

David J. Griffith's
Introduction to Quantum Mechanics
NOTES

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Part I

THEORY

Chapter 1

The Wave Function

1.1 The Schrödinger Equation

A particle's **wave function** is given by solving the **Schrödinger equation**

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

where \hbar is the Planck's constant divided by 2π

$$\hbar = \frac{h}{2\pi} = 1.05 \times 10^{-34} J \cdot s.$$

1.2 The Statistical Interpretation

The wave function is spread out in space. Born's **statistical interpretation** of the wave function says that $|\Psi(x, t)|^2$ gives the probability of finding the particle at point x , at time t

$$\int_a^b |\Psi(x, t)|^2 dx = \left\{ \begin{array}{l} \text{probability of finding the particle} \\ \text{between } a \text{ and } b, \text{ at time } t. \end{array} \right\} \quad (1.1)$$

Probability is the area under the graph of $|\Psi|^2$. The statistical interpretation introduces a kind of **indeterminacy** into quantum mechanics.

Suppose we do measure the position of the particle and we find it to be at point C . The question is where was the particle just before the measurement. There are three plausible answers to the question.

1. The **realist** position: The particle was at C .
2. The **orthodox** position: The particle wasn't really anywhere.
3. The **agnostic** position: Refuse to answer.

The experiments have decisively confirmed the orthodox interpretation. A particle simply does not have a precise position prior to measurement.

Another question: what if a second measurement is made immediately after the first? A repeated measurement must return the same value. The first

measurement radically alters the wave function so that it's now sharply peaked about C . We say that the wave function **collapses**, upon measurement, to a spike at point C .

1.3 Probability

1.3.1 Discrete Variables

Suppose a room contains fourteen people of different ages. Let $N(j)$ represent the number of people of age j . Then the total number of people in the room is

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

The **probability** of getting age j is

$$P(j) = \frac{N(j)}{N}.$$

The sum of all probabilities is 1

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

The average value of age j is

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

In quantum mechanics the average value is called **expectation value**. Generally, the average value of some function of j is given by

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

Also, we need a numerical measure of the amount of "spread" in a distribution, with respect to the average.

$$\Delta j = j - \langle j \rangle,$$

And then we take

$$\sigma^2 \equiv \langle (\Delta j)^2 \rangle.$$

The quantity is known as the **variance** of the distribution, and σ is called the **standard deviation**. And then we have

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

Taking the square root,

$$\sigma = \sqrt{\langle j^2 \rangle - \langle j \rangle^2}.$$

1.3.2 Continuous Variables

So far we are dealing with a discrete variable. We generalize the situation to continuous distributions.

$$\left\{ \begin{array}{l} \text{probability that an individual} \\ \text{lies between } x \text{ and } (x + dx) \end{array} \right\} = \rho(x)dx, \quad (1.2)$$

where $\rho(x)$ is **probability density**. The probability that x lies between a and b is given by

$$P_{ab} = \int_a^b \rho(x)dx,$$

and the rules we deduced for discrete distributions translate in the obvious way:

$$1 = \int_{-\infty}^{+\infty} \rho(x)dx,$$

$$\langle x \rangle = \int_{-\infty}^{+\infty} x\rho(x)dx,$$

$$\langle f(x) \rangle = \int_{-\infty}^{+\infty} f(x)\rho(x)dx,$$

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

1.4 Normalization

We have known that $|\Psi(x, t)|^2$ is the probability density for finding the particle at point x and at time t , then

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

If $\Psi(x, t)$ is a solution for the Schrödinger equation, then $A\Psi(x, t)$ is also a solution, where A is a constant. Thus we must pick this undetermined multiplicative factor to ensure the above equation is satisfied. This process is called **normalizing** the wave function. Physical realizable states correspond to the **square-integrable** solutions to Schrödinger equation.

The Schrödinger equation has the property that it automatically preserves the normalization of the wave function. It turns out that

$$\frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 0,$$

and hence the integral is constant (independent of time); if Ψ is normalized at $t = 0$, it stays normalized for all future time.

1.5 Momentum

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

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

If we measure the position of the particle, the first measurement will collapse the wave function to a spike at the value actually obtained, and the subsequent measurements will simply repeat the results. Thus the expectation value is the average of repeated measurements on an ensemble of identically prepared systems. We are interested in how fast $\langle x \rangle$ moves.

$$\begin{aligned} \frac{d\langle x \rangle}{dt} &= \int x \frac{\partial}{\partial t} |\Psi|^2 dx \\ &= -\frac{i\hbar}{m} \int \Psi^* \frac{\partial \Psi}{\partial x} dx. \end{aligned}$$

The expectation value of the velocity is equal to the time derivative of the expectation value of position:

$$\langle v \rangle = \frac{d\langle x \rangle}{dt}.$$

For **momentum**,

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

Then we write the expressions for $\langle x \rangle$ and $\langle p \rangle$ in a more suggestive way

$$\langle x \rangle = \int \Psi^*(x) \Psi dx.$$

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

We say that the **operator** x represents position, and the operator $(\hbar/i)(\partial/\partial x)$ represents the momentum. To calculate expectation values we "sandwich" the appropriate operator between Ψ^* and Ψ , and integrate.

All classical dynamic variables can be expressed in terms of position and momentum, say $Q(x, p)$. Then

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

1.6 The Uncertainty Principle

The **Heisenberg's uncertainty principle**

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

where σ_x is the standard deviation in x and σ_p is the standard deviation in p . Like position measurement, momentum measurements yield precise answers.

Chapter 2

Time-Independent Schrödinger Equation

2.1 Stationary States

The Schrödinger equation

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

In this chapter we assume that V is independent of t . In that case the Schrödinger equation can be solved by **separation of variables**,

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

where ψ is the function of x alone, and ϕ is a function of t alone. For separable solutions we have

$$\frac{\partial \Psi}{\partial t} = \psi \frac{d\phi}{dt}, \quad \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2 \psi}{dx^2} \phi,$$

and the Schrödinger equation reads

$$i\hbar \psi \frac{d\phi}{dt} = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} \phi + V\psi\phi.$$

Dividing by $\psi\phi$,

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

Now the left side is a function of t alone and the right side is a function of x alone. The only way this can be possibly true is that both sides are constant. We call the separation constant E .

$$i\hbar \frac{1}{\phi} \frac{d\phi}{dt} = E,$$

and

$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V = E,$$

or

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

Separation of variables has turned a partial differential equation into two ordinary differential equations. The first equation is easy to solve

$$\phi(t) = e^{-iEt/\hbar}.$$

The second equation is called the **time-independent Schrödinger equation**. There are three reasons about why we consider about the separable solutions.

1. They are **stationary states**. Although the wave function itself depend on t , the probability density does not.

$$|\Psi(x, t)|^2 = \Psi^* \Psi = \psi^* e^{iEt/\hbar} \psi e^{-iEt/\hbar} = |\psi(x)|^2.$$

And we have

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

Every expectation value is constant in time, we might drop the factor $\phi(t)$.

2. They are states of definite total energy. In classical mechanics, the total energy is called the **Hamiltonian**:

$$H(x, p) = \frac{p^2}{2m} + V(x).$$

The corresponding Hamiltonian operator, obtained by $p \rightarrow (\hbar/i)(\partial/\partial x)$ is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x).$$

Thus the time-independent Schrödinger equation can be written as

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

and the expectation value of the total energy is

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

Moreover,

$$\hat{H}^2 \psi = \hat{H}(\hat{H}\psi) = \hat{H}(E\psi) = E(\hat{H}\psi) = E^2 \psi.$$

Hence

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

So the variance of H is

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0.$$

Thus a separable solution has the property that every measurement of the total energy is certain to return the value E .

3. The general solution is a **linear combination** of separable solutions. The time-independent Schrödinger equation has the property that any linear combination of solutions is itself a solution. If the separable solutions are found, then a more general solution would be of the form

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

2.2 The Infinite Square Well

Suppose

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

A particle in this potential is completely free, except at the two ends, where an infinite force prevents it from escaping.

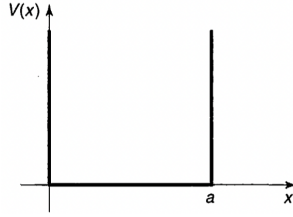


Figure 2.1: The infinite square well potential

Outside the well, $\psi(x) = 0$, as the probability of finding the particle there is 0. Inside the well, $V = 0$ and the time-independent Schrödinger equation is given by

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

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad k \equiv \frac{\sqrt{2mE}}{\hbar}.$$

This equation is the **simple harmonic oscillator** equation, and the general solution is given by

$$\psi(x) = A \sin kx + B \cos kx,$$

where A and B are constants. These constants are fixed by **boundary conditions** of the problem. Continuity of $\psi(x)$ requires that $\psi(0) = \psi(a) = 0$. Thus $\psi(0) = A \sin 0 + B \cos 0 = B$, so $B = 0$ and hence

$$\psi(x) = A \sin kx.$$

Then $\psi(a) = A \sin ka = 0$. This gives that $\sin ka = 0$ (we don't want $A = 0$ here), which means that $ka = 0, \pm\pi, \pm2\pi, \pm3\pi, \dots$. So the distinct solutions are

$$k_n = \frac{n\pi}{a}, \quad n = 1, 2, 3, \dots$$

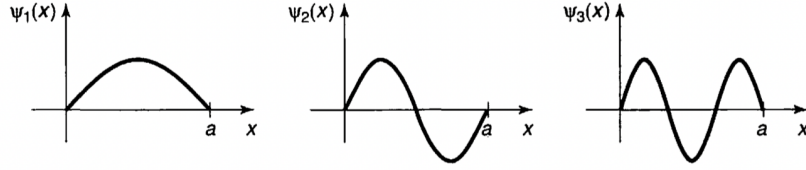


Figure 2.2: The first three stationary states of the infinite square well

Thus the possible values of E are

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}.$$

To find A , we normalize ψ :

$$\int_0^a |A|^2 \sin^2(kx) dx = |A|^2 \frac{a}{2} = 1, \quad \text{so } |A|^2 = \frac{2}{a}.$$

We just simply pick the positive real root: $A = \sqrt{2/a}$. Thus inside the well, the solutions of the Schrödinger equation are

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right).$$

The first few solutions are plotted in Figure 2.2. They look like the standing waves on a string of length a . ψ_1 , which carries the lowest energy, is called the **ground state**, the others, whose energies increase in proportion to n^2 , are called **excited states**. The functions $\psi_n(x)$ have some properties:

1. They are alternately even and odd, with respect to the center of the well.
2. As we go up in energy, each successive state has one more node.

3. They are mutually **orthogonal**, in the sense that

$$\int \psi_m(x)^* \psi_n(x) dx = 0,$$

whenever $m \neq n$. In fact we can combine orthogonality and normalization into a single statement:

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

where δ_{mn} (the so-called **Kronecker delta**) is defined as

$$\delta_{mn} = \begin{cases} 0, & \text{if } m \neq n; \\ 1, & \text{if } m = n. \end{cases}$$

We say that the ψ 's are **orthonormal**.

4. They are **complete**, in the sense that any other function, $f(x)$, can be expressed as a linear combination of them:

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

This is just the **Fourier series** for $f(x)$. The coefficients c_n can be evaluated, for a given $f(x)$, by **Fourier's trick**:

$$\int \psi_m(x)^* f(x) dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x) dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m.$$

Thus the n th coefficient in the expansion of $f(x)$ is

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

The stationary states of the infinite square well are

$$\Psi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}.$$

The most general solution to the time-independent Schrödinger equation is a linear combination of stationary states:

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

We can fit any prescribed initial wave function, $\Psi(x, 0)$, by appropriate choice of the coefficients c_n :

$$\boxed{\Psi(x, 0) = \sum_{n=1}^{\infty} c_n \psi_n(x).$$

The completeness of the ψ 's guarantees that we can always express $\Psi(x, 0)$ in this way, and the actual coefficients is determined by

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

Thus given the initial wave function $\Psi(x, 0)$, we can first compute the expansion coefficients c_n , and obtain $\Psi(x, t)$.

Loosely speaking, c_n tells us the "amount of ψ_n that is contained in Ψ ". We'll see in Chapter 3 that what $|c_n|^2$ tells us is the probability that a measurement of the energy would yield the value E_n (that is, a competent measurement will always return one of the allowed values, and $|c_n|^2$ is the probability of getting the particular value E_n). Thus

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

Moreover, the expectation value of the energy must be

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

Notice that the probability of getting a particular energy is independent of time, and so is the expectation value of H . This is a manifestation of **conservation of energy** in quantum mechanics.

2.3 The Harmonic Oscillator

A classical harmonic oscillator is a mass m attached to a spring of force constant k . The motion is governed by **Hooke's law**

$$F = -kx = m \frac{d^2x}{dt^2},$$

and the solution is

$$x(t) = A \sin(\omega t) + B \cos(\omega t),$$

where

$$\omega \equiv \sqrt{\frac{k}{m}}$$

is the angular frequency of oscillation. The potential energy is

$$V(x) = \frac{1}{2} kx^2,$$

its graph is a parabola. There's no such thing as a perfect harmonic oscillator. But practically any potential is approximately parabolic, in the neighborhood of a local minimum. We expand $V(x)$ in a **Taylor series** about the minimum:

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2} V''(x_0)(x - x_0)^2 + \dots,$$

we get

$$V(x) \approx \frac{1}{2}V''(x_0)(x - x_0)^2,$$

with an effective spring constant $k = V''(x_0)$.

The quantum problem is to solve the Schrödinger equation for the potential

$$V(x) = \frac{1}{2}m\omega x^2.$$

The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi.$$

2.3.1 Algebraic Method

Rewrite the Schrödinger equation in a more suggestive form

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

where $p \equiv (\hbar/i)d/dx$ is the momentum operator. The basic idea is to factor the Hamiltonian,

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

If these were numbers, it would be easy: $u^2 + v^2 = (iu + v)(-iu + v)$. However, p and x are operators, and operators are generally not **commute** (that is, px is not necessary equals to xp). Still this does motivate us to examine the quantities

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

The product

$$a_- a_+ = \frac{1}{2\hbar m\omega}(ip + m\omega x)(-ip + m\omega x) \quad (2.1)$$

$$= \frac{1}{2\hbar m\omega}[p^2 + (m\omega x)^2 - im\omega(xp - px)]. \quad (2.2)$$

There's an extra term $(xp - px)$. We call this the **commutator** of x and p , which is a measure of how badly they fail to commute. In general, the commutator of operators A and B is

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

Thus

$$a_- a_+ = \frac{1}{2\hbar m\omega}[p^2 + (m\omega x)^2] - \frac{i}{2\hbar}[x, p].$$

We need to figure out the commutator of x and p .

$$[x, p]f(x) = \left[x \frac{\hbar}{i} \frac{d}{dx}(f) - \frac{\hbar}{i} \frac{d}{dx}(xf) \right] = \frac{\hbar}{i} \left(x \frac{df}{dx} - x \frac{df}{dx} - f \right) = i\hbar f(x).$$

This shows that

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

This result is known as the **canonical commutation relation**. With this we have

$$a_- a_+ = \frac{1}{\hbar\omega} H + \frac{1}{2}.$$

or

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

Noticing the order of a_+ and a_- is important here:

$$a_+ a_- = \frac{1}{\hbar\omega} H - \frac{1}{2}, \quad H = \hbar\omega \left(a_+ a_- + \frac{1}{2} \right).$$

In particular,

$$[a_+, a_-] = 1.$$

Thus the Schrödinger equation takes the form

$$\hbar\omega \left(a_{\pm} a_{\mp} \pm \frac{1}{2} \right) \psi = E\psi.$$

Now here is a claim: if ψ satisfies the Schrödinger equation with energy E , then $a_+ \psi$ satisfies the Schrödinger equation with energy $(E + \hbar\omega)$, $a_- \psi$ satisfies the Schrödinger equation with energy $(E - \hbar\omega)$.

$$H\psi = E\psi, \quad H(a_+ \psi) = (E + \hbar\omega)(a_+ \psi), \quad H(a_- \psi) = (E - \hbar\omega)(a_- \psi)$$

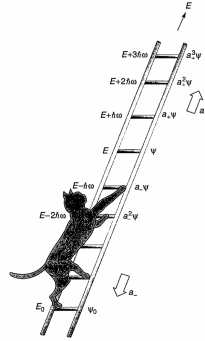


Figure 2.3: The ladder of states for the harmonic oscillator

If we find one solution, then we can generate new solutions with higher and lower energies. We call a_{\pm} **ladder operators**; a_+ is the **raising operator**, and a_- is the **lowering operator**.

