Quantum Mechanics

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Part I

Theory

1 Wave Mechanics

1.1 The Schrödinger Equation

In classical mechanics, given a particle with mass m, the goal is to determine the position function $x(t)$. Then we can obtain the its velocity, acceleration, momentum, kinetic energy, etc. In quantum mechanics, the goal is to find the particle's **wave function**, $\Psi(x,t)$, by solving the **Schrödinger equation**

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi. \tag{1.1}$$

Here $\hbar \approx 1.055 \times 10^{-34}\,\mathrm{J\cdot s} = 6.582 \times 10^{-16}\,\mathrm{eV\cdot s}$ is Planck's constant. Throughout the entire notes, assume that the particle's motion is non-relativistic, unless stated otherwise.

1.1.1 The Probability

The **statistical interpretation** of the wave function states that $|\Psi(x,t)|^2 = \Psi^*\Psi$ (where $*$ denotes the complex conjugate) gives the probability density of finding the particle at point x at time t:

$$\int_a^b |\Psi(x,t)|^2 dx = \{\text{probability of finding the particle between } a \text{ and } b, \text{ at time } t.\}$$

Since $|\Psi(x,t)|^2$ is the probability density of the particle, the integral of $|\Psi|^2$ over all space must be 1:

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1. \tag{1.2}$$

The Schrödinger equation is linear. It $\Psi(x,t)$ is a solution, then so is $A\Psi(x,t)$, where A is any complex constant. The process of finding this multipication factor A that satisfies (1.2) is called **normalization**.

Theorem 1.1. Normalization is independent of time

The Schrödinger equation has a remarkable property that it automatically preserves the normalization of the wave function, which means the normalization is independent of time,

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

Proof. Take the time-derivative of (1.2):

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

By the product rule,

$$\frac{\partial}{\partial t}|\Psi|^2 = \frac{\partial}{\partial t}(\Psi^*\Psi) = \Psi^*\frac{\partial\Psi}{\partial t} + \frac{\partial\Psi^*}{\partial t}\Psi.$$

The Schrödinger equation (1.1) reads

$$\frac{\partial\Psi}{\partial t} = \frac{i\hbar}{2m}\frac{\partial^2\Psi}{\partial x^2} - \frac{i}{\hbar}V\Psi \quad\text{and}\quad \frac{\partial\Psi^*}{\partial t} = -\frac{i\hbar}{2m}\frac{\partial^2\Psi^*}{\partial x^2} + \frac{i}{\hbar}V\Psi^*,$$

where the second equation is the complex conjugate of the first. Thus,

$$\frac{\partial}{\partial t}|\Psi|^2 = \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial^2\Psi}{\partial x^2} - \frac{\partial^2\Psi^*}{\partial x^2}\Psi\right) = \frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)\right]. \tag{1.3}$$

The integral can be evaluated:

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\Psi(x,t)|^2 dx = \frac{i\hbar}{2m}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)\Big|_{-\infty}^{+\infty}.$$

The wave function $\Psi(x,t)$ must go to zero as $x\to\pm\infty$, or the wave function would not be normalizable, so the integral is zero,

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

It means if Ψ is normalized at time $t=0$, it stays normalized for all future time. $\qquad\square$

1.1.2   The Probability Current

Let $P_{ab}(t)$ be the probability of finding the particle in the range (a,b) at time t. Taking its time-derivative and using (1.3),

$$\frac{dP_{ab}}{dt} = \frac{d}{dt}\int_a^b |\Psi|^2\,dx = \int_a^b \frac{\partial}{\partial t}|\Psi|^2\,dx = \frac{dP_{ab}}{dt} = \frac{i\hbar}{2m}\left[\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right]\Big|_a^b = J(a,t) - J(b,t),$$

where

$$J(x,t) \equiv \frac{i\hbar}{2m}\left(\frac{\partial\Psi^*}{\partial x}\Psi - \Psi^*\frac{\partial\Psi}{\partial x}\right). \tag{1.4}$$

The quantity $J(x,t)$ is known as the **probability current**. It tells the rate at which probability if flowing past the point x. If $P_{ab}(t)$ is increasing, then more probability is flowing into the region (a,b) than flowing out. If the ends are set to infinity, $(-\infty,\infty)$, the probability current is zero at both ends. Mathematically, Ψ vanishes at infinities, and so does J because it is proportional to Ψ (or Ψ^*). Physically, it means that probability is conserved when integrated over all space.

1.1.3   Momentum

The expectation value of the position x of a particle is

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\Psi(x,t)|^2 dx. \tag{1.5}$$

This expectation value means the average of measurements performed on particles all in the state Ψ. You must either find some way to return the particle to state Ψ after each measurement, or measure a collection of particles with the same state Ψ. The expectation value is the average of repeated measurements on an ensemble of identically prepared systems, not the average of repeated measurements on one and the same system.

Because of the time dependence of Ψ, $\langle x\rangle$ is often a function of time. The velocity of the expectation value of x of the particle is

$$\frac{d\langle x\rangle}{dt} = \int x\frac{\partial}{\partial t}|\Psi|^2 dx = \frac{i\hbar}{2m}\int x\frac{\partial}{\partial x}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)dx$$

where we omit the $\pm\infty$ sign. Using integration by parts and boundary condition of $\Psi\to 0$ at infinities, we get

$$\frac{d\langle x\rangle}{dt} = -\frac{i\hbar}{2m}\int\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)dx.$$

Integration by parts again on the second term gives

$$\langle v\rangle = \frac{d\langle x\rangle}{dt} = -\frac{i\hbar}{m}\int\Psi^*\frac{\partial\Psi}{\partial x}\,dx,$$

where $\langle v\rangle$ is the expectation value of the velocity. Subsequently, the expectation of momentum of the particle is defined as

$$\langle p\rangle = m\frac{d\langle x\rangle}{dt} = \int\Psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi\,dx, \tag{1.6}$$

where $-i\hbar\partial_x$ is called the **momentum operator**.

Every quantity in classical mechanics can be expressed in terms of position and momentum. For instance, the kinetic energy is

$T = p^2/2m$ or the angular momentum is $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. For any expectation value of quantity $Q(x, p)$, we can simply replace p by $-i\hbar\partial_x$ and integrate:

$$\langle Q \rangle = \int \Psi^* \hat{Q} \left(x, -i\hbar\partial_x \right) \Psi \, dx.$$

The object $Q(x, p)$ is turned to an operator when it is sandwiched between Ψ^* and Ψ. Thus, in quantum mechanics, we are working with operators rather than numbers.

Example 1.1. The expectation value of the kinetic energy

The expectation value of the kinetic energy is

$$\langle T \rangle = \int_{-\infty}^{\infty} \Psi^* \left(\frac{p^2}{2m} \right) \Psi \, dx = -\frac{\hbar^2}{2m} \int \Psi^* \frac{\partial^2 \Psi}{\partial x^2} \, dx \tag{1.7}$$

where the kinetic energy operator is

$$T = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}.$$

You may find it very familiar. Indeed, this is the first term (or the first operator) acting on Ψ on the RHS of the Schrödinger equation (1.1). The second operator acting on Ψ is V, the potential energy. Thus, the Schrödinger equation is an equation about energy.

1.1.4 The Uncertainty Principle

When constantly generating a wave on a rope, it is hard to tell "where the wave is". Instead, giving its wavelength would be satisfying. Oppositely, if we give a sudden jerk to the rope, it is easier to tell "where the wave is" than telling its wavelength. It seems like if we measure the wavelength more precisely, the position of the wave would be less precise and vice versa.

There are two formulas associated with this phenomenon. The first one is the **de Broglie formula**:

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda}. \tag{1.8}$$

The second one is Heisenberg's **uncertainty principle**:

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}, \tag{1.9}$$

where σ_x is the standard deviation of position x and σ_p is the standard deviation of momentum p. This means that if we get a very presice position of a particle (Ψ will look like a spike or more precisely a delta function), the momentum will be widely scattered and vice versa.

1.2 Stationary States

To get the quantities of interest, our goal is to solve the Schrödinger equation for Ψ. In most cases, the potential V is independent of t. Then we can solve the Schrödinger equation with **separation of variables**. We are looking for solutions that are simple products,

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

that separates the variables x and t into two functions $\psi(x)$ and $\phi(t)$. Now we can write partial derivatives of Ψ in terms of ψ, ϕ and their ordinary derivatives:

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

The Schrödinger equation then becomes

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

The LHS is a function only of t and the RHS is a function only of x. This means that both sides must be a constant. Otherwise changing one side will not affect the other and the equation will no longer be true. Define this separation constant to be E. There are two equations to solve:

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

The first equation is easy:

$$\phi(t) = e^{-iEt/\hbar}. \tag{1.10}$$

This solution specifies the time-evolution of a state as we shall see later. The second equation is called the **time-independent Schrödinger equation**,

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi.} \tag{1.11}$$

It can be solved only when $V(x)$ is specified. In quantum mechanics, we spend most of the time solving the time-independent Schrödinger equation.

Most solutions to the time-*dependent* Schrödinger equation do not take in the separable form $\psi(x)\phi(t)$, but this form is still useful. There are three reasons:

1. Although the wave function of the separable solution depends on time, $\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$, the probability density does not:

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

   These separation solutions are known as **stationary states**. It turns out that the expectation value of any quantity of interest has this property,

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

   Every expectation value is independent of time. From this we can know that in a stationary state, $\langle x\rangle$ is a constant, and so $\langle p\rangle \propto d\langle x\rangle/dt = 0$.

2. Separable states shows definite total energy. In classical mechanics, we have the **Hamiltonian**

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

   In quantum mechanics, if we substitute $p \to -i\hbar\partial_x$, then the Hamiltonian *operator* will be

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

   Thus, the time-independent Schrödinger equation can be written as

$$H\psi = E\psi. \tag{1.12}$$

   The expectation value of the total energy is

$$\langle H\rangle = \int \psi^* H\psi\,dx = E\int |\psi|^2 dx = E.$$

   Moreover, $H^2\psi = H(H\psi) = H(E\psi) = E(H\psi) = E^2\psi$. Then we also have

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

   Therefore, the variance of H is $\sigma_H^2 = \langle H^2\rangle - \langle H\rangle^2 = E^2 - E^2 = 0$. This means a separable solution has the property that every measurement of the total energy is certain to return the value E.

3. We can check that the time-independent Schrödinger equation gives infinite solutions $\{\psi_1(x), \psi_2(x), \dots\}$. Each of them is associated with a separation constant, called the **allowed energies**, $\{E_1, E_2, \dots\}$. There is a different wave function for each allowed energy:

$$\Psi_1(x,t) = \psi_1(x)e^{iE_1 t/\hbar}, \quad \Psi_2(x,t) = \psi_2(x)e^{-iE_2 t/\hbar}, \quad \dots, \quad \Psi_n(x,t) = \psi_n(x)e^{-iE_n t/\hbar}.$$

For time-dependent Schrödinger equation, any linear combination of solution is also a solution.

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}, \tag{1.13}$$

for some complex constant c_n. However, while the separable solutions are stationary states, the general solution is not. When calculating $|\Psi|^2$, the energy difference will not make the exponentials cancel out. The physical meaning of c_n is that $|c_n|^2$ gives the probability that a measurement of the energy will return the value E_n. The explanation will be available in Chapter 2.

There are several general theorems in quantum mechanics to remember:

Theorem 1.2. E must be real

For normalizable solutions, the separation constant E must be real.

Proof. Suppose $E = E_0 + i\Gamma$, where E_0 and Γ are real constants. The separable solution is

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} = \psi(x)e^{-i(E_0+i\Gamma)t/\hbar} = \psi(x)e^{-iE_0t/\hbar + \Gamma t/\hbar}.$$

Let the normalization condition hold for $t = 0$,

$$\int_{-\infty}^{\infty} |\Psi(x,0)|\,dx = \int_{-\infty}^{\infty} |\psi(x)|^2 e^{2\Gamma t/\hbar}\,dx \bigg|_{t=0} = \int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 1.$$

Apparently, when $t \neq 0$, the total probability acquires a factor of $e^{2\Gamma t/\hbar}$, which means the normalization does not hold for all t. In other words, probability is not conserved unless $\Gamma = 0$. $\qquad\square$

Theorem 1.3. Even Potential

If $V(x)$ is an even function, $V(-x) = V(x)$, then $\psi(x)$ can always be taken to be either even or odd.

Proof. Suppose $\psi(x)$ is a solution to the time-independent Schrödinger equation (1.11),

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

Now change $x \to -x$ for all operators and functions that depend on x,

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

where we used $d(-x)^2 = (-dx)^2 = dx^2$ and $V(-x) = V(x)$. This indicates that $\psi(-x)$ is also a solution. We know that any linear combination of two solutions of the Schrödinger equation is also a solution, so it is convenient to construct the even and odd solutions by

$$\psi_{\text{even}} = \psi(x) + \psi(-x) \quad\text{and}\quad \psi_{\text{odd}} = \psi(x) - \psi(-x).$$

That is, $\psi(x)$ can always taken to be even or odd. $\qquad\square$

Theorem 1.4. The minimum value of E

Classically, the energy of a system must exceed the minimum value of $V(x)$. Otherwise, the kinetic energy will be negative. This is also true in quantum mechanics: the allowed energy E must exceed the minimum value of $V(x)$ for every normalizable

solution.

Proof. The time-independent Schrödinger equation (1.11) can be rewritten in the form

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

If $E < V_{\min}$, then $V(x) - E > 0$ for all x. Mathematically, it means $\psi(x)$ and $d^2\psi/dx^2$ must have the same sign: when ψ is positive, it is concave up; when ψ is negative, it is concave down. If this happens, ψ will blow up at both infinities according to concavity, so it will not be normalizable. Thus, E must exceed the minimum value of $V(x)$ for every normalizable solution. $\qquad\square$

1.3   The Infinite Square Well

The first potential to study is the **infinite square well**:

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

The particle can move freely between 0 and a, but there is an infinite force prevents it from escaping the two ends. Outside the well, the probability of finding the particle is zero so $\psi(x) = 0$. Inside the well, we have $V(x) = 0$ and the time-independent Schrödinger equation (1.11) becomes

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

or

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

Note that $E \geq 0$ according to Theorem 1.4. This is a classical simple harmonic oscillator equation, with the general solution

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

Normally, both ψ and $d\psi/dx$ are continuous so that the Schrödinger equation (particularly $d^2\psi/dx^2$) is valid. In this case, however, as the potential goes to infinity, we can only have the first boundary condition. The continuity of ψ gives

$$\psi(0) = \psi(a) = 0.$$

This means

$$\psi(0) = A\sin 0 + B\cos 0 = B = 0 \quad \Longrightarrow \quad \psi(x) = A\sin kx.$$

For normalizable solution, $A \neq 0$, which implies that

$$\sin ka = 0 \quad \Longrightarrow \quad k_n = \frac{n\pi}{a}, \quad n = 1, 2, 3, \ldots$$

The allowed energies are

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}.} \tag{1.14}$$

We can see that a quantum particle can only have special values of energy, as opposed to a classical particle. To get A, we should normalize ψ,

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

Note that you can always multiply A by a phase factor $e^{i\theta}$ without having any physical significance. But for convenience, the normalization factor is often taken to be real. The wave function behaves like standing waves in classical mechanics, with

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right).} \tag{1.15}$$

The lowest energy is called the **ground state**. The energy of the particle increases in proportional to n^2 and these higher-energy states are called the **excited states**. Several statements can be made from (1.15). First, they are either even or odd about the center

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of the well $x = a/2$. Second, the states are **orthonormal** (orthogonal and normalized),

$$\int \psi_m^*(x)\psi_n(x)\,dx = \delta_{mn}, \quad \text{where} \quad \delta_{mn} = \begin{cases} 0, & m \neq n, \\ 1, & m = n. \end{cases}$$

Here δ_{mn} is the Kronecker delta. This can be proved by direct integration,

$$\begin{aligned}
\int \psi_m^* \psi_n\,dx &= \frac{2}{a}\int_0^a \sin\left(\frac{m\pi x}{a}\right)\sin\left(\frac{n\pi x}{a}\right)dx = \frac{1}{a}\int_0^a \left[\cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right)\right]dx \\
&= \left[\frac{1}{(m-n)\pi}\sin\left(\frac{m-n}{a}\pi x\right) - \frac{1}{(m+n)\pi}\sin\left(\frac{m+n}{a}\pi x\right)\right]_0^a \\
&= \frac{1}{\pi}\left\{\frac{\sin[(m-n)\pi]}{m-n} - \frac{\sin[(m+n)\pi]}{m+n}\right\} = \delta_{mn}.
\end{aligned}$$

Third, the set of states are **complete**, meaning that any function $f(x)$ can be written as a linear combination of them.

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

This notes will not prove completeness as they are in general much harder to prove than orthogonality. One may notice that this is just the Fourier series for $f(x)$. The coefficients c_n can be obtained by

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

By using (1.13), one can construct the most general state

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

Given an initial wave function $\Psi(x,0)$, the coefficients can be determined by Fourier's trick,

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

Example 1.2.

Suppose the (already normalized) initial wavefunction is given by

$$\Psi(x,0) = \begin{cases} \sqrt{3/a}, & 0 < x < a/3, \\ 0, & \text{otherwise.} \end{cases}$$

It can be decomposed into a linear combination of ψ_n with coefficients

$$c_n = \sqrt{\frac{2}{a}}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\Psi(x,0)\,dx = \frac{\sqrt{6}}{a}\int_0^{a/3}\sin\left(\frac{n\pi x}{a}\right)dx = \frac{\sqrt{6}}{n\pi}\left[1 - \cos\left(\frac{n\pi}{3}\right)\right].$$

This gives $\Psi(x,t)$ for future time:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n e^{-iE_n t/\hbar} = \sqrt{\frac{12}{a}}\sum_{n=1}^{\infty}\frac{1}{n\pi}\left[1 - \cos\left(\frac{n\pi}{3}\right)\right]\sin\left(\frac{n\pi x}{a}\right)e^{-in^2\pi^2\hbar t/2ma^2}.$$

Recall that $|c_n|^2$ represents the probability of getting E_n if we do a measurement on energy. For example, the probability of getting the ground state energy $E_1 = \pi^2\hbar^2/2ma^2$ is $|c_1|^2 = 3/2\pi^2$; The probability of getting the first-excited state energy is $E_2 = 2\pi^2\hbar^2/ma^2$ is $|c_2|^2 = 27/8\pi^2$; etc.

1.4 The Harmonic Oscillator*

In classical mechanics, a harmonic oscillator has a potential energy of

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2 \quad \text{with frequency} \quad \omega = \sqrt{\frac{k}{m}}.$$

For a quantum harmonic oscillator, the problem is to solve the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi. \tag{1.16}$$

There are two independent methods to solve this equation. One is by the **power series method** (analytic), a method used to study many ordinary differential equations in mathematics. The other is by using a very elegant algebraic method, which will become very important in many fields of physics.

1.4.1 Algebraic Method

Rewrite (1.16) in the form of

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

where $p = -i\hbar\, d/dx$ is the momentum operator. The idea is to factor the Hamiltonian,

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

Since p and x are operators, they in general do not commute, so there might be some problem factoring the Hamiltonian into the form $(iu + v)(-iu + v)$. However, it still worth to examine the quantities

$$a^\dagger = \frac{1}{\sqrt{2\hbar m\omega}}(-ip + m\omega x), \quad a = \frac{1}{\sqrt{2\hbar m\omega}}(ip + m\omega x). \tag{1.17}$$

Their product differs from the Hamiltonian by an extra term:

$$aa^\dagger = \frac{1}{2\hbar m\omega}[p^2 + (m\omega x)^2 - im\omega(xp - px)] = \frac{H}{\hbar\omega} - \frac{i}{2\hbar}[x,p],$$

where $[x,p] = xp - px$ is called the **commutator** of x and p. To determine this (and any) commutator, let it act on a test function $f(x)$,

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

This means $[x,p] = i\hbar$, known as the **canonical commutation relation**. Plug in $[x,p] = i\hbar$ into $aa^\dagger$,

$$aa^\dagger = \frac{H}{\hbar\omega} + \frac{1}{2} \quad \text{or} \quad H = \hbar\omega\left(aa^\dagger - \frac{1}{2}\right).$$

We can also compute the commutator for a and $a^\dagger$. The result is $[a, a^\dagger] = 1$. Hence the Hamiltonian can be equally written as

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right).$$

The Schrödinger equation in terms of $a, a^\dagger$ for the harmonic oscillator is

$$\hbar\omega\left(a^\dagger a + \frac{1}{2}\right)\psi = E\psi \quad \text{or} \quad \hbar\omega\left(aa^\dagger - \frac{1}{2}\right)\psi = E\psi. \tag{1.18}$$

Theorem 1.5. Ladder Operators

If ψ satisfies the Schrödinger equation with energy E, then $a^\dagger \psi$ satisfies the Schrödinger equation with energy $E + \hbar\omega$; $a\psi$ satisfies the Schrödinger equation with energy $E - \hbar\omega$:

$$H\psi = E\psi \quad \Longrightarrow \quad \begin{cases} H(a^\dagger \psi) = (E + \hbar\omega)(a^\dagger \psi), \\ H(a\psi) = (E - \hbar\omega)(a\psi). \end{cases}$$

Proof. Let the Hamiltonian act on $a^\dagger \psi$,

$$H(a^\dagger \psi) = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right)(a^\dagger \psi) = \hbar\omega \left(a^\dagger a a^\dagger + \frac{1}{2} a^\dagger \right)\psi = \hbar\omega a^\dagger \left(a a^\dagger + \frac{1}{2} \right)\psi.$$

Now use the commutation relation $[a, a^\dagger] = 1$, or equivalently, $a a^\dagger = 1 + a^\dagger a$,

$$H(a^\dagger \psi) = a^\dagger \left[\hbar\omega \left(a^\dagger a + 1 + \frac{1}{2} \right)\psi \right] = a^\dagger (H + \hbar\omega)\psi = a^\dagger (E + \hbar\omega)\psi = (E + \hbar\omega)(a^\dagger \psi).$$

A similar procedure can show that $a\psi$ is a solution with energy $E - \hbar\omega$. $\qquad\square$

We call $a_\pm$ as the **ladder operators**: $a^\dagger$ is the **raising operator** (or **creation operator**) and a is the **lowering operator** (or **annihilation operator**). If we find one solution, they allow us to climb up and down in energy for new solutions. However, we know that $a\psi$ is a new solution to the Schrödinger equation, but there is no guarantee that it will be normalizable (i.e. it might be zero). This happens when we apply a many times, causing the energy to become lower than zero and violating Theorem 1.4. To solve this, we claim that there is a lowest possible energy E_0 for a solution ψ_0 such that

$$a\psi_0 = 0.$$

Remember that $a\psi_0$ is a solution that is not normalizable, so ψ_0 is the ground state for the quantum harmonic oscillator. We can use this to determine ψ_0:

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

Solve this differential equation by separation of variables,

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

The final solution is a Gaussian

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

Again, the integration constant can be fixed by normalization:

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

(This integral is the famous Gaussian integral. It can be looked up in tables.) Therefore, the normalized ground state is

$$\boxed{\psi_0(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-m\omega x^2 / 2\hbar}.} \tag{1.19}$$

To determine the energy, we use

$$H\psi_0 = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right)\psi_0 = E_0 \psi_0 \quad \text{and} \quad a\psi_0 = 0.$$

This gives the ground state energy

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

By acting $a^\dagger$ on ψ_0 repeatedly and increasing the energy by $\hbar\omega$, we can generate the excited states:

$$\boxed{\psi_n(x) = A_n (a^\dagger)^n \psi_0(x), \quad E_n = \left(n + \frac{1}{2} \right)\hbar\omega.} \tag{1.20}$$

We can get the normalization constant A_n algebraically as well in terms of n. For some normalized states ψ_n and $\psi_{n\pm 1}$, we already know that

$$a^\dagger \psi_n = c_n \psi_{n+1}, \quad a\psi_n = d_n \psi_{n-1}$$

with some proportionality factors c_n and d_n.

Theorem 1.6. Hermitian conjugate of a, $a^\dagger$

a ($a^\dagger$) is the **Hermitian conjugate** of $a^\dagger$ (a). In other words, for any two functions $f(x)$ and $g(x)$ that go to zero at $\pm\infty$,

$$\int_{-\infty}^{\infty} f^*(ag)\, dx = \int_{-\infty}^{\infty} (a^\dagger f)^* g\, dx, \quad \int_{-\infty}^{\infty} f^*(a^\dagger g)\, dx = \int_{-\infty}^{\infty} (af)^* g\, dx,$$

Proof. Using integration by parts,

$$\int_{-\infty}^{\infty} f^*\left(\frac{dg}{dx}\right) dx = f^* g\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \left(\frac{df^*}{dx}\right) g\, dx = -\int_{-\infty}^{\infty} \left(\frac{df}{dx}\right)^* g\, dx.$$

Then

$$\int_{-\infty}^{\infty} f^*(a^\dagger g)\, dx = \frac{1}{\sqrt{2\hbar m\omega}} \int_{-\infty}^{\infty} f^*\left(-\hbar\frac{d}{dx} + m\omega x\right) g\, dx$$

$$= \frac{1}{\sqrt{2\hbar m\omega}} \int_{-\infty}^{\infty} \left[\left(+\hbar\frac{d}{dx} + m\omega x\right) f\right]^* g\, dx$$

$$= \int_{-\infty}^{\infty} (af)^* g\, dx.$$

$\square$

By (1.18) and (1.20), we have

$$\hbar\omega\left(a^\dagger a + \frac{1}{2}\right)\psi_n = E_n\psi_n = \left(n + \frac{1}{2}\right)\hbar\omega\psi_n, \quad \text{and} \quad \hbar\omega\left(aa^\dagger - \frac{1}{2}\right) = \left(n + \frac{1}{2}\right)\hbar\omega\psi_n,$$

or

$$a^\dagger a\psi_n = n\psi_n, \quad aa^\dagger \psi_n = (n+1)\psi_n.$$

($a^\dagger a$ is sometimes called the **number operator**.) Hence

$$|c_n|^2 \int_{-\infty}^{\infty} |\psi_{n+1}|^2\, dx = \int_{-\infty}^{\infty} (a^\dagger \psi_n)^*(a^\dagger \psi_n)\, dx = \int_{-\infty}^{\infty} (aa^\dagger \psi_n)^* \psi_n\, dx = (n+1)\int_{-\infty}^{\infty} |\psi_n|^2\, dx.$$

$$|d_n|^2 \int_{-\infty}^{\infty} |\psi_{n_1}|^2\, dx = \int_{-\infty}^{\infty} (a\psi_n)^*(a\psi_n)\, dx = \int_{-\infty}^{\infty} (a^\dagger a\psi_n)^* \psi_n\, dx = n\int_{-\infty}^{\infty} |\psi_n|^2\, dx.$$

Since we have the assumption that ψ_n and $\psi_{n\pm 1}$ are normalized, this means $|c_n|^2 = n+1$ and $|d_n|^2 = n$, and

$$\boxed{a^\dagger \psi_n = \sqrt{n+1}\,\psi_{n+1}, \quad a\psi_n = \sqrt{n}\,\psi_{n-1}.} \tag{1.21}$$

Finally, the general solution with the normalization factor is

$$\boxed{\psi_n = \frac{1}{\sqrt{n!}}(a^\dagger)^n \psi_0.} \tag{1.22}$$

The stationary states of the harmonic oscillator are also orthonormal, $\int \psi_m^* \psi_n\, dx = \delta_{mn}$. This can be proved by inserting the number operator ($a^\dagger a$):

$$\int_{-\infty}^{\infty} \psi_m^*(a^\dagger a)\psi_n\, dx = n\int_{-\infty}^{\infty} \psi_m^* \psi_n\, dx.$$

Meanwhile, by Theorem 1.6,

$$\int_{-\infty}^{\infty} \psi_m^*(a^\dagger a)\psi_n\, dx = \int_{-\infty}^{\infty} (a\psi_m)^*(a\psi_n)\, dx = \int_{-\infty}^{\infty} (a^\dagger a\psi_m)^* \psi_n\, dx = m\int_{-\infty}^{\infty} \psi_m^* \psi_n\, dx.$$

This works for any m and n, which means $\int \psi_m^* \psi_n \, dx$ vanishes unless $m = n$.

Example 1.3. The expectation value of the potential energy

This example introduces a very powerful technique and a peculiar result of the harmonic oscillator. We will use the expectation value of the potential energy as an example. To calculate $\langle V \rangle$, we will examine the integral

$$\langle V \rangle = \left\langle \frac{1}{2} m \omega^2 x^2 \right\rangle = \frac{1}{2} m \omega^2 \int_{-\infty}^{\infty} \psi_n^* \, x^2 \, \psi_n \, dx.$$

The exact form of ψ_n of the harmonic oscillator are extremely complicated. We do not want to evaluate the integral analytically. Instead, we will use the definition of ladder operators (1.17),

$$a^\dagger = \frac{1}{\sqrt{2\hbar m \omega}} (-ip + m \omega x), \quad a = \frac{1}{\sqrt{2\hbar m \omega}} (ip + m \omega x).$$

Rearranging some terms, we can write x and p in terms of $a_\pm$,

$$x = \sqrt{\frac{\hbar}{2m\omega}} (a^\dagger + a), \quad p = i\sqrt{\frac{\hbar m \omega}{2}} (a^\dagger - a). \tag{1.23}$$

Then the operator x^2 is

$$x^2 = \frac{\hbar}{2m\omega} \left(a^{\dagger 2} + a^\dagger a + a a^\dagger + a^2 \right).$$

Now using (1.21), the expectation value of $\langle V \rangle$ can be calculated easily:

$$\begin{aligned}
\langle V \rangle &= \frac{\hbar \omega}{4} \int_{-\infty}^{\infty} \psi_n^* \left(a^{\dagger 2} + a^\dagger a + a a^\dagger + a^2 \right) \psi_n \, dx \\
&= \frac{\hbar \omega}{4} \int_{-\infty}^{\infty} \psi_n^* \left[\sqrt{(n+1)(n+2)} \, \psi_{n+2} + n \psi_n + (n+1)\psi_n + \sqrt{n(n-1)} \, \psi_{n-2} \right] dx \\
&= \frac{\hbar \omega}{4} (n + 1 + n) = \frac{1}{2} \hbar \omega \left(n + \frac{1}{2} \right) = \frac{1}{2} E_n.
\end{aligned}$$

We also used the orthonormality of states, where ψ_n is orthogonal to ψ_{n+2} and ψ_{n-2}. The final result shows that the expectation value of the potential energy is half the total energy. The other half is evidently $\langle T \rangle$.

There are many more interesting properties about the quantum harmonic oscillator and ladder operators available in Appendix B.2. The section about coherent states requires some knowledge of Chapter 2, and section about 3D harmonic oscillator requires some knowledge of Chapter 4 (in particular, the hydrogen atom).

1.4.2 Analytic Method

The analytic method is to solve the Schrödinger equation by power series. Define the dimensionless variable $\xi \equiv (\sqrt{m\omega/\hbar})x$ so that

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} m \omega^2 x^2 \psi = E\psi \quad \Longrightarrow \quad \frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi, \tag{1.24}$$

where $K \equiv 2E/\hbar\omega$. At very large ξ, the equation can be approximated as

$$\frac{d^2\psi}{d\xi^2} \sim \xi^2 \psi \quad \Longrightarrow \quad \psi(\xi) \sim A e^{-\xi^2/2} + B e^{+\xi^2/2}.$$

The constant B should be set to zero or $\psi(\xi)$ blows up at infinities. This is the start of a typical power series method for solving differential equations. First analyze the large-ξ limit and get an approximated solution. The next step is crucial: we propose that the exact solution should look like

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

for some well-behaved function $h(\xi)$. The derivatives of ψ are

$$\frac{d\psi}{d\xi} = \left(\frac{dh}{d\xi} - \xi h\right)e^{-\xi^2/2} \quad \text{and} \quad \frac{d^2\psi}{d\xi^2} = \left[\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (\xi^2 - 1)h\right]e^{-\xi^2/2}.$$

Substitute into (1.24),

$$\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (K - 1)h = 0. \tag{1.25}$$

Note that the Schrödinger equation turns to another equation of $h(\xi)$. Let $h(\xi)$ be a power series in ξ:

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots = \sum_{j=0}^{\infty} a_j\xi^j.$$

The derivatives of $h(\xi)$ are

$$\frac{dh}{d\xi} = a_1 + 2a_2\xi + 3a_3\xi^2 + \cdots = \sum_{j=0}^{\infty} ja_j\xi^{j-1},$$

$$\frac{d^2h}{d\xi^2} = 2a_2 + 6a_3\xi + 12a_4\xi^2 + \cdots = \sum_{j=0}^{\infty} j(j+1)a_{j+1}\xi^{j-1} = \sum_{j=0}^{\infty}(j+1)(j+2)a_{j+2}\xi^j.$$

Then (1.25) says that

$$\sum_{j=0}^{\infty}\left[(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j\right]\xi^j = 0.$$

Since different powers of ξ, $\{1, \xi, \xi^2, \dots\}$, are linearly independent, the coefficient of each power is zero:

$$(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j = 0 \quad \Longrightarrow \quad a_{j+2} = \frac{2j+1-K}{(j+1)(j+2)}a_j. \tag{1.26}$$

With two independent coefficients a_0 and a_1, we can generate all even and odd coefficients based on this recursion formula:

$$a_2 = \frac{1-K}{2}a_0, \quad a_4 = \frac{5-K}{12}a_2 = \frac{(5-K)(1-K)}{24}a_0, \quad \dots,$$

$$a_3 = \frac{3-K}{6}a_1, \quad a_5 = \frac{7-K}{20}a_3 = \frac{(7-K)(3-K)}{120}a_1, \quad \dots.$$

The complete solution consists of $h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi)$, where

$$h_{\text{even}} = a_0 + a_2\xi^2 + a_4\xi^4 + \cdots, \quad h_{\text{odd}} = a_1\xi + a_3\xi^3 + a_5\xi^5 + \cdots.$$

There is no guarantee that the solution will be normalizable. At large j, the recursion formula is approximately

$$a_{j+2} \approx \frac{2}{j}a_j \quad \Longrightarrow \quad a_j = \frac{1}{j/2 - 1}a_{j-2} = \frac{1}{j/2 - 1}\frac{1}{j/2 - 2}a_{j-4} = \cdots \approx \frac{Ca_0}{(j/2)!}$$

for some constant C. Then

$$h(\xi) \approx C\sum_j \frac{\xi^j}{(j/2)!} \approx C\sum_j \frac{\xi^{2j}}{j!} = Ce^{\xi^2}.$$

It causes $\psi \sim e^{\xi^2/2}$ for large ξ. This is the third step: for a typical power series problem, the encounter of divergence at large ξ is almost inevitable. To solve this problem, we claim that there must be some highest j (which we will call n) such that the series terminates. That is, $a_{n+2} = 0$ for the highest some n. Since n cannot be both even and odd, we can only take h_{even} or h_{odd} from the start, while the other will be set to zero. In other words, $a_1 = 0$ if n is even, and $a_0 = 0$ if n is odd. By the recursion formula (1.26) and set $a_{n+2} = 0$, we have

$$K = 2n + 1 \quad \Longleftrightarrow \quad E_n = \left(n + \frac{1}{2}\right)\hbar\omega.$$

The quantized energy of the harmonic oscillator is recovered. Note that E_n can get arbitrary large. The key is that j can terminate at any finite number, but it needs to terminate. All of this is because e^x is an infinite series—terminating the series reduces it to a polynomial in some sense and it will then be suppressed by $e^{-\xi^2/2}$.

Of course, if we only want to solve the Schrödinger equation without caring about physics, E can definitely be continuous, and each

E has two independent solutions. However, only at specific energy E_n, the solution does not blow up at infinities. These solutions are the normalizable and physical ones. You may check this by solving the Schrödinger equation numerically for $E = (1/2 + 0.01)\hbar\omega$ and $E = (1/2 - 0.01)\hbar\omega$, and see how they diverge at infinities.

Now the recursion formula (with the constraints on K) is adjusted to

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

Polynomials generated by this recursion relation are known as **Hermite polynomials**, $H_n(\xi)$. Physicists' convention of writing Hermite polynomials is to set the coefficient of highest power of ξ to be 2^n. By this convention, the normalized stationary states for the harmonic oscillator are

$$\boxed{\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}H_n(\xi)e^{-\xi^2/2}.} \tag{1.27}$$

Hermite polynomials are studied well in mathematics. They form an orthogonal and complete set of polynomials. The orthogonality inner product is defined as

$$\int_{-\infty}^{\infty}H_m(x)H_n(x)e^{-x^2}dx = 2^n n!\sqrt{\pi}\delta_{mn}.$$

This is equivalent to the orthogonality between ψ_n in algebraic method. More information about Hermite polynomials are discussed in Appendix A.2.1.

1.5 The Free Particle

A free particle lives in a space with $V(x) = 0$ everywhere. In classical mechanics, the particle should move at constant velocity, but in quantum mechanics things get tricky. The time-independent Schrödinger equation reads

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

This is the same as the infinite square well, except the fact that there are no boundary conditions to restrict the energy. Another way to say is that the boundaries are at infinities. We shall write the general solution as

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

These are the plane wave solutions. Though they are mathematically the same as sines and cosines, they are physically different as standing wave solutions in the infinite square well. With standard time dependence $e^{-iEt/\hbar}$, the solution becomes

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

We know that the function of the combination $(x \pm vt)$ is a wave traveling at a constant speed v. The first term in the solution represents a wave travelling to the right and the second term is to the left. We can combine the two terms as

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

where

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

Their wavelength is $\lambda = 2\pi/|k|$. According to the de Broglie formula (1.8), they have momentum

$$p = \hbar k.$$

This can also be obtained by applying the momentum operator $p = -i\hbar\partial_x$ to the state. (That is, the state is also an eigenstate of p, using the language of chapter 2.) The speed of these waves is

$$v_{\text{quantum}} = \left|\frac{dx}{dt}\right| = \left|\frac{\partial\Psi_k/\partial t}{\partial\Psi_k/\partial x}\right| = \frac{\hbar k^2}{2m|k|} = \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}}.$$

The classical speed of a free particle is given by

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

This is a problem between classical free particles and quantum free particles. An even more serious problem is that the wave function of a free particle is not normalizable,

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

Here is an intuitive explanation: we know the momentum is definite, $p = \hbar k$ for each k, without uncertainty. By the uncertainty principle (1.9), the uncertainty of x is infinite. In other words, the particle is *everywhere*. Since the solution is not normalizable, a pure plane wave does not represent a physical solution. There is no particle with a definite energy or momentum.

Nonetheless, this separable solution can play a mathematical role. The general solution to the time-dependent Schrödinger equation is still the linear combination of separable solutions. This time, instead of summing over discrete index n, we integrate the solutions over the continuous variable k,

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} \, dk \tag{1.28}$$

where $(1/\sqrt{2\pi})\phi(k)dk$ works as the conventional coefficient c_n for a linear combination. For appropriate $\phi(k)$, this wave function can be normalized. Since there are a range of k's, or a range of energies and speeds, this is called a **wave packet**. Now the problem is to determine $\phi(k)$ so that it matches the initial wave function

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

This is a problem in Fourier analysis and the answer is provided by **Plancherel's theorem**

$$\boxed{f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) e^{ikx} \, dk \quad \Longrightarrow \quad F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} \, dx.} \tag{1.29}$$

$F(k)$ is called the **Fourier transform** of $f(x)$ and $f(x)$ is the **inverse Fourier transform** of $F(k)$. The purpose is to guarentee that $\Psi(x,0)$ is normalized, so the solution to $\phi(k)$ is

$$\boxed{\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx} dx.} \tag{1.30}$$

It turns out that if $\Psi(x,0)$ is normalized, so is $\phi(k)$,

$$\int_{-\infty}^{\infty} |\phi(k)|^2 dk = 1.$$

We can interpret $\phi(k)$ as the wave function of the particle in the momentum space because $p = \hbar k$. It tells the probability of finding the particle with momentum with some range of k. Furthermore, we will find that

$$\langle x \rangle = \int_{-\infty}^{\infty} \phi^*(k) \left(i \frac{\partial}{\partial k} \right) \phi(k) \, dk.$$

This means, in momentum space, $x \to i\partial_k = i\hbar\partial_p$. We can see that x and p are related by some intrinsic connection—they are **conjugate variables**. It can also be proved that $p \to p$ in momentum space just like p is x in the position space. We will see these in Chapter 2.

Now with ϕ and the concept of wave packet, we are able to explain the paradox $v_{\text{quantum}} \neq v_{\text{classical}}$. The wave packet is a superposition of plane waves e^{ikx} with amplitudes $\phi(k)$. In general, the wave packet can be seen as some envelope, while e^{ikx} themselves are ripples inside the envelope. The velocity of the envelope is the **group velocity**, while the velocity of the ripples is the **phase velocity**. Now return to the wave function,

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

where $\omega = \hbar k^2/2m$. The formula for ω as a function of k is called the **dispersion relation** of a wave packet. The phase velocity is

defined as ω/k, while the group velocity is defined as $d\omega/dk$. For our wave packet,

$$v_{\text{phase}} = \frac{\omega}{k} = \frac{\hbar k}{2m} = v_{\text{quantum}}, \quad v_{\text{group}} = \frac{d\omega}{dk} = \frac{\hbar k}{m} = v_{\text{classical}}.$$

The velocity of the wave packet envelope follows the classical velocity. This is reasonable because the particle is characterized by the envelope, not plane wave ripples.

