So the correction to the zeroth order energy

$$E^{O,P} = E_0 + \Delta E \tag{15.51}$$

for Ortho- and Parahelium will be

$$\begin{aligned}
\Delta E^{O,P} = \ & \frac{1}{2}\int d^3x_1 d^3x_2 \ \{\phi^*_{100}(x_1)\phi^*_{nlm}(x_2) \pm \phi^*_{100}(x_2)\phi^*_{nlm}(x_1)\} \\
& \times \frac{e^2}{|\vec{x}_1 - \vec{x}_2|} \{\phi_{100}(x_1)\phi_{nlm}(x_2) \pm \phi_{100}(x_2)\phi_{nlm}(x_1)\} \\
& \times <\Phi_{s=0,1}|\Phi_{s=0,1}>
\end{aligned} \tag{15.52}$$

where the plus sign is for Parahelium, and the minus sign for Orthohelium. The spin states are normalized, so $<\Phi|\Phi>=1$, and therefore, collecting like terms,

$$\begin{aligned}
\Delta E^P &= A + B \\
\Delta E^O &= A - B
\end{aligned} \tag{15.53}$$

where

$$A = \int d^3x_1 d^3x_2 \ |\phi_{100}(x_1)|^2 \frac{e^2}{r_{12}}|\phi_{nlm}(x_2)|^2 \tag{15.54}$$

and

$$B = \int d^3x_1 d^3x_2 \, [\phi_{nlm}^*(x_1)\phi_{100}(x_1)]\frac{e^2}{r_{12}}[\phi_{nlm}(x_2)\phi_{100}^*(x_2)] \tag{15.55}$$

Term A is associated with a simple, intuitive picture. If we think of the electron in state (100) as having a charge density proportional to its probability density

$$\rho_{100}(x) = -e|\phi_{100}(x)|^2 \tag{15.56}$$

and likewise for the electron in state (nlm)

$$\rho_{nlm}(x) = -e|\phi_{nlm}(x)|^2 \tag{15.57}$$

then A is simply the Couloumb interaction energy between those two charge distributions, i.e.

$$A = \int d^3x_1 d^3x_2 \, \frac{\rho_{100}(x_1)\rho_{nlm}(x_2)}{|\vec{x}_1 - \vec{x}_2|} \tag{15.58}$$

On the other hand, there is no classical picture for the origin of term B. In terms of the Feynman diagrams of relativistic quantum mechanics (see, e.g. Bjorken and Drell, vol. I), one can visualize the interaction between electrons as occuring via the transfer of a photon between them. The Coulomb interaction A comes about when the electron in the (100) state emits a photon at point x_1, which is absorbed by the electron in the (nlm) state at point x_2. The exchange interaction comes about when the electron in the (100) emits a photon at point x_1 and jumps into the (nlm) state, while the electron at point x_2 absorbs a photon, and drops into the (100) state. In other words, the particles not only exchange a photon, but in doing so they also exchange states. The diagrams are shown in Fig. [15.2] and I hope they give a hint of what is going on, but, to be honest, an explanation of what these diagrams really mean will have to wait for a course in quantum field theory.

Both the quantities A and B are positive numbers, so we can conclude that

$$E \text{ of Parahelium } (s = 0) \quad > \quad E \text{ of Orthohelium } (s = 1) \tag{15.59}$$

The intuitive reason for this fact is something like this: The $s = 1$ state is symmetric in spins, it is therefore antisymmetric in space. In spatially antisymmetric states, the electrons tend to be further apart, on average, than for the corresponding spatially symmetric states. For example, in an antisymmetric state the wavefunction vanishes at $x_1 = x_2$. Being further apart means that the repulsive potential is somewhat smaller, and hence the energy of the state is smaller. This is an example of a rule in atomic physics known as Hund's First Rule (see next section), which says that, other things being equal, the state of highest spin is the state of lowest energy.

15.3   The Periodic Table

One learns in a beginning chemistry course that chemical reactions among the elements involve electrons hopping from one atom to another, either in the form of an ionic bond (one atom captures the electron of another, as in NaCl), or a covalent bond (one or more electrons are shared between atoms, as in H_2). But, why should electrons hop back and forth between atoms? Why don't they simply sit in the lowest possible energy state of each atom, and refuse to budge unless seriously molested? The key to that question, and to understanding the curious periodicity of chemical properties among the elements, is the Pauli Exclusion Principle.

In principle, everything that can be known about an atom is contained in the wavefunctions of its energy eigenstates. For purposes of chemistry it is the atomic ground state, and particularly the ionization energy, which are important (the ionization energy is the minimum energy required to remove a single electron from the atom). Again in principle, the procedure for finding the ground state of an atom of atomic number Z is very straightforward: First, write down Schrodinger's equation for the Z-electron state

$$\left[\sum_{n=1}^{Z}\left\{-\frac{\hbar^2}{2m}\nabla_n^2 - \frac{Ze^2}{r_n}\right\} + \sum_{n>m}\frac{e^2}{|\vec{x}_n - \vec{x}_m|}\right]\Psi = E\Psi \qquad (15.60)$$

Second, find the solution, antisymmetric with respect to particle interchange, which has the lowest energy. The antisymmetry restriction is very important; the lowest energy eigenstates are not antisymmetric in general.

Unfortunately, the second part of this suggested procedure is very hard carry out in practice. The problem is that, due to the interactions among electrons, there is no way of separating variables in the many-electron Schrodinger equation. What's more, the electron interaction term is too large to be treated as a small perturbation, for which there exist systematic approximation methods.

But in the case that the number of electrons is fairly large, the theoretical physicist has another trick up his or her sleave. In condensed matter, nuclear, and particle physics this trick is known variously as the "mean field," or "self-consistent field," or "independent particle," or "random phase" approximation. In atomic physics the method is known as the "Hartree approximation." Roughly the idea is this: when each particle interacts with many other particles, the potential due to those many other particles can be treated, on average, as though it were a classical potential, in which each particle moves independently. If we knew this average potential, we could calculate the wavefunction of each particle by solving a one-particle Schrodinger equation; and, knowing the wavefunction of each particle, we could calculate the average potential. Therefore one calculates the wavefunctions "self-consisently," i.e. finding solutions which lead to a potential which give those solutions. Thats the general idea. The weakness of the approximation is that it ignores all correlations in the positions of the various particles. Still, when each particle interacts with

many other particles, ignoring these subtle correllations is often justified. We won't actually do any calculations of multi-electron atomic wavefunctions using this method (the computations are quite involved), but its still interesting and useful to see how one gets started.

The first part of the Hartree approximation is to imagine that each electron, numbered $1, 2, .., Z$ is in an individual state, denoted $\phi_1, \phi_2, ..., \phi_Z$, so the total wave-function would be

$$\Phi(1, 2, ..., Z) = \phi_1(1)\phi_2(2)...\phi_Z(Z) \tag{15.61}$$

where the arguments $1, 2, ..$ refer to the coordinates *and* spin state of the indicated particle. This is of course already in conflict with the spin-statistics theorem because Φ should be antisymmetric. In fact, the approximation can be improved by anti-symmetrizing Φ (its called the "Hartree-Fock" approximation), but the improvement is on the order of $10 - 20\%$, so we will ignore this additional complication. The Pauli Exclusion principle, however, must be respected! This is imposed by requiring that the ϕ_n are all orthogonal, or nearly so, so that no two electrons are in the same quantum state. We will also suppose, for now, that the ϕ_n are of the form

$$\phi_n(n) = \phi_n(x_n)\chi_\pm^n \tag{15.62}$$

The essence of the Hartree approximation is that the electron in the k-th state "sees" the electron in the j-th state as being a cloud of charge, with charge density given by

$$\rho(x) = -e|\phi_j(x)|^2 \tag{15.63}$$

In that case, we can write down a Schrodinger equation for the wavefunction of the k-th electron, treating the other electrons as though they were simply classical charge distributions of the form (15.63), i.e.

$$\left\{ \frac{-\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + \sum_{n \neq k} \int d^3y \frac{e^2|\phi_n(y)|^2}{|\vec{x} - \vec{y}|} \right\} \phi_k(x) = \mathcal{E}\phi_k(x) \tag{15.64}$$

To make things even simpler, the last term is approximated by its angular average, i.e.

$$\left\{ \frac{-\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + V_k(r) \right\} \phi_k(x) = \mathcal{E}\phi_k(x) \tag{15.65}$$

where[2]

$$V_k(r) = \frac{1}{4\pi} \int d\Omega \sum_{n \neq k} \int d^3y \frac{e^2|\phi_n(y)|^2}{|\vec{x} - \vec{y}|} \tag{15.66}$$

There are two important observations to make about eq. (15.65). First, it is an equation with a spherically symmetric potential. This means that the Hamiltonian

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[2]This is the Coulomb term. The Hartree approximation, because it has not been properly anti-symmetrized, misses the exchange term.

commutes with L^2, L_z, and the solutions can be labeled by same quantum numbers as the Hydrogen atom wavefunctions, i.e. (nlm). Second, the potential is no longer exactly $1/r$. When a given electron is close to the nucleus, it sees a potential $-Ze^2/r$, due to the full charge of the nuclues. However, when the electron is near the edge of the atom, it will only see a potential of strength $-e^2/r$, because the other $Z-1$ electrons are interposed, and screen the nuclear charge. As a result, energies are no longer independent of the l quantum number. In fact, for a given n, the larger values of l have a higher energy (i.e. are more weakly bound). The reason is that the higher angular momentum states are further, on the average, from the nucleus. Therefore an electron in such states sees a smaller attractive potential, and therefore has a smaller binding energy.[3]

Without solving anything, a ground-state wavefunction in the Hartree approximation is denoted by listing the energy levels that the Z electrons are in. The notation for each level is

$$n \ \mathbf{l}^N \quad \begin{cases} n = 1, 2, 3, ... & \text{principal quantum no.} \\ \mathbf{l} = s, p, d, ... & \text{spectroscopic symbol for } l = 0, 1, 2, .., n-1 \\ N = 1, 2, 3, ... & \text{number of electrons in this level } \leq 2(2l+1) \end{cases} \quad (15.67)$$

The Pauli principle tells us that the maximum value for N, at any given l, is

$$N_{max}(l) = 2(2l+1) \tag{15.68}$$

Each electron has to be in a different state, and there are $2l+1$ possible values of m for each l. Therefore there can be $2l+1$ electrons with spin up, and $2l+1$ electrons with spin down; a total of $2(2l+1)$ electrons in all. When there are exactly this many electrons in a given level, the level is said to be "filled."

The last thing needed, in order to list the electron configuration of each atomic ground state, is the actual order of the energies. In the hydrogen atom, the energies depend only on the n quantum number, but in multi-electron atoms, as just mentioned, the binding energy decreases, as l increases. This listing can only be obtained by actually carrying out the Hartree approximation, and is as follows:

$$1s, 2s, 2p, 3s, 3p, [4s, 3d], 4p, [5s, 4d], 5p, [6s, 4f, 5d], 6p, ... \tag{15.69}$$

where the levels in brackets are very close in energy. Note that there are cases, such as $4s$ and $3d$, where a level with smaller n and larger l has a higher energy than the level with higher n and smaller l. Again, this is due to the l-dependence of the energy: the

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[3]You might wonder why a spherically symmetric Hamiltonian with a $1/r$ potential has a greater degeneracy of eigenstates than Hamiltonians with other central potentials $V(r)$. The answer is that Hamiltonians with $1/r$ potentials actually have a symmetry which includes, but is greater than, spherical symmetry. Knowledge of this symmetry allows one, in the case of $1/r$ potentials, to define raising and lowering operators that change l as well as m. A full discussion of this point, however, is beyond the scope of this course.

$4s$-orbital tends to be closer to the nucleus, and hence sees a larger effective positive charge, than the $3d$-orbital, which tends to be further from the nucleus, whose charge is therefore screened to a greater extent by intervening electrons.

Knowledge of the atomic number Z of an atom, and the order of energies (15.69), allows us to immediately write down the configuration of electrons in the ground state. As an example, consider sodium, with an atomic number of $Z = 11$. Of the eleven electrons, the first two go into the $1s$ state, which is filled. Two more electrons go into the $2s$ state, which is also filled. Of the remaining seven electrons, six fill the $2p$ level, and the remaining electron occupies the 3s level. So the electron configuration is written[4]

$$\text{Na:} \quad 1s^2 \, 2s^2 \, 2p^6 \, 3s \tag{15.70}$$

Electrons in the highest energy level are known as **valence electrons**. It is these electrons that determine the chemical properties of the atom. Sodium has one valence electron, in the 3s state.

- **A Quick Tour of the Periodic Table:** The Periodic Table begins with Hydrogen, with a $1s$ electron configuration in the ground state, and an ionization enegy of 13.6 eV. The next element, Helium, has two electrons in a $1s^2$ configuration, but (as we see in Fig. [15.3]), the ionization energy has almost doubled, to 24.6 eV. The reason for this increase in ionization energy is quite simple: the charge of the nucleus is twice as big as for Hydrogen, so each of the 1s levels is more tightly bound to the nucleus. Helium will not easily give up an electron to form a molecule; moreover, since the 1s level is filled, it will not capture an electron either. This element is therefore chemically inert.

The electron configuration of the third element, Lithium, is $1s^2 \, 2s$, and the ionization energy is much less than Helium, being only 5.4 eV. Naively, since the charge of the nucleus is now $Z = 3$, one might expect the ionization energy to increase, as it did with Helium, so that Lithium would be even more inactive. It is at this point that the Exclusion Principle comes into play, with a constraint that allows chemistry to be interesting, and life to exist. Since the $1s$ level is filled, the third electron must occupy the $2s$ level. But an electron in the $2s$ level is further away from the nucleus, on average, than the two electrons in the $1s$ level, so the valence electron sees a shielded charge, which is only about $Z = 1$. Having seen this, we can estimate that the binding energy of the $2s$ electron in Lithium should be about the same as that of a $2s$ electron in Hydrogen, namely 3.4 eV. The actual binding energy (which is also the ionization energy) is in fact slightly higher than that (5.4 eV, as mentioned above), and this is because the electron in the 2s state has some amplitude for being close to the nucleus, where it would see a larger effective nuclear charge. Moving to the next element in line, Beryllium, the configuration is $1s^2 \, 2s^2$, and again the ionization

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[4]When there is only one electron in a given level, one omits the superscript, i.e. $3s \equiv 3s^1$.

energy increases because $Z = 4$, and the binding energy of each of the $2s$ states is greater. But although the $2s$ shell is filled, the $2p$ shell is quite close in energy, and the presence of a nearby atom may be enough to cause a rearrangement in which one of the $2s$ electrons goes into the $2p$ state. So Beryllium is not as chemically inert as Helium. In general, the most stable electron configurations are those for which: (i) the valence level is filled; and (ii) there is a large jump in energy to the next level; e.g. when all l levels for a given n are filled.

Roughly, then, this is the picture: The various electron levels can be lumped together into groups which have about the same energy. These groups, and the maximum number of electrons allowed in each group, are

$$
\begin{array}{lll}
1s & 2 & \text{electrons} \\
2s,\ 2p & 8 & " \\
3s,\ 3p & 8 & " \\
4s,\ 3d,\ 4p & 18 & " \\
5s,\ 4d,\ 5p & 18 & " \\
6s,\ 4f,\ 5d,\ 6p & 32 & " \\
7s,\ 6d,\ 5f, ...
\end{array}
\tag{15.71}
$$

As one goes up in Z in each group, the binding energy tends to increase, due to the fact that charge of the nucleus increases. Thus the ionization energy builds to a maximum, which is the case when all of the energy levels in a group are filled, as seen in Fig. [15.4]. These maxima occur for the **inert gases**: Helium, Neon, Argon, Krypton. However, as Z increases further and the levels of the next higher group begin to be filled, the ionization energy drops sharply from its value at the inert gas. The reason is that the sudden decrease in binding energy of the next higher shell predominates over the increase in Z. It should be noted that unless a shell is completely filled, a high ionization energy does not mean that an element is necessarily very inert. Chlorine, for example, has an ionization energy (13 eV) which is nearly as high as the inert gas Argon (15.8 eV). But the valence level of Chlorine is not filled; there is room for one more electron. And because the binding energy of the valence level is so high, it is possible for Chlorine to capture an electron, thereby filling its valence level. This is why, when Sodium and Chlorine are brought into proximity, it is energetically favorable for Sodium to lose its valence electron (this only costs 5.1 eV), which is more than compensated by a lowering of the Chlorine energy by the valence electron bound state energy (-13 eV). The positively charged Sodium ion is then bound to the negatively charged Chlorine ion by ordinary electrostatic attraction. The resulting compound, as you probably know from high school chemistry,[5] is ordinary table salt: NaCl.

The groups shown above in (15.71) are associated with rows in the period table. The first group, corresponding to the 1s level, is occupied only by Hydrogen and Helium. The next two groups are the "short" rows of the Periodic Table, and constitute

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[5]Do they still teach chemistry in high school?

the eight elements of Lithium to Neon in the upper row, and Sodium to Argon in the lower row. Next come two long rows of the periodic table, with 18 elements each: Potassium to Krypton in the upper row, and Rubidium to Xenon in the lower row. Then comes a long group of 32 elements, containing the rare earths, whose names I can never remember. The last group of the heaviest elements, containing Thorium, Uranium, and some other elements that have been created in the laboratory but which don't appear in nature, is not completely filled. The limitation on the size of the periodic table comes not from atomic physics, but from nuclear physics, since nuclei beyond some limiting Z tend to be highly radioactive, and decay an instant after they are produced.

• **Term Notation** The Hartree approximation ignores all correllations between electrons, and in particular it ignores the correllations that lead to the atomic ground state being an eigenstate of *total* spin, orbital, and spin+orbital angular momenta

$$\begin{aligned}
\vec{S} &= \vec{S}_1 + \vec{S}_2 + ... + \vec{S}_Z \\
\vec{L} &= \vec{L}_1 + \vec{L}_2 + ... + \vec{L}_Z \\
\vec{S} &= \vec{J}_1 + \vec{J}_2 + ... + \vec{J}_Z
\end{aligned} \tag{15.72}$$

In fact, the Hamiltonian commutes with J^2, L^2, S^2, and the ground state in particular has definite values of the quantum numbers J, L, S, where we use capitals letters to emphasize that these are quantum numbers for the ensemble of electrons. The **Term Notation** or **Spectroscopic Description** of a many electron state with definite quantum numbers J, L, S is given by the expression

$$^{2S+1}\mathcal{L}_J \tag{15.73}$$

where

$$\begin{array}{ccccccc}
L = & 0 & 1 & 2 & 3 & 4 & 5 & ... \\
\mathcal{L} = & S & P & D & F & G & H & ...
\end{array} \tag{15.74}$$

There exists some folklore known as **Hund's Rules** which allow one to guess, sometimes, the term description for the ground state of a given atom. In these rules, the phrase "highest (lowest) possible" means: highest (lowest) possible consistent with the exclusion principle. The rules are as follows:

Hund's Rule's

1. *Other things being equal, the lowest energy state of atomic electrons is the state with the highest S.*

2. *For a given total spin S, the lowest energy state is the state with the largest L.*

3. *For a given total S and L, if the valence level is not more than half-filled, the lowest energy state has the minimum $J = |L - S|$; if the shell is more than half-filled, the lowest energy state has $J = L + S$.*

As an example of these rules we consider Carbon, which has an atomic configuration $1s^2\, 2s^2\, 2p^2$. The filled shells have zero spin and zero orbital angular momentum (because there is no state one can make with $m^{total} \neq 0$, $S_z^{total} \neq 0$), so only the two valence electrons are relevant for determining the overall spin, orbital, and total angular momentum. The two spin $\frac{1}{2}$ electrons in the $2p$ states can combine into $S = 0$ or $S = 1$. By Hund's First Rule, the $S = 1$ value is chosen. This means (for $S_z = +1$) both electrons are spin up. They are also both in an $l = 1$ orbital, so addition of angular momentum could lead to any of the values $L = 2, 1, 0$. But because of the exclusion principle, the two spin-up electrons can't possibly have the same m values. This means that the highest and lowest weight states for adding $L_1 = 1$ and $L_2 = 1$ are excluded, since we can't have $m_1 = m_2 = \pm 1$. So this rules out $L = 2$. The highest L left, by Hund's second rule, is $L = 1$. By Hund's third rule, since the valence shell is less than half filled, $J = |L - S| = 0$. So the term notation (or "spectroscopic description") for the ground state of Carbon is $^3P_0$.

There is much more that can be deduced about the Periodic Table, atomic physics, and chemical reactions from quantum-mechanical principles. This is the subject matter of a course on Theoretical Chemistry. But there are two points that, once again, deserve special emphasis. First, the existence of chemical reactions is a consequence of the exclusion principle. Were it not for the exclusion principle, all atomic electrons would sit in the $1s$ state, becoming more and more tightly bound as Z increases. The second point is that the observed repetition of chemical properties is connected to the $2(2l + 1)$ occupancy of the s, p, d, f orbitals, and this in turn is connected to the peculiar algebra of the angular momentum operators. In short, the chemical properties of the elements are due essentially to the exclusion principle, and to the fact that two rotations, done in different orders, end up in different places. Life is a byproduct of chemistry; it's a curious thought that we owe our existence to the absolute identity of electrons, and to the non-commutative property of rotations.

Chapter 16

Live Wires and Dead Stars

Stars die. Their long lives are interesting and complex, occasionally culminating in fantastic explosions (supernovas) that can briefly outshine entire galaxies. The details are the subject matter of some other course. For us, it is sufficient to know that every "living" star balances its immense gravitational force, which tends to crush all the atoms of the star inward to a single point, with an equally enormous outward pressure, due to the heat produced by nuclear fusion. Eventually, any star will exhaust its nuclear fuel, and then the gravitational force, unopposed, crushes the atoms of the star to a fantastic density. In the course of collapse, for stars greater than about one solar mass, the atomic electrons are absorbed by protons in the nuclei, via the process

$$ e^- \ + \ p \ \rightarrow \ n \ + \ \nu \tag{16.1} $$
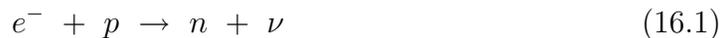
and the massless neutrinos ν, due to their weak interaction with all other matter, escape into space. At this stage, all of the particles composing the star are neutrons, the density of the star approximates that of atomic nuclei, and the dead star is known as a "neutron star." For stars with masses less than about four solar masses, that is the end of the story: the cold dead star remains as a neutron star until the end of time. But this brings up the question: what force can there possibly be, within the cold neutron star, that is capable of opposing the mighty gravitational force, which would otherwise crush all the matter of the star to a single point?

It seems incredible that all this astrophysical drama should have anything at all to do with the apparently more mundane question of why some materials conduct electricity, and some don't. Nevertheless, the physics of dead stars, and that of quite ordinary solids, are related in certain unexpected ways. Both neutron stars, and the electrons in cold metals, are examples of what are known as **degenerate Fermi gases**. We begin by taking up the question of how is it possible for certain solids to conduct electricity.

16.1   The Kronig-Penny Model

A crystalline solid is a regular array of atoms, and, at first sight, conduction of electricity is a mystery: if electrons are bound to atoms, how is possible for them to move through the solid under the influence of a small electric field? The answer is that in a crystal, not all of the electrons are actually bound to the atoms; in fact, some of the electrons in the metal behave more like a gas of free particles, albeit with some peculiar characteristics which are due to the exclusion principle.

To understand how electrons in a crystal can act as a gas, it is useful to solve for the electron energy eigenstates in a highly idealized model of a solid, known as the Kronig-Penny model, which makes the following simplifications:

S1. The solid is one-dimensional, rather than three-dimensional. The N atoms are spaced a distance a from one another. In order that there are no special effects at the boundaries, we consider a solid has no boundary at all, by arranging the atoms in a circle as shown in Fig. [16.1].

S2. Instead of a Coulomb potential, the potential of the n-th atom is represented by a delta-function attractive potential well

$$V_n(x) = -g\delta(x - x_n) \tag{16.2}$$

where x_n is the position of the n-th atom.

S3. Interactions between electrons in the 1-dimensional solid are ignored.

Obviously, these are pretty drastic simplifications. The important feature of this model, which it shares with realistic solids, is that the electrons are moving in a periodic potential. For purposes of understanding the existence of conductivity, it is the periodicity of the potential, not its precise shape (or even its dimensionality) which is the crucial feature.

Arranging the atoms in a circle, as in Fig. [16.1], means that the position variable is periodic, like an angle. Just as $\theta + 2\pi$ is the same angle as θ, so the position $x + L$ is the same position as x, where

$$L = Na \tag{16.3}$$

is the length of the solid. Let the position of the n-th particle be $x_n = na, \quad n = 0, 1, ..., N - 1$, the potential then has the form

$$V(x) = -g \sum_{n=0}^{N-1} \delta(x - na) \tag{16.4}$$

Its clear that the potential satisfies

$$V(x + a) = V(x) \tag{16.5}$$

providing that we impose the periodicity requirement that $x + L$ denotes the same point as x. The "periodic delta-function" which incorporates this requirement is given by

$$\delta(x) = \frac{1}{2\pi} \sum_m \exp\left[2\pi imx/L\right] \tag{16.6}$$

The time-independent Schrodinger equation for the motion of any one electron in this potential has the usual form

$$H\psi_k(x) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - g\sum_{n=0}^{N-1}\delta(x - na)\right]\psi_k(x) = E_k\psi_k(x) \tag{16.7}$$

Because $V(x)$ has the symmetry (16.5), it is useful to consider the translation operator first introduced in Chapter 10,

$$\begin{aligned} T_a f(x) &= \exp[ia\tilde{p}/\hbar]f(x) \\ &= f(x + a) \end{aligned} \tag{16.8}$$

Likewise,

$$\begin{aligned} T_{-a} f(x) &= \exp[-ia\tilde{p}/\hbar]f(x) \\ &= f(x - a) \end{aligned} \tag{16.9}$$

Because $\tilde{p}$ is an Hermitian operator, its easy to see (just expand the exponentials in a power series) that

$$\begin{aligned} T_a^\dagger &= T_{-a} \\ [T_a, T_{-a}] &= 0 \\ T_{-a}T_a &= 1 \end{aligned} \tag{16.10}$$

Due to the periodicity of the potential $V(x)$, the Hamiltonian commutes with the translation operators, which, as we've seen, also commute with each other, i.e.

$$[T_a, H] = [T_{-a}, H] = [T_a, T_{-a}] = 0 \tag{16.11}$$

This means (see Chapter 10) that we can choose energy eigenstates to also be eigenstates of $T_{\pm a}$, i.e.

$$\begin{aligned} T_a\psi_E(x) &= \lambda_E\psi_E(x) \\ T_{-a}\psi_E(x) &= \lambda'_E\psi_E(x) \end{aligned} \tag{16.12}$$

Therefore,

$$\begin{aligned} \lambda_E &= <\psi_E|T_a|\psi_E> \\ &= <T_a^\dagger\psi_E|\psi_E> \\ &= <T_{-a}\psi_E|\psi_E> \\ &= (\lambda'_E)^* \end{aligned} \tag{16.13}$$

But also

$$\begin{aligned}
\psi_E(x) &= T_a T_{-a} \psi_E \\
&= \lambda_E \lambda_E' \psi_E \\
&= \psi_E(x)
\end{aligned} \tag{16.14}$$

This means that $\lambda_E' = (\lambda_E)^{-1}$. Insert that fact into (16.13) and we conclude that $\lambda_E^* = (\lambda_E)^{-1}$, i.e.

$$\lambda_E = \exp(iKa) \tag{16.15}$$

for some K. In this way we arrive at

Bloch's Theorem

For potentials with the periodicity property $V(x + a) = V(x)$, each energy eigenstate of the Schrodinger equation satisfies

$$\psi(x + a) = e^{iKa}\psi(x) \tag{16.16}$$

for some value of K.

It is also easy to work out the possible values of K, from the fact that

$$\begin{aligned}
\psi(x) &= \psi(x + L) \\
&= (T_a)^N \psi(x) \\
&= \exp[iNKa]\psi(x)
\end{aligned} \tag{16.17}$$

which implies

$$K = \frac{2\pi}{Na}j \qquad j = 0, 1, 2, ..., N - 1 \tag{16.18}$$

The limiting value of j is $N - 1$, simply because

$$\exp[i2\pi\frac{j + N}{N}] = \exp[i2\pi\frac{j}{N}] \tag{16.19}$$

so $j \geq N$ doesn't lead to any further eigenvalues (j and $N - j$ are equivalent).

According to Bloch's theorem, if we can solve for the energy eigenstates in the region $0 \leq x \leq a$, then we have also solved for the wavefunction at all other values of x. Now the periodic delta function potential $V(x)$ vanishes in the region $0 < x < a$, so in this region (call it region I) the solution must have the free-particle form

$$\psi_I(x) = A\sin(kx) + B\cos(kx) \qquad E = \frac{\hbar^2 k^2}{2m} \tag{16.20}$$

But according to Bloch's theorem, in the region $-a < x < 0$ (region II),

$$\begin{aligned}
\psi_{II}(x) &= e^{-iKa}\psi_I(x+a) \\
&= e^{-iKa}[A\sin k(x+a) + B\cos k(x+a)]
\end{aligned} \tag{16.21}$$

Now we apply continuity of the wavefunction at $x = 0$ to get

$$B = e^{-iKa}[A\sin(ka) + B\cos(kb)] \tag{16.22}$$

For a delta function potential, we found last semester a discontinuity in the slope of the wavefunction at the location $(x = 0)$ of the delta function spike, namely

$$\left(\frac{d\psi}{dx}\right)_{|\epsilon} - \left(\frac{d\psi}{dx}\right)_{|-\epsilon} = -\frac{2mg}{\hbar^2}\psi(0) \tag{16.23}$$

and this condition gives us

$$kA - e^{-iKa}k[A\cos(ka) - B\sin(ka)] = -\frac{2mg}{\hbar^2}B \tag{16.24}$$

Solving eq. (16.22) for A,

$$A = \frac{e^{iKa} - \cos(ka)}{\sin(ka)}B \tag{16.25}$$

inserting into eq. (16.24) and cancelling B on both sides of the equation leads finally, after a few manipulations, to

$$\cos(Ka) = \cos(ka) - \frac{mg}{\hbar^2 k}\sin(ka) \tag{16.26}$$

This equation determines the possible values of k, and thereby, via $E = \hbar^2 k^2/2m$, the possible energy eigenvalues of an electron in a periodic potential.

Now comes the interesting point. The parameter K can take on the values $2\pi n/Na$, and $\cos(Ka)$ varies from $\cos(Ka) = +1$ ($n = 0$) down to $\cos(Ka) = -1$ ($n = N/2$), and back up to $\cos(Ka) \approx +1$ ($n = N - 1$). So the left hand side is always in the range $[-1, 1]$. On the other hand, the right hand side is *not* always in this range, and that means *there are gaps in the allowed energies of an electron in a periodic potential.* This is shown in Fig. [16.2], where the right hand side of (16.26) is plotted. Values of k for which the curve is outside the range $[-1, 1]$ correspond to regions of forbidden energies, known as **energy gaps**, while the values where the curve is inside the $[-1, 1]$ range correspond to allowed energies, known as **energy bands**. The structure of bands and gaps is indicated in Fig. [16.3]; each of the closely spaced horizontal lines is associated with a definite value of K.

In the case that we have $M > N$ non-interacting electrons, each of the electrons must be in an energy state corresponding to a line in one of the allowed energy bands. The lowest energy state would naively be that of all electrons in the lowest energy

level, but at this point we must invoke the Exclusion Principle: There can be no more than one electron in any given quantum state. Thus there can a maximum of two electrons (spin up and spin down) at any allowed energy in an energy band.

At the lowest possible temperature ($T = 0$ K), the electrons' configuration is the lowest possible energy consistent with the Exclusion Principle. A perfect **Insulator** is a crystal in which the electrons completely fill one or more energy bands, and there is a gap in energy from the most energetic electron to the next unoccupied energy level. In a **Conductor**, the highest energy band containing electrons is only partially filled.

In an applied electric field the electrons in a crystal will tend to accellerate, and increase their energy. But...they can only increase their energy if there are (nearby) higher energy states available, for electrons to occupy. If there are no nearby higher energy states, as in an insulator, no current will flow (unless the applied field is so enormous that electrons can "jump" across the energy gap). In a conductor, there are an enormous number of nearby energy states for electrons to move into. Electrons are therefore free to accellerate, and a current flows through the material.

The actual physics of conduction, in a real solid, is of course far more complex than this little calculation would indicate. Still, the Kronig-Penny model does a remarkable job of isolating the essential effect, namely, the formation of separated energy bands, which is due to the periodicity of the potential.

16.2 The Free Electron Gas

In the Kronig-Penney model, the electron wavefunctions have a free-particle form in the interval between the atoms; there is just a discontinuity in slope at precisely the position of the atoms. In passing to the three-dimensional case, we'll simplify the situation just a bit more, by ignoring even the discontinuity in slope. The electron wavefunctions are then entirely of the free particle form, with only some boundary conditions that need to be imposed at the surface of the solid. Tossing away the atomic potential means losing the energy gaps; there is only one "band," whose energies are determined entirely by the boundary conditions. For some purposes (such as thermodynamics of solids, or computing the bulk modulus), this is not such a terrible approximation.

We consider the case of N electrons in a cubical solid of length L on a side. Since the electrons are constrained to stay within the solid, but we are otherwise ignoring atomic potentials and inter-electron forces, the problem maps directly into a gas of non-interacting electrons in a cubical box. Inside the box, the Schrodinger equation for each electron has the free particle form

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = E\psi(x,y,z) \qquad (16.27)$$

While, at the boundaries, we impose the "box" conditions

$$
\begin{aligned}
\psi(0, y, z) &= \psi(L, y, z) = 0 \\
\psi(x, 0, z) &= \psi(x, L, z) = 0 \\
\psi(x, y, 0) &= \psi(x, y, L) = 0
\end{aligned}
\tag{16.28}
$$

The solution of the particle in a box is a simple generalization of the particle in a tube (Lecture 5), and the particle in a square (Lecture 10). The eigenstates are

$$
\psi_{n_1 n_2 n_3}(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin(\frac{\pi n_1}{L}x) \sin(\frac{\pi n_2}{L}y) \sin(\frac{\pi n_3}{L}z)
\tag{16.29}
$$

with energy eigenvalues

$$
E_{n_1 n_2 n_3} = \frac{\pi^2 \hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)
\tag{16.30}
$$

Suppose the solid is at temperature $T = 0$. We ask the question: (i) what is the total energy E_T of the electrons in the solid; and (ii) what is the energy E_F of the most energetic electron in the solid? The energy of the most energetic electron in a cold solid, E_F, is known as the **Fermi Energy**.

Start with E_F. The method for calculating the Fermi energy is to first suppose that we know it, and, assuming that every energy $E_{n_1 n_2 n_3} < E_F$ is filled with two electrons (spin up/down), figure out the total number of electrons in the solid. By setting this number to N, we can determine E_F.

To each eigenstate there corresponds a set of integers n_1, n_2, n_3, so each possible energy state can be represented a point in a three-dimensional space, with positive integer coordinates. Denote the maximum value of $n_1^2 + n_2^2 + n_3^2$, for the most energetic state, by R^2. The Fermi Energy is therefore

$$
E_F = \frac{\pi^2 \hbar^2}{2mL^2} R^2
\tag{16.31}
$$

Now all of the states with $E \leq E_F$ are occupied. So we need to count the number of points with integer coordinates $(n_1 n_2 n_3)$ such that

$$
n_1^2 + n_2^2 + n_3^2 \leq R^2
\tag{16.32}
$$

But since there is one site with integer coordinates per unit volume, the number of sites satisfying (16.32) is simply the volume of a one octant of a sphere of radius R (see Fig. 16.4). Since there can be no more than two electrons per site $(n_1 n_2 n_3)$, the total number of electrons with energies less than E_F, with all levels filled, is

$$
N = 2 \times \frac{1}{8} \times \frac{4}{3}\pi R^3 = \frac{1}{3}\pi R^3
\tag{16.33}
$$

According to (16.31),

$$R = \left(\frac{2mL^2}{\hbar^2\pi^2}E_F\right)^{1/2} \tag{16.34}$$

so the number of electrons, in terms of E_F, becomes

$$N = \frac{\pi}{3}L^3\left(\frac{2mE_F}{\hbar^2\pi^2}\right)^{3/2} \tag{16.35}$$

Solving for the Fermi energy, we get

$$E_F = \frac{\hbar^2\pi^2}{2m}\left(\frac{3N}{\pi L^3}\right)^{2/3} \tag{16.36}$$

But the number density of electrons, n_e, in the solid is just

$$n_e = \frac{N}{L^3} \tag{16.37}$$

Therefore, we find that the Fermi energy just depends on the electron mass and density (and not on the size of the box)

$$E_F = \frac{\hbar^2\pi^2}{2m}\left(\frac{3}{\pi}n_e\right)^{2/3} \tag{16.38}$$

Next, approximate the sum over all states with energies less than E_F by an integral

$$
\begin{aligned}
E_T &= \sum_{n_1}\sum_{n_2}\sum_{n_3} 2E_{n_1n_2n_3} \\
&\approx \int_{\vec{n}\cdot\vec{n}\leq R^2} d^3n\, 2E_{n_1n_2n_3} \\
&= \frac{\hbar^2\pi^2}{mL^2}\frac{1}{8}\int d^3n\, \vec{n}\cdot\vec{n} \\
&= \frac{\hbar^2\pi^2}{8mL^2}4\pi\int_0^R dn\, n^4 \\
&= \frac{\hbar^2\pi^3}{10mL^2}R^5
\end{aligned}
\tag{16.39}
$$

where the factor of $1/8$ in front of the integral comes, again, because the sites lie in the octant of the sphere with *positive* integer coordinates. Next from (16.33)

$$R = \left(\frac{3N}{\pi}\right)^{1/3} \tag{16.40}$$

Using $L = V^{1/3}$, where V is the volume of the solid, we get finally

$$E_T = \frac{\hbar^2\pi^3}{10m}\left(\frac{3N}{\pi}\right)^{5/3}V^{-2/3} \tag{16.41}$$

The pressure with which any object resists compression is given by

$$p = -\frac{dE_T}{dV} \tag{16.42}$$

where E_T is the energy of the object. For a cold electron gas, this is known as the **degeneracy pressure**. The bulk modulus B describes the change in pressure per fractional decrease in volume, i.e.

$$
\begin{aligned}
B &= -V\frac{dp}{dV} \\
&= -V\frac{d^2E_T}{dV^2} \\
&= \frac{\pi^3\hbar^2}{9m}\left(\frac{3N}{\pi}\right)^{5/3}V^{-5/3} \\
&= \frac{\pi^3\hbar^2}{9m}\left(\frac{3n_e}{\pi}\right)^{5/3}
\end{aligned}
\tag{16.43}
$$

Rather surprisingly, given all the unrealistic assumptions that have gone into this expression, it gives answers that compare reasonably well (within 30% in some cases) to the experimental results.