In practice, there occurs a "lowest rung" (call it ψ_0) such that

$$a_- \psi_0 = 0.$$

We can use this to determine $\psi_0(x)$:

$$\frac{1}{\sqrt{2\hbar m\omega}} \left(\hbar \frac{d}{dx} + m\omega x \right) \psi_0 = 0.$$

or

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

This could be solved easily:

$$\int \frac{d\psi_0}{\psi_0} = -\frac{m\omega}{\hbar} \int x dx \Rightarrow \ln \psi_0 = -\frac{m\omega}{\hbar} x^2 + C,$$

thus

$$\psi_0(x) = A e^{-\frac{m\omega}{2\hbar} x^2}.$$

By normalization,

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-m\omega x^2/\hbar} dx = |A|^2 \sqrt{\frac{\pi\hbar}{m\omega}}.$$

Hence,

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

To determine the energy of this state, plug it into the Schrödinger equation, $\hbar\omega (a_+ a_- + 1/2) \psi_0 = E_0 \psi_0$, and exploit the fact that $a_- \psi_0 = 0$:

$$E_0 = \frac{1}{2} \hbar\omega.$$

Now we simply apply the raising operator to generate the excited states, increasing the energy by $\hbar\omega$ with each step:

$$\boxed{\psi_n(x) = A_n (a_+)^n \psi_0(x), \quad \text{with } E_n = \left(n + \frac{1}{2} \right) \hbar\omega,}$$

where A_n is the normalization constant.

Actually by rigorous proof we have

$$a_+ \psi_n = \sqrt{n+1} \psi_{n+1}, \quad a_- \psi_n = \sqrt{n} \psi_{n-1}.$$

Thus

$$\boxed{\psi_n = \frac{1}{\sqrt{n!}} (a_+)^n \psi_0.}$$

The stationary states of the harmonic oscillator are orthogonal:

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = \delta_{mn}.$$

2.3.2 Analytic Method

2.4 The Free Particle

We now consider the free particle, i.e. $V(x) = 0$ everywhere. The time independent Schrödinger equation reads

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

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad k \equiv \frac{\sqrt{2mE}}{\hbar}.$$

The solution could be written in exponential form

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

Unlike the infinite square well, there are no boundary conditions to restrict the possible values of k ; the free particle can carry any (positive) energy.

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

Any function of x and t that depends on these variables in special combination ($x \pm vt$) represents a wave of fixed profile, traveling in the $\mp x$ -direction, at speed v . A fixed point on the waveform corresponds to a fixed value of the argument,

$$x \pm vt = \text{constant}, \quad \text{or} \quad x = \mp vt + \text{constant}.$$

Since every point on the waveform is moving along with the same velocity, its shape doesn't change as it propagates. Thus in the previous equation, the first term represents a wave travelling to the left, and the second represents a wave traveling to the right. Since they only differ by the sign in front of k , we might write

$$\Psi_k(x, t) = Ae^{i(kx - \frac{\hbar k^2}{2m}t)},$$

and

$$k \equiv \pm \frac{\sqrt{2mE}}{\hbar}. \quad \text{with} \begin{cases} k > 0 \Rightarrow & \text{traveling to the right,} \\ k < 0 \Rightarrow & \text{traveling to the left.} \end{cases}$$

The stationary states of the free particle are propagating waves, their wavelength is $\lambda = 2\pi/|k|$, and by the de Broglie formula, they carry the momentum $p = \hbar k$. The speed of the wave (the coefficient of t over the coefficient of x) is

$$v_{\text{quantum}} = \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}}.$$

The classical speed of a free particle with energy E is given by

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

However, there is a serious problem that the wave function is not normalized since

$$\int_{-\infty}^{\infty} \Psi_k^* \Psi_k dx = |A|^2 \int_{-\infty}^{\infty} dx = |A|^2(\infty).$$

Thus in this case, the separable solutions do not represent physically realizable states. A free particle cannot exist in a stationary state. Or, *there is no such thing as a free particle with a definite energy*. However, the general solution to the time-independent Schrödinger equation is still a linear combination of separable solutions:

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

Now for appropriate $\phi(k)$, this wave function can be normalized. It necessarily carries a range of k 's, and hence a range of energies and speeds. We call it a **wave packet**. The only question is how to determine $\phi(k)$ so as to match the initial wave function:

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

The answer is provided by **Plancherel's theorem**:

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

$F(k)$ is called the **Fourier transform** of $f(x)$; $f(x)$ is the **inverse Fourier transform** of $F(k)$. Thus we have

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

A wave packet is a superposition of sinusoidal functions whose amplitude is modulated by ϕ ; it consists of "ripples" contained within an envelope. What corresponds to the particle velocity is not the speed of the individual ripples (**phase velocity**), but rather the speed of the envelop (**group velocity**). The problem is to determine the group velocity of a wave packet with the general form

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

(Now it applies to any kind of wave packet, with w as a function of k). Assume that $\phi(k)$ is narrowly peaked about some particular value k_0 . By Taylor expansion,

$$w(k) \approx w_0 + w'_0(k - k_0).$$

Changing variables from k to $s \equiv k - k_0$, we have

$$\Psi(x, t) \approx \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k_0 + s) e^{i[(k_0 + s)x - (w_0 + w'_0 s)t]} dk.$$

At $t = 0$,

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k_0 + s) e^{i(k_0 + s)x} dk,$$

and at later times

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} e^{-i(w_0 - k_0 w'_0)t} \int_{-\infty}^{\infty} \phi(k_0 + s) e^{i(k_0 + s)(x - w'_0 t)} dk,$$

Except for the shift from x to $(x - w'_0 t)$, the integral is the same as the one in $\Psi(x, 0)$. Thus

$$\Psi(x, t) \approx e^{-i(w_0 - k_0 w'_0)t} \Psi(x - w'_0 t, 0).$$

Thus the wave packet moves along a speed w'_0 :

$$v_{\text{group}} = \left. \frac{dw}{dk} \right|_{k=k_0},$$

And the ordinary phase velocity

$$v_{\text{phase}} = \frac{w}{k}.$$

In our case, $w = (\hbar k^2/2m)$, thus $w/k = (\hbar k/2m)$ and $dw/dk = (\hbar k/m)$,

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

2.5 The Delta-Function Potential

2.5.1 Bound States and Scattering States

We have now encountered two different kinds of solutions to the Schrödinger equation: For the infinite square well and the harmonic oscillator they are normalizable, and labeled by a discrete index n ; for the free particle they are non-normalizable, and labeled by a continuous variable k .

In classical mechanics, suppose we have a one-dimensional time-independent potential $V(x)$. If $V(x)$ is higher than the particle's total energy E on either side, then the particle is stuck in the potential well – it rocks back and forth between the **turning points** and couldn't escape. This is called a **bound state**. If E exceeds $V(x)$ on one side, then the particle comes in from the infinity and returns to infinity. This is called a **scattering state**.

In quantum mechanics, **tunneling** allows the particle to leak through any finite potential barrier, thus only the potential at infinity matters:

$$\begin{cases} E < [V(-\infty) \text{ and } V(+\infty)] \Rightarrow \text{bound state,} \\ E > [V(-\infty) \text{ or } V(+\infty)] \Rightarrow \text{scattering state.} \end{cases}$$

In real life, most potentials go to zero at infinity, thus

$$\begin{cases} E < 0 \Rightarrow \text{bound state,} \\ E > 0 \Rightarrow \text{scattering state.} \end{cases}$$

The potentials of the infinite well and the harmonic oscillator go to infinity as $x \rightarrow \pm\infty$, they admit bound states only; the potential of the free particle is zero everywhere, it only allows scattering states.

Also note that E must exceed the minimum value of $V(x)$, for every normalizable solution to the time-independent Schrödinger equation.

2.5.2 The Delta-Function Well

The **Dirac delta function** satisfies

$$\delta(x) \equiv \begin{cases} 0, & \text{if } x \neq 0 \\ \infty, & \text{if } x = 0 \end{cases} \cdot \text{ with } \int_{-\infty}^{+\infty} \delta(x) dx = 1.$$

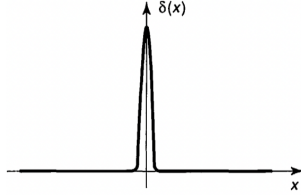


Figure 2.4: The Dirac delta function

Notice that $\delta(x - a)$ is a spike of area 1 at the point a . Thus we have

$$f(x)\delta(x - a) = f(a)\delta(x - a).$$

This give the most important property of the delta function:

$$\int_{-\infty}^{+\infty} f(x)\delta(x - a) = f(a) \int_{-\infty}^{+\infty} \delta(x - a) = f(a).$$

Under the integral sign, the value of $f(x)$ at a is picked out.

Now let's consider a potential of the form

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

where α is a positive constant. The Schrödinger equation for the delta-function well reads

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - \alpha\delta(x)\psi = E\psi;$$

it yields both bound states and scattering states. We look at the bound states first.

When $x < 0$, $V(x) = 0$, thus

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = \kappa^2\psi,$$

where

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

The general solution to the equation is

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

but the first term would blow up as $x \rightarrow -\infty$, thus $A = 0$:

$$\psi(x) = Be^{\kappa x}. \quad (x < 0).$$

In the region $x > 0$, similarly we have

$$\psi(x) = Fe^{-\kappa x}. \quad (x > 0).$$

The question is two stitch these two functions together at $x = 0$. The standard boundary conditions for ψ is

$\begin{cases} 1. \psi & \text{is always continuous;} \\ 2. d\psi/dx & \text{is continuous except at points where the potential is infinite.} \end{cases}$
--

Thus the first boundary condition tells us that $F = B$, thus

$$\psi(x) = \begin{cases} Be^{\kappa x}, & (x \leq 0). \\ Be^{-\kappa x}, & (x \geq 0); \end{cases}$$

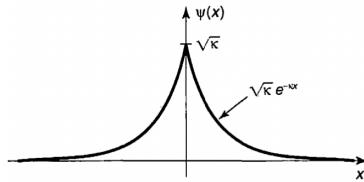


Figure 2.5: Bound state wave function for the delta-function potential

$\psi(x)$ is plotted as shown. Evidently the delta function must determine the discontinuity in the derivative of ψ , at $x = 0$. But how to prove that? We integrate the Schrödinger equation from $-\epsilon$ to $+\epsilon$, and let $\epsilon \rightarrow 0$:

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

The first integral is just $d\psi/dx$, evaluated at two end points; the last integral is 0 as $\epsilon \rightarrow 0$ evidently. Thus

$$\Delta\left(\frac{d\psi}{dx}\right) \equiv \lim_{\epsilon \rightarrow 0} \left(\frac{d\psi}{dx} \Big|_{+\epsilon} - \frac{d\psi}{dx} \Big|_{-\epsilon} \right) = \frac{2m}{\hbar^2} \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{+\epsilon} V(x)\psi(x)dx.$$

Since $V(x) = -\alpha\delta(x)$, we have

$$\Delta\left(\frac{d\psi}{dx}\right) = -\frac{2m\alpha}{\hbar^2}\psi(0).$$

In this case,

$$\frac{d\psi}{dx} \Big|_{+} = -B\kappa, \quad \frac{d\psi}{dx} \Big|_{-} = B\kappa.$$

and hence $\Delta(d\psi/dx) = -2B\kappa$. Also we have $\psi(0) = B$, thus

$$\kappa = \frac{m\alpha}{\hbar^2}.$$

Thus the allowed energy is

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

Finally we normalize ψ :

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = 2|B|^2 \int_0^{\infty} e^{-2\kappa x} dx = \frac{|B|^2}{\kappa} = 1.$$

Hence

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

Evidently the delta-function well, regardless of its strength α , has exactly one bound state:

$$\boxed{\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2}; \quad E = -\frac{m\alpha^2}{2\hbar^2}.$$

Then we consider the scattering states with $E > 0$. When $x < 0$, the Schrödinger equation reads

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

where

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

is real and positive. The solution is

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

Similarly, for $x > 0$,

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}.$$

The continuity of $\psi(x)$ at $x = 0$ requires that

$$F + G = A + B.$$

Also we have $\Delta(d\psi/dx) = ik(F - G - A + B)$ and $\psi(0) = A + B$, so the second boundary condition says

$$ik(F - G - A + B) = -\frac{2mE}{\hbar^2}(A + B),$$

or

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

In a typical scattering experiment particles are fired in from one direction, say from the left. Thus the amplitude of the wave coming in from the left will be zero: $G = 0$.

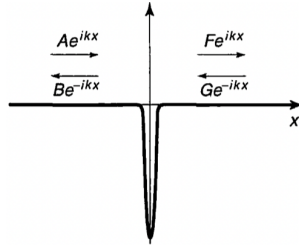


Figure 2.6: Scattering from a delta function well

A is the amplitude of the **incident wave**, B is the amplitude of the **reflected wave**, and F is the amplitude of the **transmitted wave**. Solving those equations, we have

$$B = \frac{i\beta}{1 - i\beta}A, \quad F = \frac{1}{1 - i\beta}A.$$

Actually the wave function here is not normalizable, thus the probability of finding the particle at a particular point is not well defined. However, the ratio of probabilities for the incident and reflected wave is meaningful. The relative probability that an incident particle will be reflected back is

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

R is called the **reflection coefficient**. The probability of transmission is given by the **transmission coefficient**

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

The sum of these probabilities is 1: $R + T = 1$. The above equation could also be written as

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

The higher the energy, the greater the probability of transmission. This seems reasonable. But here's still the problem: these scattering wave function are not normalizable, so they don't actually represent possible particle states. The solution is we need to form normalizable linear combinations of the stationary states. R and T should be interpreted as the approximate reflection and transmission probabilities for particles in the vicinity of E .

Now let's briefly look at the case of a delta-function barrier, by changing the sign of α . This kills the bound state. Since R and T only depends on α^2 , they are unchanged. In quantum mechanics, the particle has some nonzero probability of passing through the potential even if $E < V_{\max}$. This phenomenon is called **tunneling**. Conversely, even if $E > V_{\max}$, there are some possibility that the particle will bounce back.

2.6 The Finite Square Well

Consider the finite square well potential

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

where V_0 is a positive constant. This potential admits both bound states (with $E < 0$) and scattering states (with $E > 0$). We first look at the bound state.

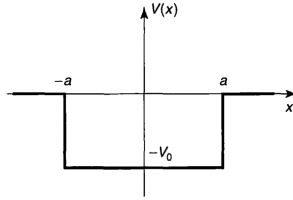


Figure 2.7: The finite square well

When $x < -a$, the potential is 0, thus the Schrödinger equation reads

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi, \quad \text{or} \quad \frac{d^2\psi}{dx^2} = \kappa^2\psi,$$

where

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

is real and positive. The general solution is $\psi(x) = A \exp(-\kappa x) + B \exp(\kappa x)$, but the first term blows up as $x \rightarrow -\infty$, so the solution is

$$\psi(x) = B e^{\kappa x}, \quad \text{for } x < -a.$$

In the region $-a < x < a$, $V(x) = -V_0$, and the Schrödinger equation reads

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - V_0\psi = E\psi, \quad \text{or } \frac{d^2\psi}{dx^2} = -l^2\psi,$$

where

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

E is negative for bound states, but it must be greater than $-V_0$, thus l is real and positive. The general solution is

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

where C and D are constants. Finally for $x > a$, similarly we have

$$\psi(x) = F e^{-\kappa x}, \quad \text{for } x > a.$$

If $V(x)$ is an even function, then $\psi(x)$ can always be taken to be either even or odd. Now here $V(x)$ is an even function. The advantage of this is that we only need to impose the boundary conditions on one side, and the other side is automatic. We here consider $\psi(x)$ as an even function.

$$\psi(x) = \begin{cases} F e^{-\kappa x}, & \text{for } x > a, \\ D \cos(lx), & \text{for } -a < x < a, \\ \psi(-x), & \text{for } x < -a. \end{cases}$$

The continuity of $\psi(x)$ at $x = a$ says that

$$F e^{-\kappa a} = D \cos(la),$$

and the continuity of $d\psi/dx$, says

$$-\kappa F e^{-\kappa a} = -l D \sin(la).$$

Then we have

$$\kappa = l \tan(la).$$

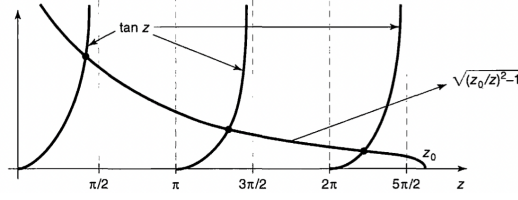
This is a formula for the allowed energies, as κ and l are both functions of E . To solve this, we let

$$z \equiv la, \quad z_0 \equiv \frac{a}{\hbar} \sqrt{2mV_0}.$$

Also we have $(\kappa^2 + l^2) = 2mV_0/\hbar^2$, thus $\kappa a = \sqrt{z_0^2 - z^2}$, and hence

$$\tan z = \sqrt{(z_0/z)^2 - 1}.$$

This is a transcendental function for z as a function of z_0 . Two limiting cases are of special interest:


 Figure 2.8: Graphic solution for $z_0 = 8$ (even state)

1. **Wide, deep well.** If z_0 is very large, the intersection occur just slightly below $z_n = n\pi/2$, with n odd, thus

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

$E + V_0$ is the energy above the bottom of the well and the right side is just the infinite square well energies (or rather half of them, since n is odd), for a well of width $2a$. Thus the finite square well goes over to the infinite square well as $V_0 \rightarrow \infty$; for any finite V_0 , there are only a finite number of bound states.