Example 1.4. The Gaussian Wave Packet

Consider a free particle with $\Psi(x,0) = Ae^{-a^2x^2}$ with A, a real. We will normalize it, find its Fourier transform, and describe its evolution in time. Here are two useful (Gaussian) integrals to remember:

$$\int_{-\infty}^{\infty} e^{-\lambda x^2} dx = \sqrt{\frac{\pi}{\lambda}}, \qquad \int_{-\infty}^{\infty} e^{-(Ax^2+Bx)} dx = \sqrt{\frac{\pi}{A}} e^{B^2/4A}.$$

First, normalize the state:

$$1 = A^2 \int_{-\infty}^{\infty} |\Psi(x,0)|^2\, dx = A^2 \int_{-\infty}^{\infty} e^{-2a^2x^2} dx = A^2 \frac{\sqrt{\pi}}{\sqrt{2}a} \implies A = \left(\frac{2a^2}{\pi}\right)^{1/4}.$$

Fourier transform $\Psi(x,0)$ to find $\phi(k)$:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx}\, dx = \frac{1}{\sqrt{2\pi}} \left(\frac{2a^2}{\pi}\right)^{1/4} \int_{-\infty}^{\infty} e^{-(a^2x^2+kx)}\, dx = \left(\frac{1}{2a^2\pi}\right)^{1/4} e^{-k^2/4a^2}.$$

Note that the Fourier transform of a Gaussian is still a Gaussian. A Gaussian distribution somewhat balances the position space and momentum space. Putting in the time dependence:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{2a^2\pi}\right)^{1/4} \int_{-\infty}^{\infty} e^{-k^2/4a^2} e^{i(kx - \frac{\hbar k^2}{2m}t)}\, dk = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{2a^2\pi}\right)^{1/4} \int_{-\infty}^{\infty} e^{-[(1/4a^2 + i\hbar t/2m)k^2 - (ix)k]}\, dk$$

$$= \left(\frac{2}{a^2\pi}\right)^{1/4} \frac{a}{\sqrt{1+2i\hbar a^2 t/m}} e^{-a^2x^2/(1+2i\hbar a^2 t/m)}.$$

We will write the probability density $|\Psi(x,t)|^2$ in a cleaner way. Let $\omega \equiv a/\sqrt{1+(2\hbar a^2 t/m)^2}$,

$$|\Psi(x,t)|^2 = \left(\frac{2}{a^2\pi}\right)^{1/2} \frac{a}{\sqrt{1+2i\hbar a^2 t/m}} \frac{a}{\sqrt{1-2i\hbar a^2 t/m}} e^{-a^2x^2/(1+2i\hbar a^2 t/m)} e^{-a^2x^2/(1-2i\hbar a^2 t/m)}$$

$$= \left(\frac{2}{a^2\pi}\right)^{1/2} \frac{a^2}{\sqrt{1+(2\hbar a^2 t/m)^2}} e^{-2a^2x^2/[1+(2\hbar a^2 t/m)^2]} = \sqrt{\frac{2}{\pi}}\, \omega e^{-2\omega^2 x^2}.$$

As time goes on, ω gets smaller. The suppression of the exponential $e^{-2\omega^2 x^2}$ dominates over ω, so $\Psi(x,t)$ is getting wider and spreading more evenly. Moreover, the particle is not "moving". Since $|\Psi(x,t)|$ is always an even function, $\langle x \rangle = 0$ and $\langle p \rangle = 0$ at all times. One can also calculate $\langle x^2 \rangle = 1/4\omega^2$ and $\langle p^2 \rangle = \hbar^2 a^2$. (Note that $\langle p^2 \rangle$ is constant over time, while $\langle x^2 \rangle$ is increasing.) Hence the uncertainty of position and momentum are $\sigma_x = 1/2\omega$ and $\hbar a$, respectively. We can check the uncertainty principle

$$\sigma_x \sigma_p = \frac{1}{2\omega}\hbar a = \left(\frac{a}{\omega}\right)\frac{\hbar}{2} \geq \frac{\hbar}{2}$$

because $\omega \leq a$ (by its definition). The uncertainty is saturated when $\omega = a$, or $t = 0$.

1.6 The Delta-Function Potential

1.6.1 Bound States and Scattering States

We now have two different kinds of solution to the time-independent Schrödinger equation:

- The solutions of the infinite square well and the harmonic oscillator are normalizable and are labeled by a discrete index n.

- For the free particle, its solutions are non-normalizable and are labeled by a continuous variable k.

In classical mechanics, a particle in a time-independent potential can have two different kinds of motion. If $V(x)$ is higher than the particle's total energy E on both side, then it is a **bound state**. If $V(x)$ is lower than E on one side (or both), then it is a **scattering state**. The two kinds of solution to the Schrödinger equation corresponds to bound and scattering states. Moreover, particles in quantum mechanics can "leak" through any finite potential barrier. For example, a particle in a quantum harmonic oscillator in its ground state has a wave function $\propto e^{-\xi^2/2}$. Since $e^{-\xi^2/2}$ is nonzero anywhere except at infinity (where the potential goes to infinity), the particle has a nonzero probability density even at places where $V(x) > E$, the classical forbidden region. Such a phenomenon is called **quantum tunneling**. Thus, the only thing matters is the potential at infinity:

$$\begin{cases} E < V(-\infty) \text{ and } V(+\infty) & \implies \quad \text{bound state,} \\ E \geq V(-\infty) \text{ or } V(+\infty) & \implies \quad \text{scattering state.} \end{cases}$$

The infinite square well and harmonic oscillator potentials go to infinity as $x \to \pm\infty$, so the particles are in bound states. The free particle has a zero potential everywhere so it is in scattering states. All bound systems have discrete energy levels; all scattering systems have continuous energy levels.

1.6.2 The Dirac Delta Function

The **Dirac delta function** (or more precisely, distribution) is defined as

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

If we multiply $\delta(x - a)$ by a well-behaved function $f(x)$, it is the same as multiplying by $f(a)$,

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

More properties are listed in Appendix B.3. The most important property of the delta function is expressed in integration: for any nonzero ϵ,

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

1.6.3 The Delta-Function Well

Consider a potential of the form

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

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

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \alpha\delta(x)\psi = E\psi \tag{1.31}$$

Because the delta-function well has $V(\pm\infty) = 0$ and $V(0) = -\infty$, the Schrödinger equation (1.31) yields both bound states ($E < 0$) and scattering states ($E > 0$).

Bound States. Observing (1.31), when $x < 0$, $V(x) = 0$, so

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

Since $E < 0$ in bound states, κ is real and positive. The general solution is

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

We must have $A = 0$, or the first term blows up at $-\infty$. The wave function for becomes

$$\psi_-(x) = Be^{\kappa x}, \quad [x < 0]$$

for some constant B. Similarly, when $x > 0$, the general solution is

$$\psi_+(x) = Fe^{-\kappa x}, \quad [x > 0]$$

for some constant F. Now we introduce the standard boundary conditions: ψ is always continuous, and $d\psi/dx$ is continuous except at points where the potential is infinite. The first condition implies that $B = F$, so

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

There will be a kink at $x = 0$ for this function. The delta function must account for this discontinuity in the derivative of ψ. To do this, we integrate the Schrödinger equation (1.31) from $-\epsilon$ to ϵ and take the limit $\epsilon \to 0$:

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

The first integral is the difference of $d\psi/dx$ evaluated at $+\epsilon$ from $-\epsilon$. The last integral is zero if we take the limit $\epsilon \to 0$. Therefore,

$$\lim_{\epsilon \to 0}\left(\frac{d\psi}{dx}\bigg|_{+\epsilon} - \frac{d\psi}{dx}\bigg|_{-\epsilon}\right) = \frac{2m}{\hbar^2}\lim_{\epsilon \to 0}\int_{-\epsilon}^{+\epsilon} V(x)\psi(x)\,dx. \tag{1.32}$$

The RHS is ordinarily zero taking the limit. However, if $V(x) = -\alpha\delta(x)$, we have

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

Since $\psi(0) = B$,

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

Then we normalize ψ:

$$1 = \int_{-\infty}^{\infty} |\psi(x)|^2 dx = 2|B|^2 \int_0^{\infty} e^{2\kappa x}dx = \frac{|B|^2}{\kappa} \implies B = \sqrt{\kappa} = \frac{\sqrt{m\alpha}}{\hbar}.$$

In conclusion, the delta-function well has exactly one bound state:

$$\boxed{\psi(x) = \frac{\sqrt{m\alpha}}{\hbar}e^{-m\alpha|x|/\hbar^2} \quad \text{and} \quad E = -\frac{m\alpha^2}{2\hbar^2}.} \tag{1.33}$$

Scattering states. Scattering states has $E > 0$. When $x < 0$, (1.31) reads

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

The general solution is

$$\psi_-(x) = Ae^{ikx} + Be^{-ikx}, \quad [x < 0].$$

Similarly,

$$\psi_+(x) = Fe^{ikx} + Ge^{-ikx}, \quad [x > 0].$$

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

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

The derivatives are

$$\begin{cases} d\psi/dx = ik(Fe^{ikx} - Ge^{-ikx}), & x > 0 \implies d\psi/dx\big|_+ = ik(F - G), \\ d\psi/dx = ik(Ae^{ikx} - Be^{-ikx}), & x < 0 \implies d\psi/dx\big|_- = ik(A - B). \end{cases}$$

Thus, $\Delta(d\psi/dx) = ik(F - G - A + B)$. With $\psi(0) = (A + B)$, the boundary condition (Equation 1.32, the integral of the Schrödinger equation (1.31)) gives

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

or

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

One can check that the bound state (1.33) is orthogonal to the scattering states (see Appendix B.3.4). There are four unknowns (A, B, F, and G) with two equations. It is not possible to solve for all of them so we should instead examine their physical significance. Given $e^{\pm ikx}$ with a time-dependent factor $e^{-iEt/\hbar}$, we can get a wave. This means that A is the amplitude of a wave coming in from the left; B is the amplitude of a wave returning to the left; F is returning to the right and G is coming from the right. In a typical scattering experiment, the particles are usually emitted from one direction. If we emit particles from the left ($G = 0$), A is then the incident wave amplitude, B is the reflected wave amplitude, and F is the transmitted wave amplitude. Writing B and F in terms of the incident wave amplitude A,

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

Since the scattering states are not normalizable, we will instead find the relative probability of the position of the particle. The relative probability that an incident particle will reflect back is

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

where R is the **reflection coefficient**. If there is a beam of particles, the quantity R gives the fraction of reflected particles. Similarly, we can find the **transmission coefficient**

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

The reflection and transmission coefficients add up to 1—there is no particle loss. (In fact, in scattering experiments other than the delta function well, transmitted particles may not have the same wavenumber k or speed v as incident particles. In this case, the reflection coefficient is $R = |B|^2/|A|^2$, but the transmission coefficient should be defined as $T \equiv 1 - R$ instead. If the transmission coefficient is defined as $T \equiv |F|^2/|A|^2$, T and R may not sum up to 1. See Example B.6) In terms of the energy E, the reflection and transmission coefficients are

$$\boxed{R = \frac{1}{1 + (2\hbar^2 E/m\alpha^2)}, \quad T = \frac{1}{1 + (m\alpha^2/2\hbar^2 E)}.} \tag{1.34}$$

Higher energy means higher probability of transmission. Classically, particles cannot reflect off a negative well, but it happens in quantum mechanics. Note that both transmission and reflection coefficient depends on α^2 instead of α, so the sign of α does not matter in this situation. Hence the delta-function well is essentially the same as a delta-function *barrier* with $\alpha > 0$ for scattering states. (The delta-function barrier does not admit any bound state though.)

1.7   The Finite Square Well

Conside the finite square well potential

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

where V_0 is a positive constant. It admits both bound states ($E < 0$) and scattering states ($E > 0$).

Bound States   When $x < -a$ the potential is zero so the Schrödinger equation is

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

or

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi, \quad \text{where} \quad \kappa = \frac{\sqrt{-2mE}}{\hbar}.$$

Like the one in the delta-function well, the general solution is

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

When $-a < x < a$ and $V(x) = -V_0$,

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

or

$$\frac{d^2\psi}{dx^2} = -\ell^2\psi, \quad \text{where} \quad \ell = \frac{\sqrt{2m(E+V_0)}}{\hbar}.$$

E must be greater than V_0 or else the kinetic energy will be negative, so ℓ is real and positive. The general solution is

$$\psi(x) = C\sin(\ell x) + D\cos(\ell x), \quad [-a < x < a].$$

(By convention, complex exponentials e^{ikx} represent traveling waves; sine and cosine are for standing waves.) When $x > a$, the general solution is

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

Now impose boundary conditions: the continuity of ψ and $d\psi/dx$ at $x = \pm a$. Note that this finite square potential is an even function. By Theorem 1.3, the wave function can be either odd or even. For even solution, we should look for the form

$$\psi(x) = \begin{cases} Fe^{-\kappa x}, & x > a, \\ D\cos(\ell x), & 0 < x < a, \\ \psi(-x), & x < 0. \end{cases}$$

The two boundary conditions at $x = a$ says

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

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

Dividing the second equation by the first gives

$$\kappa = \ell\tan(\ell a).$$

We can solve for allowed energies E with since κ and ℓ are both functions of E. However, this equation cannot be solved analytically, but we can do some approximations. To do this, consider

$$z = \ell a \quad \text{and} \quad z_0 = \frac{a}{\hbar}\sqrt{2mV_0}.$$

By definitions of κ and ℓ, we can find that $\kappa a = \ell a\tan(\ell a) = \sqrt{z_0^2 - z^2}$, and

$$\boxed{\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1.}} \tag{1.35}$$

Note that z_0 is the measure of the size of the well, characterized by both the depth V_0 and width a. We can solve the transcendental equation for z numerically and graphically. Below are some approximations for extreme cases.
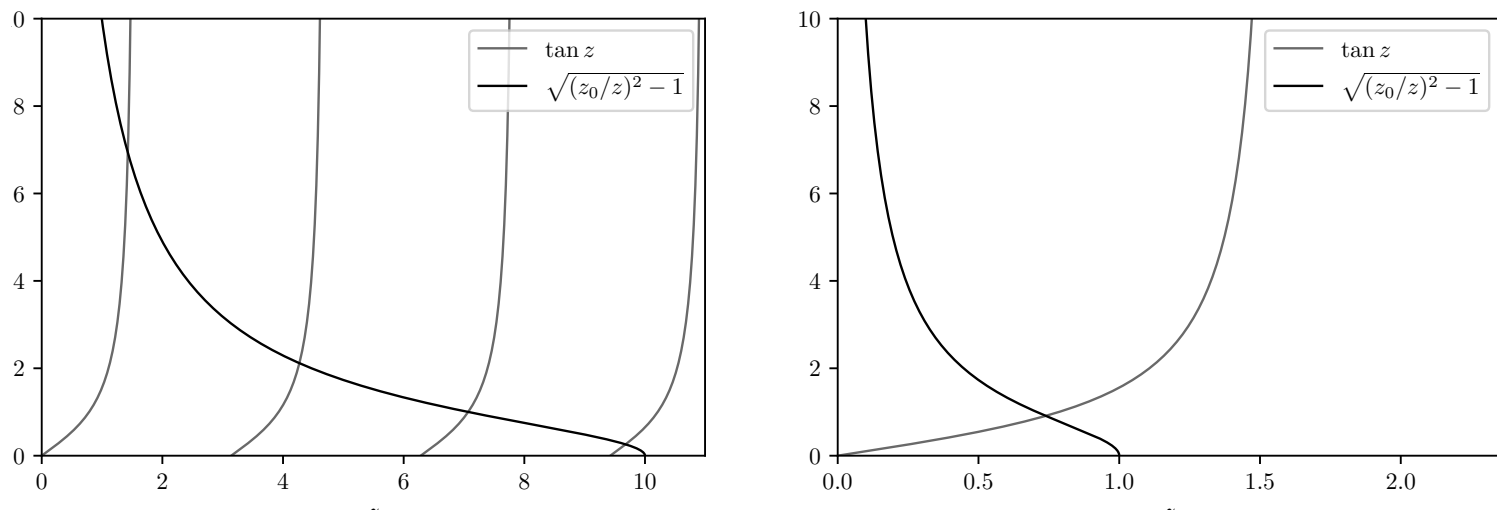
Figure 1.1: Graphical solutions to $\tan z = \sqrt{(z_0/z)^2 - 1}$. The left figure is a wide, deep well with $z_0 = 10$. The right figure is a narrow, shallow well with $z_0 = 1$.

- **Wide, deep well.** If z_0 is very large, the RHS of (1.35) is large, so $\tan z \to \infty$, or $z \simeq n\pi/2$ for $n = 1, 3, 5, \ldots$ By the definition of z,

$$z \equiv \ell a = \frac{\sqrt{2m(E + V_0)}\,a}{\hbar} \simeq \frac{n\pi}{2}.$$

  The allowed energies obey approximately

$$E_n + V_0 \simeq \frac{n^2\pi^2\hbar^2}{2m(2a)^2}, \quad n = 1, 3, 5, \ldots$$

  The LHS is the energy above the bottom of the well. The RHS is like the energy from an infinite square well with width $2a$, which is expected because the well is deep. But it is not exactly an infinite square well: for finite V_0 there are only finite numbers of allowed energies for bound states. We obtain half (only odd n) of the allowed energies for the wide, deep well; the other half is in the odd solution.

- **Narrow, shallow well.** As z_0 decreases, there will be fewer and fewer bound states, but there will at least be one bound states, no matter how weak the well becomes (see Figure 1.1, right).

The odd solutions of ψ can be solved in a similar way. We will arrive at (see Appendix B.4.1)

$$\kappa = -\ell \cot(\ell a). \tag{1.36}$$

Scattering States   Let $k = \sqrt{2mE}/\hbar$. To the left where $V(x) = 0$,

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad [x < -a].$$

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

$$\psi(x) = C\sin(\ell x) + D\cos(\ell x), \quad [-a < x < a].$$

To the right, assuming no incoming wave,

$$\psi(x) = Fe^{ikx}, \quad [x > a].$$

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

$$\begin{cases} Ae^{-ika} + B^{ika} = -C\sin(\ell a) + D\cos \ell a, & \text{[continuity of } \psi \text{ at } -a], \\ ik[Ae^{-ika} - Be^{ika}] = \ell[C\cos(\ell a) + D\sin(\ell a)], & \text{[continuity of } d\psi/dx \text{ at } -a], \\ C\sin(\ell a) + D\cos(\ell a) = Fe^{ika}, & \text{[continuity of } \psi \text{ at } +a], \\ \ell[C\cos(\ell a) - D\sin(\ell a)] = ikFe^{ika}, & \text{[continuity of } d\psi/dx \text{ at } +a]. \end{cases}$$

We are interested in B and F since they infer reflection and transmission coefficients. After a little algebra (see Appendix B.4.2), we find that

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

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

$$\boxed{T^{-1} = 1 + \frac{V_0^2}{4E(E + V_0)}\sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E + V_0)}\right).} \tag{1.37}$$

Note that $T = 1$ when the argument of sine satisfies

$$\frac{2a}{\hbar}\sqrt{2m(E_n + V_0)} = n\pi, \quad n = 1, 2, 3, \ldots$$

That is, the energies for perfect transmission are

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

exactly the energy levels for the infinite square well with width $2a$. The periodic behavior of the transmission coefficient (1.37) is known as the **Ramsauer-Townsend effect**, discovered by Carl Ramsauer and John Sealy Townsend independently in 1921 before the existence of quantum mechanics.

1.7.1 The Finite Square Barrier

A good example of tunneling is a finite square barrier:

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

where $V_0 > 0$. It looks almost the same as the finite square well, except the potential in the middle region $-a \leq x \leq a$ is flipped in sign. Since the energy must be greater than the minimum potential $V = 0$, while $V(\pm\infty) = 0$ as well, the finite square barrier admits only scattering states. There are three cases: $0 \leq E < V_0$, $E = V_0$, and $E > V_0$.

Case 1: $0 \leq E < V_0$. Let

$$k \equiv \frac{2mE}{\hbar}, \quad \kappa \equiv \frac{\sqrt{2m(V_0 - E)}}{\hbar}.$$

The solution of Schrödinger equation over all space is

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

Again, we assume that there is no incoming wave from the right.

The boundary conditions are continuity of ψ and $d\psi/dx$ at $x = \pm a$:

$$\begin{cases} Ae^{-ika} + Be^{ika} = Ce^{-\kappa a} + De^{\kappa a}, & [\text{continuity of } \psi \text{ at } -a], \\ Ae^{-ika} - Be^{ika} = \frac{\kappa}{ik}(Ce^{-\kappa a} - De^{\kappa a}), & [\text{continuity of } d\psi/dx \text{ at } -a], \\ Fe^{ika} = Ce^{\kappa a} + De^{-\kappa a}, & [\text{continuity of } \psi \text{ at } +a], \\ \frac{ik}{\kappa}Fe^{ika} = Ce^{\kappa a} - De^{-\kappa a}, & [\text{continuity of } d\psi/dx \text{ at } -a]. \end{cases}$$

After some algebra similar to those in Appendix B.4.2, we have

$$2Ae^{-ika} = Ce^{-\kappa a}\left(1 + \frac{\kappa}{ik}\right) + De^{\kappa a}\left(1 - \frac{\kappa}{ik}\right),$$

$$Ce^{-\kappa a} = \frac{1}{2}Fe^{ika}\left(1 + \frac{ik}{\kappa}\right)e^{-2\kappa a},$$

$$De^{\kappa a} = \frac{1}{2}Fe^{ika}\left(1 - \frac{ik}{\kappa}\right)e^{2\kappa a}.$$

Plug in the second and the third equation into the first one gives

$$A = Fe^{-ika}\left[\cosh(2\kappa a) + i\frac{\kappa^2 - k^2}{2k\kappa}\sinh(2\kappa a)\right].$$

The transmission coefficient is

$$T^{-1} = \frac{|A|^2}{|F|^2} = 1 + \frac{(\kappa^2 + k^2)^2}{4\kappa^2 k^2}\sinh^2(2\kappa a),$$

or, in terms of E and V_0,

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

Case 2: $E = V_0$. The wave function over all space is

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < -a, \\ Cx + D, & -a < x < a, \\ Fe^{ikx}, & x > a. \end{cases}$$

The boundary conditions are

$$\begin{cases} Ae^{-ika} + Be^{ika} = -Ca + D, & \text{[continuity of } \psi \text{ at } -a], \\ Ae^{-ika} - Be^{ika} = \frac{1}{ik}C, & \text{[continuity of } d\psi/dx \text{ at } -a], \\ Fe^{ika} = Ca + D, & \text{[continuity of } \psi \text{ at } +a], \\ ikFe^{ika} = C, & \text{[continuity of } d\psi/dx \text{ at } -a]. \end{cases}$$

We will find that $A = Fe^{ika}(1 - ika)$, and the transmission coefficent is

$$T^{-1} = \frac{|A|^2}{|F|^2} = 1 + k^2 a^2 = 1 + \frac{2ma^2 E}{\hbar^2}.$$

Case 3: $E > V_0$. This case is even simpler. Recall that in the finite square well, the scattering states all have $E + V_0 > 0$, or $E > -V_0$. In the finite square barrier with $E > V_0$, all we need to do is to change $-V_0 \to V_0$ in the finite square well transmission coefficient 1.37:

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

Compared to Case 1 ($E < V_0$), the only difference is that the hyperbolic sine is changed to ordinary sine. Actually, this can also be obtained by switching $-V_0 \to V_0$ and using the fact that $\sin(i\theta) = i\sinh\theta$ in both incident amplitude A and transmitted amplitude F. The three cases are just artifacts of solving different second order differential equations in the region $-a \leq x \leq a$.

2 FORMALISM

2.1 Review of Linear Algebra

In quantum mechanics, the state of a system is represented by its wave function, while observables are represented by operators. The natural language of quantum mechanics is linear algebra: the wave functions satisfy axioms of (abstract) vectors, and operators act on them as linear transformations. In an n-dimensional space, the vector is represented as a "ket", $|\alpha\rangle$. In an orthonormal basis, a vector can be represented by the n-tuple of its components:

$$|\alpha\rangle \to \boldsymbol{\alpha} = \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_n \end{bmatrix}.$$

The inner product of two vectors in this basis is the complex number

$$\langle \alpha | \beta \rangle = \alpha_1^* \beta_1 + \alpha_2^* \beta_2 + \cdots + \alpha_n^* \beta_n,$$

where $\langle \beta |$ is a "bra" vector. These useful notations are known as **Dirac notation** or simply **braket notation**. A linear transformation, T, is represented by a matrix,

$$|\beta\rangle = T|\alpha\rangle \to \boldsymbol{\beta} = \mathbf{T}\boldsymbol{\alpha} = \begin{bmatrix} t_{11} & t_{12} & \cdots & t_{1n} \\ t_{21} & t_{22} & \cdots & t_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ t_{n1} & t_{n2} & \cdots & t_{nn} \end{bmatrix} \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_n \end{bmatrix}.$$

A **vector space** is a set of vectors $(|\alpha\rangle, |\beta\rangle, |\gamma\rangle \ldots,)$ with a set of scalars $(a, b, c, \ldots)$, For our interests, the scalars are taken to be complex. Here are the axioms of vector spaces:

- A vector space V is closed under vector addition and scalar multiplication. The sum of any two vectors $|\alpha\rangle, |\beta\rangle \in V$ is another vector $|\gamma\rangle \in V$:

$$|\alpha\rangle + |\beta\rangle = |\gamma\rangle.$$

  The product of any scalar $a \in \mathbb{C}$ with any vector $|\alpha\rangle \in V$ is another vector $|\beta\rangle \in V$:

$$a|\alpha\rangle = |\beta\rangle.$$

- Vector addition is commutative and associative:

$$|\alpha\rangle + |\beta\rangle = |\beta\rangle + |\alpha\rangle, \quad |\alpha\rangle + (|\beta\rangle + |\gamma\rangle) = (|\alpha\rangle + |\beta\rangle) + |\gamma\rangle.$$

- There exists a zero/null vector $|0\rangle$ (or simply 0) such that $|\alpha\rangle + |0\rangle = |\alpha\rangle$ for every $|\alpha\rangle \in V$.

- For every vector $|\alpha\rangle \in V$, there exists and associated inverse vector $|-\alpha\rangle = -|\alpha\rangle$ such that $|\alpha\rangle + |-\alpha\rangle = 0$.

- Scalar multiplication is distributive with respect to vector addition and scalar addition:

$$a(|\alpha\rangle + |\beta\rangle) = a|\alpha\rangle + a|\beta\rangle, \quad (a + b)|\alpha\rangle = a|\alpha\rangle + b|\alpha\rangle.$$

- Scalar multiplication is associative with respect to ordinary multiplication of scalars: $a(b|\alpha\rangle) = (ab)|\alpha\rangle$.

- Scalar multiplication of 0 and 1 with any vector $|\alpha\rangle \in V$ satisfies

$$0|\alpha\rangle = |0\rangle, \quad 1|\alpha\rangle = |\alpha\rangle.$$

In a vector space V, it is possible to define an inner product of $|\alpha\rangle$ and $|\beta\rangle$ as $\langle\alpha|\beta\rangle$ that satisfies following axioms:

- $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^*$.

- $\langle\alpha|\alpha\rangle \geq 0$ and real for any $|\alpha\rangle \in V$.

- Inner product is distributive: $\langle\alpha|\,(a|\beta\rangle + b|\gamma\rangle) = a\,\langle\alpha|\beta\rangle + b\,\langle\alpha|\gamma\rangle$.

Suppose $|\delta\rangle = a|\alpha\rangle + b|\beta\rangle$. To turn the ket into a bra, the coefficients take the complex conjugate: $\langle\delta| = a^*\langle\alpha| + b^*\langle\beta|$. In later sections, we will know that $\langle\delta|$ is the Hermitian conjugate of $|\delta\rangle$.

For an inner product following these axioms, there are two important results: Schwarz inequality and the triangle inequality.

Theorem 2.1. Schwarz Inequality

For any two vectors $|\alpha\rangle , |\beta\rangle$ in a vector space V with a well-defined inner product,

$$|\langle\alpha|\beta\rangle|^2 \leq \langle\alpha|\alpha\rangle \langle\beta|\beta\rangle. \tag{2.1}$$

Proof. First, if $|\alpha\rangle = 0$ or $|\beta\rangle = 0$, the inequality is automatically satisfied. For $|\alpha\rangle , |\beta\rangle \neq 0$, consider a new vector

$$|\delta\rangle = |\beta\rangle - \frac{\langle\alpha|\beta\rangle}{\langle\alpha|\alpha\rangle}|\alpha\rangle \quad\Longrightarrow\quad \langle\delta| = \langle\beta| - \left(\frac{\langle\alpha|\beta\rangle}{\langle\alpha|\alpha\rangle}\right)^*\langle\alpha| = \langle\beta| - \frac{\langle\alpha|\beta\rangle^*}{\langle\alpha|\alpha\rangle}\langle\alpha|.$$

Take the inner product of $|\delta\rangle$ with itself:

$$\begin{aligned}
\langle\delta|\delta\rangle &= \left(\langle\beta| - \frac{\langle\alpha|\beta\rangle^*}{\langle\alpha|\alpha\rangle}\langle\alpha|\right)\left(|\beta\rangle - \frac{\langle\alpha|\beta\rangle}{\langle\alpha|\alpha\rangle}|\alpha\rangle\right) \\
&= \langle\beta|\beta\rangle - \frac{\langle\alpha|\beta\rangle}{\langle\alpha|\alpha\rangle}\langle\beta|\alpha\rangle - \frac{\langle\alpha|\beta\rangle^*}{\langle\alpha|\alpha\rangle}\langle\alpha|\beta\rangle + \frac{|\langle\alpha|\beta\rangle|^2}{\langle\alpha|\alpha\rangle^2}\langle\alpha|\alpha\rangle \\
&= \langle\beta|\beta\rangle - \frac{|\langle\alpha|\beta\rangle|^2}{\langle\alpha|\alpha\rangle} - \frac{|\langle\alpha|\beta\rangle|^2}{\langle\alpha|\alpha\rangle} + \frac{|\langle\alpha|\beta\rangle|^2}{\langle\alpha|\alpha\rangle} \\
&= \langle\beta|\beta\rangle - \frac{|\langle\alpha|\beta\rangle|^2}{\langle\alpha|\alpha\rangle}.
\end{aligned}$$

By the second axiom of inner product, $\langle\delta|\delta\rangle \geq 0$, so

$$\langle\beta|\beta\rangle \geq \frac{|\langle\alpha|\beta\rangle|^2}{\langle\alpha|\alpha\rangle} \quad\Longrightarrow\quad |\langle\alpha|\beta\rangle| \leq \langle\alpha|\alpha\rangle \langle\beta|\beta\rangle.$$

$\square$

Theorem 2.2. Triangle Inequality

Define the norm $\|\alpha\| = \sqrt{\langle\alpha|\alpha\rangle}$. For any two vectors $|\alpha\rangle , |\beta\rangle$ in a vector space V with a well-defined inner product,

$$\|(|\alpha\rangle + |\beta\rangle)\| \leq \|\alpha\| + \|\beta\|. \tag{2.2}$$

Proof. The square of the norm of $|\alpha\rangle + |\beta\rangle$ is

$$\|(|\alpha\rangle + |\beta\rangle)\|^2 = (\langle\alpha| + \langle\beta|)(|\alpha\rangle + |\beta\rangle) = \langle\alpha|\alpha\rangle + \langle\alpha|\beta\rangle + \langle\beta|\alpha\rangle + \langle\beta|\beta\rangle = \|\alpha\|^2 + 2\operatorname{Re}[\langle\alpha|\beta\rangle] + \|\beta\|^2 \leq \|\alpha\|^2 + 2|\langle\alpha|\beta\rangle| + \|\beta\|^2.$$

By Schwarz inequality, $|\langle\alpha|\beta\rangle| \leq \sqrt{\langle\alpha|\alpha\rangle \langle\beta|\beta\rangle} = \|\alpha\|\|\beta\|$, so

$$\|(|\alpha\rangle + |\beta\rangle)\|^2 \leq \|\alpha\|^2 + 2\|\alpha\|\|\beta\| + \|\beta\|^2 = (\|\alpha\| + \|\beta\|)^2.$$

Taking the square root,

$$\|(|\alpha\rangle + |\beta\rangle)\| \leq \|\alpha\| + \|\beta\|.$$

$\square$

2.2 Hilbert Space

Most of the vectors we encounter in quantum mechanics are actually functions in an infinite-dimensional space. In particular, the requirement that a wave function Ψ must be normalized means

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

All normalizable functions are **square-integrable functions**. The converse is not true: for example, $f(x) = 0$ is square integrable, but it cannot be normalized. The set of all square-integrable functions on a specific interval (a, b) is called $L^2(a, b)$ in mathematics, or **Hilbert space** in physics. It is contituted by functions $f(x)$ such that

$$\int_a^b |f(x)|^2 \, dx < \infty.$$

In quantum mechanics, (a, b) are $(-\infty, \infty)$ for most of the time. We define the inner product of two functions $f(x)$ and $g(x)$ as

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

We now prove that Hilbert space is indeed a vector space.

Proof. Since all "vectors" in Hilbert space are functions. Most axioms of vector spaces are automatically satisfied by properties of functions, such as commutativity, associativity, existence of a zero, etc. The main point is to show that Hilbert space is closed under vector addition. Consider any two square-integrable functions $f(x)$ and $g(x)$. We want to show $f(x) + g(x)$ is also square-integrable:

$$\int |f + g|^2 \, dx = \int (f^* + g^*)(f + g) \, dx = \int (|f|^2 + f^* g + g^* f + |g|^2) \, dx. = \int |f|^2 \, dx + \int |g|^2 \, dx + \int f^* g \, dx + \left(\int f^* g \, dx\right)^*.$$

The first two integrals are finite. The last two are also finite because Schwarz inequality (2.1) says

$$\left|\int f(x)^* g(x) \, dx\right| \leq \sqrt{\int |f(x)|^2 \, dx \int |g(x)|^2 \, dx} < \infty.$$

Closure of scalar multiplication is trivial to verify. Hence Hilbert space is a vector space. $\square$

There are several properties about functions in Hilbert space:

- The complex inner product follows
$$\langle g|f\rangle = \langle f|g\rangle^*.$$

- The inner product of $f(x)$ with itself
$$\langle f|f\rangle = \int_a^b |f(x)|^2 dx$$
is real and non-negative.

- A function is normalized if its inner product with itself is 1. Two functions are orthogonal if their inner product is 0. A set of functions, $\{f_n\}$, is **orthonormal** if
$$\langle f_m|f_n\rangle = \delta_{mn}.$$

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 $\{f_n\}$ are orthonormal, the coefficients c_n are given by

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

Note that orthonormality does not imply completeness, or vice versa. In general, completeness is much harder to prove than orthonormality.

2.3 Observables

2.3.1 Hermitian Operators

The expectation value of an observable $Q(x, p)$ can be expressed as

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

where $\hat{Q}$ is the linear operator constructed by replacing p with $-i\hbar\partial_x$ in the observable Q. In this chapter, we will refer the operator with a "hat", and the observable with no hat. In other chapters, a no-hat version represents the operator since we are dealing with quantum mechanics. For example, $\hat{H}$ and H can both represent the Hamiltonian operator.

Since the outcome of a measurement must be real, $\langle Q \rangle = \langle Q \rangle^*$. Recall that the complex conjugate of an inner product has the relation

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

This means all observables satisfy

$$\langle f | \hat{Q} f \rangle = \langle \hat{Q} f | f \rangle \quad \text{for all } f(x).$$

We call their corresponding operators **Hermitian operators**. The above condition actually leads to a seemingly stronger condition,

$$\langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle \quad \text{for all } f(x), g(x),$$

but in fact they are equivalent.

Proof. To be written. $\square$

Example 2.1. The momentum operator

The momentum operator is Hermitian:

$$\langle f | \hat{p} g \rangle = \int_{-\infty}^{\infty} f^* \left(-i\hbar \frac{dg}{dx} \right) \, dx = -i\hbar f^* g \Big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \left(-i\hbar \frac{df}{dx} \right)^* g \, dx = \langle \hat{p} f | g \rangle.$$

Here we used the fact that both f and g vanish at infinities, a property of square-integrable functions. We see that the i is necessary for the momentum operator to be Hermitian. Its complex conjugate gives a minus sign that cancels with another minus sign from integration by parts.

The **Hermitian conjugate/adjoint** of an operator $\hat{Q}$ is denoted as $\hat{Q}^\dagger$ and defined such that

$$\langle f | \hat{Q} g \rangle = \langle \hat{Q}^\dagger f | g \rangle \quad \text{for all } f(x), g(x).$$

A Hermitian operator is its own Hermitian conjugate, $\hat{Q} = \hat{Q}^\dagger$. Here are some properties regarding addition and multiplication of Hermitian operators and Hermitian conjugates:

- Hermitian conjugate of sum: $(\hat{Q} + \hat{R})^\dagger = \hat{Q}^\dagger + \hat{R}^\dagger$.

- Hermitian conjugate of scalar product: $(c\hat{Q})^\dagger = c^*\hat{Q}^\dagger$ for any complex number c.

- Hermitian conjugate of product: $(\hat{Q}\hat{R})^\dagger = \hat{R}^\dagger\hat{Q}^\dagger$. *Proof*: Using the definition of Hermitian conjugate $\langle f|\hat{Q}g\rangle = \langle \hat{Q}^\dagger f|g\rangle$,

$$\langle f|(\hat{Q}\hat{R})g\rangle = \langle f|\hat{Q}(\hat{R}g)\rangle = \langle \hat{Q}^\dagger f|\hat{R}g\rangle = \langle \hat{R}^\dagger(\hat{Q}^\dagger f)|g\rangle = \langle (\hat{R}^\dagger\hat{Q}^\dagger)f|g\rangle\,.$$

  Since f and g are arbitrary, we have $(\hat{Q}\hat{R})^\dagger = \hat{R}^\dagger\hat{Q}^\dagger$.

- From the three properties above, we know that the sum of two Hermitian operators is hermitian; for $c\hat{Q}$ to be Hermitian, c must be real; the product of two Hermitian operators $\hat{Q}$ and $\hat{R}$ is Hermitian when they commute, $[\hat{Q}, \hat{R}] = 0$.

Example 2.2. The position operator and Hamiltonian operator

The position operator is Hermitian:
$$\langle f|\hat{x}g\rangle = \int f^*(xg)\,dx = \int (xf)^*g\,dx = \langle \hat{x}f|g\rangle$$

because x is real. Similarly, the potential function $V(x)$ is assumed to be real, so it is also Hermitian. Since $[\hat{p}, \hat{p}] = 0$, $\hat{p}^2$ is a Hermitian operator. The Hamiltonian operator can be written in terms of position and momentum, $\hat{H} = \hat{p}^2/2m + V(x)$, which means it is a Hermitian operator as well.

Example 2.3. The Ladder Operators

In Theorem 1.6, we showed that the ladder operators $a^\dagger$ and a are Hermitian conjugate of each other. In more advanced books, the lowering operator is denoted simply as a, while the raising operator $a^\dagger$ is written as its Hermitian conjugate.

2.3.2   Determinate States

The **indeterminacy** of quantum mechanics means that with the same state Ψ and identically prepared systems, we cannot get the same results. A **determinate state** for an observable Q is a state in which every measurement of Q is certain to return to the same value q. There is already one example, stationary states are determinate states of the Hamiltonian: a measurement of the total energy on a particle in the stationary state Ψ_n is certain to yield the corresponding allowed energy E_n. The standard deviation of Q in a determinate state is zero (because it's determinate),

$$\sigma^2 = \langle(\hat{Q} - \langle Q\rangle)^2\rangle = \langle \Psi|(\hat{Q}-q)^2\Psi\rangle = \langle (\hat{Q}-q)\Psi|(\hat{Q}-q)\Psi\rangle = 0.$$

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

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

This is an **eigenvalue equation** for $\hat{Q}$. The wave function Ψ is an **eigenfunction** or **eigenstate** of $\hat{Q}$ and q is the corresponding **eigenvalue**. The collection of all eigenvalues of an operator is called its **spectrum**.

Example 2.4. The Schrödinger equation

We have encountered an eigenvalue equation before: the time-independent Schrödinger equation

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

In this case, the operator of interest is the Hamiltonian $\hat{H}$. Its eigenfunctions are stationary states ψ_n, and the corresponding eigenvalue is the energy E_n of the state. All allowed energies $\{E_n\}$ constitutes the spectrum of the Hamiltonian.

When two linearly independent eigenfunction share the same eigenvalue, the spectrum is called **degenerate**. Degenerate spectrum is not possible in one dimension, but we will encounter them frequently in three-dimensional problems such as the hydrogen atom (in Section 4.2).