Finally, we turn to the neutron star. The radius of the dead star is determined by a balance between the inward gravitational pressure, and the outward degeneracy pressure which is due to the fact that neutrons, like electrons, are spin $\frac{1}{2}$ objects. The degeneracy pressure is the same expression for neutron stars as it is for ordinary solids, the only difference being that the electron mass m should be replaced by the neutron mass m_n, the electron number density n_e by the neutron number density n_n, and N is the number of neutrons. The degeneracy pressure is

$$
\begin{aligned}
p_D &= -\frac{dE_T}{dV} \\
&= \frac{\hbar^2\pi^3}{15m_n}\left(\frac{3N}{\pi}\right)^{5/3}V^{-5/3} \\
&= \frac{\hbar^2\pi^3}{15m_n}\left(\frac{3n_n}{\pi}\right)^{5/3}
\end{aligned}
\tag{16.44}
$$

where E_T is the total kinetic energy of the neutrons up to the Fermi level. On the other hand, the gravitational potential energy of a sphere of constant density ρ and radius $\mathcal{R}$ is given by

$$E_G = -\frac{(4\pi)^2}{15}G\rho^2\mathcal{R}^5 \tag{16.45}$$

Using $\rho = M/V$, where M is the mass of the star, and $V = \frac{4}{3}\pi\mathcal{R}^3$, we get an expression for E_G in terms of V

$$E_G = -\frac{3}{5}\left(\frac{4\pi}{3}\right)^{1/3}GM^2V^{-1/3} \tag{16.46}$$

Then the inward gravitational pressure is

$$
\begin{aligned}
p_G &= -\frac{dE_G}{dV} \\
&= -\frac{1}{5}\left(\frac{4\pi}{3}\right)^{1/3} GM^2 V^{-4/3}
\end{aligned}
\tag{16.47}
$$

Finally, requiring that the inward (p_G) and outward (p_D) pressures balance,

$$
\frac{1}{5}\left(\frac{4\pi}{3}\right)^{1/3} GM^2 V^{-4/3} = \frac{\hbar^2 \pi^3}{15 m_n}\left(\frac{3N}{\pi}\right)^{5/3} V^{-5/3}
\tag{16.48}
$$

solving for V and then for $\mathcal{R} = (3V/4\pi)^{1/3}$, we get

$$
\mathcal{R} = \left(\frac{81\pi^{20}}{16}\right)^{1/3}\frac{\hbar^2}{Gm_n^3}N^{-1/3}
\tag{16.49}
$$

For a two solar mass star, $N = M/m_n$, R turns out to be about 10 km.

It seems from eq. (16.49) that no matter how massive the star (i.e. no matter how large N) the degeneracy pressure will always end the collapse at a finite value of R. Actually this is not quite right, because we have ignored relativistic effects. The free Schrodinger equation is based on $E = p^2/2m$, i.e. E grows quadratically with p. In fact, the correct expression in relativity is $E = \sqrt{p^2 c^2 + m^2 c^4}$, and at velocities very close to the speed of light, the energy is approximately $E \approx pc$; i.e. the energy grows only linearly with p. This means that the degeneracy pressure for relativistic neutrons is less that one would expect from the non-relativistic calculation. In fact, for stars at about four solar masses, the neutrons in the star *do* become relativistic, and the degeneracy pressure is insufficient to counter the gravitational pressure. For stars of that mass and greater, no known physical process can stop the continuing collapse, and the star becomes a black hole.

For a star with a mass somewhat less than that of the sun, the cold star never reaches the neutron star stage, since the elecron degeneracy pressure is sufficient to stabilize the star at radii on the order of 10,000 km. For masses somewhat greater than that of the sun, the electrons becomes relativistic, and the collapse continues until, for masses less than four solar masses, the star becomes a neutron star.

Before leaving the topic, it is hard to resist mentioning one last aspect of electron spin. In the 1920's Dirac wrote down a relativistic equation for electrons, which not only predicted that electrons should have spin $\frac{1}{2}$, but also predicted the magnitude of the electron magnetic moment, with g-factor $g = 2$. There was just one little problem: in addition to free electrons with positive energy

$$
E = \sqrt{p^2 c^2 + m^2 c^4}
\tag{16.50}
$$

the equation also predicted *negative* energy states

$$E = -\sqrt{p^2 c^2 + m^2 c^4} \tag{16.51}$$

This had the uncomfortable consequence that an electron could radiate energy indefinitely, as it dropped into ever lower negative energy states. To avoid this problem, Dirac postulated that every negative energy state was filled; the lowest energy state in nature being an infinite collection of negative energy electrons known as the "**Dirac sea**." theory also allowed for the possibility than a negative energy electron could absorb a photon and jump to a positive energy level, leaving an unoccupied position in the negative energy levels. It turned out that this unoccupied position would behave in every way as though it were itself a particle with the electron mass and spin, but with the opposite charge: a "**positron**." These particles were discovered by Anderson, in cosmic ray studies, just a few years after their existence was predicted by Dirac.

Its clear that electron spin, and the spin-statistics theorem, explains a lot. It enables us to understand the qualitative features of the periodic table and the existence of conduction bands in crystals. It allows us to estimate the bulk modulus of solids, and the radii of dead stars. And this is not even half the story! In addition to degenerate fermion gases, there are also degenerate boson gases, in which every particle occupies the lowest energy level. Aggregates of that kind are of crucial importance in understanding such startling phenomena as superconductivity and superfluidity. It would be nice to discuss those things also, but there are limits to the number of things one can do in a year.

Chapter 17

Time-Independent Perturbation Theory

Consider a Hamiltonian which has this form:

$$H = H_0 + \text{a little bit extra potential} \tag{17.1}$$

where H_0 is a Hamiltonian whose eigenvalue equation is already solved:

$$H_0 \phi_n^0 = E_n^0 \phi_n^0 \tag{17.2}$$

It then makes sense that the solutions to the eigenvalue equation

$$H \phi_n = E_n \phi_n \tag{17.3}$$

can be written, for each n, as

$$
\begin{aligned}
\phi_n &= \phi_n^0 + \text{a little bit extra function} \\
E_n &= E_n^0 + \text{a little bit extra constant}
\end{aligned}
\tag{17.4}
$$

An example:

$$H = -\frac{\hbar^2}{2m} \frac{d}{dx^2} + \frac{1}{2} k x^2 + \lambda x^4 \tag{17.5}$$

In this case

$$H_0 = -\frac{\hbar^2}{2m} \frac{d}{dx^2} + \frac{1}{2} k x^2 \tag{17.6}$$

is the Hamiltonian of a harmonic oscillator, whose energy eigenvalues and eigenfunctions are well known, and

$$\text{a little bit extra potential} = \lambda x^4 \tag{17.7}$$

Another example is the case of a a Hydrogen atom in an external electric field, directed (say) along the z-axis

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r} + eEz \tag{17.8}$$

This time

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} \tag{17.9}$$

is the usual Hydrogen atom Hamiltonian, and

$$\text{a little bit extra potential} = eEz \tag{17.10}$$

Of course, in each case these extra potentials can only be characterized as "a little bit extra" if the constants λ and eE are small, in some appropriate units (to be discussed further below). Lets write in general that

$$\text{a little bit extra potential} = V'(x) = \lambda V(x) \tag{17.11}$$

where λ is some constant which controls whether $V'(x)$ is small or not. Then the solutions of the eigenvalue equation (17.3) are, obviously, funtions of λ, which can be expanded in a Taylor series around $\lambda = 0$, i.e.

$$\begin{aligned}
\phi_n &= \phi_n(x, \lambda) \\
&= \phi_n^{(0)}(x) + \lambda\phi_n^{(1)}(x) + \lambda^2\phi_n^{(2)}(x) + ... \\
E_n &= E_n(\lambda) \\
&= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...
\end{aligned} \tag{17.12}$$

where

$$\begin{aligned}
E_n^{(k)} &\equiv \frac{1}{k!}\left(\frac{d^k}{dx^k}E_n(\lambda)\right)_{\lambda=0} \\
\phi_n^k(x) &\equiv \frac{1}{k!}\left(\frac{d^k}{dx^k}\phi(x,\lambda)\right)_{\lambda=0}
\end{aligned} \tag{17.13}$$

and of course

$$H = H_0 + \lambda V \tag{17.14}$$

Then the eigenvalue (17.3) becomes

$$\begin{aligned}
&(H_0 + \lambda V)(\phi_n^{(0)} + \lambda\phi_n^{(1)} + \lambda^2\phi_n^{(2)} + ...) \\
&= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...)(\phi_n^{(0)}(x) + \lambda\phi_n^{(1)}(x) + \lambda^2\phi_n^{(2)}(x) + ...)
\end{aligned} \tag{17.15}$$

Collecting like powers of λ on each side we have

$$\begin{aligned}
&H_0\phi_n^{(0)} + \lambda(H_0\phi_n^{(1)} + V\phi_n^{(0)}) + ... + \lambda^N(H_0\phi_n^{(N)} + V\phi_n^{(N-1)}) + ... \\
&= E_n^{(0)}\phi_n^{(0)} + \lambda(E_n^{(0)}\phi_n^{(1)} + E_n^{(1)}\phi_n^{0}) + \lambda^2(E_n^{(0)}\phi_n^{(2)} + E_n^{(1)}\phi_n^{(1)} + E_n^{(2)}\phi_n^{(0)}) + ... \\
&\quad + \lambda^N\sum_{j=0}^{N} E_n^{(j)}\phi_n^{(N-j)} + ...
\end{aligned} \tag{17.16}$$

or

$$
\begin{aligned}
0 &= (H_0\phi_n^{(0)} - E_n^{(0)}\phi_n^{(0)}) + \lambda(H_0\phi_n^{(1)} + V\phi_n^{(0)} - E_n^{(0)}\phi_n^{(1)} - E_n^{(1)}\phi_n^0) + ... \\
&\quad + \lambda^N(H_0\phi_n^{(N)} + V\phi_n^{(N-1)} - \sum_{j=0}^{N} E_n^{(j)}\phi_n^{(N-j)}) + ... \\
&= F^{(0)} + \lambda F^{(1)} + \lambda^2 F^2 + ... \quad\quad (17.17)
\end{aligned}
$$

Now this equation has to be true for *every* choice of λ. But since, by definition, the $E_n^{(k)}$ and $\phi_n^{(k)}(x)$ are independent of λ, we must have

$$
F^{(0)} = F^{(1)} = F^{(2)} = ... = 0 \quad\quad (17.18)
$$

which gives us an infinite set of coupled equations:

$$
\begin{aligned}
(H_0 - E_n^{(0)})\phi_n^{(0)} &= 0 \\
(H_0 - E_n^{(0)})\phi_n^{(1)} &= (E_n^{(1)} - V)\phi_n^{(0)} \\
(H_0 - E_n^{(0)})\phi_n^{(2)} &= -V\phi_n^{(1)} + E_n^{(1)}\phi_n^{(1)} + E_n^{(2)}\phi_n^{(0)} \\
... &= ... \\
(H_0 - E_n^{(0)})\phi_n^{(N)} &= -V\phi^{(N-1)} + \sum_{j=1}^{N-1} E_n^{(j)}\phi_n^{(N-j)} + E_n^N\phi_n^{(0)} \\
... &= ... \quad\quad (17.19)
\end{aligned}
$$

We already know the solution of $F^{(0)} = 0$, which is simply the set of zeroth-order (in λ) eigenstates and eigenfunctions $\{\phi_n^{(0)}, E_n^{(0)}\}$. Then the idea is input these solutions to solve the equation $F^{(1)} = 0$ for the set $\{\phi_n^{(1)}, E_n^{(1)}\}$. This provides the solution to ϕ_n, E_n up to first order in λ. We can then continue to solve these equations iteratively, and obtain the eigenstates and eigenvalues to any order in λ desired.

But we first have to deal with a slight ambiguity. Notice that if $\phi_n^{(1)}$ is a solution of

$$
(H_0 - E_n^{(0)})\phi_n^{(1)} = (E_n^{(1)} - V)\phi_n^{(0)} \quad\quad (17.20)
$$

then so is

$$
\phi_n'^{(1)} = \phi_n^{(1)} + a\phi_n^{(0)} \quad\quad (17.21)
$$

where a is any constant. There is a similar ambiguity for any $\phi_n^{(N)}$. We can get rid of this ambiguity is a simple way. We first note that the eigenvalue equation $H\phi_n = E_n\phi_n$ is a linear equation, which doesn't set the overall normalization $\langle\phi_n|\phi_n\rangle$ of the eigenstates. So lets temporarily choose the normalization such that the overlap

$$
\langle\phi_n^0|\phi_n\rangle = 1 \qu\quad (17.22)
$$

is unity, for any λ. Its easy to see, from the expansion (17.12), that this implies for each N,

$$
\langle\phi_n^0|\phi_n^{(N)}\rangle = 0 \quad\quad (17.23)
$$

and this condition eliminates the ambiguity mentioned above. Of course, after having computed $\phi_n(x)$ by the process of iteratively solving the set of $F^{(N)} = 0$ equations, we will finally have to normalize $\phi_n(x)$ in the usual way to obtain a physical state.

Lets see how this iterative process works. Suppose we have solved all the $F^{(k)} = 0$ equations up to $k = N - 1$. The $k = N$-th equation, in bra-ket notation, is

$$(H_0 - E_n^{(0)})|\phi_n^{(N)}\rangle = -V|\phi_n^{(N-1)}\rangle + \sum_{j=1}^{N-1} E_n^{(j)}|\phi_n^{(N-j)}\rangle + E_n^N|\phi_n^{(0)}\rangle \qquad (17.24)$$

To solve for $\phi_n^{(N)}$, first express it in terms of a complete set of states spanning the Hilbert space, namely, the zero-th order eigenstates of H_0

$$\phi_n^{(N)} = \sum_{i \neq n} c_{ni}^N \phi_i^{(0)} \qquad (17.25)$$

where we can neglect $i = n$ because of (17.23). Now multiply eq. (17.24) on both sides by the bra vector $\langle\phi_i^{(0)}|$, with $i \neq n$

$$\langle\phi_i^{(0)}|(H_0 - E_n^{(0)})|\phi_n^{(N)}\rangle = -\langle\phi_i^{(0)}|V|\phi_n^{(N-1)}\rangle + \sum_{j=1}^{N-1} E_n^{(j)}\langle\phi_i^{(0)}|\phi_n^{(N-j)}\rangle + E_n^N\langle\phi_i^{(0)}|\phi_n^{(0)}\rangle$$

$$(E_i^{(0)} - E_n^{(0)})\langle\phi_i^{(0)}|\phi_n^{(N)}\rangle = -\langle\phi_i^{(0)}|V|\phi_n^{(N-1)}\rangle + \sum_{j=1}^{N-1} E_n^{(j)}\langle\phi_i^{(0)}|\phi_n^{(N-j)}\rangle$$

$$(E_i^{(0)} - E_n^{(0)})c_{ni}^N = -\langle\phi_i^{(0)}|V|\phi_n^{(N-1)}\rangle + \sum_{j=1}^{N-1} E_n^{(j)}c_{ni}^{N-1} \qquad (17.26)$$

so that

$$c_{ni}^N = \frac{1}{E_n^{(0)} - E_i^{(0)}}\left[\langle\phi_i^{(0)}|V|\phi_n^{(N-1)}\rangle - \sum_{j=1}^{N-1} E_n^{(j)}c_{ni}^{N-1}\right] \qquad (17.27)$$

Therefore

$$\phi_n^{(N)} = \sum_{i \neq n} \frac{1}{E_n^{(0)} - E_i^{(0)}}\left[\langle\phi_i^{(0)}|V|\phi_n^{(N-1)}\rangle - \sum_{j=1}^{N-1} E_n^{(j)}c_{ni}^{N-1}\right]\phi_n^{(0)} \qquad (17.28)$$

is the N-th order correction to the zeroth-order wavefunction, expressed in terms of the lower order $E_n^{(j)}$ and c_{ni}^{N-1}.

Next we have to get the N-th order correction to the energy, and for this we multiply eq. (17.24) on both sides by the bra vector $\langle\phi_n^{(0)}|$

$$\langle\phi_n^{(0)}|(H_0 - E_n^{(0)})|\phi_n^{(N)}\rangle = -\langle\phi_n^{(0)}|V|\phi_n^{(N-1)}\rangle + \sum_{j=1}^{N-1} E_n^{(j)}\langle\phi_n^{(0)}|\phi_n^{(N-j)}\rangle + E_n^N\langle\phi_n^{(0)}|\phi_n^{(0)}\rangle$$

$$0 = -\langle\phi_n^{(0)}|V|\phi_n^{(N-1)}\rangle + \sum_{j=1}^{N-1} E_n^{(j)}\langle\phi_n^{(0)}|\phi_n^{(N-j)}\rangle + E_n^N\langle\phi_n^{(0)}|\phi_n^{(0)}\rangle$$

$$(17.29)$$

and making use of the constraint (17.23), we have

$$0 = -\langle \phi_n^{(0)}|V|\phi_n^{(N-1)}\rangle + E_n^{(N)} \tag{17.30}$$

Putting everything together, we have the iterative equations

$$\phi_n^{(N)} = \sum_{i\neq n} c_{ni}^N \phi_i^{(0)}$$

$$c_{ni}^N = \frac{1}{E_n^{(0)} - E_i^{(0)}} \left[\langle \phi_i^{(0)}|V|\phi_n^{(N-1)}\rangle - \sum_{j=1}^{N-1} E_n^{(j)} c_{ni}^{N-1} \right]$$

$$E_n^{(N)} = \langle \phi_n^{(0)}|V|\phi_n^{(N-1)}\rangle \tag{17.31}$$

which allows us to compute the solutions

$$\phi_n = \phi_n^{(0)} + \lambda \phi_n^{(1)} + \lambda^2 \phi_n^{(2)} + ...$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ... \tag{17.32}$$

to any desired accuracy.

Lets now work out the corrections to the energies and wavefunctions to second order in λ (it is usually not necessary to go further than this). First of all, setting $N = 1$ in (17.31)

$$c_{ni}^1 = \frac{\langle \phi_i^{(0)}|V|\phi_n^{(0)}\rangle}{E_n^{(0)} - E_i^{(0)}} \tag{17.33}$$

so that

$$\phi_n^{(1)} = \sum_{i\neq n} \frac{\langle \phi_i^{(0)}|V|\phi_n^{(0)}\rangle}{E_n^{(0)} - E_i^{(0)}} \phi_i^0 \tag{17.34}$$

and

$$E_n^{(1)} = \langle \phi_n^{(0)}|V|\phi_n^{(0)}\rangle \tag{17.35}$$

We can substitute these formulas into the $N = 2$ equations to get the second-order correction to the wavefunction,

$$\phi_n^{(2)} = \sum_{i\neq n} \frac{1}{E_n^{(0)} - E_i^{(0)}} \left[\langle \phi_i^{(0)}|V|\phi_n^{(1)}\rangle - E_n^{(1)} c_{ni}^1 \right] \phi_n^{(0)}$$

$$= \sum_{i\neq n} \frac{1}{E_n^{(0)} - E_i^{(0)}} \left[\langle \phi_i^{(0)}|V| \left\{ \sum_{k\neq n} c_{nk}^1 |\phi_k^{(0)}\rangle \right\} - E_n^{(1)} c_{ni}^1 \right] \phi_n^{(0)}$$

$$= \sum_{i\neq n} \sum_{k\neq n} \frac{1}{E_n^{(0)} - E_i^{(0)}} \frac{1}{E_n^{(0)} - E_k^{(0)}} \langle \phi_i^{(0)}|V|\phi_k^{(0)}\rangle \langle \phi_k^{(0)}|V|\phi_n^{(0)} > \phi_i^{(0)}$$

$$- \sum_{i\neq n} \frac{\langle \phi_i^{(0)}|V|\phi_n^{(0)}\rangle \langle \phi_i^{(0)}|V|\phi_n^{(0)} >}{(E_n^{(0)} - E_i^{(0)})^2} \phi_i^{(0)} \tag{17.36}$$

and the second-order correction to the energy,

$$
\begin{aligned}
E_n^2 &= \langle \phi_n^{(0)} | V | \phi_n^1 \rangle \\
&= \langle \phi_n^{(0)} | V \sum_{i \neq n} \frac{\langle \phi_i^{(0)} | V | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}} | \phi_i^{(0)} \rangle \\
&= \sum_{i \neq n} \frac{\left| \langle \phi_n^{(0)} | V | \phi_i^{(0)} \rangle \right|^2}{E_n^{(0)} - E_i^{(0)}}
\end{aligned}
\tag{17.37}
$$

You may wonder how much of this you really have to remember. The average quantum physicist can recite from from memory the result for the wavefunction to first order, and the energy to second order in λ. So these are the results to remember:

$$
\phi_n = \phi_n^{(0)} + \lambda \sum_{i \neq n} \frac{\langle \phi_i^{(0)} | V | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}} \phi_i^{(0)}
$$

$$
E_n = E_n^{(0)} + \lambda \langle \phi_n^{(0)} | V | \phi_n^{(0)} \rangle + \lambda^2 \sum_{i \neq n} \frac{\left| \langle \phi_n^{(0)} | V | \phi_i^{(0)} \rangle \right|^2}{E_n^{(0)} - E_i^{(0)}}
\tag{17.38}
$$

17.1 Validity of Perturbation Theory

Perturbation theory works when the perturbing potential V' is small compared to H_0. But...what do we mean by "small"? A good rule of thumb is that V' is small if the first order correction $\lambda \phi_n^{(1)}$ is much less than the zeroth-order wavefunction, which requires (at least) that

$$
\lambda | c_{in}^1 | \ll 1 \quad \Longrightarrow \quad \lambda \left| \frac{\langle \phi_i^{(0)} | V | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}} \right| \ll 1
\tag{17.39}
$$

In other words, the "matrix element" V'_{in} of the perturbing potential is much smaller than the corresponding energy difference

$$
|V'_{in}| \equiv \lambda | \langle \phi_i^{(0)} | V | \phi_n^{(0)} \rangle | \ll |E_n^{(0)} - E_i^0|
\tag{17.40}
$$

This is, of course, for $i \neq n$ (otherwise the energy difference is trivially zero). For $i = n$, we require that the first-order correction to the energy is small compared to the zeroth-order energy, i.e.

$$
E_n^{(1)} \ll E_n^{(0)} \quad \Longrightarrow \quad | \langle \phi_n^{(0)} | V | \phi_n^{(0)} \rangle | \ll E_n^{(0)}
\tag{17.41}
$$

17.2   Example - The Anharmonic Oscillator

Consider the Hamiltonian

$$
\begin{aligned}
H &= -\frac{\hbar^2}{2m}\frac{d}{dx^2} + \frac{1}{2}kx^2 + \lambda x^4 \\
&= H_0 + \lambda x^4
\end{aligned}
\tag{17.42}
$$

The shift in the energy, to first order in λ, is

$$
\begin{aligned}
\Delta E_n &= \lambda E_n^{(1)} \\
&= \lambda \langle n|x^4|n\rangle
\end{aligned}
\tag{17.43}
$$

where we introduce the notation, for the harmonic oscillator, that

$$
|n\rangle \equiv |\phi_n^{(0)}>
\tag{17.44}
$$

As usual in harmonic oscillator problems, it helps to express the position operator x in terms of raising and lowering operators

$$
\begin{aligned}
x &= \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger) \\
x^4 &= \left(\frac{\hbar}{2m\omega}\right)^2 (a + a^\dagger)^4 \\
&= \left(\frac{\hbar}{2m\omega}\right)^2 \Big[a^2(a^\dagger)^2 + aa^\dagger aa^\dagger + a(a^\dagger)^2 a + \\
&\quad + a^\dagger a^2 a^\dagger + a^\dagger a a^\dagger a + (a^\dagger)^2 a^2\Big] \\
&\quad + \text{non-contributing terms}
\end{aligned}
\tag{17.45}
$$

Using the raising/lowering operator properties

$$
\begin{aligned}
a^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle \\
a|n\rangle &= \sqrt{n}|n-1\rangle
\end{aligned}
\tag{17.46}
$$

we find, e.g., that

$$
\begin{aligned}
\langle n|a^2(a^\dagger)^2|n\rangle &= \sqrt{n+1}\langle n|a^2 a^\dagger|n+1\rangle \\
&= \sqrt{n+1}\sqrt{n+2}\langle n|a^2|n+2\rangle \\
&= \sqrt{n+1}(n+2)\langle n|a|n+1\rangle \\
&= (n+1)(n+2)
\end{aligned}
\tag{17.47}
$$

Evaluating all of the relevant terms in this way, we find

$$
\begin{aligned}
\langle n|x^4|n\rangle &= \left(\frac{\hbar}{2m\omega}\right)^2 \Big[(n+2)(n+1) + (n+1)^2 + n(n+1) + n(n+1) + n^2 + n(n-1)\Big] \\
&= 3\left(\frac{\hbar}{2m\omega}\right)^2 [1 + 2n(n+1)]
\end{aligned}
\tag{17.48}
$$

Then, to first order in λ

$$E_n = \hbar\omega(n + \frac{1}{2}) + 3\lambda \left(\frac{\hbar}{2m\omega}\right)^2 [1 + 2n(n+1)] \qquad (17.49)$$

which we can also express as

$$E_n = \hbar(\omega + \delta\omega)(n + \frac{1}{2}) + n^2\hbar\delta\omega \qquad (17.50)$$

where

$$\delta\omega = 6\lambda\frac{\hbar}{4m^2\omega^3} \qquad (17.51)$$

So the effect of the $\dot{x}^4$ perturbation is essentially a shift $\delta\omega$ in the angular frequency of the oscillator, together with an increase in the spacing of energy levels. Its interesting to note that no matter how small λ may be, the perturbative expansion for the energy must break down completely when n is large enough. This is because the zeroth-order energy increases only linearly with n, whereas the first-order correction increases quadratically. This breakdown of perturbation theory has a simple physical explanation. Whatever the value of λ, it is always true that $\lambda x^4 > \frac{1}{2}kx^2$ when x is large enough. But highly excited harmonic oscillator states, which have large n, spread out far from the origin $x = 0$, and therefore probe the region where the perturbing potential is larger than the zeroth-order potential. In such regions, one cannot expect perturbation theory to work, and in fact it doesn't.

17.3   Perturbation Theory in Matrix Notation

Let us define the matrix elements of an operator, in the basis of Hilbert space spanned by $\{\phi_n^{(0)}\}$, as

$$O_{ij} = \langle\phi_i^{(0)}|O|\phi_j^{(0)}\rangle \qquad (17.52)$$

In this basis, H_0 is a diagonal matrix:

$$\begin{aligned}
[H_0]_{ij} &= \langle\phi_i^{(0)}|H_0|\phi_j^{(0)}\rangle \\
&= \delta_{ij}E_j^{(0)} \\
H_0 &= \begin{bmatrix} E_1^0 & 0 & 0 & ... \\ 0 & E_2^0 & 0 & ... \\ 0 & 0 & E_3^0 & ... \\ . & . & . & ... \\ . & . & . & ... \end{bmatrix}
\end{aligned} \qquad (17.53)$$

For diagonal matrices, solving the eigenvalue problem

$$H_0\phi_n^{(0)} = E_n^{(0)}\phi_n^{(0)} \qquad (17.54)$$

is very easy. The eigenvectors are

$$\vec{\phi}_1^{(0)} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ . \\ . \end{bmatrix} \quad , \quad \vec{\phi}_2^{(0)} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ . \\ . \end{bmatrix} \quad , \quad \vec{\phi}_3^{(0)} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ . \\ . \end{bmatrix} \quad \dots \tag{17.55}$$

and the eigenvalues are the diagonal elements of the matrix.

So now the problem is to find the eigenvectors of the (non-diagonal) matrix

$$H = H_0 + V' = \begin{bmatrix} E_1^{(0)} + V_{11}' & V_{12}' & V_{13}' & \dots \\ V_{21}' & E_2^{(0)} + V_{22}' & V_{23}' & \dots \\ V_{31}' & V_{32}' & E_3^{(0)} + V_{33}' & \dots \\ . & . & . & \dots \\ . & . & . & \dots \end{bmatrix} \tag{17.56}$$

where

$$H_{ij} = \langle \phi_i^{(0)} | H_0 + V' | \phi_j^{(0)} \rangle = E_j \delta_{ij} + V_{ij}' \tag{17.57}$$

But this problem is already solved! To first order (in V') for the eigenvectors, and second order in the eigenvalues, the solution is

$$\vec{\phi}_n = \vec{\phi}_n^{(0)} + \sum_{i \neq n} \frac{V_{in}'}{E_n^{(0)} - E_i^{(0)}} \vec{\phi}_i^{(0)} + O(V'^2)$$

$$E_n = E_n^0 + V_{nn}' + \sum_{i \neq n} \frac{\left| V_{in}' \right|^2}{E_n^{(0)} - E_i^{(0)}} + O(V'^3) \tag{17.58}$$

You can see that we can apply these equations to finding the eigenstates and eigenvalues of any matrix of the form

$$M = M_0 + Q \tag{17.59}$$

where M_0 is a diagonal matrix ($M_{ij} = m_i \delta_{ij}$), and Q is a "perturbation" matrix such that

$$|Q_{ij}| \ll |m_i - m_j| \quad , \quad |Q_{ii}| \ll |m_i| \tag{17.60}$$

Its just a matter of changing notation (replace H_0 by M_0, $E_n^{(0)}$ by m_n, etc.).

Getting back to the original problem, suppose we have found the eigenstates $\{\vec{\phi}_n\}$ from by the perturbative method (eq. (17.58)), or by some other method, and then normalized the states so that

$$\vec{\phi}_n \cdot \vec{\phi}_n = 1 \tag{17.61}$$

Now suppose we use the states $\{\phi_n\}$ to span the Hilbert space, instead of the set $\{\phi_n^{(0)}\}$. Then you can easily see that in this new basis, it is the matrix H, rather than H_0, which is diagonal

$$
H = \begin{bmatrix}
E_1 & 0 & 0 & \ldots \\
0 & E_2 & 0 & \ldots \\
0 & 0 & E_3 & \ldots \\
. & . & . & \ldots \\
. & . & . & \ldots
\end{bmatrix}
\tag{17.62}
$$

because

$$
H_{ij} = \langle \phi_i | H | \phi_j \rangle = \delta_{ij} E_j
\tag{17.63}
$$

It is for this reason that the process of solving the Hamiltonian eigenvalue equation $H\phi_n = E_n\phi_n$ is often referred to as *"diagonalizing the Hamiltonian"*.

17.4 Degenerate Perturbation Theory

The energy eigenvalues of the Hydrogen atom are degenerate. The energy eigenstates ϕ_{nlm} depend on quantum numbers n, l, m, but the energy eigenvalues depend only on n. As we found back in chapter 10, this degeneracy is typical when the Hamiltonian is invariant with respect to some symmetry operations (e.g. rotation around the x, y or z axes) which don't commute with each other.

But now if we try to apply perturbation theory to a Hamiltonian with degenerate energy eigenvalues, we can immediately see that there is a problem. Consider, e.g. the first-order correction to the wavefunction

$$
\phi_n^{(1)} = \sum_{i \neq n} \frac{V_{in}}{E_n^{(0)} - E_i^{(0)}} \phi_i^{(0)}
\tag{17.64}
$$

Obviously, if there is some energy $E_k^{(0)}$ such that $E_n^{(0)} = E_k^{(0)}$, then the right-hand side of this equation is not small, it is infinite. That is not exactly a small perturbation! What can be done in this case, which is quite typical in atomic physics?

First of all, to simplify things a little bit, lets suppose that there is just one set of states with degenerate energy eigenvalues, and that these are the states $\phi_n^{(0)}$ labeled by $n = 1, 2, ..., q$, i.e.

$$
E_1^{(0)} = E_2^{(0)} = ... = E_q^{(0)}
\tag{17.65}
$$

The first-order correction to the wavefunction is derived from eq. (17.26) with $N = 1$ and $i \neq n$, and requires

$$
(E_i^{(0)} - E_n^{(0)})c_{ni}^1 = -\langle \phi_i^{(0)} | V | \phi_n^{(0)} \rangle
\tag{17.66}
$$

Now if $i, n \leq q$, then $E_i^{(0)} = E_n^{(0)}$ and the lhs of the equation is zero. But this is impossible unless

$$
\langle \phi_i^{(0)} | V | \phi_n^{(0)} \rangle = 0
\tag{17.67}
$$

for all $i, n < q$ with $i \neq n$, which is generally not the case.

The way out of this dilemma is to first notice that the set of $\{\phi_n^{(0)}, n = 1, 2, ..., q\}$ spans a finite, q-dimensional subspace of the full Hilbert space, and *any* state in this subspace is an eigenstate of H_0, with the same degenerate energy $E_1^{(0)} = E_2^{(0)} = ...$ Then let $\overline{V}$ be the Hermitian, $q \times q$ matrix, whose matrix elements are

$$\overline{V}_{ij} = \langle \phi_i^{(0)}|V|\phi_j^{(0)} \rangle \qquad i, j \leq q \tag{17.68}$$

By the usual theorems about Hermitian operators (which also apply to Hermitian matrices), the eigenstates $\{\varphi_n, n = 1, 2, ..., q\}$ of $\overline{V}$

$$\overline{V}\varphi_n = \mathcal{E}_n \varphi_n \tag{17.69}$$

span the *same* q-dimensional Hilbert space as the $\{\phi_n^{(0)}, n = 1, 2, ..., q\}$, and moreover, for $i \neq n$

$$\langle \varphi_i^{(0)}|V|\varphi_n^{(0)} \rangle = 0 \tag{17.70}$$

providing all the $\mathcal{E}_n$ are different (which we will assume).

This means that if we replace the initial set of eigenstates $\{\phi_n^{(0)}\}$ of H_0 with a new set of zeroth-order eigenstates

$$\phi_n'^{(0)} = \begin{cases} \varphi_n & n \leq q \\ \phi_n^{(0)} & n > q \end{cases} \tag{17.71}$$

then eq. (17.26) is automatically satisfied for $i, n \leq q$

$$0 = (E_i^{(0)} - E_n^{(0)})c_{ni}^1 = -\langle \phi_i'^{(0)}|V|\phi_n'^{(0)} \rangle = 0 \tag{17.72}$$

We can then consistently take

$$c_{ni}^1 = 0 \quad \text{for} \quad i, n \leq q \tag{17.73}$$

Given the new set of zeroth-order wavefunctions $\{\phi_n'^{(0)}\}$, perturbation theory can be applied exactly as in the non-degenerate case, and we find for the first order corrections that

$$\begin{aligned}
\phi_n^{(1)} &= \sum_{i>q} \frac{\langle \varphi_n|V|\phi_i^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}} \phi_i^{(0)} \quad \text{for} \quad n \leq q \\
\phi_n^{(1)} &= \sum_{i \neq n} \frac{\langle \phi_n^{(0)}|V|\phi_i'^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}} \phi_i'^{(0)} \quad \text{for} \quad n > q \\
E_n^{(1)} &= \langle \phi_n'^{(0)}|V|\phi_n'^{(0)} \rangle \\
&= \begin{cases} \mathcal{E}_n & n \leq q \\ \langle \phi_n|V|\phi_n \rangle & n > q \end{cases}
\end{aligned} \tag{17.74}$$

17.4.1   Diagonalizing the Submatrix

Equations (17.74) give the perturbative solutions to $H\phi_n = E_n\phi_n$ to first order in λ, when the first q energy eigenvalues are degenerate, providing one can solve the eigenvalue equation

$$\overline{V}\,\varphi_n = \mathcal{E}_n\varphi_n \tag{17.75}$$

Since the first q eigenstates $\{\phi_n^{(0)},\ n = 1, 2, ..., q\}$ are a basis of the q-dimensional subspace, we can write

$$\varphi_n = \sum_{i=0}^{q} a_{ni}\phi_i^{(0)} \tag{17.76}$$

Writing the $\{\phi_n^{(0)}, n = 1, 2, ..q\}$ as basis vectors, as in eq. (17.55), we can write the eigenvectors φ_n in the q-dimensional subspace in the form

$$\vec{\varphi}_n = \begin{bmatrix} a_{n1} \\ a_{n2} \\ a_{n3} \\ . \\ . \\ . \\ a_{nq} \end{bmatrix} \tag{17.77}$$

(In the full Hilbert space φ_n is an infinite-component vector, with zeros following a_{nq}.) Then, in matrix notation, the eigenvalue problem (17.75) is simply

$$\begin{bmatrix} V_{11} & V_{12} & V_{13} & . & . & V_{1q} \\ V_{21} & V_{22} & V_{23} & . & . & V_{2q} \\ V_{31} & V_{32} & V_{33} & . & . & V_{3q} \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ V_{q1} & V_{q2} & V_{q3} & . & . & V_{qq} \end{bmatrix} \vec{\varphi}_n = \mathcal{E}_n\vec{\varphi}_n \tag{17.78}$$

We have already discussed how to solve the eigenvalue problem for a 2×2 matrix, for example in solving for the eigenstates of the Pauli spin matrix σ_y in Chapter 13. In general, one first solves for the eigenvalues $\mathcal{E}_n$ by solving the **secular equation**

$$\det[\overline{V} - \mathcal{E}I] = 0 \tag{17.79}$$

where I is the $q \times q$ unit matrix. The secular equation is a q-th order polynomial which (in general) has q roots. These roots are the set of eigenvalues of the matrix $\overline{V}$, which we have denoted $\{\mathcal{E}_n\}$. Then, for each eigenvalue, we solve for the vector $\vec{\varphi}_n$ in eq. (17.78) algebraically (as illustrated for the eigenstates of σ_y in Chapter 13).

17.4.2   Example - The Two-Dimensional Harmonic Oscillator

The Hamiltonian for a harmonic oscillator in two dimensions is

$$H_0 = -\frac{\hbar^2}{2M} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right] + \frac{1}{2}k(x^2 + y^2) \tag{17.80}$$

This system is symmetric with respect to rotations (around the z-axis), reflections ($x \to -x$ and $y \to -y$), and interchange $x \to y$, $y \to x$. Its not hard to verify that these symmetries do not all commute with each other, and therefore at least some of the energy eigenvalues must be degenerate. In fact, it is easy to solve for the eigenvalues and eigenstates of H_0 by the method of separation of variables. Writing

$$H_0 = h[x] + h[y] \tag{17.81}$$

where $h[x]$ and $h[y]$ are one-dimensional harmonic oscillator Hamiltonians in the x and y coordinates respectively, and

$$\phi_{mn}^{(0)}(x, y) = \phi_m(x)\phi_n(y) \tag{17.82}$$

we end up with the one-dimensional harmonic oscillator eigenvalue equations

$$\begin{aligned} h[x]\phi_m(x) &= E_m\phi_m(x) \\ h[y]\phi_n(y) &= E_n\phi_n(y) \end{aligned} \tag{17.83}$$

with the total energy eigenvalue of $\phi_{mn}^{(0)}(x, y)$ being

$$E_{nm}^{(0)} = E_m + E_n \tag{17.84}$$

The eigenvalue equations (17.83) we have solved long ago using raising/lowering operators. In this case, we should introduce separate raising/lowering operators in the x and y coordinates, i.e.

$$\begin{aligned} a &= \frac{1}{\sqrt{2\hbar}} \left(\sqrt{M\omega}x + i\frac{p_x}{\sqrt{M\omega}} \right) \\ b &= \frac{1}{\sqrt{2\hbar}} \left(\sqrt{M\omega}y + i\frac{p_y}{\sqrt{M\omega}} \right) \end{aligned} \tag{17.85}$$

with commutator relations

$$[a, a^\dagger] = [b, b^\dagger] = 1 \tag{17.86}$$

and

$$[a, b] = [a, b^\dagger] = [a^\dagger, b] = [a^\dagger, b^\dagger] = 0 \tag{17.87}$$

In terms of these operators, the two dimensional harmonic oscillator is simply

$$H_0 = \hbar\omega(a^\dagger a + b^\dagger b + 1) \tag{17.88}$$

and the $\phi_m(x)$ and $\phi_n(y)$ are one-dimensional harmonic oscillator eigenstates. The total energy eigenvalue is the sum of $E_m + E_m$

$$
\begin{aligned}
\phi_{mn}^{(0)}(x, y) &= \phi_m(x)\phi_n(y) \\
E_{mn}^{(0)} &= \hbar\omega(m + n + 1)
\end{aligned}
\tag{17.89}
$$

Its easy to see that the energy $E_{00}^{(0)}$ is unique, that $E_{01}^{(0)} = E_{10}^{(0)}$ is two-fold degenerate, $E_{20}^{(0)} = E_{11}^{(0)} = E_{02}^{(0)}$ is three-fold degenerate, and so on (in general, the energy E_{mn}^0 is $(m + n + 1)$-fold degenerate).