2. **Shallow, narrow well.** As z_0 decreases, the bound states will be fewer, until finally, only one remains. No matter how weak the well becomes, there is always one bound state.

Then we come to the scattering states ($E > 0$). To the left, $V(x) = 0$, we have

$$\psi(x) = Ae^{-ikx} + Be^{-ikx}, \quad \text{for } x < -a,$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar}.$$

Inside the well, we have $V(x) = -V_0$,

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

where

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

To the right, assuming there's no incoming wave in this region, we have

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

Here A is the incident amplitude, B is the reflected amplitude, and F is the transmitted amplitude. There are four boundary conditions:

1. Continuity of $\psi(x)$ at $-a$:

$$Ae^{-ika} + Be^{ika} = -C \sin(la) + D \cos(la).$$

2. Continuity of $d\psi(x)/dx$ at $-a$:

$$ik[Ae^{-ika} - Be^{ika}] = l[C \cos(la) + D \sin(la)].$$

3. Continuity of $\psi(x)$ at a :

$$C \sin(la) + D \cos(la) = Fe^{ika}.$$

4. Continuity of $d\psi(x)/dx$ at a :

$$l[C \cos(la) - D \sin(la)] = ikFe^{ika}.$$

Then we have

$$B = i \frac{\sin(2la)}{2kl} (l^2 - k^2) F.$$

$$F = \frac{Ae^{-2ika}}{\cos(2la) - i \frac{k^2 + l^2}{2kl} \sin(2la)}.$$

The transmission coefficient ($T = |F|^2/|A|^2$) is given by

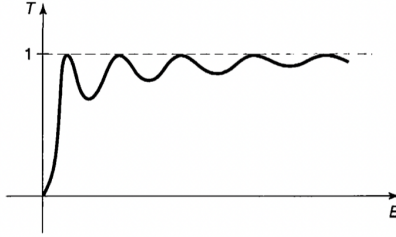


Figure 2.9: Transmission coefficient as a function of energy

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

Notice that $T = 1$ (the well becomes transparent) whenever the sine is zero, which is to say, when

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

where n is an integer. The energies for perfect transmission are given by

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

which happen to be precisely the allowed energies for the infinite square well. T is plotted as a function of the energy.

Chapter 3

Formalism

3.1 Hilbert Space

Quantum mechanics is based on two structures: *wave functions* and *operators*. The states of a system is represented by its wave function, observables are represented by operators. Wave functions satisfy the defining condition for abstract **vectors**, and operator act on them as **linear transformations**. So the natural language of quantum mechanics is **linear algebra**.

In an N -dimensional space, a vector $|\alpha\rangle$ is represented by

$$|\alpha\rangle \rightarrow \mathbf{a} = \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{bmatrix}.$$

The **inner product**, $\langle\alpha|\beta\rangle$, of two vectors is the complex number,

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

Linear transformation, T , are represented by matrices:

$$|\beta\rangle = T|\alpha\rangle \rightarrow \mathbf{b} = \mathbf{T}\mathbf{a} = \begin{bmatrix} t_{11} & t_{12} & \cdots & t_{1N} \\ t_{21} & t_{22} & \cdots & t_{2N} \\ \vdots & \vdots & & \vdots \\ t_{N1} & t_{N2} & \cdots & t_{NN} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{bmatrix}.$$

However, "vectors" we encounter in quantum mechanics are functions, and they live in infinite-dimensional spaces. To represent a physical state, the wave function Ψ must be normalized:

$$\int |\Psi|^2 dx = 1.$$

The set of all **square-integrable functions**, on a specified interval,

$$f(x) \quad \text{such that} \quad \int_a^b |f(x)|^2 dx < \infty$$

constitutes a vector space. We call it **Hilbert space**. In quantum mechanics,

Wave functions live in Hilbert space.

We define the **inner product of two functions** as follows:

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

If f and g are both square-integrable (i.e. both in Hilbert space), their inner product is guaranteed to exist. This follows the integral **Schwarz inequality**:

$$\left| \int_a^b f(x)^* g(x) dx \right| \leq \sqrt{\int_a^b |f(x)|^2 dx \int_a^b |g(x)|^2 dx}.$$

In particular we have

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

Moreover, the inner product of $f(x)$ with itself

$$\langle f|f\rangle = \int_a^b |f(x)|^2 dx$$

is real and non-negative; it's 0 only when $f(x) = 0$.

A function is **normalized** if its inner product with itself is 1; two functions are **orthogonal** if their inner product is 0; and a set of functions f_n is **orthonormal** if they are normalized and mutually orthogonal:

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

Finally, a set of functions is **complete** if any other function (in Hilbert space) can be expressed as a linear combination of them:

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

If the functions $f_n(x)$ are orthonormal, the coefficients are given by Fourier's trick:

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

3.2 Observables

3.2.1 Hermitian Operators

The expectation value of an observable $Q(x, p)$ can be expressed very neatly inner-product notation:

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

The outcome of a measurement has got to be real, thus

$$\langle Q \rangle = \langle Q \rangle^*.$$

The complex conjugate of an inner product reverses the order, thus

$$\langle \Psi | \hat{Q} \Psi \rangle = \langle \hat{Q} \Psi | \Psi \rangle.$$

This must be true for any wave function Ψ . Such operators are called **hermitian**. A stronger property is that

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

for any f and g . A hermitian operator can be applied either to the first member of an inner product or to the second with the same result, and hermitian operators naturally arise in quantum mechanics because their expectation values are real:

Observables are represented by hermitian operators.

3.2.2 Determinate States

Quantum mechanics is indeterminate: when we measure an observable Q on an ensemble of identically prepared systems, all in the same state Ψ , we do not get the same result each time. Can we get a **determinate state** for the observable Q (that is, every measurement of Q returns the same value q)? Actually, there's one example: stationary states are determinate states of the Hamiltonian.

The standard deviation of Q , in a determinate state, would be zero:

$$\sigma^2 = \langle (\hat{Q} - \langle Q \rangle)^2 \rangle = \langle \Psi | (\hat{Q} - q)^2 \Psi \rangle = \langle (\hat{Q} - q) \Psi | (\hat{Q} - q) \Psi \rangle.$$

The only function whose inner product with itself vanishes is 0, thus

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

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

Determinate states are eigenfunctions of \hat{Q} .

Eigenvalue is a number. Multiplying the eigenfunction by a constant still gives an eigenfunction. Eigenfunctions could not be 0, but eigenvalue could be 0. The collection of all the eigenvalues of an operator is called its **spectrum**. Sometime two (or more) linearly independent eigenfunctions share the same eigenvalue, in that case the spectrum is said to be **degenerate**.

3.3 Eigenfunctions of a Hermitian Operator

We now focus on the eigenfunctions of hermitian operators. If the spectrum is **discrete** (the eigenvalues are separated from each other), then the eigenfunctions lie in Hilbert space and they constitute physically realizable states. If the spectrum is **continuous** (the eigenvalues fill out an entire range) then the eigenfunctions are not realizable, and they do not represent possible wave functions, although linear combinations of them might be normalizable. Some operators have a discrete spectrum, like the Hamiltonian for the harmonic oscillator; some have only a continuous spectrum, like the free particle Hamiltonian; and some have both a discrete part and a continuous part, like the Hamiltonian for a finite square well.

3.3.1 Discrete Spectra

The normalizable eigenfunctions of a hermitian operator have two important properties:

Theorem 1 (reality): The eigenvalues are real.

Proof: Suppose $\hat{Q}f = qf$ and $\langle f|\hat{Q}f\rangle = \langle \hat{Q}f|f\rangle$. Then $q\langle f|f\rangle = q^*\langle f|f\rangle$. Since $\langle f|f\rangle$ can not be zero, thus $q = q^*$. QED

Theorem 2 (orthogonality): Eigenfunctions belonging to distinct eigenvalues are orthogonal.

Proof: Suppose $\hat{Q}f = qf$ and $\hat{Q}g = q'g$. Then $\langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle$, thus $q'\langle f|g\rangle = q\langle f|g\rangle$. Since q is real, thus $q \neq q'$. Hence $\langle f|g\rangle = 0$ must hold. QED

Then we consider about degenerate states. If two or more eigenfunctions share the same eigenvalue, any linear combination of them is an eigenfunction with the same eigenvalue. We can use the **Gram-Schmidt orthogonalization procedure** to construct orthogonal eigenfunctions within each degenerate subspace.

Axiom (completeness): The eigenfunctions of an observable operator are complete: Any function in Hilbert space can be expressed as a linear combination of them.

3.3.2 Continuous Spectra

If the spectrum of a hermitian operator is continuous, the eigenfunctions are not normalizable and Theorem 1 and 2 fail. Nevertheless, there is a sense where the three properties. Consider the following example:

Example: Find the eigenfunctions and eigenvalues of the momentum operator.

Solution: Let $f_p(x)$ be the eigenfunction and p the eigenvalue, then

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

The general solution is

$$f_p(x) = A e^{ipx/\hbar}.$$

This is not square-integrable for any complex p . But if we consider real eigenvalues, we do cover a kind of ersatz "orthonormality":

$$\int_{-\infty}^{\infty} f_{p'}^*(x) f_p(x) dx = |A|^2 \int_{-\infty}^{\infty} e^{i(p-p')x/\hbar} dx = |A|^2 2\pi\hbar \delta(p-p').$$

If we pick $A = 1/\sqrt{2\pi\hbar}$, then

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar},$$

and so that

$$\langle f_{p'} | f_p \rangle = \delta(p-p').$$

This is called the **Dirac orthonormality**.

Most important, the eigenfunctions are complete:

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

The expansion coefficient $c(p)$ is obtained by Fourier's trick:

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

Example: Find the eigenfunctions and eigenvalues of the position operator.

Solution: Let $g_y(x)$ be the eigenfunction and y the eigenvalue:

$$x g_y(x) = y g_y(x).$$

The solution is the Dirac delta function:

$$g_y(x) = A \delta(x-y).$$

This time the eigenvalue has to be real; the eigenfunctions are not square-integrable, but again they admit Dirac orthonormality:

$$\int_{-\infty}^{\infty} g_{y'}^*(x) g_y(x) dx = |A|^2 \int_{-\infty}^{\infty} \delta(x-y') \delta(x-y) = |A|^2 \delta(y-y').$$

Let $A = 1$, so

$$g_y(x) = \delta(x-y),$$

then

$$\langle g_{y'} | g_y \rangle = \delta(y-y').$$

Their eigenfunctions are also complete:

$$f(x) = \int_{-\infty}^{\infty} c(y) g_y(x) dy = \int_{-\infty}^{\infty} c(y) \delta(x-y) dy,$$

with

$$c(y) = f(y).$$

3.4 Generalized Statistical Interpretation

Generalized statistical interpretation: If we measure an observable $Q(x, p)$ on a particle in the state $\Psi(x, t)$, we are certain to get one of the eigenvalues of the hermitian operator \hat{Q} . If the spectrum of \hat{Q} is discrete, the probability of getting the particular eigenvalue q_n associated with the orthonormalized eigenfunction $f_n(x)$ is

$$|c_n|^2, \quad \text{where } c_n = \langle f_n | \Psi \rangle.$$

If the spectrum is continuous, with real eigenvalues $q(z)$ and associated Dirac-orthonormalized eigenfunctions $f_z(x)$, the probability of getting a result in the range dz is

$$|c_n|^2 dz, \quad \text{where } c(z) = \langle f_z | \Psi \rangle.$$

Upon measurement, the wave function “collapses” to the corresponding eigenstate.

The eigenfunctions of an observable operator are complete, so the wave function can be written as a linear combination of them:

$$\Psi(x, t) = \sum_n c_n f_n(x).$$

(We assume the spectrum is discrete here for simplicity.) The eigenfunctions are orthonormal, the coefficients are given by the Fourier’s trick:

$$c_n = \langle f_n | \Psi \rangle = \int f_n(x)^* \Psi(x, t) dx.$$

Qualitatively, c_n tells us how much f_n is contained in Ψ . Actually $|c_n|^2$ gives the probability of getting the particular eigenvalues q_n . The total probability has got to be one:

$$\sum_n |c_n|^2 = 1,$$

and this follows the normalization of the wave function:

$$\begin{aligned} 1 = \langle \Psi | \Psi \rangle &= \left\langle \left(\sum_{n'} c_{n'} f_{n'} \right) \middle| \left(\sum_n c_n f_n \right) \right\rangle = \sum_{n'} \sum_n c_{n'}^* c_n \langle f_{n'} | f_n \rangle \\ &= \sum_{n'} \sum_n c_{n'}^* c_n \delta_{n'n} = \sum_n c_n^* c_n = \sum_n |c_n|^2. \end{aligned}$$

Similarly, the expectation value of Q should be the sum over all possible outcomes of the eigenvalue times the probability of getting that eigenvalue:

$$\langle Q \rangle = \sum_n q_n |c_n|^2.$$

This is derived by

$$\langle Q \rangle = \langle \Psi | \hat{Q} \Psi \rangle = \left\langle \left(\sum_{n'} c_{n'} f_{n'} \right) \middle| \left(\hat{Q} \sum_n c_n f_n \right) \right\rangle,$$

since $\hat{Q}f_n = q_n f_n$,

$$\langle Q \rangle = \sum_{n'} \sum_n c_{n'}^* c_n q_n \langle f_{n'} | f_n \rangle = \sum_{n'} \sum_n c_{n'}^* c_n q_n \delta_{n'n} = \sum_n q_n |c_n|^2.$$

A measurement of x on a particle in state Ψ must return one of the eigenvalues of the position operator. Actually every real number y is an eigenvalue of x and the corresponding eigenfunction is $g_y(x) = \delta(x - y)$. Then

$$c(y) = \langle g_y | \Psi \rangle = \int_{-\infty}^{\infty} \delta(x - y) \Psi(x, t) dx = \Psi(y, t),$$

so the probability of getting a result in the range dy is $|\Psi(y, t)|^2 dy$, which is the original statistical interpretation. And for momentum,

$$c(p) = \langle f_p | \Psi \rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \Psi(x, t) dx.$$

We give it a special name and symbol: the **momentum space wave function**, $\Phi(p, t)$, which is the Fourier transform of the **position space wave function** $\Psi(x, t)$:

$$\begin{aligned} \Phi(p, t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \Psi(x, t) dx, \\ \Psi(x, t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ipx/\hbar} \Phi(p, t) dp. \end{aligned}$$

The probability that a measurement of momentum would yield a result in the range dp is

$$|\Phi(p, t)|^2 dp.$$

3.5 The Uncertainty Principle

3.5.1 Proof of the Generalized Uncertainty Principle

For any observable A , we have

$$\sigma_A^2 = \langle (\hat{A} - \langle A \rangle) \Psi | (\hat{A} - \langle A \rangle) \Psi \rangle = \langle f | f \rangle,$$

where $f \equiv (\hat{A} - \langle A \rangle) \Psi$. Likewise, for any other observable B ,

$$\sigma_B^2 = \langle g | g \rangle,$$

where $g \equiv (\hat{B} - \langle B \rangle) \Psi$. Using the Schwarz inequality

$$\sigma_A^2 \sigma_B^2 = \langle f | f \rangle \langle g | g \rangle \geq |\langle f | g \rangle|^2.$$

For any complex number z ,

$$|z|^2 = [\text{Re}(z)]^2 + [\text{Im}(z)]^2 \geq [\text{Im}(z)]^2 = \left[\frac{1}{2i} (z - z^*) \right]^2.$$

Thus letting $z = \langle f|g\rangle$,

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} [\langle f|g\rangle - \langle g|f\rangle] \right)^2.$$

By calculation we have

$$\langle f|g\rangle = \langle \hat{A}\hat{B}\rangle - \langle A\rangle\langle B\rangle, \quad \langle g|f\rangle = \langle \hat{B}\hat{A}\rangle - \langle B\rangle\langle A\rangle.$$

so

$$\langle f|g\rangle - \langle g|f\rangle = \langle \hat{A}\hat{B}\rangle - \langle \hat{B}\hat{A}\rangle = \langle [\hat{A}, \hat{B}] \rangle,$$

where

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

To be conclude,

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

This is called the **generalized uncertainty principle**. For example, we have

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

thus

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

This is the original Heisenberg uncertainty principle. In fact there is an uncertainty principle for every pair of observables whose operators do not commute – we call them **incompatible observables**. Incompatible observables do not have common eigenfunctions, but they do admit complete sets of simultaneous eigenfunctions.