2.4 Vectors and Operators; Matrix Mechanics

2.4.1 Bases in Hilbert Space

For an ordinary 3-dimensional vector $\mathbf{u}$, it can be represented by three components (u_x, u_y, u_z) with respect to a basis $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$:

$$\mathbf{u} = u_x \hat{\mathbf{x}} + u_y \hat{\mathbf{y}} + u_z \hat{\mathbf{z}}.$$

The components can be determined by the inner product of $\mathbf{u}$ and each basis vector,

$$u_x = \hat{\mathbf{x}} \cdot \mathbf{u}, \quad u_y = \hat{\mathbf{y}} \cdot \mathbf{u}, \quad u_z = \hat{\mathbf{z}} \cdot \mathbf{u}.$$

Alternatively, if we change the original basis to a new one $\hat{\mathbf{x}}', \hat{\mathbf{y}}', \hat{\mathbf{z}}'$, the vector is still the same, but its component will be different in general,

$$u_x' = \hat{\mathbf{x}}' \cdot \mathbf{u}, \quad u_y' = \hat{\mathbf{y}}' \cdot \mathbf{u}, \quad u_z' = \hat{\mathbf{z}}' \cdot \mathbf{u}.$$

In quantum mechanics, a state of a system is represented by a vector, $|S(t)\rangle$. It can be expressed in different bases:

- $\Psi(x, t)$ is the x-component in the expansion of $|S(t)\rangle$ in the basis of position eigenfunctions ($|x\rangle = \delta(x - y)$ in position space),

$$\Psi(x, t) = \langle x | S(t) \rangle \quad \Longleftrightarrow \quad |S(t)\rangle = \int \Psi(y, t) \delta(x - y) \, dy.$$

- $\Phi(p, t)$ is the p-component in the expansion of $|S(t)\rangle$ in the basis of momentum eigenfunctions ($|p\rangle = e^{ipx/\hbar}/\sqrt{2\pi\hbar}$ in position space),

$$\Phi(p, t) = \langle p | S(t) \rangle \quad \Longleftrightarrow \quad |S(t)\rangle = \int \Phi(p, t) \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \, dp.$$

- $c_n(t)$ (assuming discrete) is the energy-component in the expansion of $|S(t)\rangle$ in the basis of Hamiltonian eigenfunctions ($|n\rangle = \psi_n(x)$ in position space),

$$c_n(t) = \langle n | S(t) \rangle \quad \Longleftrightarrow \quad |S(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar} \psi_n(x).$$

Operators that represent observables are linear transformations acting on a vector. Consider a (discrete) orthonormal basis $|e_n\rangle$, (which can be $|n\rangle$, the eigenfunctions of $\hat{H}$), and two vectors $|\alpha\rangle$ and $|\beta\rangle$. They can be expressed in this basis as

$$|\alpha\rangle = \sum_n a_n |e_n\rangle, \quad |\beta\rangle = \sum_n b_n |e_n\rangle, \quad \text{where} \quad a_n = \langle e_n | \alpha \rangle, \quad b_n = \langle e_n | \beta \rangle.$$

Consider an operator $\hat{Q}$ and let $|\beta\rangle = \hat{Q}|\alpha\rangle$. If $\hat{Q}$ can be represented by a matrix with matrix elements Q_{mn} in the basis $|e_n\rangle$, then

$$|\beta\rangle = \hat{Q}|\alpha\rangle \quad \Longrightarrow \quad \sum_n b_n |e_n\rangle = \sum_n a_n \hat{Q}|e_n\rangle.$$

Taking the inner product with $|e_m\rangle$ on both sides,

$$\sum_n b_n \langle e_m | e_n \rangle = \sum_n a_n \langle e_m | \hat{Q} | e_n \rangle \quad \Longrightarrow \quad b_m = \sum_n \langle e_m | \hat{Q} | e_n \rangle a_n.$$

We identify the quantity $\langle e_m | \hat{Q} | e_n \rangle$ as the matrix element Q_{mn} of Q so that the above relation represent ordinary matrix multiplication,

$$b_m = \sum_n Q_{mn} a_n, \quad Q_{mn} \equiv \langle e_m | \hat{Q} | e_n \rangle. \tag{2.3}$$

> **Theorem 2.3. Hermitian matrix**
>
> The matrix representation of a Hermitian operator $\hat{Q}$ is equal to its transpose complex conjugate,
>
> $$Q_{mn} = \langle \boldsymbol{e}_m | \hat{Q} | \boldsymbol{e}_n \rangle = \langle \boldsymbol{e}_m | \hat{Q} \boldsymbol{e}_n \rangle = \langle \hat{Q} \boldsymbol{e}_m | \boldsymbol{e}_n \rangle = \langle \boldsymbol{e}_n | \hat{Q} \boldsymbol{e}_m \rangle^* = \langle \boldsymbol{e}_n | \hat{Q} | \boldsymbol{e}_m \rangle^* = Q_{nm}^*.$$
>
> This can also be applied to column vectors, so $|\alpha\rangle^\dagger = \langle\alpha|$.

The matrix elements Q_{mn} tells how te components transform, and it is determined only by the basis $|\boldsymbol{e}_n\rangle$ and the operator $\hat{Q}$. If a system admits only a finite number N of linearly independent states, a general state $|S(t)\rangle$ can be represented as a column vector of N components. Operators are $N \times N$ matrices. These are the basics for **matrix mechanics**. Important matrices are presented in Appendix A.3. One advantage of matrix mechanics is that once we find all matrix elements of Q in a given basis, it provides a method other than solving differential equations to find eigenvalues. In general, finding the eigenvalues of a matrix is much simpler.

2.4.2 Dirac Notation

A ket $|\beta\rangle$ is a vector. Think of a column vector in ordinary vector space or a function in Hilbert space. A bra $\langle\alpha|$ is a linear function of vectors that live in the **dual space** of the vector space in which $|\beta\rangle$ lives in. When a bra $\langle\alpha|$ hits a ket $|\beta\rangle$, it returns a scalar, the inner product $\langle\alpha|\beta\rangle$. In ordinary vector space, $\langle\alpha|$ is a row vector, and $\langle\alpha|\beta\rangle$ is the usual dot product. In Hilbert space, the bra $\langle f|$ is

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

where $[\cdots]$ is for a ket vector (a function).

There are two important operators in Dirac notation. The first one is the **projection operator** $\hat{P}$. For a normalized vector $|\alpha\rangle$, the projection operator

$$\hat{P} \equiv |\alpha\rangle\langle\alpha| \tag{2.4}$$

projects any other vector that lies along $|\alpha\rangle$. For example,

$$\hat{P}|\beta\rangle = |\alpha\rangle\langle\alpha|\beta\rangle = (\langle\alpha|\beta\rangle)|\alpha\rangle.$$

The projection along $|\alpha\rangle$ is $\langle\alpha|\beta\rangle$, as expected. Note that once $\hat{P} = |\alpha\rangle\langle\alpha|$ acts on $|\beta\rangle$, the inner product $\langle\alpha|\beta\rangle$ is just a number, which commutes with anything and thus can be moved around.

> **Example 2.5. Eigenvalues and eigenvectors of the projection operator**
>
> It is known that $\hat{P}^n = \hat{P}$. For any vector $|\beta\rangle$,
>
> $$\hat{P}^2|\beta\rangle = \hat{P}(\hat{P}|\beta\rangle) = \hat{P}(\langle\alpha|\beta\rangle|\alpha\rangle) = \langle\alpha|\beta\rangle\,(\hat{P}|\alpha\rangle) = \langle\alpha|\beta\rangle\,\langle\alpha|\alpha\rangle|\alpha\rangle = \langle\alpha|\beta\rangle|\alpha\rangle = \hat{P}|\beta\rangle,$$
>
> and the same for higher powers. To find the eigenvalues and eigenvectors of $\hat{P}$, let $\hat{P}|\beta\rangle = \lambda|\beta\rangle$. Then
>
> $$\hat{P}^2|\beta\rangle = \lambda\hat{P}|\beta\rangle = \lambda^2|\beta\rangle.$$
>
> Since $\hat{P}^2 = \hat{P}$, we must have $\lambda^2 = \lambda$. The eigenvalues are $\lambda = 0$ and $\lambda = 1$. If $\hat{P} = |\alpha\rangle\langle\alpha|$, any vector orthogonal to $|\alpha\rangle$ is an eigenvector with eigenvalue $\lambda = 0$; any multiple of $|\alpha\rangle$ is an eigenvector with eigenvalue $\lambda = 1$.

The second one is the **identity operator**,

$$1 = \sum_n |\boldsymbol{e}_n\rangle\langle\boldsymbol{e}_n|, \tag{2.5}$$

provided that $\{|e_n\rangle\}$ is a discrete orthonormal basis. For example, if 1 act on any vector $|\alpha\rangle$, it produces the same vector,

$$1|\alpha\rangle = \sum_n |e_n\rangle\langle e_n|\alpha\rangle = \sum_n (\langle e_n|\alpha\rangle)|e_n\rangle = |\alpha\rangle\,.$$

If $\{|e_z\rangle\}$ is a continuous orthonormal basis, $\langle e_z|e_z'\rangle = \delta(z - z')$, then the identity operator is

$$1 = \int |e_z\rangle\langle e_z|\, dz. \tag{2.6}$$

The most significant advantage of the identity operator is that we can insert it into the expression anywhere because identity commutes with everything. We will see examples of it in the following section.

For a general operator $\hat{Q}$, it is possible to construct functions of operators. They are defined by the power series expansion. For example,

$$e^{\hat{Q}} \equiv 1 + \hat{Q} + \frac{1}{2}\hat{Q}^2 + \frac{1}{3!}\hat{Q}^3 + \cdots$$

$$\frac{1}{1 - \hat{Q}} \equiv 1 + \hat{Q} + \hat{Q}^2 + \hat{Q}^3 + \cdots$$

$$\ln\left(1 + \hat{Q}\right) \equiv \hat{Q} - \frac{1}{2}\hat{Q}^2 + \frac{1}{3}\hat{Q}^3 - \frac{1}{4}\hat{Q}^4 + \cdots$$

Theorem 2.4. Spectral decomposition

Let $\hat{Q}$ be an operator with a complete set of orthonormal eigenvectors $\{|e_n\rangle\}$ with corresponding eigenvalues q_n:

$$\hat{Q}|e_n\rangle = q_n|e_n\rangle\,.$$

Then $\hat{Q}$ can be written in terms of its **spectral decomposition**:

$$\hat{Q} = \sum_n q_n\,|e_n\rangle\langle e_n|\,. \tag{2.7}$$

A function of $\hat{Q}$ can be spectral decomposed as

$$f(\hat{Q}) = \sum_n f(q_n)\,|e_n\rangle\langle e_n|\,.$$

Proof. Consider an arbitrary vector $|\alpha\rangle$,

$$|\alpha\rangle = \sum_n c_n|e_n\rangle\,, \quad c_n = \langle e_n|\alpha\rangle\,.$$

We can do this because $\{|e_n\rangle\}$ is complete and orthonormal. Then

$$\hat{Q}|\alpha\rangle = \sum_n c_n\hat{Q}|e_n\rangle = \sum_n \langle e_n|\alpha\rangle\, q_n|e_n\rangle = \sum_n q_n|e_n\rangle\langle e_n|\alpha\rangle = \left(\sum_n q_n|e_n\rangle\langle e_n|\right)|\alpha\rangle\,.$$

Since $|\alpha\rangle$ can be any vector,

$$\hat{Q} = \sum_n q_n\,|e_n\rangle\langle e_n|\,.$$

Powers of $\hat{Q}$ bring powers of q_n when acting on $\hat{Q}$ itself,

$$\hat{Q}^2 = \sum_n q_n\hat{Q}\,|e_n\rangle\langle e_n| = \sum_n q_n^2\,|e_n\rangle\langle e_n|\,, \quad \hat{Q}^3 = \sum_n q_n^3\,|e_n\rangle\langle e_n|\,, \dots$$

Hence $f(\hat{Q})$ in terms of a power series of $\hat{Q}$ brings the power series of eigenvectors inside the sum:

$$f(\hat{Q}) = \sum_n f(q_n)\,|e_n\rangle\langle e_n|\,.$$

$\square$

2.4.3   Changing Bases in Dirac Notation

With the identity operator, we can easily represent a state in different bases. In particular, we are interested in position space, momentum space, and energy space. The identity operator is

$$1 = \int dx \, |x\rangle\langle x| = \int dp \, |p\rangle\langle p| = \sum_n |n\rangle\langle n| \,.$$

For a state vector $|S(t)\rangle$, acting the identity operator on it gives the wave functions in corresponding space:

$$|S(t)\rangle = \int dx \, |x\rangle\langle x|S(t)\rangle \equiv \int \Psi(x,t)|x\rangle \, dx$$

$$|S(t)\rangle = \int dp \, |p\rangle\langle p|S(t)\rangle \equiv \int \Phi(p,t)|p\rangle \, dp$$

$$|S(t)\rangle = \sum_n |n\rangle\langle n|S(t)\rangle \equiv \sum_n c_n(t)|n\rangle \,.$$

Example 2.6. Energy-space wave function

The coefficients $c_n(t)$ is the energy-space wave function of the state $|S(t)\rangle$. Suppose we know the position-space wave function as $\Psi(x,t)$, and we would like to know the energy-space wave function $c_n(t)$. Using the identity operator, the transformation rule is

$$c_n(t) = \langle n|S(t)\rangle = \langle n| \left(\int dx \, |x\rangle\langle x| \right) |S(t)\rangle = \int dx \, \langle n|x\rangle \, \langle x|S(t)\rangle \,.$$

Because $\langle x|S(t)\rangle = \Psi(x,t)$ and $\langle x|n\rangle = \psi_n(x)$, the nth energy eigenstate in position space, the transformation rule becomes

$$c_n(t) = \int \psi_n(x)^* \Psi(x,t) \, dx.$$

Consider two incompatible observables A and B with eigenstates $\{|e_a\rangle\}$ and $\{|e_b\rangle\}$, respectively. Both set of eigenstates are complete and orthonormal, so either of them serve as a basis of Hilbert space. Suppose $\{|e_a\rangle\}$ is the old basis, and $\{|e_b\rangle\}$ is the new basis. For a more general change of basis, we want to find the **transformation operator** that connects the old basis to the new one.

Theorem 2.5. Unitary Transformation

Given two sets of orthonormal and complete basis vectors $\{|e_a\rangle\}$ and $\{|e_b\rangle\}$, there exist a unitary operator U (i.e. $\hat{U}^\dagger \hat{U} = \hat{U}\hat{U}^\dagger = I$) such that

$$\left|e_b^1\right\rangle = \hat{U}\left|e_a^1\right\rangle, \quad \left|e_b^2\right\rangle = \hat{U}\left|e_a^2\right\rangle, \dots$$

Proof. The operator $\hat{U} = \sum_i \left|e_b^i\right\rangle\!\left\langle e_a^i\right|$ satisfies all the requirements. First, applying $\hat{U}$ to $\left|a^j\right\rangle$ gives

$$\hat{U}\left|e_a^j\right\rangle = \sum_i \left|e_b^i\right\rangle\!\left\langle e_a^i\middle|e_a^j\right\rangle = \sum_i \left|e_b^i\right\rangle \delta_{ij} = \left|e_b^j\right\rangle \,.$$

Second, $\hat{U}$ is unitary:

$$\hat{U}^\dagger \hat{U} = \sum_i \sum_j |e_a^j\rangle\langle e_b^j|e_b^i\rangle\langle e_a^i| = \sum_i \sum_j \left|e_a^j\right\rangle \delta_{ij} \left\langle e_a^i\right| = \sum_i \left|e_a^i\right\rangle\!\left\langle e_a^i\right| = 1.$$

$\square$

Furthermore, we can construct the matrix representation of $\hat{U}$ in the basis $\{|e_a\rangle\}$. The matrix elements are $\langle e_a^m|U|e_a^n\rangle = \langle e_a^m|e_b^n\rangle$. Suppose we have an arbitrary vector $|\alpha\rangle$ with known coefficients in the old basis,

$$|\alpha\rangle = \sum_i \left\langle e_a^i\middle|\alpha\right\rangle \left|e_a^i\right\rangle \,.$$

To get the expansion coefficients in the new basis, take the inner product of $|\alpha\rangle$ with $\left|e_b^i\right\rangle$,

$$\langle e_b^i|\alpha\rangle = \sum_j \langle e_b^i|e_a^j\rangle\langle e_a^j|\alpha\rangle = \sum_j \langle e_a^i|U^\dagger|e_a^j\rangle\langle e_a^j|\alpha\rangle\,.$$

In matrix notation, $\langle e_a^j|\alpha\rangle$ is the jth component of the column vector $|\alpha\rangle$, and $\langle e_a^i|U^\dagger|e_a^j\rangle$ is the matrix element $U_{ij}^\dagger$. As expected, components transform inversely as basis (since $U^\dagger = U^{-1}$). The transformation of a matrix Q from the old basis to new basis can be obtained as follows. The new matrix element is

$$\langle e_b^i|\hat{Q}|e_b^j\rangle = \sum_{m,n} \langle e_b^i|e_a^m\rangle\langle e_a^m|\hat{Q}|e_a^n\rangle\langle e_a^n|e_b^j\rangle = \sum_{m,n} \langle e_a^i|\hat{U}^\dagger|e_a^m\rangle\langle e_a^m|\hat{Q}|e_a^n\rangle\langle e_a^n|\hat{U}|e_a^j\rangle\,,$$

where we inserted two identity operators in the first equality. The final expression contains a double sum of three set of matrix elements, U_{im}, Q_{mn}, and U_{nj}. In matrix form, this is known as a **similarity transformation**:

$$Q' = U^\dagger Q U.$$

2.5 The Uncertainty Principle

2.5.1 The Generalized Uncertainty Principle

Theorem 2.6. Generalized Uncertainty Principle

For observables A and B, their uncertainties σ_A and σ_B satisfy the relation

$$\sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle\right)^2. \tag{2.8}$$

Proof. For an observable A, its uncertainty (squared) is defined as

$$\sigma_A^2 \equiv \langle(A-\langle A\rangle)^2\rangle = \langle\Psi|(\hat{A}-\langle A\rangle)^2\Psi\rangle = \langle(\hat{A}-\langle A\rangle)\Psi|(\hat{A}-\langle A\rangle)\Psi\rangle = \langle f|f\rangle\,, \quad \text{where} \quad f \equiv (\hat{A}-\langle A\rangle)\Psi.$$

For another observable B,

$$\sigma_B^2 = \langle g|g\rangle\,, \quad \text{where} \quad g \equiv (\hat{B}-\langle B\rangle)\Psi.$$

By Schwarz inequality (2.1),

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

For any complex number z,

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

Setting $z = \langle f|g\rangle$,

$$\sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}[\langle f|g\rangle - \langle g|f\rangle]\right)^2. \tag{2.9}$$

The inner product of $|f\rangle$ and $|g\rangle$ is

$$\begin{aligned}
\langle f|g\rangle &= \langle(\hat{A}-\langle A\rangle)\Psi|(\hat{B}-\langle B\rangle)\Psi\rangle = \langle\Psi|(\hat{A}-\langle A\rangle)(\hat{B}-\langle B\rangle)\Psi\rangle \\
&= \langle\Psi|(\hat{A}\hat{B} - \hat{A}\langle B\rangle - \hat{B}\langle A\rangle + \langle A\rangle\langle B\rangle)\Psi\rangle \\
&= \langle\Psi|\hat{A}\hat{B}\Psi\rangle - \langle B\rangle\langle\Psi|\hat{A}\Psi\rangle - \langle A\rangle\langle\Psi|\hat{B}\Psi\rangle + \langle A\rangle\langle B\rangle\langle\Psi|\Psi\rangle \\
&= \langle\hat{A}\hat{B}\rangle - \langle B\rangle\langle A\rangle - \langle A\rangle\langle B\rangle + \langle A\rangle\langle B\rangle \\
&= \langle\hat{A}\hat{B}\rangle - \langle A\rangle\langle B\rangle.
\end{aligned}$$

In the second equality, we use the Hermiticity of $\hat{A} - \langle A \rangle$. Similarly, the inner product of $|g\rangle$ and $|f\rangle$ is

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

Then

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

Plug this into (2.9), we get the generalized uncertainty principle:

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

$\square$

Example 2.7. Heisenberg uncertainty principle

The commutator of the position and the momentum operator is $[\hat{x}, \hat{p}] = i\hbar$. Therefore,

$$\sigma_x^2 \sigma_p^2 \geq \left(\frac{1}{2i} i\hbar \right)^2 = \left(\frac{\hbar}{2} \right)^2 \quad \Longrightarrow \quad \sigma_x \sigma_p \geq \frac{\hbar}{2}.$$

The commutator plays an important role in quantum mechanics. Useful Commutation relations are listed in Appendix A.1. We say that two observables A and B are **compatible** when their operators commute, $[\hat{A}, \hat{B}] = 0$. When two operators commute, they share the same set of eigenfunctions. Physically, it means you can determine both observables simultaneously.

2.5.2 The Generalized Ehrenfest Theorem

There is another form of the uncertainty principle called the **energy-time uncertainty principle**:

$$\Delta E \Delta t \geq \frac{\hbar}{2}.$$

If we are doing nonrelativistic quantum mechanics, the observables, particularly position, momentum and energy, are all dynamical variables. They are measurable characteristics of a system at given time. However, time is not a dynamical variable. Time is the independent variable, so the interpretation of the energy-time uncertainty principle is a little different. The term Δt does not mean the standard deviation, it is actually the time it takes the system to change substantially.

Consider an observable with time dependence $Q(x, p, t)$. The time-derivative of its expectation value is

$$\frac{d}{dt}\langle Q \rangle = \frac{d}{dt}\langle \Psi | \hat{Q}\Psi \rangle = \left\langle \frac{\partial \Psi}{\partial t} \middle| \hat{Q}\Psi \right\rangle + \left\langle \Psi \middle| \frac{\partial \hat{Q}}{\partial t} \Psi \right\rangle + \left\langle \Psi \middle| \hat{Q} \frac{\partial \Psi}{\partial t} \right\rangle.$$

The Schrödinger equation says

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

Hence

$$\frac{d}{dt}\langle Q \rangle = -\frac{1}{i\hbar}\langle \hat{H}\Psi | \hat{Q}\Psi \rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle + \frac{1}{i\hbar}\langle \Psi | \hat{Q}\hat{H}\Psi \rangle.$$

Note that $\hat{H}$ is Hermitian, $\langle \hat{H}\Psi | \hat{Q}\Psi \rangle = \langle \Psi | \hat{H}\hat{Q}\Psi \rangle$, so we can combine the first and third term to a commutator,

$$\boxed{\frac{d}{dt}\langle Q \rangle = \frac{i}{\hbar}\langle [\hat{H}, \hat{Q}] \rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle.} \tag{2.10}$$

This is sometimes called the **Generalized Ehrenfest Theorem**. If Q does not depend explicitly on time (which is true in most cases), the rate of change of its expectation value is determined by the commutator of $\hat{Q}$ and the Hamiltonian. When $\hat{Q}$ commutes with $\hat{H}$, then Q is a conserved quantity.

Example 2.8. Special Cases

1. Let $\hat{Q} = \langle \Psi | \Psi \rangle = 1$. Evidently $[\hat{H}, 1] = 0$. The generalized Ehrenfest theorem infers the conservation of normalization:

$$\frac{d}{dt} \langle \Psi | \Psi \rangle = 0.$$

2. Let $\hat{Q} = \hat{H}$, then $[\hat{H}, \hat{H}] = 0$. If the Hamiltonian does not have explicit time dependence, then we have the conservation of energy:

$$\frac{d}{dt} \langle H \rangle = 0.$$

3. Let $\hat{Q} = x$. We can recover the definition of momentum expectation value (referring the commutator to A.1),

$$[H, x] = -\frac{i\hbar p}{m} \quad \Longrightarrow \quad \frac{d\langle x \rangle}{dt} = \frac{i}{\hbar} \left(-\frac{i\hbar \langle p \rangle}{m} \right) = \frac{\langle p \rangle}{m}.$$

4. Let $\hat{Q} = p$. We can recover the original Ehrenfest theorem (quantum version of Newton's second law, see Theorem B.2),

$$[H, p] = \left[\frac{p^2}{2m} + V, p \right] = [V, p] = i\hbar \frac{\partial V}{\partial x} \quad \Longrightarrow \quad \frac{d\langle p \rangle}{dt} = \frac{i}{\hbar} \left(i\hbar \left\langle \frac{\partial V}{\partial x} \right\rangle \right) = -\left\langle \frac{\partial V}{\partial x} \right\rangle.$$

Assuming that $\hat{Q}$ is independent of time, the general uncertainty principle (2.8) says

$$\sigma_H^2 \sigma_Q^2 \geq \left(\frac{1}{2i} \langle [\hat{H}, \hat{Q}] \rangle \right)^2 = \left(\frac{1}{2i} \frac{\hbar}{i} \frac{d\langle Q \rangle}{dt} \right)^2 = \left(\frac{\hbar}{2} \right)^2 \left(\frac{d\langle Q \rangle}{dt} \right)^2 \quad \Longrightarrow \quad \sigma_H \sigma_Q \geq \frac{\hbar}{2} \left| \frac{d\langle Q \rangle}{dt} \right|.$$

Define the uncertainty in energy to and that in time to be

$$\Delta E \equiv \sigma_H \quad \text{and} \quad \Delta t \equiv \frac{\sigma_Q}{|d\langle Q \rangle / dt|}$$

so that $\Delta E \Delta t \geq \hbar/2$. Since $\sigma_Q = |d\langle Q \rangle / dt| \Delta t$, Δt means the amount of time it takes the expectation value of Q to change by one standard deviation. If ΔE is small, then all observables change slowly. Conversely, if any observable is changing rapidly, then ΔE is large.

2.6 Eigenfunctions of a Hermitian Operator

There are two kinds of spectrum of a Hermitian operator: discrete (eigenvalues are separated from one another) and continuous (eigenvalues fill out the entire range and the eigenfunctions will not be normalizable). The Hamiltonian of an infinite square well and the harmonic oscillator falls into the first category. Free particle Hamiltonian falls into the second category. The Hamiltonian of a finite square well has both discrete and continuous spectrum.

2.6.1 Discrete Spectra

The normalizable eigenfunctions of a Hermitian operator have several properties:

- Their eigenvalues are *real*. Consider the eigenvalue equation $\hat{Q} f = q f$. If $\hat{Q}$ is Hermitian, then

$$\langle f | \hat{Q} f \rangle = \langle \hat{Q} f | f \rangle \quad \Longrightarrow \quad q \langle f | f \rangle = q^* \langle f | f \rangle.$$

  An eigenfunction $|f\rangle$ is not allowed to be zero by definition, so $q = q^*$.

- Eigenfunctions belonging to distinct eigenvalues are *orthogonal*. Suppose $\hat{Q} f = q f$ and $\hat{Q} g = q' g$, with $q \neq q'$ and $\hat{Q}$ Hermitian. Then $\langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle$ implies $q' \langle f | g \rangle = q \langle f | g \rangle$, or

$$\langle f | g \rangle = 0.$$

- The eigenfunctions of any observable are *complete*. That is, any function in Hilbert space can be written as a linear combination of them. This will be taken as an axiom in quantum mechanics.

For example, the stationary states of the infinite square well or the harmonic oscillator are orthogonal because they are eigenfunctions of the Hamiltonian with distinct eigenvalues (energies). Each set of eigenfunctions is complete so we can use Fourier's trick.

An **anti-Hermitian** or **skew-Hermitian** operator is an operator equal to its minus Hermitian conjugate: $\hat{Q}^\dagger = -\hat{Q}$. Here are a few properties of an anti-Hermitian operator. It is helpful to compare them with those of a Hermitian operator.

- The expectation value of an anti-Hermitian operator is *imaginary*:

$$\langle Q \rangle = \langle \psi | \hat{Q} \psi \rangle = \langle \hat{Q}^\dagger \psi | \psi \rangle = -\langle \hat{Q} \psi | \psi \rangle = -\langle \psi | \hat{Q} \psi \rangle^* = -\langle Q \rangle^*.$$

- The eigenvalues of an anti-Hermitian operatr is *imaginary*. Consider the eigenvalue equation $\hat{Q}f = qf$. If $\hat{Q}^\dagger = -\hat{Q}$,

$$\langle f | \hat{Q} f \rangle = -\langle \hat{Q} f | f \rangle \quad \Longrightarrow \quad q \langle f | f \rangle = -q^* \langle f | f \rangle.$$

$q = -q^*$ indicates that q is imaginary.

- Eigenfunctions belonging to distinct eigenvalues are *orthogonal*. Suppose $\hat{Q}f = qf$ and $\hat{Q}g = q'g$, with $q \neq q'$ and $\hat{Q}$ anti-Hermitian. Then $\langle f | \hat{Q} g \rangle = -\langle \hat{Q} f | g \rangle$ implies $q' \langle f | g \rangle = -q^* \langle f | g \rangle = q \langle f | g \rangle$, or

$$\langle f | g \rangle = 0.$$

- The commutator of two Hermitian operators or two anti-Hermitian operators is anti-Hermitian. If $\hat{Q} = \hat{Q}^\dagger$, $\hat{R} = \hat{R}^\dagger$,

$$[\hat{Q}, \hat{R}]^\dagger = (\hat{Q}\hat{R} - \hat{R}\hat{Q})^\dagger = \hat{R}^\dagger \hat{Q}^\dagger - \hat{Q}^\dagger \hat{R}^\dagger = \hat{R}\hat{Q} - \hat{Q}\hat{R} = -[\hat{Q}, \hat{R}].$$

If $\hat{Q} = -\hat{Q}^\dagger$, $\hat{R} = -\hat{R}^\dagger$,

$$[\hat{Q}, \hat{R}]^\dagger = \hat{R}^\dagger \hat{Q}^\dagger - \hat{Q}^\dagger \hat{R}^\dagger = (-\hat{R})(-\hat{Q}) - (-\hat{Q})(-\hat{R}) = \hat{R}\hat{Q} - \hat{Q}\hat{R} = -[\hat{Q}, \hat{R}].$$

- Any operator $\hat{Q}$ can be written as a sum of a Hermitian operator $\hat{A}$ and an anti-Hermitian operator $\hat{B}$. In terms of $\hat{Q}$ and its adjoint $\hat{Q}^\dagger$,

$$\hat{A} = \frac{1}{2}(\hat{Q} + \hat{Q}^\dagger), \quad \hat{B} = \frac{1}{2}(\hat{Q} - \hat{Q}^\dagger) \quad \Longrightarrow \quad \hat{Q} = \hat{A} + \hat{B}.$$

2.6.2 Continuous Spectra

If the spectrum is continuous, it is not normalizable, but the properties of reality, orthogonality, and completeness may still hold.

Example 2.9. Eigenfunctions of the momentum operator

The momentum operator is $-i\hbar\partial_x$. Let $f_p(x)$ be the eigenfunction and p the eigenvalue. We can get an eigenvalue equation

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

The general solution is

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

The delta function can be written as (B.8)

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}dk.$$

It is reasonable to assume that the momentum eigenvalue p is real. Then

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

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

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

Hence

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

This is the orthonormality—the Kronecker delta just becomes a Dirac delta. We can call this **Dirac orthonormality**. The eigenfunctions are also complete if the sum is replaced by an integral:

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

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

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

Physically, the eigenfunctions of momentum are free particles. They are sinusoidal with wavelength

$$\lambda = \frac{2\pi\hbar}{p},$$

which is just the de Broglie formula.

Example 2.10. Eigenfunctions of the position operator

Let $f_x(x)$ be the eigenfunction and x' be the eigenvalue:

$$x f_x(x) = x' f_x(x).$$

We see that $f_x(x)$ is a weird function: multiplying $f_x(x)$ by x gives a scaling $f_x(x)$. It turns out that $f_x(x)$ is the delta function:

$$f_x(x) = \delta(x-x').$$

It is continuous (as x' can be any real number), and is not normalizable: $\int \delta^2(x-x')\, dx = \delta(x'-x') = \delta(0) = \infty$. For two eigenfunctions $\delta(x-a)$ and $\delta(x-b)$, they also follow Dirac orthonormality,

$$\int_{-\infty}^{\infty} \delta(x-a)\delta(x-b)\, dx = \delta(b-a).$$

In three dimensions, the eigenfunction of $\hat{\mathbf{r}} = (x, y, z)$ are the three-dimensional delta functions,

$$\delta^3(\mathbf{r} - \mathbf{r}') = \delta(x-x')\delta(y-y')\delta(z-z'),$$

where the eigenvalue is $\mathbf{r}'$. Evidently, $\hat{x}, \hat{y}, \hat{z}$ are compatible observables because

$$x\delta^3(\mathbf{r} - \mathbf{r}') = x'\delta^3(\mathbf{r} - \mathbf{r}'), \quad y\delta^3(\mathbf{r} - \mathbf{r}') = y'\delta^3(\mathbf{r} - \mathbf{r}'), \quad z\delta^3(\mathbf{r} - \mathbf{r}') = z'\delta^3(\mathbf{r} - \mathbf{r}').$$

In other words, position operators commute:

$$[x_i, x_j] = 0.$$

2.7 Position, Momentum, and Translation

2.7.1 Translation Operators

Consider an operation that translates a well-localized state $|x'\rangle = \delta(x - x')$ to another one $|x' + dx'\rangle = \delta(x - x' - dx')$. This operation is called an **infinitesimal translation** by dx', denoted by $\hat{\mathcal{T}}$,

$$\hat{\mathcal{T}}(dx')|x'\rangle = |x' + dx'\rangle.$$

Here we examine the infinitesimal translation on an arbitrary state $|\alpha\rangle$:

$$\hat{\mathcal{T}}(dx')|\alpha\rangle = \hat{\mathcal{T}}(dx') \int dx' \, |x'\rangle\langle x'|\alpha\rangle = \int dx' \, |x' + dx'\rangle\langle x'|\alpha\rangle.$$

Since the integral runs over all space, it is equivalent to write

$$\hat{\mathcal{T}}(dx')|\alpha\rangle = \int dx' \, |x'\rangle\langle x' - dx'|\alpha\rangle.$$

In other words, the translated wave function (in position space) of $\hat{\mathcal{T}}(dx')|\alpha\rangle$ is obtained by replacing all x' with $x' - dx'$. Properties of an infinitesimal translation operator (in three dimensions) includes:

1. Unitarity: for the translated state to conserve probability,

$$1 = \langle \alpha|\alpha\rangle = \langle \alpha|\hat{\mathcal{T}}^\dagger(d\mathbf{r}')\hat{\mathcal{T}}(d\mathbf{r}')|\alpha\rangle \implies \hat{\mathcal{T}}^\dagger(d\mathbf{r}')\hat{\mathcal{T}}(d\mathbf{r}') = 1.$$

2. Successive translation: two infinitesimal translation operators can be written as a single one, with the translation being the (vector) sum

$$\hat{\mathcal{T}}(d\mathbf{r}_1)\hat{\mathcal{T}}(d\mathbf{r}_2) = \hat{\mathcal{T}}(d\mathbf{r}_1 + d\mathbf{r}_2).$$

3. The inverse of a translation is $\hat{\mathcal{T}}^{-1}(d\mathbf{r}') = \hat{\mathcal{T}}(-d\mathbf{r}')$.

4. As $d\mathbf{r}' \to 0$, the infinitesimal translation operator becomes the identity operator.

We claim that an infinitesimal translation operator can be written in the form

$$\hat{\mathcal{T}}(d\mathbf{r}') = 1 - i\hat{\mathbf{K}} \cdot d\mathbf{r}',$$

where $\hat{\mathbf{K}} = (\hat{K}_x, \hat{K}_y, \hat{K}_z)$ and its components are Hermitian operators, $\hat{\mathbf{K}} = \hat{\mathbf{K}}^\dagger$.

Proof. The unitarity of $\hat{\mathcal{T}}(d\mathbf{r}')$ follows by

$$\hat{\mathcal{T}}^\dagger(d\mathbf{r}')\hat{\mathcal{T}}(d\mathbf{r}') = (1 + i\hat{\mathbf{K}}^\dagger \cdot d\mathbf{r}')(1 - i\hat{\mathbf{K}} \cdot d\mathbf{r}') = 1 - i(\hat{\mathbf{K}} - \hat{\mathbf{K}}^\dagger) \cdot d\mathbf{r}' + \mathcal{O}(d\mathbf{r}'^2) = 1.$$

Two successive translation can be combined into a single one,

$$\hat{\mathcal{T}}(d\mathbf{r}_1)\hat{\mathcal{T}}(d\mathbf{r}_2) = (1 - i\hat{\mathbf{K}} \cdot d\mathbf{r}_1)(1 - i\hat{\mathbf{K}} \cdot d\mathbf{r}_2) = 1 - i\hat{\mathbf{K}} \cdot (d\mathbf{r}_1 + d\mathbf{r}_2) + \mathcal{O}(d\mathbf{r}_1 d\mathbf{r}_2) = \hat{\mathcal{T}}(d\mathbf{r}_1 + d\mathbf{r}_2).$$

The third and fourth property are trivially satisfied. $\qquad\square$

Now we investigate the relation between $\hat{\mathbf{K}}$ and the position operator $\hat{\mathbf{r}}$. Specifically, we are interested in the commutator of them. Note that

$$[\hat{\mathbf{r}}, \hat{\mathcal{T}}(d\mathbf{r}')]|\mathbf{r}'\rangle = [\hat{\mathbf{r}}\hat{\mathcal{T}}(d\mathbf{r}') - \hat{\mathcal{T}}(d\mathbf{r}')\hat{\mathbf{r}}]|\mathbf{r}'\rangle = \hat{\mathbf{r}}|\mathbf{r}' + d\mathbf{r}'\rangle - \mathbf{r}'\hat{\mathcal{T}}(d\mathbf{r}')|\mathbf{r}'\rangle = (\mathbf{r}' + d\mathbf{r}')|\mathbf{r}' + d\mathbf{r}'\rangle - \mathbf{r}'|\mathbf{r}' + d\mathbf{r}'\rangle = d\mathbf{r}'|\mathbf{r}' + d\mathbf{r}'\rangle.$$

Rewrite $|\mathbf{r}' + d\mathbf{r}'\rangle$ back to $\hat{\mathcal{T}}(d\mathbf{r}')|\mathbf{r}'\rangle$,

$$[\hat{\mathbf{r}}, \hat{\mathcal{T}}(d\mathbf{r}')] = d\mathbf{r}'\hat{\mathcal{T}}(d\mathbf{r}')|\mathbf{r}'\rangle = d\mathbf{r}'(1 - i\hat{\mathbf{K}} \cdot d\mathbf{r}')|\mathbf{r}'\rangle \simeq d\mathbf{r}'|\mathbf{r}'\rangle,$$

where the second-order term are neglected as $d\mathbf{r}' \to 0$. Because $\{|\hat{\mathbf{r}}'\rangle\}$ form a complete and orthonormal basis, the fact that

$[\hat{\mathbf{r}}, \hat{\mathcal{T}}(d\mathbf{r}')] = d\mathbf{r}'$ holds for $\hat{\mathbf{r}}'$ means that it holds for any function. Therefore, we have the commutation relation

$$[\hat{\mathbf{r}}, \hat{\mathcal{T}}(d\mathbf{r}')] = d\mathbf{r}'. \tag{2.11}$$

In terms of $\hat{\mathbf{K}}$, (2.11) can be expressed as

$$-i\hat{\mathbf{r}}\hat{\mathbf{K}} \cdot d\mathbf{r}' + i\hat{\mathbf{K}} \cdot d\mathbf{r}'\hat{\mathbf{r}} = d\mathbf{r}' \quad \text{or} \quad [\hat{\mathbf{r}}, \hat{\mathbf{K}} \cdot d\mathbf{r}'] = i\, d\mathbf{r}'.$$

This is a vector commutator, so it must hold for all component. For example, if we let $d\mathbf{r}' = \hat{\mathbf{x}}\, dx$, then $\hat{\mathbf{K}} \cdot d\mathbf{r}' = K_x\, dx$ and $\hat{\mathbf{r}}$ must also point in the x-direction, $\hat{\mathbf{r}} = \hat{x}\hat{\mathbf{x}}$. Otherwise, the component does not match. Doing this for all components gives a very important commutator:

$$[\hat{x}_i, \hat{K}_j] = i\delta_{ij}.$$

2.7.2   Momentum as a Generator of Translation

In classical mechanics, momentum is the generator of an infinitesimal translation. An infinitesimal translation is a canonical transformation

$$\mathbf{q}_{\text{new}} \equiv \mathbf{Q} = \mathbf{q} + d\mathbf{q}, \quad \mathbf{p}_{\text{new}} \equiv \mathbf{P} = \mathbf{p},$$

where $\mathbf{p}$ and $\mathbf{P}$ are the corresponding momenta of $\mathbf{q}$ and $\mathbf{Q}$, respectively. Such a canonical transformation can be obtained from the generating function

$$F(\mathbf{q}, \mathbf{P}) = \mathbf{q} \cdot \mathbf{P} + \mathbf{p} \cdot d\mathbf{q}.$$

Moreover, $\mathbf{q} \cdot \mathbf{P}$ is the generating function for the identity transformation, so $F(\mathbf{q}, \mathbf{P})$ is almost the same as $\hat{\mathcal{T}}(d\mathbf{r}') = 1 - i\hat{\mathbf{K}} \cdot d\mathbf{r}'$. We should speculate that whether $\hat{\mathbf{K}}$ has to do with the momentum operator. It turns out that $\hat{\mathbf{K}}$ is the wavenumber operator $\hat{\mathbf{k}} = \hat{\mathbf{p}}/\hbar$, where $\hat{\mathbf{p}}$ is the momentum operator. Hence the infinitesimal translation operator is related to $\mathbf{p}$ by

$$\hat{\mathcal{T}}(d\mathbf{r}') = 1 - \frac{i\mathbf{p}}{\hbar} \cdot d\mathbf{r}'. \tag{2.12}$$

One reason for this factor of $\hbar$ is that the product of position and momentum has dimensions of angular momentum (or action). The second reason is the de Broglie formula $p = h/\lambda = 2\pi\hbar/\lambda = \hbar k$. The commutation relation (2.11) becomes:

$$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}.$$

A finite translation can be seen as an infinite number of infinitesimal translations. Suppose $\hat{\mathcal{T}}(\Delta x'\hat{\mathbf{x}})|\mathbf{r}'\rangle = |\mathbf{r}' + \Delta x'\hat{\mathbf{x}}\rangle$ denotes a finite translation of Δx in the x-direction. Then if we let $\Delta x/N$ be the infinitesimal, and apply it N times,

$$\hat{\mathcal{T}}(\Delta x'\hat{\mathbf{x}}) = \lim_{N\to\infty}\left(1 - \frac{i\hat{p}_x\Delta x'}{N\hbar}\right)^N = e^{-i\hat{p}_x\Delta x'/\hbar}.$$

Physically, successive translations in different directions commute,

$$\hat{\mathcal{T}}(dy'\hat{\mathbf{y}})\hat{\mathcal{T}}(dx'\hat{\mathbf{x}}) = \hat{\mathcal{T}}(dx'\hat{\mathbf{x}})\hat{\mathcal{T}}(dy'\hat{\mathbf{y}}) = \hat{\mathcal{T}}(dx'\hat{\mathbf{x}} + dy'\hat{\mathbf{y}}).$$

Writing the commutator up to second order

$$[\hat{\mathcal{T}}(dx'\hat{\mathbf{x}}), \hat{\mathcal{T}}(dy'\hat{\mathbf{y}})] = [(1 - i\hat{p}_x\, dx'/\hbar), (1 - i\hat{p}_y\, dy'/\hbar)] = -\frac{[\hat{p}_x, \hat{p}_y]\, dx'dy'}{\hbar^2}.$$

Because translations in different directions commute (and of course they commute in the same direction), this requires $[\hat{p}_x, \hat{p}_y] = 0$, or more generally,

$$[p_i, p_j] = 0.$$

This implies that p_x, p_y, and p_z are mutually compatible observables. There exist eigenstates $|\mathbf{p}'\rangle$ such that $\hat{\mathbf{p}}|\mathbf{p}'\rangle = \mathbf{p}'|\mathbf{p}'\rangle$. Meanwhile, infinitesimal translation operators share these eigenstates,

$$\hat{\mathcal{T}}(d\mathbf{r}')|\mathbf{p}'\rangle = \left(1 - \frac{i\hat{\mathbf{p}} \cdot d\mathbf{r}'}{\hbar}\right)|\mathbf{p}'\rangle = \left(1 - \frac{i\mathbf{p}' \cdot d\mathbf{r}'}{\hbar}\right)|\mathbf{p}'\rangle.$$

2.7.3   The Canonical Commutation Relation

Now we found three commutation relations

$$[\hat{x}_i, \hat{x}_j] = 0, \quad [\hat{p}_i, \hat{p}_j] = 0, \quad [\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij}. \tag{2.13}$$

They are known as the **canonical commutation relations**. The classical analog of commutator is the Poisson brackets. For two functions $A(q_i, p_i)$ and $B(q_i, p_i)$, their Poisson bracket is defined as

$$\{A, B\} \equiv \sum_i \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right).$$

It turns out that in quantum mechanics, if all relations involving the Poisson bracket $\{\cdot, \cdot\}$ turns into $[\cdot, \cdot]/i\hbar$ and with observables to corresponding operators, the relations still hold. Such a rule is sometimes called Dirac's quantization rule. For example,

$$\{x_i, p_j\} = \delta_{ij} \quad \Longrightarrow \quad [\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij}.$$

More examples include

$$
\begin{aligned}
\{A, A\} &= 0 & \Longrightarrow \quad [\hat{A}, \hat{A}] &= 0, \\
\{A, B\} &= -\{B, A\} & \Longrightarrow \quad [\hat{A}, \hat{B}] &= -[\hat{B}, \hat{A}], \\
\{A, c\} &= 0 & \Longrightarrow \quad [\hat{A}, c] &= 0 \quad \text{for} \quad \text{constant } c, \\
\{A + B, C\} &= \{A, C\} + \{B, C\} & \Longrightarrow \quad [\hat{A} + \hat{B}, \hat{C}] &= [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}], \\
\{A, BC\} &= \{A, B\}C + B\{A, C\} & \Longrightarrow \quad [\hat{A}, \hat{B}\hat{C}] &= [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}], \\
\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} &= 0 & \Longrightarrow \quad [\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] &= 0.
\end{aligned}
$$

The last relation is known as the **Jacobi identity**.