Now introduce a perturbing potential $V' = \lambda xy$,

$$
H = H_0 + \lambda xy
\tag{17.90}
$$

As an exercise in degenerate perturbation theory, we will now compute the correction to the energies $E_{10}^{(0)} = E_{01}^{(0)}$ of the first excited states.

The first two excited states with degenerate energy eigenvalues, ϕ_{10} and ϕ_{01}, span a two-dimensional subspace of the Hilbert space. Our first task is to find the eigenstates of the 2×2 matrix

$$
\overline{V} = \begin{bmatrix} \langle\phi_{10}|xy|\phi_{10}\rangle & \langle\phi_{10}|xy|\phi_{01}\rangle \\ \langle\phi_{01}|xy|\phi_{10}\rangle & \langle\phi_{01}|xy|\phi_{01}\rangle \end{bmatrix}
\tag{17.91}
$$

Using

$$
xy = \frac{1}{2\beta^2}(a + a^\dagger)(b + b^\dagger) \qquad \beta \equiv \sqrt{\frac{M\omega}{\hbar}}
\tag{17.92}
$$

we get

$$
\begin{aligned}
\langle\phi_{10}|xy|\phi_{10}\rangle &= \frac{1}{2\beta^2}\langle\phi_1(x)|(a + a^\dagger)|\phi_1(x)\rangle\langle\phi_0(y)|(b + b^\dagger)|\phi_0(y)\rangle = 0 \\
\langle\phi_{01}|xy|\phi_{01}\rangle &= \frac{1}{2\beta^2}\langle\phi_0(x)|(a + a^\dagger)|\phi_0(x)\rangle\langle\phi_1(y)|(b + b^\dagger)|\phi_1(y)\rangle = 0 \\
\langle\phi_{10}|xy|\phi_{01}\rangle &= \frac{1}{2\beta^2}\langle\phi_1(x)|(a + a^\dagger)|\phi_0(x)\rangle\langle\phi_0(y)|(b + b^\dagger)|\phi_1(y)\rangle = \frac{1}{2\beta^2} \\
\langle\phi_{01}|xy|\phi_{10}\rangle &= \frac{1}{2\beta^2}\langle\phi_0(x)|(a + a^\dagger)|\phi_1(x)\rangle\langle\phi_1(y)|(b + b^\dagger)|\phi_0(y)\rangle = \frac{1}{2\beta^2}
\end{aligned}
\tag{17.93}
$$

and therefore

$$
\overline{V} = \frac{1}{2\beta^2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}
\tag{17.94}
$$

The problem of finding the eigenvectors and eigenvalues ("diagonalizing") the matrix $\overline{V}$ is pretty much the same as solving the eigenvalue problem for the Pauli matrix σ_x. First we solve the secular equation

$$
\det[\overline{V} - \mathcal{E}I] = \mathcal{E}^2 - \left(\frac{1}{2\beta^2}\right)^2 = 0
\tag{17.95}
$$

to find two roots

$$\mathcal{E}_\pm = \pm\frac{1}{2\beta^2} \tag{17.96}$$

corresponding to eigenstates

$$\phi_+ = a\phi_{10} + b\phi_{01}$$
$$\phi_- = c\phi_{10} + d\phi_{01} \tag{17.97}$$

We find these eigenstates by solving

$$\frac{1}{2\beta^2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} a \\ b \end{bmatrix} = \frac{1}{2\beta^2}\begin{bmatrix} a \\ b \end{bmatrix}$$
$$\frac{1}{2\beta^2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} c \\ d \end{bmatrix} = -\frac{1}{2\beta^2}\begin{bmatrix} c \\ d \end{bmatrix} \tag{17.98}$$

subject to the condition that

$$\langle\phi_+|\phi_+\rangle = a^2 + b^2 = 1$$
$$\langle\phi_-|\phi_-\rangle = c^2 + d^2 = 1 \tag{17.99}$$

The solutions are

$$\phi_+ = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}$$
$$= \frac{1}{\sqrt{2}}[\phi_{10} + \phi_{01}]$$
$$\phi_- = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}$$
$$= \frac{1}{\sqrt{2}}[\phi_{10} - \phi_{01}] \tag{17.100}$$

Instead of two degenerate energies, $E_{10} = E_{01}$, we now have energy eigenvalues to first order in λ

$$H\phi_+ = E_+\phi_+$$
$$H\phi_- = E_-\phi_- \tag{17.101}$$

where $E = E^{(0)} + \lambda\mathcal{E}$, i.e.

$$E_+ = E_{10} + \frac{\lambda}{2\beta^2}$$
$$E_- = E_{10} - \frac{\lambda}{2\beta^2} \tag{17.102}$$

We say that the degeneracy is "lifted at first order" by the perturbation.

17.4.3   Example - The Stark Effect

The Stark Effect is a splitting of spectral lines due to the (partial) lifting of atomic energy level degeneracy by an external electric field.

Let us suppose that the electric field is directed along the z-axis. The Hamiltonian of the Hydrogen atom is then

$$
\begin{aligned}
H_0 &= \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} \right) - eE_z z \\
&= H_0 + \lambda V
\end{aligned}
\tag{17.103}
$$

where this time

$$
\lambda = eE_z \quad \text{and} \quad V = z
\tag{17.104}
$$

Since the ground state energy is non-degenerate (only the ϕ_{100} state has this energy at zero-th order), the lifting of degeneracy first occurs at $n = 2$. There are four states at $n = 2$ with the same energy $E_2^{(0)}$

$$
|\phi_{nlm}\rangle = |nlm\rangle = |200\rangle , \quad |211\rangle , \quad |210\rangle , \quad |21-1\rangle
\tag{17.105}
$$

which span a 4×4 subspace of Hilbert space. We first have to compute the 4×4 $\overline{V}$ matrix with matrix elements $\langle 2l_1 m_1|z|2l_2 m_2\rangle$.

Consider the case $m_1 \neq m_2$. Then

$$
\langle 2l_1 m_1|z|2l_2 m_2\rangle \sim \int_0^{2\pi} d\phi e^{i(m_2-m_1)} = 0
\tag{17.106}
$$

since $z = r\cos(\theta)$ doesn't depend on ϕ. Therefore only terms with $m_1 = m_2$ are non-zero. Next, consider $l_1 = l_2$, where we find

$$
\langle 2lm|z|2lm\rangle \sim \int d\Omega |Y_{lm}|^2 \cos(\theta) = 0
\tag{17.107}
$$

This is essentially because $|Y_{lm}|^2 > 0$ is an even function around $\theta = \pi/2$, while $\cos(\theta)$ is an odd function for reflections around $\pi/2$.

Thus, the only non-zero matrix elements in this subspace are

$$
\begin{aligned}
\langle 210|z|200\rangle &= \langle 200|z|210\rangle \\
&= \int dr r^2 \int d\Omega \phi_{200} z \phi_{210} \\
&= \int dr r^2 \int d\Omega \frac{2}{(2a_0)^{3/2}}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} Y_{00} \times \\
&\quad \times r\cos(\theta)\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}Y_{10}(\theta,\phi) \\
&= 3a_0
\end{aligned}
\tag{17.108}
$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius. The secular equation is then

$$\det[\overline{V} - \mathcal{E}I]$$

$$= \det \begin{bmatrix} \langle 200|z|200\rangle - \mathcal{E} & \langle 200|z|211\rangle & \langle 200|z|210\rangle & \langle 200|z|21-1\rangle \\ \langle 211|z|200\rangle & \langle 211|z|211\rangle - \mathcal{E} & \langle 211|z|210\rangle & \langle 211|z|21-1\rangle \\ \langle 210|z|200\rangle & \langle 210|z|211\rangle & \langle 210|z|210\rangle - \mathcal{E} & \langle 210|z|21-1\rangle \\ \langle 21-1|z|200\rangle & \langle 21-1|z|211\rangle & \langle 21-1|z|210\rangle & \langle 21-1|z|21-1\rangle - \mathcal{E} \end{bmatrix}$$

$$= \det \begin{bmatrix} -\mathcal{E} & 0 & 3a_0 & 0 \\ 0 & -\mathcal{E} & 0 & 0 \\ 3a_0 & 0 & -\mathcal{E} & 0 \\ 0 & 0 & 0 & -\mathcal{E} \end{bmatrix}$$

$$= \mathcal{E}^4 - (3a_0)^2 \mathcal{E}^2$$

$$= 0 \tag{17.109}$$

The roots of the secular equation are

$$\mathcal{E} = 0, \ 3a_0, \ -3a_0 \tag{17.110}$$

Therefore the 4-fold degenerate E_2 energy level splits into three (not four) levels

$$E_2 \implies \begin{cases} E_2 + 3a_0 e E_z \\ E_2 \\ E_2 - 3a_0 e E_z \end{cases} \tag{17.111}$$

Because the subspace is four-dimensional, but the perturbation results only in three distinct energies, the degeneracy is not entirely lifted; a subset of states in this 4D subspace still have degenerate energies.

Next we figure out the eigenstates corresponding to the $n = 2$ energy eigenvalues at first order. We can always express a general state in the subspace spanned by the zeroth-order $n = 2$ state as a superposition

$$|\psi\rangle = a|\phi_{200}\rangle + b|\phi_{211}\rangle + c|\phi_{210}\rangle + d|\phi_{20-1}\rangle \tag{17.112}$$

In vector notation, we can write

$$\vec{\psi} = \begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} \tag{17.113}$$

and the eigenvalue equation

$$\overline{V}\psi = \mathcal{E}\psi \tag{17.114}$$

becomes

$$\begin{bmatrix} 0 & 0 & 3a_0 & 0 \\ 0 & 0 & 0 & 0 \\ 3a_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} = \mathcal{E} \begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} \tag{17.115}$$

There are three values of $\mathcal{E}$ to consider:

Case I: $\mathcal{E} = 3a_0$

Matrix multiplication on the left hand side of (17.115) gives us

$$3a_0 \begin{bmatrix} c \\ 0 \\ a \\ 0 \end{bmatrix} = 3a_0 \begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} \tag{17.116}$$

from which we conclude that

$$c = a \ , \quad b = d = 0 \tag{17.117}$$

Normalization of

$$\vec{\phi} = \begin{bmatrix} a \\ 0 \\ a \\ 0 \end{bmatrix} \tag{17.118}$$

gives us $a = 1/\sqrt{2}$. So to first order in $\lambda = eE_z$ we have an eigenstate

$$|\phi\rangle_{E_{2+}} = \frac{1}{\sqrt{2}} \Big[|\phi_{200}\rangle + |\phi_{210}\rangle \Big] \tag{17.119}$$

for energy eigenvalue

$$E_{2+} = E_2^{(0)} + 3ea_0 E_z \tag{17.120}$$

Case II: $\mathcal{E} = -3a_0$

$$3a_0 \begin{bmatrix} c \\ 0 \\ a \\ 0 \end{bmatrix} = -3a_0 \begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} \tag{17.121}$$

and therefore

$$c = -a \ , \quad b = d = 0 \tag{17.122}$$

Normalization of

$$\vec{\phi} = \begin{bmatrix} a \\ 0 \\ -a \\ 0 \end{bmatrix} \tag{17.123}$$

still gives $a = 1/\sqrt{2}$, leading to the eigenstate

$$|\phi\rangle_{E_{2-}} = \frac{1}{\sqrt{2}}\Big[|\phi_{200}\rangle - |\phi_{210}\rangle\Big] \qquad (17.124)$$

for energy eigenvalue

$$E_{2-} = E_2^{(0)} - 3ea_0 E_z \qquad (17.125)$$

Case III: $\mathcal{E} = 0$

Finally, we consider $\mathcal{E} = 0$, and eq. (17.115) becomes

$$3a_0 \begin{bmatrix} c \\ 0 \\ a \\ 0 \end{bmatrix} = 0 \qquad (17.126)$$

This time, we can only conclude that $a = c = 0$, and that any normalized eigenstate of the form

$$|\phi\rangle_{E_2} = a|\phi_{211}\rangle + b|\phi_{21-1}\rangle \qquad (17.127)$$

has an energy eigenvalue

$$E_2 = E_2^{(0)} \qquad (17.128)$$

The normalization condition in this case only tells us that

$$a^2 + b^2 = 1 \qquad (17.129)$$

and therefore the linearly independent eigenstates with energy E_2 span a two-dimensional subspace of the full Hilbert space. Thus the perturbation does not remove *all* of the degeneracy in energy eigenvalues; there is still some left.

The reason that there is still some degeneracy left, as seen in the $\mathcal{E} = 0$ case, is that there is still some symmetry left after the external electric field is applied. For an electric field directed along the z-axis, the Hamiltonian is still invariant with respect to rotations around the z-axis, as well as reflections along the x and y-axes; the result is some remnant degeneracy in the energy eigenvalues.

Chapter 18

Time-Dependent Perturbation Theory

Thus far we have always assumed that the potential $V(x)$ in the Schrodinger equation is time-independent. But nothing in this world is completely time independent, and some of the most interesting, and technologically important, aspects of atomic physics concern the interaction of atoms with electromagnetic radiation. Electromagnetic waves consist of orthogonal electric and magnetic fields which oscillate, at any point, harmonically in time. If the field strength is small enough, then the associated electrostatic potential can be viewed as a small, time-varying perturbation to the usual Hamiltonian of the atom. So to understand the effect of electromagnetic waves on atomic electrons, we need to develop methods for dealing with time-dependent perturbations of the atomic potential.

Let us then consider time-dependent Hamiltonians of the form

$$H = H_0 + \lambda V(x, t) \tag{18.1}$$

where we assume that the eigenstates of H_0, now denoted φ_n,

$$H_0 \varphi_n(x) = E_n \varphi_n(x) \tag{18.2}$$

are known. Denote the corresponding energy-eigenstate solutions of the time-dependent Schrodinger equation by

$$\psi_n(x, t) = \varphi_n(x) e^{-i\omega_n t} \qquad \omega_n = \frac{E_n}{\hbar} \tag{18.3}$$

Just to have a definite picture in mind, we might imagine that the φ_n are the energy eigenstates of the Hydrogen atom, and the time-varying potential $\lambda V(x, t)$ is the electrostatic potential, at point x, of an incident electromagnetic wave. The question we are interested in answering is this: If the electron starts out at time t_0 in

a given orbital φ_n, what is the probability that the incident radiation will result in the electron being found in the orbital φ_m at some later time t?

To begin with, since the states $\{\psi_n(x,t)\}$ span the Hilbert space at any time t, we can always expand the solution of the time-dependent Schrodinger equation $\psi(x,t)$, at any time t, in that basis:

$$\psi(x,t) = \sum_n c_n(t)\psi_n(x,t) \tag{18.4}$$

The initial value problem, i.e. "given $\psi(x,0)$, find $\psi(x,t)$," can be phrased as: given $\{c_n(0)\}$, find $\{c_n(t)\}$. Substituting (18.4) into the time-dependent Schrodinger equation

$$i\hbar \frac{d}{dt}\psi = (H_0 + \lambda V)\psi \tag{18.5}$$

to get

$$i\hbar \sum_n \left(\frac{dc_n}{dt} - i\omega_n c_n\right)\psi_n = \sum_n \left(\hbar\omega_n + \lambda V\right)c_n\psi_n \tag{18.6}$$

Cancelling terms on each side proportional to $\hbar\omega_n$, and going to ket notation

$$i\hbar \sum_n \frac{dc_n}{dt}|\psi_n\rangle = \sum_n \lambda V c_n|\psi_n\rangle \tag{18.7}$$

Multiply both sides by $\langle\psi_k|$

$$i\hbar \frac{dc_k}{dt} = \lambda \sum_n \langle\psi_k|V|\psi_n\rangle c_n \tag{18.8}$$

Obviously, the solutions $c_n = c_n(t)$ are are actually functions of both time *and* λ. We can therefore expand the c_n in a Taylor series around $\lambda = 0$

$$
\begin{aligned}
c_k(t) &= c_k^{(0)} + \lambda c_k^{(1)}(t) + \lambda^2 c_k^{(2)}(t) + ... \\
c_k^{(n)}(t) &= \frac{1}{n!}\left(\frac{d^n c_k}{d\lambda^n}\right)_{\lambda=0}
\end{aligned}
\tag{18.9}
$$

Substituting this expansion into (18.8)

$$i\hbar \left[\frac{dc_k^{(0)}}{dt} + \lambda\frac{dc_k^{(1)}}{dt} + \lambda^2\frac{dc_k^{(2)}}{dt} + ...\right] = \sum_n \langle\psi_k|V|\psi_n\rangle \left[\lambda c_n^{(0)} + \lambda^2 c_n^1 + \lambda^3 c_n^{(2)} + ...\right] \tag{18.10}$$

and equating equal powers of λ on the right and left-hand sides gives an infinite set of equations

$$i\hbar \frac{dc_k^{(0)}}{dt} = 0$$

$$ i\hbar \frac{dc_k^{(1)}}{dt} = \sum_n \langle \psi_k | V | \psi_n \rangle c_n^{(0)} $$

$$ i\hbar \frac{dc_k^{(2)}}{dt} = \sum_n \langle \psi_k | V | \psi_n \rangle c_n^{(1)} $$

$$ ... = ... $$

$$ i\hbar \frac{dc_k^{(m+1)}}{dt} = \sum_n \langle \psi_k | V | \psi_n \rangle c_n^{(m)} $$

$$ ... = ... \tag{18.11} $$

This set can be solved iteratively, starting from knowledge of the set $\{c_n^{(0)}\}$.

Suppose that initially (say at $t \to -\infty$), before the perturbation is turned on, the system was in an energy eigenstate of the unperturbed Hamiltonian φ_l. For example, in the case we have in mind, perhaps the electron of a Hydrogen atom is in some definite orbital before a laser, aimed at the atom, is turned on. Then we have

$$ c_n(t \to -\infty) = c_n^{(0)} = \delta_{nl} \tag{18.12} $$

Substituting into the equation for $dc_k^{(1)}/dt$,

$$ i\hbar \frac{dc_k^{(1)}}{dt} = \langle \psi_k | V | \psi_l \rangle \tag{18.13} $$

which is integrated to yield

$$ c_k^{(1)}(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} dt_1 \langle \psi_k(t_1) | V(t_1) | \psi_l(t_1) \rangle \tag{18.14} $$

Likewise,

$$ i\hbar \frac{dc_k^{(2)}}{dt} = \sum_n \langle \psi_k | V | \psi_l \rangle c_n^{(1)} \tag{18.15} $$

is integrated to

$$ c_k^{(2)}(t) = \frac{1}{i\hbar} \sum_{n_1} \int_{-\infty}^{t} dt_1 \langle \psi_k(t_1) | V(t_1) | \psi_{n_1}(t_1) \rangle c_{n_1}^{(1)}(t_1) \tag{18.16} $$

inserting (18.14)

$$ c_k^{(2)}(t) = \left(\frac{1}{i\hbar} \right)^2 \sum_{n_1} \int_{-\infty}^{t} dt_1 \langle \psi_k(t_1) | V(t_1) | \psi_{n_1}(t_1) \rangle \int_{-\infty}^{t_1} dt_2 \langle \psi_{n_1}(t_2) | V(t_2) | \psi_l(t_2) \rangle \tag{18.17} $$

By induction, its not hard to see that

$$ c_k^{(m)}(t) = \left(\frac{1}{i\hbar} \right)^m \sum_{n_1, n_2, ..., n_{m-1}} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 ... \int_{-\infty}^{t_{m-1}} dt_m \langle \psi_k(t_1) | V(t_1) | \psi_{n_1}(t_1) \rangle \times $$

$$ \times \quad \langle \psi_{n_1}(t_2) | V(t_2) | \psi_{n_2}(t_2) \rangle \langle \psi_{n_2}(t_3) | V(t_3) | \psi_{n_3}(t_3) \rangle ... \langle \psi_{n_{m-1}}(t_m) | V(t_m) | \psi_l(t_m) \rangle \tag{18.18} $$

or, using

$$\begin{aligned} |\psi_n(t)\rangle &= e^{-i\omega_n t}|\varphi_n\rangle \\ \langle\psi_n(t)| &= e^{i\omega_n t}\langle\varphi_n| \end{aligned}$$

(18.19)

we have in general

$$c_k^{(m)}(t) = \left(\frac{1}{i\hbar}\right)^m \sum_{n_1,n_2,\dots,n_{m-1}} \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \dots \int_{-\infty}^{t_{m-1}} dt_m$$

$$e^{i(\omega_k-\omega_{n_1})t_1} e^{i(\omega_{n_1}-\omega_{n_2})t_2} \dots e^{i(\omega_{n_{m-1}}-\omega_l)t_m} \times$$

$$\times \langle\varphi_k|V(t_1)|\varphi_{n_1}\rangle\langle\varphi_{n_1}|V(t_2)|\varphi_{n_2}\rangle\langle\varphi_{n_2}|V(t_3)|\varphi_{n_3}\rangle\dots\langle\varphi_{n_{m-1}}|V(t_m)|\varphi_l\rangle$$

(18.20)

In what follows, we really only need the coefficients $c_k(t)$ to first order in λ:

$$c_k^{(1)}(t) = \frac{1}{i\hbar} \int_{-\infty}^t dt' e^{i(\omega_k-\omega_l)t'} \langle\varphi_k|V(t')|\varphi_l\rangle$$

(18.21)

It is also often the case that the perturbing potential factorizes into time and space-dependent pieces,

$$\lambda V(x,t) = \lambda v(x)f(t)$$

(18.22)

so that to first order

$$c_k(t) = \delta_{kl} + \lambda c_k^{(1)}(t) = \delta_{kl} + \lambda\langle\varphi_k|v|\varphi_l\rangle\frac{1}{i\hbar}\int_{-\infty}^t dt' e^{i(\omega_k-\omega_l)t'} f(t')$$

(18.23)

Then the transition probability $P_{l\to k}$ for the system, initially in state ψ_l at time $t \to -\infty$, to be found in a different state ψ_k, $k \ne l$ at time t, is just

$$\begin{aligned} P_{l\to k} &= \left|\langle\psi_k(t)|\psi(t)\rangle\right|^2 \\ &= \left|c_k(t)\right|^2 \\ &= \lambda^2\frac{1}{\hbar^2}\left|\langle\varphi_k|v|\varphi_l\rangle\right|^2 \left|\int_{-\infty}^t dt' e^{i(\omega_k-\omega_l)t'} f(t')\right|^2 \end{aligned}$$

(18.24)

18.1 Harmonic Perturbations

As already mentioned, the electric potential associated with electromagnetic radiation varies harmonically in time. Let us then consider a time-dependent potential of the form

$$\lambda V(x,t) = \begin{cases} 0 & t \le 0 \\ \lambda v(r)2\cos(\omega t) & t > 0 \end{cases}$$

(18.25)

Again we imagine that the system is in the state ψ_l at $t \le 0$, so that $c_k(0) = c_k^0 = \delta_{kl}$. Substituting (18.25) into (18.23) gives us, for $k \ne l$,

$$
\begin{aligned}
c_k(t) &= \lambda c_k^{(1)}(t) \\
&= \lambda \langle \varphi_k | v | \varphi_l \rangle \frac{1}{i\hbar} \int_0^t dt'\; e^{i(\omega_k - \omega_l)t'} \left[e^{i\omega t'} + e^{-i\omega t'} \right] \\
&= -\lambda \langle \varphi_k | v | \varphi_l \rangle \frac{1}{i\hbar} \left[\frac{e^{i(\omega_{kl} - \omega)t} - 1}{\omega_{kl} - \omega} + \frac{e^{i(\omega_{kl} + \omega)t} - 1}{\omega_{kl} + \omega} \right] \\
&= -2i\lambda \langle \varphi_k | v | \varphi_l \rangle \frac{1}{\hbar} \left[\frac{e^{i(\omega_{kl} - \omega)t/2}}{\omega_{kl} - \omega} \sin[\frac{1}{2}(\omega_{kl} - \omega)t] + \right. \\
&\quad \left. + \frac{e^{i(\omega_{kl} + \omega)t/2}}{\omega_{kl} + \omega} \sin[\frac{1}{2}(\omega_{kl} + \omega)t] \right]
\end{aligned}
\tag{18.26}
$$

where we have defined

$$
\omega_{kl} = \omega_k - \omega_l = \frac{E_k - E_l}{\hbar}
\tag{18.27}
$$

Clearly, the transition probability $P_{lk} = |c_k|^2$ is going to be largest when the angular frequency ω of the perturbing potential is equal to either ω_{kl} or $-\omega_{kl}$, i.e

$$
\begin{array}{lll}
\hbar\omega = E_k - E_l & \text{``absorbtion''} & (E_k > E_l) \\
\hbar\omega = E_l - E_k & \text{``stimulated emission''} & (E_l > E_k)
\end{array}
\tag{18.28}
$$

The terms "absorbtion" and "stimulated emission" refer to atomic electrons in the field of an electromagnetic wave. According to the Einstein-Bohr picture, the incoming radiation consists of photons, each of energy $E = hf = \hbar\omega$. An electron, initially in an orbital with energy E_l, absorbs a photon of energy $\hbar\omega$ from the incoming electromagnetic radiation, and jumps into a higher energy state $E_k = E_l + \hbar\omega$. This is the absorbtion case.

But from our result (18.25) we draw some conclusions which cannot easily be anticipated from the Bohr model. The first surprise is that, in addition to absorbtion, where the electron gobbles up a photon and jumps to a higher energy, there is also the phenomenon of stimulated emission, in which the incoming radiation "stimulates" an electron in an excited state with energy E_l to jump down to a *lower* energy state with energy E_k. In this case the electron does not absorb a photon (in fact it emits one, although we cannot demonstrate that here). The two cases are illustrated in Fig. 18.1. There is no simple classical picture of stimulated emission; it is an intrinically quantum-mechanical process. Nevertheless, the fact that such a process is required was deduced by Albert Einstein long before the development of modern quantum mechanics based on the Schrodinger equation. Einstein's reasoning was based on the necessities of thermal equilibrium: if absorbtion is possible, stimulated emission is also required. Quantum theory must be consistent with statistical mechanics, and happily the mysterious stimulated emission turns out to be a prediction of the theory.

The second surprise is that although the transition from E_l to E_k by absorbtion is most probable when the incoming radiation has an angular frequency $\omega = (E_k - E_l)/\hbar$, the probability is non-zero away from this value also. In fact, for E_k less than but close to E_l, the transition probability as a function of time is roughly

$$P_{lk}(t) = \lambda^2 \left| \langle \varphi_k | v | \varphi_l \rangle \right|^2 \frac{4}{\hbar^2} \frac{\sin^2 \frac{1}{2}(\omega_{kl} - \omega)t}{(\omega_{kl} - \omega)^2} \tag{18.29}$$

Fig. 18.2 is a graph of the function

$$g(\omega_{kl} - \omega) = \frac{\sin^2 \frac{1}{2}(\omega_{kl} - \omega)t}{(\omega_{kl} - \omega)^2} \tag{18.30}$$

at a fixed time t (it has the same functional form as the intensity vs. distance of a one-slit diffraction pattern). The central peak has a half-width of $2\pi/t$, which means that the expected relation for energy conservation, i.e.

$$E_k = E_l + \hbar\omega \tag{18.31}$$

is only satisfied in the $t \to \infty$ limit. For any finite t, there is a finite probability for (18.31) to be violated. It seems as though we have lost energy conservation! How is this possible?

Of course there is really no breakdown of energy conservation. The *apparent* breakdown, in this case, comes from the assumption that the electromagnetic radiation incident on the atom only contains photons of definite energy $\hbar\omega$; and this assumption actually conflicts with the Heisenberg Uncertainty Principle. Lets see how this works. First of all, if we write

$$\omega_{kl} = \omega + \Delta\omega \tag{18.32}$$

then there will normally only be a transition between orbitals by absorbtion if $\Delta\omega$ is within the "central peak"

$$\Delta\omega \approx \pm \frac{2\pi}{t} \tag{18.33}$$

so the apparent violation of energy conservation is of the order

$$\Delta E = \hbar\Delta\omega = \frac{2\hbar\pi}{t} \tag{18.34}$$

Now by assumption, the perturbing potential was turned on at $t = 0$, so the portion of the electromagnetic wave, containing the photon absorbed by the electron, has an extension in space of $\Delta x = ct$. The electromagnetic wave itself can be thought of as the wavefunction of the photon (a concept which can only be made precise in the framework of relativistic quantum field theory), and this means that if the extension

of the wave is ct, then the photon is localized within this region before absorbtion. Therefore, by the Uncertainty Principle, the photon has an uncertainty in momentum

$$\Delta p \sim \frac{h}{\Delta x} = \frac{h}{ct} \tag{18.35}$$

Using the relativistic relation between energy and momentum for massless particles, $E = pc$, the photons in the beam therefore have an uncertainty in energy of order

$$\Delta E = \frac{2\pi\hbar}{t} \tag{18.36}$$

But this is the same magnitude as the apparent "violation" of energy conservation in (18.31). We conclude that there is no violation at all, and that the failure of the Bohr relation to hold exactly is just a consequence of the Uncertainty Principle applied to photons, which tells us that the energy of photons in an electromagnetic wave of frequency f is not exactly hf, if the wave has a finite extension in space.

Another puzzling fact is the existence of *spontaneous emission* of photons by electrons. This occurs when an electron in an excited orbital emits a photon, and drops to a lower energy orbital, without being subjected to electromagnetic radiation or any other external potential. An external radiation field of the right frequency speeds up (or "stimulates") the process, but emission will occur in any case, eventually. But this fact directly contradicts the notion that the wave functions $\varphi_n(x)$ are eigenstates of energy, and therefore stationary. A stationary state, excited or not, is by definition independent of time; it cannot change unless acted on by an external perturbation.

As it happens, the excited states of the Hydrogen atom are not really eigenstates of energy after all. Non-relativistic quantum mechanics, as taught in this course, is only an approximation to the real world; in particular it is an approximation in which the electromagnetic field is treated classically. In the theory of quantum electrodyamics, an electron is in constant interaction with the quantized electromagnetic field *even in the absence of an external electromagnetic wave.* Excited states of the Hydrogen atom are not eigenstates in quantum electrodynamics, but instead have some uncertainty in energy. From our discussion of the time-energy uncertainty relation in the first semester, it is clear that this uncertainty is related to the average time it takes for the state to change in some noticeable way, e.g. to emit a photon. Let us call this average time τ. Then the uncertainty ΔE in a given atomic orbital is given by

$$\Delta E \approx \frac{\hbar}{\tau} \tag{18.37}$$

The uncertainty in the energy of atomic orbitals leads to a corresponding broadening (spread in frequencies) of the photons emitted in electron transitions between those orbitals.

Finally, I want to mention briefly (and inadequately) a clever and technologically important application of stimulated emission. This is the laser, whose acronym

(as you surely know) stands for "**L**ight **A**mplification by **S**timulated **E**mission of **R**adiation". The simplest version of the scheme involves an atom with three energy levels, of energies $E_2 > E_1 > E_3$, with the property that electrons which are excited (from the ground state at E_0) to level E_2 tend to rapidly (within about 10 ns) emit a photon and fall into the E_1 level, which is comparatively long-lived; on the order of micro- to milli-seconds before emitting a photon. The idea with lasers (or their microwave relatives, the masers), is to excite a great many electrons from the ground state into the E_2 state, from which they fall into the E_1 orbital. With enough energy expended, it is possible to obtain a "population inversion"; i.e. more electrons in the excited state at E_1 than in the ground state. What then happens is that electrons falling from E_1 to the ground state emit photons, and these photons cause other electrons to make the transition to the ground state by stimulated emission. The photons which stimulate the emission, and the emitted photons, have about the same energy (and therefore frequency), and they are in phase. Thus the light is extremely coherent. This is in contrast to the light emitted by thermal radiation (e.g. by a light bulb), where the relative phase in the wavefunction of different photons is random, the black-body distribution of frequencies is broad, and the light is said to be incoherent.

18.1.1   Fermi's Golden Rule

We have seen that the probability of an absorbtion transition is given by the expression

$$P_{lk}(t) = \lambda^2 \left| \langle \varphi_k | v | \varphi_l \rangle \right|^2 \frac{4}{\hbar^2} \frac{\sin^2 \frac{1}{2}(\omega_{kl} - \omega)t}{(\omega_{kl} - \omega)^2} \tag{18.38}$$

with a similar expression for stimulated emission ($\omega_{kl} - \omega \to \omega_{kl} + \omega$). It seems that this expression could be simplified, in the $t \to \infty$ limit, using the identity

$$f(0) = \int d\omega\, f(\omega)\delta(\omega) = \lim_{t \to \infty} \int d\omega\, f(\omega) \frac{2}{\pi} \frac{\sin^2 \frac{1}{2}\omega t}{t\omega^2} \tag{18.39}$$

or, loosely speaking

$$\delta(\omega) = \lim_{t \to \infty} \frac{2}{\pi} \frac{\sin^2 \frac{1}{2}\omega t}{t\omega^2} \tag{18.40}$$

Using this identity, it seems that we can express the transition probability in the $t \to \infty$ limit as

$$P_{lk} = \lambda^2 \frac{2\pi t}{\hbar^2} \left| \langle \varphi_k | v | \varphi_l \rangle \right|^2 \delta(\omega \pm \omega_{kl}) \tag{18.41}$$

At this point we have to stop, because something appears to have gone wrong. A probability proportional to a Dirac δ-function is clearly a breakdown of the notion that a perturbation is supposed to be a small correction.

So lets back up a bit. It is often the case that there is a group K of final states $\{\varphi_{k'}, k' \in K\}$ which have nearly the same energies, i.e.

$$E_{k'} = E_k + \epsilon \qquad (k', k \in K) \tag{18.42}$$

and nearly the same matrix elements

$$\langle \varphi_{k'}|v|\varphi_l \rangle \approx \langle \varphi_k|v|\varphi_l \rangle \qquad (k', k \in K) \tag{18.43}$$

For example, the electron final state might lie in a (conduction) band of energies. Or, for a single atom, we might take into account the possibility that since the energy of an excited orbital is not precise, there is a continuum of possible energies for the emitted photon. Another possibility is the scattering of an electron by a potential, where there is a continuum of possible final momenta $\vec{p}$ with the same energy $E = p^2/2m$. In this situation, we may be interested in the transition probability to any one of a set of final states K in the energy range $[E_k, E_k + \Delta]$.