3.5.2 The Minimum-Uncertainty Wave Packet

A question is: what is the most general minimum-uncertainty wave packet? Suppose that we have $g(x) = ia f(x)$, $a \in \mathbb{R}$. For the position-momentum uncertainty principle this becomes:

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

which is a differential equation for Ψ as a function of x . The solution is

$$\Psi(x) = A e^{-a(x - \langle x \rangle)^2 / 2\hbar} e^{i\langle p \rangle x / \hbar}.$$

The minimum-uncertainty wave packet is a Gaussian.

3.5.3 The Energy-Time Uncertainty Principle

3.6 Dirac Notation

The state of a system in quantum mechanics is represented by a vector $|s(t)\rangle$, that lives out there in Hilbert space, but we can express it with respect to any bases. The wave function $\Psi(x, t)$ is the coefficient in the expansion of $|s\rangle$ in the basis of position eigenfunctions:

$$\Psi(x, t) = \langle x|s(t)\rangle$$

(with $|x\rangle$ standing for the eigenfunction of \hat{x} with eigenvalue x), and the momentum space wavefunction $\Phi(p, t)$ is the expansion of $|s\rangle$ in the basis of momentum eigenfunctions:

$$\Phi(p, t) = \langle p|s(t)\rangle$$

(with $|p\rangle$ standing for the eigenfunction of \hat{p} with eigenvalue p). Or we can expand $|s\rangle$ in the basis of energy eigenfunctions (suppose the spectrum is discrete):

$$c_n(t) = \langle n|s(t)\rangle$$

(with $|n\rangle$ standing for the n -th eigenfunction of \hat{H}). Those are three different ways of describing the same vector:

$$\begin{aligned}\Psi(x, t) &= \int \Psi(y, t) \delta(x - y) dy = \int \phi(p, t) \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} dp \\ &= \sum c_n e^{iE_n t/\hbar} \psi_n(x).\end{aligned}$$

Operators (observables) are linear transformations which transform one vector into another:

$$|\beta\rangle = \hat{Q}|\alpha\rangle.$$

Vectors are represented, with respect to a particular basis $\{|e_n\rangle\}$, by their components,

$$|\alpha\rangle = \sum_n a_n |e_n\rangle, \quad a_n = \langle e_n|\alpha\rangle; \quad |\beta\rangle = \sum_n b_n |e_n\rangle, \quad b_n = \langle e_n|\beta\rangle.$$

Operators are represented by their **matrix elements**

$$\langle e_m|\hat{Q}|e_n\rangle \equiv Q_{mn}.$$

Thus we have

$$\sum_n b_n |e_n\rangle = \sum_n a_n \hat{Q}|e_n\rangle,$$

or

$$\sum_n b_n \langle e_m|e_n\rangle = \sum_n a_n \langle e_m|\hat{Q}|e_n\rangle,$$

and hence,

$$b_m = \sum_n Q_{mn} a_n.$$

The matrix elements tells how the components transform.

Dirac proposed to chop the bracket notation for the inner product $\langle\alpha|\beta\rangle$ into two pieces, **bra** $\langle\alpha|$ and **ket** $|\beta\rangle$. The latter is a vector, while the former is a *linear function* of vectors. In a function space, the bra can be thought of as an instruction to integrate:

$$\langle f| = \int f^*[\dots] dx.$$

In a finite-dimensional vector space, the vectors are expressed as columns,

$$|\alpha\rangle = \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{bmatrix},$$

and the corresponding bra is a row vector:

$$\langle\alpha| = (a_1^*, a_2^*, \dots, a_n^*).$$

The collection of all bras constitutes another vector space: **dual space**.

The operator

$$\hat{P} \equiv |\alpha\rangle\langle\alpha|$$

picks out the portion of any other vector that lies along $|\alpha\rangle$:

$$\hat{P}|\beta\rangle = \langle\alpha|\beta\rangle|\alpha\rangle;$$

we call it the **projection operator** onto the one-dimensional subspace spanned by $|\alpha\rangle$. If $\{|e_n\rangle\}$ is a discrete orthogonal basis,

$$\langle e_m|e_n\rangle = \delta_{mn},$$

then

$$\sum_n |e_n\rangle\langle e_n| = 1,$$

which shows it's an identical operator. Similarly, if $\{|e_z\rangle\}$ is a Dirac orthonormalized continuous basis,

$$\langle e_z|e_{z'}\rangle = \delta_{z-z'},$$

then

$$\int |e_z\rangle\langle e_z| = 1.$$

Chapter 4

Quantum Mechanics in Three Dimensions

4.1 Schrödinger Equation in Spherical Coordinates

The Schrödinger equation says

$$i\hbar \frac{\partial \psi}{\partial t} = H\Psi,$$

where H is the Hamiltonian operator obtained from the classical energy

$$\frac{1}{2}mv^2 + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V.$$

By the standard prescription,

$$p_x \rightarrow \frac{h}{i} \frac{\partial}{\partial x}, \quad p_y \rightarrow \frac{h}{i} \frac{\partial}{\partial y}, \quad p_z \rightarrow \frac{h}{i} \frac{\partial}{\partial z},$$

or

$$\boxed{\mathbf{p} \rightarrow \frac{h}{i} \nabla.}$$

Thus

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

where

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

is the **Laplacian**. The potential V and the wave function Ψ are functions of $\mathbf{r} = (x, y, z)$ and t . The probability of finding the particle in the infinitesimal volume $d^3\mathbf{r} = dxdydz$ is $|\Psi(\mathbf{r}, t)|^2 d^3r$, and the normalization condition is

$$\int |\Psi|^2 d^3r = 1.$$

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

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

where the spatial wave function ψ_n satisfies the time-independent Schrödinger equation:

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

The general solution to the Schrödinger equation is

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

where c_n are determined by the initial wave function $\Psi(\mathbf{r}, 0)$.

4.1.1 Separation of Variables

It's nature to adopt **spherical coordinates** (r, θ, ϕ) in the 3D Schrödinger equation. The Laplacian takes the form

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

Then the time-independent Schrödinger equation reads

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

Then we look for solutions that are separable into products:

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

Put it into the previous equation, we have

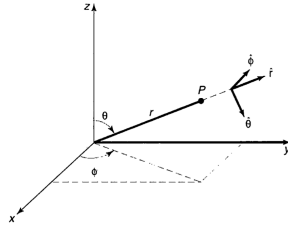


Figure 4.1: Spherical coordinates

$$-\frac{\hbar^2}{2m} \left[\frac{Y}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] + VRY = ERY.$$

Then

$$\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} + \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = 0.$$

The first term depends only on r , and the remainder only depends on θ and ϕ , so each must be a constant. Thus we have

$$\begin{aligned} \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] &= l(l+1); \\ \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} &= -l(l+1). \end{aligned}$$

4.1.2 The Angular Equation

From the previous equation we have

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

We try separation of variables:

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

Plugging this in, we have

$$\left\{ \frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1) \sin^2 \theta \right\} + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = 0.$$

The first term is a function only of θ and the second is a function only of ϕ , so each must be a constant:

$$\begin{aligned} \frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1) \sin^2 \theta &= m^2; \\ \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} &= -m^2. \end{aligned}$$

The ϕ equation is easy:

$$\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi \quad \Rightarrow \quad \Phi(\phi) = e^{im\phi}.$$

When ϕ advances by 2π , we return to the same point in space, thus we require

$$\Phi(\phi + 2\pi) = \Phi(\phi).$$

This means that $\exp[im(\phi + 2\pi)] = \exp(im\phi)$, or $\exp(2\pi im) = 1$. Thus m must be an integer:

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

The solution for the θ equation is

$$\Theta(\theta) = AP_l^m(\cos \theta),$$

where $P_l^m(\cos \theta)$ is the **associated Legendre function** defined by

$$P_l^m(\cos \theta) \equiv (1 - x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x),$$

and $P_l(x)$ is the l th **Legendre polynomial**, defined by the **Rodrigues formula**:

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l.$$

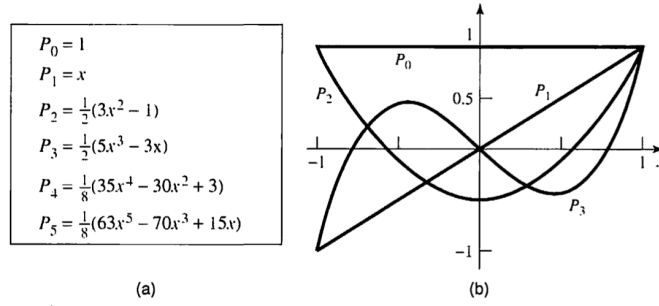


Figure 4.2: The first few Legendre polynomials

l must be a non-negative integer for the Rodrigues formula to make sense; also for $|m| > l$, $P_l^m = 0$. Thus for any given l , there are $(2l + 1)$ possible values of m :

$$l = 0, 1, 2, \dots; \quad m = 0, \pm 1, \pm 2, \dots, \pm l.$$

Now the volume element in the spherical coordinates is

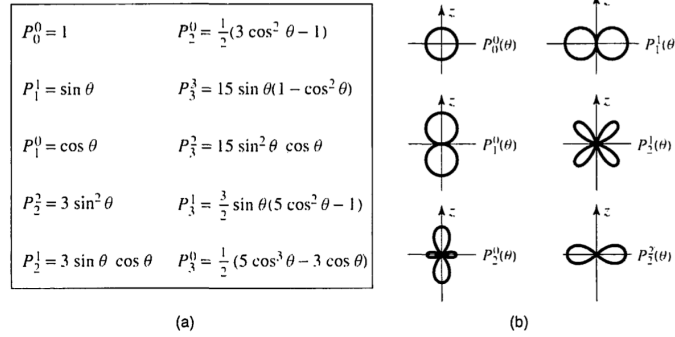
$$d^3\mathbf{r} = r^2 \sin \theta \, dr \, d\theta \, d\phi,$$

so the normalization condition becomes

$$\int |\psi|^2 r^2 \sin \theta \, dr \, d\theta \, d\phi = \int |R|^2 r^2 \, dr \int |Y|^2 \sin \theta \, d\theta \, d\phi = 1.$$

We normalize R and Y separately:

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


 Figure 4.3: Some associated Legendre functions, $P_l^m(\cos \theta)$

The normalized angular wave functions are called **spherical harmonics**:

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^m(\cos \theta),$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. They are orthogonal:

$$\int_0^{2\pi} \int_0^\pi [Y_l^m(\theta, \phi)]^* [Y_{l'}^{m'}(\theta, \phi)] \sin \theta d\theta d\phi = \delta_{ll'} \delta_{mm'}.$$

We call l the **azimuthal quantum number** and m the **magnetic quantum number**.

4.1.3 The Radial Equation

The angular function $Y(\theta, \phi)$ is the same for all spherically symmetric potentials; the actual shape of the potential $V(r)$ affects only the radial part of the wave function $R(r)$. Let $u(r) \equiv rR(r)$, we have the **radial equation**:

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

This is identical in form to the one-dimensional Schrödinger equation except the **effective potential**

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

$(\hbar^2/2m)[l(l+1)/r^2]$ is called the **centrifugal term**, which tends to throw the particle outward. The normalization becomes

$$\int_0^\infty |u|^2 dr = 1.$$

4.2 The Hydrogen Atom

From Coulomb's law, the potential energy of the electron in the hydrogen atom is

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

and the radial equation is

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

4.2.1 The Radial Wave Function

Let

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

Then we have

$$\frac{1}{\kappa^2} \frac{d^2 u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \frac{1}{r} + \frac{l(l+1)}{(\kappa r)^2} \right] u.$$

We introduce

$$\rho \equiv \kappa r, \quad \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa},$$

then

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

We then examine the asymptotic form of the solutions. As $\rho \rightarrow \infty$, approximately we have

$$\frac{d^2 u}{d\rho^2} = u.$$

The general solution is

$$u(\rho) = Ae^{-\rho} + Be^{\rho},$$

we need $B = 0$. Then

$$u(\rho) \approx Ae^{-\rho}$$

for large ρ . On the other hand, as $\rho \rightarrow 0$, approximately we have

$$\frac{d^2 u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u.$$

The general solution is

$$u(\rho) = C\rho^{l+1} + D\rho^{-l},$$

we need $D = 0$. Thus

$$u(\rho) \approx C\rho^{l+1}$$

for small ρ . We introduce a new function $v(\rho)$ to peel off the asymptotic behavior:

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho).$$

We have

$$\frac{du}{d\rho} = \rho^l e^{-\rho} \left[(l+1-\rho)v + \rho \frac{dv}{d\rho} \right],$$

and

$$\frac{d^2u}{d\rho^2} = \rho^l e^{-\rho} \left\{ \left[-2l-2+\rho + \frac{l(l+1)}{\rho} \right] v + 2(l+1-\rho) \frac{dv}{d\rho} + \rho \frac{d^2v}{d\rho^2} \right\}.$$

In terms of $v(\rho)$, the radial equation reads

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

Assume the solution $v(\rho)$ can be expressed as a power series in ρ :

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

Our problem is to determine the coefficients. Differentiate term by term:

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j.$$

Differentiating again, we have

$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}.$$

Insert into the radial equation, we obtain

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

This is a recursion formula which determines the coefficients. We start with c_0 (by normalization) and hence the other c_j 's.

For a large j , the recursion formula says

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j.$$

Suppose for a moment that this were *exact*. Then

$$f_j = \frac{2^j}{j!} c_0,$$

so

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho},$$

and hence

$$u(\rho) = c_0 \rho^{l+1} e^\rho,$$

which blows up at large ρ . The series must terminate. There must occur some maximal integer j_{\max} , such that

$$c_{j_{\max}+1} = 0.$$

Evidently

$$2(j_{\max} + l + 1) - \rho_0 = 0.$$

Defining

$$n \equiv j_{\max} + l + 1,$$

where n is the **principal quantum number**, we have

$$\rho_0 = 2n.$$

Since

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

so the allowed energies are

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

This is the **Bohr formula**.

We also find that

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0 \hbar^2} \right) \frac{1}{n} = \frac{1}{\alpha n},$$

where

$$\alpha \equiv \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.529 \times 10^{-10} m$$

is the **Bohr radius**. It follows that

$$\rho = \frac{r}{\alpha n}.$$

The spatial wave functions for hydrogen are labeled by three quantum numbers (n , l , and m):

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi),$$

where

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

and $v(\rho)$ is a polynomial of degree $j_{\max} = n - l - 1$ in ρ , whose coefficients are determined by the recursion formula

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j.$$

The **ground state** is the case where $n = 1$, then

$$E_1 = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6\text{eV}.$$

This shows that the **binding energy** of hydrogen is 13.6eV. And $l = 0, m = 0$, so

$$\psi_{100}(r, \theta, \phi) = R_{10}(r)Y_0^0(\theta, \phi).$$

The recursion formula truncates after the first term ($j = 0$ yields $c_1 = 0$), so $v(\rho)$ is a constant (c_0) and then

$$R_{10}(r) = \frac{c_0}{a} e^{-r/a}.$$

Normalizing it, we have

$$\int_0^\infty |R_{10}|^2 r^2 dr = \frac{|c_0|^2}{a^2} \int_0^\infty e^{-2r/a} r^2 dr = |c_0|^2 \frac{a}{4} = 1,$$

so $c_0 = 2/\sqrt{a}$. Meanwhile $Y_0^0 = 1/\sqrt{4\pi}$, and hence the ground state of hydrogen is

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^2}} e^{-r/a}.$$

If $n = 2$, the energy is

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

which is the first excited state. If $l = 0$, the recursion relation gives

$$c_1 = -c_0, \quad c_2 = 0,$$

so $v(\rho) = c_0(1 - \rho)$ and therefore

$$R_{20}(r) = \frac{c_0}{2a} \left(1 - \frac{r}{2a} \right) e^{-r/2a}.$$

If $l = 1$, the recursion formula terminates the series after a single term; $v(\rho)$ is a constant, and

$$R_{21} = \frac{c_0}{4a^2} r e^{-r/2a}.$$

For arbitrary n , the possible values of l are

$$l = 0, 1, 2, \dots, n-1,$$

and for each l there are $(2l+1)$ possible values of m , so the total degeneracy of the energy level E_n is

$$d(n) = \sum_{l=1}^{n-1} (2l+1) = n^2.$$

The polynomial $v(\rho)$ can be written as

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho),$$

where

$$L_{q-p}^p(x) \equiv (-1)^p \left(\frac{d}{dx} \right)^p L_q(x)$$

is an **associated Laguerre polynomial** and

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

is the q th **Laguerre polynomial**. The normalized wave functions are

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na} \right)^l [L_{n-l-1}^{2l+1}(2r/na)] Y_l^m(\theta, \phi).$$

4.2.2 The Spectrum of Hydrogen

For a hydrogen atom, the electron may undergo a **transition** to other stationary state, either by absorbing energy and moving up to a higher-energy state, or by giving off energy and moving down. The result is that a container of hydrogen give off photons, whose energy corresponds to the difference in energy between the initial and final states:

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

By the **Planck formula**, the energy of a photon is

$$E_\gamma = h\nu = h \frac{c}{\lambda}.$$

Thus we have

$$\frac{1}{\lambda} = R \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right),$$

where

$$R \equiv \frac{m}{4\pi\hbar^2} \left(\frac{e^2}{4\pi\epsilon + 0} \right)^2 = 1.097 \times 10^7 \text{m}^{-1}$$

is known as the **Rydberg constant** and the equation is the **Rydberg formula** for the spectrum of hydrogen.