2.8   Generalized Statistical Interpretation

The **generalized statistical interpretation** is the foundation of quantum mechanics, just like the Schrödinger equation.

Theorem 2.7. Generalized Statistical Interpretation

It is certain to get one of the eigenvalues of the Hermitian operator $\hat{Q}(x, -i\hbar\partial_x)$ when measuring an observable $Q(x, p)$ on a particle in the state $\Psi(x, t)$. For discrete spectrum, the probability of getting an eigenvalue q_n associated with the orthonormalized eigenfunction $f_n(x)$ is

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

For continuous spectrum with eigenvalue $q(z)$ and eigenfunction $f_z(x)$, the probability of getting a result in the range dz is

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

After one measures and obtains an eigenvalue q_n, the state of the system collapses to the corresponding eigenstate f_n.

To view this in a more direct way, assume that the spectrum is discrete (as it is easy to generalized into continuous one). The eigenfunctions are complete, which means the wave function can be written as the linear combination of them,

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

The coefficients are given by Fourier's trick:

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

Essentially, the coefficient c_n (or more precisely, $|c_n|^2$), tells how much f_n is contained in Ψ. The sum of all $|c_n|^2$ is one:

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

which can be shown with wave function normalization,

$$1 = \langle \Psi | \Psi \rangle = \left\langle \left(\sum_m c_m f_m \right) \middle| \left(\sum_n c_n f_n \right) \right\rangle = \sum_m \sum_n c_m^* c_n \langle f_m | f_n \rangle = \sum_m \sum_n c_m^* c_n \delta_{mn} = \sum_n c_n^* c_n = \sum_n |c_n|^2.$$

The expectation value of Q should be

$$\langle Q \rangle = \langle \Psi | \hat{Q} \Psi \rangle = \left\langle \left(\sum_m c_m f_m \right) \middle| \left(\hat{Q} \sum_n c_n f_n \right) \right\rangle = \sum_m \sum_n c_m^* c_n q_n \langle f_m | f_n \rangle = \sum_m \sum_n c_m^* c_n q_n \delta_{mn} = \sum_n q_n |c_n|^2.$$

From the equation $\langle Q \rangle = \sum_n q_n |c_n|^2$ and the definition of expectation value, we can recognize $|c_n|^2$ to be the probability of yielding q_n when measuring Q in the state Ψ. We will generalize these statements to continuous spectrum by considering the following two examples: position and momentum measurement.

Example 2.11. Position measurement

It is known that the eigenvalue of the position operator x is a real number y, with corresponding eigenfunction $g_y(x) = \delta(x - y)$. The coefficient $c(y)$ is given by

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

According to the generalized statistical interpretation, the probability of observing the particle in range dy is $|c(y)|^2 \, dy$, or $|\Psi(y, t)|^2 \, dy$. This is just how we interpret the wave function at the beginning!

Example 2.12. Momentum measurement: the momentum space

The eigenvalue of the momentum operator $-i\hbar \partial_x$ is $f_p(x) = e^{ipx/\hbar}/\sqrt{2\pi\hbar}$. The coefficient $c(p)$ is

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

The quantity $\Phi(p, t)$ is important; we call it the **momentum space wave function**. By Plancherel's theorem, the position space wave function $\Psi(x, t)$ and $\Phi(p, t)$ are Fourier transform and inverse Fourier transform of each other,

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \Psi(x, t) \, dx \quad \Longleftrightarrow \quad \Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ipx/\hbar} \Phi(p, t) \, dp. \tag{2.14}$$

According to the generalized statistical interpretation, the probability of measuring the momentum of the particle in range dp is $|\Phi(p, t)|^2 \, dp$. The discussion of $\Phi(p, t)$, the position and momentum operator in momentum space are presented in Appendix B.5.2.

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3 QUANTUM DYNAMICS

3.1 Time Evolution and the Schrödinger Equation

3.1.1 The Time-Evolution Operator

Consider a system represented by a state vector $|\psi(t_0)\rangle$ at time t_0. In general, it evolves with time and become a new state $|\psi(t)\rangle$ at time $t > t_0$. We require that $\lim_{t \to t_0} |\psi(t)\rangle = |\psi(t_0)\rangle$. The evolution of the state is related to the **time-evolution operator** $U(t, t_0)$:

$$|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle.$$

The time-evolution operator is very similar to translation operators $\mathcal{T}$, because time evolution can be seen as a translation in time. To see this, here are some properties of the time-evolution operator:

1. Unitarity: the evolved state conserves probability,

   $$1 = \langle\psi(t)|\psi(t)\rangle = \langle\psi(t_0)|U^\dagger(t, t_0)U(t, t_0)|\psi(t_0)\rangle = \langle\psi(t_0)|\psi(t_0)\rangle \implies U^\dagger(t, t_0)U(t, t_0) = 1.$$

2. Composition property (like successive translation): the time evolution from t_0 to t_2 is the same as that first from t_0 to t_1 and then from t_1 to t_2,

   $$U(t_2, t_0) = U(t_2, t_1)U(t_1, t_0), \quad t_2 > t_1 > t_0.$$

3. For an infinitesimal time-evolution operator $U(t_0 + dt, t_0)$, its effect reduces to the identity when $dt \to 0$,

   $$\lim_{dt \to 0} U(t_0 + dt, t_0) = 1.$$

To satisfy all these properties, the infinitesimal time-evolution operator should look like

$$U(t_0 + dt, t_0) = 1 - i\Omega \, dt,$$

where Ω is a Hermitian operator. In general, Ω does not depend on time. If it does, then it should be evaluated as $t = t_0$ in the time-evolution operator. To find out what Ω is, note that it should have dimensions of frequency. In classical mechanics, we know that the Hamiltonian is the generator of time evolution, so we propose that $\Omega = H/\hbar$ to match both the dimension and its classical counterpart. (This is also similar to the fact that momentum is the generator of translation.) Thus, the infinitesimal time-evolution operator can be expressed as

$$U(t_0 + dt, t_0) = 1 - \frac{iH}{\hbar} \, dt. \tag{3.1}$$

3.1.2 The Schrödinger Equation

Using the composition property of the time-evolution operator, we can write

$$U(t + dt, t_0) = U(t + dt, t)U(t, t_0) = \left(1 - \frac{iH \, dt}{\hbar}\right)U(t, t_0).$$

Rearranging some terms,

$$U(t + dt, t_0) - U(t, t_0) = -i\left(\frac{H}{\hbar}\right) dt \, U(t, t_0).$$

Taking the limit $dt \to 0$, we get the **Schrödinger equation for the time-evolution operator**:

$$\boxed{i\hbar \frac{\partial}{\partial t} U(t, t_0) = HU(t, t_0).} \tag{3.2}$$

If we let this equation act on an initial state vector $|\psi(t_0)\rangle$ that does not depend on time,

$$i\hbar\frac{\partial}{\partial t}U(t,t_0)|\psi(t_0)\rangle = HU(t,t_0)|\psi(t_0)\rangle \quad \Longrightarrow \quad i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle.$$

This is the usual Schrödinger equation we are familiar with. Previously, we solve the Schrödinger equation for $|\psi(t)\rangle$. Now, if we can solve for $U(t,t_0)$ using (3.2) and know how it acts on $|\psi(t)\rangle$, the state at time t is known. To solve (3.2), there are three cases:

- **Case 1.** If the Hamiltonian operator is independent of time, then the solution to (3.2) is an exponential,

$$U(t,t_0) = e^{-iH(t-t_0)/\hbar}. \tag{3.3}$$

The usual technique for differential equation works here even though H is an operator. This can be proved by expanding $e^{-iH(t-t_0)/\hbar}$ in Taylor series. In this chapter, we shall assume that H is time-independent.

- **Case 2.** If the Hamiltonian operator is time-dependent, but $H(t)$ at different times commute, then we directly solve

$$U(t+dt,t_0) - U(t,t_0) = -i\left(\frac{H}{\hbar}\right)dt\,U(t,t_0) \quad \Longrightarrow \quad \frac{dU}{U} = -\frac{i}{\hbar}H\,dt.$$

Integrating both sides, we can get

$$U(t,t_0) = \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t}dt'\,H(t')\right]. \tag{3.4}$$

If H is time-independent, this reduces to case 1, $U(t,t_0) = e^{-iH(t-t_0)/\hbar}$, as expected.

- **Case 3.** If the Hamiltonian operator is time-dependent and $H(t)$ at different times do not commute, then

$$U(t,t_0) = 1 + \sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^{n}\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\cdots\int_{t_0}^{t_{n-1}}dt_n\,H(t_1)H(t_2)\cdots H(t_n). \tag{3.5}$$

This result is known as the **Dyson series**, developed by F. J. Dyson in quantum field theory. We will not prove this now.

3.1.3 Energy Eigenstates

We would like to find the effect of the time-evolution operator (3.3) on an arbitrary initial state $|\psi\rangle$. Suppose we work in the energy basis $\{|n\rangle\}$, where $|n\rangle$ are eigenstates of the Hamiltonian: $H|n\rangle = E_n|n\rangle$. Using the identity operator, the time-evolution operator can be written as (taking $t_0 = 0$)

$$U(t,0) = \sum_{n'}\sum_{n}|n'\rangle\langle n'|\,e^{-iHt/\hbar}\,|n\rangle\langle n| = \sum_{n,n'}|n'\rangle\langle n'|n\rangle\,e^{-iE_nt/\hbar}\,\langle n| = \sum_{n}|n\rangle\,e^{-iE_nt/\hbar}\,\langle n|.$$

($e^{iE_nt/\hbar}$ is just a number; it commutes with any kets.) If the initial state can be expanded as

$$|\psi(0)\rangle = \sum_{n}|n\rangle\langle n|\psi\rangle = \sum_{n}c_n|n\rangle,$$

when the effect of the time evolution operator is

$$|\psi(t)\rangle = e^{-iHt/\hbar}|\psi(0)\rangle = \sum_{n}|n\rangle\langle n|\psi(0)\rangle\,e^{-iE_nt/\hbar}.$$

Hence the new expansion coefficient becomes $c_n(t) = c_n(0)e^{-iE_nt/\hbar}$, which we already know from the Schrödinger equation using separation of variables. If the initial state is an energy eigenstate $|n'\rangle$, then the evolved state

$$|\psi(t)\rangle = \sum_{n}|n\rangle\langle n|n'\rangle\,e^{-iE_nt/\hbar} = |n'\rangle\,e^{-iE_{n'}t/\hbar}$$

is still an energy eigenstate. This is what we called stationary states in Chapter 1, as we can find that the expectation value of any observable A in stationary states is independent of t: let $|\psi(0)\rangle = |n\rangle$, so $|\psi(t)\rangle = |n\rangle\,e^{-iE_nt/\hbar}$. Then the expectation value of Q is

$$\langle Q\rangle = \langle\psi(t)|Q|\psi(t)\rangle = \langle n|e^{iE_nt/\hbar}Qe^{-iE_nt/\hbar}|n\rangle = \langle n|Q|n\rangle.$$

3.1.4 The Correlation Amplitude

Consider a state $|\psi\rangle$ that changes from $|\psi(0)\rangle$ to $|\psi(t)\rangle = U(t,0)|\psi(0)\rangle$. We are interested in how similar $|\psi(t)\rangle$ is to $|\psi(0)\rangle$. The "similarity" is given by their inner product,

$$C(t) \equiv \langle\psi(0)|\psi(t)\rangle = \langle\psi(0)|U(t,0)|\psi(0)\rangle. \tag{3.6}$$

$C(t)$ is known as the **correlation amplitude**, which measures the correlation between $|\psi\rangle$ at different times. If $|\psi(0)\rangle = |n\rangle$ is an eigenstate of H, then the correlation amplitude is always unity:

$$C(t) = \langle n|U(t,0)|n\rangle = e^{-iE_n t/\hbar}.$$

Physically, it means that stationary states at different times are identical, up to a phase factor that does not affect the probability. More generally, $|\psi\rangle$ is a superposition of $\{|n\rangle\}$. The correlation amplitude generalize to

$$C(t) = \left(\sum_{n'} c_{n'}^* \langle n'|\right)\left(\sum_n c_n e^{-iE_n t/\hbar}|n\rangle\right) = \sum_{n,n'} c_{n'}^* c_n e^{-iE_n t/\hbar}\delta_{nn'} = \sum_n |c_n|^2 e^{-iE_n t/\hbar}.$$

3.2 The Schrödinger versus the Heisenberg Picture

So far all our analysis of states and operators (observables) are in the **Schrödinger picture**, where states evolve with time and operators are time-independent (in general). There is another formulation of quantum mechanics called the **Heisenberg picture**, where states do not evolve with time but operators do.

3.2.1 Unitary Operators

We have encountered two unitary operators U that transform the state: the translation operator $\mathcal{T}(d\mathbf{r})$ and the time-evolution operator $U(t,t_0)$. One important property of a unitary transformation is that they changes states, but not inner products: for $|\alpha\rangle \to U|\alpha\rangle$ and $|\beta\rangle \to U|\beta\rangle$,

$$\langle\alpha|\beta\rangle \to \langle\alpha|U^\dagger U|\beta\rangle = \langle\alpha|\beta\rangle.$$

Then we know how $\langle\alpha|Q|\beta\rangle$ must change when U affect states:

$$\langle\alpha|Q|\beta\rangle \to (\langle\alpha|U^\dagger)Q(U|\beta\rangle) = \langle\alpha|(U^\dagger Q U)|\beta\rangle.$$

The last equality is from associativity, which suggests that there are two ways to approach unitary transformations:

1. $|\alpha\rangle \to U|\alpha\rangle$, with operators unchanged;

2. $Q \to U^\dagger Q U$, with states unchanged.

Now we specify U to be the time-evolution operator $U(t,t_0)$. Approach 1 follows the Schrödinger picture, while Approach 2 follows the Heisenberg picture. Again, we set $t_0 = 0$ for convenience, and from (3.3)

$$U(t,0) \equiv U(t) = e^{-iHt/\hbar}.$$

We denote the Schrödinger picture observable by a superscript (S), and the Heisenberg picture observable by (H). The Heisenberg picture observable is related to the Schrödinger picture one by

$$Q^{(H)}(t) \equiv U^\dagger(t)Q^{(S)}U(t). \tag{3.7}$$

At $t = 0$, observables in both pictures are identical, $Q^{(H)}(0) = Q^{(S)}$. In the Heisenberg picture, the state is unchanged after $t = 0$, $|\psi(t)\rangle_H = |\psi(0)\rangle$. In the Schrödinger picture, $|\psi(t)\rangle_S = U(t)|\psi(0)\rangle$. The expectation value $\langle Q\rangle$ is the same in both pictures:

$$\langle\psi(t)|Q^{(S)}|\psi(t)\rangle_S = \langle\psi(0)|U^\dagger Q^{(S)}U|\psi(0)\rangle = \langle\psi(t)|Q^{(H)}(t)|\psi(t)\rangle_H.$$

3.2.2 The Heisenberg Equation of Motion

Assuming that an observable $Q^{(S)}$ (in the Schrödinger picture) does not depend explicitly on time. In the Heisenberg picture, its time-derivative, using (3.7), is

$$\frac{dQ^{(H)}}{dt} = \frac{\partial U^\dagger}{\partial t} Q^{(S)} U + U^\dagger Q^{(S)} \frac{\partial U}{\partial t} = -\frac{1}{i\hbar} U^\dagger H Q^{(S)} U + \frac{1}{i\hbar} U^\dagger Q^{(S)} H U,$$

where (3.2) is used. Inserting the identity $1 = UU^\dagger$ in the two terms,

$$\frac{dQ^{(H)}}{dt} = -\frac{1}{i\hbar} U^\dagger H U U^\dagger Q^{(S)} U + \frac{1}{i\hbar} U^\dagger Q^{(S)} U U^\dagger H U = \frac{1}{i\hbar} [Q^{(H)}, U^\dagger H U].$$

Now the operator $U^\dagger H U$ can be seen as the Hamiltonian operator in the Heisenberg picture. However, we assume that $U = e^{-iHt/\hbar}$, which obviously commutes with H, so

$$H^{(H)} = U^\dagger H U = U^\dagger U H = H.$$

The Hamiltonian is the same in both pictures. Then we obtain

$$\boxed{\frac{dQ^{(H)}}{dt} = \frac{1}{i\hbar} [Q^{(H)}, H].} \tag{3.8}$$

Equation (3.8) is known as the **Heisenberg equation of motion**. It is the analog to the generalized Ehrenfest theorem (2.10) in the Schrödinger picture. Note that the Heisenberg equation of motion obeys Dirac's quantization rule. In classical mechanics, if Q is a function of q_i and p_i but not t explicitly, then it follows the classical equation of motion:

$$\frac{dQ}{dt} = \{Q, H\}.$$

Again, when the Poisson bracket is replaced by the commutator (with a factor of $1/i\hbar$), the classical equation of motion is quantized. This is the relation between the Heisenberg picture and classical mechanics. Below are two examples that we already encountered in wave mechanics, but this time in the Heisenberg picture. Here are two useful commutator formulas:

$$[x_i, f(\mathbf{r}, \mathbf{p})] = i\hbar \frac{\partial f}{\partial p_i}, \quad [p_i, g(\mathbf{r}, \mathbf{p})] = -i\hbar \frac{\partial g}{\partial x_i}.$$

Combining them with (3.8), we obtain

$$\frac{dx_i}{dt} = \frac{\partial H}{\partial p_i}, \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial x_i}, \tag{3.9}$$

which are just Hamilton's equations in classical mechanics.

Example 3.1. The free particle revisited

The Hamiltonian of the free particle is

$$H = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}.$$

Since $[p_i, p_j] = 0$, applying (3.8) to p_i means that

$$\frac{dp_i}{dt} = \frac{1}{i\hbar} [p_i, H] = 0.$$

The momentum of a free particle is conserved, as expected. The rate of change of position is

$$\frac{dx_i}{dt} = \frac{\partial H}{\partial p_i} = \frac{p_i}{m},$$

which is just $\mathbf{p} = m\mathbf{v}$.

Example 3.2. Ehrenfest theorem revisited

A more general Hamiltonian takes the form

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

Applying (3.8) gives

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial x_i} = -\frac{\partial V}{\partial x_i}, \quad \frac{dx_i}{dt} = \frac{\partial H}{\partial p_i} = \frac{p_i}{m}.$$

We can obtain the second time-derivative by using the Heisenberg equation of motion again:

$$\frac{d^2 x_i}{dt^2} = \frac{1}{i\hbar}\left[\frac{dx_i}{dt}, H\right] = \frac{1}{i\hbar}\left[\frac{p_i}{m}, H\right] = \frac{1}{m}\frac{dp_i}{dt}.$$

Combining this with $dp_i/dt = -\partial V/\partial x_i$, we obtain Newton's second law in vectorial form,

$$m\frac{d^2 \mathbf{r}}{dt^2} = -\nabla V(\mathbf{r}).$$

All these operators are in the Heisenberg picture. To get a result that work in all pictures, we take the expectation value (using Heisenberg state $|\psi(t)\rangle_H = |\psi(0)\rangle$ for the Heisenberg picture),

$$m\frac{d^2}{dt^2}\langle \mathbf{r} \rangle = -\langle \nabla V(\mathbf{r}) \rangle.$$

This is the **Ehrenfest theorem**. (It is originally derived in wave mechanics by Ehrenfest in 1927. The derivation in the Heisenberg picture is presented here as an example.)

3.2.3   Basis Vectors

The state vector does not evolve with time in the Heisenberg picture, but the basis vector does. We know that the set of all eigenstates $\{|e_n\rangle\}$ of an observable Q can be used as a basis. The defining eigenvalue equation is

$$Q^{(S)}|e_n\rangle_S = q_n|e_n\rangle_S$$

at $t = 0$. In the Schrödinger picture, Q does not change with time. Thus, the basis vectors $|e_n\rangle_S$ should not change with time either so that this eigenvalue equation at $t = 0$ is satisfied.

In the Heisenberg picture, the operator is time-dependent: $Q^{(H)}(t) = U^\dagger(t)Q^{(S)}U(t)$. We multiply the eigenvalue equation on both sides by $U^\dagger$ on the left,

$$U^\dagger Q^{(S)}|e_n\rangle_S = U^\dagger q_n|e_n\rangle_S = q_n U^\dagger|e_n\rangle_S.$$

Then insert the identity $1 = UU^\dagger$ on the LHS,

$$U^\dagger Q^{(S)}UU^\dagger|e_n\rangle_S = q_n U^\dagger|e_n\rangle_S \quad \Longrightarrow \quad Q^{(H)}(U^\dagger|e_n\rangle_S) = q_n(U^\dagger|e_n\rangle_S).$$

This is another eigenvalue equation, which suggests that $U^\dagger|e_n\rangle_S \equiv |e_n\rangle_H$ should be the basis vectors in the Heisenberg picture. Because of $U^\dagger$ instead of U, the basis vectors in the Heisenberg picture transform oppositely as the state vectors in the Schrödinger picture. The equivalence of the Schrödinger and the Heisenberg picture are shown in various aspects:

- The eigenvalues, in both pictures, are always the constant q_n from the eigenvalue equation.

- The expansion coefficients of a state in both pictures are also the same:

$$c_n(t) = \begin{cases} \langle e_n|\psi(t)\rangle_S = \langle e_n|\,(U|\psi(0)\rangle), & \text{[Schrödinger]}, \\ \langle e_n|\psi(t)\rangle_H = (\langle e_n|\,U)|\psi(0)\rangle, & \text{[Heisenberg]}. \end{cases}$$

In the language of linear algebra, no matter we rotate the state vector by an angle θ or rotate the basis vector by an angle $-\theta$, the cosine of the angle between them is the same.

- The spectral decomposition (2.7) is also consistent in the Heisenberg picture:

$$Q^{(H)}(t) = \sum_n q_n |e_n\rangle\langle e_n|_H = \sum_n q_n U^\dagger |e_n\rangle\langle e_n| U = U^\dagger Q^{(S)} U,$$

which reproduces the definition (3.7).

3.2.4 The Simple Harmonic Oscillator Revisited

It is instructive to work with a concrete example in the Heisenberg picture. We shall choose the harmonic oscillator as an example since we are already familiar with it. We first list out some basic definitions and results of operators in vectorial notation.

- Operators: the ladder operators, number operator, and Hamiltonian

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{ip}{m\omega}\right), \quad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(x - \frac{ip}{m\omega}\right), \quad N = a^\dagger a, \quad H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 = \hbar\omega\left(N + \frac{1}{2}\right).$$

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a), \quad p = i\sqrt{\frac{m\hbar\omega}{2}}(a^\dagger - a).$$

- Commutation relations:

$$[a, a^\dagger] = 1, \quad [N, a] = -a, \quad [N, a^\dagger] = a^\dagger, \quad [H, a] = -\hbar\omega a, \quad [H, a^\dagger] = -\hbar\omega a^\dagger.$$

- Operators acting on eigenstates of H:

$$N|n\rangle = n|n\rangle, \quad H|n\rangle = \left(n + \frac{1}{2}\right)\hbar\omega|n\rangle, \quad a|n\rangle = \sqrt{n}|n-1\rangle, \quad a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle.$$

- Matrix elements:

$$\langle n'|a|n\rangle = \sqrt{n}\,\delta_{n',n-1}, \quad \langle n'|a^\dagger|n\rangle = \sqrt{n+1}\,\delta_{n',n+1},$$

$$\langle n'|x|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}(\sqrt{n+1}\,\delta_{n',n+1} + \sqrt{n}\,\delta_{n',n-1}), \quad \langle n'|p|n\rangle = i\sqrt{\frac{m\hbar\omega}{2}}(\sqrt{n+1}\,\delta_{n',n+1} - \sqrt{n}\,\delta_{n',n-1}).$$

We now study the time-dependent operators x, p, a, and $a^\dagger$. For simplicity, we write operators as $Q^{(H)}(t) \to Q$. By the Heisenberg equation of motion (3.8) or Hamilton's equations (3.9),

$$\frac{dp}{dt} = -\frac{\partial H}{\partial x} = -m\omega^2 x, \quad \frac{dx}{dt} = \frac{\partial H}{\partial p} = \frac{p}{m}, \quad \frac{da}{dt} = \frac{1}{i\hbar}[a, H] = -i\omega a, \quad \frac{da^\dagger}{dt} = \frac{1}{i\hbar}[a^\dagger, H] = i\omega a^\dagger.$$

The number operator and Hamiltonian are time-independent in the Heisenberg picture because $[N, H] = 0$ and $[H, H] = 0$. The (x, p) equations are coupled differential equations, but they are equivalent to $(a, a^\dagger)$ equations, which are uncoupled already. The solutions are

$$a(t) = a(0)e^{-i\omega t}, \quad a^\dagger(t) = a^\dagger(0)e^{i\omega t}$$

In terms of x and p,

$$x(t) + \frac{ip(t)}{m\omega} = x_0 e^{-i\omega t} + \frac{ip_0}{m\omega}e^{-i\omega t}, \quad x(t) - \frac{ip(t)}{m\omega} = x_0 e^{i\omega t} - \frac{ip_0}{m\omega}e^{i\omega t}.$$

Solving this system of equations for $x(t)$ and $p(t)$, we obtain

$$x(t) = x_0\cos\omega t + \frac{p_0}{m\omega}\sin\omega t, \quad p(t) = -m\omega x_0\sin\omega t + p_0\cos\omega t. \tag{3.10}$$

The operators x and p oscillates with frequency ω. For an alternative derivation, see Appendix B.2.3. Though x and p oscillates, their expectation value in any stationary states do not oscillate. In fact, both $\langle x\rangle$ and $\langle p\rangle$ vanish in those energy eigenstates. To obtain oscillations in $\langle x\rangle$ and $\langle p\rangle$, a state constructed with a superposition of energy eigenstates is required. The superposition that most imitates the classical oscillator (oscillating without destroying the shape) are the coherent states discussed in Appendix B.2.2.

3.3 Wave Mechanics in Three Dimensions

3.3.1 The Schrödinger Equation in Three Dimensions

We turn back to the Schrödinger picture and wave mechanics and generalize it to three dimensions. The operator form of the Schrödinger equation is

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t}, \quad \text{where} \quad H = \frac{p^2}{2m} + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V.$$

In quantum mechanics, all we need to do is to replace p_i with operators:

$$p_x \to -i\hbar\partial_x, \quad p_y \to -i\hbar\partial_y, \quad p_z \to -i\hbar\partial_z, \quad \text{or} \quad \mathbf{p} \to -i\hbar\nabla.$$

So the Schrödinger equation in three dimensions is

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}.} \tag{3.11}$$

By replacing the kinetic energy term with Laplacian, our analysis is not restricted to Cartesian coordinates anymore. The wave functions and the potential are now functions of $\mathbf{r}$ and t. If the potential is independent of time, then the time-independent Schrödinger equation and its general solutions are

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \quad \text{with} \quad \Psi(\mathbf{r},t) = \sum_n c_n\psi_n(\mathbf{r})e^{iE_n t/\hbar}.$$

Finally, the probability density of finding a particle is $\rho(\mathbf{r},t) = |\Psi|^2 d^3\mathbf{r}$. The normalization condition requires

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

There are several results in the first three chapters that can be generalized to three-dimensional cases:

- We have the full canonical commutation relations:

$$[r_i, p_j] = -[p_i, r_j] = i\hbar\delta_{ij}, \quad [r_i, r_j] = [p_i, p_j] = 0.$$

- The three-dimensional version of **Ehrenfest theorem** (see proof at Theorem B.2 for one-dimensional version; it is straightforward to generalize to 3 dimensions):

$$\langle\mathbf{p}\rangle = m\frac{d\langle\mathbf{r}\rangle}{dt}, \quad \text{and} \quad \frac{d\langle\mathbf{p}\rangle}{dt} = -\langle\nabla V\rangle.$$

- The probability current in three dimensions is (see derivation in Appendix B.6.5)

$$\mathbf{J}(\mathbf{r},t) = -\frac{i\hbar}{2m}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) = \frac{\hbar}{m}\,\text{Im}[\Psi^*\nabla\Psi]. \tag{3.12}$$

  The continuity equation for probability holds:

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{J} = 0, \quad \text{and} \quad \int \mathbf{J}(\mathbf{r},t)\,d^3\mathbf{r} = \frac{\langle\mathbf{p}\rangle}{m}.$$

- From the canonical commutation relations and generalized uncertainty principle (2.8), we have

$$\sigma_x\sigma_{p_x} \geq \frac{\hbar}{2}, \quad \sigma_y\sigma_{p_y} \geq \frac{\hbar}{2}, \quad \sigma_z\sigma_{p_z} \geq \frac{\hbar}{2}.$$

  Note that there is no restrictions on measuring x and p in different directions. The uncertainty relation holds only for x and p in the same direction.

Here are two examples of one-dimensional potential that are generalized to 3 dimensions: the 3D infinite square well and 3D harmonic oscillator. Degeneracy appears in both cases because they have a lot of symmetry.

Example 3.3. The three-dimensional infinite square well

The three-dimensional infinite square well has the potential

$$V(x, y, z) = \begin{cases} 0, & 0 \le x, y, z \le a; \\ \infty, & \text{otherwise.} \end{cases}$$

(This is also called "particle in a box".) The stationary states can be found using separation of variables. The time-independent Schrödinger equation inside the well is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) = E\psi.$$

Consider the separable solution $\psi(x, y, z) = X(x)Y(y)Z(z)$. Substitute ψ into the Schrödinger equation and divide both sides by $\psi = XYZ$ and $-\hbar^2/2m$,

$$\frac{1}{X}\frac{d^2 X}{dx^2} + \frac{1}{Y}\frac{d^2 Y}{dy^2} + \frac{1}{Z}\frac{d^2 Z}{dz^2} = -\frac{2m}{\hbar^2}E.$$

The RHS is a constant, so each term on the LHS is also a constant. Let the separation constant be k_x^2, k_y^2, and k_z^2,

$$\frac{d^2 X}{dx^2} = -k_x^2 X, \quad \frac{d^2 Y}{dy^2} = -k_y^2 Y, \quad \frac{d^2 Z}{dz^2} = -k_z^2 Z, \quad \text{and} \quad E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2).$$

Now we have reduce a three-dimensional problem to three one-dimensional problems. They are already solved in the 1D infinite square well. The solution is

$$X(x) = A_x \sin\left(\frac{n_x \pi x}{a}\right), \quad Y(y) = A_y \sin\left(\frac{n_y \pi y}{a}\right), \quad Z(z) = A_z \sin\left(\frac{n_z \pi z}{a}\right), \quad k_i = \frac{n_i \pi}{a}.$$

Putting back to $\psi(x, y, z)$ and normalizing, we have the stationary states and their corresponding energies,

$$\psi(x, y, z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right), \quad E = \frac{\pi^2 \hbar^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2),$$

where $n_x, n_y, n_z = 1, 2, 3, \ldots$ In three-dimensional cases, degeneracy starts to appear. For example, the energy is the same for ψ_{112}, ψ_{121}, and ψ_{211}, where the substripts denotes (n_x, n_y, n_z).

Example 3.4. The three-dimensional harmonic oscillator

The three-dimensional harmonic oscillator has a radial potential and a separable potential at the same time:

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

Due to this property, it can solved using separation of variables in both Cartesian and spherical coordinates. We will use Cartesian coordinates to find its stationary states and energies. The time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) + \frac{1}{2}m\omega^2(x^2 + y^2 + z^2)\psi = E\psi.$$

Let $\psi(x, y, z) = X(x)Y(y)Z(z)$. Substitute into the equation and divide both sides by $\psi = XYZ$,

$$\left(-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2 X}{dx^2} + \frac{1}{2}m\omega^2 x^2\right) + \left(-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2 Y}{dy^2} + \frac{1}{2}m\omega^2 y^2\right) + \left(-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2 Z}{dz^2} + \frac{1}{2}m\omega^2 z^2\right) = E.$$

Each bracket on the LHS is a constant. Called them E_x, E_y, and E_z, respectively, and $E_x + E_y + E_z = E$. We then have

$$-\frac{\hbar^2}{2m}\frac{d^2 X}{dx^2} + \frac{1}{2}m\omega^2 x^2 X = E_x X, \quad -\frac{\hbar^2}{2m}\frac{d^2 Y}{dy^2} + \frac{1}{2}m\omega^2 y^2 Y = E_y Y, \quad -\frac{\hbar^2}{2m}\frac{d^2 Z}{dz^2} + \frac{1}{2}m\omega^2 z^2 Z = E_z Z.$$

These are three one-dimensional harmonic oscillators. I am not writing down their stationary states, but their energies are simple,

$$E_x = \left(n_x + \frac{1}{2}\right)\hbar\omega, \quad E_y = \left(n_y + \frac{1}{2}\right)\hbar\omega, \quad E_z = \left(n_z + \frac{1}{2}\right)\hbar\omega \quad \implies \quad E = \left(n + \frac{3}{2}\right)\hbar\omega,$$

where $n \equiv n_x + n_y + n_z$ and $n_x, n_y, n_z = 0, 1, 2, 3, \dots$ The degeneracy of E_n is just the way to sum three non-negative integers to n. Let's say for a particular n, if $n_x = n$, then $n_y = n_z = 0$; there is only one way. If $n_x = n - 1$, then either $n_y = 0, n_z = 1$ or $n_y = 1, n_z = 0$; there are two ways. If $n_x = n - 2$, then $n_y = 0, n_z = 2$, or $n_y = 1, n_z = 1$, or $n_y = 2, n_z = 0$; there are three ways, and so on. The degeneracy is

$$d(n) = 1 + 2 + 3 + \cdots + (n + 1) = \frac{(n+1)(n+2)}{2}.$$

Because the three-dimensional harmonic oscillator also has a radial potential, it can be solved in spherical coordinates. The power series method is presented in Appendix B.2.6.

3.3.2   The Statistical Interpretation

To satisfy $|\Psi(\mathbf{r}, t)|^2 = \rho(\mathbf{r}, t)$, we can write any wave function as

$$\Psi(\mathbf{r}, t) = \sqrt{\rho(\mathbf{r}, t)}\, e^{iS(\mathbf{r}, t)/\hbar},$$

where $S(\mathbf{r}, t)$ is a real function and $\rho > 0$ for a probability density. We are interested in the physical interpretation of S. Let us calculate the probability current in terms of ρ and S. Using (3.12),

$$\Psi^* \nabla \Psi = \sqrt{\rho}\, \nabla \sqrt{\rho} + \frac{i}{\hbar} \rho \nabla S \quad \implies \quad \mathbf{J} = \frac{\hbar}{m} \text{Im}[\Psi^* \nabla \Psi] = \frac{\rho \nabla S}{m}.$$

We see that $\mathbf{J}$ is proportional to ∇S, which contains two types of information: strength and direction. First, spatial variation of the phase of the wave function shows the strength of $\mathbf{J}$. Second, the direction of $\mathbf{J}$ at some point $\mathbf{r}$ is normal to the surface of a constant phase that goes through that point, a property of the gradient.

Example 3.5. The probability current of a plane wave.

Consider a three-dimensional plane wave (a free particle wave function)

$$\Psi(\mathbf{r}, t) = e^{i(\mathbf{p} \cdot \mathbf{x} - Et)/\hbar},$$

where $\mathbf{p}$ is the momentum of the particle. In this case, $S = \mathbf{p} \cdot \mathbf{x} - Et$, and $\nabla S = \mathbf{p}$. Evidently, larger momentum of the particle gives rise to a larger probability flux. In classical mechanics, we know that $\mathbf{p} = m\mathbf{v}$. Now since $\nabla S = \mathbf{p}$, we can define the "velocity" of the particle as $\mathbf{v} \equiv \nabla S/m$. The probability current then becomes $\mathbf{J} = \rho \mathbf{v}$. The continuity equation reads

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0,$$

which is analogous to the one in fluid dynamics when ρ is the mass density, or the one in electrodynamics when ρ is the charge density. However, this cannot be taken too seriously because velocity (or momentum) and position cannot be simultaneously determined in quantum mechanics.

3.3.3   The Classical Limit

Let us see what happens when we plug in $\Psi(\mathbf{r}, t) = \sqrt{\rho}\, e^{iS/\hbar}$ into the Schrödinger equation (3.11)

$$-\frac{\hbar^2}{2m} \nabla^2 \left(\sqrt{\rho}\, e^{iS/\hbar}\right) + V\sqrt{\rho}\, e^{iS/\hbar} = i\hbar \frac{\partial}{\partial t}\left(\sqrt{\rho}\, e^{iS/\hbar}\right).$$

The Laplacian can be calculated as follows:

$$\nabla \Psi = \left(\nabla \sqrt{\rho} + \frac{i}{\hbar} \sqrt{\rho} \nabla S \right) e^{iS/\hbar},$$

$$\nabla^2 \Psi = \nabla \cdot \left[\left(\nabla \sqrt{\rho} + \frac{i}{\hbar} \sqrt{\rho} \nabla S \right) e^{iS/\hbar} \right] = e^{iS/\hbar} \nabla \cdot \left(\nabla \sqrt{\rho} + \frac{i}{\hbar} \sqrt{\rho} \nabla S \right) + \left(\nabla \sqrt{\rho} + \frac{i}{\hbar} \sqrt{\rho} \nabla S \right) \cdot \nabla e^{iS/\hbar}$$

$$= e^{iS/\hbar} \left[\nabla^2 \sqrt{\rho} + \frac{i}{\hbar} (\nabla \sqrt{\rho}) \cdot (\nabla S) + \frac{i}{\hbar} \sqrt{\rho} \nabla^2 S \right] + \left[\frac{i}{\hbar} (\nabla \sqrt{\rho}) \cdot (\nabla S) - \frac{1}{\hbar^2} \sqrt{\rho} |\nabla S|^2 \right] e^{iS/\hbar}$$

Substituting into the Schrödinger equation,

$$-\frac{\hbar^2}{2m} \left[\nabla^2 \sqrt{\rho} + \frac{2i}{\hbar} (\nabla \sqrt{\rho}) \cdot (\nabla S) - \frac{1}{\hbar^2} \sqrt{\rho} |\nabla S|^2 + \frac{i}{\hbar} \sqrt{\rho} \nabla^2 S \right] + V \sqrt{\rho} = i\hbar \left(\frac{\partial \sqrt{\rho}}{\partial t} + \frac{i}{\hbar} \sqrt{\rho} \frac{\partial S}{\partial t} \right).$$

In the classical limit, $\hbar$ can be regarded as a small quantity. Collecting terms to the lowest order in $\hbar$ (in this case, the zeroth order) in the Schrödinger equation, we get a differential equation for S:

$$\boxed{\frac{1}{2m} |\nabla S(\mathbf{r}, t)|^2 + V(\mathbf{r}) + \frac{\partial S(\mathbf{r}, t)}{\partial t} = 0.} \tag{3.13}$$

But this is the **Hamilton-Jacobi equation** in classical mechanics, where $S(\mathbf{r}, t)$ is **Hamilton's principal function**. Thus, in the $\hbar \to 0$ limit, classical mechanics is contained in the Schrödinger equation. For a stationary state, the time-evolution is governed by $e^{-iEt/\hbar}$. This corresponds to the classical system with a constant Hamiltonian. In this system, Hamilton's principal function is separable:

$$S(\mathbf{r}, t) = W(\mathbf{r}) - Et, \tag{3.14}$$

where $W(\mathbf{r})$ is called **Hamilton's characteristic function**. The momentum in the classical Hamilton-Jacobi theory is $\mathbf{p} = \nabla S = \nabla W$, which is again consistent with our result in Example 3.5.