Let us define the *density of final states*

$$g(E)\delta E \equiv \text{no. of states with energies in the range } [E, E + \delta E] \tag{18.44}$$

Then the transition probability to some member of this set of final states is the integral

$$P_{lK}(t) = \lambda^2 \int_{E_k}^{E_k+\Delta} dE_{k'} g(E_{k'}) \left| \langle \varphi_{k'}|v|\varphi_l \rangle \right|^2 \frac{4}{\hbar^2} \frac{\sin^2 \frac{1}{2}(\omega_{k'l} - \omega)t}{(\omega_{k'l} - \omega)^2} \tag{18.45}$$

For large t, the integrand is very strongly peaked near $E_{k'} = E_l + \hbar\omega$, and we can assume that the matrix element of $v(x)$, and the density of final states $g(E_{k'})$ is nearly constant within the very narrow range of energies in the peak. Then we have

$$P_{lK}(t) = \lambda^2 g(E_k) \left| \langle \varphi_k|v|\varphi_l \rangle \right|^2 \frac{4}{\hbar^2} \int_{E_k}^{E_k+\Delta} dE_{k'} \frac{\sin^2 \frac{1}{2}(\omega_{k'l} \pm \omega)t}{(\omega_{k'l} \pm \omega)^2} \tag{18.46}$$

The quick way to do the integral is to use the large-time limit (18.40)

$$\lim_{t\to\infty} \frac{\sin^2 \frac{1}{2}(\omega_{kl} \pm \omega)t}{(\omega_{kl} \pm \omega)^2} = \frac{1}{2}\pi t \delta(\omega \pm \omega_{kl}) \tag{18.47}$$

and we find that

$$P_{lK}(t) = t \frac{2\pi}{\hbar} g(E_k) \left| \langle \varphi_k|v|\varphi_l \rangle \right|^2 \tag{18.48}$$

The **transition rate** is defined as the probability of transition per unit time. Therefore, differentiating (18.48) wrt t, we derive

Fermi's Golden Rule

The transition rate to some member of a set of "energy-conserving" states with $E_k \approx E_l + \hbar\omega$ is given, after sufficient time, by

$$\Gamma_{lk} = \frac{2\pi}{\hbar} g(E_k) \left| \langle \varphi_k|v|\varphi_l \rangle \right|^2 \tag{18.49}$$

We will postpone application of this rule until we study scattering. However, some examples of the density of final states is called for. Lets begin with the harmonic oscillator in two dimensions, where the energy eigenvalues were found to be

$$E_{n_1 n_2} = \hbar\omega(n_1 + n_2 + 1) = \hbar\omega N \tag{18.50}$$

where $N = n_1 + n_2 + 1$ is an integer in the range $[1, \infty)$ and the degeneracy of each energy is N-fold. Then the number of states lying between $E = \hbar\omega N$ and $E + \Delta E = \hbar\omega(N + \Delta N)$ is approximately

$$
\begin{aligned}
n &= N\Delta N \\
&= \frac{E}{\hbar\omega} \frac{\Delta E}{\hbar\omega} \\
&= \frac{E}{\hbar^2\omega^2}\Delta E \\
&= g(E)\Delta E
\end{aligned}
\tag{18.51}
$$

From this we conclude that for the two-dimensional harmonic oscillator

$$g(E) = \frac{E}{\hbar^2\omega^2} \tag{18.52}$$

A second example is that of a particle in a cubical box of length L. In this case, proceeding as in our discussion of the free electron gas,

$$
\begin{aligned}
E_{n_1 n_2 n_3} &= \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}(n_1^2 + n_2^2 + n_3^2) \\
&= \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2) \\
&= \frac{\pi^2\hbar^2}{2mL^2}R^2
\end{aligned}
\tag{18.53}
$$

The number of states n which lie between R and $R + \Delta R$ is given by the volume of an octant of a spherical shell

$$
\begin{aligned}
n &= \frac{1}{8}\left[\frac{4}{3}\pi(R + \Delta R)^3 - \frac{4}{3}\pi R^3\right] \\
&= \frac{1}{2}\pi R^2\Delta R + O(\Delta R^3)
\end{aligned}
\tag{18.54}
$$

But from (18.53)

$$R = \left(\frac{2mL^2}{\pi^2\hbar^2}\right)^{1/2} E^{1/2} \tag{18.55}$$

so also

$$\Delta R = \frac{1}{2}\left(\frac{2mL^2}{\pi^2\hbar^2}\right)^{1/2} E^{-1/2}\Delta E \tag{18.56}$$

Substituting this expression for R and ΔR into (18.54)

$$
\begin{aligned}
n &= \frac{1}{2}\pi\left(\frac{2mL^2}{\pi^2\hbar^2}\right)E\frac{1}{2}\left(\frac{2mL^2}{\pi^2\hbar^2}\right)^{1/2}E^{-1/2}\Delta E \\
&= \frac{\pi}{4}\left(\frac{2mL^2}{\pi^2\hbar^2}\right)^{3/2}E^{1/2}\Delta E
\end{aligned}
\tag{18.57}
$$

and from this we read off the density of final states

$$
g(E) = \frac{\pi}{4}\left(\frac{2mL^2}{\pi^2\hbar^2}\right)^{3/2}E^{1/2}
\tag{18.58}
$$

18.2 Adiabatic Perturbations

Next we consider the situation where the perturbation is turned on very slowly, so that dV'/dt is negligible (in a sense to be explained shortly). Then, starting from the first order term

$$
c_k^{(1)}(t) = \frac{1}{i\hbar}\int_{-\infty}^{t}dt'V_{kl}(t')e^{i\omega_{kl}t'}
\tag{18.59}
$$

we integrate by parts

$$
\begin{aligned}
c_k^{(1)}(t) &= \frac{1}{i\hbar}\int_{-\infty}^{t}dt'V_{kl}(t')\frac{1}{i\omega_{kl}}\frac{\partial}{\partial t'}e^{i\omega_{kl}t'} \\
&= -\frac{1}{\hbar\omega_{kl}}\int_{-\infty}^{t}dt'V_{kl}(t')\frac{\partial}{\partial t'}e^{i\omega_{kl}t'} \\
&= -\frac{1}{\hbar\omega_{kl}}\left[V_{kl}(t)e^{i\omega_{kl}t} - \int_{-\infty}^{t}dt'\frac{\partial V_{kl}}{\partial t'}e^{i\omega_{kl}t'}\right]
\end{aligned}
\tag{18.60}
$$

Then assuming the time derivative of the potential is negligible,

$$
\begin{aligned}
c_k^{(1)}(t) &\approx -\frac{1}{\hbar\omega_{kl}}V_{kl}(t)e^{i\omega_{kl}t} \\
&= -\frac{\langle\varphi_k|V(t)|\varphi_l\rangle}{E_k^{(0)} - E_l^0}e^{i\omega_{kl}t}
\end{aligned}
\tag{18.61}
$$

The solution to the time-dependent Schrodinger equation, to first order, is

$$
\psi(x,t) = \psi_l(x,t) + \lambda\sum_{k\neq l}\frac{\langle\varphi_k|V(t)|\varphi_l\rangle}{E_l^{(0)} - E_k^0}e^{i\omega_{kl}t}\psi_k(x,t)
\tag{18.62}
$$

and using

$$
\psi_k(x,t) = \varphi_k(x)e^{-i\omega_k t}
\tag{18.63}
$$

we get

$$\psi(x,t) = e^{-i\omega_l t}\left[\varphi_l(x) + \lambda \sum_{k\neq l} \frac{\langle\varphi_k|V(t)|\varphi_l\rangle}{E_l^{(0)} - E_k^0}\varphi_k(x)\right] \tag{18.64}$$

Notice that the expression inside the [...] brackets is the k-th eigenstate, to first order in λ, of the Hamiltonian

$$H = H_0 + V'(x) \tag{18.65}$$

where

$$V'(x) = \lambda V(x,t) \tag{18.66}$$

Likewise, the energy expectation value at time t, given by

$$
\begin{aligned}
E(t) &= \langle\psi(t)|H_0 + \lambda V(t)|\psi(t)\rangle \\
&= E_l^0 + \lambda\langle\varphi_l|V(t)|\varphi_l\rangle + \left\{\langle\varphi_l|H_0\sum_{k\neq l}\frac{\langle\varphi_k|V(t)|\varphi_l\rangle}{E_l^{(0)} - E_k^0}|\varphi_k\rangle + \right. \\
&\quad +\text{hermitian conjugate}\Big\} \\
&= E_l^0 + \lambda\langle\varphi_l|V(t)|\varphi_l\rangle + \left\{\sum_{k\neq l}\langle\varphi_l|H_0|\varphi_k\rangle\frac{\langle\varphi_k|V(t)|\varphi_l\rangle}{E_l^{(0)} - E_k^0}\right. \\
&\quad +\text{hermitian conjugate}\Big\} \\
&= E_l^0 + \lambda\langle\varphi_l|V(t)|\varphi_l\rangle
\end{aligned} \tag{18.67}
$$

We recognize this as the same result as in time-independent perturbation theory, for a perturbing potential $V'(x) = \lambda V(x,t)$

To sum it up, for very slowly varying ("adiabatic") potentials, the prescription is simple: First solve the time-independent Schrodinger equation

$$[H_0 + \lambda V(x,t)]\phi_l(x,t) = E_l(t)\phi_l(x,t) \tag{18.68}$$

where the time variable t in the above equation is just treated as a fixed parameter, subject to the condition

$$\lim_{\lambda\to 0} \phi_l(x,t) = \varphi_l(t) \tag{18.69}$$

To first order in λ, the result is

$$
\begin{aligned}
\phi_l(x,t) &= \varphi_l(x) + \lambda\sum_{k\neq l}\frac{\langle\varphi_k|V(t)|\varphi_l\rangle}{E_l^{(0)} - E_k^0}\varphi_k(x) \\
E_l(t) &= E_l^0 + \lambda\langle\varphi_l|V(t)|\varphi_l\rangle
\end{aligned} \tag{18.70}
$$

and

$$\psi(x,t) = \phi_l(x,t)e^{-iE_l(t)/\hbar} \tag{18.71}$$

Note that since $E_l(t)$ varies in time, the energy of the system is not conserved, even after long times. But, you may ask, did we not prove from the Schrodinger equation, back in the last semester, that $\partial_t \langle H \rangle = 0$? Actually, if you look back at the derivation, it assumed that the potential $V(x)$ was time-independent. If the potential depends on time, there is no reason for the energy to be constant. Of course, if we would treat *everything* quantum-mechanically, including the source of the potential, then the energy of the entire system must be conserved. But thats another story.

18.2.1 Example

Consider a particle of mass m, initially (time $t = 0$) in its ground state in a one-dimensional box of length L; i.e.

$$\varphi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2} \tag{18.72}$$

Suppose that the walls of the box move apart from each other very slowly, so that the adiabatic assumption is justified, and that after some long time t the walls are a distance αL apart.

We don't even need perturbation theory to solve this problem. All that is required is to solve the time independent Schrodinger equation (exactly) at time t. The result is

$$\varphi_1(x,t) = \sqrt{\frac{2}{\alpha L}} \sin\left(\frac{\pi x}{\alpha L}\right)$$

$$E_1(t) = \frac{\pi^2 \hbar^2}{2m\alpha^2 L^2} \tag{18.73}$$

You can see that the particle has an energy loss

$$\Delta E = \frac{\pi^2 \hbar^2}{2mL^2}\left(1 - \frac{1}{\alpha^2}\right) \tag{18.74}$$

which has a simple classical interpretation: The particle in the box exerts a pressure on the walls. As the walls move, the particle does positive work, and loses energy. Thats a good thing; otherwise steam and automobile engines wouldn't work! Gas molocules ultimately obey the laws of quantum mechanics. In pushing a piston, they had better give up some of their energy to the piston, otherwise it would be hard to understand how quantum mechanics would be consistent with the principles of heat engine design, that were worked out in the 19th century.

18.2.2   Validity

Before leaving the topic, its necessary to have some criterion for the validity of the adiabatic method: what do we mean by saying that the potential is "slowly varying"? Slowly varying compared to what?

Lets go back to the integration-by-parts formula, and assume that the perturbing potential was turned on at $t = 0$

$$c_k^1(t) = -\frac{1}{\hbar\omega_{kl}} \left[V_{kl}(t)e^{i\omega_{kl}t} - \int_0^t dt' \frac{\partial V_{kl}}{\partial t'} e^{i\omega_{kl}t'} \right] \tag{18.75}$$

Making the rough assumption that $\frac{\partial V_{kl}}{\partial t}$ is nearly constant in time, we can carry out the time integration to get

$$c_k^1(t) = -\frac{1}{\hbar\omega_{kl}} \left[V_{kl}(t)e^{i\omega_{kl}t} - \frac{1}{i\omega_{kl}}\frac{\partial V_{kl}}{\partial t} 2\sin[\frac{1}{2}\omega_{kl}t]e^{i\omega_{kl}t/2} \right] \tag{18.76}$$

We are only justified in dropping the term proportional to the time derivative of V_{kl} if

$$\left| V_{kl}(t) \right| \gg \left| \frac{2}{\omega_{kl}}\frac{\partial V_{kl}}{\partial t} \right| \tag{18.77}$$

So this is the necessary condition for the validity of the adiabatic approximation.

18.3   Sudden Perturbations

Finally, let us consider the other extreme of time-dependent perturbation, namely, the case where the potential changes instantly (or nearly so, e.g. by someone flipping a switch):

$$V'(x,t) = \begin{cases} 0 & t < 0 \\ V'(x) & t \geq 0 \end{cases} \tag{18.78}$$

We will suppose that the possible energy eigenstates and eigenvalues both before and after $t = 0$ are known:

$$\begin{aligned} H_0\phi_n &= E_n\phi_n \\ H\phi_n' &= E_n'\phi_n' \\ H &= H_0 + V'(x,t) \end{aligned} \tag{18.79}$$

Possibly $\{\phi_n', E_n'\}$ can determined by time-independent perturbation theory, or are even known exactly (for some simple forms of $V'(x)$).

Consider a system which is in an initial state

$$\psi_{in}(x, t = 0^-) \tag{18.80}$$

at a moment $(t = 0^-)$ just before the perturbation is switched on. With this initial condition, we want to know what the wavefunction will be at any time $t > 0$, and in particular the probability of finding any particle energy eigenvalue E'_k.

This is actually quite simple. First of all, at any time $t > 0$, the solution to the time-dependent Schrodinger equation has the general form

$$\psi(x, t > 0) = \sum_n c_n \phi'_n(x) e^{-iE_n t/\hbar} \qquad (18.81)$$

Then continuity of the wavefunction in time, and particularly continuity at time $t = 0$, requires that

$$\psi_{in}(x, t = 0^-) = \sum_n c_n \phi'_n(x) \qquad (18.82)$$

This equation determines all the c_n in the usual way (go to bra-ket notation, and multiply on the left by $\langle \phi'_k |$

$$c_k = \langle \phi'_k | \psi_{in}(t = 0^-) \rangle \qquad (18.83)$$

The probability of measuring energy E'_k at any time $t > 0$ is then

$$
\begin{aligned}
P(E_k) &= \left| \langle \phi'_k | \psi(t) \rangle \right|^2 \\
&= \left| c_k \right|^2 \\
&= \left| \langle \phi'_k | \psi_{in}(t = 0^-) \rangle \right|^2 \qquad (18.84)
\end{aligned}
$$

18.3.1   Example

We consider the potential

$$V(x, t) = \begin{cases} \frac{1}{2} k x^2 & t < 0 \\ \frac{1}{2} k' x^2 & t \geq 0 \end{cases} \qquad (18.85)$$

So for any time t the Hamiltonian is that of a harmonic oscillator (which is exactly soluble) but with spring constant k at $t < 0$, and k' at $t > 0$.

Suppose the particle is in its ground state at times $t < 0$. What is the probability that the particle is in an excited state at $t > 0$?

Clearly the probability of being in an excited state is is related to the probability $P(E'_0)$ of remaining in the ground state, i.e.

$$P_{ex} = 1 - P(E'_0) = 1 - |c_0|^2 \qquad (18.86)$$

The ground states before and after $t = 0$ are

$$
\begin{aligned}
\phi_0(x) &= \left(\frac{mk}{\pi^2 \hbar^2} \right)^{1/8} \exp\left[-\frac{1}{2} \sqrt{mk} x^2 / \hbar \right] \\
\phi'_0(x) &= \left(\frac{mk'}{\pi^2 \hbar^2} \right)^{1/8} \exp\left[-\frac{1}{2} \sqrt{mk'} x^2 / \hbar \right] \qquad (18.87)
\end{aligned}
$$

Then

$$
\begin{aligned}
c_0 &= \langle \phi_0' | \phi_0 \rangle \\
&= \left(\frac{m}{\pi^2 \hbar^2} \right)^{1/4} (kk')^{1/8} \int dx \exp\left[-\frac{1}{2}(\sqrt{mk} + \sqrt{mk'})x^2/\hbar \right] \\
&= \sqrt{2} \frac{(kk')^{1/8}}{(\sqrt{k} + \sqrt{k'})^{1/2}}
\end{aligned}
\tag{18.88}
$$

so that

$$
P(E_0') = 2 \frac{(kk')^{1/4}}{\sqrt{k} + \sqrt{k'}}
\tag{18.89}
$$

Its interested to plug in some numbers. Suppose that the spring constant changes drastically at $t = 0$, by a factor of 16, i.e.

$$
k' = \frac{k}{16}
\tag{18.90}
$$

We might expect that such a large change would be very likely to kick the particle out of the ground state. but in fact, one finds in this case that $P(E_0') = \frac{4}{5}$, so that there is actually only a 20% chance that the particle is found in an excited state after time $t = 0$.

Chapter 19

The WKB and Variational Methods

(In Preparation)

Chapter 20

Scattering Theory

Chapter 21

Quantum Mechanics as Linear Algebra

I have stressed throughout the course that physical states in quantum mechanics are represented by vectors (in Hilbert Space), that observables are associated with linear operators, and that linear operators have a matrix representation. This suggests that the equations of quantum mechanics can be expressed in the terminology and notation of linear algebra, i.e. vectors and matrices. This chapter will explore the linear algebra/quantum mechanics connection in more detail. In addition, we will study Dirac's prescription for quantizing an arbitrary mechanical system.

It may help to have in mind the main theme. We saw in Lecture 7 that every linear operator $\tilde{O}$ has a matrix representation $O(x, y)$, where

$$O(x, y) = \tilde{O}\delta(x - y) \tag{21.1}$$

This is actually only one of an infinite number of possible matrix representations of $\tilde{O}$; it is known as the x-representation (or position-representation). As we will see, there exist other useful representations of operators, among them the p- (momentum-)representation, and the E- (energy-)representation. Each matrix representation is associated with a different set of orthonormal basis vectors in Hilbert Space, and each set of orthonormal basis vectors are the eigenstates of some complete set of linear operators. At the end of the chapter, you should aim for a good understanding of the last sentence.

We begin with a quick review of some basic facts about vectors and matrices.

21.1   Review of Vectors and Matrices

A D-dimensional column vector is a set of D complex numbers arranged in a column

$$\begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ . \\ . \\ . \\ v_D \end{bmatrix} \tag{21.2}$$

and a D-dimensional row vector is a set of D complex numbers arranged in a row

$$[w_1, w_2, w_3, ..., w_D] \tag{21.3}$$

To save typing, I will use $D = 2$ when displaying row and column vectors explicitly.

For each column vector, and one each row vector, there is defined an **inner product**

$$[w_1, w_2] \cdot \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = w_1 v_1 + w_2 v_2$$

$$= \sum_{i=1}^{D} w_i v_i \tag{21.4}$$

To each column vector, there is a corresponding row vector (and vice-versa)

$$\begin{bmatrix} v_1 \\ v_2 \end{bmatrix} \Longrightarrow [v_1^*, v_2^*] \tag{21.5}$$

The norm $|v|$ of a vector v is defined as the square-root of the inner product of the column vector with its corresponding row vector

$$|v|^2 = [v_1^*, v_2^*] \cdot \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \sum_{i=1}^{D} v_i^* v_i \tag{21.6}$$

A matrix M is a $D \times D$ square array of complex numbers

$$M = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} \tag{21.7}$$

which transforms column vectors v into column vectors v' according to the rule

$$\begin{bmatrix} v_1' \\ v_2' \end{bmatrix} = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix}$$

$$= \begin{bmatrix} m_{11} v_1 + m_{12} v_2 \\ m_{21} v_1 + m_{22} v_2 \end{bmatrix} \tag{21.8}$$

or, for each component of the transformed column vector,

$$v'_i = \sum_{j=1}^{D} m_{ij} v_j \tag{21.9}$$

Likewise, a matrix transforms row vectors according to the rule

$$
\begin{aligned}
[w'_1, w'_2] &= [w_1, w_2] \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} \\
&= [(w_1 m_{11} + w_2 m_{21}), (w_1 m_{12} + w_2 m_{22})]
\end{aligned} \tag{21.10}
$$

or, for each component of the transformed row vector

$$w'_i = \sum_{j=1}^{D} w_j m_{ji} \tag{21.11}$$

Two matrices A and B can be multiplied to form a third matrix $C = AB$ according to the rule

$$
\begin{aligned}
\begin{bmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{bmatrix} &= \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} \\
&= \begin{bmatrix} a_{11} b_{11} + a_{12} b_{21} & a_{11} b_{12} + a_{12} b_{22} \\ a_{21} b_{11} + a_{22} b_{21} & a_{21} b_{12} + a_{22} b_{22} \end{bmatrix}
\end{aligned} \tag{21.12}
$$

or, in terms of matrix components,

$$c_{ij} = \sum_{k=1}^{D} a_{ik} b_{kj} \tag{21.13}$$

The **Hermitian Conjugate** $M^\dagger$ of a matrix M, with components m_{ij} is the transpose complex conjugate of M, i.e.

$$M^\dagger = \begin{bmatrix} m_{11}^* & m_{21}^* \\ m_{12}^* & m_{22}^* \end{bmatrix} \tag{21.14}$$

or, in general, if we denote by $[A]_{ij}$ the i, j component of the matrix A,

$$[M^\dagger]_{ij} = [M]_{ji}^* \tag{21.15}$$

The **Determinant** of a matrix M is the sum of products of components

$$\det(M) = \sum_{i_1=1}^{D} \sum_{i_2}^{D} ... \sum_{i_D=1}^{D} \epsilon_{i_1 i_2 ... i_D} m_{1 i_1} m_{2 i_2} m_{3 i_3} .... m_{D i_D} \tag{21.16}$$

where

$$\epsilon_{i_1 i_2 ... i_D} = \begin{cases} +1 & \text{if } i_1 i_2 ... i_D \text{ an even permutation of } 123...D \\ -1 & \text{if } i_1 i_2 ... i_D \text{ an odd permutation of } 123...D \\ 0 & \text{otherwise} \end{cases} \qquad (21.17)$$

In particular, for a 2×2 matrix

$$\det \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} = m_{11} m_{22} - m_{12} m_{21} \qquad (21.18)$$

Two very important classes of matrices are the Hermitian matrices, which have the property

$$H = H^\dagger \qquad (21.19)$$

or, in components,

$$[H]_{ij} = [H]^*_{ji} \qquad (21.20)$$

and the unitary matrices, which have the property

$$U^\dagger = U^{-1} \qquad (21.21)$$

By U^{-1}, we mean a matrix with the property that

$$U U^{-1} = I \qquad (21.22)$$

where I is the unit matrix

$$I = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad (21.23)$$

In terms of components

$$[I]_{ij} = \delta_{ij} \qquad (21.24)$$

Hermitian 2×2 matrices have the form

$$H = \begin{bmatrix} a & c + id \\ c - id & b \end{bmatrix} \qquad (21.25)$$

where a, b, c, d are real numbers. A unitary 2×2 matrix has the form

$$U = e^{i\theta} \begin{bmatrix} a + ib & -c + id \\ c + id & a - ib \end{bmatrix} \qquad \text{where} \quad a^2 + b^2 + c^2 + d^2 = 1 \qquad (21.26)$$

In general, for any D, a unitary matrix can be written

$$\begin{aligned} U & = e^{iH} \\ & = \sum_{n=0}^{\infty} \frac{i^n}{n!} H^n \qquad (21.27) \end{aligned}$$

where H is an Hermitian matrix.

The **Eigenvalue Equation** for a matrix M is the relation $Mu = \lambda u$, or

$$\begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \lambda \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \tag{21.28}$$

In components, the eigenvalue equation reads

$$\sum_{j=1}^{D} m_{ij} u_j = \lambda u_i \tag{21.29}$$

The solutions of this equation are a set of normalized **eigenvectors** $u^{(n)}$ and corresponding eigenvalues λ

$$\{u^{(n)}, \lambda^n\} = \left\{ \begin{bmatrix} u_1^{(n)} \\ u_2^{(n)} \end{bmatrix} \quad \lambda^{(n)} \right\} \tag{21.30}$$

where the superscript $n = 1, 2, .., D$ labels the different, linearly independent solutions. If there are k linearly independent solutions with the same eigenvalue, then that eigenvalue is said to be k-fold degenerate.[1] The eigenvalue equation can also be written

$$(M - \lambda I)u = 0 \tag{21.31}$$

• **To Find the Eigenvalues:** Take the determinant of $M - \lambda I$ and set it to zero, i.e.

$$det(M - \lambda I) = \det \begin{bmatrix} m_{11} - \lambda & m_{12} \\ m_{21} & m_{22} - \lambda \end{bmatrix} = 0 \tag{21.32}$$

In general this is a D-th order polynomial in λ, with D solutions $\lambda_1, \lambda_2, ..., \lambda_D$, which are in general complex. If k eigenvalues are the same, there is a k-fold degeneracy.

• **To Find the Eigenvectors:** To find the eigenvector $u^{(n)}$ corresponding to a given eigenvalue λ_n, solve the simultaneous set of equations

$$\begin{aligned} m_{11} u_1^{(n)} + m_{12} u_2^{(n)} &= \lambda_n u_1^{(n)} \\ m_{21} u_2^{(n)} + m_{22} u_2^{(n)} &= \lambda_n u_2^{(n)} \end{aligned} \tag{21.33}$$

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[1]Of course, if D=2, then an eigenvalue can be no more than 2-fold degenerate.

or, in the case of a $D \times D$ matrix, solve the D simultaneous equations

$$\sum_{j=1}^{D} m_{ij} u_j^{(n)} = \lambda_n u_i^{(n)} \qquad (i = 1, 2, 3, ..., D) \tag{21.34}$$

The general solution of this equation, in terms of determinants, is given in any linear algebra book. The solution is denoted $u^{(n)}$, and should be normalized so that

$$[u_1^*, u_2^*] \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \sum_{i=1}^{D} u_i^* u_i = 1 \tag{21.35}$$

Theorem

The eigenvalues of a Hermitian matrix are all real. Any two eigenvectors of a Hermitian matrix, which correspond to different eigenvalues, are orthogonal.

Proof: Let $u^{(m)}$ and $u^{(n)}$ be two eigenvectors of a Hermitian matrix H, with eigenvalues λ_n, λ_m respectively. Consider the quantity

$$Q = \sum_{ij} (u_i^n) * H_{ij} u_j^{(m)} \tag{21.36}$$

Since u^m is an eigenvector, we know that

$$\sum_j H_{ij} u_j^{(m)} = \lambda_m u_i^{(m)} \tag{21.37}$$

so

$$Q = \lambda_m \sum_i (u_i^{(n)})^* u_i^{(m)} = \lambda_m u^{(n)} \cdot u^{(m)} \tag{21.38}$$

On the other hand, we can write Q as

$$Q = \sum_{ij} \left(H_{ij}^* u_i^{(n)} \right)^* u_j^{(m)} \tag{21.39}$$

Because H is an Hermitian matrix,

$$H_{ij}^* = H_{ji} \tag{21.40}$$

so

$$\begin{aligned} Q &= \sum_{ij} \left(H_{ji} u_i^{(n)} \right)^* u_j^{(m)} \\ &= \sum_j (\lambda_n u_j^{(n)})^* u_j^{(m)} \\ &= \lambda_n^* u^{(n)} \cdot u^{(m)} \end{aligned} \tag{21.41}$$

Therefore

$$\lambda_n^* u^{(n)} \cdot u^{(m)} = \lambda_m u^{(n)} \cdot u^{(m)} \tag{21.42}$$

For $n = m$, this implies

$$\lambda_n \quad \text{is real for all } n \tag{21.43}$$

which proves the first part of theorem. For $n \neq m$, and $\lambda_n \neq \lambda_m$, it also implies

$$u^{(n)} \cdot u^{(m)} = 0 \qquad \lambda_n \neq \lambda_m \tag{21.44}$$

which proves the second part of theorem.

- **Example** Lets find the eigenvalues and eigenvectors of the Hermitian matrix

$$H = \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} \tag{21.45}$$

First, to find the eigenvalues

$$\det \begin{bmatrix} -\lambda & i \\ -i & -\lambda \end{bmatrix} = \lambda^2 - 1 = 0 \tag{21.46}$$

so the eigenvalues are

$$\lambda_1 = +1 \qquad \lambda_2 = -1 \tag{21.47}$$

Note that these are both real, in agreement with theorem above. Then solve for the eigenvector u_1

$$\begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} \begin{bmatrix} u_1^1 \\ u_2^1 \end{bmatrix} = \begin{bmatrix} u_1^1 \\ u_2^1 \end{bmatrix}$$
$$\begin{bmatrix} i u_2^1 \\ -i u_1^1 \end{bmatrix} = \begin{bmatrix} u_1^1 \\ u_2^1 \end{bmatrix} \tag{21.48}$$

which has the solution

$$u_2^1 = -i u_1^1 \quad \text{or} \quad u^1 = \begin{bmatrix} u_1^1 \\ -i u_1^1 \end{bmatrix} \tag{21.49}$$

Finally, we determine u_1^1 by normalization

$$1 = u^1 \cdot u^1 = |u_1^1|^2 + |-i u_1^1|^2 = 2|u_1^1|^2$$
$$\implies u_1 = \frac{1}{\sqrt{2}} \tag{21.50}$$

so

$$\lambda_1 = +1 \qquad u^1 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix} \tag{21.51}$$

The procedure for $\lambda_2 = -1$ is identical:

$$\begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} \begin{bmatrix} u_1^2 \\ u_2^2 \end{bmatrix} = - \begin{bmatrix} u_1^2 \\ u_2^2 \end{bmatrix}$$

$$\begin{bmatrix} iu_2^2 \\ -iu_1^2 \end{bmatrix} = \begin{bmatrix} -u_1^2 \\ -u_2^2 \end{bmatrix} \tag{21.52}$$

And this time $u_2^2 = iu_1^2$. Normalizing to determine u_1^2, we find

$$\lambda_2 = -1 \qquad u^2 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix} \tag{21.53}$$

Note that the inner product

$$u^1 \cdot u^2 = \frac{1}{2}[1, i] \begin{bmatrix} 1 \\ i \end{bmatrix} = 1 + i^2 = 0 \tag{21.54}$$

vanishes, so u^1 and u^2 are orthogonal, again as predicted by theorem.

21.2   Linear Algebra in Bra-Ket notation

The definition of a column vector as a set of numbers is clearly not adequate as a definition of the word "vector" in physics. Take, for example, the electric field E, which is a three-dimensional vector quantity. In a particular set of xyz cartesian coordinates, the vector E may be *represented* by the three components

$$\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \tag{21.55}$$

but there is nothing sacred about any particular set of coordinates, and if we rotate to another coordinate frame, the same vector E will have three different components

$$\begin{bmatrix} E'_{x'} \\ E'_{y'} \\ E'_{z'} \end{bmatrix} \tag{21.56}$$

In classical mechanics and electromagnetism, a vector quantity is just denoted, e.g., by a boldface symbol $\mathbf{E}$ or by an arrow $\vec{E}$. This is the quantity which, *in a particular reference frame*, is represented by a D-dimensional column vector.

   Laws of motion are fundamental, reference frames are not, and one of the objectives of vector notation is to express the laws of classical physics in coordinate-independent form; e.g. Newton's Law of motion, and Ampere's Law

$$\vec{F} = m\vec{a} \quad \text{and} \quad \nabla \times \vec{B} = \mu_0 \vec{j} \tag{21.57}$$

are true in any system of cartesian coordinates. Vector notation, with the associated concepts of **grad**, **div**, and **curl**, is an elegant and useful way of avoiding the clutter of coordinate indices, and displaying the content of dynamical equations in the most direct way. In classical physics, vectors are usually three- (or in relativity, four-) dimensional, and their components are real-valued. In quantum theory, the vectors of interest are usually infinite-dimensional, and their components are typically complex-valued. Bra-ket notation, introduced by Dirac, aims to accomplish for quantum theory what vector notation does for classical mechanics; namely, to express the laws of motion as directly as possible, in a way that is independent of the (irrelevant) reference frame.

   Because the vectors in quantum mechanics can have complex components, it is important to distinguish between vectors whose components are column vectors, and vectors whose components are row vectors. The former are the "ket" vectors $|v>$, the latter the "bra" vectors $<v|$. There is a one-to-one correspondence between bra and ket vectors. If the components (in some reference frame) of a ket vector are given by

$$|v > \leftrightarrow \begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ . \\ . \\ . \\ v_D \end{bmatrix} \tag{21.58}$$

then the components of the corresponding bra vector are

$$< v| \leftrightarrow [v_1^*, v_2^*, v_3^*, ..., v_D^*] \tag{21.59}$$

The symbol $\leftrightarrow$ is used to remind us that the values of the components depend on the choice of reference frame; they are only a particular representation of the bra-ket vectors. The bra-ket vectors themselves, like $\vec{F}$ or $\vec{E}$, are meaningful independent of the basis chosen.

   A **Linear Vector Space** is a collection of vectors $\{|v>\}$, which is complete under vector addition, i.e. if $|v^1>$ and $|v^2>$ belong to the space, so does the combination

$$a|v^1 > +b|v^2 > \tag{21.60}$$

where a and b are any constants. There is also defined an inner product $< u|v >$ between bra and ket vectors

$$< u|v >=< v|u >^*$$
(21.61)

with the bi-linearity property

$$[a < q| + b < r|][c|s > +d|t >] = ac < q|s > +ad < q|t > +bc < r|s > +bd < r|t >$$
(21.62)

where a, b, c, d are all constants.

In order to distinguish quantitatively between vectors in the vector space, it is important to introduce what amounts to a reference frame, called a **basis**. A basis for a D-dimensional vector space is a set of D orthonormal vectors $\{|e_n >, \quad n = 1, 2, ..., D\}$

$$< e_n|e_m >= \delta_{mn}$$
(21.63)

such that any element of the vector space can be written as a linear combination

$$|v >= \sum_{m=1}^{D} v_m|e_m >$$
(21.64)

This expression is completely analogous to the expansion of vectors that is often seen in classical mechanics

$$\vec{F} = F_x\vec{i} + F_y\vec{j} + F_z\vec{k}$$
(21.65)

where $\vec{i}, \vec{j}, \vec{k}$ are unit vectors in the x,y,and z-directions respectively.

Taking the inner product of eq. (21.64) with the bra vector $< e_n|$

$$< e_n|v >=< e_n| \sum_{m=1}^{D} v_m|e_m >$$
(21.66)

and using the bi-linearity property (21.62)

$$< e_n|v >= \sum_{m=1}^{D} v_m < e_n|e_m >$$
(21.67)

and the orthonormality property (21.63)

$$< e_n|v >= \sum_{m=1}^{D} v_m\delta_{nm}$$
(21.68)

we find:

The Component (or "Wavefunction") of Vector $|v >$ in the basis $\{|e_n >\}$

$$v_n =< e_n|v >$$
(21.69)

Of course, in calling the components of a vector a "wavefunction", we are antici-pating the use of eq. (21.69) in quantum mechanics.

Next, we want to know the components of the bra-vector $< v|$ corresponding to $|v>$. Writing

$$< v| = \sum_m c_m < e_m| \qquad (21.70)$$

taking the inner product with $|e_n>$, and again using the bilinearity (21.62) and orthonormality (21.63) properties, we find

$$c_n =< v|e_n > \qquad (21.71)$$

Then, using the fact that $< u|v >=< v|u >^*$ (eq. (21.61)), and eq. (21.69)

$$c_n = v_n^* \qquad (21.72)$$

Therefore, in a given orthonormal basis $\{e_n\}$, the corresponding bra and ket vectors have the form

$$
\begin{aligned}
|v > &= \sum_n v_n |e_n > \\
< v| &= \sum_n v_n^* < e_n|
\end{aligned}
\qquad (21.73)
$$

The fact that the components of the bra vector are the complex conjugate of the components of the ket vector is in agreement with what was already been stated in equations (21.58) and (21.59).

• **Linear Operators**   Just as a function f is a rule for taking any number (x) and turning it into another number y (i.e. $y = f(x)$), so an an operator M is a rule for taking any vector $|v>$ into turning it into some other vector $|v'>$,

$$|v > \rightarrow |v' >= M|v > \quad \text{or} \quad |Mv > \qquad (21.74)$$

A **Linear Operator** has the property

$$M[a|v > +b|u >] = aM|v > +bM|u > \qquad (21.75)$$

for any vectors $|u>$, $|v>$ and constants a, b. Because of this property, we can determine what a linear operator M does to any vector $|v>$ by specifying what it does to any basis vector $|e_n>$:

$$
\begin{aligned}
|v' >= M|v > &= M \sum_j v_j |e_j > \\
&= \sum_j v_j M|e_j >
\end{aligned}
\qquad (21.76)
$$

Since both $|v' >$ and $M|e_i >$ are ket vectors, they must have an expansion in basis vectors which we write as

$$|v' >= \sum_k v'_k |e_k > \tag{21.77}$$

and

$$M|e_j >= \sum_k m_{kj} |e_k > \tag{21.78}$$

Substituting into (21.76) gives

$$\sum_k v'_k |e_k >= \sum_i \sum_k v_i m_{ki} |e_k > \tag{21.79}$$

Taking the inner product of both sides with the bra vector $< e_i|$, and using again the bi-linearity property and orthonormality properties (21.62), (21.63)

$$
\begin{aligned}
< e_i| \sum_k v'_k |e_k > &= < e_i| \sum_j \sum_k v_j m_{kj} |e_k > \\
\sum_k v'_k < e_i|e_k > &= \sum_j \sum_k v_j m_{kj} < e_i|e_k > \\
\sum_k v'_k \delta_{ik} &= \sum_j \sum_k v_j m_{kj} \delta_{ik} \\
v'_i &= \sum_j m_{ij} v_j \tag{21.80}
\end{aligned}
$$

But this is just the rule, in components, for multiplying a column vector by a matrix. This means that, in a given basis, *the action of a linear operator on vectors is equivalent to matrix multiplication.* In fact, taking the inner product of both sides of eq. (21.78) with the bra vector $< e_i|$, we find

The Matrix Element of Operator M in the basis $\{|e_n >\}$

$$m_{ij} =< e_i|M|e_j > \tag{21.81}$$

Next, it is useful to introduce a linear operation L on bras and kets which is represented symbollically by

$$L = |u >< v| \tag{21.82}$$

The meaning of this symbol is that L operating on *any* ket $|w >$ will turn it into another ket, proportional to $|u >$, by taking an inner product on the left

$$
\begin{aligned}
L|w > &= (|u >< v|)|w >= |u > (< v|w >) \\
&= (< v|w >)|u > \tag{21.83}
\end{aligned}
$$

Likewise L acts on bra vectors $< q|$ by taking an inner product on the right

$$
\begin{aligned}
< q|L &= < q|(|u >< v|) \\
&= < q|u >< v|
\end{aligned}
\tag{21.84}
$$

We now show that *any* linear operator can be expressed as a linear combination of $|u >< v|$ symbols. Begin with the identity operator I, defined such that

$$
I|v >= |v > \quad \text{and} \quad < u|I =< u|
\tag{21.85}
$$

for all $< u|$, $|v >$ in the vector space. It is easy to see that such an operator can be written, in a given basis $\{|e_i >\}$ as

$$
I = \sum_n |e_n >< e_n|
\tag{21.86}
$$

Check this:

$$
\begin{aligned}
I|v > &= \left(\sum_n |e_n >< e_n| \right) \left(\sum_k v_k |e_k > \right) \\
&= \sum_n \sum_k v_k |e_n > \delta_{nk} \\
&= \sum_k v_k |e_k > \\
&= |v >
\end{aligned}
\tag{21.87}
$$

Likewise

$$
\begin{aligned}
< u|I &= \left(\sum_k u_k < e_k| \right) \left(\sum_n |e_n >< e_n| \right) \\
&= \sum_k \sum_n u_k \delta_{kn} < e_n| \\
&= \sum_k u_k < e_k| \\
&= < u|
\end{aligned}
\tag{21.88}
$$

Finally, if M is any linear operator

$$
IM = MI = M
\tag{21.89}
$$

because

$$
IM|v >= I|Mv >= |Mv >= M|v >
\tag{21.90}
$$

and

$$
MI|v >= M|v >
\tag{21.91}
$$

We are now ready to express any linear operator M in terms of $|u><v|$ symbols. We have

$$
\begin{aligned}
M &= IMI \\
&= \left(\sum_i |e_i><e_i| \right) M \left(\sum_j |e_j><e_j| \right) \\
&= \sum_{ij} |e_i><e_i|M|e_j><e_j| \\
&= \sum_{ij} m_{ij}|e_i><e_j| \tag{21.92}
\end{aligned}
$$

Exercise: Let

$$
\begin{aligned}
|v'> &= M|v> \\
<u'| &= <u|M \tag{21.93}
\end{aligned}
$$

where we denote the components of the bra-ket vectors shown as

$$
\begin{aligned}
|v> &= \sum_i v_i|e_i> \\
|v'> &= \sum_i v_i'|e_i> \\
<u| &= \sum_i u_i <e_i| \\
<u'| &= \sum_i u_i' <e_i| \tag{21.94}
\end{aligned}
$$

Using the bra-ket representation of M in eq. (21.92), show that the components $v_i \to v_i'$ by matrix multiplication of a column vector, and $u_i \to u_i'$ by matrix multiplication of a row vector.

Exercise: Let $\{e_n\}$ and $\{e_m'\}$ be two different bases for the same vector space. Show that the $D \times D$ matrix whose elements are

$$
U_{ij} = <e_i|e_j'> \tag{21.95}
$$

is a unitary matrix.

In general, the bra vector which corresponds to $M|v>$ is not the same as $<v|M$, i.e.

$$
<Mv| \neq <v|M \tag{21.96}
$$

The Hermitian conjugate $M^\dagger$ of a linear operator M is defined to be that operator with the property

$$< Mv| =< v|M^\dagger \qquad (21.97)$$

for any bra vector. That means, in particular,

$$
\begin{aligned}
M_{ij}^\dagger &= < e_i|M^\dagger|e_j > \\
&= < Me_i|e_j > \\
&= < e_j|Me_i >^* \\
&= < e_j|M|e_i >^* \\
&= M_{ji}^* \qquad (21.98)
\end{aligned}
$$

This is the definition of the Hermitian conjugate of a matrix, given in the previous section. Therefore, *the matrix elements of the operator $M^\dagger$ are simply the hermitian conjugate of the matrix elements of the operator M*. As in the case of matrices, an **Hermitian Operator** is an operator which is its own Hermitian conjugate, ie.

$$M^\dagger = M \qquad (21.99)$$

An Hermitian operator therefore has the property that

$$< v|M =< Mv| \qquad (21.100)$$

An eigenvalue equation for the linear operator M has the form

$$M|v^n >= \lambda_n|v^n > \qquad (21.101)$$

This becomes a matrix equation, in the basis $\{|e_n >\}$, by taking the inner product of both sides of the equation with $< e_i|$:

$$
\begin{aligned}
< e_i|M|v^n > &= \lambda_n < e_i|v^n > \\
< e_i| \left(\sum_{lj} M|e_l >< e_j| \right) |v^n > &= \lambda_n v_i^n \\
\sum_j M_{ij} v_j^n &= \lambda_n v_i^n \qquad (21.102)
\end{aligned}
$$

which is the same as the matrix eigenvalue equation, in components, seen in the previous section.