4.3 Angular Momentum

Classically, the angular momentum of a particle is given by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p},$$

which equals to

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x.$$

The corresponding operators are obtained by $p_x \rightarrow -i\hbar\partial/\partial x$, $p_y \rightarrow -i\hbar\partial/\partial y$, $p_z \rightarrow -i\hbar\partial/\partial z$.

4.3.1 Eigenvalues

The operators L_x and L_y do not commute:

$$\begin{aligned} [L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] \\ &= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z]. \end{aligned}$$

The only operators that fail to commute here are x with p_x , y with p_y , and z with p_z . So the middle two terms drop out and we have

$$[L_x, L_y] = yp_x[p_z, z] + xp_y[z, p_z] = i\hbar(xp_y - yp_x) = i\hbar L_z.$$

This shows that

$$\boxed{[L_x, L_y] = i\hbar L_z; \quad [L_y, L_z] = i\hbar L_x; \quad [L_z, L_x] = i\hbar L_y.}$$

By the generalized uncertainty principle,

$$\sigma_{L_x}^2 \sigma_{L_y}^2 \geq \left(\frac{1}{2i} \langle i\hbar L_z \rangle \right)^2 = \frac{\hbar^2}{4} \langle L_z \rangle^2,$$

or

$$\sigma_{L_x} \sigma_{L_y} \geq \frac{\hbar}{2} |\langle L_z \rangle|.$$

The square of the total angular momentum

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2,$$

does commute with L_x :

$$[L^2, L_x] = 0.$$

It follows that

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

or

$$[L^2, \mathbf{L}] = 0.$$

Thus L^2 is compatible with each component of \mathbf{L} , and we can hope to find simultaneous eigenstates of L^2 and L_z :

$$L^2 f = \lambda f \quad \text{and} \quad L_z f = \mu f.$$

Let

$$L_{\pm} \equiv L_x \pm iL_y.$$

The commutator with L_z is

$$[L_z, L_{\pm}] = [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm i(-i\hbar L_x) = \pm\hbar(L_x \pm iL_y),$$

so

$$[L_z, L_{\pm}] = \pm\hbar L_{\pm}.$$

And also we have

$$[L^2, L_{\pm}] = 0.$$

We claim that if f is an eigenfunction of L^2 and L_z , so also is $L_{\pm}f$:

$$L^2(L_{\pm}f) = L_{\pm}(L^2f) = L_{\pm}(\lambda f) = \lambda(L_{\pm}f),$$

so $L_{\pm}f$ is an eigenfunction of L^2 , with the same eigenvalue λ . And since

$$\begin{aligned} L_z(L_{\pm}f) &= (L_z L_{\pm} - L_{\pm} L_z)f + L_{\pm} L_z f = \pm\hbar L_{\pm}f + L_{\pm}(\mu f) \\ &= (\mu \pm \hbar)(L_{\pm}f), \end{aligned}$$

so $L_{\pm}f$ is an eigenfunction of L_z with the new eigenvalue $\mu \pm \hbar$. We call L_+ the raising operator and L_- the lowering operator. Eventually we will reach a state for which the z -component exceeds the total. So there must be a top rung f_t for the "ladder":

$$L_+ f_t = 0.$$

Let $\hbar l$ be the eigenvalue of L_z at this top rung:

$$L_z f_t = \hbar l f_t; \quad L^2 f_t = \lambda f_t.$$

Now

$$\begin{aligned} L_{\pm} L_{\mp} &= (L_x \pm iL_y)(L_x \mp iL_y) = L_x^2 + L_y^2 \mp i(L_x L_y - L_y L_x) \\ &= L^2 - L_z^2 \mp i(i\hbar L_z), \end{aligned}$$

or

$$L^2 = L_{\pm} L_{\mp} + L_z^2 \mp \hbar L_z.$$

It follows that

$$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z) f_t = (0 + \hbar^2 l^2 + \hbar^2 l) f_t = \hbar^2 l(l+1) f_t,$$

and hence

$$\lambda = \hbar^2 l(l+1).$$

This tells us the eigenvalue of L^2 in terms of the maximum eigenvalue of L_z .

There's also a bottom rung, f_b , such that

$$L_- f_b = 0.$$

Let $\hbar\bar{l}$ be the eigenvalue of L_z at this bottom rung:

$$L_z f_b = \hbar\bar{l} f_b; \quad L^2 f_b = \lambda f_b.$$

Then we have

$$L^2 f_b = (L_+ L_- + L_z^2 - \hbar L_z) f_b = (0 + \hbar^2 \bar{l}^2 - \hbar^2 \bar{l}) f_b = \hbar^2 \bar{l}(\bar{l} - 1) f_b,$$

and therefore

$$\lambda = \hbar^2 \bar{l}(\bar{l} - 1).$$

We see that $l(l+1) = \bar{l}(\bar{l}-1)$. This means that $\bar{l} = -l$. The eigenvalues of L_z are $m\hbar$, where m goes from $-l$ to $+l$ in N integers steps. In particular, it follows that $l = -l + N$, and hence $l = N/2$. So l must be an integer or a half-integer. The eigenfunctions are characterized by the number l and m :

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m; \quad L_z f_l^m = \hbar m f_l^m,$$

where

$$l = 0, 1/2, 1, 3/2, \dots; \quad m = -l, -l+1, \dots, l-1, l.$$

For a given value of l , there are $2l+1$ different values of m .

4.3.2 Eigenfunctions

Rewrite L_x , L_y and L_z in spherical coordinates. Now $\mathbf{L} = (\hbar/\mathbf{r})(\mathbf{r} \times \nabla)$, and the gradient is

$$\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi};$$

also, $\mathbf{r} = r\hat{r}$, thus

$$\mathbf{L} = \frac{\hbar}{i} \left[r(\hat{r} \times \hat{r} \frac{\partial}{\partial r} + (\hat{r} \times \hat{\theta}) \frac{\partial}{\partial \theta} + (\hat{r} \times \hat{\phi}) \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right].$$

Also we have $(\hat{r} \times \hat{r}) = 0$, $(\hat{r} \times \hat{\theta}) = \hat{\phi}$, and $(\hat{r} \times \hat{\phi}) = -\hat{\theta}$, then

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

The unit vector $\hat{\theta}$ and $\hat{\phi}$ can be written as Cartesian components:

$$\begin{aligned} \hat{\theta} &= (\cos \theta \cos \phi) \hat{i} + (\cos \theta \sin \phi) \hat{j} - (\sin \theta) \hat{k}; \\ \hat{\phi} &= -(\sin \phi) \hat{i} + (\cos \phi) \hat{j}. \end{aligned}$$

Thus

$$\mathbf{L} = \frac{\hbar}{i} \left[(-\sin \phi \hat{i} + \cos \phi \hat{j}) \frac{\partial}{\partial \theta} - (\cos \theta \cos \phi \hat{i} + \cos \theta \sin \phi \hat{j} - \sin \theta \hat{k}) \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right].$$

Evidently we have

$$L_x = \frac{\hbar}{i} \left(-\sin \phi \frac{\partial}{\partial \theta} - \cos \phi \cot \theta \frac{\partial}{\partial \phi} \right),$$

$$L_y = \frac{\hbar}{i} \left(+\cos \phi \frac{\partial}{\partial \theta} - \sin \phi \cot \theta \frac{\partial}{\partial \phi} \right),$$

and

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}.$$

We introduce the raising and lowering operators:

$$L_{\pm} = L_x \pm iL_y = \frac{\hbar}{i} \left[(-\sin \phi \pm i \cos \phi) \frac{\partial}{\partial \theta} - (\cos \phi \pm i \sin \phi) \cot \theta \frac{\partial}{\partial \phi} \right].$$

Since $\cos \phi \pm i \sin \phi = e^{\pm i\phi}$, thus

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

In particular,

$$L_+ L_- = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \phi^2} + i \frac{\partial}{\partial \phi} \right),$$

and hence

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

Now we need to determine $f_l^m(\theta, \phi)$, which is an eigenfunction of L^2 , with eigenvalue $\hbar^2 l(l+1)$:

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

This is just the angular equation. f_l^m is also an eigenfunction of L_z , with eigenvalue $m\hbar$:

$$L_z f_l^m = \frac{\hbar}{i} \frac{\partial}{\partial \phi} f_l^m = \hbar m f_l^m.$$

This is just the azimuthal equation. We have already solved this systems and the result is spherical harmonic $Y_l^m(\theta, \phi)$. We conclude that spherical harmonics

are eigenfunctions of L^2 and L_z . When we are solving the Schrödinger equation by separation of variables, we are inadvertently constructing simultaneous eigenfunctions of the three commuting operators H , L^2 and L_z :

$$H\psi = E\psi, \quad L^2\psi = \hbar^2 l(l+1)\psi, \quad L_z\psi = \hbar m\psi.$$

Rewrite the Schrödinger equation more compactly:

$$\frac{1}{2mr^2} \left[-\hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + L^2 \right] \psi + V\psi = E\psi.$$

4.4 Spin

In classical mechanics, a rigid object admits two kinds of angular momentum: **orbital** ($\mathbf{L} = \mathbf{r} \times \mathbf{p}$), associated with the motion of the center of mass, and **spin** ($\mathbf{S} = I\boldsymbol{\omega}$), associated with the motion about the center of mass. In quantum mechanics, the elementary particles carry **intrinsic** angular momentum (\mathbf{S}) in addition to their extrinsic angular momentum (\mathbf{L}).

The theory of spin begins with the fundamental commutation relations:

$$[S_x, S_y] = i\hbar S_z; \quad [S_y, S_z] = i\hbar S_x; \quad [S_z, S_x] = i\hbar S_y.$$

The eigenvectors of S^2 and S_z satisfy:

$$S^2|s\,m\rangle = \hbar^2 s(s+1)|s\,m\rangle; \quad S_z|s\,m\rangle = \hbar m|s\,m\rangle;$$

and

$$S_{\pm}|s\,m\rangle = \hbar\sqrt{s(s+1) - m(m\pm 1)}|s\,(m\pm 1)\rangle,$$

where

$$S_{\pm} \equiv S_x \pm iS_y,$$

and

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots; \quad m = -s, -s+1, \dots, s-1, s.$$

It happens that every elementary particle has a specific and immutable value of s , which we call **the spin** of that particular series: pi mesons have spin 0; electrons have spin 1/2; photons have spin 1; deltas have spin 3/2; gravitons have spin 2; and so on. The orbital angular momentum number l can take on any integer value you please, and will change from one to another with the system is perturbed. But s is fixed for any given particle.

4.4.1 Spin 1/2

The most important case is $s = 1/2$, since this is the spin of the particles that make up ordinary matter (protons, neutrons, and electrons), as well as all quarks and all leptons. There are two eigenstates: $|\frac{1}{2}\,\frac{1}{2}\rangle$, which we call **spin up** (\uparrow) and $|\frac{1}{2}\,(-\frac{1}{2})\rangle$, which we call **spin down** (\downarrow). Using these as basis vectors, the

general state of a spin 1/2 particle can be expressed as a two-element column matrix (**spinor**):

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-,$$

with

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

representing spin up and spin down respectively.

The spin operators become 2×2 matrix:

$$S^2\chi_+ = \frac{3}{4}\hbar^2\chi_+ \quad S^2\chi_- = \frac{3}{4}\hbar^2\chi_-.$$

We write

$$S^2 = \begin{pmatrix} c & d \\ e & f \end{pmatrix},$$

and hence

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

This gives that

$$S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

Similarly, since

$$S_z\chi_+ = \frac{\hbar}{2}\chi_+, \quad S_z\chi_- = -\frac{\hbar}{2}\chi_-,$$

then

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Meanwhile, since

$$S_+\chi_- = \hbar\chi_+, \quad S_-\chi_+ = \hbar\chi_-, \quad S_+\chi_+ = S_-\chi_- = 0,$$

then

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

Now $S_{\pm} = S_x \pm iS_y$, so $S_x = (1/2)(S_+ + S_-)$ and $S_y = (1/2i)(S_+ - S_-)$ and hence

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

Write $S = (\hbar/2)\sigma$, where

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

These are called **Pauli spin matrices**. Notice that S_x , S_y , S_z and S^2 are all *hermitian* and they represent observables. However, S_- and S_+ are not hermitian and they are not observables. The eigenspinors of S_z are

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

If we measure S_z on a particle in the general state χ , we can get $+\hbar/2$ with probability $|a|^2$, or $-\hbar/2$ with probability $|b|^2$. Since the spinor must be normalized, then

$$|a|^2 + |b|^2 = 1.$$

If we measure S_x , we can solve that the eigenvalues of S_x are also $+\hbar/2$ and $-\hbar/2$. And the normalized eigenspinors are

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

The general spinor χ can be expressed as a linear combination of them:

$$\chi = \left(\frac{a+b}{\sqrt{2}} \right)^2 \chi_+^{(x)} + \left(\frac{a-b}{\sqrt{2}} \right)^2 \chi_-^{(x)}.$$

4.4.2 Electron in a Magnetic Field

A spinning charged particle constitutes a magnetic dipole. Its **magnetic dipole moment** μ is proportional to its spin angular momentum \mathbf{S} :

$$\mu = \gamma \mathbf{S},$$

where γ is called the **gyromagnetic ratio**. When a magnetic dipole is placed in a magnetic field \mathbf{B} , it experience a torque, $\mu \times \mathbf{B}$, which tends to line it up parallel to the field. The energy associated with the torque is

$$H = -\mu \cdot \mathbf{B},$$

so the Hamiltonian of a spinning charged particle at rest in a magnetic field is

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

4.4.3 Addition of Angular Momenta

Suppose we now have two spin 1/2 particles. Each can have spin up or spin down, so there are four possibilities in all:

$$\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow.$$

We want to find out the total angular momentum of the system. Let

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

Then

$$\begin{aligned} S_z \chi_1 \chi_2 &= (S_z^{(1)} + S_z^{(2)}) \chi_1 \chi_2 = (S_z^{(1)} \chi_1) \chi_2 + \chi_1 (S_z^{(2)} \chi_2) \\ &= (\hbar m_1 \chi_1) \chi_2 + \chi_1 (\hbar m_2 \chi_2) = \hbar(m_1 + m_2) \chi_1 \chi_2. \end{aligned}$$

So the quantum number m for the composite system is just $m_1 + m_2$:

$$\begin{aligned} \uparrow\uparrow: m &= 1; \\ \uparrow\downarrow: m &= 0; \\ \downarrow\uparrow: m &= 0; \\ \downarrow\downarrow: m &= -1. \end{aligned}$$

Now we find that $s = 1$. But we also find that there is an extra state with $m = 0$. To solve this problem, we apply the lowering operator $S_- = S_-^{(1)} + S_-^{(2)}$ to the state $\uparrow\uparrow$:

$$S_-(\uparrow\uparrow) = \hbar(\uparrow\downarrow + \downarrow\uparrow).$$

The three states with $s = 1$ are

$$\left\{ \begin{array}{l} |1\ 1\rangle = \uparrow\uparrow \\ |1\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1\ -1\rangle = \downarrow\downarrow \end{array} \right\} \quad s = 1 \text{ (triplet).}$$

This is called the **triplet** combination. Meanwhile, the orthogonal state with $m = 0$ carries $s = 0$:

$$\left\{ |0\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \right\} \quad s = 0 \text{ (singlet).}$$

We claim that the combination of two spin $1/2$ particles can carry a total spin of 1 or 0, depending on whether they occupy the triplet or the singlet configuration. It can be proved that

$$S^2|1\ 0\rangle = 2\hbar^2|1\ 0\rangle, \quad S^2|0\ 0\rangle = 0.$$

A more complex problem is that: if we combine spin s_1 with spin s_2 , what total spins s can we get? The answer is that we can get every spin from $(s_1 + s_2)$ down to $|s_2 - s_1|$ in integer steps:

$$s = (s_1 + s_2), (s_1 + s_2 - 1), \dots, |s_1 - s_2|.$$

The combined state $|s\ m\rangle$ with total spin s and z -component m will be some linear combination of the composite states $|s_1\ m_1\rangle|s_2\ m_2\rangle$:

$$|s\ m\rangle = \sum_{m_1+m_2=m} C_{m_1 m_2 m}^{s_1 s_2 s} |s_1\ m_1\rangle |s_2\ m_2\rangle.$$

The constants $C_{m_1 m_2 m}^{s_1 s_2 s}$ are called **Clebsch-Gordan coefficients**.