3.4 Propagators and Feynman Path Integrals

3.4.1 Propagators in Wave Mechanics

In the Schrödinger picture, the general state $|\psi\rangle$ can be expressed in the basis of energy eigenstates $\{|n\rangle\}$:

$$|\psi(t)\rangle = e^{-iH(t-t_0)/\hbar} |\psi(t_0)\rangle = e^{-iH(t-t_0)/\hbar} \sum_n |n\rangle \langle n|\psi(t_0)\rangle = \sum_n |n\rangle \langle n|\psi(t_0)\rangle \, e^{-iE_n(t-t_0)/\hbar}.$$

We can obtain the wave function of it by projecting it in the position space,

$$\langle \mathbf{r}|\psi(t)\rangle = \sum_n \langle \mathbf{r}|n\rangle \langle n|\psi(t_0)\rangle \, e^{-iE_n(t-t_0)/\hbar} \quad \Longrightarrow \quad \Psi(\mathbf{r}, t) = \sum_n c_n(t_0) \psi_n(\mathbf{r}) e^{-iE_n(t-t_0)/\hbar},$$

where $\psi_n(\mathbf{r}) = \langle \mathbf{r}|n\rangle$ and $|\mathbf{r}\rangle$ are eigenstates of the position operator $\mathbf{r}$. The coefficients $c_n(t_0)$ can be obtained by

$$\langle n|\psi(t_0)\rangle = \int d^3\mathbf{r} \, \langle n|\mathbf{r}\rangle \langle \mathbf{r}|\psi(t_0)\rangle, \quad \text{or} \quad c_n(t_0) = \int d^3\mathbf{r} \, \psi_n^*(\mathbf{r}) \Psi(\mathbf{r}, t),$$

which is our usual Fourier's trick. We can combine all of these to write the wave function as

$$\Psi(\mathbf{r}, t) = \sum_n \langle \mathbf{r}|n\rangle \left[\int d^3\mathbf{r}' \, \langle n|\mathbf{r}'\rangle \langle \mathbf{r}'|\psi(t_0)\rangle \right] e^{-iE_n(t-t_0)/\hbar} = \int d^3\mathbf{r}' \sum_n \langle \mathbf{r}|n\rangle \langle n|\mathbf{r}'\rangle \, e^{-iE_n(t-t_0)/\hbar} \Psi(\mathbf{r}', t) \equiv \int d^3\mathbf{r}' \, K(\mathbf{r}, t; \mathbf{r}', t_0) \Psi(\mathbf{r}', t_0),$$

where the quantity

$$K(\mathbf{r}, t; \mathbf{r}', t_0) \equiv \sum_n \langle \mathbf{r}|n\rangle \langle n|\mathbf{r}'\rangle \, e^{-iE_n(t-t_0)/\hbar} \tag{3.15}$$

is called the **propagator** in wave mechanics. Alternatively, the inner products in (3.15) are wave functions in the position space,

$$K(\mathbf{r}, t; \mathbf{r}', t_0) = \sum_n \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') e^{-iE_n(t-t_0)/\hbar}. \tag{3.16}$$

There are several properties of the propagator:

1. The propagator depends only on the potential V in the Hamiltonian which determines $|n\rangle$, but not on the initial wave function. The time evolution of the wave function is predicted if both $K(\mathbf{r}, t; \mathbf{r}', t_0)$ and $\psi(\mathbf{r}', t_0)$ are known. This means Schrödinger's wave mechanics is a perfectly causal theory.

2. The propagator solves the Schrödinger equation (3.11) in $\mathbf{r}$ and t, with $\mathbf{r}'$ and t_0 held constant. This is because $\langle \mathbf{r}|n\rangle = \psi_n(\mathbf{r})$ with the time dependence factor $e^{-iE_n t/\hbar}$ solves the time-dependent Schrödinger equation, and the propagator is just a superposition of them.

3. When $t \to t_0$, the propagator reduces to the Dirac orthonormality:

$$\lim_{t \to t_0} K(\mathbf{r}, t; \mathbf{r}', t_0) = \sum_n \langle \mathbf{r}|n\rangle\langle n|\mathbf{r}'\rangle = \langle \mathbf{r}|\mathbf{r}'\rangle = \delta^3(\mathbf{r} - \mathbf{r}').$$

From (3.15),

$$K(\mathbf{r}, t; \mathbf{r}', t_0) = \sum_n \langle \mathbf{r}|e^{-iH(t-t_0)/\hbar}|n\rangle\langle n|\mathbf{r}'\rangle.$$

Invoking the identity operator $1 = \sum_n |n\rangle\langle n|$, it is more convenient to express the propagator as

$$K(\mathbf{r}, t; \mathbf{r}', t_0) = \langle \mathbf{r}|e^{-iH(t-t_0)/\hbar}|\mathbf{r}'\rangle = \langle \mathbf{r}|U(t, t_0)|\mathbf{r}'\rangle. \tag{3.17}$$

Theorem 3.1. Propagator as a Green's function

The propagator (3.15), with the boundary condition $K(\mathbf{r}, t; \mathbf{r}', t_0) = 0$ for $t < t_0$, is the Green's function for the time-dependent Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) - i\hbar\frac{\partial}{\partial t}\right] K(\mathbf{r}, t; \mathbf{r}', t_0) = -i\hbar\delta^3(\mathbf{r} - \mathbf{r}')\delta(t - t_0).$$

Proof. The propagator with the boundary condition above can be written as a single function $\tilde{K}$, where

$$\tilde{K}(\mathbf{r}, t; \mathbf{r}', t_0) = K(\mathbf{r}, t; \mathbf{r}', t_0)\theta(t - t_0),$$

where $\theta(t - t_0)$ is the Heaviside step function (mentioned in Appendix B.3.2) with the "step" at $t = t_0$. Let us define the differential operator of the Schrödinger equation:

$$\hat{\mathcal{S}} \equiv -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) - i\hbar\frac{\partial}{\partial t}.$$

We already know that ordinary propagator K without the boundary condition solves the Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) - i\hbar\frac{\partial}{\partial t}\right] K(\mathbf{r}, t; \mathbf{r}', t_0) = \hat{\mathcal{S}} K(\mathbf{r}, t; \mathbf{r}', t_0) = 0.$$

However, the boundary condition provides a discontinuity via the step function, so when $\hat{\mathcal{S}}$ acts on $\tilde{K}$,

$$\hat{\mathcal{S}}\tilde{K}(\mathbf{r}, t; \mathbf{r}', t_0) = \theta(t - t_0)\underbrace{\hat{\mathcal{S}}K(\mathbf{r}, t; \mathbf{r}', t_0)}_{} - i\hbar K(\mathbf{r}, t; \mathbf{r}', t_0)\frac{\partial}{\partial t}\theta(t - t_0) = -i\hbar K(\mathbf{r}, t; \mathbf{r}', t_0)\frac{\partial}{\partial t}(t - t_0).$$

The derivative of the step function is the delta function, $\partial\theta(t - t_0)/\partial t = \delta(t - t_0)$, so

$$\hat{\mathcal{S}}\tilde{K}(\mathbf{r}, t; \mathbf{r}', t_0) = -i\hbar K(\mathbf{r}, t; \mathbf{r}', t_0)\delta(t - t_0).$$

By the property of the delta function, $K(\mathbf{r}, t; \mathbf{r}', t_0)\delta(t - t_0) = K(\mathbf{r}, t_0; \mathbf{r}', t_0)$. Meanwhile, from the property 3 of the propagator, we know that $K(\mathbf{r}, t_0; \mathbf{r}', t_0) = \delta^3(\mathbf{r} - \mathbf{r}')$. Therefore,

$$\hat{\mathcal{S}}\tilde{K}(\mathbf{r}, t; \mathbf{r}', t_0) = -i\hbar\delta^3(\mathbf{r} - \mathbf{r}')\delta(t - t_0).$$

$\square$

Now we shall see some examples of the propagator when $V(\mathbf{r})$ is specified.

Example 3.6. The free particle propagator

Consider the free particle in one-dimension, $V(x) = 0$ everywhere. The eigenstates of H are simultaneous eigenstates of the momentum, with the energy eigenvalue purely kinetic. According to Example 2.9, the momentum eigenstates are

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}, \quad \text{with} \quad E_p = \frac{p^2}{2m}.$$

Equation (3.16) refers to the propagator as the sum of discrete n, but the free particle has a continuous spectra, so the sum turns to an integral over p,

$$K(x,t;x',t_0) = \int_{-\infty}^{\infty} dp\, f_p(x) f_p^*(x') e^{-iE_p(t-t_0)/\hbar} = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp\, e^{ip(x-x')/\hbar - ip^2(t-t_0)/2m\hbar}.$$

This integral can be evaluated by completing the square in the exponent using $\int e^{-(ax^2+bx)} dx = \sqrt{\pi/a}\, e^{b^2/4a}$. The result is

$$K(x,t;x',t_0) = \sqrt{\frac{m}{2\pi i\hbar(t-t_0)}}\, e^{im(x-x')^2/2\hbar(t-t_0)}. \tag{3.18}$$

Example 3.7. The harmonic oscillator propagator

The one-dimensional harmonic oscillator has discrete energy eigenstates (1.27)

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}, \quad \xi = \sqrt{\frac{m\omega}{\hbar}} x, \quad E_n = \left(n + \frac{1}{2}\right)\hbar\omega.$$

Though the energy E_n are simple, the eigenstates $\psi_n(x)$ involve Hermite polynomials and Gaussians, which are not very easy to deal with. The propagator of the harmonic oscillator is:

$$K(x,t;x',t_0) = \sqrt{\frac{m\omega}{2\pi i\hbar \sin[\omega(t-t_0)]}} \exp\left\{\frac{im\omega}{2\hbar \sin[\omega(t-t_0)]}[(x^2 + x'^2)\cos[\omega(t-t_0)] - 2xx']\right\}. \tag{3.19}$$

Appendix B.2.4 presents a detailed method using ladder operators to find the propagator. Even though the propagator is ugly, we can still see that it is a periodic function of t with frequency ω, or period $2\pi/\omega$. This means $K(x, t_0 + 2n\pi/\omega; x', t_0) = K(x, t_0; x', t_0) = \delta(x - x')$: the wave function $\Psi(\mathbf{r}, t)$ returns to its original state $\Psi(\mathbf{r}, t_0)$ once every $2\pi/\omega$. Taking the limit $\omega \to 0$ (no potential), we can recover the free particle propagator (3.18).

Here are two integrals of the propagator to study. For simplicity, we set $t_0 = 0$. The first one is the integral of $K(\mathbf{r}, t; \mathbf{r}', t_0)$ with $\mathbf{r} = \mathbf{r}'$: by (3.15),

$$G(t) \equiv \int d^3\mathbf{r}'\, K(\mathbf{r}', t; \mathbf{r}', 0) = \int d^3\mathbf{r}' \sum_n |\langle \mathbf{r}'|n\rangle|^2 e^{-iE_n t/\hbar} = \sum_n e^{-iE_n t/\hbar}. \tag{3.20}$$

This is the trace of the time-evolution operator in the position-representation if we use (3.17). But Trace is an representation-independent quantity, so is $G(t)$—we can evaluate it in any representation. The quantity (3.20) looks a lot like the partition function in statistical mechanics if we define $\beta = it/\hbar$, and

$$G(t) = \sum_n e^{-\beta E_n} \equiv Z.$$

The second integral is the Laplace transform of $G(t)$:

$$\tilde{G}(E) = -\frac{i}{\hbar} \int_0^\infty dt\, G(t) e^{iEt/\hbar} = -\frac{i}{\hbar} \int_0^\infty dt \sum_n e^{-iE_n t/\hbar} e^{iEt/\hbar} = -\frac{i}{\hbar} \sum_n \frac{\hbar}{i(E - E_n)} e^{i(E-E_n)t/\hbar}\Big|_0^\infty.$$

This integral cannot be evaluated if the integrand is purely oscillatory. Nonetheless, if we let $E \to E + i\epsilon$, where ϵ is small, then in the limit $\epsilon \to 0$,

$$\tilde{G}(E) = \sum_n \frac{1}{(E - E_n) + i\epsilon} e^{-\epsilon t/\hbar} e^{i(E-E_n)t/\hbar}\Big|_0^\infty = \sum_n \frac{1}{E - E_n}. \tag{3.21}$$

In this case, in the complex plane of E, the spectrum E_n are simple poles of $\tilde{G}(E)$. Studying the analytic properties of $\tilde{G}(E)$ gives information about E_n.

3.4.2 The Transition Amplitude

Consider an eigenstate $|q\rangle = |\psi(t_0)\rangle$ of an observable Q. At some later time $t > t_0$, it is at a state $|\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle$, which may not be an eigenstate of Q anymore. We can take the inner product of $|\psi(t)\rangle$ with another eigenstate $|q'\rangle$ to get the **transition amplitude** from $|q\rangle$ to $|q'\rangle$:

$$\langle q'|\psi(t)\rangle = \langle q'|U(t,t_0)|q\rangle \tag{3.22}$$

The transition amplitude tells us how much of $|q\rangle$, after some time, is contained in a (not necessarily the same) eigenstate $|q'\rangle$.

Recall that basis vectors in the Heisenberg picture evolve oppositely with time, $|e_n\rangle_H = U^\dagger|e_n\rangle_S$. We define the position eigenbasis in the Heisenberg picture to be $|\mathbf{r},t\rangle \equiv U^\dagger(t)|\mathbf{r}\rangle = e^{iHt/\hbar}|\mathbf{r}\rangle$. Then from the definition of the propagator (3.17),

$$K(\mathbf{r},t;\mathbf{r}',t_0) = \langle \mathbf{r}|e^{-iHt}e^{iHt_0}|\mathbf{r}'\rangle \equiv \langle \mathbf{r},t|\mathbf{r}',t_0\rangle \tag{3.23}$$

in the Heisenberg picture. The propagator then can be seen as a transition amplitude for a state in $|\mathbf{r}'\rangle$, to a new position $|\mathbf{r}\rangle$. Physically, it is the amplitude of a particle well-localized at a spacetime coordinate $(\mathbf{r}',t_0)$ to another coodinate $(\mathbf{r},t)$.

For a more symmetric notation, we shall write $|\mathbf{r}',t_0\rangle \to |\mathbf{r}',t'\rangle$, because there is nothing special about t_0. In the Heisenberg picture, we have the identity operator

$$1 = \int d^3\mathbf{r}\,|\mathbf{r},t\rangle\langle \mathbf{r},t| = \int d^3\mathbf{r}'\,|\mathbf{r}',t'\rangle\langle \mathbf{r}',t'|\,.$$

We are allowed to insert them anywhere we like. Then we can explore the **composition property** of the transition amplitude:

$$\langle \mathbf{r}'',t''|\mathbf{r},t\rangle = \int d^3\mathbf{r}'\,\langle \mathbf{r}'',t''|\mathbf{r}',t'\rangle\langle \mathbf{r}',t'|\mathbf{r},t\rangle\,, \quad (t'' > t' > t).$$

This divides the time evolution from t to t'' in two parts: from t to t', and t' to t''. We can of course divide those time intervals into smaller pieces:

$$\langle \mathbf{r}''',t'''|\mathbf{r},t\rangle = \int d^3\mathbf{r}''\int d^3\mathbf{r}'\,\langle \mathbf{r}''',t'''|\mathbf{r}'',t''\rangle\langle \mathbf{r}'',t''|\mathbf{r}',t'\rangle\langle \mathbf{r}',t'|\mathbf{r},t\rangle\,.$$

Feynman, in 1948, suggested that we can divide time intervals into infinitesimal ones: $t' = t + dt$, $t'' = t' + dt$, and so on. This led to a new formulation of quantum mechanics, called the **path integral formulation**.

3.4.3 From Dirac to the Path Integral Formulation

We will consider one-dimensional problems for now and adopt the notation $(x,t) \to (x_1,t_1)$, $(x',t') \to (x_2,t_2)$, $(x'',t'') \to (x_3,t_3)$, etc. There are N intervals between t_1 to t_N, so

$$t_j - t_{j-1} = \delta t = \frac{t_N - t}{N-1}.$$

The composition property of the transition amplitude says

$$\langle x_N,t_N|x_1,t_1\rangle = \int dx_{N-1}\int dx_{N-2}\cdots\int dx_2\,\langle x_N,t_N|x_{N-1},t_{N-1}\rangle\langle x_{N-1},t_{N-1}|x_{N-2},t_{N-2}\rangle\cdots\langle x_2,t_2|x_1,t_1\rangle\,. \tag{3.24}$$

It is a problem involving fixed end points, but infinite number of paths. In classical mechanics, we find the *unique* physical path that extremizes the action, $\delta S = 0$, and Lagrange's equations of motion are obtained. On the contrary, in quantum mechanics, (3.24) is the sum over *all* possible paths in a spacetime coordinate.

Feynman attacks this problem from classical mechanics, inspired by Dirac's paper "The Lagrangian in Quantum Mechanics". In his paper, Dirac remarked that

$$\exp\left[\frac{i}{\hbar}\int_{t_1}^{t_2} dt\,\mathcal{L}_c(x,\dot{x})\right] \quad \text{corresponds to} \quad \langle x_2,t_2|x_1,t_1\rangle\,,$$

where $\mathcal{L}_c$ is the classical Lagrangian, and where the meaning of the phrase "corresponds to" is mysterious.

Here we introduce a new notation of the classical action:

$$S(n, n-1) \equiv \int_{t_{n-1}}^{t_n} dt\, \mathcal{L}_c(x, \dot{x}). \tag{3.25}$$

In this integral, we are evaluating some particular path, not a sum over all possible paths. We want something for $\langle x_N, t_N | x_1, t_1 \rangle$, so the idea is multiply all the exponentials from t_1 to t_N:

$$\prod_{n=2}^{N} \exp\left[\frac{iS(n, n-1)}{\hbar}\right] = \exp\left[\frac{i}{\hbar} \sum_{n=2}^{N} S(n, n-1)\right] = e^{iS(N,1)/\hbar}.$$

This is still not $\langle x_N, t_N | x_1, t_1 \rangle$. We need to integrate over all paths,

$$\langle x_N, t_N | x_1, t_1 \rangle \sim \sum_{\text{all paths}} e^{iS(N,1)/\hbar}.$$

The $\sim$ sign is required because both our reasoning and the result are not precise. First, the dimensions is not correct, as $\langle x_N, t_N | x_1, t_1 \rangle$ should have dimensions of 1/length (from the normalization condition). So let us make $e^{iS/\hbar}$ acquire some weighting factor,

$$\langle x_n, t_n | x_{n-1}, t_{n-1} \rangle = \frac{1}{w(\delta t)} e^{iS(n,n-1)/\hbar}. \tag{3.26}$$

The weighting factor $w(\delta t)$ is assumed to have dimensions of length, and depend only on δt but not $V(x)$. Moreover, we take the limit $\delta t \to 0$, so we can approximate the action as

$$S(n, n-1) = \int_{t_{n-1}}^{t_n} dt \left[\frac{1}{2}m\dot{x}^2 - V(x)\right] = \delta t \left[\frac{1}{2}m\left(\frac{x_n - x_{n-1}}{\delta t}\right)^2 - V\left(\frac{x_n + x_{n-1}}{2}\right)\right].$$

Example 3.8. The free particle transition amplitude

The free particle has $V = 0$. The transition amplitude (3.26) is

$$\langle x_n, t_n | x_{n-1}, t_{n-1} \rangle = \frac{1}{w(\delta t)} e^{im(x_n - x_{n-1})^2/2\hbar\delta t}.$$

Note that the exponential part is the same as the free particle propagator (3.18). When $\delta t \to 0$, the transition amplitude becomes a delta function,

$$\lim_{t_n \to t_{n-1}} \langle x_n, t_n | x_{n-1}, t_{n-1} \rangle = \langle x_n | x_{n-1} \rangle = \delta(x_n - x_{n-1}).$$

According to Equation (B.5), it is known that the delta function is a limit of the Gaussian with standard deviation going to zero:

$$\lim_{\delta t \to 0} \sqrt{\frac{m}{2\pi i\hbar\delta t}} e^{im(x_n - x_{n-1})^2/2\hbar\delta t} = \delta(x_n - x_{n-1}).$$

We can identify the weighting factor to be

$$\frac{1}{w(\delta t)} = \sqrt{\frac{m}{2\pi i\hbar\delta t}}. \tag{3.27}$$

Since we asserted that $\delta(\delta t)$ does not depend on $V(x)$, (3.27) works for all potentials, and

$$\langle x_n, t_n | x_{n-1}, t_{n-1} \rangle = \sqrt{\frac{m}{2\pi i\hbar\delta t}} e^{iS(n,n-1)/\hbar}.$$

The transition amplitude, from t_1 to t_N, is then

$$\langle x_N, t_N | x_1, t_1 \rangle = \lim_{N \to \infty} \left(\frac{m}{2\pi i\hbar\delta t}\right)^{(N-1)/2} \int dx_{N-1} \int dx_{N-2} \cdots \int dx_2 \prod_{n=2}^{N} e^{iS(n,n-1)/\hbar}.$$

If we define an infinite-dimensional integral operator

$$\int_{x_1}^{x_N} \mathcal{D}[x(t)] \equiv \lim_{N \to \infty} \left(\frac{m}{2\pi i \hbar \delta t} \right)^{(N-1)/\hbar} \int dx_{N-1} \int dx_{N-2} \cdots \int dx_2,$$

we can express the transition amplitude compactly as

$$\boxed{\langle x_N, t_N | x_1, t_1 \rangle = \int_{x_1}^{x_N} \mathcal{D}[x(t)] \exp \left[\frac{i}{\hbar} \int_{t_1}^{t_N} dt \, \mathcal{L}_c(x, \dot{x}) \right].} \tag{3.28}$$

This expression is known as **Feynman's path integral**. We will now show that (3.28) is equivalent to the propagator in wave mechanics (3.15) by showing that $\langle x_N, t_N | x_1, t_1 \rangle$ satisfies the Schrödinger equation in the variables (x_N, t_N).

Proof. First,

$$\langle x_N, t_N | x_1, t_1 \rangle = \int dx_{N-1} \, \langle x_N, t_N | x_{N-1}, t_{N-1} \rangle \langle x_{N-1}, t_{N-1} | x_1, t_1 \rangle$$

$$= \int_{-\infty}^{\infty} dx_{N-1} \sqrt{\frac{m}{2\pi i \hbar \delta t}} \exp \left[\frac{im}{2\hbar} \frac{(x_N - x_{N-1})^2}{\delta t} - \frac{iV\delta t}{\hbar} \right] \langle x_{N-1}, t_{N-1} | x_1, t_1 \rangle.$$

Define $\xi = x_N - x_{N-1}$, and let $x_N \to x$ and $t_N \to t + \delta t$,

$$\langle x, t + \delta t | x_1, t_1 \rangle = \sqrt{\frac{m}{2\pi i \hbar \delta t}} \int_{-\infty}^{\infty} d\xi \, \exp \left(\frac{im\xi^2}{2\hbar \delta t} - \frac{iV\delta t}{\hbar} \right) \langle x - \xi, t | x_1, t_1 \rangle.$$

When δt is small, the main contribution to this integral is from $\xi \simeq 0$ as seen from Equation (B.5). Thus, we can expand terms in powers of ξ and δt:

$$\langle x, t | x_1, t_1 \rangle + \delta t \frac{\partial}{\partial t} \langle x, t | x_1, t_1 \rangle \simeq \sqrt{\frac{m}{2\pi i \hbar \delta t}} \int_{-\infty}^{\infty} d\xi \, e^{im\xi^2/2\hbar \delta t} \left(1 - \frac{iV\delta t}{\hbar} + \cdots \right) \left[\langle x, t | x_1, t_1 \rangle + \frac{\xi^2}{2} \frac{\partial^2}{\partial x^2} \langle x, t | x_1, t_1 \rangle + \cdots \right].$$

Note that there is no linear term in ξ because odd powers of ξ makes the integrand odd, and their integrals over all space vanish. There are two useful Gaussian integrals:

$$\int_{-\infty}^{\infty} d\xi \, e^{im\xi^2/2\hbar \delta t} = \sqrt{\frac{m}{2\pi i \hbar \delta t}} \quad \text{and} \quad \int_{-\infty}^{\infty} d\xi \, \xi^2 e^{im\xi^2/2\hbar \delta t} = \sqrt{2\pi} \left(\frac{i\hbar \delta t}{m} \right)^{3/2}.$$

The first integral indicates that the leading term involving $\langle x, t | x_1, t_1 \rangle$ cancel on both sides. To first order, we are left with (using the second integral)

$$\delta t \frac{\partial}{\partial t} \langle x, t | x_1, t_1 \rangle \simeq \sqrt{\frac{m}{2\pi i \hbar \delta t}} \left[\sqrt{2\pi} \left(\frac{i\hbar \delta t}{m} \right)^{3/2} \right] \frac{1}{2} \frac{\partial^2}{\partial x^2} \langle x, t | x_1, t_1 \rangle - \frac{iV\delta t}{\hbar} \langle x, t | x_1, t_1 \rangle.$$

Simplifying both sides, and taking the limit $\delta t \to 0$ so that $\simeq$ becomes an $=$,

$$\delta t \frac{\partial}{\partial t} \langle x, t | x_1, t_1 \rangle = \frac{i\hbar \delta t}{2m} \frac{\partial^2}{\partial x^2} \langle x, t | x_1, t_1 \rangle - \frac{iV\delta t}{\hbar} \langle x, t | x_1, t_1 \rangle.$$

Multiplying both sides by $i\hbar/\delta t$, we arrive at exactly the time-dependent Schrödinger equation for the propagator:

$$i\hbar \frac{\partial}{\partial t} \langle x, t | x_1, t_1 \rangle = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \langle x, t | x_1, t_1 \rangle + V \langle x, t | x_1, t_1 \rangle.$$

$\square$

We are able to use Feynman's path integral to compute $\langle x_n, t_n | x_{n-1}, t_{n-1} \rangle$ and hence the propagators once $V(x)$ is specified. For the harmonic oscillator, for example, see Appendix B.2.5. The path integral formulation is not very useful in non-relativistic quantum mechanics. However, it is a very powerful technique in other fields of physics, such as quantum field theory and statistical mechanics.

3.5 Potentials and Gauge Transformations

3.5.1 Constant Potentials

It is well-known that changing the zero point potential energy, $V(\mathbf{r}) \to V(\mathbf{r}) + V_0$ with V_0 constant, does not affect the physics involved. For example, only the gradient of the potential is involved in Newton's second law: $m\ddot{\mathbf{r}} = -\nabla V$. It turns out that it work the same in quantum mechanics: only the difference in potential is relevant.

We shall work in the Schrödinger picture. Consider two potentials $V(\mathbf{r})$ and $\tilde{V}(\mathbf{r}) = V(\mathbf{r}) + V_0$, or

$$H = \frac{p^2}{2m} + V(\mathbf{r}), \quad \text{and} \quad \tilde{H} = \frac{p^2}{2m} + V(\mathbf{r}) + V_0.$$

Let $|\psi(t)\rangle$ be a state in the potential $V(\mathbf{r})$, and $|\tilde{\psi}(t)\rangle$ be a state in the potential $\tilde{V}(\mathbf{r})$. Also, let both states coincide at t_0: $|\psi(t_0)\rangle = |\tilde{\psi}(t_0)\rangle$. The state $|\tilde{\psi}(t)\rangle$ is governed by the time-evolution operator,

$$|\tilde{\psi}(t)\rangle = e^{-i\tilde{H}(t-t_0)/\hbar}|\tilde{\psi}(t_0)\rangle = e^{-iV_0(t-t_0)/\hbar}e^{-iH(t-t_0)/\hbar}|\psi(t_0)\rangle = e^{-iV_0(t-t_0)/\hbar}|\psi(t)\rangle.$$

The time dependence of the two states differ by only a phase factor. For stationary states, changing $V \to V + V_0$ just means $E \to E + V_0$, which is totally reasonable. In quantum mechanics, measurable quantities are expectation values of observables. We can immediately see that the phase factor $e^{-iV_0(t-t_0)/\hbar}$ disappears when we compute expectation values:

$$\langle \tilde{Q} \rangle = \langle \tilde{\psi}(t)|Q|\tilde{\psi}(t)\rangle = \langle \psi(t)|e^{iV_0(t-t_0)/\hbar}Qe^{-iV_0(t-t_0)/\hbar}|\psi(t)\rangle = \langle \psi(t)|Q|\psi(t)\rangle = \langle Q \rangle.$$

This means adding a constant potential to the original one is a **gauge transformation** in quantum mechanics. Moreover, if the potential $V_0(t)$ is time-dependent but spatially uniform, it changes the phase factor,

$$|\tilde{\psi}(t)\rangle = \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} dt\, V_0(t')\right]|\psi(t)\rangle,$$

but still does not affect expectation values. We can see the time-dependent flat potential $V_0(t)$ as choosing a new zero point energy at each t. However, the potential difference is measurable when the two states interfere at some point and become one single state. The expectation value of the whole state acquires an oscillatory term $\cos(\phi_1 - \phi_2)$, where

$$\phi_1 - \phi_2 = \frac{1}{\hbar}\int_{t_i}^{t_f} dt\, [V_2(t) - V_1(t)].$$

This is an effect special to quantum mechanics. In classical mechanics, $\hbar \to 0$, the oscillation becomes too rapid to be observed, as we can only observe the time-average intensity classically.

3.5.2 Gravity in Quantum Mechanics

In Newtonian gravity, the equation of motion is Newton's second law,

$$m\ddot{\mathbf{r}} = -m\nabla\Phi_g,$$

where Φ_g is the gravitational potential. The mass terms cancel. Because the inertial mass and gravitational mass are numerically equal, it is likely that the mass of an object will cancel in equations in Newtonian gravity.

In quantum mechanics, if we plug in $V = m\Phi_g$ into the Schrödinger equation,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + m\Phi_g\right)\Psi = i\hbar\frac{\partial\Psi}{\partial t} \quad \Longrightarrow \quad \left(-\frac{\hbar^2}{2m^2}\nabla^2 + \Phi_g\right)\Psi = \frac{i\hbar}{m}\frac{\partial\Psi}{\partial t}.$$

Note that $\hbar$ and m always appear in pairs in the form $\hbar/m$. They no longer cancel in the equation. For observable effects, such as expectation values, the Ehrenfest theorem (B.2) gives the answer

$$\frac{d\langle \mathbf{p} \rangle}{dt} = -\langle \nabla V \rangle \quad \Longrightarrow \quad \frac{d^2}{dt^2}\langle \mathbf{r} \rangle = -\nabla\Phi_g.$$

Neither $\hbar$ nor m appears, so this is not special to quantum mechanics. The nontrivial gravitational effect in quantum mechanics is hard to study because gravity is too weak. Readers can search for **gravity-induced quantum inference** to see nontrivial effects

of gravity in quantum mechanics.

3.5.3 Electromagnetism in Quantum Mechanics

Consider the time-independent scalar potential and vector potential, $\phi(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$. They are related to the electric and magnetic fields by

$$\mathbf{E} = -\nabla\phi, \quad \mathbf{B} = \nabla \times \mathbf{A}.$$

In classical electromagnetism, the Hamiltonian of a particle of charge q is

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi. \tag{3.29}$$

In quantum mechanics, both $\phi(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ are functions of the position operator $\mathbf{r}$ of the particle.

The Heisenberg Picture. In the Heisenberg picture, the dynamics of $\mathbf{r}$ is given by (3.9),

$$\frac{dx_i}{dt} = \frac{\partial H}{\partial p_i} = \frac{1}{m}(p_i - qA_i).$$

This is the velocity of the particle, from which we can define the **mechanical momentum**, $\mathbf{\Pi}$, of the particle to be

$$\mathbf{\Pi} \equiv m\frac{d\mathbf{r}}{dt} = \mathbf{p} - q\mathbf{A}. \tag{3.30}$$

We should distinguish (3.30) from the canonical momentum $\mathbf{p}$. The commutator relation of components of the mechanical momentum can be easily obtained. For example, consider the x- and y-component: because $[p_i, p_j] = 0$ and $[A_i, A_j] = 0$,

$$[\Pi_x, \Pi_y] = [p_x - qA_x, p_y - qA_y] = [p_x, p_y] - q([p_x, A_y] + [A_x, p_y]) + q^2[A_i, A_j] = -\frac{q}{c}\left[-i\hbar\frac{\partial A_y}{\partial x} + i\hbar\frac{\partial A_x}{\partial y}\right].$$

The last quantity is the z-component of $\nabla \times \mathbf{A}$, which is just B_z. Thus, the commutation relation for the mechanical momentum is

$$[\Pi_i, \Pi_j] = i\hbar q\epsilon_{ijk}B_k \tag{3.31}$$

We can compute the second-derivative of $\mathbf{r}$ and get the force law: for the x-component for example,

$$\begin{aligned}
m\frac{d^2x}{dt^2} = \frac{d\Pi_x}{dt} &= \frac{1}{i\hbar}[\Pi_x, H] = \frac{1}{2i\hbar m}[\Pi_x, \Pi_x^2 + \Pi_y^2 + \Pi_z^2] + \frac{q}{i\hbar}[\Pi_x, \phi] \\
&= \frac{1}{2i\hbar m}([\Pi_x, \Pi_y]\Pi_y + \Pi_y[\Pi_x, \Pi_y] + [\Pi_x, \Pi_z]\Pi_z + \Pi_z[\Pi_x, \Pi_z]) + \frac{q}{i\hbar}[p_x, \phi] \\
&= \frac{q}{2m}(B_z\Pi_y + \Pi_yB_z - B_y\Pi_z - \Pi_zB_y) - q\frac{\partial\phi}{\partial x}.
\end{aligned}$$

We can switch the mechanical momentum back to velocity using (3.30), $\Pi_i = mv_i$, and

$$m\frac{d^2x}{dt^2} = \frac{q}{2}(B_zv_y + v_yB_z - B_yv_z - v_zB_y) - q\frac{\partial\phi}{\partial x} = \frac{q}{2}[(\mathbf{v}\times\mathbf{B})_x - (\mathbf{B}\times\mathbf{v})_x] - q(\nabla\phi)_x.$$

Recognizing that $-\nabla\phi = \mathbf{E}$, we obtain the **Lorentz force law** in quantum mechanics,

$$m\frac{d^2\mathbf{r}}{dt^2} = q\left[\mathbf{E} + \frac{1}{2}(\mathbf{v}\times\mathbf{B} - \mathbf{B}\times\mathbf{v})\right]. \tag{3.32}$$

This reduces to $m\ddot{\mathbf{r}} = q(\mathbf{E} + \mathbf{v}\times\mathbf{B})$ when $\mathbf{v}$ (or $\mathbf{\Pi}$) commutes with $\mathbf{B}$ in the classical electromagnetism.

The Schrödinger Picture. The Schrödinger equation for a charged particle in ϕ and $\mathbf{A}$ is

$$\frac{1}{2m}\left[(-i\hbar\nabla - q\mathbf{A})^2 + q\phi\right]\Psi = i\hbar\frac{\partial\Psi}{\partial t}.$$

The Hamiltonian has ∇ replaced by $\nabla - iq\mathbf{A}/\hbar$. Note that ∇ acts on both $\mathbf{A}(\mathbf{r})$ and $\Psi(\mathbf{r}, t)$, as there is a square in the Hamiltonian. We still define the probability current via the continuity equation $\dot{\rho} + \nabla \cdot \mathbf{J} = 0$, where $\rho = |\Psi|^2$. This leads to the probability current

(derived in Appendix B.6.6)

$$\mathbf{J} = \frac{\hbar}{m} \operatorname{Im}[\Psi^* \nabla \Psi] - \frac{q\mathbf{A}}{m} |\Psi|^2.$$

This is expected because it is just the ordinary probability current (3.12) with $\nabla \to \nabla - iq\mathbf{A}/\hbar$. When Ψ is written as $\sqrt{\rho}\, e^{iS/\hbar}$, the probability current becomes

$$\mathbf{J} = \frac{\rho}{m} (\nabla S - q\mathbf{A}). \tag{3.33}$$

With the extra term $-q\mathbf{A}|\Psi|^2/m$ in $\mathbf{J}$, its integral over all space turns to

$$\int \mathbf{J}(\mathbf{r}, t)\, d^3\mathbf{r} = \frac{\langle \mathbf{p} \rangle}{m} - \frac{q\langle \mathbf{A} \rangle}{m} = \frac{\langle \mathbf{\Pi} \rangle}{m}.$$

Gauge Transformations. In classical electromagnetism, any electric and magnetic fields that solve Maxwell's equations (including time-dependent ones) can be written as

$$\mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}.$$

One can check that the general gauge transformation of potentials that leaves both $\mathbf{E}$ and $\mathbf{B}$ unchanged has the form

$$\phi \to \phi - \frac{\partial \lambda}{\partial t}, \quad \mathbf{A} \to \mathbf{A} + \nabla \lambda,$$

for any scalar function $\lambda(\mathbf{r}, t)$. In this section, we will work with the gauge transformation $\phi \to \phi$ and $\mathbf{A} \to \mathbf{A} + \nabla \lambda$ only. The classical Hamilton's equations are

$$\frac{dx_i}{dt} = \frac{\partial H}{\partial p_i}, \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial x_i},$$

where H are specified by (3.29). In general, the canonical momentum p_i is not a gauge-invariant quantity, unlike $\mathbf{E}$ and $\mathbf{B}$. On the contrary, the position x_i and $\Pi_i = m\, dx_i/dt$ are gauge-invariant quantities because they specify the physical trajectory of a particle. In other words, $\mathbf{p}$ compensates the change in $\mathbf{A}$ by (3.30) to leave $\mathbf{\Pi}$ unchanged.

Returning to quantum mechanics, we expect that both $\langle \mathbf{r} \rangle$ and $\langle \mathbf{\Pi} \rangle$ are gauge-invariant, while $\langle \mathbf{p} \rangle$ is not. Thus, for a state $|\psi\rangle$ in $\mathbf{A}$ and another state $|\psi\rangle$ in $\tilde{\mathbf{A}} = \mathbf{A} + \nabla \lambda$, we assume that

$$\langle \psi | \mathbf{r} | \psi \rangle = \langle \tilde{\psi} | \mathbf{r} | \tilde{\psi} \rangle, \quad \langle \psi | (\mathbf{p} - q\mathbf{A}) | \psi \rangle = \langle \tilde{\psi} | (\mathbf{p} - q\tilde{\mathbf{A}}) | \tilde{\psi} \rangle, \quad \text{and} \quad \langle \psi | \psi \rangle = \langle \tilde{\psi} | \tilde{\psi} \rangle = 1.$$

Suppose there is an operator $\mathcal{G}$ such that relates $|\tilde{\psi}\rangle = \mathcal{G}|\psi\rangle$. Then our assumptions require $\mathcal{G}$ to satisfy

$$\mathcal{G}^\dagger \mathbf{r} \mathcal{G} = \mathbf{r}, \quad \mathcal{G}^\dagger (\mathbf{p} - q\mathbf{A} - q\nabla \lambda) \mathcal{G} = \mathbf{p} - q\mathbf{A}, \quad \text{and} \quad \mathcal{G}^\dagger \mathcal{G} = 1.$$

We claim that

$$\mathcal{G} = e^{iq\lambda(\mathbf{r})/\hbar} \tag{3.34}$$

meets the conditions.

Proof. The unitary condition $\mathcal{G}^\dagger \mathcal{G} = 1$ is trivial. $\mathcal{G}$ is a function of $\mathbf{r}$, which commutes with $\mathbf{r}$, so $\mathcal{G}^\dagger \mathbf{r} \mathcal{G} = \mathcal{G}^\dagger \mathcal{G} \mathbf{r} = \mathbf{r}$. The condition for $\mathbf{\Pi}$ is also satisfied:

$$\begin{aligned}
\mathcal{G}^\dagger (\mathbf{p} - q\mathbf{A} - q\nabla \lambda) \mathcal{G} &= e^{-iq\lambda/\hbar} (\mathbf{p} - q\mathbf{A} - q\nabla \lambda) e^{iq\lambda/\hbar} \\
&= e^{-iq\lambda/\hbar} [\mathbf{p}, e^{iq\lambda/\hbar}] + e^{-iq\lambda/\hbar} e^{iq\lambda/\hbar} \mathbf{p} - q\mathbf{A} - q\nabla \lambda \\
&= -e^{-iq\lambda/\hbar} [i\hbar \nabla (e^{iq\lambda/\hbar})] + \mathbf{p} - q\mathbf{A} - q\nabla \lambda \\
&= q\nabla \lambda + \mathbf{p} - q\mathbf{A} - q\nabla \lambda \\
&= \mathbf{p} - q\mathbf{A}.
\end{aligned}$$

One can also verify that $\tilde{\Psi}(\mathbf{r}, t) = e^{iq\lambda(\mathbf{r})/\hbar} \Psi(\mathbf{r}, t)$ satisfy the Schrödinger equation with $\tilde{\mathbf{A}} = \mathbf{A} + \nabla \lambda$. The ideas are the same. $\qquad \square$

With an additional phase factor, $\tilde{\Psi}(\mathbf{r}, t) = e^{iq\lambda(\mathbf{r})/\hbar} \Psi(\mathbf{r}, t)$. In terms of ρ and S, the probability density ρ is unchanged, but S is transformed to $S + q\lambda$. Evidently, the probability current (3.33) is gauge-invariant when $S \to S + q\lambda$ and $\mathbf{A} \to \mathbf{A} + \nabla \lambda$, which is also expected.