Theorem

The eigenvalues of an Hermitian operator are real. Eigenstates corresponding to different eigenvalues are orthogonal.

This is theorm proved in the last section for matrices. Below we simply run through the proof once again (it was also seen in Lecture 7) in bra-ket notation:

$$
\begin{aligned}
< v^n|M|v^m > &= \lambda_m < v^n|v^m > \\
< Mv^n|v^m > &= \\
< v^m|Mv^n >^* &= \\
(\lambda_n < v^m|v^n >)^* &= \\
\lambda_n^* < v^n|v^m > &= \lambda_m < v^n|v^m >
\end{aligned}
\tag{21.103}
$$

For $n = m$, this implies that λ_n is real. For $n \neq m$ and $\lambda_n \neq \lambda_m$, it implies that $< v^n|v^m >= 0$; i.e. the two vectors are orthogonal. This proves theorem.

Theorem

If the eigenvalues of a linear operator are non-degenerate, then the normalized eigenstates form a basis in the linear vector space.

The eigenvalues λ_n are obtained by solving the D-th order polynomial

$$
\det[M_{ij} - \lambda\delta_{ij}] = 0
\tag{21.104}
$$

A D-th order polynomial has D roots, unless two or more roots coincide, in which case there is a degeneracy. Since the eigenvalue equation is a linear equation, it means that if $|v^n >$ is an eigenvector, so is $|v'^n >= N|v^n >$. Choose N so that

$$
|v'^n| = 1
\tag{21.105}
$$

Then, if the eigenvalues are non-degenerate, by theorem above it means that

$$
< v^m|v^n >= \delta_{nm} \quad \text{for} \quad n, m = 1, 2, 3, ..., D
\tag{21.106}
$$

and D orthonormal vectors form a basis for a D-dimensional linear vector space.

Since the eigenvectors $\{v^n\}$ of an Hermitian matrix M form a basis for the linear vector space, we can represent any linear operator O in the space in terms of its matrix elements in the "M-basis", i.e.

$$
O_{mn} =< v^m|O|v^n >
\tag{21.107}
$$

and

$$
O = \sum_{mn} O_{mn}|v^m >< v^n|
\tag{21.108}
$$

In particular, the matrix elements of M in the M-basis form a diagonal matrix

$$
\begin{aligned}
M_{mn} &= <v^m|M|v^n> \\
&= \lambda_n \delta_{mn}
\end{aligned}
\tag{21.109}
$$

and therefore

$$
\begin{aligned}
M &= \sum_{mn} \lambda_n \delta_{mn} |v^m><v^n| \\
&= \sum_n \lambda_n |v^n><v^n|
\end{aligned}
\tag{21.110}
$$

For this reason, solving the eigenvalue equation $M|v^n> = \lambda_n|v^n>$ is sometimes refered to as "diagonalizing" the operator M, since the matrix M_{mn} is a diagonal matrix in the basis spanned by the the eigenvectors $\{|v^n>\}$

21.3 Hilbert Space

Hilbert space is an infinite-dimensional, linear vector space. The eigenvectors (or eigenstates) of any Hermitian operator, having an infinite number of non-degenerate eigenvalues, form a basis in Hilbert space.

So far we have encountered the eigenvalue equation for Hilbert space operators in three versions. First, there is the "operator-acting-on-a-function" version

$$
\tilde{O}\psi_n(x) = \lambda_n \psi_n(x)
\tag{21.111}
$$

Second, the "matrix-multiplication" version is

$$
\int dy\, O(x,y)\psi_n(y) = \lambda_n \psi(x)
\tag{21.112}
$$

where the matrix element $O(x,y)$ was defined by the operator O acting on a delta-function

$$
O(x,y) = \tilde{O}\delta(x-y)
\tag{21.113}
$$

Finally, there is the abstract "bra-ket" version, which holds just as well in finite dimensional linear vector spaces

$$
O|\psi_n> = \lambda_n|\psi_n>
\tag{21.114}
$$

We ask: what is the relationship of the first two forms of the eigenvalue equation with the third "bra-ket" form, and, in particular, what is the relationship between the ket vector $|\psi>$ and the wavefunction $\psi(x)$? The answer, briefly, is that the first two forms are the eigenvalue equation in the x-representation, and the wavefunction $\psi(x)$ gives the components of the state vector $|\psi>$ in the x-representation.

The x-**representation** refers to the basis in Hilbert Space spanned by the eigenstates of the position operator X. The eigenvalues of X are all the real numbers $x \in [-\infty, \infty]$, and we will denote the (normalized) ket vector corresponding to an eigenvalue x_0 simply as $|x_0>$, i.e.

$$X|x_0 >= x_0|x_0 > \tag{21.115}$$

Since the ket vectors form an orthonormal basis, it means that

$$< x|y >= \delta(x - y) \tag{21.116}$$

and also that

$$I = \int dy |y >< y| \tag{21.117}$$

is the identity operator. To go from the bra-ket form (21.114) of the eigenvalue equation to the matrix form (21.112), we use the identity operator I

$$
\begin{aligned}
O|\psi_n > &= \lambda_n|\psi_n > \\
OI|\psi_n > &= \lambda_n|\psi_n > \\
\int dy \, O|y >< y|\psi_n > &= \lambda_n|\psi_n >
\end{aligned}
\tag{21.118}
$$

and take the inner-product of both sides of the equation with the bra $< x|$

$$\int dy \, < x|O|y >< y|\psi_n > = \lambda_n < x|\psi_n > \tag{21.119}$$

Comparing the forms (21.119) with (21.112) shows that we must identify

$$O(x, y) \equiv < x|O|y > \tag{21.120}$$

as the **Matrix Element of O in the X-Representation**, and

$$\psi_n(x) \equiv < x|\psi_n > \tag{21.121}$$

as the **Wavefunction of State $|\psi_n >$ in the X-Representation**. If we go one step further, and write

$$O(x, y) = \tilde{O}\delta(x - y) \tag{21.122}$$

where $\tilde{O}$ is an operator acting on functions of the variable x, and then substitute this expression into the matrix form of the eigenvalue eq. (21.112), we get the original form (21.111).

Most of the calculations done in elementary quantum mechanics are carried out in the position basis, i.e. using the first form (21.111) of the eigenvalue equation, and solving for wavefunctions in the x-representation. Nevertheless, there is nothing sacred about the x-representation, and other representations are sometimes useful. Among these are the p-representation, the harmonic-oscillator representation, and

various angular-momentum representations. The harmonic-oscillator representation is frequently used in quantum field theory, and the angular-momentum representations will be employed shortly, in our discussion of spin and addition of angular momentum.

Suppose we have an Hermitian operator O with a set of eigenstates and non-degenerate eigenvalues satisying

$$O|\phi_n> = o_n|\phi_n> \tag{21.123}$$

Then the wavefunction of any state $|\psi>$ in the O-representation is the inner product

$$\psi(n) = <\phi_n|\psi> \tag{21.124}$$

and the matrix element of any linear operator M in the O-representation is given by

$$M_{ij}^O = <\phi_i|M|\phi_j> \tag{21.125}$$

We will consider as examples four operators: position X,

$$X|x_0> = x_0|x_0> \qquad x_0 \in [-\infty, \infty] \tag{21.126}$$

momentum P,

$$P|p_0> = p_0|p_0> \qquad p_0 \in [-\infty, \infty] \tag{21.127}$$

the harmonic oscillator Hamiltonian H^{ho},

$$H^{ho}|\varphi_n> = E_n|\varphi_n> \qquad E_n = \hbar\omega(n + \frac{1}{2}) \tag{21.128}$$

and the square well Hamiltonian H^{sq},

$$H^{sq}|\phi_i> = E_i|\phi_i> \qquad E_i = n^2\frac{\hbar^2}{2mL^2} \tag{21.129}$$

From the matrix elements and eigenfunctions of these operators in the X-representation, we can construct the matrix elements and eigenstates in other representations. All our work so far has been in the X-representation, so we begin there.

- **The X-representation**

Taking the inner product of the eigenvalue equation $X|y> = y|y>$ with the bra $<x|$, we get immediately the matrix elements

$$
\begin{aligned}
<x|X|y> &= y <x|y> \\
&= y\delta(x-y) \\
&= x\delta(x-y)
\end{aligned}
\tag{21.130}
$$

The other operators, $\{P,\ H^{ho},\ H^{sq}\}$, we define by their matrix elements in the X-representation

$$
\begin{aligned}
<x|P|y> &= \tilde{p}\delta(x-y) \qquad \tilde{p} = -i\hbar\frac{\partial}{\partial x} \\
<x|H^{ho}|y> &= \left\{\frac{\tilde{p}^2}{2m} + \frac{1}{2}kx^2\right\}\delta(x-y) \\
<x|H^{sq}|y> &= \left\{\frac{\tilde{p}^2}{2m} + V^{sq}(x)\right\}\delta(x-y) \qquad (21.131)
\end{aligned}
$$

(where $V^{sq}(x)$ is the square-well potential). We note once again that all of these matrix elements have the form

$$
O(x,y) = \tilde{O}\delta(x-y) \qquad (21.132)
$$

and therefore the matrix eigenvalue equation

$$
\int dy\ <x|O|y><y|\psi_n> = \lambda_n <x|\psi_n> \qquad (21.133)
$$

becomes the operator-acting-on-a-function form

$$
\begin{aligned}
\tilde{O}\int dy\ \delta(x-y)\psi_n(y) &= \lambda_n\psi_n(x) \\
\tilde{O}\psi_n(x) &= \lambda_n\psi_n(x) \qquad (21.134)
\end{aligned}
$$

In this form, we have already solved for the eigenstates of X, P, H^{ho}, H^{sq}:

$$
\begin{aligned}
\text{position eigenstates}\quad \psi_{x_0}(x) &= <x|x_0> = \delta(x-x_0) \\
\text{momentum eigenstates}\quad \psi_{p_0}(x) &= <x|p_0> = \frac{1}{\sqrt{2\pi\hbar}}e^{ip_0 x/\hbar} \\
\text{harm. osc. eigenstates}\ \varphi_n x &= <x|\varphi_n> = \frac{1}{\sqrt{n!}}(a^\dagger)^n e^{-m\omega x^2/2\hbar} \\
\text{sq. well eigenstates}\quad \phi_n(x) &= <x|\phi_n> = \sqrt{\frac{1}{2L}}\sin\left[\frac{n\pi x}{L}\right] \qquad (21.135)
\end{aligned}
$$

The only new thing is the insight that the wavefunction of a state in the X-representation is an inner product $\psi(x) = <x|\psi>$.

Given these matrix elements and wavefunctions in the x-representation, we can find the matrix elements and wavefunctions in other representations. First, however, we check the validity of the operator identity

$$
[X,P] = i\hbar I \qquad (21.136)
$$

as a matrix equation in the X-representation:

$$
\begin{aligned}
< x|[X,P]|y > \ &= \ < x|XP|y > - < x|PX|y > \\
&= \ < x|XIP|y > - < x|PIX|y > \\
&= \ < x|X \left\{ \int dx \, |z> <z| \right\} P|y > - < x|P \left\{ \int dx \, |z> <z| \right\} X|y > \\
&= \ \int dz \ [< x|X|z> <z|P|y > - < x|P|z> <z|X|y >] \\
&= \ \int dz \left[x\delta(x-z) \left(-i\hbar \frac{\partial}{\partial z} \delta(z-y) \right) - \left(-i\hbar \frac{\partial}{\partial x} \delta(x-z) \right) z\delta(z-y) \right] \\
&= \ -i\hbar \left[x\frac{\partial}{\partial x}\delta(x-y) - y\frac{\partial}{\partial x}\delta(x-y) \right] \\
&= \ -i\hbar\delta(x-y) \left[-\frac{\partial}{\partial x}x + y\frac{\partial}{\partial x} \right] \\
&= \ i\hbar\delta(x-y) \tag{21.137}
\end{aligned}
$$

(In the next to last line, the derivative is understood to be acting on some function of x standing to to the right). This example is an illustration of the fact that *the matrix representation of a product of operators is equal to the product of matrix representations of each operator*, i.e.

$$
\begin{aligned}
< \phi_m|AB|\phi_n > \ &= \ \sum_k < \phi_m|A|\phi_k> <\phi_k|B|\phi_n > \\
[AB]_{mn} \ &= \ \sum_k A_{mk}B_{kn} \tag{21.138}
\end{aligned}
$$

- **The P-representation**

Taking the inner product of the eigenvalue equation $P|p_0>= p_0|p_0>$ with the bra $< p|$, we have the momentum eignfunctions in the momentum-representation

$$
\psi_{p_0}(p) =< p|p_0 >= \delta(p-p_0) \tag{21.139}
$$

The eigenstates of position are given by

$$
\begin{aligned}
\psi_{x_0}(p) \ &= \ < p|x_0 > \\
&= \ < x_0|p >^* \\
&= \ \psi_p(x)^* \\
&= \ \frac{1}{\sqrt{2\pi\hbar}}e^{-ip_0x/\hbar} \tag{21.140}
\end{aligned}
$$

An in general, any state whose eigenfunction is $\psi(x)$ in the x-representation will have an eigenfunction $\psi(p)$ in the p-representation given by

$$
\begin{aligned}
\psi(p) &= <p|\psi> \\
&= <p|I\psi> \\
&= <p|\left\{\int dx\ |x><x|\right\}|\psi> \\
&= \int dx <p|x><x|\psi> \qquad\qquad (21.141)
\end{aligned}
$$

or, using the result above for $<p|x>$,

$$
\psi(p) = \frac{1}{\sqrt{2\pi\hbar}}\int dx\psi(x)e^{-ipx/\hbar} \qquad\qquad (21.142)
$$

In other words, the momentum-space (P-representation) wavefunction is the Fourier transform of the position-space (X-representation) wavefunction.

Next, we compute matrix elements of operators. For the momentum operator

$$
<p_1|P|p_2> = p_2 <p_1|p_2> = p_1\delta(p_1 - p_2) \qquad\qquad (21.143)
$$

i.e. the momentum operator is *diagonal* ($= 0$ for $p_1 \neq p_2$) in the momentum representation. Writing

$$
<p|P|p'> = \tilde{p}\delta(p - p') \qquad\qquad (21.144)
$$

we see that

$$
\tilde{p} = p \qquad\qquad (21.145)
$$

For the position operator, we again use the identity operation

$$
\begin{aligned}
<p_1|X|p_2> &= <p_1|IXI|p_2> \\
&= <p_1|\left\{\int dx\ |x><x|\right\}X\left\{\int dy\ |y><y|\right\}|p_2> \\
&= \int dxdy\ <p|x><x|X|y><y|p_2> \\
&= \frac{1}{2\pi\hbar}\int dxdy\ x\delta(x-y)e^{(ip_2y - ip_1x)/\hbar} \\
&= \frac{1}{2\pi\hbar}\int dx\ xe^{i(p_2 - p_1)/\hbar} \\
&= i\hbar\frac{\partial}{\partial p_1}\frac{1}{2\pi\hbar}\int dx\ e^{i(p_2-p_1)/\hbar} \\
&= i\hbar\frac{\partial}{\partial p_1}\delta(p_1 - p_2) \qquad\qquad (21.146)
\end{aligned}
$$

or

$$
<p|X|p'> = \tilde{x}\delta(p - p') \qquad\qquad (21.147)
$$

where

$$\tilde{x} = i\hbar \frac{\partial}{\partial p} \tag{21.148}$$

In general, one can show that in the p-representation

$$< p_1 | X^n | \phi_2 >= \left(i\hbar \frac{\partial}{\partial p_1} \right)^n \delta(p_1 - p_2) \tag{21.149}$$

The matrix element of a Hamiltonian with potential $V(x)$ therefore takes the form

$$< p | H | p' >= \tilde{H} \delta(p - p') \tag{21.150}$$

where

$$\tilde{H} = \frac{p^2}{2m} + V \left[i\hbar \frac{\partial}{\partial p} \right] \tag{21.151}$$

The Schrodinger equation in the momentum representation is obtained by starting from

$$i\hbar \partial_t |\psi >= H |\psi > \tag{21.152}$$

and taking the inner product with the bra $< p|$

$$
\begin{aligned}
i\hbar \partial_t < p|\psi > &= < p|H|\psi > \\
i\hbar \partial_t < p|\psi > &= < p|H \left\{ \int dp' \; |p' >< p'| \right\} |\psi > \\
&= \int dp' < p|H|p' > \psi(p') \\
&= \tilde{H} \int dp' \delta(p - p') \psi(p')
\end{aligned} \tag{21.153}
$$

so finally

$$i\hbar \partial_t \psi(p, t) = \left\{ \frac{p^2}{2m} + V \left[i\hbar \frac{\partial}{\partial p} \right] \right\} \psi(p, t) \tag{21.154}$$

is the Schrodinger equation in this representation. Unless the potential is either zero (the free particle) or quadratic (the harmonic oscillator), this form of the Schrodinger equation is usually higher than 2nd order in derivatives, and therefore harder to solve than the corresponding equation in the X-representation.

Exercise: Verify eq. (21.149).

Exercise: Using eq. (21.146), verify that

$$< p | [X, P] | p' >= i\hbar \delta(p - p') \tag{21.155}$$

- **The Harmonic Oscillator Representation**

We next consider a basis for Hilbert Space consisting of the eigenstates $|\varphi_n >$ of the Harmonic oscillator Hamiltonian H^{ho}. The Hilbert Space we have discussed so far consists of the physical states of a particle moving in one dimension. The Harmonic Oscillator representation is just a basis in that space, and can be used whether or not the particle is actually moving in a harmonic oscillator potential (although that would be the most useful application).

From the orthonormality of eigenstates of a Hermitian operator, the wavefunction of the eigenstate $|\varphi_n >$ is

$$\varphi_n(m) = < \varphi_m|\varphi_n > = \delta_{mn} \qquad m = 0, 1, 2, ... \tag{21.156}$$

In other words, the wavefunction of eigenstates of the harmonic oscillator, in the harmonic oscillator representation, can be represented as infinite-dimensional column vectors:

$$\varphi_0 = \begin{bmatrix} 1 \\ 0 \\ 0 \\ . \\ . \\ . \end{bmatrix} \qquad \varphi_1 = \begin{bmatrix} 0 \\ 1 \\ 0 \\ . \\ . \\ . \end{bmatrix} \qquad \varphi_2 = \begin{bmatrix} 0 \\ 0 \\ 1 \\ . \\ . \\ . \end{bmatrix} ..... \tag{21.157}$$

In fact, because $n = 0, 1, 2, ...$ is a discrete index, all "eigenfunctions"
$\psi(n) = < \varphi_n|\psi >$ can be thought of as the components of a column vector. In particular, an eigenfunction of position $|x >$, in the HO-representation, is

$$
\begin{aligned}
\psi_x(n) &= < \varphi_n|x > \\
&= < x|\varphi_n >^* \\
&= \varphi_n(x) \tag{21.158}
\end{aligned}
$$

In other words, an eigenstate of position has the form of a column vector

$$\psi_x = \begin{bmatrix} \varphi_0(x) \\ \varphi_1(x) \\ \varphi_2(x) \\ . \\ . \\ . \end{bmatrix} \tag{21.159}$$

Then the orthogonality of position eigenstates implies

$$\delta(x - y) = < x|y >$$

$$= \; [\varphi_0^*(x), \varphi_1^*(x), \varphi_2^*(x), ...] \begin{bmatrix} \varphi_0(y) \\ \varphi_1(y) \\ \varphi_2(y) \\ . \\ . \\ . \end{bmatrix} \quad (21.160)$$

Taking the inner product of the row and column vectors, we get the identity

$$\sum_{n=0}^{\infty} \varphi_n^*(x)\varphi_n(y) = \delta(x-y) \quad (21.161)$$

Next we turn to the matrix elements of operators. Taking the inner product of the eigenvalue equation $H^{ho}|\varphi_n> = E_n|\varphi_n>$ with the bra $<\varphi_m|$ gives

$$H_{mn}^{ho} \equiv <\varphi_m|H^{ho}|\varphi_n> = E_n\delta_{mn} \quad (21.162)$$

i.e. H_{mn}^{ho} is a diagonal matrix

$$H^{ho} = \begin{bmatrix} E_1 & 0 & 0 & . & . & . \\ 0 & E_2 & 0 & . & . & . \\ 0 & 0 & E_3 & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{bmatrix} \quad (21.163)$$

The matrix representations X_{mn} and P_{mn} are easily obtained using the raising and lowering operator relations

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

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

$$a^\dagger|\phi_n> = \sqrt{n+1}|\phi_{n+1}>$$

$$a|\phi_n> = \sqrt{n}|\phi_{n-1}> \quad (21.164)$$

Then

$$X_{mn} = \sqrt{\frac{\hbar}{2m\omega}}\left[<\varphi_m|a^\dagger|\varphi_n> + <\varphi_m|a|\varphi_m>\right]$$

$$= \sqrt{\frac{\hbar}{2m\omega}}\left[\sqrt{n+1}\delta_{m,n+1} + \sqrt{n}\delta_{m,n-1}\right] \quad (21.165)$$

and likewise

$$P_{mn} = i\sqrt{\frac{m\omega\hbar}{2}}\left[\sqrt{n+1}\delta_{m,n+1} - \sqrt{n}\delta_{m,n-1}\right] \quad (21.166)$$

or

$$X = \sqrt{\frac{\hbar}{2m\omega}} \begin{bmatrix} 0 & 1 & 0 & . & . & . \\ 1 & 0 & \sqrt{2} & . & . & . \\ 0 & \sqrt{2} & 0 & \sqrt{3} & . & . \\ 0 & 0 & \sqrt{3} & 0 & \sqrt{4} & . \\ . & . & . & . & . & . \end{bmatrix}$$

$$P = \sqrt{\frac{m\omega\hbar}{2}} \begin{bmatrix} 0 & -i & 0 & . & . & . \\ i & 0 & -i\sqrt{2} & . & . & . \\ 0 & i\sqrt{2} & 0 & -i\sqrt{3} & . & . \\ 0 & 0 & i\sqrt{3} & 0 & -i\sqrt{4} & . \\ . & . & . & . & . & . \end{bmatrix} \quad (21.167)$$

Notice that the matrix representations of H^{ho}, X, and P, are all Hermitian.

Exercise: Using the matrix representations (21.165) and (21.166), show that

$$< \varphi_m |[X, P]| \varphi_n > = \delta_{mn} \quad (21.168)$$

- **The Square Well Representation**

This representation is only useful for a Hilbert Space in which the position-space wavefunctions are constrained to be zero outside a finite range $x \in [0, L]$. Such as situation occurs if the particle is trapped in a tube of finite length. Like the harmonic oscillator Hamiltonian H^{ho}, the square well Hamiltonian H^{sq} has a discrete set of eigenvalues and eigenvectors, so that "wavefunctions" are the components of infinite-dimensional column vectors, and operators are represented by $\infty \times \infty$ matrices.

From the orthonormality of eigenstates of a Hermitian operator, the wavefunction of the square-well eigenstate $|\phi_n >$ is

$$\phi_n(m) = < \phi_m |\phi_n > = \delta_{mn} \qquad m = 1, 2, 3, ... \quad (21.169)$$

which are the components of ∞-dimensional column vectors:

$$\phi_1 = \begin{bmatrix} 1 \\ 0 \\ 0 \\ . \\ . \\ . \end{bmatrix} \qquad \phi_2 = \begin{bmatrix} 0 \\ 1 \\ 0 \\ . \\ . \\ . \end{bmatrix} \qquad \phi_3 = \begin{bmatrix} 0 \\ 0 \\ 1 \\ . \\ . \\ . \end{bmatrix} ..... \quad (21.170)$$

These look just like the eigenstates of the harmonic oscillator Hamiltonian φ_n in the HO-representation, but of course they correspond to very different states. An eigenfunction of position $|x>$, in the square-well representation, is

$$
\begin{aligned}
\psi_x(n) &= <\phi_n|x> \\
&= <x|\phi_n>^* \\
&= \phi_n(x) \\
&= \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)
\end{aligned}
\tag{21.171}
$$

As a column vector, an eigenstate of position has the form

$$
\psi_x = \sqrt{\frac{2}{L}}
\begin{bmatrix}
\sin\left(\frac{\pi x}{L}\right) \\
\sin\left(\frac{2\pi x}{L}\right) \\
\sin\left(\frac{3\pi x}{L}\right) \\
. \\
. \\
.
\end{bmatrix}
\tag{21.172}
$$

The orthogonality of position eigenstates implies

$$
\begin{aligned}
\delta(x-y) &= <x|y> \\
&= [\phi_1^*(x),\phi_2^*(x),\phi_3^*(x),...]
\begin{bmatrix}
\phi_1(y) \\
\phi_2(y) \\
\phi_3(y) \\
. \\
. \\
.
\end{bmatrix}
\end{aligned}
\tag{21.173}
$$

Taking the inner product of the row and column vectors, we get another identity, analogous to (21.161)

$$
\frac{2}{L}\sum_{n=1}^{\infty}\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi y}{L}\right) = \delta(x-y)
\tag{21.174}
$$

As in the case of the harmonic oscillator, the matrix elements of the square-well Hamiltonian in the square-well representation is diagonal:

$$
H_{mn}^{sq} \equiv <\phi_m|H^{sq}|\phi_n> = E_n\delta_{mn}
\tag{21.175}
$$

i.e., as a matrix

$$
H^{sq} =
\begin{bmatrix}
E_1 & 0 & 0 & . & . & . \\
0 & E_2 & 0 & . & . & . \\
0 & 0 & E_3 & . & . & . \\
. & . & . & . & . & . \\
. & . & . & . & . & . \\
. & . & . & . & . & .
\end{bmatrix}
\tag{21.176}
$$

where this time

$$E_n = n^2 \frac{\hbar^2 \pi^2}{2mL^2} \tag{21.177}$$

The matrix representations X_{mn} is given by

$$X_{mn} = \langle \phi_m | X | \phi_n \rangle \tag{21.178}$$

which is best evaluated in the X-representation, which we already know should be

$$\begin{aligned} X_{mn} &= \int dx \, \phi_m^*(x) x \phi_n(x) \\ &= \frac{1}{2L} \int_0^L dx \, x \sin \frac{m\pi x}{L} \sin \frac{n\pi x}{L} \end{aligned} \tag{21.179}$$

To go from the bra-ket expression (21.178) to its x-representation (21.179), we use again the identity operator

$$\begin{aligned} X_{mn} &= \langle \phi_m | IXI | \phi_n \rangle \\ &= \langle \phi_m | \left\{ \int dx \, | x \rangle \langle x | \right\} X \left\{ \int dy \, | y \rangle \langle y | \right\} | \phi_n \rangle \\ &= \int dx \int dy \, \langle \phi_m | x \rangle \langle x | X | y \rangle \langle y | \phi_n \rangle \\ &= \int dx \int dy \, \phi_m^*(x) x \delta(x - y) \phi_n(y) \end{aligned} \tag{21.180}$$

Carrying out the y-integration, we obtain eq. (21.179). Carrying out the x-integration, we finally obtain

$$X_{mn} = \begin{cases} -\frac{8Lmn}{\pi^2(n^2 - m^2)^2} & (n - m) \text{ odd} \\ 0 & (n - m) \text{ even} \\ \frac{L}{2} & n = m \end{cases} \tag{21.181}$$

Similarly, the momentum operator in the square-well representation is

$$\begin{aligned} P_{mn} &= \langle \phi_m | P | \phi_n \rangle \\ &= \int dx dy \, \phi_m^*(x) \left(-i\hbar \frac{\partial}{\partial x} \delta(x - y) \right) \phi_n(y) \\ &= \int dx \, \phi_n^*(x) \left(-i\hbar \frac{\partial}{\partial x} \right) \phi_n(x) \end{aligned} \tag{21.182}$$

which is evaluated to be

$$P_{mn} = -i\hbar \begin{cases} \frac{4nm}{L(n^2 - m^2)} & (n - m) \text{ odd} \\ 0 & (n - m) \text{ even} \end{cases} \tag{21.183}$$

Written out as $\infty \times \infty$ matrices, X and P are

$$
X = L \begin{bmatrix}
\frac{1}{2} & -\frac{16}{9\pi^2} & 0 & . & . & . \\
-\frac{16}{9\pi^2} & \frac{1}{2} & \frac{48}{25\pi^2} & . & . & . \\
0 & -\frac{48}{25\pi^2} & \frac{1}{2} & . & . & . \\
. & . & . & . & . & . \\
. & . & . & . & . & . \\
. & . & . & . & . & .
\end{bmatrix}
$$

$$
P = \frac{i\hbar}{L} \begin{bmatrix}
0 & \frac{8}{3} & 0 & . & . & . \\
-\frac{8}{3} & 0 & \frac{24}{5} & . & . & . \\
0 & -\frac{24}{5} & 0 & . & . & . \\
. & . & . & . & . & . \\
. & . & . & . & . & . \\
. & . & . & . & . & .
\end{bmatrix}
\tag{21.184}
$$

which are both clearly Hermitian.

Exercise: Calculate the 11 matrix element of the $[X, P]$ commutator approximately, in the square well representation, using

$$
[X, P]_{mn} = \sum_{k=1}^{\infty} [X_{mk} P_{kn} - P_{mk} X_{kn}]
\tag{21.185}
$$

Carry out the sum over k to $k = 16$.

- **The Angular Momentum Representation**

As a final example, we consider the Hilbert space spanned by the eigenstates of angular momentum

$$
\begin{aligned}
J^2 |jm> &= j(j+1)\hbar^2 |jm> \\
J_z |jm> &= m\hbar |jm>
\end{aligned}
\tag{21.186}
$$

In the special case that j is an integer, the inner product of $|jm>$ with eigenstates of angles $|\theta, \phi>$ gives the spherical harmonics

$$
Y_{jm}(\theta, \phi) = < \theta\phi|jm >
\tag{21.187}
$$

The spherical harmonics are the wavefunctions of eigenstates of angular momentum in the "angle basis," spanned by the the set $\{|\theta, \phi>\}$ of angle eigenstates (a rigid rotator in an angle eigenstates has a definite angular position θ, ϕ However, the angular momentum algebra also allows for half-integer eigenvalues $j = 1/2$, $3/2$, ... In particular, the $j = 1/2$ case is important for describing the spin angular momentum

of the electron. In that case the $|\theta, \phi>$ basis is inadequate, and the use of the angular momentum basis $|jm>$ becomes indispensible.

The eigenstates of angular momentum are written as unit column vectors

$$
\varphi_{00} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ . \\ . \\ . \\ . \\ . \\ . \end{bmatrix}
$$

$$
\varphi_{\frac{1}{2},\frac{1}{2}} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ . \\ . \\ . \\ . \\ . \\ . \end{bmatrix}
\qquad
\varphi_{\frac{1}{2},-\frac{1}{2}} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ . \\ . \\ . \\ . \\ . \end{bmatrix}
$$

$$
\varphi_{11} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ . \\ . \\ . \end{bmatrix}
\qquad
\varphi_{10} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ . \\ . \\ . \end{bmatrix}
\qquad
\varphi_{00} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ . \\ . \end{bmatrix}
\qquad (21.188)
$$

Using eq. (21.186) above, and also the angular momementum raising and lowering operators

$$
\begin{aligned}
J_-|jm> &= \sqrt{(j+m)(j-m+1)}\hbar|j, m-1 > \\
J_+|jm> &= \sqrt{(j-m)(j+m+1)}\hbar|j, m+1 >
\end{aligned}
\qquad (21.189)
$$

we get the matrix elements

$$
\begin{aligned}
\left[J^2\right]_{jm,j'm'} &= j(j+1)\hbar^2 \delta_{jj'}\delta_{mm'} \\
[J_z]_{jm,j'm'} &= m\hbar\delta_{jj'}\delta_{mm'}
\end{aligned}
$$

$$[J_-]_{jm,j'm'} = \sqrt{(j'+m')(j'-m'+1)}\hbar\delta_{jj'}\delta_{m,m'-1}$$

$$[J_+]_{jm,j'm'} = \sqrt{(j'-m')(j'+m'+1)}\hbar\delta_{jj'}\delta_{m,m'+1} \qquad (21.190)$$

In the form of $\infty \times \infty$ matrices these are

$$J^2 = \hbar^2 \begin{bmatrix} 0 & . & . & . & . & . & . & . & . \\ . & \frac{3}{4} & 0 & . & . & . & . & . & . \\ . & 0 & \frac{3}{4} & . & . & . & . & . & . \\ . & . & . & 2 & 0 & 0 & . & . & . \\ . & . & . & 0 & 2 & 0 & . & . & . \\ . & . & . & 0 & 0 & 2 & . & . & . \\ . & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & . \end{bmatrix}$$

$$J_z = \hbar \begin{bmatrix} 0 & . & . & . & . & . & . & . & . \\ . & \frac{1}{2} & 0 & . & . & . & . & . & . \\ . & 0 & -\frac{1}{2} & . & . & . & . & . & . \\ . & . & . & 1 & 0 & 0 & . & . & . \\ . & . & . & 0 & 1 & 0 & . & . & . \\ . & . & . & 0 & 0 & 1 & . & . & . \\ . & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & . \end{bmatrix}$$

$$J_+ = \hbar \begin{bmatrix} 0 & . & . & . & . & . & . & . & . \\ . & 0 & 1 & . & . & . & . & . & . \\ . & 0 & 0 & . & . & . & . & . & . \\ . & . & . & 0 & \sqrt{2} & 0 & . & . & . \\ . & . & . & 0 & 0 & \sqrt{2} & . & . & . \\ . & . & . & 0 & 0 & 0 & . & . & . \\ . & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & . \end{bmatrix}$$

$$J_- = \hbar \begin{bmatrix} 0 & . & . & . & . & . & . & . & . \\ . & 0 & 0 & . & . & . & . & . & . \\ . & 1 & 0 & . & . & . & . & . & . \\ . & . & . & 0 & 0 & 0 & . & . & . \\ . & . & . & \sqrt{2} & 0 & 0 & . & . & . \\ . & . & . & 0 & \sqrt{2} & 0 & . & . & . \\ . & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & . \end{bmatrix} \qquad (21.191)$$

We can also write the operators J_x and J_y as matrices, using the identities

$$J_x = \frac{1}{2}(J_+ + J_-)$$

$$J_y = -\frac{i}{2}(J_+ - J_-) \qquad (21.192)$$

Often, in dealing with problems in atomic, nuclear, or particle physics, we are interested only in a finite subspace of Hilbert space consisting of eigenstates of a definite total angular momentum; i.e. definite value of the quantum number j. For example, the spin angular momentum of an electron corresponds to $j = \frac{1}{2}$, and nothing can ever change that value, short of annihilating the electron. So it makes sense to restrict considerations to the $j = \frac{1}{2}$ subspace of Hilbert space, spanned by the two eigenstates

$$|j = \frac{1}{2}, m = \frac{1}{2} > \quad \text{and} \quad |j = \frac{1}{2}, m = -\frac{1}{2} > \tag{21.193}$$

In this subspace, the angular momentum operators are

$$
\begin{aligned}
J^2 &= \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad J_z = \frac{1}{2}\hbar \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \\
J_+ &= \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \\
J_- &= \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}
\end{aligned}
\tag{21.194}
$$

Using eq. (21.192), we can write the angular momentum operators J_x, J_y, J_z in the $j = \frac{1}{2}$ subspace as

$$J_x = \frac{\hbar}{2}\sigma_x \qquad J_y = \frac{\hbar}{2}\sigma_y \qquad J_z = \frac{\hbar}{2}\sigma_z \tag{21.195}$$

where the matrices

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{21.196}$$

are known as the **Pauli Spin Matrices**. They will be useful in our later discussion of electron spin.

21.4   Canonical Quantization

Quantum mechanics as presented in previous chapters has been formulated in the x-representation. Let us review how we go from the classical mechanics of a particle moving in one dimension, to the corresponding quantum theory: The transition is made as follows:

$$
\begin{array}{cc}
\underline{\text{Classical}} & \underline{\text{Quantum}} \\
- - - - - - - - - - & - - - - - - - - - - - - \\
\text{physical state } (x,p) & \text{wavefunction } \psi(x) \qquad cc \\
\text{Observables } O = O(x,p) & \text{Operators } \tilde{O} = \tilde{O}(\tilde{x}, \tilde{p}) \\
\partial_t x = \frac{\partial H}{\partial p}, \quad \partial_t p = -\frac{\partial H}{\partial x} & i\hbar \partial_t \psi(x,t) = \tilde{H}(\tilde{x}, \tilde{p})\psi(x,t)
\end{array}
\tag{21.197}
$$

and, in addition, we make the crucial identification of $\tilde{x}$ and $\tilde{p}$ as the following operators, acting on functions of x

$$\begin{aligned}
\tilde{x}f(x) &= xf(x) \\
\tilde{p}f(x) &= -i\hbar\frac{\partial}{\partial x}f(x)
\end{aligned}$$
(21.198)

All of this was deduced from the wave equation for De Broglie waves, the Born interpretation, and the Ehrenfest Principle. From the discussion in this chapter, we see that the wavefunction $\psi(x)$ is the wavefunction of a state in the x-representation, the operators $\tilde{x}$ and $\tilde{p}$ operate exclusively on such wavefunctions.