Chapter 5

Identical Particles

5.1 Two-Particles Systems

For a *single* particle, $\Psi(\mathbf{r}, t)$ is a function of spatial coordinates \mathbf{r} and the time t . The state of a *two-particle* system is a function of the coordinates of particle one (\mathbf{r}_1), the coordinates of particle two (\mathbf{r}_2) and the time:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t).$$

The time evolution is determined by the Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi,$$

where H is the Hamiltonian for the whole system:

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

And $|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2$ is the probability of finding particle 1 in the volume $d^3\mathbf{r}_1$ and particle 2 in the volume $d^3\mathbf{r}_2$. Thus Ψ must be normalized:

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

For time-independent potentials, we can obtain a complete set of solutions by separations of variables:

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

where the spatial wave function satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V\psi = E\psi,$$

and E is the total energy of the system.

5.1.1 Bosons and Fermions

Suppose particle 1 is in the state $\psi_a(\mathbf{r})$ and particle 2 is in the state $\psi_b(\mathbf{r})$ (we ignore spin for this moment). In this case $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is a simple product:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r})\psi_b(\mathbf{r}).$$

This assumes that we can tell the particles apart. However, in quantum mechanics, all electrons are *utterly identical*.

Quantum mechanics neatly accommodates the existence of particles that are *indistinguishable in principle*: We construct a wave function that is non-committal as to which particle is in which state. There are two ways to do it:

$$\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r})\psi_b(\mathbf{r}) \pm \psi_b(\mathbf{r})\psi_a(\mathbf{r})].$$

The theory admits two kinds of identical particles: **bosons**, for which we use the plus sign, and **fermions**, for which we use the minus sign. All particles with *integer* spin are bosons and all particles with *half* integer spin are fermions. This connects **spin and statistics**.

It follows that *two identical cannot occupy the same state*. If $\psi_a = \psi_b$, then

$$\psi_{-}(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r})\psi_a(\mathbf{r}) - \psi_a(\mathbf{r})\psi_a(\mathbf{r})] = 0.$$

This is the **Pauli exclusion principle**.

Define the **exchange operator** P , which interchanges the two particles:

$$Pf(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1).$$

Clearly we have $P^2 = 1$, and the eigenvalues of P are ± 1 . Thus if two particles are identical, the Hamiltonian must treat them the same: $m_1 = m_2$ and $V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_2, \mathbf{r}_1)$. It follows that P and H are compatible observables:

$$[P, H] = 0,$$

and hence we can find a complete set of functions that are simultaneous eigenstates of both. This means that we can find solutions to the Schrödinger equation that are either symmetric (eigenvalue +1) or antisymmetric (eigenvalue -1) under exchange:

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

This is called the **symmetrization requirement**.

5.1.2 Exchange Forces

Suppose one particle is in state $\psi_a(x)$ and the other is in state $\psi_b(x)$ and these two states are orthogonal and normalized. If the two particles are distinguishable, and number 1 is the one in state ψ_a , then the combined wave function is

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2).$$

If they are bosons, the composite wave function is

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)];$$

and if they are fermions, it is

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)].$$

We want to calculate the expectation value of the square of the separation distance between the two particles:

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle.$$

Case 1: Distinguishable particles. We have

$$\langle x_1^2 \rangle = \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_a,$$

(the expectation value of x^2 in the one-particle state ψ_a)

$$\langle x_2^2 \rangle = \int |\psi_a(x_1)|^2 dx_1 \int x_2^2 |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_b,$$

and

$$\langle x_1 x_2 \rangle = \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 = \langle x \rangle_a \langle x \rangle_b.$$

Thus

$$\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b.$$

The answer would be the same if particle 1 is in state ψ_b and particle 2 is in state ψ_a .

Case 2: Identical particles. We have

$$\begin{aligned} \langle x_1^2 \rangle &= \frac{1}{2} \left[\int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 \right. \\ &\quad + \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \\ &\quad \pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int \psi_b(x_2)^* \psi_a(x_2) dx_2 \\ &\quad \left. \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0] = \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b). \end{aligned}$$

Similarly,

$$\langle x_1^2 \rangle_d = \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b),$$

since we can't tell the two particles apart. Also

$$\begin{aligned}
\langle x_1 x_2 \rangle &= \frac{1}{2} \left[\int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 \right. \\
&\quad + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \\
&\quad \pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) dx_2 \\
&\quad \left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\
&= \frac{1}{2} [\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a + \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}] \\
&= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2,
\end{aligned}$$

where

$$\langle x \rangle_{ab}^2 \equiv \int x \psi_a(x)^* \psi_b(x) dx.$$

Then we have

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2|\langle x \rangle_{ab}|^2.$$

Comparing the two cases, we see that the difference resides in the final term:

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2|\langle x \rangle_{ab}|^2.$$

Identical bosons tend to be closer together and identical fermions farther apart, than distinguishable particles in the same two states. Notice that $\langle x \rangle_{ab}$ vanishes unless the two wave function actually *overlap*. As a particle matter, it's okay to pretend that electrons with non-overlapping wave functions are distinguishable.

When there is some overlap of the wave functions, the system behaves as though there were a "force attraction" between identical bosons and a "force of repulsion" between identical fermions. We call it an **exchanging force**, which is a geometrical consequence of the symmetrization requirement.

5.2 Atoms

A neutral atom of atomic number Z consists of a heavy nucleus with electric charge Ze , surrounded by Z electrons, each with mass m and charge $-e$. The Hamiltonian for this system is

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

The problem is to solve the Schrödinger equation

$$H\psi = E\psi$$

for the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$. Since electrons are identical fermions, not all solutions are acceptable and only those for which the complete state

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)\chi(\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_Z)$$

is antisymmetric with respect to interchange of any two electrons. That is, no two electrons can occupy the same state. However, the Schrödinger equation cannot be solved exactly. In practice, approximation methods are required.

5.2.1 Helium

For helium, $Z = 2$. Then the Hamiltonian is written as

$$H = \left[-\frac{\hbar^2}{2m} \nabla_1^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{2e^2}{r_1} \right] + \left[-\frac{\hbar^2}{2m} \nabla_2^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{2e^2}{r_2} \right] + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}.$$

This consists of two *hydrogenic* Hamiltonians (with nuclear charge $2e$). If we ignore the last term, the Schrödinger equation separates and the solution can be written as products of hydrogen wave functions:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2),$$

only with half the Bohr radius and four times the Bohr energies. And the total energy would be

$$E = 4(E_n + E_{n'}),$$

where $E_n = -13.6/n^2 \text{ eV}$. In particular, the ground state would be

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a},$$

and its energy is

$$E_0 = 8(-13.6 \text{ eV}) = -109 \text{ eV}.$$

Since ψ_0 is a symmetric function, the spin state has to be antisymmetric, so the ground state of helium should be a singlet configuration. The actual ground state of helium is indeed a singlet, but the experimentally determined energy is -78.975 eV .

The excited states of helium consist of one electron in the hydrogenic ground state and the other in an excited state:

$$\psi_{nlm}\psi_{100}.$$

We can construct both symmetric and antisymmetric combinations; the former go with the antisymmetric configuration (the singlet), and they are called **parahelium**; while the latter require a symmetric spin configuration (the triplet), and they are known as **orthohelium**. The ground state is parahelium and the excited states come in both forms.

5.2.2 The Periodic Table

5.3 Solid

In the solid state, a few of the loosely bound outermost **valence** electrons in each atom become detached, and roam around throughout the material, no longer subject only to the Coulomb field of a specific nucleus, but rather to the combined potential of the entire crystal lattice.

5.3.1 The Free Electron Gas

Now suppose we have a rectangular solid with dimensions l_x, l_y, l_z and imagine that an electron inside experiences no forces at all, except at the impenetrable walls:

$$V(x, y, z) \begin{cases} 0, & \text{if } 0 < x < l_x, 0 < y < l_y, 0 < z < l_z; \\ \infty, & \text{otherwise.} \end{cases}$$

The Schrödinger equation

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

separates in Cartesian coordinates: $\psi(x, y, z) = X(x)Y(y)Z(z)$, with

$$-\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} = E_x X; \quad -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} = E_y Y; \quad -\frac{\hbar^2}{2m} \frac{d^2 Z}{dz^2} = E_z Z,$$

and $E = E_x + E_y + E_z$. We let

$$k_x \equiv \frac{\sqrt{2mE_x}}{\hbar}; \quad k_y \equiv \frac{\sqrt{2mE_y}}{\hbar}; \quad k_z \equiv \frac{\sqrt{2mE_z}}{\hbar}.$$

Then we can obtain the general solutions

$$\begin{aligned} X(x) &= A_x \sin(k_x x) + B_x \cos(k_x x), \\ Y(y) &= A_y \sin(k_y y) + B_y \cos(k_y y), \\ Z(z) &= A_z \sin(k_z z) + B_z \cos(k_z z). \end{aligned}$$

The boundary conditions require that $X(0) = Y(0) = Z(0) = 0$, thus $B_x = B_y = B_z = 0$; and also we have $X(l_x) = Y(l_y) = Z(l_z) = 0$, then

$$k_x l_x = n_x \pi, \quad k_y l_y = n_y \pi, \quad k_z l_z = n_z \pi,$$

where each n is a positive integer. Then the normalized wave functions are

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right),$$

and the allowed energies are

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) = \frac{\hbar^2 k^2}{2m},$$

where k is the magnitude of the **wave vector**, $\mathbf{k} \equiv (k_x, k_y, k_z)$.

Now we imagine a three-dimensional space with axes k_x , k_y and k_z , and planes drawn in at $k_x = (\pi/l_x), (2\pi/l_x), \dots$, at $k_y = (\pi/l_y), (2\pi/l_y), \dots$, and at $k_z = (\pi/l_z), (2\pi/l_z), \dots$, each intersection point represents a distinct one-particle stationary state. Each block in this grid, and hence each state, occupies a volume

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$$

of " k -space, where $V \equiv l_x l_y l_z$ is the volume of the object itself. Suppose our sample contains N atoms, and each atom contributes q free electrons. Electrons are identical fermions, so only two of them can occupy any given state. They will fill up one octant of a *sphere* in k -space whose radius k_F is determined by the fact that each pair of electrons requires a volume π^3/V :

$$\frac{1}{8} \left(\frac{4\pi}{3} k_F^3 \right) = \frac{Nq}{2} \left(\frac{\pi^3}{V} \right).$$

Thus

$$k_F = (3\rho\pi^2)^{1/3},$$

where

$$\rho \equiv \frac{Nq}{V}$$

is the free electron density.

The boundary separating occupied and unoccupied states in k -space is called the **Fermi surface**. The corresponding energy is called the **Fermi energy** E_F . For a free electron gas

$$E_F = \frac{\hbar^2}{2m} (3\rho\pi^2)^{2/3}.$$

The total energy of the electron gas can be calculated as follows: a shell of thickness dk contains a volume

$$\frac{1}{8} (4\pi k^2) dk,$$

so the number of electron states in the shell is

$$\frac{2[(1/2)\pi k^2 dk]}{\pi^3/V} = \frac{V}{\pi^2} k^2 dk.$$

Each of these states carries an energy $\hbar^2 k^2/2m$, so the energy of the shell is

$$dE = \frac{\hbar^2 k^2}{2m} \frac{V}{\pi^2} k^2 dk,$$

and then the total energy is

$$E_{\text{tot}} = \frac{\hbar^2 V}{2\pi^2 m} \int_0^{k_F} k^4 dk = \frac{\hbar^2 k_F^5 V}{10\pi^2 m} = \frac{\hbar^2 (3\pi^2 Nq)^{5/3}}{10\pi^2 m} V^{-2/3}.$$

In particular, the quantum mechanical energy exerts a pressure on the walls. If the box expands by an amount dV , the total energy decreases:

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

and this shows up as work done on the outside ($dW = PdV$) by the quantum pressure P .

$$P = \frac{2}{3} \frac{E_{\text{tot}}}{V} = \frac{2}{3} \frac{\hbar^2 k_F^5}{10\pi^2 m} = \frac{(3\pi^2)^{2/3} \hbar^2}{5m} \rho^{5/3}.$$

This is called **degeneracy pressure**.

5.3.2 Band Structure

Now suppose we have a periodic potential in one-dimension:

$$V(x+a) = V(x).$$

Bloch's theorem states that for such a potential the solutions to the Schrödinger equation

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

can be taken to satisfy the condition

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

for some constant K , which is independent of x . We wrap the x -axis around in a circle and connect it onto its tail, after a large number $N \approx 10^{23}$ of periods; formally we impose the boundary condition

$$\psi(x+Na) = \psi(x).$$

It follows that

$$e^{iNka}\psi(x) = \psi(x),$$

so $e^{iNKa} = 1$, which is $NKa = 2\pi n$, and then

$$K = \frac{2\pi n}{Na}.$$

The virtue of Bloch's theorem is that we only need to solve the Schrödinger equation within a single cell; recursive application of the Bloch's theorem generates the solution everywhere else.

Now suppose the potential consists of a long string of delta-function spikes (the Dirac comb):

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

In the region $0 < x < a$ the potential is zero, so

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

or

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

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar}.$$

Then the general solution is

$$\psi(x) = A \sin(kx) + B \cos(kx), \quad (0 < x < a).$$

According to the Bloch's theorem, we have

$$\psi(x) = e^{iKa} [A \sin(kx) + B \cos(kx)], \quad (-a < x < 0).$$

At $x = 0$, ψ must be continuous, thus

$$B = e^{-iKa} [A \sin(ka) + B \cos(ka)];$$

its derivative suffers a discontinuity proportional to the strength of the delta function:

$$kA - e^{-iKa} k [A \cos(ka) - B \sin(ka)] = \frac{2m\alpha}{\hbar^2} B.$$

Solving those two equations we have

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

This determines the possible values of k and the allowed energies. Let

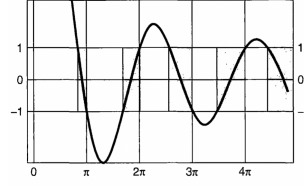
$$z \equiv ka, \quad \beta \equiv \frac{m\alpha a}{\hbar^2},$$

so the RHS can be written as

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

We plot $f(z)$ for the case $\beta = 10$. Notice that the range of $f(z)$ is $(-1, +1)$ due to the range of $\cos(Ka)$. These **gaps** represent *forbidden energies*, and they are separated by **bands** of *allowed energies*. $\cos(Ka) = \cos(2\pi n/N)$, and N is a huge number. Imagine we draw N horizontal lines on the figure, and the intersection of each of these lines with $f(z)$ yields an allowed energies. Evidently there are N states in each band.

In practice we will have Nq electrons, where q is the number of free electrons per atom. Because of the Pauli exclusion principle, only two electrons can

Figure 5.1: Graph of $f(z)$

occupy a given state. So if $q = 1$, they will half fill the first band, if $q = 2$ they will completely fill the first band, and if $q = 3$ they will half fill the second band, and so on.

If a band is entirely filled, it takes a relatively large energy to excite an electron, since it has to jump across the forbidden zone. Such material are called **insulators**. If a band is partly filled, it take very little energy to excite an electron, and such material are called **conductors**. If we **dope** an insulator with a few atoms of larger or smaller q , this puts some extra electrons into the next higher band or creates some holes in the previously filled one, allowing for weak electric currents to flow, such material are called **semiconductors**.

5.4 Quantum Statistical Mechanics

The **fundamental assumption of statistical mechanics** is that in **thermal equilibrium** every distinct state with the same total energy E is equally probable. Random thermal motions constantly shift energy from one particle to another, and from one form to another, but the total is fixed by conservation of energy. The assumption is that this continual redistribution of energy does not favor any particular state. The **temperature** T is a measure of the total energy of a system in thermal equilibrium. The only new twist introduced to quantum mechanics has to do with *how we count the distinct states*.