Example 3.9. Magnetic monopole

Maxwell's equations says that magnetic fields are generated either by moving charges or varying electric fields. The equation $\nabla \cdot \mathbf{B} = 0$ is Maxwell's equation comes from empirical results, so there is no theoretical proof that a magnetic monopole or **magnetic monopole** cannot exist.

Suppose a point magnetic monopole exist, and $\nabla \cdot \mathbf{B} = \mu_0 \rho_M$, analogous to Gauss's law $\nabla \cdot \mathbf{E} = \rho/\epsilon_0$. The constants μ_0 and ϵ_0 are permeability and permittivity of free space, respectively, and $c = 1/\sqrt{\mu_0 \epsilon_0}$. Then there is a "Coulomb's law" for the static magnetic field generated by a magnetic point charge e_M:

$$\mathbf{B} = \frac{\mu_0 e_M}{4\pi r^2} \hat{\mathbf{r}}.$$

Classically, the vector potential $\mathbf{A}$ is often proposed by the divergence-free nature of $\mathbf{B}$: because the divergence of a curl is always zero, so $\nabla \cdot \mathbf{B} = 0$ implies $\mathbf{B} = \nabla \times \mathbf{A}$ for some vector potential $\mathbf{A}$. But now with a magnetic charge, $\nabla \cdot \mathbf{B} = 0$ no longer holds. If we still stick to $\mathbf{B} = \nabla \times \mathbf{A}$, we can propose that the vector potential

$$\mathbf{A} = \frac{\mu_0 e_M (1 - \cos\theta)}{4\pi r \sin\theta} \hat{\boldsymbol{\phi}}$$

does the job. This indeed produces $\mathbf{B} = \mu_0 e_M \hat{\mathbf{r}}/4\pi r^2$, but $\mathbf{A}$ blows up at $\theta = \pi$. Unlike $r = 0$ (where $\mathbf{B}$ also blows up), $\theta = \pi$ is not an allowed singularity for $\mathbf{A}$. In fact, there is no single expression of $\mathbf{A}$ that can produce an inverse-square law while remaining non-singular except at $r = 0$. One may suggest that we can use a combined expression for $\mathbf{A}$:

$$\begin{cases} \mathbf{A}_1 = \dfrac{\mu_0 e_M (1 - \cos\theta)}{4\pi r \sin\theta} \hat{\boldsymbol{\phi}}, & \theta \leq \pi - \epsilon, \\ \mathbf{A}_2 = -\dfrac{\mu_0 e_M (1 + \cos\theta)}{4\pi r \sin\theta} \hat{\boldsymbol{\phi}}, & \theta \geq \epsilon. \end{cases}$$

In other words, $\mathbf{A}_1$ works except inside the cone $\theta = \pi - \epsilon$ around the negative z-axis, while $\mathbf{A}_2$ works except inside the cone $\theta = \epsilon$ around the positive z-axis. The combined $\mathbf{A}_1$ and $\mathbf{A}_2$ gives the correct $\mathbf{B}$ everywhere. Note that there is an overlap region $\epsilon \leq \theta \leq \pi - \epsilon$, where we are allowed to use both $\mathbf{A}_1$ and $\mathbf{A}_2$ to produce the same magnetic field. This means $\mathbf{A}_1$ and $\mathbf{A}_2$ are related by a gauge transformation:

$$\mathbf{A}_2 = \mathbf{A}_1 + \nabla\lambda \quad \Longrightarrow \quad \nabla\lambda = -\frac{\mu_0 e_M}{2\pi r \sin\theta} \hat{\boldsymbol{\phi}}.$$

We can find that (using gradient in spherical coordinates)

$$\lambda(\mathbf{r}) = -\frac{\mu_0 e_M \phi}{2\pi},$$

and the corresponding wave functions for a particle of charge e inside the magnetic field are related by (3.34),

$$\Psi_2 = e^{-i\mu_0 q e_M \phi/2\pi\hbar} \Psi_1.$$

The equator $\theta = \pi/2$ is always contained in the overlapping region. To make physical sense, in spherical coordinates (r, θ, ϕ), both wave functions should satisfy $\Psi(\phi + 2\pi) = \Psi(\phi)$ because $\phi + 2\pi$ and ϕ represent the same azimuthal angle in space. This impose a periodic boundary condition:

$$e^{-i\mu_0 q e_M (2\pi)/2\pi\hbar} = 1 \quad \Longrightarrow \quad \frac{\mu_0 q e_M}{2\pi\hbar} = n, \quad n = 0, \pm 1, \pm 2, \dots$$

With the elementary (electric) charge e, the magnetic charge should come in units of

$$e_M/n = \frac{2\pi\hbar}{\mu_0 e} = \frac{2\pi\epsilon_0 \hbar c^2}{e}.$$

In conclusion, quantum mechanics does not say whether magnetic monopoles exist. It predicts that *if* they exist, the magnitude of magnetic charge must be quantized in terms of other fundamental constants: e, $\hbar$, c, and ϵ_0. Conversely, if magnetic monopoles exist, they may explain why electric charges are quantized.

4 THEORY OF ANGULAR MOMENTUM

4.1 The Schrödinger Equation

4.1.1 Spherical Coordinates

Many potential in the universe is a radial potential. The main goal of this chapter is to solve the hydrogen atom, which also has a potential as a function of radius (from electron to the nucleus). Thus we will use spherical coordinates (r, θ, ϕ). The Laplacian in spherical coordinates is

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

Then the time-independent Schrödinger equation is

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

As usual, we first look for separable solutions: $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$. Put this into the Schrödinger equation,

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

Dividing by RY and multiplying by $-2mr^2/\hbar^2$ on both sides:

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

The first bracket depends only on r, while the second depends only on θ and ϕ, so each must be a constant. It is convenient to let the separation constant be $\ell(\ell + 1)$, where ℓ can be any complex number (for now). We get two equations: (4.1) is the radial part, and (4.2) is the angular part.

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = \ell(\ell + 1); \tag{4.1}$$

$$\frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = -\ell(\ell + 1). \tag{4.2}$$

4.1.2 The Angular Equation

Multiplying the angular equation (4.2) by $Y \sin^2 \theta$,

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

Again, try separation of variables: $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$. Substitute in and divide by $\Theta\Phi$ on both sides,

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

The first term depends only on θ and the second only on ϕ, so each is a constant, which we shall define as m^2. This gives one equation for θ and one for ϕ.

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + \ell(\ell+1)\sin^2\theta = m^2 \quad\Longrightarrow\quad \frac{d}{d\theta}\left(\sin^2\theta\frac{d\Theta}{d\theta}\right) + [\ell(\ell+1)\sin^2\theta - m^2]\Theta = 0; \tag{4.3}$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \quad\Longrightarrow\quad \frac{d^2\Phi}{d\phi^2} = -m^2\Phi. \tag{4.4}$$

The ϕ-equation (4.4) is sometimes called the **azimuthal equation**. Its solution is $\Phi(\phi) = e^{im\phi}$. Here m can be positive or negative, and the integration constant can be absorbed into Θ function. In space, two points are the same if ϕ advances by 2π, so a periodic boundary condition is imposed on Φ,

$$\Phi(\phi + 2\pi) = \Phi(\phi) \quad\text{or}\quad e^{im(\phi+2\pi)} = e^{im\phi}.$$

This means that m is an integer: $m = 0, \pm 1, \pm 2, \pm 3, \dots$ The θ-equation (4.3) is a well-studies equation, called **associated Legendre equation**, in mathematics. The solution is

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

where $P_\ell^m(x)$ is the **associated Legendre polynomials** defined by (assuming $m \geq 0$)

$$P_\ell^m(x) \equiv (-1)^m(1-x^2)^{m/2}\left(\frac{d}{dx}\right)^m P_\ell(x), \quad P_\ell^{-m} = (-1)^m\frac{(\ell-m)!}{(\ell+m)!}P_\ell^m, \tag{4.5}$$

and $P_\ell(x)$ is the ℓth **Legendre polynomial**, defined by the **Rodrigues formula**:

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell. \tag{4.6}$$

(For more information about Legendre polynomials, see Appendix A.2.3 and A.2.4.) Notice that ℓ is a non-negative integer. Also, if $|m| > \ell$, then $P_\ell^m = 0$, so for any given ℓ, there are $(2\ell+1)$ possible values of m:

$$\ell = 0, 1, 2, \dots; \quad m = -\ell, -\ell+1, \dots, -1, 0, 1, \dots, \ell-1, \ell.$$

The volume element in spherical coordinates is $d^3\mathbf{r} = r^2\sin\theta\, dr\, d\theta\, d\phi$. Then the normalization becomes

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

It is convenient to set

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

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

$$\boxed{Y_\ell^m(\theta,\phi) = \epsilon\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}e^{im\phi}P_\ell^m(\cos\theta),} \tag{4.7}$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. Spherical harmonics are mutually orthogonal and complete, so they form a basis for angular wave functions. (See Appendix A.2.5 for more information.) The angular wave function $Y(\theta,\phi)$ works for all spherically symmetric potentials. Historically, ℓ is named **azimuthal quantum number** and m is the **magnetic quantum number**.

4.1.3 The Radial Equation

The spherically symmetric potential, $V(r)$, affects only the radial wave function. The radial part (4.1) is

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

Let $u(r) \equiv rR(r)$ so that $R = u/r$, $dR/dr = [r(du/dr) - u]/r^2$, $(d/dr)[r^2(dR/dr)] = r\, d^2u/dr^2$. Then the equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu. \tag{4.8}$$

This is the **radial equation**. We write it in the same form as the one-dimensional Schrödinger equation, but with the potential replaced by the **effective potential**,

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

The extra term aside from the ordinary potential is the **centrifugal term**. In classical mechanics, this term creates a centrifugal barrier for a particle with nonzero angular momentum, which means that such a particle cannot reach an arbitrarily small radius. The normalization condition becomes

$$\int_0^\infty |R|^2 r^2 \, dr = 1 \implies \int_0^\infty |u|^2 dr = 1.$$

The radial equation (4.8) can be solved once the potential is specified.

4.2 The Hydrogen Atom⋆

By Coulomb's law, the potential energy of an electron attracted by a proton is

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

where e is the elementary charge, and $\epsilon_0 = 8.854 \times 10^{-12}\,\text{kg}^{-1}\,\text{m}^{-3}\,\text{s}^4\,\text{A}^2$ is the permittivity of free space. The radial equation specified by this potential is

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} \right] u = Eu, \tag{4.9}$$

where $m = m_e$ is the mass of the electron. The Coulomb potential admits both bound states and scattering states. The hydrogen atom is represented by bound states. (The bound states by themselves do not form a complete set of wave functions.)

4.2.1 The Radial Wave Function

Define a real parameter $\kappa \equiv \sqrt{-2mE}/\hbar$ and divide (4.9) by E,

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

Make another change of variable $\rho \equiv \kappa r$ and define the constant $\rho_0 \equiv me^2/2\pi\epsilon_0\hbar^2\kappa$ so that

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right] u. \tag{4.10}$$

We will use the similar analytic method as in Section 1.4.2 to solve this equation. First, examine the asymptotic solution.

As $\rho \to \infty$,

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

The second term Be^ρ blows up as $\rho \to \infty$, so $B = 0$. The solution becomes

$$u(\rho) \sim Ae^{-\rho} \quad \text{for large } \rho.$$

As $\rho \to 0$,

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

The second term $D\rho^{-\ell}$ blows up as $\rho \to 0$, so $D = 0$. The solution becomes

$$u(\rho) \sim C\rho^{\ell+1} \quad \text{for small } \rho.$$

These asymptotic behaviors suggest that we can introduce a new function $v(\rho)$ such that

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

Compute the first and second derivative of u in terms of v:

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

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

The radial equation (4.10) in terms of v becomes

$$\rho\frac{d^2v}{d\rho^2} + 2(\ell + 1 - \rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell + 1)]v = 0. \tag{4.11}$$

Applying the power series method: assume the solution $v(\rho)$ to be expressed in power series and the goal is to determine c_j,

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

Differentiating v gives (and changing the dummy index $j \to j + 1$):

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

Insert these expressions into the radial equation (4.11):

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + 2(\ell+1)\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j - 2\sum_{j=0}^{\infty} jc_j\rho^j + [\rho_0 - 2(\ell+1)]\sum_{j=0}^{\infty} c_j\rho^j = 0.$$

For each j, the coefficients of ρ^j must vanish because polynomials are linearly independent. The recursion formula for coefficients c_j is,

$$j(j+1)c_{j+1} + 2(\ell+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(\ell+1)]c_j = 0 \implies c_{j+1} = \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)}c_j.$$

The normalization condition determines the appropriate c_0. The next step is to see the behavior of $v(\rho)$ For large j. For large j, the coefficient becomes

$$c_{j+1} \simeq \frac{2j}{j(j+1)}c_j = \frac{2}{j+1}c_j \implies c_j \simeq \frac{2^j}{j!}c_0.$$

This means

$$v(\rho) \simeq c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!}\rho^j = c_0 e^{2\rho} \quad \text{and} \quad u(\rho) = c_0 \rho^{\ell+1}e^\rho,$$

which blows up at large ρ. Recall that this is exactly the asymptotic behavior we don't want. This indicates that the series must terminate at some integer $j_{\max}$ such that

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

From the recursive formula for c_j, we have

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

Define

$$n \equiv j_{\max} + \ell + 1, \quad \rho_0 = 2n.$$

Here n is known as the **principal quantum number**. Because $j_{\max}$ is a non-negative integer, the azimuthal quantum number ℓ must be an integer less than n: $0 \le \ell \le n-1$. From the definitions $\rho_0 = me^2/2\pi\epsilon_0\hbar^2\kappa$ and $\kappa = \sqrt{-2mE}/\hbar$, we can relate the energy E to ρ_0,

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

The allowed energies are obtained by substituting $\rho_0 = 2n$,

$$\boxed{E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots} \tag{4.12}$$

This is the famous **Bohr formula**, obtained by Bohr with semi-classical physics in 1913. Nonetheless, the Schrödinger equation produces the same result in 1926. Relating κ to E_n,

$$\kappa = \frac{\sqrt{-2mE_n}}{\hbar} = \left(\frac{me^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{n} = \frac{1}{an}, \quad \rho = \frac{r}{an},$$

where

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10}\,\text{m} \tag{4.13}$$

is the **Bohr radius**. With the Bohr radius, the ground state energy E_1 can be written as

$$E_1 = -\frac{e^2}{8\pi\epsilon_0 a} = -\frac{\hbar^2}{2ma^2} = -13.6\,\text{eV}. \tag{4.14}$$

Even though the radial wave function involves $\ell(\ell+1)$, the allowed energies are independent of ℓ. The spatial wave functions for the hydrogen atom are labeled with three quantum numbers (n, ℓ, m).

$$\psi_{nlm}(r, \theta, \phi) = R_{n\ell}(r)Y_\ell^m(\theta, \phi), \quad \text{where} \quad R_{n\ell}(r) = \frac{1}{r}\rho^{\ell+1}e^{-\rho}v(\rho),$$

and $v(\rho)$ is a polynomial of degree $j_{\max} = n - \ell - 1$ whose coefficients are

$$c_{j+1} = \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)}c_j = \frac{2(j+\ell+1-n)}{(j+1)(j+2\ell+2)}c_j.$$

Fortunately, $v(\rho)$ is a well-known function studied in mathematics. It can be written as

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

Here $L_q^p(x)$ is called **associated Laguerre polynomial**, and

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

is the qth **Laguerre polynomial**. For more information about Laguerre polynomials, associated Laguerre polynomials, and radial wave functions $R_{n\ell}$, see Appendix A.2.6, A.2.7, A.2.8, respectively. Finally, the normalized hydrogen wave functions, all in one piece, specified by three quantum numbers (n, ℓ, m), are

$$\boxed{\psi_{n\ell m} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}}\, e^{-r/na}\left(\frac{2r}{na}\right)^\ell \left[L_{n-\ell-1}^{2\ell+1}(2r/na)\right] Y_\ell^m(\theta, \phi).} \tag{4.15}$$

These wave functions are mutually orthogonal for all (n, ℓ, m), but the bound states are not complete,

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

For the first few hydrogen wave functions, see Appendix A.2.9. There are several conclusions that can be drawn from the wave functions:

- All $|\psi_{n\ell m}|^2$ have azimuthal symmetry, i.e. there is no difference in x or y regarding the probability density. They also have parity symmetry about the xy-plane. These results means that $\langle x \rangle = \langle y \rangle = \langle z \rangle = 0$ for *all* states. All $\ell = 0$ states are radially symmetric. As we will see in Section 4.4, they are states with zero angular momentum.

- The expectation values $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$ are nonzero. Particularly, $\langle r^2 \rangle$ is independent of m, but $\langle z^2 \rangle$ has a close connection with m: states with larger $|m|$ have smaller $\langle z^2 \rangle$. Equivalently, states with larger $|m|$ have larger $\langle x^2 \rangle = \langle y^2 \rangle$ (azimuthal symmetry) because $\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$.

4.2.2   The Spectrum of Hydrogen

If a hydrogen is in a stationary state $|n, \ell, m\rangle$, then it *should* stay there forever. However, if a light shines on it, for example, it may undergo **transition** from one state to another. Absorbing a photon typically raises the energy, and emitting a photon lowers the energy. Let's say the electron in a hydrogen atom emits a photon, jumping from an initial state ψ_f to a final state ψ_i. The energy of the photon E_γ can only carry certain values,

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

The **Planck formula** says that $E_\gamma = h\nu$, where ν is the frequency of the photon. The wavelength $\lambda = c/\nu$ of the photon is given by the **Rydberg formula**

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

(4.16)

where

$$R_H \equiv \frac{m_e}{4\pi\hbar^3 c} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \approx 1.097 \times 10^7 \, \text{m}^{-1}$$

is the **Rydberg constant**.

It turns out that the hydrogen wave functions are good wave functions of a **hydrogenic atom** if you vary some constants. A hydrogenic atom consists of a single electron orbiting a nucleus with Z protons. For example, an atom with $Z = 2$ and one electron is an ionized helium. To calculate the energy levels, the Bohr radius, and the Rydberg constant, just replace e^2 with Ze^2 in their formulas. (Note that we do not replace e with Ze because the e^2 factor has one e from the proton, and the other from the electron.) The results are

$$E_n(Z) = Z^2 E_n, \quad a(Z) = \frac{a}{Z}, \quad \text{and} \quad R(Z) = Z^2 R.$$

In practice, we often assume that the proton is infinitely heavy comparing to the electron ($m_p \gg m_e$), and the Rydberg constant R_H becomes R_∞. R_H is slightly smaller than R_∞ (by $\sim 0.1\%$).

4.2.3   Comments

Before we move on to angular momentum, there are a few things to remember from the hydrogen atom:

1. It is definitely not required to remember Legendre polynomials or spherical harmonics, but you need to know the ϕ dependence of the wave function, which is $e^{im\phi}$. And remember that Y_0^0 is a constant.

2. You need to know the limits of ℓ and m since they carry physical meanings as we will discuss in later sections. First, for a given energy level n, the energy does not depend on ℓ even though there are $\ell(\ell+1)$ in the radial equation. The azimuthal quantum number ℓ ranges from 0 to $n-1$ for each n, and the magnetic quantum number m ranges from $-\ell$ to ℓ for each ℓ.

3. From the second point we can know the degeneracy of an energy level E_n: there are $n-1$ possible values for ℓ, and for each ℓ there are $(2\ell + 1)$ possible values for m, so

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

   Later we will know that by Pauli exclusion principle, one can insert two electrons with opposite spins for the same (n, ℓ, m), so the total degeneracy is $2n^2$ instead. This number has significant impact on chemistry.

4. Gravity has the same form of potential energy as the hydrogen atom. Appendix B.6.1 is an interesting discussion of the Earth-Sun system as a gravitational analog to the hydrogen atom.

5. Though hydrogen atom has an ugly wave function, it is the *only* atom with an analytic solution for now. Solving the Schrödinger equation for any other atoms requires either approximation or numerical methods.

4.3   The Rotation Operator

4.3.1   Finite vs. Infinitesimal Rotations

Consider **finite rotations** in three dimensions—rotations of a finite angle ϕ around the x-, y-, and z-axis. It is well known that the 3×3 rotation matrices R_x, R_y, and R_z are given by

$$R_x(\phi) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & -\sin\phi \\ 0 & \sin\phi & \cos\phi \end{bmatrix}, \quad R_y(\phi) = \begin{bmatrix} \cos\phi & 0 & \sin\phi \\ 0 & 1 & 0 \\ -\sin\phi & 0 & \cos\phi \end{bmatrix}, \quad R_z(\phi) = \begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

(4.17)

The rotation of a three-dimensional vector $\mathbf{v}$, around the z-axis, for example, transforms by $\mathbf{v}' = R_z(\phi)\mathbf{v}$. The rotation matrices are orthogonal matrices, $R^T R = R R^T = 1$, which means that they do not change the magnitude of a vector. Finite rotations around different axes do not commute.

Infinitesimal rotations, characterized by an infinitesimal angle $\epsilon \to 0$, can be obtained by expanding the rotation matrices:

$$R_x(\epsilon) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 - \epsilon^2/2 & -\epsilon \\ 0 & \epsilon & 1 - \epsilon^2/2 \end{bmatrix}, \quad R_y(\epsilon) = \begin{bmatrix} 1 - \epsilon^2/2 & 0 & \epsilon \\ 0 & 1 & 0 \\ -\epsilon & 0 & 1 - \epsilon^2/2 \end{bmatrix}, \quad R_z(\epsilon) = \begin{bmatrix} 1 - \epsilon^2/2 & -\epsilon & 0 \\ \epsilon & 1 - \epsilon^2/2 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

where we keep terms up to second order in ϵ. Infinitesimal rotations do commute to first order in ϵ, but not to second order:

$$R_x(\epsilon)R_y(\epsilon) = \begin{bmatrix} 1 - \epsilon^2/2 & 0 & \epsilon \\ \epsilon^2 & 1 - \epsilon^2/2 & -\epsilon \\ -\epsilon & \epsilon & 1 - \epsilon^2/2 \end{bmatrix}, \quad R_y(\epsilon)R_x(\epsilon) = \begin{bmatrix} 1 - \epsilon^2/2 & \epsilon^2 & \epsilon \\ 0 & 1 - \epsilon^2/2 & -\epsilon \\ -\epsilon & \epsilon & 1 - \epsilon^2/2 \end{bmatrix}.$$

More importantly, the commutator of R_x and R_y shows that

$$R_x(\epsilon)R_y(\epsilon) - R_y(\epsilon)R_x(\epsilon) = \begin{bmatrix} 0 & -\epsilon^2 & 0 \\ \epsilon^2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \simeq R_z(\epsilon^2) - 1. \tag{4.18}$$

4.3.2 Fundamental Commutation Relations of Angular Momentum

In quantum mechanics, a physical system is represented by a state vector $|\psi\rangle$. The rotated state, denoted as

$$|\psi\rangle_R = \mathcal{D}(R)|\psi\rangle,$$

is expected to be different from the original state $|\psi\rangle$. ($\mathcal{D}$ for *Drehung*, or rotation, in German.) We want to study $\mathcal{D}(R)$ as an infinitesimal rotation. We have experience in the infinitesimal translation operator (2.12) and infinitesimal time-evolution operator (3.1):

$$\mathcal{T}(d\mathbf{r}') = 1 - \frac{i\mathbf{p}}{\hbar} \cdot d\mathbf{r}', \quad U(t + dt, t_0) = 1 - \frac{iH}{\hbar} dt.$$

Observing the similarity in these operators: the momentum $\mathbf{p}$ is the generator of translation $d\mathbf{r}'$; the Hamiltonian H is the generator of time evolution dt. From classical mechanics, we know that angular momentum is the generator of rotation. Since rotation is characterized by an angle and an axis of rotation, we define the infinitesimal rotation operator to be

$$\mathcal{D}(\hat{\mathbf{n}}, d\phi) = 1 - \frac{i\mathbf{J} \cdot \hat{\mathbf{n}}}{\hbar} d\phi, \tag{4.19}$$

where $\mathbf{J}$ is a Hermitian operator (not to be confused with probability current), $\hat{\mathbf{n}}$ is a unit vector characterizing the axis of rotation, and $d\phi$ is an infinitesimal angle. We will find that $\mathbf{J}$ stands for any type of angular momentum. It can be orbital angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, or spin $\mathbf{S}$, or a combination of them. Because the concept of spin does not have a classical counterpart, we shall take (4.19) as the basic.

As usual, a finite rotation can be seen as adding successive infinitesimal rotations about the same axis. For example, a finite rotation about the z-axis is

$$\mathcal{D}_z(\phi) = \lim_{N \to \infty} \left[1 - \frac{iJ_z\phi}{N\hbar} \right]^N = e^{-iJ_z\phi/\hbar} = 1 - \frac{iJ_z\phi}{\hbar} - \frac{J_z^2\phi^2}{2\hbar^2} + \cdots. \tag{4.20}$$

Now we are in the position to derive the commutation relation for angular momentum. Consider a rotation $\mathcal{D}(\epsilon)$ for a small angle ϵ around the x-axis. Keeping terms up to second order in ϵ, we find that

$$\mathcal{D}_x(\epsilon) = e^{-iJ_x\epsilon/\hbar} \simeq 1 - \frac{iJ_x\epsilon}{\hbar} - \frac{J_x^2\epsilon^2}{2\hbar^2}.$$

In analogous to (4.18), we require $[\mathcal{D}_x(\epsilon), \mathcal{D}_y(\epsilon)] = \mathcal{D}_z(\epsilon^2) - 1$:

$$\left(1 - \frac{iJ_x\epsilon}{\hbar} - \frac{J_x^2\epsilon^2}{2\hbar^2} \right)\left(1 - \frac{iJ_y\epsilon}{\hbar} - \frac{J_y^2\epsilon^2}{2\hbar^2} \right) - \left(1 - \frac{iJ_y\epsilon}{\hbar} - \frac{J_y^2\epsilon^2}{2\hbar^2} \right)\left(1 - \frac{iJ_x\epsilon}{\hbar} - \frac{J_x^2\epsilon^2}{2\hbar^2} \right) = 1 - \frac{iJ_z\epsilon^2}{\hbar} - 1.$$

All first-order terms on the LHS cancel. Equating the second-order terms, we find that

$$[J_x, J_y] = i\hbar J_z.$$

Rotations about the other axis are similar, and we conclude that

$$\boxed{[J_i, J_j] = i\hbar \epsilon_{ijk} J_k.}$$

(4.21)

They are known as the **fundamental commutation relations of angular momentum**.

4.3.3 The Effect of the Rotation Operator

Consider a system in state $|\psi\rangle$. The state after rotation, by an angle ϕ around the z-axis for example, is

$$|\psi\rangle_R = \mathcal{D}_z(\phi)|\psi\rangle, \quad \mathcal{D}_z(\phi) = e^{-iJ_z\phi/\hbar}.$$

To see the effect of $\mathcal{D}_z$, we compute the expectation value of J_x, J_y, and J_z. J_z is simple, because $[J_z, \mathcal{D}_z(\phi)] = 0$,

$$\langle J_z \rangle_R = \langle \psi | J_z | \psi \rangle_R = \langle \psi | \mathcal{D}_z^\dagger(\phi) J_z \mathcal{D}_z(\phi) | \psi \rangle = \langle \psi | e^{iJ_z\phi/\hbar} J_z e^{-iJ_z\phi/\hbar} | \psi \rangle = \langle \psi | J_z | \psi \rangle = \langle J_z \rangle.$$

For J_x,

$$\langle J_x \rangle_R = \langle \psi | J_x | \psi \rangle_R = \langle \psi | \mathcal{D}_z^\dagger(\phi) J_x \mathcal{D}_z(\phi) | \psi \rangle = \langle \psi | e^{iJ_z\phi/\hbar} J_x e^{-iJ_z\phi/\hbar} | \psi \rangle.$$

Using the Baker-Hausdorff lemma (B.1),

$$\begin{aligned}
e^{iJ_z\phi/\hbar} J_x e^{-iJ_z\phi/\hbar} &= J_x + \frac{i\phi}{\hbar}[J_z, J_x] + \frac{i^2\phi^2}{2!\hbar^2}[J_z, [J_z, J_x]] + \frac{i^3\phi^3}{3!\hbar^3}[J_z, [J_z, [J_z, J_x]]] + \cdots \\
&= J_x + \frac{i\phi}{\hbar}(i\hbar J_y) - \frac{\phi^2}{2!\hbar^2}(\hbar^2 J_x) - \frac{i\phi^3}{3!\hbar^3}(i\hbar^3 J_y) + \cdots \\
&= J_x \left[1 - \frac{\phi^2}{2!} + \cdots \right] - J_y \left[\phi - \frac{\phi^3}{3!} + \cdots \right] \\
&= J_x \cos\phi - J_y \sin\phi.
\end{aligned}$$

Hence

$$\langle J_x \rangle_R = \langle J_x \rangle \cos\phi - \langle J_y \rangle \sin\phi.$$

Similarly for J_y, we can find that

$$\langle J_y \rangle_R = \langle J_y \rangle \cos\phi + \langle J_x \rangle \sin\phi.$$

Compactly, if we write these expectation values as a column vector $\langle \mathbf{J} \rangle$, then applying a finite rotation operator is equivalent to a matrix multiplication by a 3×3 rotation matrix $R_z(\phi)$:

$$\langle \mathbf{J} \rangle_R = \begin{bmatrix} \langle J_x \rangle_R \\ \langle J_y \rangle_R \\ \langle J_z \rangle_R \end{bmatrix} = \begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \langle J_x \rangle \\ \langle J_y \rangle \\ \langle J_z \rangle \end{bmatrix} = R_z(\phi) \langle \mathbf{J} \rangle.$$

4.4 Orbital Angular Momentum

4.4.1 Eigenvalues

Classically, the angular momentum of a particle is the cross product of position and momentum,

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad \text{or} \quad L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x$$

The quantum operators are obtained by changing $p_i \rightarrow -i\hbar\partial_i$. The components of angular momentum do not commute. They follow the cyclic commutation relations

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y. \tag{4.22}$$

This means we cannot simultaneously determine any two components of angular momentum. The square of the total angular momentum $L^2 \equiv L_x^2 + L_y^2 + L_z^2$ commutes with L_i. For example,

$$\begin{aligned}
[L^2, L_x] &= \cancel{[L_x^2, L_x]} + [L_y^2, L_x] + [L_z^2, L_x] \\
&= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z \\
&= L_y(-i\hbar L_z) + (-i\hbar L_z)L_y + L_z(i\hbar L_y) + (i\hbar L_y)L_z \\
&= 0.
\end{aligned}$$

In a more compact way, we can write $[L^2, \mathbf{L}] = 0$. This means L^2 is compatible with each component of $\mathbf{L}$: they have the same eigenfunctions. Let f be their common eigenfunction,

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

Define the "ladder operator" for angular momentum $L_\pm \equiv L_x \pm iL_y$. Its commutator with L_z and L^2 are

$$[L_z, L_\pm] = \pm\hbar L_\pm \quad \text{and} \quad [L^2, L_\pm] = 0.$$

It follows with a conclusion: if f is an eigenfunction of L^2 and L_z, then so is $L_\pm f$. The eigenvalues are λ and $\mu + \hbar$ respectively.

$$L^2(L_\pm f) = L_\pm(L^2 f) = L_\pm(\lambda f) = \lambda(L_\pm f).$$

$$L_z(L_\pm f) = [L_z, L_\pm]f + L_\pm L_z f = \pm\hbar L_\pm f + L_\pm(\mu f) = (\mu \pm \hbar)(L_\pm f).$$

The raising operator L_+ raises the eigenvalue of L_z by $\hbar$, while the lowering operator L_- lowers the that by $\hbar$, but they have no effect on the eigenvalue of L^2. There is an identity that will be used later,

$$L^2 = L_\pm L_\mp + L_z^2 \pm \hbar L_z \tag{4.23}$$

The z-component angular momentum cannot be arbitrarily large because it cannot exceed the total angular momentum. Hence there exists a top boundary f_t such that $L_+ f_t = 0$. There should also exist a bottom boundary f_b for the same reason, $L_- f_b = 0$. Let $\hbar\ell$ be the maximum eigenvalue of L_z with corresponding eigenfunction f_t,

$$L_z f_t = \hbar\ell f_t, \quad L^2 f_t = \lambda f_t.$$

With (4.23) and the fact that $L_+ f_t = 0$, we have

$$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z)f_t = (0 + \hbar^2\ell^2 + \hbar^2\ell)f_t = \hbar^2\ell(\ell+1)f_t \quad \Longrightarrow \quad \lambda = \hbar^2\ell(\ell+1).$$

By the same token, let $\hbar\bar{\ell}$ be the minimum eigenvalue of L_z with eigenfunction f_b,

$$L_z f_b = \hbar\bar{\ell} f_b, \quad L^2 f_b = \lambda f_b,$$

and using (4.23),

$$L^2 f_b = (L_+ L_- + L_z^2 - \hbar L_z)f_b = (0 + \hbar^2\bar{\ell}^2 - \hbar^2\bar{\ell})f_b = \hbar^2\bar{\ell}(\bar{\ell}-1)f_b \quad \Longrightarrow \quad \lambda = \hbar^2\bar{\ell}(\bar{\ell}-1).$$

Comparing $\lambda = \hbar^2\ell(\ell+1)$ and $\lambda = \hbar^2\bar{\ell}(\bar{\ell}-1)$, this means either

$$\bar{\ell} = \ell + 1 \quad \text{or} \quad \boxed{\bar{\ell} = -\ell}$$

The first relation is physically invalid because the minimum eigenvalue cannot be higher than the maximum one. Since $L_\pm$ raises or lower the angular momentum in z-direction by integers of $\hbar$, we define m that goes from $-\ell$ to $+\ell$ in N integer steps. The the eigenvalues of L_z are $m\hbar$ and $\ell = N/2$. The eigenfunctions are characterized by ℓ and m:

$$\boxed{L^2 f_\ell^m = \hbar^2\ell(\ell+1)f_\ell^m, \quad L_z f_\ell^m = m\hbar f_\ell^m.} \tag{4.24}$$

where $\ell = 0, 1/2, 1, 3/2, \ldots$, and $m = -\ell, -\ell + 1, \ldots, \ell - 1, \ell$. In conclusion, we start with *only* the commutation relations for angular momemtum (4.22), we know the eigenvalues of L^2 and L_z. For a given ℓ, there are $2\ell + 1$ values for m. (This should be familiar.)

4.4.2 Eigenfunctions

To get eigenfunctions, write angular momentum in spherical coordinates first,

$$\mathbf{L} = -i\hbar(\mathbf{r} \times \nabla), \quad \text{where} \quad \mathbf{r} = r\hat{\mathbf{r}}, \quad \nabla = \hat{\mathbf{r}}\frac{\partial}{\partial r} + \hat{\boldsymbol{\theta}}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\boldsymbol{\phi}}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}.$$

By some algebra we get

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

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

This means:

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

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

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

Now is to determine the eigenfunction $f_\ell^m(\theta, \phi)$. It is an eigenfunction of L^2 with eigenvalue $\hbar^2\ell(\ell+1)$, and of L_z with eigenvalue $m\hbar$:

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

$$L_z f_\ell^m = -i\hbar\frac{\partial}{\partial \phi}f_\ell^m = m\hbar f_\ell^m.$$

The first one is precisely the angular equation (4.2), while the second one is the azimuthal equation (4.4). This indicates that the spherical harmonic $Y_\ell^m(\theta, \phi)$ are the eigenfunctions. We now have arrived three conclusions:

$$H\psi = E\psi, \quad L^2\psi = \hbar^2\ell(\ell+1)\psi, \quad L_z\psi = m\hbar\psi. \tag{4.25}$$

The Schrödinger equation can be written in terms of angular momentum:

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

The only problem here is that the algebraic theory of angular momentum can have ℓ as half integers, but separation of variables only yields integers.

Some Useful Results

1. Recall that the ladder operators for the harmonic oscillator takes an eigenstate to another with some constants

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \quad \text{and} \quad a|n\rangle = \sqrt{n}|n-1\rangle.$$

The angular momentum ladder operators also have such features (see proof in Appendix B.6.2),

$$L_+ Y_\ell^m = \hbar\sqrt{\ell(\ell+1) - m(m+1)}Y_\ell^{m+1} \quad \text{and} \quad L_- Y_\ell^m = \hbar\sqrt{\ell(\ell+1) - m(m-1)}Y_\ell^{m-1}.$$

2. With the cononical commutation relation, if is straight forward to prove more commutation relations for angular momentum:

$$[L_z, x] = i\hbar y, \quad [L_z, y] = -i\hbar x, \quad [L_z, z] = 0,$$

$$[L_z, p_x] = i\hbar p_y, \quad [L_z, p_y] = -i\hbar p_x, \quad [L_z, p_z] = 0.$$

$$[L_z, r^2] = 0, \quad [L_z, p^2] = 0.$$

L commutes with the Hamiltonian if the potential is radially symmetric, (This can also be seen from equation 4.25.)

$$[\mathbf{L}, H] = 0, \quad \text{where} \quad H = \frac{p^2}{2m} + V(r).$$

Finally, the commutator $[L_+, L_-] = 2\hbar L_z$, analogous to $[a^\dagger, a] = 1$.

3. For a particle in a potential $V(\mathbf{r})$, the rate of change of the expectation value of the orbital angular momentum is equal to the expectation value of the torque:

$$\frac{d\langle \mathbf{L} \rangle}{dt} = \langle \boldsymbol{\tau} \rangle, \quad \text{where} \quad \boldsymbol{\tau} = \mathbf{r} \times (-\nabla V).$$

This is the rotational analog to Ehrenfest theorem. It is also true that $d\langle \mathbf{L} \rangle/dt = 0$ for any spherically symmetric potential (conservation of angular momentum). Proofs are available in Appendix B.6.3.

4.5   Spin

In classical mechanics, there are two kinds of angular momentum: $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ and $\mathbf{S} = I\boldsymbol{\omega}$. For example, the spin of the Earth is just the total angular momenta of rocks and dusts around Earth's spin axis. In quantum mechanics, we can have electrons orbiting around the nuclei (extrinsic/orbital angular momentum). However, since electrons is a point particle, classical spin does not apply to them, but we still define an intrinsic angular momentum called **spin** for electrons. The algebraic theory of spin is a copy of the one of angular momentum,

$$[S_x, S_y] = i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y, \quad \text{or} \quad [S_i, S_j] = i\hbar \epsilon_{ijk} S_k.$$

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

$$S_\pm|s, m\rangle = \hbar\sqrt{s(s+1) - m(m \pm 1)}|s, (m \pm 1)\rangle \quad \text{where} \quad S_\pm = S_x \pm iS_y$$

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

The eigenstates of spin cannot be expressed as functions in position space.

4.5.1   Pauli Spin Matrices

The simplest spin system is a spin-1/2 particle. There are two eigenstates for S_z:

$$|0\rangle = \left|\tfrac{1}{2}, \tfrac{1}{2}\right\rangle \quad (\text{spin up } \uparrow), \quad \text{and} \quad |1\rangle = \left|\tfrac{1}{2}, -\tfrac{1}{2}\right\rangle \quad (\text{spin down } \downarrow).$$

In matrix mechanics, the general state can be expressed as a **spinor** (a two-element column matrix):

$$\chi = \begin{bmatrix} a \\ b \end{bmatrix} = a\chi_+ + b\chi_- \quad \text{where} \quad \chi_+ = |0\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \chi_- = |1\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

Meanwhile, the spin operators become 2×2 matrices,

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

The matrix elements of S^2, S_z, $S_\pm$, and then S_x and S_y can be determined in the S_z-basis,

$$S^2 = \frac{3}{4}\hbar^2\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad S_z = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad S_+ = \hbar\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, \quad S_- = \hbar\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}.$$

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

We can write S_x, S_y and S_z as $S_i = (\hbar/2)\sigma_i$, where

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \qquad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \qquad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{4.26}$$

These are known as the **Pauli spin matrices**. The eigenspinors of S_z are χ_+ with eigenvalue $+\hbar/2$, and χ_- with eigenvalue $-\hbar/2$. For a general state χ, we will measure $\hbar/2$ with probability $|a|^2$, or $-\hbar/2$ with probability $|b|^2$.

Example 4.1. Eigenspinors of S_x and S_y

If we want to measure S_x, we need to know its eigenvalues and eigenspinors.

$$\begin{vmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{vmatrix} = 0 \implies \lambda = \pm \frac{\hbar}{2}.$$

The eigenspinors are

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

The general spinor in terms of $\chi_+^{(x)}$ and $\chi_-^{(x)}$ is

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

The probability of measuring $+\hbar/2$ is $(1/2)|a+b|^2$; the probability of getting $-\hbar/2$ is $(1/2)|a-b|^2$. By similar methods, we can get the eigenspinors for S_y,

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

For general spin matrices along any vector $\hat{\mathbf{r}}$, see Appendix A.3.3.

Here are some properties of the Pauli spin matrices σ_i for $i = x, y, z$:

- They are Hermitian and traceless matrices with determinant -1:

$$\sigma_i^\dagger = \sigma_i, \quad \det(\sigma_i) = -1, \quad \text{Tr}(\sigma_i) = 0.$$

- They square to the identity, and they mutually *anti-commute*. These two statements can be summarized as $\{\sigma_i, \sigma_j\} = 2\delta_{ij}$, where $\{\sigma_i, \sigma_j\} \equiv \sigma_i \sigma_j + \sigma_j \sigma_i$.

- The commutator of the Pauli spin matrices is $[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k$.

