David J. Griffith's

Introduction to Quantum Mechanics

NOTES

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Contents

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

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

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

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

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

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

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

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

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.

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

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

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

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**,

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

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

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

1.6 The Uncertainty Principle

The **Heisenberg's uncertainty principle**

$$\boxed{\sigma_x \sigma_p \leq \frac{\hbar}{2},}$$

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

Chapter 2

Time-Independent Schrödinger Equation

2.1 Stationary States

The Schrödinger equation

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

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 $p\to(\hbar/i)(\partial/\partial x)$ 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

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

   Moreover,

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

   Hence

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

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

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

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.

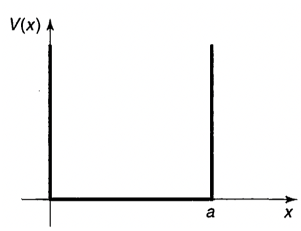

Figure 2.1: The infinite square well potential

Outside the well, $\psi(x) = 0$, as the probability of finding the particle there is 0. Insider 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 $ka = 0, \pm\pi, \pm 2\pi, \pm 3\pi, ...$So the distinct solutions are

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

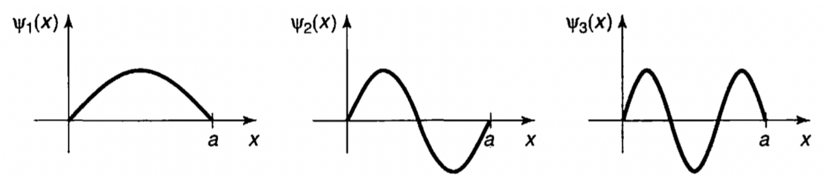

Figure 2.2: The first three stationary states of the infinite square well

Thus the possible values of E are

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

To find A, we normalize ψ:

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

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

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

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

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

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 nth 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

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

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:

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

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

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

The product

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

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

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

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

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

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

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 $(E - \hbar\omega)$.

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

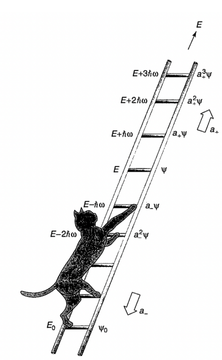

Figure 2.3: The ladder of states for the harmonic oscillator

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:

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

thus

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

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, $\hbar\omega\left(a_+a_- + 1/2\right)\psi_0 = E_0\psi_0$, 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

Tired. Mastering one method is already tough enough. Let me finish this section later.

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,

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

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 left. 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 Brogile 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:

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

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**:

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

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

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

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 $dw/dk = (\hbar k/m)$,

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

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:

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

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 $x \to \pm\infty$, 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

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

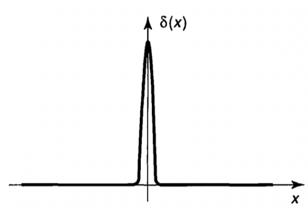

Figure 2.4: The Dirac delta function

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 $x \to -\infty$, 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

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

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

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

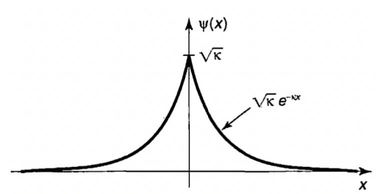

Figure 2.5: Bound state wave function for the delta-function potential

$\psi(x)$ 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 $\epsilon \to 0$:

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

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

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

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,

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

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:

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

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

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

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: $G = 0$.

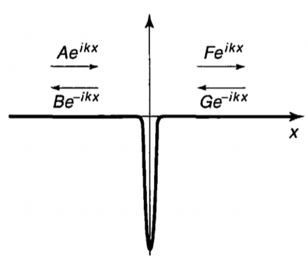

Figure 2.6: Scattering from a delta function well

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 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

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

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

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

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.

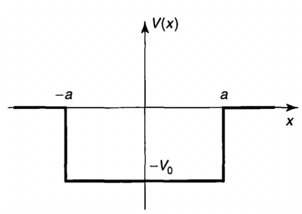

Figure 2.7: The finite square well

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 $x \to -\infty$, so the solution is

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

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 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

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

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.

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

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

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

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

$$-\kappa Fe^{-\kappa a} = -lD\sin(la).$$

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

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

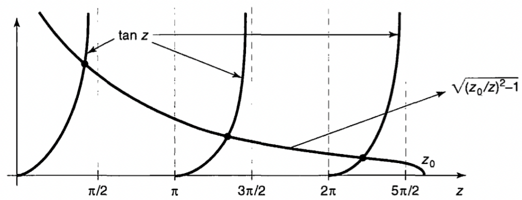

Figure 2.8: Graphic solution for $z_0 = 8$ (even state)

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:

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 $V_0 \to \infty$; 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

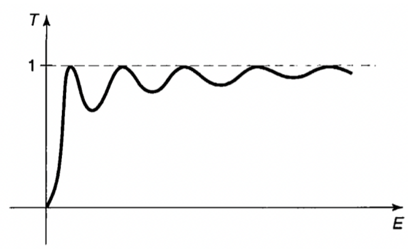

Figure 2.9: Transmission coefficient as a function of energy

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

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

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:

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

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,

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

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

$$\boxed{\textbf{Wave functions live in Hilbert space.}}$$

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**:

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

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:

$$\boxed{\textbf{Observables are represented by hermitian operators.}}$$

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

$$\boxed{\textbf{Determinate states are eigenfunctions of } \boldsymbol{\hat{Q}}.}$$

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 holds. 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

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

The general solution is
$$f_p(x) = Ae^{ipx/\hbar}.$$
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

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

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

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

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** $\Psi(x, t)$:

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

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 comp;ex number z,

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

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

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

where

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

To be conclude,

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

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 $g(x) = iaf(x), a \in \mathbb{R}$. For the position-momentum uncertainty principle this becomes:

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

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

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

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:

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

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:

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

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:

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

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,

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

or

$$\boxed{\boldsymbol{p} \to \frac{h}{i}\nabla.}$$

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 $\boldsymbol{r} = (x, y, z)$ and t. The probability of finding the particle in the infinitesimal volume $d^3\boldsymbol{r} = dxdydz$ is $|\Psi(\boldsymbol{r},t)|^2 d^3r$, 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

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

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

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

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

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

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

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

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

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

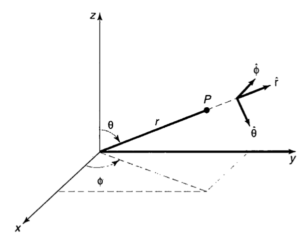

Figure 4.1: Spherical coordinates

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:

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

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

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:

$$m = 0, \pm1, \pm2, ...$$

The θ equation,