5.4.1 An Example

5.4.2 The General Case

Consider an arbitrary potential, for which the one-particle energies are E_1, E_2, \dots , with degeneracies d_1, d_2, \dots (i.e. there are d_n distinct one-particle states with energy E_n). Suppose we put N particles with the same mass into the potential. We are interested in the configuration (N_1, N_2, N_3, \dots) for which there are N_1 particles with energy E_1 , N_2 particles with E_2 , and so on. We are wondering how many different ways can this be achieved.

First we assume that the particles are *distinguishable*. The number of ways to put N_1 particles, selected from a total population of N , into a bin containing d_1 distinct options is

$$C_N^{N_1} d_1^{N_1},$$

where $C_N^{N_1}$ is the **binomial coefficient**. Now for bin 2, there are only $(N - N_1)$ particles left, so the number would be

$$C_{N-N_1}^{N_2} d_2^{N_2}.$$

Then the total number should be

$$Q(N_1, N_2, N_3, \dots) = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}.$$

For *identical fermions*, it doesn't matter which particle are in which states. Only one particle can occupy a given state. There are $C_{d_n}^{N_n}$ ways to choose the N_n occupied states in the n th bin, so

$$Q(N_1, N_2, N_3, \dots) = \prod_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n - N_n)!}.$$

Then we consider the case of *identical bosons*. Then for the n th bin, we need to assign N_n identical particles to d_n different states. Then we have

$$Q(N_1, N_2, N_3, \dots) = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}.$$

5.4.3 The Most Probable Configuration

The *most probable configuration* is the one that can be achieved in the largest number of different ways - that is $Q(N_1, N_2, N_3, \dots)$ is a maximum, subject to the constraints

$$\sum_{n=1}^{\infty} N_n = N,$$

and

$$\sum_{n=1}^{\infty} N_n E_n = E.$$

The problem can be solved by the **Lagrange multipliers**. Let

$$Q \equiv \ln(Q) + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right],$$

where α and β are Lagrange multipliers.

If the particles are *distinguishable*, then we have

$$G = \ln(N!) + \sum_{n=1}^{\infty} [N_n \ln(d_n) - \ln(N_n!)] + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right].$$

Introduce the **Stirling's approximation**:

$$\ln(z!) \approx z \ln(z) - z, \quad z \gg 1.$$

Then we may write

$$G \approx \sum_{n=1}^{\infty} [N_n \ln(d_n) - N_n \ln(N_n) + N_n - \alpha N_n - \beta E_n N_n] + \ln(N!) + \alpha N + \beta E.$$

It follows that

$$\frac{\partial G}{\partial N_n} = \ln(d_n) - \ln(N_n) - \alpha - \beta E_n = 0.$$

We conclude that the most probable occupation numbers for distinguishable particles are

$$N_n = d_n e^{-(\alpha + \beta E_n)}.$$

If the particles are *identical fermions*, then we have

$$\begin{aligned} G = & \sum_{n=1}^{\infty} \{ \ln(d_n!) - \ln(N_n!) - \ln[(d_n - N_n)!] \} \\ & + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]. \end{aligned}$$

Applying the Stirling's approximation again, we have

$$\frac{\partial G}{\partial N_n} = -\ln(N_n) + \ln(d_n - N_n) - \alpha - \beta E_n = 0.$$

Thus the most probable occupation numbers for identical fermions are

$$N_n = \frac{d_n}{e^{(\alpha + \beta E_n)} + 1}.$$

If the particles are *identical bosons*, then

$$\begin{aligned} G = & \sum_{n=1}^{\infty} \{ \ln[(N_n + d_n - 1)!] - \ln(N_n!) - \ln[(d_n - 1)!] \} \\ & + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]. \end{aligned}$$

Again we use the Stirling's approximation:

$$\frac{\partial G}{\partial N_n} = \ln(N_n + d_n - 1) - \ln(N_n) - \alpha - \beta E_n = 0.$$

Thus the most probable occupation numbers for identical bosons are

$$N_n = \frac{d_n - 1}{e^{(\alpha + \beta E_n)} - 1}.$$

5.4.4 Physical Significance of the Coefficients

For the free electron gas, the allowed energies are

$$E_k = \frac{\hbar^2}{2m} k^2,$$

where

$$\mathbf{k} = \left(\frac{\pi n_x}{l_x}, \frac{\pi n_y}{l_y}, \frac{\pi n_z}{l_z} \right).$$

The number of states in the shell is

$$d_k = \frac{1}{8} \frac{4\pi k^2 dk}{\pi^3/V} = \frac{V}{2\pi^2} k^2 dk.$$

For distinguish particle, the first constraint is

$$N = \frac{V}{2\pi^2} e^{-\alpha} \int_0^\infty e^{-\beta \hbar^2 k^2 / 2} / k^2 dk = V e^{-\alpha} \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2}.$$

Thus

$$e^{-\alpha} = \frac{N}{V} \left(\frac{2\pi\beta\hbar^2}{m} \right)^{3/2}.$$

And the second constraint is

$$E = \frac{V}{2\pi^2} e^{-\alpha} \frac{\hbar^2}{2m} \int_0^\infty e^{-\beta \hbar^2 k^2 / 2} / k^4 dk = \frac{3V}{2\beta} \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2}.$$

This gives that

$$E = \frac{3N}{2\beta}.$$

Also we have

$$\frac{E}{N} = \frac{3}{2} k_B T,$$

where k_B is the Boltzmann constant. Then

$$\beta = \frac{1}{k_B T}.$$

Replace α by the **chemical potential**

$$\mu(T) \equiv -\alpha k_B T.$$

Then the most probable number of particles in a particular state with energy ϵ :

$n(\epsilon) = \begin{cases} \frac{e^{-(\epsilon-\mu)/k_B T}}{e^{(\epsilon-\mu)/k_B T} + 1} \\ \frac{1}{e^{(\epsilon-\mu)/k_B T} - 1} \end{cases}$	MAXWELL-BOLTZMANN
	FERMI-DIRAC
	BOSE-EINSTEIN

The **Maxwell-Boltzmann distribution** is the classical result, for *distinguishable* particles; the **Fermi-Dirac distribution** applies to *identical fermions* and the **Bose-Einstein distribution** is for *identical bosons*.

5.4.5 The Blackbody Spectrum

We can conclude some properties of photons, which are identical bosons with spin 1:

1. The energy of a photon is related to its frequency by the Planck formula:
 $E = h\nu = \hbar\omega$.
2. The wave number k is related to the frequency by $k = 2\pi/\lambda = \omega/c$.
3. Only two spin states occur (the quantum number m can be +1 or -1).
4. The number of photons is not a conserved quantity; when the temperature rises, the number of photons per unit volume increases.

The most probable occupation number for photons is

$$N_\omega = \frac{d_k}{e^{\hbar\omega/k_B T} - 1}.$$

For free photons in a box of volume V , d_k is given by

$$d_k = \frac{V}{\pi^2 c^3} \omega^2 d\omega.$$

So the energy density $N_\omega \hbar\omega/V$ in the frequency range $d\omega$ is $\rho(\omega)d\omega$, where

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/k_B T} - 1)}.$$

This is Planck's formula for the **blackbody spectrum**, giving the energy per unit volume, per unit frequency, for an electromagnetic field in equilibrium at temperature T .

Part II

APPLICATION

Chapter 6

Time-Independent Perturbation Theory

6.1 Nondegenerate Perturbation Theory

6.1.1 General Formulation

Suppose we have solved the time-independent Schrödinger equation for some potential:

$$H^0 \psi_n^0 = E_n^0 \psi_n^0,$$

obtaining a complete set of orthonormal eigenfunctions ψ_n^0 :

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm},$$

and the corresponding eigenvalues E_n^0 . Now we *perturb* the potential slightly and we'd like to find the new eigenfunctions and eigenvalues:

$$H \psi_n = E_n \psi_n.$$

Perturbation theory is a systematic procedure for obtaining *approximate* solutions to the perturbed problem, by building on the known exact solutions to the *unperturbed* case.

Write the new Hamiltonian as the sum of two terms:

$$H = H^0 + \lambda H',$$

where H' is the perturbation. Then we write ψ_n and E_n as power series in λ :

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots ;$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots ,$$

where E_n^1 is the **first-order correction** to the n th eigenvalue, and ψ_n^1 is the first-order correction to the n th eigenfunctions; E_n^2 and ψ_n^2 are the **second-order corrections** and so on. We plug those equations into $H \psi_n = E_n \psi_n$, then

$$(H^0 + \lambda H')[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots)[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots],$$

or

$$\begin{aligned} H^0 \psi_n^0 + \lambda(H^0 \psi_n^1 + H' \psi_n^0) + \lambda^2(H^0 \psi_n^2 + H' \psi_n^1) + \dots \\ = E_n^0 \psi_n^0 + \lambda(E_n^0 \psi_n^1 + E_n^1 \psi_n^0) + \lambda^2(E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0) + \dots \end{aligned}$$

To lowest order (λ^0) this yields $H^0 \psi_n^0 = E_n^0 \psi_n^0$. To first order (λ^1),

$$H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0.$$

To second order (λ^2),

$$H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0,$$

and so on.

6.1.2 First-Order Theory

We take the inner product of the first-order equation with ψ_n^0 ,

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle.$$

Since H^0 is Hermitian, then

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle = \langle H^0 \psi_n^0 | \psi_n^1 \rangle = \langle E_n^0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle,$$

and this cancels the first term of RHS. Also we have $\langle \psi_n^0 | \psi_n^0 \rangle = 1$, then

$$\boxed{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle.}$$

This is the fundamental result of first-order perturbation theory; it says that the first-order correction to the energy is the expectation value of the perturbation, in the unperturbed state.

To find the first-order correction to the wave function, we rewrite the first-order equation:

$$(H^0 - E_n^0) \psi_n^1 = -(H' - E_n^1) \psi_n^0.$$

The unperturbed wave functions constitute a complete set, so ψ_n^1 can be expressed as a linear combination of them:

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0.$$

Putting this into the previous equation and we have

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = -(H' - E_n^1) \psi_n^0.$$

Taking the inner product with ψ_l^0 ,

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_l^0 | \psi_m^0 \rangle = -\langle \psi_l^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle.$$

If $l \neq n$, we get

$$(E_l^0 - E_n^0)c_l^{(n)} = -\langle \psi_l^0 | H' | \psi_n^0 \rangle,$$

or

$$c_m^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}.$$

Thus

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0.$$

6.1.3 Second-Order Energies

Again we take the inner product of the second order equation with ψ_n^0 :

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle.$$

Similarly we have

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle = \langle H^0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle,$$

and also $\langle \psi_n^0 | \psi_n^0 \rangle = 1$, thus

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle.$$

Since

$$\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0,$$

then

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | H' | \psi_m^0 \rangle.$$

Or

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}.$$

This is the fundamental result of the second-order perturbation theory.

6.2 Degenerate Perturbation Theory

If the unperturbed states are degenerate, i.e., two or more distinct states share the same energy, then the ordinary perturbation theory fails.

6.2.1 Two-Fold Degeneracy

Suppose that

$$H^0\psi_a^0 = E^0\psi_a^0, \quad H^0\psi_b^0 = E^0\psi_b^0, \quad \langle\psi_a^0|\psi_b^0\rangle = 0,$$

with ψ_a^0, ψ_b^0 both normalized. Any linear combination of these two states

$$\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0$$

is still an eigenstate of H^0 , with the same eigenvalue E^0 :

$$H^0\psi^0 = E^0\psi^0.$$

We want to solve the Schrödinger equation

$$H\psi = E\psi,$$

with $H = H_0 + \lambda H'$ and

$$\psi_n = \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \cdots;$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots.$$

Plugging these into the Schrödinger equation, we have

$$H^0 E^0 + \lambda(H'\psi^0 + H^0\psi^1) + \cdots = E^0\psi^0 + \lambda(E^1\psi^0 + E^0\psi^1) + \cdots.$$

At order λ we have

$$H'\psi^0 + H^0\psi^1 = E^1\psi^0 + E^0\psi^1.$$

Taking the inner product with ψ_a^0 :

$$\langle\psi_a^0|H'\psi^0\rangle + \langle\psi_a^0|H^0\psi^1\rangle = E^1\langle\psi_a^0|\psi^0\rangle + E^0\langle\psi_a^0|\psi^1\rangle.$$

Since H^0 is hermitian, similarly, the first term on LHS cancels the first term on RHS. Then we may have

$$\alpha\langle\psi_a^0|H'|\psi_a^0\rangle + \beta\langle\psi_a^0|H'|\psi_b^0\rangle = \alpha E^1.$$

Or

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1,$$

where

$$W_{ij} \equiv \langle\psi_i^0|H'|\psi_j^0\rangle.$$

Similarly, the inner product with ψ_b^0 yields

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1.$$

Solving those two equations and noting that $W_{ba} = W_{ab}^*$, we can conclude that

$$E_{\pm}^1 = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right].$$

This is the fundamental result of degenerate perturbation theory. If $\alpha = 0$ or $\beta = 0$, we can exactly obtain the nondegenerate perturbation theory.

Theorem: Let A be a hermitian operator that commutes with H^0 and H' . If ψ_a^0 and ψ_b^0 (the degenerate eigenfunctions of H^0) are also eigenfunctions of A , with distinct eigenvalues, and

$$A\psi_a^0 = \mu\psi_a^0, \quad A\psi_b^0 = \nu\psi_b^0, \quad \mu \neq \nu,$$

then $W_{ab} = 0$.

So if we have degenerate states, look around for some hermitian operator A that commutes with H^0 and H' ; pick as our unperturbed states ones that are simultaneously eigenfunctions of H^0 and A . Then use the ordinary first-order perturbation theory. If we cannot find such operator, then we just use the two-fold degenerate theory.

6.2.2 Higher-Order Degeneracy

In the previous subsection we assume that the degeneracy was two-fold. Rewrite the equations in matrix form:

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}.$$

In the case of n -fold degeneracy, we look for the eigenvalues of the $n \times n$ matrix

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle.$$

In linear algebra, finding the "good" unperturbed wave functions amounts to constructing a basis in the degenerate subspace that diagonalizes the matrix W .

6.3 The Fine Structure of Hydrogen

Fine structure is a correction to the motion of nucleus, due to two distinct mechanisms: a **relativistic correction**, and **spin-orbit coupling**. Compared to the Bohr energies, fine structure is a tiny perturbation - smaller by a factor of α^2 , where

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137.036}$$

is the **fine structure constant**.