- For a vector $\mathbf{a}$ in three-dimensions, $\sigma \cdot \mathbf{a}$ is defined as

$$\sigma \cdot \mathbf{a} \equiv \sum_k a_k \sigma_k = \begin{bmatrix} a_3 & a_1 - ia_2 \\ a_1 + ia_2 & -a_3 \end{bmatrix}.$$

Then there is an important identity: for any two three-dimensional vectors $\mathbf{a}$ and $\mathbf{b}$,

$$(\sigma \cdot \mathbf{a})(\sigma \cdot \mathbf{b}) = \mathbf{a} \cdot \mathbf{b} + i\sigma \cdot (\mathbf{a} \times \mathbf{b}).$$

To show this, we use the commutation and anti-commutation relation,

$$\sum_i \sigma_i a_i \sum_j \sigma_j b_j = \sum_{i,j} (\sigma_i \sigma_k) a_i b_j = \sum_{i,j} \left(\frac{1}{2}\{\sigma_i, \sigma_j\} + \frac{1}{2}[\sigma_i, \sigma_j] \right) a_i b_j = \sum_{i,j} (\delta_{ij} + i\epsilon_{ijk}\sigma_k) a_i b_j = \mathbf{a} \cdot \mathbf{b} + i\sigma \cdot (\mathbf{a} \times \mathbf{b}).$$

If $\mathbf{a}$ is real, then $(\sigma \cdot \mathbf{a})^2 = |\mathbf{a}|^2$. This will be useful in the next section.

4.5.2   Matrix Representation of the Rotation Operator

Working with a spin-1/2 particle as an example, we can study the matrix representation of $\mathcal{D}(\hat{\mathbf{n}}, \phi)$. Similar to (4.20), a finite rotation operator for a rotation, by an angle ϕ around the axis $\hat{\mathbf{n}}$, can be written as an exponential,

$$\mathcal{D}(\hat{\mathbf{n}}, \phi) = e^{-i\mathbf{S}\cdot\hat{\mathbf{n}}\phi/\hbar} = e^{-i\sigma\cdot\hat{\mathbf{n}}\phi/2} = \left[1 - \frac{(\sigma\cdot\hat{\mathbf{n}})^2}{2!}\left(\frac{\phi}{2}\right)^2 + \frac{(\sigma\cdot\hat{\mathbf{n}})^4}{4!}\left(\frac{\phi}{2}\right)^4 - \cdots \right] - i\left[(\sigma\cdot\hat{\mathbf{n}})\frac{\phi}{2} - \frac{(\sigma\cdot\hat{\mathbf{n}})^3}{3!}\left(\frac{\phi}{2}\right)^3 + \cdots \right].$$

Because $(\sigma\cdot\hat{\mathbf{n}})^2 = |\hat{\mathbf{n}}|^2 = 1$, we have

$$(\sigma\cdot\hat{\mathbf{n}})^n = \begin{cases} 1, & n \text{ odd,} \\ \sigma\cdot\hat{\mathbf{n}}, & n \text{ even.} \end{cases}$$

Then the rotation operator becomes

$$\mathcal{D}(\hat{\mathbf{n}}, \phi) = \left[1 - \frac{(\phi/2)^2}{2!} + \frac{(\phi/2)^4}{4!} - \cdots \right] - i(\sigma\cdot\hat{\mathbf{n}})\left[(\phi/2) - \frac{(\phi/2)^3}{3!} + \cdots \right] = 1\cos(\phi/2) - i\sigma\cdot\hat{\mathbf{n}}\sin(\phi/2),$$

where all the 1's above represent the 2×2 identity matrix. Explicitly,

$$\mathcal{D}(\hat{\mathbf{n}}, \phi) = \begin{bmatrix} \cos(\phi/2) - in_z\sin(\phi/2) & -(in_x + n_y)\sin(\phi/2) \\ -(in_x - n_y)\sin(\phi/2) & \cos(\phi/2) + in_z\sin(\phi/2) \end{bmatrix}. \tag{4.27}$$

The argument $\phi/2$ is interesting. (Recall that the factor $1/2$ comes from $s = 1/2$ of the particle.) For example, if we choose to rotate the state by $\phi = 2\pi$, then for any vector $\hat{\mathbf{n}}$,

$$\mathcal{D}(\hat{\mathbf{n}}, 2\pi) = -1.$$

This means that rotating a spin-1/2 particle by 360° flips the state. It requires a rotation of 720° to get back to the original state.

4.5.3   Electron in a Magnetic Field

A charged particle's **magnetic dipole moment** $\boldsymbol{\mu}$ is proportional to its spin $\mathbf{S}$,

$$\boldsymbol{\mu} = \gamma\mathbf{S}.$$

where γ is the **gyromagnetic ratio**. When a magnetic dipole is placed in a magnetic field $\mathbf{B}$, it experienced a torque $\boldsymbol{\mu} \times \mathbf{B}$ which lines the dipole moment to the field. The Hamiltonian of a spinning charged particle is

$$H = -\boldsymbol{\mu}\cdot\mathbf{B} = -\gamma\mathbf{B}\cdot\mathbf{S} = -\gamma[S_xB_x + S_yB_y + S_zB_z].$$

Example 4.2. Larmor precession

Consider a spin-1/2 particle at rest in a uniform magnetic field $\mathbf{B} = B_0\hat{\mathbf{z}}$. The Hamiltonian of the particle is

$$H = -\gamma B_0 S_z = -\frac{\gamma B_0\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

The eigenstates of the Hamiltonian are also χ_+ and χ_-, with energies $E_\pm = \mp\gamma B_0\hbar/2$. The lower energy state has spin (or dipole moment) parallel to the field, the same as the classical case. The general solution to the time-dependent Schrödinger equation is

$$i\hbar\frac{\partial\chi}{\partial t} = H\chi \implies \chi(t) = a\chi_+ e^{-iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar} = \begin{bmatrix} ae^{i\gamma B_0 t/2} \\ be^{-i\gamma B_0 t/2} \end{bmatrix}.$$

The constants a and b are determined by $\chi(0)$ and $|a|^2 + |b|^2 = 1$. It is convenient to set a and b real, and write $a = \cos(\alpha/2)$ and $b = \sin(\alpha/2)$. The general state is

$$\chi(t) = \begin{bmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{bmatrix}.$$

The expectation value of $\mathbf{S}$ can be calculated:

$$
\begin{aligned}
\langle S_x \rangle &= \langle \chi(t)|S_x|\chi(t) \rangle \\
&= \begin{bmatrix} \cos(\alpha/2)e^{-i\gamma B_0 t/2} & \sin(\alpha/2)e^{i\gamma B_0 t/2} \end{bmatrix} \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{bmatrix} \\
&= \frac{\hbar}{2} \sin\alpha \cos(\gamma B_0 t).
\end{aligned}
$$

Similarly,

$$
\langle S_y \rangle = -\frac{\hbar}{2}\sin\alpha \sin(\gamma B_0 t), \quad \langle S_z \rangle = \frac{\hbar}{2}\cos\alpha.
$$

We see that $\langle S \rangle$ has a constant angle α with the z-axis, and precesses about the field at the **Larmor frequency**,

$$
\omega = \gamma B_0. \tag{4.28}
$$

This is consistent with the classical Larmor frequency in electromagnetism.

Example 4.3. The Stern-Gerlach experiment

If the magnetic field is inhomogeneous, there will be a force on a magnetic dipole:

$$
\mathbf{F} = \nabla(\boldsymbol{\mu} \cdot \mathbf{B}).
$$

Consider a beam of neutral atoms (neutral to avoid Lorentz force) traveling in the y-direction in a magnetic field

$$
\mathbf{B}(x, y, z) = -\alpha x \hat{\mathbf{x}} + (B_0 + \alpha z)\hat{\mathbf{z}},
$$

where B_0 is a strong uniform field and α is a small deviation. The force on the atoms is

$$
\mathbf{F} = \gamma\alpha\left(-S_x\hat{\mathbf{x}} + S_z\hat{\mathbf{z}}\right).
$$

Because of the Larmor precession about $\mathbf{B}_0$, $\langle S_x \rangle$ has a rapid oscillation and averages the force to zero in the x-direction. Thus the net force is in the z-direction,

$$
F_z = \gamma\alpha S_z.
$$

The atoms deflects according to their spin angular momentum. The beam splits into $2s+1$ streams, which shows the quantization of angular momentum in quantum mechanics. If you have a $s = 1/2$ particle (like silver atom), you would get a perfect half-split of the beam.

4.6   SO(3), SU(2), and Euler Rotations

4.6.1   Special Orthogonal Group

Previously we saw that the rotation matrices (4.17) are 3×3 special orthogonal matrices, where special means determinant 1, and orthogonal means $R^T R = R R^T = 1$. The general rotation matrices R that does not restrict to coordinate axes can be studied more easily using group theory. Successive rotations are just multiplication of rotation matrices—this will be the composition rule. We first check that the set of all 3×3 special orthogonal matrices, with the composition rule being ordinary matrix multiplication, satisfy all group axioms:

1. Closure: the product of two orthogonal matrices is another orthogonal matrix,

$$
(R_1 R_2)(R_1 R_2)^T = R_1(R_2 R_2^T)R_1^T = R_1 R_1^T = 1, \quad \det(R_1 R_2) = \det R_1 \det R_2 = 1 \cdot 1 = 1.
$$

2. Associativity: satisfied by the property of ordinary matrix multiplication.

3. The existence of the identity: the identity for rotation means no rotation,

$$R1 = 1R = R, \quad 1^T 1 = 1, \quad \det 1 = 1.$$

4. The existence of an inverse: because orthogonal matrices are defined by $RR^T = R^T R = 1$, the inverse of R is just $R^{-1} = R^T$. R^T also has determinant 1, $\det R^T = \det R = 1$. Physically, R^{-1} is a rotation in the opposite direction of R.

Such a group is called the **special orthogonal group** SO(3), S for special, O for orthogonal, and 3 for three dimensions.

4.6.2 Special Unitary Group

Now we return back to the matrix representation of the rotation operator (4.27). One can check that $\mathcal{D}(\hat{\mathbf{n}}, \phi)$ is a unitary matrix with determinant 1, or special. The most general 2×2 special unitary matrix can be specified by two complex numbers,

$$U(a, b) = \begin{bmatrix} a & b \\ -b^* & a^* \end{bmatrix}, \quad \text{with} \quad |a|^2 + |b|^2 = 1.$$

There are three (real valued) degrees of freedom: one need four real numbers to specify two complex numbers a and b, but there is a constraint $|a|^2 + |b|^2 = 1$ that reduce the degrees of freedom to 3 three real numbers. In the case of $\mathcal{D}(\hat{\mathbf{n}}, \phi)$,

$$a = \cos(\phi/2) - in_z \sin(\phi/2), \quad b = -n_y \sin(\phi/2) - in_x \sin(\phi/2).$$

Again, there are three degrees of freedom: all four of ϕ, n_x, n_y, and n_z are real, but there is a constraint $n_x^2 + n_y^2 + n_z^2 = 1$. Historically, the two complex numbers a and b are known as **Kayley-Klein parameters**. The set of all 2×2 special unitary matrices, with the composition rule being ordinary matrix multiplication, forms a group:

1. Closure: the product of two special unitary matrices is another special unitary matrix,

$$U(a_1, b_1)U(a_2, b_2) = \begin{bmatrix} a_1 & b_1 \\ -b_1^* & a_1^* \end{bmatrix}\begin{bmatrix} a_2 & b_2 \\ -b_2^* & a_2^* \end{bmatrix} = \begin{bmatrix} a_1 a_2 - b_1 b_2^* & a_1 b_2 + a_2^* b_1 \\ -a_1^* b_2^* - a_2 b_1^* & a_1^* a_2^* - b_1^* b_2 \end{bmatrix} = U(a_1 a_2 - b_1 b_2^*, a_1 b_2 + a_2^* b_1),$$

$$\det[U(a_1, b_1)U(a_2, b_2)] = \det U(a_1, b_1) \det U(a_2, b_2) = 1 \cdot 1 = 1.$$

2. Associativity: satisfied by the property of ordinary matrix multiplication.

3. The existence of the identity: the identity special unitary matrix is $1 = U(1, 0)$, which evidently has determinant 1.

4. The existence of an inverse: the inverse of $U(a, b)$ is $U^{-1}(a, b) = U^\dagger(a, b) = U(a^*, -b)$.

Such a group is called the **special unitary group** SU(2), S for special, U for unitary, and 2 for two dimensions.

We use both SO(3) and SU(2) to describe rotations. It seems like SO(3) and SU(2) are **isomorphic**, or one-to-one between two groups. But we know that a rotation using the rotation matrix $R(2\pi)$ and $R(4\pi)$ both result in the identity. In contrast, a rotation using $\mathcal{D}(\hat{\mathbf{n}}, 2\pi)$ gives -1, and $\mathcal{D}(\hat{\mathbf{n}}, 4\pi)$ is the identity. Hence the correspondence between SU(2) and SO(3) is infact two-to-one. We say that they are *locally* isomorphic.

4.6.3 Euler Rotations

To be written.

4.7 Density Operators, Pure vs. Mixed Ensembles

4.7.1 Ensemble Averages and the Density Operator

A **pure ensemble** is a collection of physical systems such that every member is characterized by the same state vector $|\psi\rangle$. A **mixed ensemble** can have members in various states $|\psi^i\rangle$, weighted by a relative/fractional population w_i. The fractional population should sum up to 1:

$$\sum_i w_i = 1.$$

Be sure to distinguish w_i with the coefficients a and b of a state like $\chi = a\chi_+ + b\chi_-$. The spinor χ stands for a state for one particular physical system (such as a particle), and $|a|^2$ and $|b|^2$ represent the probability of measuring χ_+ and χ_-, respectively. In a collection of physical systems, even for spin-1/2 particles, we can have 50% of them in χ_+, 25% of them in $\chi_+^{(x)}$, and 25% of them in $\chi_+^{(y)}$.

Consider a large mixed ensemble. We are interested in the average measurement of an observable Q on this ensemble. Such an average is called the **ensemble average** of A, defined by

$$[Q] \equiv \sum_i w_i \langle \psi^i|Q|\psi^i\rangle = \sum_i w_i \langle \psi^i| \sum_n q_n |q_n\rangle\langle q_n|\psi^i\rangle = \sum_{i,n} w_i q_n |\langle q_n|\psi^i\rangle|^2, \tag{4.29}$$

where $|q_n\rangle$ are eigenstates of Q and we used spectral decomposition (2.7) to rewrite Q. Note that $\langle \psi^i|Q|\psi^i\rangle$ is the usual expectation value of *one* physical system in $|\psi^i\rangle$; $|\langle q_n|\psi^i\rangle|^2$ is the probability or $|\psi^i\rangle$ to be found in $|q_n\rangle$, and w_i tells the probability of finding a physical system in $|\psi^i\rangle$ among the ensemble.

Consider a more general basis $\{|e_n\rangle\}$ (not necessarily the eigenbasis of Q). By inserting two identity operators, the ensemble average is

$$[Q] = \sum_i w_i \sum_m \sum_n \langle \psi^i|e_m\rangle\langle e_m|Q|e_n\rangle\langle e_n|\psi^i\rangle = \sum_{m,n} \left(\sum_i w_i \langle e_n|\psi^i\rangle\langle \psi^i|e_m\rangle \right) \langle e_m|Q|e_n\rangle .$$

The sum in the parenthesis does not depend on the observable A but only on the ensemble. We define the **density operator** ρ:

$$\rho \equiv \sum_i w_i |\psi^i\rangle\langle \psi^i| . \tag{4.30}$$

Then the sum in the parenthesis is the matrix element of the **density matrix**,

$$\rho_{mn} = \langle e_m|\rho|e_n\rangle = \sum_i w_i \langle e_m|\psi^i\rangle\langle \psi^i|e_n\rangle , \tag{4.31}$$

and the ensemble average can be written simply as

$$[A] = \sum_{m,n} \langle e_n|\rho|e_m\rangle\langle e_m|Q|e_n\rangle = \sum_n \langle e_n|\rho Q|e_n\rangle = \text{tr}(\rho Q). \tag{4.32}$$

Equation (4.32) is powerful, because the trace is a representation-independent quantity. We can evaluate $\text{tr}(\rho Q)$ in any convenient basis. By (4.30), the density operator is evidently Hermitian because w_i is real. Also, the trace of the density operator is 1:

$$\text{tr}(\rho) = \sum_{i,n} w_i \langle e_n|\psi^i\rangle\langle \psi^i|e_n\rangle = \sum_{i,n} w_i \langle \psi^i|e_n\rangle\langle e_n|\psi^i\rangle = \sum_i w_i \langle \psi^i|\psi^i\rangle = 1.$$

Example 4.4. A pure ensemble

A pure ensemble has all members in one state $|\psi\rangle$, with $w = 1$. The density operator is just

$$\rho = |\psi\rangle\langle \psi| .$$

It is obvious that $\rho^2 = \rho$, or $\rho(\rho - 1) = 0$. We can find the eigenvalues of this density operator: for an eigenvector $|\mathbf{v}\rangle$,

$$\rho(\rho - 1)|\mathbf{v}\rangle = \lambda(\lambda - 1)|\mathbf{v}\rangle = 0 \quad \implies \quad \lambda = 0, 1.$$

Meanwhile, the trace of the density operator is $\text{tr}(\rho) = 1$. Since the trace is the sum of all eigenvalues, the density matrix (after diagonalization) has every matrix element 0, except a 1 at any diagonal entry,

$$\rho = \begin{bmatrix} 0 & & & & & & & & \\ & 0 & & & & & & & \\ & & \ddots & & & & & & \\ & & & 0 & & & & & \\ & & & & 1 & & & & \\ & & & & & 0 & & & \\ & & & & & & 0 & & \\ & & & & & & & \ddots & \\ & & & & & & & & 0 \end{bmatrix}$$

For example, a beam of spin-1/2 particles completely polarized in χ_+ (spin up) has the density matrix

$$\rho = \left| \tfrac{1}{2}, \tfrac{1}{2} \right\rangle\!\!\left\langle \tfrac{1}{2}, \tfrac{1}{2} \right| = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \begin{bmatrix} 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}.$$

4.7.2 Time Evolution of Ensembles

To be written.

4.7.3 Continuum Generalizations

To be written.

4.7.4 Quantum Statistics

To be written.

4.8 Addition of Angular Momenta

The angular momenta in quantum mechanics do not add up in a classical way. Suppose there are two particles, one with spin s_1 and the other s_2. Now, consider the s_1 particle in state $|s_1, m_1\rangle$, and the s_2 particle in state $|s_2, m_2\rangle$. Their composite state is denoted as $|s_1, m_1\rangle|s_2, m_2\rangle$. We can then have four eigenvalue relations,

$$S_1^2 |s_1, m_1\rangle|s_2, m_2\rangle = s_1(s_1 + 1)\hbar^2 |s_1, m_1\rangle|s_2, m_2\rangle,$$
$$S_2^2 |s_1, m_1\rangle|s_2, m_2\rangle = s_2(s_2 + 1)\hbar^2 |s_1, m_1\rangle|s_2, m_2\rangle,$$
$$S_{1z} |s_1, m_1\rangle|s_2, m_2\rangle = m_1\hbar |s_1, m_1\rangle|s_2, m_2\rangle,$$
$$S_{2z} |s_1, m_1\rangle|s_2, m_2\rangle = m_2\hbar |s_1, m_1\rangle|s_2, m_2\rangle.$$

We want to know the total angular momentum (the net spin s, and the net z-component m) of the system,

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2.$$

The net z-component is simple:

$$S_z |s_1, m_1\rangle|s_2, m_2\rangle = (S_{1z} + S_{2z}) |s_1, m_1\rangle|s_2, m_2\rangle = \hbar(m_1 + m_2) |s_1, m_1\rangle|s_2, m_2\rangle = \hbar m |s_1, m_1\rangle|s_2, m_2\rangle.$$

This means $m = m_1 + m_2$. The total spin is a bit complicated. Here is an example. Consider two spin-1/2 particle, so there are four possibilities:

$$\begin{cases} |\uparrow\uparrow\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle\left|\frac{1}{2}, \frac{1}{2}\right\rangle, & m = 1, \\ |\uparrow\downarrow\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle\left|\frac{1}{2}, -\frac{1}{2}\right\rangle, & m = 0, \\ |\downarrow\uparrow\rangle = \left|\frac{1}{2}, -\frac{1}{2}\right\rangle\left|\frac{1}{2}, \frac{1}{2}\right\rangle, & m = 0, \\ |\downarrow\downarrow\rangle = \left|\frac{1}{2}, -\frac{1}{2}\right\rangle\left|\frac{1}{2}, -\frac{1}{2}\right\rangle, & m = -1. \end{cases}$$

There is an extra state with $m = 0$ as m ranges from -1 to 1, so we cannot say $s = 1$ immediately. This indicates that this basis may not be the best basis to find the total spin s. The first state and the last state with single m seem to be right, so we will try to apply the lowering operator $S_- = S_{1-} + S_{2-}$ to the state $|\uparrow\uparrow\rangle$,

$$\begin{aligned} S_- \left|\frac{1}{2}, \frac{1}{2}\right\rangle\left|\frac{1}{2}, \frac{1}{2}\right\rangle &= \left(S_{1-}\left|\frac{1}{2}, \frac{1}{2}\right\rangle\right)\left|\frac{1}{2}, \frac{1}{2}\right\rangle + \left|\frac{1}{2}, \frac{1}{2}\right\rangle\left(S_{2-}\left|\frac{1}{2}, \frac{1}{2}\right\rangle\right) \\ &= \hbar\left(\left|\frac{1}{2}, -\frac{1}{2}\right\rangle\left|\frac{1}{2}, \frac{1}{2}\right\rangle + \left|\frac{1}{2}, \frac{1}{2}\right\rangle\left|\frac{1}{2}, -\frac{1}{2}\right\rangle\right) \\ &= \hbar(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle). \end{aligned}$$

You may check that applying S_- again to this state gives $\downarrow\downarrow$. It follows that these three states are good basis for $s = 1$:

$$s = 1 \text{ (triplet)} \begin{cases} |1, 1\rangle = |\uparrow\uparrow\rangle \\ |1, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |1, -1\rangle = |\downarrow\downarrow\rangle \end{cases} \tag{4.33}$$

This is the **triplet** combination. There should be another state with $m = 0$, and it turns out to be the **singlet** state with $s = 0$,

$$s = 0 \text{ (singlet)} \quad |0, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \tag{4.34}$$

Applying S_- to $|0, 0\rangle$ gives zero as desired.

These are the four basis, expressed in the combined angular momentum notation $|s, m\rangle$. The combination of two spin-1/2 partiles can only carry a total spin of 1 or 0. In fact, the total spin of particles with spin s_1 and s_2 can be

$$s = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \ldots, |s_1 - s_2|. \tag{4.35}$$

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

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

The constants $C^{s_1 s_2 s}_{m_1 m_2 m}$ are the **Clebsch-Gordan coefficients** (available in Appendix A.4.1). Note that the Clebsch-Gordan table uses j to denote the spin instead of s. This is because this section is about addition of *angular momenta*, so the above discussion also applies to orbital angular momenta, or a combination of spin and orbital. Usually, we use j to denote any kinds of angular momentum.

Example 4.5.

If two particles of spin 2 and spin 1 contributes a total spin 3, and its z-component is 0, then

$$|3, 0\rangle = \frac{1}{\sqrt{5}}|2, 1\rangle|1, -1\rangle + \sqrt{\frac{3}{5}}|2, 0\rangle|1, 0\rangle + \frac{1}{\sqrt{5}}|2, -1\rangle|1, 1\rangle.$$

In principle, m_1 can range from -2 to 2 and m_2 can range from -1 to 1. However, since we know the final particle has $m = 0$, m_1 cannot be ± 2 because m_2 does not have ± 2. There are only three possible choices. From the combined state, we know a measuremnt of $S_z^{(1)}$ can return a value $\hbar$ with probability 1/5, or 0 with probability 3/5, or $-\hbar$ with probability 1/5.

5 IDENTICAL PARTICLES

5.1 Two-Particle Systems

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 hamiltonian for the whole system is now

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

The normalization is now

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

If the potential is time-independent, we can still get separable solutions,

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

There are two special cases that a two-particle problem can be reduces to a one-particle problem:

1. Noninteracting particles with external force characterized by a separable potential: the potential and the wave function are in the form

$$V(\mathbf{r}_1, \mathbf{r}_2) = V_1(\mathbf{r}_1) + V_2(\mathbf{r}_2), \quad \psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2).$$

   In this case, $\psi_a(\mathbf{r}_1)$ and $\psi_b(\mathbf{r}_2)$ each satisfies the one particle Schrödinger equation,

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi_a(\mathbf{r}_1) + V_1(\mathbf{r}_1)\psi_a(\mathbf{r}_1) = E_a\psi_a(\mathbf{r}_1),$$

$$-\frac{\hbar^2}{2m_2}\nabla_2^2\psi_b(\mathbf{r}_2) + V_b(\mathbf{r}_2)\psi_b(\mathbf{r}_2) = E_b\psi_b(\mathbf{r}_2).$$

   Obviously $E = E_a + E_b$, so
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)e^{-i(E_a + E_b)t/\hbar} = \Psi_a(\mathbf{r}_1, t)\Psi_b(\mathbf{r}_2, t).$$

   Note that any linear combination of $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$ is also a solution.

2. Central potentials without external force: the particles interact only with each other,

$$V(\mathbf{r}_1, \mathbf{r}_2) \rightarrow V(|\mathbf{r}_1 - \mathbf{r}_2|).$$

   An example would be the hydrogen atom. This two-body problem can be reduced to a one-body problem as in classical mechanics. This is shown in Appendix B.7.1.

5.1.1 Bosons and Fermions

Consider two non-interacting particles. Let particle 1 be in the state $\psi_a(\mathbf{r})$, and particle 2 be in the state $\psi_b(\mathbf{r})$. We will ignore spin for now. This is the first case described above: $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is a simple product,

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

This assume that we can distinguish particle 1 from particle 2. However, in quantum mechanics, particles are indistinguishable in principle. For example, electrons look identical: an electron made from particle accelerators is the same as an electron produced in beta decays. You can only compute the probability of finding *one* particle at $\mathbf{r}_1$ and finding *one* particle at $\mathbf{r}_2$. Note that if you swap

the identical particles, the probability does not change.

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2.$$

This gives two kinds of states:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1) \quad \text{or} \quad \psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1).$$

There cannot be an arbitrary phase factor $e^{i\phi}$ even though the probability statement above still holds. This is because when you swap the two particles *twice*, they must be in the original state. To solve this problem, we construct a wave function that does not restrict particles to a fixed state:

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

This give two kinds of identical particles: **bosons** (with plus sign) and **fermions** (with minus sign). You may check that bosons have a symmetric wave function under the exchange of $\mathbf{r}_1$ and $\mathbf{r}_2$, and fermions have an anti-symmetric wave function. All particles with integer spin are bosons and those with half integer spin are fermions. They have very different statistical properties. This is called the **spin statistics theorem**, which can be proved in relativistic quantum mechanics. In non-relativistic quantum mechanics, this is taken as an axiom. Two identical fermions cannot occupy the same state. If $\psi_a = \psi_b$, then

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

which is not a legal state. This is the famous **Pauli exclusion principle**. To construct fermionic state and bosonic state of more than two particles, see Appendix B.7.2.

5.1.2 Exchange Forces

As a one-dimensional example, suppose one particle is in state $\psi_a(x)$ and the other is in $\psi_b(x)$, assuming that the states are orthogonal and normalized. We are to calculate the expectation value of the square of the distance between 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

The wave function is $\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$.

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

where $\langle x^2 \rangle_a$ is the expectation value of x^2 in the one-particle state ψ_a. Similarly,

$$\langle x_2^2 \rangle = \langle x^2 \rangle_b \quad \text{and} \quad \langle x_1 x_2 \rangle = \langle x \rangle_a \langle x \rangle_b.$$

Thus,

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

Case 2: Identical particles

The wave functions are

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

Note that if two bosons are in the same state ($\psi_a = \psi_b$), the normalization factor is $1/2$ instead of $1/\sqrt{2}$,

$$\psi_+ = \frac{1}{2}[\psi_a(x_1)\psi_a(x_2) + \psi_a(x_2)\psi_a(x_1)] = \psi_a(x_1) + \psi_a(x_2).$$

Calculate the expectation value:

$$\langle x_1^2 \rangle = \frac{1}{2}\left[\langle x^2 \rangle_a \pm \langle \psi_a(x_1)|x_1^2|\psi_b(x_2)\rangle \langle \psi_b(x_2)|\psi_a x_2\rangle \pm \langle \psi_b(x_1)|x_1^2|\psi_a(x_1)\rangle \langle \psi_a(x_2)|\psi_b(x_2)\rangle + \langle x^2 \rangle_b\right]$$

$$= \frac{1}{2}\left[\langle x^2 \rangle_a + \langle x^2 \rangle_b\right] = \langle x_2^2 \rangle.$$

$\langle x_2^2 \rangle = \langle x_1^2 \rangle$ makes sense because you cannot distinguish identical particles. The next term is what makes the difference,

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

where $\langle x \rangle_{ab} \equiv \langle \psi_a|x|\psi_b \rangle$. Putting all terms together,

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

This means identical bosons tend to be closer together and identical fermions are farther apart, than distinguishable particles in the same two states. The term $\langle x \rangle_{ab}$ vanishes unless the two wave functions overlap. For example, if one hydrogen atom is far apart from another hydrogen atom, the electrons behave like distinguishable particles. However, if the two atoms are close to each other when they form hydrogen molecule H_2, there can be forces of attraction or repulsion. We call this kind of force resulted from symmetry the **exchange force**. It is actually not a force but only a quantum mechanical phenomenon.

5.1.3   Spin

Again, consider the hydrogen molecule H_2 and assume all particles are in ground states. If electrons were bosons, the exchange force will concentrate electrons toward the middle and will consequently attract the protons inward. It seems like it can account for the covalent bond. But electrons are fermions instead, which means they should tear the molecule apart.

Now we bring in the spin. The complete state of the electron is instead a product of the spatial wave function and a spinor:

$$
\psi(\mathbf{r})\chi(\mathbf{s}).
$$

The complete state of a two-particle state is then

$$
|\psi\rangle = \psi(\mathbf{r}_1, \mathbf{r}_2)\chi(m_1, m_2).
$$

A state with two fermions is antisymmetric with respect to the whole wave function,

$$
\psi(\mathbf{r}_1, \mathbf{r}_2)\chi(m_1, m_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)\chi(m_2, m_1).
$$

This gives many possibilities. For example, two electrons can be in the same (symmetric) spatial state, but opposite (anti-symmetric) spin states like the singlet configuration. Another state can have two electrons with anti-symmetric spatial wave function, but symmetric spin states, such as the triplet configuration. This achieves covalent bonds, we need the spatial wave function to be symmetric so that the exchange force is attractive. In other words, we need the spinor to be antisymmetric, so the singlet state can lead to the bonding. The triplet will lead to anti-bonding since the spatial wave function in this case is anti-symmetric.

5.1.4   Generalized Symmetrization Principle

Define the **exchange operator** P that interchanges the two particles in a state:

$$
P|1,2\rangle = |2,1\rangle.
$$

Obviously, $P^2|1,2\rangle = P|2,1\rangle = |1,2\rangle$, so $P^2 = I$. The eigenvalues of P are thus ± 1. If two particles are identical $(m_1 = m_2 = m)$, the Hamiltonian will treat them the same.

$$
H(1,2) = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + V(\mathbf{r}_1, \mathbf{r}_2, t) = -\frac{\hbar^2}{2m}(\nabla_2^2 + \nabla_1^2) + V(\mathbf{r}_2, \mathbf{r}_1, t) = H(2,1).
$$

Then

$$
[P, H]|1,2\rangle = P[H(1,2)|1,2\rangle] - H(1,2)[P|1,2\rangle] = H(2,1)|2,1\rangle - H(1,2)|2,1\rangle = 0.
$$

By (2.10), $d\langle P \rangle/dt = 0$, or P is a conserved quantity. If the initial state is anti-symmetric, it will stay anti-symmetric forever. The **symmetrization axiom** requires that identical particles states should satisfy

$$|1, 2\rangle = \pm |2, 1\rangle .$$

More generally, the state should be symmetric or anti-symmetric under the interchange of any two particles:

$$\boxed{|1, 2, \ldots, i, \ldots, j, \ldots, n\rangle = \pm |1, 2, \ldots, j, \ldots, i, \ldots, n\rangle .}\tag{5.1}$$

5.2 Atoms

A neutral atom of atomic number Z has Hamiltonian

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

The term in curly brackets represents the kinetic and potential energy of the jth electron in the electric field of the nucleus. The second sum is the potential energy from repulsion of the electrons. The Schrödinger equation $H\psi = E\psi$ cannot be solved exactly except for the case $Z = 1$ (hydrogen). By now, we can only use approximation methods.

5.2.1 Helium

The Hamiltonian of the helium atom is

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

If we ignore the last repulsion term, the solution will be the products of hydrogen wave functions since there are no mutual interactions:

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

The radius of electrons are now half the Bohr radius ($a(Z) = a/Z$), and the energy of each electron is four times the Bohr energy ($E_n(Z) = Z^2 E_n$). With two electrons, the energy is eight times $-13.6\,\text{eV}$.

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3}e^{-2(r_1+r_2)/a},$$

$$E_0 = 8(-13.6\,\text{eV}) = -109\,\text{eV}.$$

This is far from the actual ground state energy of helium ($-78.975\,\text{eV}$) because we ignored electron repulsion. Observe that ψ_0 is a symmetric wave function, the spin state should be anti-symmetric. Thus, the ground state of helium should have two electrons occupying the same spatial state, but opposite spin orientations.

5.2.2 The Periodic Table

Again, if we ignore electron repulsion, wave functions for heavier atoms can be approximated in the same way as we did for helium. Electrons will occupy one-particle hydrogenic states (n, ℓ, m) called **orbitals**. Due to the Pauli exclusion principle, only two electrons can occupy the same orbital, one spin up and one spin down. The nth shell can have $2n^2$ electrons. The rows of the Periodic Table corresponds to each shell, but the rows have length 2, 8, 8, 18, 18, etc. instead if 2, 8, 18, 32, 50, etc.

Helium atom fills $n = 1$ shell, so the next atom (lithium) has one electron in the $n = 2$ shell. The question is will the third electron choose $\ell = 0$ or $\ell = 1$. If there were no electron repulsion, the $\ell = 0$ and $\ell = 1$ have the same energy, and the third electron is free to choose both. Now with the electron repulsion, the electron will choose the lowest possible value of ℓ. This is because the angular momentum tends to throw electrons outward (recall the centrifugal barrier), making them affected more by inner electrons' screening. Imagine you are an electron. When you are in $\ell = 0$ state with no orbital angular momentum, hence close to the nucleus, you will see more positive nucleus in the electron cloud. If you are in $\ell = 1$, which throws you away from the nucleus, the electron cloud screens the nucleus. In other words, you would instead see something like a particle with charge of $+e$. The potential energy in this case is a

lot higher, making it unfavorable. Therefore, the third electron occupies the orbial $(2, 0, 0)$. Beryllium also fills this orbital but with opposite spin. Boron fills the fifth electron in $\ell = 1$. The $n = 2$ shell is completely filled when we reach neon.

In the $n = 3$ shell, the same goes all the way to argon, and then there should be 10 atoms with $n = 3$ and $\ell = 2$. But the screening effect is so strong that it overlaps the next shell, so potassium and calcium choose $n = 4$, $\ell = 0$ with no orbital angular momentum. Then scandium through zinc chooses back to $n = 3$, $\ell = 2$ because $n = 4$, $\ell = 1$ states have higher energies. These are qualitative reasoning and results known as the **aufbau principle**. More rules, such as **Hund's rule** (described in Appendix B.7.3), are used to regulate the filling of electrons for more complicated atoms.

In chemistry, the state of electrons is often written in terms of the **electron configuration**. The following are the rules:

1. Each ℓ has a designated letter: s for $\ell = 0$, p for $\ell = 1$, d for $\ell = 2$, and f for $\ell = 3$. After that just follow the alphabetical order, g, h, i, (skipping j), k, l, etc.

2. The energy level n is specified simply by numbers, written before the letters representing ℓ. For example, the second energy level has $n = 2$.

3. The number of electrons in an orbital is written as the superscript of ℓ.

Here is an example: $1s^2 \, 2s^2 \, 2p^3$ is the electron configuration of nitrogen ($Z = 7$). The first 1 indicates the first energy level. There is only $\ell = 0$ available for $n = 1$, so this orbital is called $1s$. There are two electrons in this orbital, which is shown in the superscript of $1s^2$. Similarly, $2s^2$ represents two electrons in $n = 2$, $\ell = 0$ states; $2p^3$ represents three electrons in $n = 2$, $\ell = 1$ states. Note that the electron configuration does not indicate the magnetic quantum number.

In atomic physics, it is more common to express the configuration in terms of the *total* orbital angular momentum quantum number L, the *total* spin quantum number S, and the *grand total* (orbital plus spin) J. The configuration is shown as the **term symbol**:

$$^{2S+1}L_J,$$

where S and J are some numbers, and L are the letters (the same rule as in chemistry, except capitalized). For example, the configuration for nitrogen is $^4S_{3/2}$. Hund's rule will tell you how to find these numbers and letters.

5.3   Solids

In the solid state, the outermost valence electrons in each atom become delocalized. This section introduces two models, both ignoring electron-electron repulsion:

- The electron gas theory of Sommerfeld: make a *very bold* assumption that ignores all forces except the boundary ones, and treats the electrons as particles in a box.

- Bloch's theory: has a periodic potential representing the electrical attraction of regularly spaced nuclei.

5.3.1   The Free Electron Gas

Suppose the object is a rectangular solid with dimensions L_x, L_y, L_z with potential

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < L_x, \ 0 < y < L_y, \text{ and } 0 < z < L_z \\ \infty, & \text{otherwise} \end{cases}$$

From example 4.1, we know the solutions and energies. (just replace the a's with L_x, L_y, and L_z.)

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y}\right) \sin\left(\frac{n_z \pi}{L_z} z\right).$$

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**, $\mathbf{k} = (k_x, k_y, k_z)$.

Imagine a three-dimensional space with bases k_x, k_y, k_z and with grids $k_i = (\pi/L_i), (2\pi/L_i), (3\pi/L_i), \dots$. Each block (each state), occupies a volume in k-space

$$V_{\text{state}} = \frac{\pi^3}{L_x L_y L_z} = \frac{\pi^3}{V}$$

where $V = L_x L_y L_z$ is the volume of the object. Suppose the object contains N atoms, each contributing q free electrons. Only 2 electrons can occupy one state. Assuming N is large, we can approximate the electrons filling up an octant (because $k_x, k_y, k_z > 0$) of a sphere in k-space with radius k_{F}:

$$\frac{1}{8}\left(\frac{4}{3}\pi k_{\text{F}}^3\right) = \frac{Nq}{2}\left(\frac{\pi^3}{V}\right) \quad \Longrightarrow \quad k_{\text{F}} = (3\rho\pi^2)^{1/3},$$

where $\rho = Nq/V$ is the **free electron density**. The factor of $1/2$ accounts for the number of spin states for each spatial state. For example, a ground state of 4 electrons only fills 2 spatial states because each spatial state can hold two electrons. The boundary separating occupied and unoccupied states in k-space is called the **Fermi surface**. The corresponding energy is the **Fermi energy**,

$$E_{\text{F}} = \frac{\hbar^2}{2m}(3\rho\pi^2)^{2/3}.$$

Note that the Fermi energy depends only on the electron density in the volume. To calculate the total energy, consider a shell in the first octant with thickness dk which has volume

$$V_{\text{shell}} = \frac{1}{8}(4\pi k^2)dk = \frac{1}{2}\pi k^2 dk.$$

The number of electrons in this shell is

$$2 \cdot \frac{V_{\text{shell}}}{V_{\text{state}}} = \frac{2[(1/2)\pi k^2 dk]}{\pi^3/V} = \frac{V}{\pi^2}k^2 dk.$$

The energy of the shell is

$$dE = \frac{\hbar^2 k^2}{2m}\frac{V}{\pi^2}k^2 dk,$$

so 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 thermodynamics, the pressure is related to energy and volume by

$$P = -\left(\frac{\partial E}{\partial V}\right)_N = \frac{2}{3}\frac{\hbar^2(3\pi^2 Nq)^{5/3}}{10\pi^2 m}V^{-5/3} = \frac{2}{3}\frac{E_{\text{tot}}}{V} = \frac{(3\pi^2)^{2/3}\hbar^2}{5m}\rho^{5/3}. \tag{5.2}$$

This pressure is often called the **degeneracy pressure** of an electron (or other Fermi) gas. It does not arise from electron-electron repulsion. Instead, it is a sole result of Pauli exclusion principle.