Now, although the x-representation is extremely *useful* in quantum mechanics, it is no more *fundamental* than, say, a choice of cartesian coordinates in classical mechanics. The point of vector notation in classical mechanics is to write dynamical equations which hold in any reference frame. Now we would like to do the same for quantum mechanics. Up to a point, this is easy; its just a question of replacing the wavefunction $\psi(x)$ by the ket vector $|\psi>$, i.e.

$$\begin{array}{cc}
\underline{\text{Classical}} & \underline{\text{Quantum}} \\
- - - - - - - - - & - - - - - - - - - \\
(x,p) & |\psi> \\
O(x,p) & O(X,P) \\
\partial_t x = \frac{\partial H}{\partial p}, \quad \partial_t q = -\frac{\partial H}{\partial x} & i\hbar\partial_t|\psi> = H(X,P)|\psi>
\end{array} \qquad cc$$
(21.199)

But what do we now say about operators X and P, without referring directly to the x-representation? The answer is that the correct, representation-independent statement is just the commutator

$$[X,P] = i\hbar I$$
(21.200)

which can be deduced from the Ehrenfest principle and the Schrodinger equation as follows: Beginning from the Ehrenfest condition

$$< \frac{\partial H}{\partial p} > = \partial_t < x >$$
(21.201)

or

$$< \psi|\frac{\partial H}{\partial P}|\psi > = \partial_t < \psi|X|\psi >$$
(21.202)

and applying the Schrodinger equation in bra-ket form

$$\begin{aligned}
\partial_t|\psi> &= \frac{1}{i\hbar}H|\psi> \\
\partial_t <\psi| &= -\frac{1}{i\hbar}<\psi|H
\end{aligned}$$
(21.203)

we get

$$< \psi | \frac{\partial H}{\partial P} | \psi > = < \psi | \frac{1}{i\hbar}[X,H] | \psi > \qquad (21.204)$$

Likewise, the second Ehrenfest equation

$$< -\frac{\partial H}{\partial x} > = \partial_t < p > \qquad (21.205)$$

leads to

$$< \psi | -\frac{\partial H}{\partial X} | \psi > = < \psi | \frac{1}{i\hbar}[P,H] | \psi > \qquad (21.206)$$

Comparing the rhs and lhs of eqs. (21.204) and (21.206) leads us to require, as operator identities,

$$
\begin{aligned}
[X,H] &= i\hbar \frac{\partial H}{\partial P} \\
[P,H] &= -i\hbar \frac{\partial H}{\partial X}
\end{aligned}
\qquad (21.207)
$$

Let us assume that $H[X,P]$ can be expressed as a sum of products of operators X and P. Of course X commutes with powers of X, and P commutes with powers of P. [2] Now suppose that $[X,P] = i\hbar I$. Then

$$
\begin{aligned}
[X,P^n] &= XPP...P - PP...PX \\
&= PXP...P + i\hbar P^{n-1} - PP...PX \\
&= PPX...P + 2i\hbar P^{n-1} - PP...PX \\
&\quad . \\
&\quad . \\
&= ni\hbar P^{n-1} \\
&= i\hbar \frac{\partial}{\partial P} P^n
\end{aligned}
\qquad (21.208)
$$

In the same way,

$$
\begin{aligned}
[P,X^n] &= PXX...X - XX...XP \\
&= XPX...X - i\hbar X^{n-1} - XX...XP \\
&\quad . \\
&\quad . \\
&= -ni\hbar P^{n-1} \\
&= -i\hbar \frac{\partial}{\partial X} X^n
\end{aligned}
\qquad (21.209)
$$

---

[2]This is because X and X^n have the same set of eigenstates, and likewise for P and P^n.

Given that $H = H(P, X)$ can be expressed as a polynomial in X and P, the relation (21.207) follows.

To find the operators $\tilde{x}$ and $\tilde{p}$ in x-representation (which is also sometimes refered to as the **Schrodinger Representation**), we use the definition of the X-representation as the basis consisting of X eigenstates

$$X|x_0 >= x_0|x_0 > \tag{21.210}$$

so that

$$
\begin{aligned}
X(x, y) & = & < x|X|y > \\
& = & < Xx|y > \quad \text{(hermiticity of } X) \\
& = & x < x|y > \quad (|x > \quad \text{an eigenstate of } X) \\
& = & x\delta(x - y) \quad \text{(orthonormality)}
\end{aligned}
\tag{21.211}
$$

Then $P(x, y)$ is determined by the condition that

$$
\begin{aligned}
i\hbar\delta(x - y) & = & < x|[X, P]|y > \\
& = & \int dz \, [X(x, z)P(z, y) - P(x, z)X(z, y)] \\
& = & (x - y)P(x, y)
\end{aligned}
\tag{21.212}
$$

and this condition is satisfied by

$$P(x, y) = i\hbar\frac{\partial}{\partial x}\delta(x - y) \tag{21.213}$$

as was shown above. Then writing, as before

$$O(x, y) = \tilde{O}\delta(x - y) \tag{21.214}$$

so that

$$< x|O|\psi >= \tilde{O}\psi(x) \tag{21.215}$$

we have shown, simply from the commutation relation (21.200) and the eigenvalue equation (21.210) that

$$
\begin{aligned}
\tilde{x}\psi(x) & = & x\psi(x) \\
\tilde{p}\psi(x) & = & -i\hbar\frac{\partial}{\partial x}\psi(x)
\end{aligned}
\tag{21.216}
$$

We are now ready to present the procedure, first enunciated by Dirac, for quantizing any mechanical system. The procedure is known as **Canonical Quantization**, and goes as follows:

- **Canonical Quantization, or, Quantum Mechanics in a Nutshell**

1. Begin with a system with a set of coordinates and momenta $\{q^a, p_a\}$, whose dynamics is described by a Hamiltonian $H = H(p, q)$.

2. Physical states become vectors $|\psi>$ in a Hilbert space.

3. All observables are associated with Hermitian operators acting on vectors in Hilbert space. In particular, the coordinates q^a and momenta p_a correspond to operators

$$q^a \to Q^a \qquad p_a \to P_a \tag{21.217}$$

which satisy commutation relations

$$
\begin{aligned}
{[Q^a, Q^b]} &= 0 \\
{[P_a, P_b]} &= 0 \\
{[Q^a, P_b]} &= i\hbar \delta_{ab} I
\end{aligned}
\tag{21.218}
$$

4. Physical states evolve in time according to the Schrodinger equation

$$i\hbar |\psi> = H[P, Q]|\psi> \tag{21.219}$$

5. The expectation value $< O >$ of an observable $O(p, q)$, for a system in state $|\psi>$, is given by

$$< O > = < \psi | O[P, Q] |\psi> \tag{21.220}$$

Expressed in this way, the passage from classical to quantum mechanics is simple: its just a question of imposing commutation relations between Q and P, and postulating the Schrodinger equation. In none of these steps is there any committment to any particular basis in Hilbert space. Practical calculations, however, are usually carried out in the Schrodinger representation. The reason is simple: the momentum operator P appears only quadratically in the Hamiltonian, but the coordinates Q generally appear (in the potential $V(Q)$) in more complicated ways. It then makes sense to work in a basis which are eigenstates of the complicated part ($V(Q)$) of the Hamiltonian. The Schrodinger representation (or Q-representation) is defined by the basis of Q-eigenstates

$$Q^a |\{q\}> = q^a |\{q\}> \tag{21.221}$$

The wavefunction in Schrodinger representation is

$$\psi(q) = < \{q\}|\psi> \tag{21.222}$$

and

$$
\begin{aligned}
Q^a[\{q\},\{q'\}] &= q^a \delta^D(q - q') \\
P_a[\{q\},\{q'\}] &= -i\hbar \frac{\partial}{\partial q^a} \delta^D(q - q')
\end{aligned}
\tag{21.223}
$$

Using these matrix elements in the Schrodinger equation

$$
i\hbar < \{q\}|\psi > = < \{q\}|H|\psi >
\tag{21.224}
$$

leads to the Schrodinger equation in Schrodinger representation

$$
i\hbar\psi(q) = H\left[\{-i\hbar\frac{\partial}{\partial q^a}\},\{q^a\}\right]\psi(q)
\tag{21.225}
$$

which is normally the most useful form of this equation.

21.5 Poisson Brackets

Let $Q = Q(q, p)$ be some observable depending on the canonical coordinates and momenta $\{q^a, p_a\}$. Using Hamilton's equations and the chain rule for differentiation, the variation in time of this quantity is

$$
\begin{aligned}
\partial_t Q &= \sum_a \left[\frac{\partial Q}{\partial q^a}\frac{\partial q^a}{\partial t} + \frac{\partial Q}{\partial p_a}\frac{\partial p_a}{\partial t}\right] \\
&= \sum_a \left[\frac{\partial Q}{\partial q^a}\frac{\partial H}{\partial p_a} - \frac{\partial Q}{\partial p_a}\frac{\partial H}{\partial q^a}\right] \\
&= [Q, H]_{PB}
\end{aligned}
\tag{21.226}
$$

where we have defined the **Poisson Bracket** of any two observables $A(p, q)$ and $B(p, q)$ as

$$
[A, B]_{PB} = \sum_a \left[\frac{\partial A}{\partial q^a}\frac{\partial B}{\partial p_a} - \frac{\partial A}{\partial p_a}\frac{\partial B}{\partial q^a}\right]
\tag{21.227}
$$

Note, in particular, that

$$
[q^a, q^b]_{PB} = 0 \quad [p_a, p_b]_{PB} = 0 \quad [q^a, p_b]_{PB} = \delta_{ab}
\tag{21.228}
$$

An important feature of the Poisson bracket of two observables is that it always has the same value, no matter which set of conjugate coordinates and momentum are used. Normally there are many possible choices of coordinates and momenta. For example, for motion of baseball in three dimensions, we could use the cartesian coordinates x, y, z, and then obtain the conjugate momenta

$$
p_x = \frac{\partial L}{\partial \dot{x}} \quad p_y = \frac{\partial L}{\partial \dot{y}} \quad p_z = \frac{\partial L}{\partial \dot{z}}
\tag{21.229}
$$

but of course one could also express the Lagrangian in spherical coordinates r, θ, ϕ, and obtain conjugate momenta

$$p_r = \frac{\partial L}{\partial \dot{r}} \quad p_\theta = \frac{\partial L}{\partial \dot{\theta}} \quad p_\phi = \frac{\partial L}{\partial \dot{\phi}} \tag{21.230}$$

It is a theorem of classical mechanics that the Poisson Brackets of any two quantities do not depend of the choice of canonical coordinates and momenta. Therefore, any equation expressed in terms of Poisson Brackets holds true for every possible choice of $\{q^a, p_a\}$.

Now, from the Schrodinger equation we have

$$
\begin{aligned}
\partial_t < Q > &= \partial_t < \psi | Q | \psi > \\
&= \frac{1}{i\hbar} < \psi | (QH - HQ) | \psi > \\
&= < \psi | \frac{1}{i\hbar} [Q, H] | \psi >
\end{aligned}
\tag{21.231}
$$

Comparing this equation to the classical equation of motion

$$\partial_t Q = [Q, H]_{PB} \tag{21.232}$$

suggests that the classical-to-quantum transition is obtained by associating the Poisson brackets of classical observables with the commutators of corresponding operators, according to the rule

$$[A, B]_{PB} \rightarrow \frac{1}{i\hbar} [A, B] \tag{21.233}$$

Making this identification for the Poisson brackets (21.228) brings us again to the basic operator commutator equations

$$
\begin{aligned}
[Q^a, Q^b] &= 0 \\
[P_a, P_b] &= 0 \\
[Q^a, P_b] &= i\hbar \delta_{ab} I
\end{aligned}
\tag{21.234}
$$

of canonical quantization. This beautiful and deep connection between the Poisson brackets of classical mechanics, and the commutators of operators in quantum mechanics, was first pointed out by Dirac.

Chapter 22

The EPR Paradox and Bell's Theorem

No man is an island...

John Donne

Suppose we have a baseball in Philadelphia, and a football in Detroit, and we want to specify the physical state of the combined baseball-football system. In classical physics, this is done by first specifying the state of the baseball (its mass, composition, location, velocity...), and then specifying, in a similar way, the state of the football. There are no baseball+football states that *can't* be described in this way. If we decide to change the physical state of the football (by giving it a kick, say) then of course this will not very much affect the state of the far away baseball.

The point here is that the physical states of composite systems in classical physics are **separable**, in the sense that the description of the state of the whole system can always be reduced to a specification of the state of the parts. Suppose, instead of sports equipment, we consider the state of a system of two equal mass particles, which is represented by a point in 12-dimensional phase space $\{\vec{x}_1, \vec{x}_2, \vec{p}_1, \vec{p}_2\}$. Obviously, this state completely determines, and is determined by, the physical state $\{\vec{x}_1, \vec{p}_1\}$ of particle 1, and the physical state $\{\vec{x}_2, \vec{p}_2\}$ of particle 2. Moreover, if particle 1 is not in interaction with particle 2, then measurement of its location and/or momentum will not in any way affect the position or momentum of particle 2.

Physical states of composite systems, which have the same "common sense" property of separability, certainly exist in quantum mechanics. For example, suppose particle 1 is in state ψ_A and particle 2 is in state ψ_B. Then the state of the combined $1 - 2$ system is determined to be

$$\psi(x_1, x_2) = \psi_A(x_1)\psi_B(x_2) \tag{22.1}$$

Likewise, if particle 1 is in state ψ_C, and particle 2 is in state ψ_D, the combined

system is in state

$$\psi(x_1, x_2) = \psi_C(x_1)\psi_D(x_2) \tag{22.2}$$

But what do we make of the (normalized) superposition

$$\psi(x_1, x_2) = a\psi_A(x_1)\psi_B(x_2) + b\psi_C(x_1)\psi_D(x_2) \tag{22.3}$$

According to the principles of quantum mechanics, physical states are normalized vectors in Hilbert space, and the sum of two vectors is another vector. If that vector is normalized, it is a physical state too. So the wavefunction (22.3) is, from this point of view, entirely kosher: it is a physically allowed state of the two-particle system. But then if we ask: what is the state of particle 1, when the two-particle system is in state (22.3), we discover that we can't answer the question! Particle 1 is not in state ψ_A, nor is it in state ψ_C; neither is it in a linear combination such as $c\psi_A(x_1) + d\psi_C(x_1)$. The fact is, the state of particle 1 has become entangled with that of particle 2; it is impossible to specify the state of either particle separately, even if the two particles are non-interacting, and very far apart.

The fact that the quantum states of composite systems can be inseparable (or **entangled**) in this way was first noticed by Einstein, Podolsky, and Rosen ("EPR") in 1933. The consequences of this entanglement are truly mind-bending, even by the generous mind-bending standards of quantum mechanics.

22.1   The EPR Paradox

Einstein, Podolsky and Rosen were of the opinion that quantum mechanics is in some way incomplete, because it leads to (what they considered to be) a paradox in certain circumstances. To illustrate their point, we consider the following experiment (Fig. 22.1). Every time a button is pushed, two spin 1/2 particles are ejected, in opposite directions, each particle eventually passing through a detector which measures the spin of the particle along a given axis. The detectors can be rotated, so that the spin along any axis, in particular along the x- and z-axes, can be measured. After many trials, the following result is reported:

  A. Both detectors are set to measure spin along the z-axis. Whenever the spin of the particle on the left is found to be spin up, and this occurs 50% of the time, the spin of the particle on the right is found to be spin down. Likewise, whenever the particle on the left is found to be spin down, which is the other 50% of the time, the particle on the right is found to be spin up.

This means that by measuring the z-component of the spin of the particle on the left, we can determine the z-component of the spin of the particle on the right, without actually *interacting* with the particle on the right. Suppose, in a particular run, that the particle which moves to the left (which we'll now call "L") is found to be spin-up. Since the measurement on the left (goes the EPR argument) couldn't possibly

affect the spin of the other particle ("R") on the right, and yet we *know* that R is spin-down, it must be that R was spin down even *before* we made the measurement of L. Therefore, the spin state of the particles before entering the detectors must have been

$$\psi_1 = \alpha_z^L \beta_z^R \tag{22.4}$$

where α_z, β_z refer to spin up and down states, respectively, along the z-axis. For future reference, lets recall from Lecture 13 that

$$\alpha_z = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad \beta_z = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{22.5}$$

and

$$\alpha_x = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \qquad \beta_x = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix} \tag{22.6}$$

Now, by the same reasoning, if the particle on the left were found to be spin down, then the 2-particle state would have been be

$$\psi_2 = \beta_z^L \alpha_z^R \tag{22.7}$$

even before the measurement was made. According to (A), in half the runs the particles are in state ψ_1, and in the other half they are in state ψ_2.

This reasoning seems pretty solid, but now a troubling discovery is made. After many more runs, it is found that

B. When both detectors are set to measure spin in the x-direction, the two particles are *never* found to each have spin up, or each have spin down.

The problem is that, if the particles were initially in state ψ_1, then the probability that a measurement would find both spins up in the x-direction is

$$
\begin{aligned}
|<\alpha_x^L \alpha_x^R|\psi_1>|^2 &= |<\alpha_x^L|\alpha_z^L><\alpha_x^R|\beta_z^R>|^2 \\
&= \frac{1}{4} \tag{22.8}
\end{aligned}
$$

Likewise, if the particles were initially in state ψ_2, the probability to find both spins up in the x-direction would be

$$
\begin{aligned}
|<\alpha_x^L \alpha_x^R|\psi_2>|^2 &= |<\alpha_x^L|\beta_z^L><\alpha_x^R|\alpha_z^R>|^2 \\
&= \frac{1}{4} \tag{22.9}
\end{aligned}
$$

Then if the particles are half the time in state ψ_1, and half the time in state ψ_2, the total probability for finding both particles with spin up along the x-axis is simply the average of the two probabilities, i.e.

$$
\begin{aligned}
P(\text{up up})_{x-axis} &= \frac{1}{2}|<\alpha_x^L \alpha_x^R|\psi_1>|^2 + \frac{1}{2}|<\alpha_x^L \alpha_x^R|\psi_2>|^2 \\
&= \frac{1}{4} \tag{22.10}
\end{aligned}
$$

in total contradiction to the reported fact (B)! Conclusion: no experiment should report both results (A) *and* (B).

And yet, as EPR pointed out, there are quantum-mechanical states which lead to precisely these results. Suppose that the 2-particles, before reaching the detectors, are in a spin-0 state

$$
\begin{aligned}
\psi &= \frac{1}{\sqrt{2}}(\psi_1 - \psi_2) \\
&= \frac{1}{\sqrt{2}}(\alpha_z^L \beta_z^R - \beta_z^L \alpha_z^R) \qquad (22.11)
\end{aligned}
$$

Then the probability to find L with spin up and R with spin down along the z-axis is

$$
\begin{aligned}
P(\text{up down})_{z-axis} &= |< \alpha_z^L \beta_z^R | \psi >|^2 \\
&= \frac{1}{2} \left| < \alpha_z^L \beta_z^R | \psi_1 > - < \alpha_z^L \beta_z^R | \psi_2 > \right|^2 \\
&= \frac{1}{2}(1 - 0)^2 \\
&= \frac{1}{2} \qquad (22.12)
\end{aligned}
$$

Likewise, the probability to find L with spin down and R with spin up in the direction is

$$
\begin{aligned}
P(\text{down up})_{z-axis} &= |< \beta_z^L \alpha_z^R | \psi >|^2 \\
&= \frac{1}{2} \left| < \beta_z^L \alpha_z^R | \psi_1 > - < \beta_z^L \alpha_z^R | \psi_2 > \right|^2 \\
&= \frac{1}{2}(0 - 1)^2 \\
&= \frac{1}{2} \qquad (22.13)
\end{aligned}
$$

These two probabilitites are exactly what is reported in (A). Then we compute the probability to find both L and R with spin up along the x-axis

$$
\begin{aligned}
P(\text{up up})_{z-axis} &= |< \alpha_x^L \alpha_x^R | \psi >|^2 \\
&= \frac{1}{2} \left| < \alpha_x^L \alpha_x^R | \psi_1 > - < \alpha_x^L \alpha_x^R | \psi_2 > \right|^2 \\
&= \frac{1}{2} \left| < \alpha_x^L | \alpha_z^L >< \alpha_x^R | \beta_z^R > - < \alpha_x^L | \beta_z^L >< \alpha_x^R | \alpha_z^R > \right|^2 \\
&= \frac{1}{2}(\frac{1}{2} - \frac{1}{2})^2 \\
&= 0 \qquad (22.14)
\end{aligned}
$$

which is the same as result (B).

Now if both (A) and (B) are true, it means that before any measurement takes place, R is neither in state β_z^R (as in state ψ_1), nor in state α_z^R (as in ψ_2), because this would contradict (B). So, suppose we measure the spin of L along the z-axis, and it is found to be in spin up. At that point, we know that R is now spin down. But we have already concluded that before the measurement took place, R was neither spin up nor spin down. This means that, although R was not in a spin-down state initially, it must have "jumped" into a spin-down state after L was found in spin up, *even if, at the time of measurement, L and R were very far apart*! But how could a measurement of L, which perhaps is in Philadelphia, influence the state of R, which is maybe in Detroit? This is the EPR "paradox," which led Einstein, Podolsky, and Rosen to conclude that the quantum mechanical description of nature is somehow incomplete.

22.2   Bell's Theorem

Quantum mechanics might be wrong, but so far there is no evidence of that. So in what way could it be incomplete? One possibility is that, contrary to everything said so far in this course, the physical state of a particle is *not* completely specified by its wavefunction. Perhaps the particle also has some other, "hidden" degrees of freedom, which determine with certainty, rather than probabilistically, the outcome of any measurement of the particle. The probabilistic nature of quantum mechanics, according to this view, is simply due to our ignorance of the actual values of these "hidden variables."

If the hidden variable idea were true, it seems that we might be able to wriggle out of the EPR paradox. Denote the hidden variable by μ, and suppose the following values imply the following results of spin measurements along the z and x-axes, respectively:

$$
\begin{array}{llllll}
\mu = 1 & \text{leads to} & \text{up}_z & \text{or} & \text{up}_x \\
\mu = 2 & " & \text{up}_z & " & \text{down}_x \\
\mu = 3 & " & \text{down}_z & " & \text{up}_x \\
\mu = 4 & " & \text{down}_z & " & \text{down}_x
\end{array}
\tag{22.15}
$$

Then we could explain (A) and (B), for example, by saying that the two particles come out of the apparatus only with the hidden variable combinations

$$
(\mu^L, \mu^R) = (1, 4) \ \text{ or } \ (4, 1) \ \text{ or } \ (2, 3) \ \text{ or } \ (3, 2)
\tag{22.16}
$$

Of course this is not yet a theory, only an idea for a theory, but the idea itself was squelched by a celebrated theorem proved by J. Bell in 1964, which essentially says the following:

Bell's Theorem

No local hidden variable theory can agree with all of the predictions of quantum mechanics.

The restriction to a local theory means that theory does not contain any non-local "action-at-a-distance" interactions or, equivalently, any effects which propagate from one place to another at greater than the speed of light. This means that a measurement of L cannot affect the hidden variables of R; at least, not before the time required for light to travel from the left detector to the particle on the right.

Only one example is needed of a quantum-mechanical prediction that cannot be reproduced by a hidden variable theory; this is enough to prove the theorem. The example I will give here is due to Mermin.

Consider the experimental setup shown in Fig. 22.2. This is very much like the previous setup, in that when a button is pushed, two particles emerge, one traveling to the detector on the right, and one to the detector on the left. On each detector there is a switch, and two lights, one red and one green. When the switch is in position 1 then the detector measures some observable, O_1 say, and, depending on the value found, the light flashes either red or green. Likewise, when the switch is in position 2, the detector measures some other observable, O_2 say. Again, depending on the value found, the light flashes red or green. In our previous example, $O_1 = S_z$, and $O_2 = S_x$, and we could have arranged that the light flashes red for spin up, and green for spin down.

After many runs, the following results are found:

A. In runs in which the detectors have different switch settings, the lights on each detector never *both* flash green; i.e. $12GG$ and $21GG$ never occur.[1]

B. In runs in which both switches are set to 2, one finds that 9% of the time both lights flash green ($22GG$).

C. In runs in with both switches are set to 1, both lights never flash red, i.e. $11RR$ never occurs.

Now we'll imagine that these results can be explained by assuming that each particle comes out of the apparatus in a definite state, with some definite values of the hidden variables. From result (A), we can conclude that if one of the particles is in a state which would cause a switch 2 detector to flash green, then the other particle is in a state which would cause a switch 1 detector to flash red. If this were not the case, then occasionally one would find $12GG$ and $21GG$, which, it is asserted, never occurs. It follows that in those $22GG$ runs where both lights flash green, each

---

[1]Where, e.g., $12RG$ means: the switch on the left-hand detector is set to 1, the switch on the right-hand detector is set to 2, the light on the left-hand detector flashes red, the light on the right-hand detector flashes green.

particle must have been in a state which would cause a type 1 detector to flash red. So, if we set both switches to 1, we would expect to see $11RR$ exactly as many times as one sees $22GG$, namely, 9% of the time. But according to result (C), $11RR$ never occurs! Therefore, no hidden variable theory can be consistent with all three results (A), (B), and (C). Can quantum theory ever predict such results?

Lets denote the eigenstates of observable O_1 by the kets

$$|1G > \quad \text{and} \quad |1R > \tag{22.17}$$

The meaning of the notation is that when a particle is in an eigenstate $|1G >$, it causes the light on a switch 1 detector to flash green, and so on. Now suppose operator O_2 is chosen such that its eigenstates are related to the eigenstates of O_1 in the following way:

$$|2G > \;\; = \;\; \sqrt{\frac{3}{5}}|1G > +\sqrt{\frac{2}{5}}|1R >$$

$$|2R > \;\; = \;\; -\sqrt{\frac{2}{5}}|1G > +\sqrt{\frac{3}{5}}|1R > \tag{22.18}$$

Suppose further that the apparatus is designed such that the particles leaving the apparatus are in the state

$$|\Psi >= \sqrt{\frac{3}{8}}|1R >_l |1G >_r +\sqrt{\frac{3}{8}}|1G >_l |1R >_r -\frac{1}{2}|1G >_l |1G >_r \tag{22.19}$$

where the subscript r means that the state refers to the particle on the right, and l refers to the particle on the left.

With observable O_2 and state Ψ chosen in this way, then by following the standard rules of quantum theory we can compute the probabilities for finding outcomes GG, RR, RG, and GR, for switch settings 12, 21, 22, and 11. These probabilities are shown in Fig. 22.3 They are in complete agreement with the asserted results (A), (B) and (C) above.

In this way, Bell's Theorem is proven. There *are* physical states in quantum mechanics which lead to predictions that can *never* be reproduced by a local hidden variables theory. These physical states are always of the "entangled" form, in which it is impossible to deduce the state of either particle separately.

Of course, the example constructed here, although sufficient to prove theorem, is rather special. Bell's theorem, in more generality, states that if the measured values of various observables violate certain inequalities, then those results cannot be explained by any local hidden variables theory. This brings us to an experimental question: Maybe quantum mechanics is wrong! Can we actually observe, in the laboratory, results which violate the Bell inequalities (i.e. cannot be explained by local hidden variable theories)?

The relevant experiments were performed by Aspect and his collaborators in the 1970s. The two particles were two photons produced by the decay of Positronium (an electron-positron bound state). All of the quantum-mechanical predictions were confirmed. The mysterious non-local behavior of quantum theory, in which a measurement of particle 1 somehow causes the distant particle 2 to jump into a state of definite spin, cannot be explained by a local hidden variables theory.

Problem -   Given the state (22.19) and the O_2 eigenstates in eq. (22.18), derive the probabilities shown in Fig. 22.3.

Problem -   Suppose the two particles are electrons, and $O_1 = S_z$ is the spin component along the z-axis, with the green light flashing for $s_z = 1/2$, and the red light flashing for $s_z = -1/2$. Assume that O_2 measures the spin component $S_e = \vec{S} \cdot \vec{e}$ along some direction, specified by a unit vector

$$\vec{e} = \begin{bmatrix} a \\ b \\ c \end{bmatrix} \tag{22.20}$$

Again, the light flashes green for spin up along $\vec{e}$, and red for spin down. With this information, and eq. (22.18), find the direction $\vec{e}$.

22.3   Entangled States for "Quantum Radio"?

The EPR paradox and Bell's Theorem refer to experiments performed on particles in entangled states. Its easiest to define such states by what they are not.

Let $\Psi(x_1, x_2)$ denote a two-particle state. The state is **separable** if has the form

$$\Psi(x_1, x_2) = \psi(x_1)\varphi(x_2) \tag{22.21}$$

If it does not have this form, then the state is inseparable, or "**entangled**." Now suppose we are going to measure some observable A of particle 1, with eigenstates

$$\tilde{A}\phi_n(x_1) = \lambda_n \phi_n(x_1) \tag{22.22}$$

and, for simplicity, suppose the eigenvalues $\{\lambda_n\}$ are non-degenerate. Then we can always write $\Psi(x_1, x_2)$, whether separable or entangled, in the form

$$\Psi(x_1, x_2) = \sum_n c_n \phi_n(x_1)\varphi_n(x_2) \tag{22.23}$$

where

$$c_n \varphi_n(x_2) = \int dx_1 \phi_n^*(x_1) \Psi(x_1, x_2) \qquad (22.24)$$

Defined in this way, the states $\{\varphi_n(x_2)\}$ do not have to be orthogonal, they do not even have to be different states. If all the $\{\varphi_n(x_2)\}$ are the same state, then $\Psi(x_1, x_2)$ is separable. If at least some of the $\{\varphi_n(x_2)\}$ are different, then $\Psi(x_1, x_2)$ is entangled.

Now we make the measurement of observable A on particle 1, and one of the eigenvalues, $\lambda = \lambda_k$ say, is obtained. This means that particle 1 has jumped into the state $\phi_k(x_1)$. But, if the intial state is entangled, it *also* means that particle 2 has jumped into state $\varphi_k(x_2)$, which it was not in before. In other words, the entire two-particle state $\Psi(x_1, x_2)$ has "jumped" into state $\phi_k(x_1)\varphi_k(x_2)$, even if particles 1 and 2 are far apart, and a measurement is performed only on particle 1. This certainly seems like a non-local influence, and Bell's Theorem prevents the "cheap" explanation that particle 2 was really in state $\varphi_k(x_2)$ (perhaps supplemented by some "hidden" variables) all along.

Its natural to suppose that if a measurement at detector 1 causes something to happen to the distant particle 2, then this effect could be used to send messages, instantaneously, between the observer at detector 1 and the observer at detector 2. But if instantaneous (or in general, faster than light) communication were possible, then according to special relativity it should also be possible to send messages backwards in time. This would have some interesting practical applications. A typical scenario is as follows:

The four accomplices had planned it for years, after coming into possession of two pairs of super-secret - and highly illegal - quantum radios. Now for the payoff. John, the ringleader, stands at the betting window of a major racetrack, while his wife, Mary, waits impatiently on the planet Mars. The third participant, Rajiv, is piloting a rocketship which is heading towards Earth at a very substantial fraction of the speed of light. His partner, Fatima, is on another rocketship, moving parallel to Rajiv and at equal speed towards Mars. The objective of all these preparations is for John to learn the name of the winning horse at the Kentucky Derby, before the race is actually run.

The worldlines of all four participants are indicated on a spacetime diagram shown in Fig. 22.4. At point A in Fig. 22.4, the race has just ended.

"Niels Bohr", a long shot paying 200 to 1, has come in first. As Rajiv's rocket streaks overhead, John signals the name of the winning horse to him. Rajiv then uses his quantum radio to send this information instantaneously to Fatima.

However, as we know from relativity theory, simultaneity is relative to reference frame. In the John-Mary rest frame, events A and A', are simultaneous, and B and

B' are simultaneous, but A is later than B and B'. Not so in the Rajiv-Fatima rest frame: for them, events A and B' are simultaneous.

When Rajiv signals the name of the winning horse to Fatima, she receives this information at spacetime point B', just as her rocket is passing Mars. Fatima relays the important information to Mary, and then Mary contacts John, again by quantum radio, and transfers the message instantaneously (in the John-Mary rest frame) to Earth. The message reaches John at spacetime point B, several minutes before the race is to begin. John places a very large bet on "Niels Bohr" to win, and ...

Lets leave the story there. Could entangled states be used to send instantaneous messages in this way, even in principle? To answer this question, we again consider the apparatus shown in Fig. 22.2. John is at detector 1. Mary is at detector 2, but has an arsenal of laboratory equipment available to her, and can measure any observable she likes. Is there some observation which she could perform on the right-hand particles, which would tell her

I. whether John has turned on his detector; or

II. if John's detector is on, whether the switch is on setting 1 or setting 2?

The entangled state of the particles coming out of the detector can always be written in the form

$$|\Psi> = c_R|1R>_l \, |\psi>_r \, + c_G|1G>_l \, |\psi'> \qquad (22.25)$$

where, since this is an entangled state, $\psi \neq \psi'$. Mary has decided to measure the observable Q. Suppose first that John has turned off his detector. In that case Mary finds

$$
\begin{aligned}
<Q> \;\; &= \;\; <\Psi|Q|\Psi> \\
&= \;\; [c_R^* <1R|_l <\psi|_r + c_G^* <1G|_l <\psi'|_r] \, Q \, [c_R|1R>_l \, |\psi_r> \, + c_G|1G>_l \, |\psi'>_r] \\
&= \;\; |c_R|^2 <\psi|Q|\psi> \, + |c_G|^2 <\psi'|Q|\psi'> \qquad (22.26)
\end{aligned}
$$

where we have used the orthogonality

$$<1M|1N> = \delta_{MN} \qquad M = R \text{ or } G, \;\; N = R \text{ or } G \qquad (22.27)$$

Now John turns on his detector, with the switch setting at 1. When he makes a measurement, the two particles will be

$$
\begin{array}{lll}
\text{either in state} & |1R>|\psi>, & \text{with probability} \;\; |c_R|^2 \\
\text{or else in state} & |1G>|\psi'>, & \text{with probability} \;\; |c_G|^2
\end{array}
\qquad (22.28)
$$

If the right-hand particle is in state $|\psi>$, the expectation value for observable Q is $<\psi|Q|\psi>$; while if the particle is in state $|\psi'>$, the value is is $<\psi'|Q|\psi'>$. After many runs, the average value obtained must be

$$
\begin{aligned}
<Q> &= \text{Prob. to find 1R} \times <\psi|Q|\psi> + \text{Prob. to find 1G} \times <\psi'|Q|\psi'> \\
&= |c_R|^2 <\psi|Q|\psi> + |c_G|^2 <\psi'|Q|\psi'>
\end{aligned}
\tag{22.29}
$$

which is the same as result (22.26). Therefore Mary can't tell if John had turned on his detector, if the switch setting is at 1. What if John sets the switch to setting 2?

In general, the "switch 1" eigenstates $\{|1R>, |1G>\}$ and the "switch 2" eigenstates $\{|2R>, |2G>\}$ are simply different basis vectors for the left-hand particle Hilbert Space, related by a unitary transformation

$$
|1M> = \sum_{M=R,G} U_{MN} |2N>
\tag{22.30}
$$

where we recall that the unitarity property

$$
\delta_{MN} = \sum_J U_{NJ} U_{MJ}^*
\tag{22.31}
$$

follows from orthonormality

$$
\begin{aligned}
\delta_{MN} &= <1M|1N> \\
&= \sum_K U_{MK}^* <2K| \sum_J U_{NJ} |2J> \\
&= \sum_J U_{MJ}^* U_{NJ}
\end{aligned}
\tag{22.32}
$$

We can therefore write the entangled state $|\Psi>$ as

$$
\begin{aligned}
|\Psi> &= \sum_{M=R,G} [c_R U_{RM} |\psi>_r + c_G U_{GM} |\psi'>_r] |2M>_l \\
&= \sum_{M=R,G} b_M |2M>_l |\varphi_M>_r
\end{aligned}
\tag{22.33}
$$

where

$$
b_M |\varphi_M> \equiv c_R U_{RM} |\psi>_r + c_G U_{GM} |\psi'>_r
\tag{22.34}
$$

Then, after John makes his measurement, the particles will be

$$
\begin{array}{lll}
\text{either in state} & |2R>|\varphi_R>, & \text{with probability} \quad |b_R|^2 \\
\text{or else in state} & |2G>|\varphi_G>, & \text{with probability} \quad |b_G|^2
\end{array}
\tag{22.35}
$$

After many runs, the expectation value $<Q>$ is found by Mary to be

$$
<Q> = \text{Prob. to find 2R} \times <\varphi_R|Q|\varphi_R> + \text{Prob. to find 2G} \times <\varphi_G|Q|\varphi_G>
$$

$$
\begin{aligned}
&= \sum |b_M|^2 < \varphi_M|Q|\varphi_M > \\
&= \sum_M [c_R^* U_{RM}^* < \psi|_r + c_G^* U_{GM}^* < \psi'|_r] \, Q \, [c_R U_{RM}|\psi >_r + c_G U_{GM}|\psi' >_r] \\
&= \sum_M \big[|c_R|^2 U_{RM}^* U_{RM} < \psi|Q|\psi > + |c_G|^2 U_{GM}^* U_{GM} < \psi'|Q|\psi' > \\
&\quad\, + c_R^* c_G U_{RM}^* U_{GM} < \psi|Q|\psi' > + \text{c.c.}\big] \\
&= |c_R|^2 < \psi|Q|\psi > + |c_G|^2 < \psi'|Q|\psi' > \qquad\qquad (22.36)
\end{aligned}
$$

where, in the last step, we have used the unitarity property (22.32).

The conclusion is that nothing Mary can measure will tell her whether John has turned on his apparatus, or what observable he is measuring. This is a very general result, and can be easily extended to more complicated situations. There is no such thing as a "quantum radio;" entangled states can never be used to transfer information across long distances at a speed faster than light. One can never determine, just by a measurement on one of the particles, whether the state of the system is entangled, or whether is has become disentangled by a faraway measurement. The "entangled" nature of entangled states, and their strange, non-local properties, can only be appreciated when comparing measurements made on the *entire* system, rather than any one of its parts.

22.4   For Whom the Bell('s Theorem) Tolls

Entangled states are the norm, not the exception, in quantum mechanics. Generally speaking, when any two systems come into interaction, the resulting state of the combined system will be entangled. In this technical sense of quantum inseparability, the poet was right: no man is an island. No electron is an island either.

As we have seen, the existence of entangled states means that a measurement of one system can cause the second system, perhaps very distant from the first, to jump into one or another quantum state. It is time to return to the EPR criticism: *"Isn't this situation paradoxical? Doesn't it imply that something must be wrong with quantum theory?"*

Now first of all, as pointed out by Niels Bohr in his response to EPR, this situation is not really a paradox. The non-locality pointed out by EPR is certainly very, very strange. But quantum non-locality is not actually a paradox in the sense of being a logical contradiction.

"Well then, doesn't this non-local behavior violate theory of Relativity?" According to relativity theory, after all, no signal can propagate faster than the speed of light, so how can the state of particle 2 change instantaneously, in the laboratory reference frame, upon measurement of particle 1? Here we must be careful - the relativistic prohibition is against *information* propagating faster than the speed of light. If such propagation were possible, it would also be possible to send messages backwards in time, which would raise many other (authentic!) paradoxes. However,

we have just seen that the observer at detector 2 can never, by simply observing one of the particles, conclude anything about the settings of detector 1. Non-locality is not a violation of relativity in the sense of information transfer.

At this point, it is worth noting is that non-locality is not really unique to entangled states; some kind of non-local effect occurs in almost any measurement. Consider, for example a single particle, whose wavepacket $\psi(x)$ is distributed uniformly in a large, dark room, filled with particle detectors. At a given time $t = 0$ the detectors are suddenly all switched on and, just as suddenly, the position of the particle is measured. This means that the wavepacket of the particle, which was spread all over the room at $t < 0$, suddenly collapses to a narrow gaussian in the region of one of the detectors at $t = 0$. This is known as the "collapse of the wavefunction", and it also seems to be a form of non-local behavior. If we think of the particle wavepacket as some sort of fluid, by what mechanism does it instantaneously collapse?

Now, in volume 1 of these notes I have urged you to avoid thinking of the wavefunction as representing some sort of material fluid. There are just too many difficulties inherent in that kind of picture. Rather, one should think of Hilbert Space, rather than ordinary space, as being the arena of dynamics, where the state (vector) of a system evolves continuously, according to the Schrodinger equation, by rotation. This change of arena alleviates a lot of the problems associated with non-locality. On the other hand, I also said that a measurement causes the state to "jump," probabilistically, into one of a number of eigenstates of the quantity being measured.

Its time to face up to the real problem, the hard problem: By what process does a measurement cause a state to suddenly jump to one of a set of states? Can this behavior itself be explained quantum mechanically? This *very* puzzling issue has not been settled to this day. It is known as the Problem of Measurement.