6.3.1 The Relativistic Correction

The first term in the Hamiltonian represents the kinetic energy. The relativistic formula for kinetic energy is

$$T = \frac{mc^2}{\sqrt{1 - (v/c)^2}} - mc^2 = \sqrt{p^2c^2 + m^2c^4} - mc^2 = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots$$

Then the lowest-order relativistic correction to the Hamiltonian is

$$H'_r = -\frac{p^4}{8m^3c^2}.$$

In the first-order perturbation theory, the correction to E_n is given by the expectation value of H' in the unperturbed state:

$$E_r^1 = \langle H'_r \rangle = -\frac{1}{8m^3c^2} \langle \psi | p^4 | \psi \rangle = -\frac{1}{8m^3c^2} \langle p^2 \psi | p^2 \psi \rangle.$$

The Schrödinger equation says

$$p^2 \psi = 2m(E - V)\psi,$$

and hence

$$E_r^1 = -\frac{1}{2mc^2} \langle (E - V)^2 \rangle = -\frac{1}{2mc^2} [E^2 - 2E\langle V \rangle + \langle V^2 \rangle].$$

For hydrogen, $V(r) = -(1/4\pi\epsilon_0)e^2/r$, then

$$E_r^1 = -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right].$$

We can find that

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a}, \quad \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l + 1/2)n^3 a^2}.$$

Then

$$E_r^1 = -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{n^2 a} + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{(l + 1/2)n^3 a^2} \right].$$

This could be simplified as

$$E_r^1 = -\frac{(E_n)^2}{2mc^2} \left[\frac{4n}{l + 1/2} - 3 \right].$$

Note that we use the nondegenerate theory in this calculation, since the perturbation is spherically symmetrical and it commutes with L^2 and L_z . Moreover

6.3.2 Spin-Orbit Coupling

The electrons orbit around the nucleus. From the electron's point of view, the proton is circling around it. The orbiting positive charge sets up a magnetic field \mathbf{B} in the electron frame, which exerts a torque on the spinning electron, tending to align its magnetic moment $\boldsymbol{\mu}$ along the direction of the field. The Hamiltonian is

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

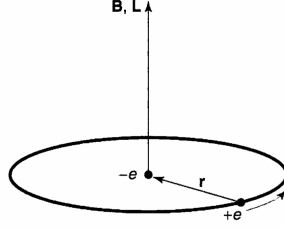


Figure 6.1: The hydrogen atom from the electron's prospective

The magnetic field generated by the proton can be calculated from the Biot-Savart law:

$$B = \frac{\mu_0 I}{2r}.$$

The proton can be considered as a continuous current loop. Thus the effective current is $I = e/T$. Moreover, the orbital angular momentum of the electron is $L = mvr = 2\pi mr^2/T$. Since \mathbf{B} and \mathbf{L} point in the same direction, then

$$\mathbf{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \mathbf{L}.$$

The magnetic dipole moment of an electron is given by Dirac:

$$\boldsymbol{\mu}_e = -\frac{e}{m} \mathbf{S}.$$

Putting this together, and if we consider the kinematic correction, known as the **Thomas precession**, we have

$$H'_{\text{so}} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}.$$

This is called the **spin-orbit interaction**. One may find that H'_{so} commute with L^2 , S^2 and the total angular momentum

$$\mathbf{J} \equiv \mathbf{L} + \mathbf{S},$$

and hence these quantities are conserved. Now the eigenstates of L^2 , S^2 , J^2 and J_z are “good” states to use in the perturbation theory. And

$$J^2 = (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S},$$

so

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2).$$

Thus the eigenvalues of $\mathbf{L} \cdot \mathbf{S}$ are

$$\frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)].$$

Of course $s = 1/2$. Meanwhile, we have

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l+1/2)(l+1)n^3a^2},$$

and then

$$E_{\text{so}}^1 = \frac{(E_n)^2}{mc^2} \frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)}.$$

Adding both the relativistic correction and the spin-orbit coupling we have

$$E_{\text{fs}}^1 = \frac{(E_n)^2}{mc^2} \left(3 - \frac{4n}{j+1/2} \right).$$

Combining this with the Bohr formula, we obtain the result for the energy levels of hydrogen with fine structure included:

$$E_{nj} = -\frac{13.6\text{eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right) \right].$$

Fine structure breaks the degeneracy in l (for a given n , the different allowed values of l do not carry the same energy), but it still preserves degeneracy in j . And the “good” quantum numbers are n , l , s , j , and m_j .

6.4 The Zeeman Effect

When an atom is placed in a uniform external magnetic field \mathbf{B}_{ext} , the energy levels are shifted. This is known as the **Zeeman effect**. For a single electron, the perturbation is

$$H'_Z = -(\boldsymbol{\mu}_l + \boldsymbol{\mu}_s) \cdot \mathbf{B}_{\text{ext}},$$

where

$$\boldsymbol{\mu}_s = -\frac{e}{m} \mathbf{S}$$

is the magnetic dipole moment associated with the electron spin, and

$$\boldsymbol{\mu}_l = -\frac{e}{2m} \mathbf{L}$$

is the dipole moment associated with orbital motion. Thus

$$H'_Z = \frac{e}{2m} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}_{\text{ext}}.$$

The nature of the Zeeman splitting depends critically on the strength of the external field in comparison with the internal field that gives rise to spin-orbit coupling. If $B_{\text{ext}} \ll B_{\text{int}}$, then fine structure dominates, and H'_Z can be treated as a small perturbation. And if $B_{\text{ext}} \gg B_{\text{int}}$, then the Zeeman effect dominates, and fine structure becomes the perturbation.

6.4.1 Weak-Field Zeeman Effect

If $B_{\text{ext}} \ll B_{\text{int}}$, the fine structure dominates: the “good” quantum numbers are n, l, j and m_j (not m_l and m_s ; because in the presence of spin-orbit coupling, \mathbf{L} and \mathbf{S} are not separately conserved). In the first order theory, the Zeeman correction to the energy is

$$E_Z^1 = \langle n l j m_j | H'_Z | n l j m_j \rangle = \frac{e}{2m} \mathbf{B}_{\text{ext}} \cdot \langle \mathbf{L} + 2\mathbf{S} \rangle.$$

Now $\mathbf{L} + 2\mathbf{S} = \mathbf{J} + \mathbf{S}$. The time average value of \mathbf{S} is just its projection along \mathbf{J} :

$$\mathbf{S}_{\text{ave}} = \frac{(\mathbf{S} \cdot \mathbf{J})}{J^2} \mathbf{J}.$$

Since $\mathbf{L} = \mathbf{J} - \mathbf{S}$, thus $L^2 = J^2 + S^2 - 2\mathbf{S} \cdot \mathbf{J}$,

$$\mathbf{S} \cdot \mathbf{J} = \frac{1}{2}(J^2 + S^2 - L^2) = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - l(l+1)].$$

Then

$$\langle \mathbf{L} + 2\mathbf{S} \rangle = \left\langle \left(1 + \frac{(\mathbf{S} \cdot \mathbf{J})}{J^2} \right) \mathbf{J} \right\rangle = \left[1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right] \langle \mathbf{J} \rangle.$$

The coefficient is called the **Landé g-factor**, g_J .

We choose the z -axis to lie along B_{ext} , then

$$E_Z^1 = \mu_B g_J B_{\text{ext}} m_j,$$

where

$$\mu_B \equiv \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \text{ eV/T}$$

is the **Bohr magneton**. The total energy is the sum of the fine-structure part and the Zeeman part.

6.4.2 Strong-Field Zeeman Effect

If $B_{\text{ext}} \gg B_{\text{int}}$, the Zeeman effect dominates. Let the z -axis along B_{ext} , then the “good” quantum numbers are n, l, m_l and m_s (not j and m_j ; because in the presence of the external torque, the total angular momentum is not conserved, but L_z and S_z are). The Zeeman Hamiltonian is

$$H'_Z = \frac{e}{2m} B_{\text{ext}} (L_z + 2S_z),$$

and the unperturbed energies are

$$E_{nm_l m_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{\text{ext}} (m_l + 2m_s).$$

In the first-order perturbation theory, the fine-structure correction to these levels is

$$E_{\text{fs}}^1 = \langle n l m_l m_s | (H'_r + H'_{\text{so}}) | n l m_l m_s \rangle.$$

The relativistic contribution is the same as before; for the spin-orbit term, we have

$$\langle \mathbf{S} \cdot \mathbf{L} \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle = \hbar^2 m_l m_s.$$

Putting these together we have

$$E_{\text{fs}}^1 = \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left\{ \frac{3}{4n} - \left[\frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right] \right\}.$$

The total energy is the sum of the Zeeman part and the fine structure contribution.

6.4.3 Intermediate-Field Zeeman Effect

6.5 Hyperfine Splitting

The proton constitutes a magnetic dipole:

$$\boldsymbol{\mu}_p = \frac{g_p e}{2m_p} \mathbf{S}_p.$$

According to classical electrodynamics, a dipole $\boldsymbol{\mu}$ sets up a magnetic field

$$\mathbf{B} = \frac{\mu_0}{4\pi r^3} [3(\boldsymbol{\mu} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \boldsymbol{\mu}] + \frac{2\mu_0}{3} \boldsymbol{\mu} \delta^3(\mathbf{r}).$$

The Hamiltonian of the electron in the magnetic field due to the proton's magnetic dipole moment is

$$H'_{\text{hf}} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \frac{[3(\mathbf{S}_p \cdot \hat{\mathbf{r}})(\mathbf{S}_e \cdot \hat{\mathbf{r}}) - \mathbf{S}_p \cdot \mathbf{S}_e]}{r^3} + \frac{\mu_0 g_p e^2}{3m_p m_e} \mathbf{S}_p \cdot \mathbf{S}_e \delta^3(\mathbf{r}).$$

The first-order correction to the energy is the expectation value of the perturbing Hamiltonian:

$$E_{\text{hf}}^1 = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \left\langle \frac{[3(\mathbf{S}_p \cdot \hat{\mathbf{r}})(\mathbf{S}_e \cdot \hat{\mathbf{r}}) - \mathbf{S}_p \cdot \mathbf{S}_e]}{r^3} \right\rangle + \frac{\mu_0 g_p e^2}{3m_p m_e} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle |\psi(0)|^2.$$

In the ground state, the wave function is spherically symmetrical, thus the first expectation value vanishes. We also find that $|\psi_{100}(0)|^2 = 1/(\pi a^3)$, then

$$E_{\text{hf}}^1 = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle$$

in the ground state. This is called **spin-spin coupling**. In this case, the individual spin angular momenta are not conserved; the “good” states are eigenvectors of the total spin

$$\mathbf{S} \equiv \mathbf{S}_e + \mathbf{S}_p.$$

We square this to get

$$\mathbf{S}_p \cdot \mathbf{S}_e = \frac{1}{2}(S^2 - S_e^2 - S_p^2).$$

Since the electron and proton both have spin $1/2$, so $S_e^2 = S_p^2 = (3/4)\hbar^2$. In the triplet state (spins parallel), the total spin is 1, and then $S^2 = 2\hbar^2$; in the singlet state the total spin is 0, and then $S^2 = 0$. Thus

$$E_{\text{hf}}^1 = \frac{4g_p\hbar^4}{2m_pm_e^2c^2a^4} \begin{cases} +1/4, & \text{(triplet);} \\ -3/4, & \text{(singlet).} \end{cases}$$

Spin-spin coupling breaks the spin degeneracy of the ground state, lifting the triplet configuration and depressing the singlet. The energy gap is

$$\Delta E = \frac{4g_p\hbar^4}{2m_pm_e^2c^2a^4} = 5.88 \times 10^{-6} \text{eV}.$$

The frequency of the proton emitted in a transition from the triplet to the singlet state is

$$\nu = \frac{\Delta E}{\hbar} = 1420 \text{MHz}.$$

Chapter 7

The Variational Principle

7.1 Theory

Suppose we want to calculate the ground state energy E_{gs} for a system described by the Hamiltonian H . However, we cannot solve the time-independent Schrödinger equation. The **variational principle** gets an *upper bound* for E_{gs} . Pick *any normalized function* ψ , we have

$$E_{\text{gs}} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle.$$

This means that the expectation value of H , in the state ψ is certain to overestimate the ground state energy. Note that this technique only applies to ground state.

7.2 The Ground State of Helium

The Hamiltonian for the helium atom is

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

The measured ground state energy of helium is

$$E_{\text{gs}} = -78.975\text{eV} \quad (\text{experimental}).$$

We want to reproduce the value theoretically. The trouble comes from the electron-electron repulsion

$$V_{ee} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

If we ignore this term, H splits into two independent hydrogen Hamiltonians. The solution is just the product of the hydrogenic wave functions:

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) \equiv \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}.$$

The energy is $8E_1 = -109$ eV. Now we apply the variational principle and use ψ_0 as the trial wave function. Then

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle,$$

where

$$\langle V_{ee} \rangle = \frac{e^2}{4\pi\epsilon_0} \left(\frac{8}{\pi a^3} \right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2 = 34 \text{ eV}$$

after calculation. Then $\langle H \rangle = -75$ eV.

A more realistic way is that, consider each electron represents a cloud of negative charge which partially shields the nucleus, so that the other electron actually sees an effective nuclear charge (Z) that is less than 2. We use a trial function of the form

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}.$$

We treat Z as a variational parameter, picking the value that minimizes H (however in the variational method we never touch the Hamiltonian itself). The Hamiltonian is

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

The expectation value of H is

$$\langle H \rangle = 2Z^2 E_1 + 2(Z-2) \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle.$$

We may find that

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a}, \quad \langle V_{ee} \rangle = \frac{5Z}{8a} \left(\frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5Z}{4} E_1.$$

Putting all this together, we have

$$\langle H \rangle = [-2Z^2 + (27/4)Z] E_1.$$

The lowest upper bound occurs when $\langle H \rangle$ is minimized:

$$\frac{d}{dZ} \langle H \rangle = [-4Z + (27/4)] E_1 = 0.$$

Then $Z = \frac{27}{16} = 1.69$. Plugging this into the energy, we have

$$\langle H \rangle = \frac{1}{2} \left(\frac{3}{2} \right)^6 E_1 = -77.5 \text{ eV}.$$

7.3 The Hydrogen Molecule Ion

A hydrogen molecule ion H_2^+ consists of a single electron in the Coulomb field of two protons. Assume for the moment that the protons are fixed by a distance R apart. The Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right),$$

where r_1 and r_2 are the distances to the electron from the respective protons.

Imagine that the ion is formed by taking a hydrogen atom in its ground state

$$\psi_0(\mathbf{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}.$$

And then we bring the second proton in from infinity, and put it at a distance R away from the first proton. We consider a trial function of the form

$$\psi = A[\psi_0(r_1) + \psi_0(r_2)].$$

First we need to normalize the function:

$$1 = |A|^2 \left[\int |\psi_0(r_1)|^2 d^3\mathbf{r} + \int |\psi_0(r_2)|^2 d^3\mathbf{r} + 2 \int \psi_0(r_1)\psi_0(r_2) d^3\mathbf{r} \right].$$

The first two integrals are 1. We let

$$I \equiv \langle \psi_0(r_1) | \psi_0(r_2) \rangle = \frac{1}{\pi a^3} \int e^{-(r_1+r_2)/a} d^3\mathbf{r}.$$

Suppose proton 1 is at the origin and proton 2 is on the z -axis at the point R . Then

$$r_1 = r, \quad r_2 = \sqrt{r^2 + R^2 - 2rR \cos \theta}.$$

Therefore,

$$I = \frac{1}{\pi a^3} \int e^{-r/a} e^{-\sqrt{r^2 + R^2 - 2rR \cos \theta}/a} r^2 \sin \theta \, dr \, d\theta \, d\phi.$$

Evaluating this integral, we have

$$I = e^{-R/a} \left[1 + \left(\frac{R}{a}\right) + \frac{1}{3} \left(\frac{R}{a}\right)^2 \right].$$

I is called an **overlap** integral, which measures the amount by which $\psi_0(r_1)$ overlaps $\psi_0(r_2)$. Then the normalization factor is

$$|A|^2 = \frac{1}{2(1+I)}.$$

Then we need to calculate $\langle H \rangle$ in the trial state. Note that

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_1}\right)\psi_0(r_1) = E_1\psi_0(r_1).$$

Same for r_2 . Then we have

$$\begin{aligned} H\psi &= A \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right] [\psi_0(r_1) + \psi_0(r_2)] \\ &= E_1\psi - A \left(\frac{e^2}{4\pi\epsilon_0} \right) \left[\frac{1}{r_2}\psi_0(r_1) + \frac{1}{r_1}\psi_0(r_2) \right]. \end{aligned}$$

Then we have

$$\langle H \rangle = E_1 - 2|A|^2 \left(\frac{e^2}{4\pi\epsilon_0} \right) \left[\left\langle \psi_0(r_1) \left| \frac{1}{r_2} \right| \psi_0(r_1) \right\rangle + \left\langle \psi_0(r_1) \left| \frac{1}{r_1} \right| \psi_0(r_2) \right\rangle \right],$$

where

$$D \equiv a \left\langle \psi_0(r_1) \left| \frac{1}{r_2} \right| \psi_0(r_1) \right\rangle$$

is the **direct integral** and

$$X \equiv a \left\langle \psi_0(r_1) \left| \frac{1}{r_1} \right| \psi_0(r_2) \right\rangle$$

is the **exchange integral**. The results are

$$D = \frac{a}{R} - \left(1 + \frac{R}{a}\right) e^{-2R/a}, \quad X = \left(1 + \frac{R}{a}\right) e^{-R/a}.$$

Putting these together, we have

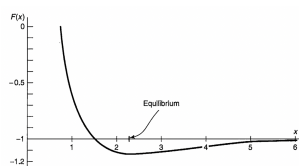
$$\langle H \rangle = \left[1 + 2 \frac{D+X}{1+I} \right] E_1$$

There is also potential energy associated with the proton-proton repulsion:

$$V_{pp} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} = -\frac{2a}{R} E_1.$$

To be conclude, the total energy of the system, in units of $-E_1$ and expressed as a function of $x \equiv R/a$ is less than

$$F(x) = -1 + \frac{2}{x} \left\{ \frac{(1 - (2/3)x^2)e^{-x} + (1+x)e^{-2x}}{1 + (1+x + (1/3)x^2)e^{-x}} \right\}.$$

Figure 7.1: The function $F(x)$

The function is plotted as shown. We find that bonding occurs, for there exists a region where the graph goes below -1. This is a covalent bond, with the electron shared equally by the two protons. The calculated binding energy is 1.8 eV, and the experimental value is 2.8 eV.

Chapter 8

The WKB Approximation

The **WKB** (Wentzel, Kramers, Brillouin) method is a technique for obtaining approximate solutions to the time-independent Schrödinger equation in one-dimension.