Chapter 23

The Problem of Measurement

I was pleased to be able to answer immediately, and I did. I said I didn't know.

Mark Twain

More than seventy years have passed since the invention of quantum mechanics. It is a little disquieting that in all that time, despite its triumphant application to atomic, nuclear, sub-nuclear, and condensed matter physics, no general agreement has been reached on what quantum theory really *means*. This could indicate one of two things. First, it may be that quantum theory is wrong in some unexpected way, and this fact will someday be discovered by experiment. The other possibility is that the problem to be discussed in this Lecture is not really a scientific question, which can ultimately be settled by either calculation or experiment, but is more a philosophical issue, in which arguments for or against various views are destined to be endlessly refined, but no general consensus will ever be reached. In either case, the interpretation of quantum mechanics is a deep and fascinating subject. In this Lecture I will try to give a brief outline of the main contending views, although I cannot hope, in this short space, to do justice to any one of them.

23.1   Mixtures and Pure States

What does a measurement *do*?

We have asked that question before, back in Lecture 7. The answer is: If the detector is designed to measure some observable O, it will leave the measured object, at least for an instant, in a zero-uncertainty state $\Delta O = 0$ of that observable, i.e., in an eigenstate of the operator O, and record the eigenvalue found.

Suppose, once again, that the object is an electron, and the detector is a Stern-Gerlach apparatus which measures the electron spin in the z-direction. A red light goes on if the electron is spin-up, a green light goes on if it is spin down. The electron

exits the apparatus, which is enclosed in a black box, in an eigenstate of S_z (see Fig. 22.2).

Whenever we know the physical state of an object, the object is said to be in a "**pure state**." Suppose that the electron is in a "pure state" entering the apparatus, i.e. its state is known to be

$$\phi = A\alpha_z + B\beta_z \tag{23.1}$$

where, for simplicity, we disregard the x, y, z degrees of freedom and concentrate on the spin. Then, if the detector has been switched on, *but before we look inside the black box*, the electron exiting the detector must be

$$\begin{array}{ll} \text{either in state} & \alpha_z, \text{ with probability } |A|^2 \\ \text{or else in state} & \beta_z, \text{ with probability } |B|^2 \end{array} \tag{23.2}$$

This is an example of a "**mixed state**" or "**mixture**." In general, if the state of an object is not known with certainty, but it *is* known that the object is in one of a number of possible states, together with the probability of being in each state, then the object is said to be in a mixed state.

John, who has set up this experiment, has left the lab for the day. Mary, knowing John's forgetful nature, goes to check that the detector inside the black box has been switched off, thereby conserving the very expensive electronics inside. To her consternation, she discovers that the box has already been locked by the janitor, who has the only key. Can she tell, without opening the box, whether the detector inside the box is on of off?

It is always possible to distinguish between a pure state and a mixture. Suppose Mary measures, on the beam of electrons emerging from the box, the value of the observable Q. If the detector is switched off, then the particles emerging from the detector remain in the inital state ϕ, so that

$$\begin{aligned} <Q>_{pure} &= <\phi|Q|\phi> \\ &= |A|^2 <\alpha_z|Q|\alpha_z> + |B|^2 <\beta_z|Q|\beta_z> \\ &\quad + A^*B <\alpha_z|Q|\beta_z> + B^*A <\beta_z|Q|\alpha_z> \end{aligned} \tag{23.3}$$

while for the mixture

$$\begin{aligned} <Q>_{mix} &= \text{Prob. to find spin up} \times <\alpha_z|Q|\alpha_z> + \text{Prob. to find spin down} \times <\beta_z|Q|\beta_z> \\ &= |A|^2 <\alpha_z|Q|\alpha_z> + |B|^2 <\beta_z|Q|\beta_z> \end{aligned} \tag{23.4}$$

The difference between the pure and mixed-state results is called the "**interference term**"

$$\begin{aligned} <Q>_{int} &= <Q>_{pure} - <Q_{mix}> \\ &= A^*B <\alpha_z|Q|\beta_z> + B^*A <\beta_z|Q|\alpha_z> \end{aligned} \tag{23.5}$$

and reflects the fact that the pure state ψ, unlike the mixture (23.2), is not really in one or the other state α_z or β_z. Of course, the interference term will vanish if α_z and β_z are eigenstates of Q, e.g. if $Q = S_z$. Otherwise, the interference term is not zero. Thus, all Mary has to do is run the beam of electrons emerging from the first detector into a second detector, which measures electron spin in the x-direction; from the resulting $< S_x >$ she can learn whether or not the first detector has been switched off.

Problem - For $Q = S_x$, calculate $< Q >_{pure}$ for the pure state (23.1) with $A = -B = 1/\sqrt{2}$, and for the corresponding mixture.

The fact that mixtures can always be distinguished from pure states, at least in principle, also holds good for entangled pure states. Consider, for example, the pure state

$$\Psi = \sum_i c_i \phi_i(x_1) \varphi_i(x_2) \tag{23.6}$$

and the mixture

$$M = \{\text{particle in } one \text{ of the states} \quad \phi_i(x_1)\varphi_i(x_2) \quad \text{with probability} \quad |c_i|^2\} \tag{23.7}$$

Suppose, for simplicity, that all these states are orthonormal, i.e.

$$< \phi_i|\phi_j > = < \varphi_i|\varphi_j > = \delta_{ij} \tag{23.8}$$

and that A is an observable of particle 1, and B an observable of particle 2. It is easy to see that if we measure *only* A, or *only* B, that the mixture M and the pure state Ψ give exactly the same answer, namely

$$
\begin{aligned}
< A > &= \sum_i |c_i|^2 < \phi_i|A|\phi_i > \\
< B > &= \sum_i |c_i|^2 < \varphi_i|B|\varphi_i >
\end{aligned} \tag{23.9}
$$

However, if we measure the expectation value of the product AB, then we find that the pure state predicts

$$< AB >_{pure} = \sum_{ij} c_i^* c_j < \psi_i|A|\psi_j >< \varphi_i|B|\varphi_j > \tag{23.10}$$

while for the mixture

$$< AB >_{mix} = \sum_i |c_i|^2 < \psi_i|A|\psi_i >< \varphi_i|B|\varphi_i > \tag{23.11}$$

The interference term is

$$< AB >_{int} = \sum_{i \neq j} c_i^* c_j < \psi_i|A|\psi_j >< \varphi_i|B|\varphi_j > \tag{23.12}$$

and it is non zero providing the matrices

$$A_{ij} \equiv < \psi_i|A|\psi_j > \quad \text{and} \quad B_{ij} \equiv < \varphi_i|B|\varphi_j > \tag{23.13}$$

are both non-diagonal.

From this discussion we extract the following conclusions:

1. In principle, it is always possible to distinguish experimentally between a mixture and a pure state;

2. To distinguish between pure and mixed states of composite systems, one must make measurements on each of the components.

Thus, to the question, "what does a measurement *do*?," our tentative response is: "it leaves the measured system in a mixed state." More precisely, if the detector makes a measurement of observable Q whose eigenstates are $\{\phi_i\}$, and if the the particle as it enters the detector is in the one-particle pure-state

$$\psi = \sum_i c_i \phi_i \tag{23.14}$$

then the particle, immediately after detection, will be in the mixed state

$$M = \{\text{particle in one of the states} \quad \phi_i \quad \text{with probability} \quad |c_i|^2\} \tag{23.15}$$

23.2   The Problem of Measurement

The problem of measurement is the problem that no closed system, evolving according to the Schrodinger equation, can ever make a transition from a pure state to a mixed state. A measurement, as we have described it, can therefore never occur if *all* relevant objects (the detector as well as the detected object) obey the Schrodinger equation.

In order to explain how a detector works, one would begin by analyzing the interaction between the detector and the particle, and describe the evolution of the particle-detector system in terms of some (probably very complicated) Hamiltonian, involving the degrees of freedom of both the particle and the detector. But to understand why there is a problem connected with the measurement process, one doesn't need to know anything about this complicated Hamiltonian. It is enough to simply assume that an appropriate Hamiltonian exists such that, if the particle starts out in

an eigenstate of the relevant observable, then the corresponding eigenvalue is some-
how registered by the detector. Once again, take the measurement of electron spin as
an example. The detector is designed to measure S_z. This means that if the initial
state of the particle-detector system is

$$|\Psi_0 >= |up > |ready > \tag{23.16}$$

where $|up >$ means the electron is in a spin-up state, and $|ready >$ means that the
detector has been switched on, then the interaction between the electron and detector
leaves the combined system in the final state

$$|\Psi_f >= |up > |red > \tag{23.17}$$

where $|red >$ indicates that red light on the detector is on. It is assumed that the
transition from the intial to final state is adequately explained by the Schrodinger
equation, and thus we write, schematically,

$$|up > |ready > \longrightarrow |up > |red > \tag{23.18}$$

Similarly, if the particle starts in a spin-down state,

$$|down > |ready > \longrightarrow |down > |green > \tag{23.19}$$

Now for the crucial point. The Schrodinger equation is a *linear* equation. This
means that if

$$\psi_a(x,t) \quad \text{and} \quad \psi_b(x,t) \tag{23.20}$$

are both solutions of the Schrodinger equation, and if the intial state is

$$\Psi_0 = A\psi_a(x,0) + B\psi_b(x,0) \tag{23.21}$$

then the corresponding final state (at time $t = T$, say) is

$$\Psi_f = A\psi_a(x,T) + B\psi_b(x,T) \tag{23.22}$$

Suppose, then, that the electron entering the detector is in the spin state

$$|\psi >= A|up > +B|down > \tag{23.23}$$

so that the initial particle-detector state is

$$\begin{aligned}
|\Psi_0 > &= |\psi > |ready > \\
&= A|up > |ready > +B|down > |ready >
\end{aligned} \tag{23.24}$$

Then, from the linearity of the Schrodinger equation, we can conclude that the
particle-detector system must end up in the entangled final state

$$|\Psi >= A|up > |red > +B|down > |green > \tag{23.25}$$

THIS IS A PURE STATE, NOT A MIXTURE! A mixture, for the particle-detector
system would be

$$M = \begin{cases} \text{either in state} & |up>|red>, & \text{with probability} & |A|^2 \\ \text{or else in state} & |down>|green>, & \text{with probability} & |B|^2 \end{cases} \quad (23.26)$$

We have seen that pure states can always be distinguished, in principle, from mix-
tures. Then we are forced to conclude, after the measurement process has supposedly
taken place, that the light on the detector is neither flashing red, nor green, but is
somehow in a superposition of the two possible states!

When we add a human observer to the system, the quantum-mechanical assault
on common-sense only gets worse. Denote the initial state of the observer by the ket
"$|waiting>$." When the observer sees a red light flash, her state changes to a new
state, denoted $|I\ saw\ red>$; likewise, if the green light flashes, the observer is left
in the state $|I\ saw\ green>$. The Hamiltonian describing the interaction between
particle, detector, and observer is assumed to lead to

$$|up>|ready>|waiting> \longrightarrow |up>|red>|I\ saw\ red> \quad (23.27)$$

Similarly, if the particle starts in a spin-down state,

$$|down>|ready>|waiting> \longrightarrow |down>|green>|I\ saw\ green> \quad (23.28)$$

Then, if the instead the particle starts off in the superposition of spin states $|\psi>$ of
eq. (23.23), so the initial state of the combined system is

$$\begin{aligned} |\Psi_0> &= |\psi>|ready>|waiting> \\ &= A|up>|ready>|waiting> +B|down>|ready>|waiting> \end{aligned} \quad (23.29)$$

Then, by the linearity of the Schrodinger equation, we are forced to conclude that
the particle-detector-observer system ends up in the entangled final state

$$|\Psi_f> = A|up>|red>|I\ saw\ red> +B|down>|green>|I\ saw\ green> \quad (23.30)$$

The observer has also ended up in a quantum superposition, in which she is neither in
the $|I\ saw\ red>$ state, nor in the $|I\ saw\ down>$ state. And this strange conclusion
is deduced simply from the assumption that a particle in a spin up (down) state
always leads the observer to an "I saw red (green)" state, and from the linearity of
the Schrodinger equation.

Its time to stand back and reconsider. A simple line of reasoning, founded on the
well-established principles of quantum mechanics, has led us to a nonsensical result.
It is not just that the conclusion is counter-intuitive; by now you should be used to
that. Rather, the problem is that the apparent conclusion is just *wrong*: Human
beings never find themselves in superpositions of this kind. There must, somewhere,
be an error in our reasoning. But where?

23.3   The "Classic" Views (I): von Neumann

The simplest answer was given by von Neumann, who urges us to follow the chain of events into the brain of the observer. The detector is in a superposition of "red light/green light" states, and it emits photons in a superposition of the corresponding frequencies. The photons reach the retina of the observer, and certain neurons are left in a superposition of excited/un-excited states. The message from the retina travels to the cerebral cortex; very large collections of neurons are now in quantum superpositions, and the brain remains in such a superposition until, at some point, a *sensation* occurs. At the instant of conscious perception, the observer, the detector, and even the particle, jump into one or the other of the "up/down, red/green" states.

What von Neumann is suggesting is that human consciousness causes the wavefunction to "collapse," with a certain probablity, into one or another of the possible neural states; the collapse of the wavefunction occurs due to the awareness of the observer. It follows, since the Schrodinger equation can never cause a wavefunction to collapse (i.e. cause a pure state to go to a mixture), that the mental function described as "awareness" or "conciousness" cannot be described by the Schrodinger equation; it is not a physical process in the usual sense.

The notion that there is something special about conciousness, and that it cannot be explained by the dynamical laws that govern all other physical processes, is anathema to most scientists. It is reminiscent of vitalism; a theory which held that one must look beyond the usual laws of physics and chemistry to explain the processes which occur in living organisms. This theory was, of course, long ago discredited by spectacular advances in molecular biology.

Still, von Neumann's idea should not be rejected out of hand. Philosophers have argued for centuries about the so-called mind/body problem, and there exist sophisticated arguments to the effect that, e.g., a computer following a complicated algorithm to simulate some aspect of human behavior can never actually "understand" what it is doing.[1] In the absence of any well-established "Theory of Consciousness," it is not entirely obvious that awareness can be explained entirely in terms of the dynamics of molecules obeying the Schrodinger equation. von Neumann argues that mental processes simply *cannot* be explained in this way, due to the absence of superimposed mental states. His argument, although obviously radical, cannot be immediately dismissed.

23.4   The "Classic" Views (II): Bohr

Niels Bohrs' view (a.k.a. "the Copenhagen Interpretation") is that the wavefunction which represents the physical state of a microscopic object does not refer to the state

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[1] A fascinating and recent exposition of this point of view is found in the book *Shadows of the Mind*, by Roger Penrose.

of the object in isolation from the observer. Rather, the wavefunction is a compact representation of the observer's *information* about the observables of a given object, and merely describes the possible outcome of a series of measurements. Put another way, the wavefunction does not refer to "physical reality" per se, in the absence of an observer; it serves only to predict and correllate measurements. If there is no observer, then no meaning can be attached to a quantum-mechanical wavefunction. From this point of view, the "collapse" of the wavefunction does not describe a new physical process; it is just a change in the information available to the observer, obtained by measurement.

The main criticism that can be leveled at Bohr's interpretation is that it becomes meaningless to speak of the physical state of an object in the absence of an observer. How, then, can we describe quantum-mechanical processes that may have occured in nature prior to the evolution of human beings, or events which, for one reason or another, may have escaped human scrutiny? In classical physics, every object in the Universe has a physical state, a definite position and momentum, regardless of whether or not human beings are around to measure that state. Not so for quantum mechanics, at least in the Bohr interpretation. It is impossible, in this view, to imagine that any object is in any definite quantum state, without at least an implicit reference to the Observer.

The fact that human observers are somehow an essential feature of the quantum-mechanical description of nature is, for some, a very troubling aspect of Bohr's view. In general, the Copenhagen interpretation has something of the flavor of logical positivism, a philosophy which holds that the purpose of science is to correllate measurements, rather than describe some "objective" reality. "Objective reality," in the positivist view, is a meaningless concept, and science should be formulated entirely in terms of quantities which can be measured directly. This view, in the hands of Mach and others, had considerable influence on physics in the early 20th century, and certainly the Copenhagen interpretation show traces of this influence.

It is a little distressing to think that science is not about Nature, but only about correllating measurements. Still, the consistency of the Copenhagen interpretation, and its ability to evade puzzles connected with the apparent non-local "collapse" of entangled wavefunctions, should not be underestimated. To the extent that there is an "official" interpretation of quantum theory, it would be the Copenhagen view.

In Preparation:

23.5 The Many-Universe Interpretation

23.6 Non-Local Hidden Variables: The Bohm Theory

23.7 Decoherence and Consistent Histories

Chapter 24

The Feynman Path Integral

In classical physics the Euler-Lagrange equations are derived from the condition that the action $S[x(t)]$ should be stationary. These second order equations are equivalent to the first order Hamilton equations of motion, which are obtained by taking appropriate derivatives of the Hamiltonian function $H[q, p]$. Now the Hamiltonian is a quantity that we have encountered frequently in these pages. But what about the action? It would be surprising if something so fundamental to classical physics had no part at all to play in quantum theory. In fact, the action has the central role in an alternative approach to quantum mechanics known as the "path-integral formulation."

Lets start with the concept of a propagator. Given the wavefunction $\psi(x, t)$ at time t, the wavefunction at any later time $t + T$ can be expressed as

$$\psi(x, t + T) = \int dy \, G_T(x, y)\psi(y, t) \qquad (24.1)$$

where $G_T(x, y)$ is known as the *propagator*, and of course it depends on the Hamiltonian of theory. In fact, given a time-independent Hamiltonian with eigenstates

$$H\phi_n(x) = E_n\phi_n(x) \qquad (24.2)$$

its easy to see that

$$G_T(x, y) = \sum_n \phi_n(x)\phi_n^*(y)e^{-iE_nT} \qquad (24.3)$$

Richard Feynman, in 1948, discovered a very beautiful expression for the propagator in terms of an integral over all paths that the particle can follow, from point y at time t, to point x at time $t + T$, with an integrand

$$e^{iS[x(t)]/\hbar} \qquad (24.4)$$

As we will see, his expression can be taken as a new way of quantizing a mechanical system, equivalent to the "canonical" approach based on exchanging observables for operators.

To see how a sum over paths comes in, lets suppose that we knew the propagator, for *any* Hamiltonian, when the time difference $T = \epsilon$ is tiny, i.e.

$$\psi(x, t + \epsilon) = \int dy \; G_\epsilon(x, y)\psi(y, t) \tag{24.5}$$

In that case, we could get the propagator for large time differences by using the propagator successively, i.e.

$$\psi(x, t + 2\epsilon) = \int dy dx_1 \; G_\epsilon(x, x_1)G_\epsilon(x_1, y)\psi(y, t)$$

$$\psi(x, t + 3\epsilon) = \int dy dx_2 dx_1 \; G_\epsilon(x, x_2)G_\epsilon(x_2, x_1)G_\epsilon(x_1, y)\psi(y, t) \tag{24.6}$$

and by induction

$$\psi(x, t + N\epsilon) = \int dy \int \left(\prod_{i=1}^{N-1} dx_n \right) G_\epsilon(x, x_{N-1})G_\epsilon(x_{N-1}, x_{N-2})...G_\epsilon(x_1, y)\psi(y, t) \tag{24.7}$$

So the propagator, for the time difference $T = N\epsilon$, has the form

$$G_T(x, y) = \int \left(\prod_{i=1}^{N-1} dx_n \right) G_\epsilon(x, x_{N-1})G_\epsilon(x_{N-1}, x_{N-2})...G_\epsilon(x_1, y) \tag{24.8}$$

Now a set of points:

$$
\begin{array}{lll}
y & \text{at time} & t \\
x_1 & \text{at time} & t + \epsilon \\
x_2 & \text{at time} & t + 2\epsilon \\
... & .... & .... \\
x_{N-1} & \text{at time} & t + (N-1)\epsilon \\
x & \text{at time} & t + T
\end{array}
\tag{24.9}
$$

connected by straight lines, as shown in Fig. 24.1, is a path between point (y, t) and point $(x, t + T)$. The integral in eq. (24.8) is therefore a sum over all paths between these two points, which consist of N straight-line segments of equal time-duration $\epsilon = T/N$. Clearly, as $N \to \infty$, any continuous path between (y, t) and $(x, t + T)$ can be approximated to arbitrary precision.

Its clear, then, that a propagator can be represented by a sum over paths. The problem is to find an expression for $G_\epsilon(x, y)$, which doesn't involve first solving the eigenvalue equation (24.2) and plugging the result into (24.3). Fortunately, if ϵ is very small, we can deduce $G_\epsilon(x, y)$ from the time-dependent Schrodinger equation. First, approximate the time-derivative with a finite difference

$$i\hbar \frac{\psi(x, t + \epsilon) - \psi(x, t)}{\epsilon} \approx H\psi(x, t) \tag{24.10}$$

so that

$$
\begin{aligned}
\psi(x, t + \epsilon) &= \left(1 + \frac{\epsilon}{i\hbar}H\right)\psi(x, t) + O(\epsilon^2) \\
&= \left(1 - i\frac{\epsilon}{\hbar}V + \frac{i\epsilon\hbar}{2m}\frac{d^2}{dx^2} + O(\epsilon^2)\right)\psi(x, t) \\
&= e^{-i\epsilon V(x)/\hbar}\left(\psi(x, t) + \frac{i\epsilon\hbar}{2m}\psi''(x, t)\right) + O(\epsilon^2) \quad (24.11)
\end{aligned}
$$

Now lets write $y = x + \eta$, and expand $\psi(y, t)$ in eq. (24.5) in a Taylor series

$$
\begin{aligned}
\psi(x, t + \epsilon) &= \int dy \, G_\epsilon(x, y)\psi(y, t) \\
&= \int d\eta \, G_\epsilon(x, x + \eta)\left[\psi(x) + \psi'(x)\eta + \frac{1}{2}\psi''(x)\eta^2 + ...\right] \quad (24.12)
\end{aligned}
$$

Comparing (24.11) and (24.12) we see that, to first order in ϵ, the propagator $G_\epsilon(x, x + \eta)$ must satisfy

$$
\begin{aligned}
\int d\eta \, G_\epsilon(x, x + \eta) &= e^{-i\epsilon V(x)/\hbar} \\
\int d\eta \, G_\epsilon(x, x + \eta)\eta &= 0 \\
\int d\eta \, G_\epsilon(x, x + \eta)\eta^2 &= \frac{i\epsilon\hbar}{m} \quad (24.13)
\end{aligned}
$$

Its also clear from (24.5) that, in the $\epsilon \to 0$ limit, the propagator must become a delta function, i.e.

$$
\lim_{\epsilon \to 0} G_\epsilon(x, x + \eta) = \delta(\eta) \quad (24.14)
$$

Therefore, $G_\epsilon(x, x + \eta)$ is a delta sequence. We have seen two examples of delta sequences in Lecture 4; one involved the integral of e^{ikx} over a finite range, the other was a gaussian. The gaussian delta-sequence, together with the first of the conditions in eq. (24.13), motivates trying, as an ansatz

$$
G_\epsilon(x, x + \eta) = e^{-i\epsilon V(x)/\hbar}\sqrt{\frac{A}{\pi}}e^{-A\eta^2} \quad (24.15)
$$

which will be a delta-sequence if $A \to \infty$ as $\epsilon \to 0$. It is easy to check that this ansatz satisfies the first and second conditions in (24.13). The constant A is determined by the third condition

$$
\begin{aligned}
\frac{i\epsilon\hbar}{m} &= \sqrt{\frac{A}{\pi}}\int d\eta \, \eta^2 e^{-A\eta^2} \\
&= \frac{1}{2A} \quad (24.16)
\end{aligned}
$$

Solving for A, and recalling $\eta = x - y$, we finally have to first order in ϵ,

$$G_\epsilon(x, y) = \left(\frac{m}{2i\pi\epsilon\hbar}\right)^{1/2} \exp\left[i\frac{\epsilon}{\hbar}\left\{\frac{1}{2}m\left(\frac{x-y}{\epsilon}\right)^2 - V(x)\right\}\right] \qquad (24.17)$$

The expression above for $G_\epsilon(x, y)$ is not exact; there are $O(\epsilon^2)$ corrections. If we insert this expression into eq. (24.8), the result for $G_T(x, y)$ will not be exact either: the product of T/ϵ terms will give an overall error of order ϵ. However, we can get the *exact* result for $G_T(x, y)$ by taking the $N \to \infty$ ($\epsilon = \frac{T}{N} \to 0$) limit

$$
\begin{aligned}
G_T(x, y) \\
&= \lim_{N\to\infty} \int \left(\prod_{i=1}^{N-1} dx_n\right) G_\epsilon(x, x_{N-1})G_\epsilon(x_{N-1}, x_{N-2})...G_\epsilon(x_1, y) \\
&= \lim_{N\to\infty} \int \left(\prod_{i=1}^{N-1} dx_n\right) \left(\frac{m}{2i\pi\epsilon\hbar}\right)^{N/2} \exp\left[\frac{i}{\hbar}\sum_{n=1}^{N} \epsilon\left(\frac{1}{2}m\frac{(x_n - x_{n-1})^2}{\epsilon^2} - V(x_n)\right)\right] (24.18)
\end{aligned}
$$

where we have defined $x_0 \equiv y$ and $x_N \equiv x$. We now introduce the notation for the integral over all possible paths

$$\int Dx(t) \equiv \lim_{N\to\infty} \int \left(\prod_{i=1}^{N-1} dx_i\right) \left(\frac{m}{2i\pi\epsilon\hbar}\right)^{N-1/2} \qquad (24.19)$$

and note that in the $\epsilon \to 0$ limit

$$
\begin{aligned}
\lim_{N\to\infty} \sum_{n=1}^{N} \epsilon\left(\frac{1}{2}m\frac{(x_n - x_{n-1})^2}{\epsilon^2} - V(x_n)\right) &= \int_t^{t+T} dt\left(\frac{1}{2}m\dot{x}^2 - V(x)\right) \\
&= S[x(t)] \qquad (24.20)
\end{aligned}
$$

where $S[x(t)]$ is the action functional defined back in Lecture 1. At last we have arrived at the **Feynman Path Integral**

$$G_T(x, y) = \int Dx(t)\, e^{iS[x(t)]/\hbar} \qquad (24.21)$$

In words, this equation says that the amplitude for a particle to propagate from point y at time t to point x at time $t + T$ is given by the integral over all possible paths running between those two points, with each path weighted by the amplitude e^{iS}, where S is the action of the given path. Of course, the *precise* meaning of $\int Dx(t)$, the sum over paths, must be given in terms of a limit, namely, the limit of a multiple integral, as the number of integrals goes to infinity. But recall that the *precise* meaning of an ordinary integral is also in terms of a limit: the limit of a sum over very many points, as the number of points tends to infinity.

24.1 The Free Particle Propagator

One might wonder if the path-integral formulation is useful: Is it really possible to carry out an infinite multiple integral? The answer is yes, if the integrand is gaussian. *Any* gaussian integral can be done, no matter whether it is a single integral, a multiple integral, or a path integral.

As an example, we will work out the propagator for a free particle by two methods: first, by using eq. (24.3), and, second, from the Feynman path integral. For a free particle

$$
\begin{aligned}
\phi_p(x) &= \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar} \\
E_p &= \frac{p^2}{2m}
\end{aligned}
\tag{24.22}
$$

so eq. (24.3) becomes

$$
G_T(x,y) = \int \frac{dp}{2\pi\hbar} \ \exp\left[-\frac{iT}{2m\hbar}p^2 + \frac{i(x-y)}{\hbar}p\right]
\tag{24.23}
$$

Using the gaussian integral formula

$$
\int dp \ e^{-ap^2+bp} = \sqrt{\frac{\pi}{a}}e^{b^2/4a}
\tag{24.24}
$$

we find

$$
\begin{aligned}
G_T(x,y) &= \frac{1}{2\pi\hbar}\left(\frac{\pi}{iT/(2m\hbar)}\right)^{1/2} \exp\left[-\frac{(x-y)^2/\hbar^2}{4iT/(2m\hbar)}\right] \\
&= \left(\frac{m}{2i\pi\hbar T}\right)^{1/2} \exp\left[i\frac{m(x-y)^2}{2\hbar T}\right]
\end{aligned}
\tag{24.25}
$$

Now lets try to compute the same quantity by the path-integral method. We have

$$
G_T(x,y) = \lim_{N\to\infty} B^{-N} \int dx_{N-1}dx_{N-2}...dx_1 \ \exp\left[-\frac{m}{2i\hbar\epsilon}\sum_{n=1}^{N}(x_n - x_{n-1})^2\right]
\tag{24.26}
$$

where

$$
B = \left(\frac{2\pi i\epsilon\hbar}{m}\right)^{1/2}
\tag{24.27}
$$

Factors like $(x_k - x_{k-1})^2$ couple together the integrals together. What we need is a change of variables which will uncouple them, so that we can do the integrals one-by-one. This is accomplished by the change of variables

$$
\begin{aligned}
z_k &= x_k - x_{k-1} \\
\sum_{n=1}^{N-1} z_k &= x_{N-1} - y
\end{aligned}
\tag{24.28}
$$

(recall that $x = x_N$, $y = x_0$), and let

$$a = \frac{m}{2i\epsilon\hbar} \tag{24.29}$$

Then

$$
\begin{aligned}
G_T(&x,y) \\
&= \lim_{N\to\infty} B^{-N} \int dz_{N-1}dz_{N-2}...dz_1 \, \exp\left[-a(x - x_{N-1})^2 - a\sum_{k=1}^{N-1} z_k^2\right] \\
&= \lim_{N\to\infty} B^{-N} \int dz_{N-1}dz_{N-2}...dz_1 \, e^{-a\sum_{k=1}^{N-1} z_k^2} \exp\left[-a(x - y - \sum_{k=1}^{N-1} z_k)^2\right] \\
&= \lim_{N\to\infty} B^{-N} \int dz_{N-1}dz_{N-2}...dz_1 \, e^{-a\sum_{k=1}^{N-1} z_k^2} \int du \, e^{-a(x-y-u)^2} \delta\left[u - \sum_{k=1}^{N-1} z_k\right] \\
&= \lim_{N\to\infty} B^{-N} \int dz_{N-1}dz_{N-2}...dz_1 \, e^{-a\sum_{k=1}^{N-1} z_k^2} \int du \, e^{-a(x-y-u)^2} \int \frac{dq}{2\pi} e^{iq(u-\sum_{k=1}^{N-1} z_k)} \\
&= \lim_{N\to\infty} B^{-N} \int \frac{dq}{2\pi} \int du \, e^{-a(x-u-y)^2} e^{iqu} \prod_{n=1}^{N-1} \int dz_k e^{-az_k^2 + iqz_k} \tag{24.30}
\end{aligned}
$$

At this point, we again use the gaussian integral formula to do each of the $N-1$ integrals over the $\{z_k\}$. This gives us

$$
\begin{aligned}
G_T(x,y) &= \lim_{N\to\infty} B^{-N} \int \frac{dq}{2\pi} \int du \, e^{-a(x-u-y)^2} e^{iqu} \left[\sqrt{\frac{\pi}{a}} e^{-q^2/4a}\right]^{N-1} \\
&= \left(\frac{\pi}{a}\right)^{(N-1)/2} \lim_{N\to\infty} B^{-N} \int \frac{dq}{2\pi} \int du \, e^{-a(x-u-y)^2} e^{iqu} e^{-(N-1)q^2/4a} \tag{24.31}
\end{aligned}
$$

Finally, in rapid succession, we do the gaussian integrals over q and then u,

$$
\begin{aligned}
G_T(x,y) &= \lim_{N\to\infty} B^{-N} \left(\frac{\pi}{a}\right)^{(N-1)/2} \frac{1}{2\pi} \sqrt{\frac{\pi}{(N-1)/4a}} \int du \, e^{-a(x-u-y)^2} \exp[-\frac{u^2}{4(N-1)/4a}] \\
&= \lim_{N\to\infty} B^{-N} \left(\frac{\pi}{a}\right)^{(N-1)/2} \frac{1}{2\pi} \sqrt{\frac{\pi}{(N-1)/4a}} \int du \, e^{-a(x-u-y)^2} e^{-a(x-y)^2/(N-1)} \\
&= \lim_{N\to\infty} B^{-N} \left(\frac{\pi}{a}\right)^{(N-1)/2} \frac{1}{2\pi} \sqrt{\frac{4a\pi}{(N-1)}} \sqrt{\frac{\pi}{a}} e^{-a(x-y)^2/(N-1)} \tag{24.32}
\end{aligned}
$$

Inserting the expression for B, we get

$$
\begin{aligned}
G_T(x,y) &= \lim_{N\to\infty} \left[\frac{m}{2\pi i\hbar\epsilon}\right]^{N/2} \left[\frac{2\pi i\epsilon\hbar}{m}\right]^{N/2} \sqrt{\frac{a}{\pi(N-1)}} e^{-a(x-y)^2/(N-1)} \\
&= \lim_{N\to\infty} \sqrt{\frac{m}{2\pi i\hbar\epsilon(N-1)}} \exp\left[-\frac{m(x-y)^2}{2i\hbar\epsilon(N-1)}\right] \tag{24.33}
\end{aligned}
$$

and finally, using $T = N\epsilon$, we have in the $N \to \infty$ limit

$$G_T(x, y) = \sqrt{\frac{m}{2\pi i \hbar T}} e^{im(x-y)^2/(2\hbar T)} \tag{24.34}$$

which is in perfect agreement with the expression obtained using eq. (24.3).

24.2 Stationary Phase and the Functional Derivative

A function f is a kind of input/output device. Input is a number x, output is another number $f(x)$. A generalization of the concept of function is the **functional**, which is also an input/output device. Input is a function $f(x)$, output is a number $F[f(x)]$. An example of a functional is the action $S[x(t)]$. Input is trajectory, $x(t)$, between times t_1 and t_2. Output is a number, the action of the trajectory

$$S[x(t)] = \int_{t_1}^{t_2} dt \left\{ \frac{1}{2} m \dot{x}^2 - V(x(t)) \right\} \tag{24.35}$$

An ordinary integral sums the values of a function over all points in a certain range. A *functional integral* sums the values of a functional over all functions in a certain range. The Feynman path integral

$$\int Dx(t) \, e^{iS[x(t)]/\hbar} \tag{24.36}$$

is a functional integral.

If there is such a thing as integration of a functional, one expects also a corresponding concept of differentiation, which would express how fast the functional changes when its argument (the function), changes in a certain way. The *functional derivative* is defined, in analogy to ordinary derivatives, in the following way:

$$\frac{\delta F}{\delta f(x)} \equiv \lim_{\epsilon \to 0} \frac{F[f(x') + \epsilon \delta(x - x')] - F[f(x')]}{\epsilon} \tag{24.37}$$

This quantity is essentially a measure of how fast the functional changes when its argument (the function) is changed in the region of point $x' = x$. Most of the usual lore about ordinary derivatives, e.g. the chain rule, holds true for functional derivatives as well. A particular, very important case is when the functional depends only on the value of the input function at one particular point, e.g. $F(f) = f(y)$. In this case

$$
\begin{aligned}
\frac{\delta}{\delta f(x)} f(y) &= \lim_{\epsilon \to 0} \frac{(f(y) + \epsilon \delta(y - x)) - f(y)}{\epsilon} \\
&= \delta(x - y) \tag{24.38}
\end{aligned}
$$

This example generalizes in a straightforward way

$$
\begin{aligned}
\frac{\delta}{\delta f(x)} f^n(y) &= \lim_{\epsilon \to 0} \frac{(f(y) + \epsilon\delta(y - x))^n - f^n(y)}{\epsilon} \\
&= n f^{n-1}(y)\delta(x - y) \\
\frac{\delta}{\delta f(x)} R(f(y)) &= \lim_{\epsilon \to 0} \frac{R(f(y) + \epsilon\delta(y - x)) - R(f(y))}{\epsilon} \\
&= \frac{\partial R(f(y))}{\partial f(y)}\delta(x - y) \quad\quad (24.39)
\end{aligned}
$$

Functional differentiation is the easiest and quickest way to derive the Euler-Lagrange equations of motion, from the condition

$$
\frac{\delta S}{\delta x(t)} = 0 \quad\quad (24.40)
$$

that the action should be stationary with respect to an infinitesmal change of path. This works as follows:

$$
\begin{aligned}
0 &= \frac{\delta S}{\delta x(t)} \\
&= \frac{\delta}{\delta x(t)} \int dt' \left\{ \frac{1}{2} m\dot{x}^2 - V(x(t')) \right\} \\
&= \int dt' \left\{ \frac{1}{2} m \frac{\delta}{\delta x(t)}\dot{x}^2 - \frac{\delta}{\delta x(t)} V(x(t')) \right\} \quad\quad (24.41)
\end{aligned}
$$

Now, using the definition of the functional derivative and the properties of delta functions, we have

$$
\begin{aligned}
m\frac{\delta}{\delta x(t)}\dot{x}^2 &= \lim_{\epsilon \to 0} \frac{[\partial_{t'}(x(t') + \epsilon\delta(t - t'))]^2 - (\partial_{t'}x(t'))^2}{\epsilon} \\
&= 2\dot{x}(t')\partial_{t'}\delta(t - t') \\
&= -2\partial_{t'}^2 x(t')\delta(t - t') \quad\quad (24.42)
\end{aligned}
$$

Then

$$
\begin{aligned}
0 &= \int dt' \left\{ -m\partial_{t'}^2 x(t')\delta(t - t') - \frac{\partial V(x(t'))}{\partial x(t')}\delta(t - t') \right\} \\
&= -m\partial_t^2 x - \frac{\partial V}{\partial x} \quad\quad (24.43)
\end{aligned}
$$

which is, of course, Newton's Law of motion $F = ma$.

To get a little more practice with functional derivatives, lets find the equations of motion for a wave on a string. Denote the wavefunction of the string (which in this

case just means the displacement of the string at point x and time t, by $\phi(x,t)$. The action of the string is known to be

$$S[\phi] = \mu \int dt' \int dx' \left\{ \frac{1}{2}(\partial_{t'}\phi(x',t'))^2 - \frac{v^2}{2}(\partial_{x'}\phi(x',t'))^2 \right\} \tag{24.44}$$

where μ is the string mass per unit length. Then the equation of motion for the string is found from the condition that the action is stationary with respect to small variations in $\phi(x,t)$, i.e.

$$
\begin{aligned}
0 &= \frac{\delta}{\delta\phi(x,t)} S[\phi(x',t')] \\
&= \lim_{\epsilon \to 0} \frac{S[\phi(x',t') + \epsilon\delta(x-x')\delta(t-t')] - S[\phi(x',t')]}{\epsilon} \\
&= \mu \int dt' \int dx' \left\{ \frac{1}{2}\frac{\delta}{\delta\phi(x,t)}(\partial_{t'}\phi(x',t'))^2 - \frac{v^2}{2}\frac{\delta}{\delta\phi(x,t)}(\partial_{x'}\phi(x',t'))^2 \right\} \\
&= \mu \int dt' dx' \left\{ \partial_{t'}\phi(x',t')\partial_{t'}\frac{\delta\phi(x',t')}{\delta\phi(x,t)} - v^2\partial_{x'}\phi(x',t')\partial_{x'}\frac{\delta\phi(x',t')}{\delta\phi(x,t)} \right\} \tag{24.45}
\end{aligned}
$$

and using

$$\frac{\delta\phi(x',t')}{\delta\phi(x,t)} = \delta(x-x')\delta(t-t') \tag{24.46}$$

and the property

$$f(x)\partial_x\delta(x-y) = -[\partial_x f(x)]\delta(x-y) \tag{24.47}$$

we obtain

$$0 = \mu \int dx' dt' \left\{ -\partial_{t'}^2\phi(x',t') + v^2\partial_{x'}^2\phi(x',t') \right\} \delta(x-x')\delta(t-t') \tag{24.48}$$

which finally leads us to the classical equation of motion, namely, the wave equation

$$\frac{\partial^2\phi}{\partial t^2} - v^2\frac{\partial^2\phi}{\partial x^2} = 0 \tag{24.49}$$

Its now easy to understand the relationship between the Feynman path integral and classical physics. Lets ask the question of which paths, out of all possible paths between two points (x_1, t_1) and (x_2, t_2), give the largest contribution to the path integral

$$\int Dx(t) \, e^{iS[x(t)]/\hbar} \tag{24.50}$$

Now the contribution of each path to the integral has the same magnitude, since $e^{iS/\hbar}$ is just a complex number of modulus 1. However, if $S \gg \hbar$, then for most paths a small variation $\delta x(t)$ in the path will cause an enormous change in the phase $S/\hbar$ the integrand. Therefore, the contributions from nearby paths oscillate wildly in phase,

and tend to cancel each other out. The exception is for paths in the vicinity of a path where the phase $S/\hbar$ is stationary. For paths in that vicinity, the contributions to the functional integral have nearly the same phase, and hence sum up contructively. But the path where the phase is stationary is the path $x_{cl}(t')$ such that

$$\left(\frac{\delta S}{\delta x(t)}\right)_{x=x_{cl}} = 0 \qquad (24.51)$$

As we have seen, this is just the condition that the path $x_{cl}(t)$ is a solution of the classical equations of motion. Therefore, for $S \gg \hbar$, *the path integral is dominated by paths in the immediate vicinity of the classical trajectory $x_{cl}(t)$.* In the limit $\hbar \to 0$, *only* the classical path (and paths infitesmally close to the classical path) contributes. The "semiclassical" or WKB approximation to the Feynman path integral is, in fact, the approximation of evaluating the integral in the neighborhood single configuration $x_{cl}(t)$, i.e.

$$\begin{aligned} G_T(x, y) &= \int Dx(t) \, e^{iS[x(t)]/\hbar} \\ &\approx \text{prefactor} \times e^{iS[x_{cl}(t)]/\hbar} \end{aligned} \qquad (24.52)$$

where the prefactor is a numerical term which comes from integrating over small variations δx around $x_{cl}(t)$.

Problem - For some problems, the WKB approximation works extremely well, even if $S[x, t]$ is not so large compared to $\hbar$. Apply this approximation to find the propagator of a free particle, and compare it to the exact result.

24.3 Operators from Path Integrals

Given a trajectory, $x(t)$, one can always define a momentum, $m\dot{x}(t)$. Then a natural way to define a momentum operator acting on a wavefunction at time t_f is in terms of the path-integral

$$\tilde{p}\psi(x_f, t_f) \equiv \int dy \int Dx(t) \, m\dot{x}(t_f) e^{iS/\hbar} \psi(y, t_0) \qquad (24.53)$$

where the paths run from (x_0, t_0) to (x_f, t_f), and $\psi(x, t_0)$ is the wavefunction at any earlier time $t_0 < t_f$. Let us take $t = t_f$ and $t_0 = t - \epsilon$, and then go to the limit $\epsilon \to 0$. In that case

$$\begin{aligned} \tilde{p}\psi(x, t) &\equiv \lim_{\epsilon \to 0} \int dy \, m \frac{(x - y)}{\epsilon} G_\epsilon(x, y)\psi(y, t - \epsilon) \\ &= \lim_{\epsilon \to 0} \int dy \, m \frac{(x - y)}{\epsilon} \left(\frac{m}{2\pi i \epsilon \hbar}\right)^{1/2} \exp\left[i\frac{m}{2\epsilon\hbar}(x - y)^2 - i\frac{\epsilon}{\hbar}V(x)\right] \psi(y, t - \epsilon) \\ &= \lim_{\epsilon \to 0} \int dy \, m \frac{(x - y)}{\epsilon} \left(\frac{m}{2\pi i \epsilon \hbar}\right)^{1/2} \exp\left[i\frac{m}{2\epsilon\hbar}(x - y)^2\right] \psi(y, t - \epsilon) \qquad (24.54) \end{aligned}$$

where we have dropped the term in the exponent proportional to $V(x)$, since that term is negligible in the $\epsilon \to 0$ limit. Now change variables to $z = y - x$. Then

$$\tilde{p}\psi(x,t)$$

$$= \lim_{\epsilon \to 0} \left(\frac{m}{2\pi i\epsilon\hbar}\right)^{1/2} \frac{m}{\epsilon} \int dz \, (-z) \exp\left[i\frac{m}{2\epsilon\hbar}z^2\right] \psi(x+z, t-\epsilon)$$

$$= \lim_{\epsilon \to 0} \left(\frac{m}{2\pi i\epsilon\hbar}\right)^{1/2} \frac{m}{\epsilon} \int dz \, (-z) \exp\left[i\frac{m}{2\epsilon\hbar}z^2\right] \psi(x, t-\epsilon) + \psi'(x, t-\epsilon)z + O(z^2)]$$

$$= -\lim_{\epsilon \to 0} \left(\frac{m}{2\pi i\epsilon\hbar}\right)^{1/2} \frac{m}{\epsilon}\frac{d\psi}{dx} \int dz \, z^2 \exp\left[i\frac{m}{2\epsilon\hbar}z^2\right] \qquad (24.55)$$

The term proportional to z drops out in the integration, because z is an odd function whereas the exponent is even. Also, terms of order z^3 and higher disappear in the $\epsilon \to 0$ limit. Performing the gaussian integral and taking the $\epsilon \to 0$ limit we finally obtain

$$\tilde{p}\psi(x,t) = -\lim_{\epsilon \to 0} \left(\frac{m}{2\pi i\epsilon\hbar}\right)^{1/2} \frac{m}{\epsilon}\frac{d\psi}{dx}\left(-\frac{\pi}{im/(2\epsilon\hbar)}\right)^{1/2} \frac{i\epsilon\hbar}{m}$$

$$= -i\hbar\frac{d\psi}{dx} \qquad (24.56)$$

which is the same rule that we had deduced previously, in Lecture 5, from Ehrenfest's principle.

Problem - Use the same analysis to find the operator corresponding to $\tilde{p}^2$. Note that, if you use only a single integral as above, and just replace

$$m\frac{(x-y)}{\epsilon} \quad \text{by} \quad m^2\frac{(x-y)^2}{\epsilon^2} \qquad (24.57)$$

something goes wrong! Can you figure out how to fix it?

24.4   Path-Integration as Quantization

Having derived the path-integral from the Schrodinger equation, one can of course go in the other direction, i.e. derive the Schrodinger equation starting from the concept of an integration over paths. We have seen that path-integrals with gaussian integrands can be evaluated exactly; integrands with non-gaussian terms can often be evaluated approximately by a perturbation technique. We have also seen that path-integrals lead to the usual form of the momentum operator. Logically, the path-integral approach is an alternative to canonical quantization based on commutators; either method can be used to quantize a classical theory.

Why then, have we spent the whole year following the Schrodinger equation approach? Why not begin with path-integral, and solve bound-state and scattering problems by that method? In fact, such an approach to teaching non-relativistic quantum mechanics can be and has been followed, by Feynman himself. The results are enshrined in a textbook by Feynman and Hibbs. However, no other elementary textbook, and not many instructors, have followed Feynman's example. The reason is simply that, in non-relativistic quantum mechanics, the path-integral is a rather cumbersome procedure for solving problems, as compared to the Schrodinger equation.

In *relativistic* quantum field theory, however, the situation is different: for very many problems it is the path-integral technique which is easier to use, and better adapted than operator methods to the thorny technicalities that are encountered. As a bonus, the path-integral formulation is naturally suited to various non-perturbative approximation methods, such as the Monte Carlo procedure, in cases where perturbation theory cannot be applied. Finally, there are interesting and deep connections between quantum field theory, based on the Feynam path integral, and statistical mechanics, based on the analysis of a partition function. But this is a long story, to be taught in another, more advanced, course.

Chapter 25

A Glimpse of Quantum Field Theory

25.1 The Quantization of Sound

Strike a solid at any point, and you generate a sound wave traveling through the solid. On a microscopic level, a solid is a regular arrangement of atoms, and a sound wave is simply a particular vibration of those atoms. But the motion of atoms should be treated quantum mechanically. What, then, is the quantum mechanics of sound?

As usual, simplify. Our model will be a one-dimensional solid with periodic boundary conditions. This is similar to the Kronig-Penney model, except the atoms are allowed to vibrate. There are N atoms; the coordinate of the n-th atom is x_n, and its classical equilibrium position is x_{n0}. Periodic boundary conditions mean that $x_{n+N} = x_n$. Denote the displacement of the n-th atom from its equilibrium position by

$$q_n = x_n - x_{n0} \tag{25.1}$$

Assuming only nearest-neighbor atoms interact, we can write the potential as a sum of two-body potentials, which we expand in Taylor series

$$
\begin{aligned}
V &= \sum_{n=1}^{N} f(q_{n+1} - q_n) \\
&= \sum_{n=1}^{N} [f(0) + f'(0)(q_{n+1} - q_n) + \frac{1}{2}f''(0)(q_{n+1} - q_n)^2 + ...] \tag{25.2}
\end{aligned}
$$

The constant term is physically irrelevant, so set $f(0) = 0$ for convenience. Due to the periodic boundary conditions $q_{N+1} = q_1$,

$$\sum_{n=1}^{N}(q_{n+1} - q_n) = 0 \tag{25.3}$$

so the second term is also zero. Then the potential must have the form

$$V = \frac{1}{2} K \sum_{n=1}^{N} (q_{n+1} - q_n)^2 \tag{25.4}$$

for small displacements of the atoms around equilibrium, where $K \equiv f''(0)$. The Hamiltonian is

$$H = \sum_{n=1}^{N} \left[\frac{1}{2m} p_n^2 + \frac{1}{2} K (q_{n+1} - q_n)^2 \right] \tag{25.5}$$

where p_n is the momentum of the n-th atom. Upon quantization,

$$p_n \rightarrow -i\hbar \frac{\partial}{\partial x_n} = -i\hbar \frac{\partial}{\partial q_n} \tag{25.6}$$

and the N-body Schrodinger equation for the solid is

$$\sum_{n=1}^{N} \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q_n^2} + \frac{1}{2} K (q_{n+1} - q_n)^2 \right] \Psi[\{q_i\}] = E \Psi[\{q_i\}] \tag{25.7}$$

The system has a ground state, denoted Ψ_0. Quantized sound waves can only correspond to excited states of the system.

The Schrodinger equation above is a partial differential equation in $N \sim 10^{23}$ variables. The only chance of solving it is by the method of separation of variables. Introduce the finite Fourier transform

$$q_n = \frac{1}{\sqrt{N}} \sum_{k=-(N-1)/2}^{(N-1)/2} Q_k \exp[i \frac{2\pi n}{N} k]$$

$$p_n = \frac{1}{\sqrt{N}} \sum_{k=-(N-1)/2}^{(N-1)/2} P_k \exp[i \frac{2\pi n}{N} k] \tag{25.8}$$

which automatically incorporates periodic boundary conditions. Using the identity

$$\sum_{n=1}^{N} \exp[i \frac{2\pi (k - k')}{N} n] = N \delta_{kk'} \tag{25.9}$$

we can write the inverse transform

$$Q_k = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} q_n \exp[-i \frac{2\pi k}{N} n]$$

$$P_k = \frac{1}{\sqrt{N}} \sum_{k=-(N-1)/2}^{(N-1)/2} p_n \exp[-i \frac{2\pi k}{N} n] \tag{25.10}$$

By taking the complex conjugate of these inverse transforms, and using the fact that q_n and p_n are real numbers, we see that

$$Q_k^* = Q_{-k} \qquad P_k^* = P_{-k} \tag{25.11}$$

The wonderful thing about this transformation is that the Hamiltonian, written in terms of Q_k, P_k, is separable, i.e.

$$
\begin{aligned}
\sum_n q_n^2 &= \frac{1}{N}\sum_n\sum_{k_1}\sum_{k_2} Q_{k_1}Q_{k_2}\exp[i\frac{2\pi(k_1+k_2)}{N}n] \\
&= \sum_k Q_k Q_{-k} \\
\sum_n p_n^2 &= \frac{1}{N}\sum_n\sum_{k_1}\sum_{k_2} P_{k_1}P_{k_2}\exp[i\frac{2\pi(k_1+k_2)}{N}n] \\
&= \sum_k P_k P_{-k} \\
\sum_n q_{n+1}q_n &= \frac{1}{N}\sum_n\sum_{k_1}\sum_{k_2} Q_{k_1}Q_{k_2}\exp[i\frac{2\pi(k_1+k_2)}{N}n]e^{i2\pi k_1/N} \\
&= \sum_k Q_k Q_{-k} e^{i2\pi k/N} \\
&= \sum_k Q_k Q_{-k}\cos[2\pi k/N]
\end{aligned}
\tag{25.12}
$$

Put it all together,

$$H = \sum_k \left\{ \frac{1}{2m}P_k P_{-k} + K[1-\cos(\frac{2\pi}{N})]Q_k Q_{-k} \right\} \tag{25.13}$$

We still need to know the commutation relations between P and Q:

$$
\begin{aligned}
[Q_k, P_{k'}] &= \frac{1}{N}\sum_n\sum_{n'}[q_n, p_{n'}]\exp[-i\frac{2\pi}{N}(kn+k'n')] \\
&= i\hbar\delta_{k,-k'}
\end{aligned}
\tag{25.14}
$$

Thus,

$$P_k = -i\hbar\frac{\partial}{\partial Q_{-k}} \tag{25.15}$$

In this way the Hamiltonian of the 1-dimensional solid has been rewritten as a sum of harmonic oscillator Hamiltonians

$$H = \sum_k \left[\frac{1}{2m}P_k P_{-k} + \frac{1}{2}\sigma_k Q_k Q_{-k} \right] \tag{25.16}$$

where

$$\frac{1}{2}\sigma_k \equiv K[1-\cos(\frac{2\pi k}{N})] \tag{25.17}$$

As in the ordinary harmonic-oscillator problem, we solve $H\Psi = E\Psi$ by introducing raising-lowering operators

$$
\begin{aligned}
a_k &= \sqrt{\frac{m\omega_k}{2\hbar}}\left[Q_k + \frac{i}{m\omega_k}P_k\right] \\
a_k^\dagger &= \sqrt{\frac{m\omega_k}{2\hbar}}\left[Q_{-k} - \frac{i}{m\omega_k}P_{-k}\right] \\
Q_k &= \sqrt{\frac{\hbar}{m\omega_k}}(a_k + a_{-k}^\dagger) \\
P_k &= \frac{1}{2i}\sqrt{2\hbar m\omega_k}(a_k - a_{-k}^\dagger)
\end{aligned}
\tag{25.18}
$$

where

$$
\omega_k = \sqrt{\frac{\sigma_k}{m}} \tag{25.19}
$$

In terms of these operators, one finds that

$$
H = \sum_k \hbar\omega_k\left(a_k^\dagger a_k + \frac{1}{2}\right) \tag{25.20}
$$

where

$$
[a_k, a_{k'}^\dagger] = \delta_{k,k'} \tag{25.21}
$$

The problem has been reduced to solving the dynamics of a set of uncoupled harmonic oscillators; one oscillator for each wavenumber k in the range $-\frac{1}{2}(N-1) \le k \le \frac{1}{2}(N-1)$.

All lowering operators annihilate the harmonic-oscillator ground state, so we require that, for all wavenumbers k

$$
a_k\Psi_0[Q] = 0 \tag{25.22}
$$

or

$$
\hbar\frac{\partial}{\partial Q_{-k}}\Psi_0 = -m\omega_k Q_k\psi_0 \tag{25.23}
$$

This equation can be solved by inspection, and we have, for the ground state of the solid,

$$
\begin{aligned}
\Psi_0 &= N\exp\left[-\frac{m}{\hbar}\sum_k \omega_k Q_k Q_{-k}\right] \\
&= N\exp\left[-\frac{\sqrt{m}}{\hbar}\sum_k \{2K(1-\cos(\frac{2\pi k}{N}))\}^{1/2}Q_k Q_k^*\right]
\end{aligned}
\tag{25.24}
$$

with ground-state (or "zero-point") energy

$$
E_0 = \sum_k \frac{1}{2}\hbar\omega_k \tag{25.25}
$$

In classical physics, there are no sound vibrations at all in a solid at zero temperature; each atom is at rest in its equilibrium position $x_n = x_{n0}$. Quantum-mechanically, of course, the atoms cannot be in such a position eigenstate, because, due to the Uncertainty Principle, this would imply an infinite kinetic energy for each atom. Thus, even at zero temperature, the atoms have a finite kinetic/potential energy of vibration, which is why E_0, the vibational energy at zero temperature, is sometimes called the "zero-point" energy

To get the excited states, its sufficient to observe that

$$[H, a_k^\dagger] = \hbar\omega_k a_k^\dagger \quad\implies\quad Ha_k^\dagger = a_k^\dagger(H + \hbar\omega_k) \tag{25.26}$$

Repeated use of this commutator shows us that

$$H\Psi_{n_a n_b \ldots n_p} = E_{n_a n_b \ldots n_p}\Psi_{n_a n_b \ldots n_p} \tag{25.27}$$

where

$$\Psi_{n_a n_b \ldots n_p} = (a_{k_a}^\dagger)^{n_a}(a_{k_b}^\dagger)^{n_b}\ldots(a_{k_p}^\dagger)^{n_p}\Psi_0 \tag{25.28}$$

are the wavefunctions of the excited energy eigenstates, and

$$E_{n_a n_b \ldots n_p} = n_a\hbar\omega_a + n_b\hbar\omega_b + \ldots + n_p\hbar\omega_p + E_0 \tag{25.29}$$

Interpretation: A glance at (25.8) shows that Q_k is essentially the amplitude of a vibrational (sound) wave of wavenumber k, propagating through the solid. Suppose we try to excite such waves in the solid, by striking it at some given frequency. In classical physics, the corresponding sound waves could have any energy at all, depending on how vigorously we strike the solid. But quantum-mechanically, we have just discovered that the energy of such sound waves is quantized in units of $\hbar\omega_k$; i.e. the energy that can be added to the solid, by exciting vibrations of wavenumber k, can only be one of the possible values

$$\Delta E = n\hbar\omega_k \tag{25.30}$$

Where have we seen this equation before? It is, of course, Planck's condition for the energy in a radiation field, where $\omega_k = 2\pi f$ is the angular frequency of the radiation. Einstein's interpretation of Planck's formula, back in 1905, was that the energy of the radiation field of a given frequency is subdivided in the form of *photons*, each of which propagates through space like a particle of energy hf. By quantizing the oscillations of a solid, we have found the same phenomenon. The energy of sound vibrations of a solid, of a given wavenumber, is carried in the form of particle-like excitations known as **phonons**, which propagate through the solid with momentum proportional to wavenumber k, and energy equal to $\hbar\omega_k$. For this reason, we drop the "raising/lowering" operator terminology, and refer to $a_k^\dagger$ and a_k as **creation/destruction** operators, respectively, because they create/destroy individual phonons in the solid.

Of course, a phonon isn't "really" a particle, in the sense that one could trap such an object, extract it from the solid, and (say) look at it under a microscope. What is "really" in the solid are the atoms which compose it. Phonons, even though they carry energy and momentum, and even though they scatter (like particles) off impurities in the solid and off one another, are merely convenient labels for the quantized vibrational states of the underlying solid.

What to say, then, about photons? Are they, or are they not, elementary particles?

25.2   The Quantization of Light

Quantum mechanics began with Planck's discovery that the energy of an electromagnetic field must be divisible in units of hf. Then came Einstein's identification of those units as particles, "photons." Then came the Compton effect, the Bohr atom, De Broglie waves, the Schrodinger equation...and then came a lot, some of which we have touched on in this course. Now its time to return to the beginning. *Why* is the energy of a radiation field quantized in units of hf? What happens if we apply the principles of quantum mechanics, which was developed to describe the motion of electrons and other particles, to the dynamics of the electromagnetic field?

First of all, what are the degrees of freedom of the system we are quantizing? An electron only has a few: the position degrees of freedom (x, y, z), and the spin state. The electromagnetic field, on the other hand, has an electric field $\vec{E}$ and a magnetic field $\vec{B}$ defined at every point in space; the number of degrees of freedom must be infinite! But how many independent degrees of freedom are there, exactly, per point?

A first guess might be that there are six degrees of freedom per point, namely the three components of the electric field, and the three components of the magnetic field. But this can't be right. First of all, not all of the components of $\vec{E}$ and $\vec{B}$ are independent (think of the no-monopole equation $\nabla \cdot B = 0$). Secondly, Maxwell's equations are first-order differential equations, which means that they must be Hamiltonian, rather than Euler-Lagrange, equations of motion. This implies that some of the E, B fields are actually canonical "momenta", rather than canonical "coordinates."

The key to obtaining the degrees of freedom corresponding to canonical coordinates is the introduction of the *4-vector potential* $A_\mu(x) = \{A_0, A_1, A_2, A_3\}$. Often A_0 is called the "scalar potential," and the remaining three components $\vec{A} = \{A_1, A_2, A_3\}$ are referred to as the "3-vector potential," or just "vector potential." In terms of the 4-vector potential, the electric and magnetic field strengths are expressed as

$$\begin{aligned}
\vec{E} &= -\nabla A_0 - \partial_t \vec{A} \\
\vec{B} &= \nabla \times \vec{A}
\end{aligned} \tag{25.31}$$

Written in this form, the E, B fields automatically satisy the the no-monopole equation, and also Faraday's Law. All that is necessary is to write an action as a functional

of A_μ, whose stationarity condition supplies the other two of Maxwell's equations, namely Gauss' and Ampere's Law

(Note: From here on, I am going to adopt a system of units which is popular among particle physicists, in which $\hbar = c = 1$.)

This action is given by

$$
\begin{aligned}
S &= \int dt \, L[A, \dot{A}] \\
&= \frac{1}{2} \int dt \int d^3x \, [\vec{E}^2 - \vec{B}^2] \\
&= \frac{1}{2} \int dt \int d^3x \, [(\nabla A_0 - \partial_t \vec{A})^2 - (\nabla \times \vec{A})^2]
\end{aligned}
\tag{25.32}
$$

Its easy to check that the two remaining Maxwell equations (Gauss' Law and Ampere's Law) are given by the stationary phase condition

$$
\begin{aligned}
\frac{\delta S}{\delta A_0} &= 0 \implies \nabla \cdot \vec{E} = 0 \\
\frac{\delta S}{\delta A_k} &= 0 \implies \partial_t E - \nabla \times B = 0
\end{aligned}
\tag{25.33}
$$

This action can be used for Feynman path-integral quantization of the electromagnetic field, but let us instead derive a Schrodinger equation. For that purpose we would like to go the Hamiltonian formulation, but at this stage we encounter a stupid technical complication. In order to go from the action to the Hamiltonian, we have to define momenta

$$
P_\mu = \frac{\delta L}{\delta \dot{A}_\mu}
\tag{25.34}
$$

The problem is that the Lagrangian contains no time derivative of the scalar potential A_0. This means that $P_0 = 0$!

In this course, the fact that $P_0 = 0$ is just an annoying technicality, which we have to deal with in some way before proceeding. There is actually a considerable body of theory on this precisely this sort of phenomenon in what are known as "constrained dynamical systems," but, to make a long story short, what it indicates is that not all field configurations A_μ are physically distinguishable. Let A_μ be a field configuration, and A'_μ be another field configuration. If one can find a function $\phi(x, t)$ such that the two field configurations are related by **gauge transformation**

$$
A'_\mu(x, t) = A_\mu(x, t) + \partial_\mu \phi(x, t)
\tag{25.35}
$$

then A and A' have exactly the same electric and magnetic fields. They are, therefore, physically equivalent. Four degrees of freedom per point is still too much, at least one

degree of freedom is redundant; a given set of E, B fields does not uniquely specify the vector potential. So let us use the gauge freedom to eliminate one more degree of freedom, by imposing an additional condition $F[A] = 0$ on the A-fields. Some popular examples are

$$
\begin{aligned}
A_0 &= 0 && \text{temporal gauge} \\
A_3 &= 0 && \text{axial gauge} \\
\nabla \cdot \vec{A} &= 0 && \text{Coulomb gauge} \\
\partial^\mu A_\mu &= 0 && \text{Landau gauge}
\end{aligned}
\tag{25.36}
$$

For our purposes, the most convenient gauge is temporal gauge, $A_0 = 0$, because this immediately solves the $P_0 = 0$ problem. If we remove A_0 from the start, then of course it has no corresponding momentum. However, we then lose the Gauss Law, because this is derived by varying S with respect to A_0. So what we have to do is impose the Gauss Law $\nabla \cdot E = 0$ as a supplementary condition on our initial data, before solving the other equations of motion. In quantum theory, one requires that Gauss' Law is satisfied as an operator equation

$$
(\nabla \cdot E)\Psi = 0 \tag{25.37}
$$

on all physical states.

All of this business with gauge invariance just looks like a nasty technicality which complicates the quantization of electromagnetism, and so it is. It is only in a more advanced course, on quantum field theory, that one learns that the principle of gauge invariance is one of the jewels of theoretical physics; it is our guiding light in constructing theories of the the strong, weak, electromagnetic (and even gravitational) interactions.

Having decided to use the gauge transformation to set $A_0 = 0$, we proceed to construct the Hamiltonian. The main difference in procedure, compared to that in Lecture 1, is that ordinary derivatives are replaced by functional derivatives. Thus

$$
\begin{aligned}
P_i &= \frac{\delta L}{\delta \dot{A}_i} \\
&= \dot{A}_i \\
&= E_i
\end{aligned}
\tag{25.38}
$$

and

$$
\begin{aligned}
H &= \left\{ \int d^3x \; P_i(x)\dot{A}_i(x) \right\} - L \\
&= \frac{1}{2} \int d^3x \; [\vec{E}^2 + \vec{B}^2] \\
&= \frac{1}{2} \int d^3x \; [\vec{P}^2 + (\nabla \times \vec{A})^2]
\end{aligned}
\tag{25.39}
$$

Its worth stressing that in Hamiltonian formulation, in $A_0 = 0$ gauge, the canonical variables are $\{A_i, E_i\}$, with the electric field $E_i = P_i$ as the momentum variable conjugate to the 3-vector potential A_i. Ampere's Law follows from the Hamilton equations of motion

$$
\begin{aligned}
\dot{A}_i(x) &= \frac{\delta H}{\delta P_i(x,t)} \\
&= E_i(x) = P_i(x) \\
\dot{P}_i(x) &= -\frac{\delta H}{\delta A_i(x)} \\
&= (\nabla \times \vec{B}(x))_i
\end{aligned}
\tag{25.40}
$$

which, taken together, give

$$
\partial_t \vec{E} - \nabla \times \vec{B} = 0
\tag{25.41}
$$

Of the remaining three Maxwell equations, Faraday's Law and $\nabla \cdot \vec{B} = 0$ are identities, which follow from expressing E, B in terms of the vector potential A. The remaining Gauss Law, $\nabla \cdot \vec{E} = 0$, we have agreed to carry along separately without deriving it from the Hamiltonian; this was the price for imposing $A_0 = 0$.

Now quantize. The Schrodinger equation and the momentum operator can be derived, as before, from Ehrenfest's principle

$$
\begin{aligned}
\partial_t < A_i > &= < \frac{\delta H}{\delta P_i(x,t)} > \\
\partial_t < P_i > &= - < \frac{\delta H}{\delta A_i(x,t)} >
\end{aligned}
\tag{25.42}
$$

but there are no surprises, and in the end one finds that, just as in ordinary quantum mechanics

$$
\begin{aligned}
\partial_t \Psi[A] &= H\Psi[A] \\
H &= \int d^3x \, [\vec{P}^2 + (\nabla \times \vec{A})^2] \\
P_i(x) &= -i\frac{\delta}{\delta A_i(x)}
\end{aligned}
\tag{25.43}
$$

Note that

$$
\begin{aligned}
[A_i(x), P_j[x']] &= [A_i(x), E_j(x')] \\
&= i\delta_{ij}\delta(x - x')
\end{aligned}
\tag{25.44}
$$

is the generalization of $[x, p] = i\hbar$ in non-relativistic quantum mechanics. We still have to impose the Gauss Law constraint, and this is done by imposing the corresponding operator constraint

$$
(\nabla \cdot E)\Psi = -i\partial_i \frac{\delta}{\delta A_i}\Psi = 0
\tag{25.45}
$$

Only states satisfying this condition, in $A_0 = 0$ gauge, are to be regarded as physical states.

To see what the Gauss Law constraint implies, lets subdivide the vector potential into a transverse part A^T and a longitudinal part A^L:

$$A_i(x) = A_i^T(x) + A_i^L(x) \tag{25.46}$$

where

$$\nabla \cdot A^T = 0 \qquad \nabla \times A^L = 0 \tag{25.47}$$

Define also

$$
\begin{aligned}
E_i(x) &= E_i^T(x) + E_i^L(x) \\
&= -i\frac{\delta}{\delta A^T(x)} - i\frac{\delta}{\delta A^L(x)}
\end{aligned}
\tag{25.48}
$$

The Gauss Law constraint becomes

$$
\begin{aligned}
0 &= \nabla \cdot E\Psi \\
&= \nabla \cdot E^L\Psi \\
&= -i\partial_i \frac{\delta}{\delta A_i^L}\Psi
\end{aligned}
\tag{25.49}
$$

which is satisfied if Ψ is independent of the longitudinal degree of freedom A^L, i.e.

$$\Psi[A_i] = \Psi[A^T] \tag{25.50}$$

As in the case of the one-dimensional solid, we want to be able to separate variables, and write the Hamiltonian as a sum of harmonic oscillators. Again, this is done by going to the Fourier-transformed variables

$$
\begin{aligned}
A_i(x) &= A_i^T(x) + A_i^L(x) \\
&= \int \frac{d^3k}{(2\pi)^3} \, [A_i^T(k) + A_i^L(k)]e^{ikx}
\end{aligned}
\tag{25.51}
$$

with

$$\vec{k} \cdot \vec{A}^T = 0 \qquad \vec{k} \times \vec{A}^L = 0 \tag{25.52}$$

The Fourier component $\vec{A}(k)$ can be regarded as the amplitude of a wave traveling in the $\vec{k}$ direction. $\vec{A}^T$ is the component perpendicular to the direction of propagation, while $\vec{A}^L$ is the component parallel to the direction of propagation.

Substitute the Fourier-transformed $A^{L,T}$ and $E^{L,T}$ into the Hamiltonian, and we find that it takes the form

$$H = \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \, [E_i^T(k)E_i^T(-k) + E_i^L(k)E_i^L(-k) + k^2 A_i^T(k)A_i^T(-k)] \tag{25.53}$$

But $E^L = -i\delta/\delta A^L$, and we have seen that $\Psi[A]$ doesn't depend on A^L, by the Gauss Law constraint. So the time-independent Schrodinger equation becomes

$$\frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \left[-\frac{\delta^2}{\delta A_i^T(k)\delta A_i^T(-k)} + k^2 A_i^T(k)A_i^T(-k) \right] \Psi[A^T] = E\Psi[A^T] \qquad (25.54)$$

Once again, the Hamiltonian has the form of a sum over harmonic oscillator terms. The ground-state solution, which must be a gaussian for any system of uncoupled harmonic oscillators, can be written down almost by inspection:

$$\Psi_0[A] = N \exp\left[-\frac{1}{2} \int d^3k |k| A_i^T(k) A_i^T(-k) \right] \qquad (25.55)$$

and this can easily be converted back to a functional of $A(x)$:

$$\begin{aligned}
\Psi_0 &= N \exp\left[-\frac{1}{2} \int d^3k \frac{1}{|k|} (k \times A^T(k)) \cdot (k \times A^T(-k)) \right] \\
&= N \exp\left[-\frac{1}{2} \int d^3k \left(4\pi \int \frac{d^3z}{(2\pi)^3} \frac{1}{z^2} e^{ikz} \right) \left(\int d^3x_1 \, i\nabla_{x_1} \times A(x_1) e^{ikx_1} \right) \right. \\
&\quad \left. \cdot \left(\int d^3x_2 \, i\nabla_{x_2} \times A(x_2) e^{-ikx_2} \right) \right]
\end{aligned} \qquad (25.56)$$

Integration over k and z leads, finally, to one of my favorite equations in physics, the ground state wavefunctional of the electromagnetic field

$$\Psi_0[A] = N \exp\left[-\frac{1}{4\pi} \int d^3x d^3y \frac{\vec{B}(x) \cdot \vec{B}(y)}{|x-y|^2} \right] \qquad (25.57)$$

Substituting this state back into the Schrodinger equation, we easily find the zero-point ground state energy

$$E_0 = \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} |k| \delta^3(0) \qquad (25.58)$$

which is infinite. This infinity is not surprising, because we are quantizing an infinite number of degrees of freedom, each of which has a finite zero-point energy.

The ground state of a quantum field theory is known, quite rightly, as the "vacuum" state; it is the lowest energy state attainable. It also shows us that the vacuum is not "nothing." Even in the absence of any sources, even in the lowest energy state possible, there are still quantum fluctuations of the electromagnetic field. In the end, this is a consequence of the Uncertainty Principle. If the vector potential were everywhere vanishing, so that the uncertainty $\Delta A = 0$, the uncertainty of the electric field (the conjugate momentum) would be infinite. This would give an energy expectation value even more strongly divergent than E_0; each degree of freedom would contribute

an infinite amount of energy. The ground state (25.57) is the lowest energy com-
promise, consistent with the Uncertainty Principle, between the energy due to the
"potential" term $\vec{B}^2$, and the energy due to the "kinetic" term $\vec{E}^2$, in the quantized
Hamiltonian.

To find the excited state wavefunctionals and energies, we need to introduce raising
and lowering operators. Since the degrees of freedom, both in the Hamiltonian and in
the physical states, are the transverse components of the vector potential, we need to
extract these from the full vector potential. To this end, for a given $\vec{k}$, let us introduce
two unit (polarization) vectors which are orthogonal to $\vec{k}$ and to each other:

$$\begin{aligned}
\vec{\epsilon}^\lambda(k) \cdot \vec{\epsilon}^{\lambda'}(k) &= \delta_{\lambda\lambda'} \\
\vec{\epsilon}^\lambda(k) \cdot \vec{k} &= 0
\end{aligned} \tag{25.59}$$

where the superscipts are $\lambda = 1, 2$. Then we can always write a transverse vector $\vec{A}^T$
or $\vec{E}^T$ as a superposition of vectors in the $\vec{\epsilon}^1$ and $\vec{\epsilon}^2$ directions. Now introduce the
creation/destruction operators

$$\begin{aligned}
a(k, \lambda) &= \frac{1}{\sqrt{2|k|}} \epsilon_i^\lambda(k) \left[|k| A_i(k) + \frac{\delta}{\delta A_i(-k)} \right] \\
&= \frac{1}{\sqrt{2|k|}} \epsilon_i^\lambda(k) \left[|k| A_i^T(k) + \frac{\delta}{\delta A_i^T(-k)} \right] \\
a^\dagger(k, \lambda) &= \frac{1}{\sqrt{2|k|}} \epsilon_i^\lambda(k) \left[|k| A_i(-k) - \frac{\delta}{\delta A_i(k)} \right] \\
&= \frac{1}{\sqrt{2|k|}} \epsilon_i^\lambda(k) \left[|k| A_i^T(-k) - \frac{\delta}{\delta A_i^T(k)} \right]
\end{aligned} \tag{25.60}$$

It is straighforward to verify that

1. these operators have the standard raising/lowering commutation relations

$$[a(k, \lambda), a(k', \lambda')] = \delta_{\lambda\lambda'} \delta^3(x - x') \tag{25.61}$$

2. the destruction operators all annihilate the ground state

$$a(k, \lambda)\Psi_0 = 0 \quad \text{for all} \quad k \tag{25.62}$$

3. the Hamiltonian can be expressed, in terms of these operators, as

$$H = \int d^3k \, |k| \sum_{\lambda=1,2} [a^\dagger(k, \lambda) a(k, \lambda) + \frac{1}{2}\delta^3(0)] \tag{25.63}$$

4. The creation operator and the Hamiltonian satisfy the commutation relation

$$[H, a^\dagger(k, \lambda)] = |k| a^\dagger(k, \lambda) \tag{25.64}$$

Problem: Verify these statements.

Making use of items (2) and (4) above, it follows that the excited energy eigenstates

$$H \Psi_{n_a n_b \dots n_p} = E_{n_a n_b \dots n_p} \Psi_{n_a n_b \dots n_p} \tag{25.65}$$

of the quantized electromagnetic field have the form

$$\Psi_{n_a n_b \dots n_p} = (a^\dagger(k_a, \lambda))^{n_a} (a^\dagger(k_b, \lambda))^{n_b} \dots (a^\dagger(k_p, \lambda))^{n_p} \Psi_0 \tag{25.66}$$

with energy eigenvalues

$$E_{n_a n_b \dots n_p} = n_a |k_a| + n_b |k_b| + \dots + n_p |k_p| + E_0 \tag{25.67}$$

Restoring the factors of $\hbar$ and the speed of light c, this expression is really

$$
\begin{aligned}
E_{n_a n_b \dots n_p} &= n_a \hbar c |k_a| + n_b \hbar c |k_b| + \dots + n_p \hbar c |k_p| + E_0 \\
&= n_a \hbar \omega_a + n_b \hbar \omega_b + \dots + n_p \hbar \omega_p + E_0 \\
&= n_a h f_a + n_b h f_b + \dots + n_p h f_p + E_0
\end{aligned} \tag{25.68}
$$

where f is the frequency of radiation with a wavevector of modulus $|k|$.

In classical physics, any amount of energy can be stored in an electromagnetic field of a given frequency f. The energy of the field is proportional to the square of the amplitude, and the amplitude is proportional to the strength of the source. What we learn from quantizing the electromagnetic field is that, as in an ordinary harmonic oscillator, the energy (above the ground state) that can be stored at any given frequency comes in multiples of hf, i.e.

$$\Delta E = n h f \tag{25.69}$$

This rule, that the energy of an electromagnetic field at each frequency is quantized, brings us full circle: it explains black-body radiation, it explains the photoelectric effect, it gives us the formulae of Planck and Einstein. But we have learned quite a bit more: we have learned what a photon *is*. It is an excited vibrational quantum state of the underlying electromagnetic field, much as phonons in a solid are excited quantum vibrational states of the underlying atoms. There is still more: it is believed that *all* of the elementary particles are essentially excited states of quantized fields. Combine quantum mechanics with classical field theory, and particles - or, at least, excited states which carry energy and momentum and seem to behave in every way like point particles - are the inevitable result. In particular, combine quantum theory with Maxwell's equations, and out come photons. The beauty and the staggering implications of this result can hardly be overstated. It is the reason that modern elementary particle theory is essentially the theory of quantized fields.