5.3.2 Band Structure

The actual potential of the solids are periodic because of the evenly spaced nuclei. Consider a simplest model called **Dirac comb** consisting of evenly spaced spikes:

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

where N is the number of spikes, a is the space in between, and α is some positive constant. Again, we assume N is large to the order of 10^{23}, so the edge effect can be ignored. To solve the Schrödinger equation,

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

we need to use **Bloch's theorem**: for a periodic potential $V(x+a) = V(x)$, the solution satisfies

$$\psi(x+a) = e^{iqa}\psi(x),$$

for some constant q that is independent of x, but may depend on E. Later we will find that q is real, so the probability density is periodic

$$|\psi(x+a)|^2 = |\psi(x)|.$$

Proof. Define the "displacement" operator:

$$Df(x) = f(x+a).$$

For a periodic potential,

$$[D, H] = 0,$$

so the eigenfunctions of H are simultaneously eigenfunctions of D:

$$D\psi(x) = \psi(x+a) = \lambda\psi(x), \quad \text{and} \quad \lambda \neq 0.$$

Thus, for any nonzero complex number, it can be expressed as

$$\lambda = e^{iqa}.$$

$\square$

For a finite solids, impose the boundary condition

$$\psi(x+Na) = \psi(x) \quad \Longrightarrow \quad e^{iNqa}\psi(x) = \psi(x),$$

We can solve for q,

$$q = \frac{2\pi n}{Na}, \quad (n = 0, \pm 1, \pm 2, \dots).$$

Note that q is a real number, so even though $\psi(x)$ is not periodic, $|\psi(x)|^2$ is:

$$|\psi(x+a)|^2 = |\psi(x)|^2.$$

Now, all we need to do is to solve for the cell $0 \leq x < a$. The recursive formula will generates the solution everywhere else. In the region $0 < x < a$, the potential is zero, so

$$\psi(x) = A\sin(kx) + B\cos(kx), \quad k = \frac{\sqrt{2mE}}{\hbar}.$$

According to Bloch's theorem, the wave function in the cell immediately to the left of the origin is

$$\psi(x) = e^{-iqa}[A\sin k(x+a) + B\cos k(x+a)], \quad (-a < x < 0).$$

The continuity of ψ at $x = 0$ gives

$$B = e^{-iqa}[A\sin(ka) + B\cos(ka)].$$

The discontinuity of $d\psi/dx$ at $x = 0$ (same as what we did for Dirac-delta well with the sign before α flipped) gives

$$kA - e^{-iqa}k[A\cos(ka) - B\sin(ka)] = \frac{2m\alpha}{\hbar^2}B. \tag{5.3}$$

Solve for A and B and substitute back to (5.3), we find

$$\cos(qa) = \cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka).$$

This equation determines k and hence the allowed energies. Let

$$z = ka, \quad \text{and} \quad \beta = \frac{m\alpha a}{\hbar^2},$$

the RHS of the equation can be simplified as

$$f(z) = \cos(z) + \beta\frac{\sin(z)}{z}.$$

If we plot $f(z)$ we should reject the parts outside the range $(-1, +1)$ because $|\cos(qa)| \leq 1$. The gaps represent forbidden energies

and they are separated by **bands** of allowed energies.

If there are more than one electron ($q > 1$) in the potential, according to the Pauli exclusion principle, the first electron will fill half of the first band. The second electron will fill another half. The third electron will fill half of the second band and so on. The bands accounts for the nature of substances:

- Insulator: if a band is completely filled, it requires a relatively large energy to excite an electron because it has to jump across the forbidden zone.

- Conductor: if a band is only partly filled, it takes very little energy to excite an electron.

- Semiconductor: if the bap is of an intermediate size. Random thermal energy can help the electron jump from one band to another.

The band structure model is different from the free electron gas model. According to the free electron gas model, there are no large gaps between energy levels—every solid should be a metal/conductor. It is these large gaps in the band structure that make solids to have various conductivities.

Part II

Applications

6 TIME-INDEPENDENT PERTURBATION THEORY

6.1 Non-degenerate Perturbation Theory

6.1.1 General Formulation

Suppose we have solved the time-independent Schrödinger equation,

$$H^0 \psi_n^0 = E_n^0 \psi_n^0,$$

and obtained a complete set of orthonormal eigenfunctions ψ_n^0 with corresponding eigenvalues E_n^0. Now perturb the potential, and we want to find the new eigenvalues and eigenstates, we will use **perturbation theory** to approximate solutions.

Consider a new Hamiltonian:

$$H = H^0 + \lambda H',$$

where H' is the perturbation and H^0 is the original Hamiltonian. The total Hamiltonian H is a function of λ, and so are E_n and ψ_n, the energies and eigenfunctions of H. We can write $\psi_n(\lambda)$ and $E_n(\lambda)$ as power series of λ, similar to a Taylor expansion,

$$\psi_n(\lambda) = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots,$$
$$E_n(\lambda) = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots.$$

The superscripts indicate nth-order corrections. The "coefficients" $\psi_n^1, \psi_n^2, \ldots$ and $E_n^1, E_n^2, \ldots$ are yet unknown. To determine them, we need to solve the Schrödinger equation by simply plugging in $\psi_n(\lambda)$ and $E_n(\lambda)$ into $H\psi_n = E_n\psi_n$:

$$(H^0 + \lambda H')[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots)[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots].$$

Collecting like powers of λ,

$$H^0 \psi_n^0 + \lambda(H^0 \psi_n^1 + H' \psi_n^0) + \lambda^2(H^0 \psi_n^2 + H' \psi_n^1) + \cdots = E_n^0 \psi_n^0 + \lambda(E_n^0 \psi_n^1 + E_n^1 \psi_n^0) + \lambda^2(E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0) + \cdots \qquad (6.1)$$

This is rather a set of equations—for each power of λ, the coefficients must be equal.

6.1.2 First-Order Theory

The zeroth-order equation $H^0 \psi_n^0 = E_n^0 \psi_n^0$ is not interesting, since it is a known information. We will start with the first order. From (6.1), the first order approximation has

$$H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0. \qquad (6.2)$$

Taking inner product of (6.2) with $\langle \psi_n^0 |$ on both sides,

$$\langle \psi_n^0 | H^0 | \psi_n^1 \rangle + \langle \psi_n^0 | H' | \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle.$$

Since H^0 is Hermitian (i.e. $\langle \psi_n^0 | H^0 = E_n^0 \langle \psi_n^0 |$), and the unperturbed basis is orthonormal $\langle \psi_n^0 | \psi_n^0 \rangle = 1$, we have

$$E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + \langle \psi_n^0 | H' | \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \quad \implies \quad \boxed{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle.} \qquad (6.3)$$

Hence the first-order perturbation theory says that the first-order correction to the energy is the expectation value of the perturbation in the unperturbed state. One property of the first-order perturbation is the accurate prediction of the energy when an energy level is lifted. That is, if the potential is lifted by a constant V_0, the first-order correction to the energy is exactly V_0,

$$E_n^1 = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0.$$

To find the first-order correction to the wave function, rewrite (6.2) as

$$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0. \tag{6.4}$$

Recall that ψ_n^0 form a complete set, so ψ_n^1 must be a linear combination of them:

$$\psi_n^1 = \sum_{m \neq n} c_{mn} \psi_m^0.$$

Note that $m \neq n$ means that c_{nn} can be omitted, or set to zero. This is because adding a $\alpha\psi_n^0$ for arbitrary α to ψ_n^1 does not affect (6.4) because $(H^0 - E_n^0)(\psi_n^1 + \alpha\psi_n^0) = (H^0 - E_n^0)\psi_n^1 + \alpha(E_n^0 - E_n^0)\psi_n^0 = (H^0 - E_n^0)\psi_n^1$. Putting the sum back to (6.4) and using the fact that $H^0\psi_m^0 = E^0\psi_m^0$,

$$\sum_{m \neq n} (E_m^0 - E_n^0)c_{nm}\psi_m^0 = -(H' - E_n^1)\psi_n^0.$$

Taking the inner product on both sides with $\langle \psi_\ell^0 |$,

$$\sum_{m \neq n} (E_m^0 - E_n^0)c_{mn} \langle \psi_\ell^0 | \psi_m^0 \rangle = - \langle \psi_\ell^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_\ell^0 | \psi_n^0 \rangle,$$

or

$$\sum_{m \neq n} (E_m^0 - E_n^0)c_{mn}\delta_{\ell m} = - \langle \psi_\ell^0 | H' | \psi_n^0 \rangle + E_n^1 \delta_{\ell n}.$$

If $\ell = n$, then the LHS is zero and the equation becomes the energy equation (6.3). If $\ell \neq n$, then

$$(E_\ell^0 - E_n^0)c_{\ell n} = - \langle \psi_\ell^0 | H' | \psi_n^0 \rangle \implies c_{mn} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}.$$

Thus, the first-order correction to the wave function is

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0. \tag{6.5}$$

Notice that $m \neq n$ makes the denominator nonzero, as long as the unperturbed energy spectrum is non-degenerate. If different unperturbed states are degenerate, we need degenerate perturbation theory.

Example 6.1. Increased spring constant

Recall that the allowed energies for the harmonic oscillator $V(x) = kx^2/2$ are

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

where $\omega = \sqrt{k/m}$. Now let the spring constant increase slightly, $k \to (1 + \epsilon)k$. The exact new energies are

$$E_n' = \left(n + \frac{1}{2}\right)\hbar\omega', \quad \text{where} \quad \omega' = \sqrt{\frac{(1 + \epsilon)k}{m}} = \omega\sqrt{1 + \epsilon}.$$

The new energy can be expressed as a power series of ϵ. To the first order of ϵ,

$$E_n' = \left(n + \frac{1}{2}\right)\hbar\omega\sqrt{1 + \epsilon} = E_n\left(1 + \frac{\epsilon}{2}\right) + \mathcal{O}(\epsilon^2).$$

The first-order correction to the energy is thus $E_n^1 = \epsilon E_n/2$. The result is exactly predicted by the perturbation theory. We know that the change in the Hamiltonian is $H' = \epsilon k x^2/2 = \epsilon V$, so

$$\langle n|H'|n\rangle = \epsilon \langle n|V|n\rangle = \frac{\epsilon E_n}{2} = E_n^1.$$

Here we used the fact that the expectation value of the potential energy is exactly equal to half the total energy, discussed in Example 1.3.

6.1.3 Second-Order Energies

According to (6.1), the second order equation is

$$H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0. \tag{6.6}$$

Again, taking the inner product with $\langle\psi_n^0|$:

$$\langle\psi_n^0|H^0|\psi_n^2\rangle + \langle\psi_n^0|H'|\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^2\rangle + E_n^1\langle\psi_n^0|\psi_n^1\rangle + E_n^2\langle\psi_n^0|\psi_n^0\rangle.$$

By Hermiticity of H^0 and $\langle\psi_n^0|\psi_n^0\rangle = 1$,
$$E_n^2 = \langle\psi_n^0|H'|\psi_n^1\rangle - E_n^1\langle\psi_n^0|\psi_n^1\rangle.$$

Since $|\psi_n^1\rangle$ is a linear combination of $|\psi_m^0\rangle$ according to (6.5),

$$\langle\psi_n^0|\psi_n^1\rangle = \sum_{m\neq n} c_{mn}\langle\psi_n^0|\psi_m^0\rangle = 0.$$

Thus, the second-order energy E_n^2 is

$$E_n^2 = \langle\psi_n^0|H'|\psi_n^1\rangle = \sum_{m\neq n} c_{mn}\langle\psi_n^0|H'|\psi_m^0\rangle = \sum_{m\neq n}\frac{\left|\langle\psi_m^0|H'|\psi_n^0\rangle\right|^2}{E_n^0 - E_m^0}. \tag{6.7}$$

We can also calculate second-order wave functions and higher-order energies, but second order is useful enough. In following sections, we will in general focus on first- and second-order energies and only first-order wave function in perturbation.

6.2 Degenerate Perturbation Theory

Two states ψ_a^0 and ψ_b^0 are degenerate if they share the same energy. Recall that the first-order correction to the perturbed state is

$$\psi_n^1 = \sum_{m\neq n}\frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{E_n^0 - E_m^0}\psi_m^0.$$

If the unperturbed states are degenerate, the denominator becomes zero when $E_a = E_b$ even though $a \neq b$. In other words, ψ_n^1 blows up unless $\langle\psi_a^0|H'|\psi_b^0\rangle = 0$.

6.2.1 Good States

Suppose

$$H^0\psi_a^0 = E^0\psi_a^0, \quad H^0\psi_b^0 = E^0\psi_b^0, \quad \langle\psi_a^0|\psi_b^0\rangle = \delta_{ab}.$$

Because ψ_a and ψ_b are degenerate, any linear combination of ψ_a^0 and ψ_b^0 is also an eigenstate of H^0 with eigenvalue E^0. We want to find **good states** ψ_+ and ψ_- that are linear combinations of ψ_a^0 and ψ_b^0 such that they set $\langle\psi_+^0|H'|\psi_-^0\rangle = 0$. Then we can use the ordinary perturbation theory. Before talking about the general method to find good states, let's see how can we guess the good states.

> **Theorem 6.1.**
>
> Let A be a Hermitian operator that commutes with H^0 and H'. If the degenerate eigenstates of H^0 (ψ_a^0 and ψ_b^0) are also eigenstates of A, with distinct eigenvalues,
>
> $$A\psi_a^0 = a\psi_a^0, \quad A\psi_b^0 = b\psi_b^0, \quad a \neq b,$$
>
> then ψ_a^0 and ψ_b^0 are good states to use in perturbation theory.

Proof. Since $[A, H'] = 0$, we have $\langle \psi_a^0 | [A, H'] | \psi_b^0 \rangle = 0$. Expanding the commutator,

$$\langle \psi_a^0 | AH' | \psi_b^0 \rangle - \langle \psi_a^0 | H'A | \psi_b^0 \rangle = \langle A\psi_a^0 | H' | \psi_b^0 \rangle - \langle \psi_a^0 | H' | A\psi_b^0 \rangle = 0.$$

Since A is Hermitian, a and b are real, so

$$(a - b) \langle \psi_a^0 | H' | \psi_b^0 \rangle = 0.$$

By the assumption $a \neq b$, we have $\langle \psi_a^0 | H' | \psi_b^0 \rangle$. The states ψ_a^0 and ψ_b^0 are good states. $\qquad \square$

Once we have the good states, we can use non-degenerate perturbation theory. Things to remember from this theorem is A commutes with H^0 and H', A is Hermitian, and its eigenvalues are distinct. Note that the degenerate eigenstates of A are not necessarily eigenstates of H'.

6.2.2 Two-Fold Degeneracy

There are some cases in which we are unable to guess the good states directly. Here is a more general way to find good states. Let the good states be expressed as a linear combination

$$\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0,$$

where ψ_a and ψ_b are not good states. When we are working with good states (but for now they are unknown), we can use the ordinary perturbation theory. We want to solve the Schrödinger equation $H\psi = E\psi$ with $H = H^0 + \lambda H'$ and

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \cdots, \quad \psi = \psi^0 + \lambda\psi^1 + \lambda^2\psi^2 + \cdots$$

Collecting like powers to first order gives the first-order equation

$$H^0\psi^1 + H'\psi^0 = E^0\psi^1 + E^1\psi^0. \tag{6.8}$$

Taking the inner product with $\langle \psi_a^0 |$:

$$\cancel{\langle \psi_a^0 | H^0 | \psi^1 \rangle} + \langle \psi_a^0 | H' | \psi^0 \rangle = \cancel{E^0 \langle \psi_a^0 | \psi^1 \rangle} + E^1 \langle \psi_a^0 | \psi^0 \rangle.$$

Using Hermiticity of H^0 and orthonormality of ψ_a^0 and ψ_b^0,

$$\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = \alpha E^1.$$

One will find that $\langle \psi_a^0 | H' | \psi_a^0 \rangle = H'_{aa}$ and $\langle \psi_a^0 | H' | \psi_b^0 \rangle = H'_{ab}$ are just matrix elements of H' in the $| \psi_a^0 \rangle$ and $| \psi_b^0 \rangle$ basis. The equation can be written as

$$\alpha H'_{aa} + \beta H'_{ab} = \alpha E^1. \tag{6.9}$$

Similarly, taking the inner product of first order equation with ψ_b^0 gives

$$\alpha H'_{ba} + \beta H'_{bb} = \beta E^1. \tag{6.10}$$

Writing in matrix form, (6.8) reduces to an eigenvalue equation:

$$\begin{bmatrix} H'_{aa} & H'_{ab} \\ H'_{ba} & H'_{bb} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E^1 \begin{bmatrix} \alpha \\ \beta \end{bmatrix}.$$

The value of E^1 and the good states are the eigenvalues and eigenvectors of H' in the $|\psi_a\rangle$ and $|\psi_b\rangle$ basis. The energies are

$$E^1_\pm = \frac{1}{2}\left[H'_{aa} + H'_{bb} \pm \sqrt{(H'_{aa} - H'_{bb})^2 + 4|H_{ab}|^2} \right], \tag{6.11}$$

where we used $H'_{ba} = H^*_{ab}$. In reality, the perturbation will break the degeneracy. The unperturbed degeneracy will split into two states with two distinct energies. To first order, the two energies are $E_0 + E_+$ and $E_0 + E_-$. Then when we turn off the perturbation, the two states will fall to the two good states.

6.2.3   Higher-Order Degeneracy

Let the good states be linear combinations of n arbitrary (degenerate) set of states $|\psi_i^0\rangle$,

$$|\psi^0\rangle = \sum_{i=1}^n \alpha_i |\psi_i^0\rangle$$

for n-fold degeneracy. By the same procedure, suppose we are working with good states and arrive at (6.8),

$$H^0 |\psi^1\rangle + H' |\psi^0\rangle = E^0 |\psi^1\rangle + E^1 |\psi^0\rangle.$$

Take the inner product with ψ_j^0,

$$\cancel{\langle\psi_j^0|H^0|\psi^1\rangle} + \langle\psi_j^0|H'|\psi^0\rangle = \cancel{E^0\langle\psi_j^0|\psi^1\rangle} + E^1\langle\psi_j^0|\psi^0\rangle.$$

Using the linear combination,

$$\sum_{i=1}^n \alpha_i \langle\psi_j^0|H'|\psi_i^0\rangle = E^1 \sum_{i=1}^n \alpha_i \langle\psi_j^0|\psi_i^0\rangle = E^1\alpha_j.$$

The LHS are just matrix elements in the $|\psi_i^0\rangle$ basis, so

$$\sum_{i=1}^n H'_{ji}\alpha_i = E^1\alpha_j.$$

In matrix notation, this is the eigenvalue problem

$$H'|\alpha\rangle = E^1|\alpha\rangle.$$

The first-order correction to the energy are eigenvalues of H', while $|\alpha\rangle$ are the good states in the $|\psi_i^0\rangle$ basis with components α_i. This is the same conclusion arrived from the case of two-fold degeneracy. In general, only some of the eigenstates of H^0 are degenerate, and some are not. To use non-degenerate perturbation theory, we need to find good states that diagonalize H' for the "degenerate part" of H^0.

Example 6.2. Two-fold degeneracy for a three-level system

Consider the perturbed Hamiltonian

$$H = V_0 \begin{bmatrix} 1-\epsilon & 0 & 0 \\ 0 & 1 & \epsilon \\ 0 & \epsilon & 2 \end{bmatrix} \implies H^0 = V_0 \begin{bmatrix} 1 & & \\ & 1 & \\ & & 2 \end{bmatrix} \quad \text{and} \quad H' = V_0\epsilon \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix},$$

where V_0 is constant, and ϵ is some small number ($\epsilon \ll 1$). Since H^0 is diagonal, its eigenvalues are the diagonal entries and eigenvectors are unit basis vectors:

$$E_a^0 = V_0, \quad |\psi_a^0\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad E_b^0 = V_0, \quad |\psi_b^0\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad E_c^0 = 2V_0, \quad |\psi_c^0\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}.$$

To find the exact eigenvalues of H, we should solve for the characteristic equation

$$0 = \begin{vmatrix} V_0(1-\epsilon) - E & 0 & 0 \\ 0 & V_0 - E & V_0\epsilon \\ 0 & V_0\epsilon & 2V_0 - E \end{vmatrix} = (V_0 - V_0\epsilon - E)[(V_0 - E)(2V_0 - E) - V_0^2\epsilon^2].$$

The solutions are

$$E_1 = (1-\epsilon)V_0, \quad E_2 = \frac{3 - \sqrt{4\epsilon^2 + 1}}{2}V_0, \quad E_3 = \frac{3 + \sqrt{4\epsilon^2 + 1}}{2}V_0.$$

To second order of ϵ, the energies E_2 and E_3 can be expanded as

$$E_2 \approx \frac{V_0}{2}\left(3 - 1 - 2\epsilon^2\right) V = (1 - \epsilon^2)V_0 \quad E_3 \approx \frac{V_0}{2}\left(3 + 1 + 2\epsilon^2\right) = (2 + \epsilon^2)V_0.$$

Among the eigenstates of H^0, only $|\psi_c^0\rangle$ is non-degenerate. We shall use non-degenerate perturbation theory for it. There is no first-order energy correction: $E_c^1 = \langle\psi_c^0|H'|\psi_c^0\rangle = 0$. The second-order energy correction by (6.7) is

$$E_c^2 = \frac{\left|\langle\psi_a^0|H'|\psi_c^0\rangle\right|^2}{E_c^0 - E_a^0} + \frac{\left|\langle\psi_b^0|H'|\psi_c^0\rangle\right|^2}{E_c^0 - E_b^0} = 0 + \frac{(V_0\epsilon)^2}{2V_0 - V_0} = V_0\epsilon^2.$$

This is consistent with $E_1 \approx (2 + \epsilon^2)V_0$ in part (b). The eigenstates $|\psi_a^0\rangle$ and $|\psi_b^0\rangle$ of H^0 are degenerate. By degenerate perturbation theory, we should fine the eigenvalues of H' for the degenerate part of H^0. That is, the first-order corrections of energy are eigenvalues of

$$H' = V_0\epsilon \begin{bmatrix} -1 & 0 \\ 0 & 0 \end{bmatrix}.$$

By inspection, the eigenvalues are $E_+ = 0$ (consistent with E_2 to first order) and $E_- = -V_0\epsilon$ (consistent exactly with E_3).

6.3 The Fine Structure of Hydrogen

The Hamiltonian of the hydrogen atom is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}.$$

We call this atom the "Bohr atom". First let's review list some known results from the Bohr atom: the energy levels are given by $E_n^0 = -13.6\,\text{eV}/n^2$. The eigenstates are $\psi_{n\ell m}$, given by (4.15) and in Appendix A.2.9. The radius of the hydrogen atom is given by the order of Bohr radius: $a = 4\pi\epsilon_0\hbar^2/me^2$. Degeneracies occur for each given n, with the number of degeneracy states n^2 (without spin), or $2n^2$ (with spin).

The solution to the Bohr atom is slightly different from the actual one. There is a tiny perturbation called **fine structure** with two corrections: **relativistic correction** and **spin-orbit coupling**.

6.3.1 The Relativistic Correction

Then how large is this perturbation, i.e., how far is the speed of electron from the speed of light:

$$p \sim \frac{\hbar}{a} \implies v \sim \frac{\hbar}{m_e a}, \implies \frac{v}{c} \sim \frac{\hbar}{m_e a c} = \alpha.$$

The constant α is known as the **fine structure constant**,

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}. \tag{6.12}$$

It shows that relativistic effects of the electron in hydrogen is small, but not negligible. Let $m = m_e$. The kinetic energy operator in quantum mechanics comes from the classical expression. The relativistic kinetic energy and momentum are

$$T = \frac{mc^2}{\sqrt{1-(v/c)^2}} - mc^2 \quad \text{and} \quad p = \frac{mv}{\sqrt{1-(v/c)^2}}.$$

The momentum and kinetic energy are related by $T = \sqrt{p^2 c^2 + m^2 c^4} - mc^2$. For small relativistic effects, $pc \ll mc^2$ for a particle so we can expand the kinetic energy in powers of (p/mc),

$$T = mc^2 \left[\sqrt{1 + \left(\frac{p}{mc}\right)^2} - 1 \right] = mc^2 \left[1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 + \cdots - 1 \right] = \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \cdots$$

The lowest-order relativistic correction to the Hamiltonian is then

$$H'_r = -\frac{p^4}{8m^3 c^2}.$$

The hydrogen atom is highly degenerate due to its spherically symmetric potential. However, the perturbation H'_r is also spherically symmetric, so H'_r also commutes with L^2 and L_z just like H does. Moreover, the *set* of eigenvalues taken together of L^2 and L_z are distinct for each state $\psi_{n\ell m}$. Thus, Theorem 6.1 says that $\psi_{n\ell m}$ are themselves good states, and n, ℓ, m are the good quantum numbers. They allow us to use non-degenerate perturbation theory.

According to first-order perturbation theory,

$$E_r^1 = \langle H'_r \rangle = -\frac{1}{8m^3 c^2} \langle \psi | p^4 | \psi \rangle = -\frac{1}{8m^3 c^2} \langle p^2 \psi | p^2 \psi \rangle.$$

By the unperturbed Schrödinger equation, $p^2 \psi = 2m(E^0 - V)\psi$, so

$$E_r^1 = -\frac{1}{8m^3 c^2} \langle 2m(E^0 - V)\psi | 2m(E^0 - V)\psi \rangle = -\frac{1}{2mc^2} \langle (E^0 - V)^2 \rangle = -\frac{1}{2mc^2}[(E^0)^2 - 2E^0\langle V \rangle + \langle V^2 \rangle].$$

For hydrogen, this is specified to

$$E_r^1 = -\frac{1}{2mc^2}\left[(E_n^0)^2 + 2E_n^0\left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right],$$

where E_n^0 is the Bohr energy and the expectation values of $1/r$ and $1/r^2$ can be calculated (see Feynman-Hellmann Theorem B.9 and Appendix B.8.1),

$$\left\langle\frac{1}{r}\right\rangle = \frac{1}{n^2 a}, \quad \left\langle\frac{1}{r^2}\right\rangle = \frac{1}{(\ell + 1/2)n^3 a^2}.$$

Eliminating a using the definition of Bohr radius (4.13) and rewrite everything in terms of E_n^0 using (4.12), we have

$$E_r^1 = -\frac{(E_n^0)^2}{2mc^2}\left[\frac{4n}{\ell + 1/2} - 3\right]. \tag{6.13}$$

6.3.2 Spin-Orbit Coupling

For an electron in an atom, the proton is circling around it in the electron frame. The proton generates a magnetic field $\mathbf{B}$ at electron's position, which exerts a torque on the spinning electron. The magnetic moment $\boldsymbol{\mu}$ of the electron tends to align with the field, and the Hamiltonian is

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

Now is to figure out the magnetic field of the proton and the dipole moment of the electron. Think of the proton as a continuous current loop. By Biot-Savart Law:

$$B = \frac{\mu_0 I}{2r},$$

where $I = e/T$ and T is the period of the orbit. The orbital angular momentum of the electron in the frame of the proton is $L = rmv = 2\pi mr^2/T$. Meanwhile, $\mathbf{B}$ and $\mathbf{L}$ are in the same direction, so

$$\mathbf{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \mathbf{L},$$

where we use $c = 1/\sqrt{\epsilon_0 \mu_0}$.

The magnetic dipole moment of a spinning electron is proportional to its spin angular momentum, with the proportionality constant the gyromagnetic ratio γ. Using classical electrodynamics, we can derive the gyromagnetic ratio. Consider a charge q evenly distributed on a ring of r that rotates with a period T. The magnetic dipole moment is defined as the product of current and area:

$$\mu = \frac{q\pi r^2}{T}.$$

The angular momentum is the product of moment of inertia and angular velocity:

$$S = \frac{2\pi mr^2}{T}.$$

Hence the gyromagnetic ratio is $\mu/S = q/2m$, which is independent of r and T. This means the ratio holds for all kinds of distribution of charge as long as the mass-charge ratio has rotational symmetry around the direction of $\mathbf{S}$. The directions of $\boldsymbol{\mu}$ and $\mathbf{S}$ are the same (or opposite if the charge is negative), so

$$\boldsymbol{\mu} = \left(\frac{q}{2m}\right)\mathbf{S}. \tag{6.14}$$

However, the electron's magnetic moment is twice the classical value according to Dirac's relativistic theory of the electron that we will not derive here:

$$\boldsymbol{\mu}_e = -\frac{e}{m}\mathbf{S}. \tag{6.15}$$

Returning back to the Hamiltonian,

$$H = \boldsymbol{\mu} \cdot \mathbf{B} = \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}.$$

These analysis are all in non-inertial system. To make this inertial, the correction is known as the **Thomas precession**:

$$H'_{\text{so}} = \left(\frac{e^2}{8\pi\epsilon_0}\right) \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}.$$

This is the **spin-orbit interaction**. Coincidentally, the Thomas precession factor $1/2$ cancels with Dirac's modified gyromagnetic ratio factor 2, which makes the result exactly the same as a classical model.

With spin-orbit coupling, the Hamiltonian no longer commutes with $\mathbf{L}$ and $\mathbf{S}$, but commutes with L^2 and S^2 and the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ (see proofs in Appendix B.8.2). Hence these quantities are conserved and eigenstates $\psi_{\ell sj}$ of L^2, S^2 and J^2 are considered good states (the states $|j, m_j\rangle$ can be obtained using the Clebsch-Gordan Table). Now we have

$$J^2 = (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S} \implies \mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2).$$

and the eigenvalues of $\mathbf{L} \cdot \mathbf{S}$ are then

$$\lambda_{\ell sj} = \frac{\hbar^2}{2}[j(j+1) - \ell(\ell+1) - s(s+1)].$$

The expectation value of $1/r^3$ calculated as (see also Appendix B.8.1)

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{\ell(\ell+1/2)(\ell+1)n^3 a^3}.$$

Thus, with $s = 1/2$ for electrons,

$$E^1_{\text{so}} = \langle \psi_{\ell sj} | H'_{\text{so}} | \psi_{\ell sj} \rangle = \frac{e^2}{8\pi\epsilon_0} \frac{\lambda_{\ell sj}}{m^2 c^2} \left\langle \frac{1}{r^3} \right\rangle = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2 c^2} \frac{(\hbar^2/2)[j(j+1) - \ell(\ell+1) - 3/4]}{\ell(\ell+1/2)(\ell+1)n^3 a^3}.$$

Expressing in terms of E^0_n,

$$E^1_{\text{so}} = \frac{(E^0_n)^2}{mc^2} \left\{ \frac{n[j(j+1) - \ell(\ell+1) - 3/4]}{\ell(\ell+1/2)(\ell+1)} \right\}. \tag{6.16}$$

Though with different mechanisms, the relativistic correction and the spin-orbit coupling have the same order (E_n^2/mc^2). The complete fine-structure correction is just adding them together (see derivation in Appendix B.8.3)

$$E_{\text{fs}}^1 = \frac{(E_n^0)^2}{2mc^2}\left(3 - \frac{4n}{j+1/2}\right).$$

(6.17)

Combining this with the Bohr formula, the grand result for the energy levels of hydrogen is

$$\boxed{E_{nj} = -\frac{13.6\,\text{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right].}$$

(6.18)

The fine structure changes the degeneracy in ℓ to degeneracy in j. The good quantum numbers are n, ℓ, s, j, and m_j. The exact fine structure of hydrogen can be obtained by relativistic quantum mechanics using Dirac equation without perturbation theory. I will write it here:

$$E_{nj} = mc^2\left\{\left[1 + \left(\frac{\alpha}{n - (j+1/2) + \sqrt{(j+1/2)^2 - \alpha^2}}\right)^2\right]^{-1/2} - 1\right\}.$$

(6.19)

Expanding (6.19) to order α^4 recovers (6.18).

6.4   The Zeeman Effect

When an atom is placed in an uniform external magnetic field $\mathbf{B}_{\text{ext}}$, its energy levels are shifted, known as the **Zeeman effect**. We will study the Zeeman effect on hydrogen with fine structure corrections.

$$H_Z' = -(\boldsymbol{\mu}_\ell + \boldsymbol{\mu}_s)\cdot\mathbf{B}_{\text{ext}} \quad \text{where} \quad \boldsymbol{\mu}_s = -\frac{e}{m}\mathbf{S} \quad \text{and} \quad \boldsymbol{\mu}_\ell = -\frac{e}{2m}\mathbf{L}.$$

The magnetic moment $\boldsymbol{\mu}_s$ is from spin according to (6.15) and $\boldsymbol{\mu}_\ell$ is from orbital angular momentum according to (classical, 6.14). Plug these into the perturbation, we obtain the full perturbation

$$H_Z' = \frac{e}{2m}(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{B}_{\text{ext}}.$$

(6.20)

An electrical analog to the Zeeman effect is the **Stark effect**, where the electron is placed in an external electric field $\mathbf{E}_{\text{ext}}$. See discussion in B.8.6.

6.4.1   Weak-Field Zeeman Effect

In the weak-field limit $\mathbf{B}_{\text{ext}} \ll \mathbf{B}_{\text{int}}$, the fine structure dominates over the Zeeman effect. Since we already get all informations from the fine structure, we shall treat $H_{\text{Bohr}} + H_{\text{fs}}'$ as unperturbed Hamiltonian and H_Z' as the perturbation. The eigenstates of the fine structure are degenerate in ℓ and m_j for the same n and j. Fortunately, we can choose $\mathbf{B}_{\text{ext}}$ to point in the z-direction so that H_Z' commutes with J_z and L^2. Then $|n,\ell,j,m_j\rangle$ are good states by Theorem 6.1 because they are uniquely determined by eigenvalues of J_z and L^2, namely m_j and ℓ (more precisely, $\ell(\ell+1)$). The first-order correction on energy is

$$E_Z^1 = \langle n,\ell,j,m_j|H_Z'|n,\ell,j,m_j\rangle = \frac{e}{2m}B_{\text{ext}}\hat{\mathbf{z}}\cdot\langle\mathbf{L} + 2\mathbf{S}\rangle = \frac{e}{2m}B_{\text{ext}}\hat{\mathbf{z}}\cdot\langle\mathbf{J} + \mathbf{S}\rangle.$$

The spin expectation is can be found by the Wigner-Eckart theorem (B.8, see derivation in Appendix B.8.4). The result is

$$\langle\mathbf{S}\rangle = \frac{\mathbf{S}\cdot\mathbf{J}}{|J|}\hat{\mathbf{e}}_J = \frac{\mathbf{S}\cdot\mathbf{J}}{J^2}\mathbf{J}.$$

An intuitive way of understanding this is that $\mathbf{L}$ and $\mathbf{S}$ are rapidly precessing around a fix vector $\mathbf{J}$ because it is conserved. Then the average value of $\mathbf{S}$ is its projection along $\mathbf{J}$. Now

$$\mathbf{S}\cdot\mathbf{J} = \frac{1}{2}(J^2 + S^2 - L^2) = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - \ell(\ell+1)].$$

Thus,

$$\langle\mathbf{L} + 2\mathbf{S}\rangle = \left\langle\left(1 + \frac{\mathbf{S}\cdot\mathbf{J}}{J^2}\right)\mathbf{J}\right\rangle = \left[1 + \frac{j(j+1) - \ell(\ell+1) + s(s+1)}{2j(j+1)}\right]\langle\mathbf{J}\rangle.$$

The term in the square bracket is called the **Landé g-factor**, g_J:

$$E_Z^1 = \frac{\hbar e}{2m} m_j g_J B_{\text{ext}} = \mu_{\text{B}} g_J B_{\text{ext}} m_j,$$
(6.21)

where $\mu_{\text{B}} \equiv e\hbar/2m = 5.788 \times 10^{-5}\,\text{eV/T}$ is the **Bohr magneton**. For example, the ground state ($n = 1$, $\ell = 0$, $j = 1/2$ and $g_J = 2$) splitting has energy correction from the Zeeman effect $\pm\mu_{\text{B}} B_{\text{ext}}$.

6.4.2 Strong-Field Zeeman Effect

In the strong field limit, $\mathbf{B}_{\text{ext}} \gg \mathbf{B}_{\text{int}}$, take the perturbation to be H_{fs}' and the unperturbed Hamiltonian to be

$$H_{\text{Bohr}} + H_Z' = H_{\text{Bohr}} + \frac{e}{2m} B_{\text{ext}}(L_z + 2S_z) \quad \Longrightarrow \quad E_{nm_\ell m_s} = -\frac{13.6\,\text{eV}}{n^2} + \mu_{\text{B}} B_{\text{ext}}(m_j + m_s).$$

This energy is obtained from the basis $|n, \ell, m_\ell, m_s\rangle$. Again, H_{fs}' commutes with L^2 and J_z, resolving the degeneracy in ℓ and $m_j + m_s = m_\ell + 2m_s$ respectively. Thus, $|n, \ell, m_\ell, m_s\rangle$ are good states. The first-order correction in energy is

$$E_{\text{fs}}^1 = \langle n, \ell, m_\ell, m_s|(H_r' + H_{\text{so}}')|n, \ell, m_\ell, m_s\rangle.$$

The relativistic correction is still (6.13). The spin-orbit coupling correction requires

$$\langle \mathbf{S} \cdot \mathbf{L} \rangle = \langle S_x\rangle\langle L_x\rangle + \langle S_y\rangle\langle L_y\rangle + \langle S_z\rangle\langle L_z\rangle = \hbar^2 m_\ell m_s$$

because $\langle S_x\rangle = \langle S_y\rangle = \langle L_x\rangle = \langle L_y\rangle$ for eigenstates of S_z and L_z. Note that we are allowed to separate $\langle S_x L_x\rangle = \langle S_x\rangle\langle L_x\rangle$ because orbital angular momentum and spin are in different spaces, i.e. $|m_\ell, m_s\rangle = |m_\ell\rangle|m_s\rangle$. Putting all these together (see Appendix B.8.5),

$$E_{\text{fs}}^1 = \frac{13.6\,\text{eV}}{n^3}\alpha^2\left\{\frac{3}{4n} - \left[\frac{\ell(\ell+1) - m_\ell m_s}{\ell(\ell+1/2)(\ell+1)}\right]\right\}.$$
(6.22)

6.5 Hyperfine Splitting in Hydrogen

To be written.

7 THE VARIATIONAL PRINCIPLE

7.1 Theory

There could be occasions where we cannot solve the time-independent Schrödinger equation but we want to find the ground state energy E_{gs}. The **variational principle** can give an upper bound for E_{gs}. Usually, this is very close to the exact value.

Theorem 7.1. The Variational Principle

For *any* normalized wave function ψ,
$$E_{\text{gs}} \leq \langle \psi|H|\psi \rangle = \langle H \rangle.$$

The expectation value of H in an incorrect state ψ is an overestimation of the ground state energy.

Proof. Since the (unknown) eigenfunctions of H form a complete set, we can express ψ as a linear combination of them:

$$\psi = \sum_n c_n \psi_n, \quad \text{with} \quad H\psi_n = E_n \psi_n.$$

Since ψ is normalized,

$$1 = \langle \psi|\psi \rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m|\psi_n \rangle = \sum_n |c_n|^2.$$

Meanwhile,

$$\langle H \rangle = \left\langle \sum_m c_m \psi_m \middle| H \middle| \sum_n c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* E_n c_n \langle \psi_m|\psi_n \rangle = \sum_n E_n |c_n|^2.$$

By definition, the ground state energy is the smallest eigenvalue of H, so $E_{\text{gs}} \leq E_n$. Hence

$$\langle H \rangle \geq E_{\text{gs}} \sum_n |c_n|^2 = E_{\text{gs}}.$$

$\square$

In principle, we can try all wave functions in the Hilbert space and the one with the lowest $\langle H \rangle$ will be the ground state. This is definitely not practical, so here we shall build some intuition on how to pick ψ:

- Observe the Hamiltonian

$$H = \frac{p^2}{2m} + V.$$

  The expectation value of the Hamiltonian can be separated into two parts: $\langle T \rangle + \langle V \rangle$. The kinetic energy term is related to the derivatives of the wave function. It tells us that the ideal wave function should not have many oscillations—we need to minimize the number of nodes. The potential energy term restricts where should most of the wave function be located, because particles do not want to be in high potential regions.

- The second technique is to introduce parameters. Then we have access to all this type of wave functions and it allows us to pick the best parameter that minimize $\langle H \rangle$. We will see examples below.

- There are many common/popular trial wave functions that satisfy the two points above. They include all the (normalizable) solutions to potentials discussed in Chapter 1: standing waves $\sin(x/a)$ with boundary conditions, Gaussian e^{-bx^2}, exponential decay $e^{-\alpha|x|}$, etc. However, the exponential decay $e^{-\alpha|x|}$ has a very sutble and interesting problem as a trial wave function. See Appendix B.9.1 (after mastering the following examples).

Example 7.1. The Harmonic Oscillator

Find the ground state energy for the one-dimensional harmonic oscillator:

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

We know that the ground state should not have nodes. Moreover, the potential is symmetric about $x = 0$, which suggests that the wave function is centered at $x = 0$. A popular trial wave function that satisfies both requirements is a Gaussian:

$$\psi(x) = \left(\frac{2b}{\pi}\right)^{1/4} e^{-bx^2},$$

where b is a constant and the coefficient ensures that the wave function is normalized. Since $\langle H \rangle = \langle T \rangle + \langle V \rangle$, we will calculate them separately.

$$\langle T \rangle = -\frac{\hbar^2}{2m}\sqrt{\frac{2b}{\pi}}\int_{-\infty}^{\infty} e^{-bx^2}\frac{d^2}{dx^2}\left(e^{-bx^2}\right)dx = \frac{\hbar^2 b}{2m}.$$

$$\langle V \rangle = \frac{1}{2}m\omega^2\sqrt{\frac{2b}{\pi}}\int_{-\infty}^{\infty} x^2 e^{-2bx^2}dx = \frac{m\omega^2}{8b}.$$

Thus,

$$\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}.$$

Assume that $\langle H \rangle \geq E_{\text{gs}}$ for any b, we shall minimize $\langle H \rangle$ to get the tightest bound:

$$\frac{d}{db}\langle H \rangle = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \quad \Longrightarrow \quad b = \frac{m\omega}{2\hbar}.$$

Putting this back to $\langle H \rangle$, we find

$$\langle H \rangle_{\text{min}} = \frac{1}{2}\hbar\omega,$$

which is exactly the ground state energy of the harmonic oscillator. Note that we find the exact ground state energy because the set of trial wave functions already contains the ground state of the harmonic oscillator.

Example 7.2. The Delta Potential Well

Find the ground state energy for the delta-function potential:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\delta(x).$$

We know that the true ground state should be $\psi \propto e^{-b|x|}$, but let's use the Gaussian wave function as the trial function again to see what happens. The kinetic energy is known in the previous example. The potential energy is

$$\langle V \rangle = -\alpha\sqrt{\frac{2b}{\pi}}\int_{-\infty}^{\infty} e^{-bx^2}\delta(x)\,dx = -\alpha\sqrt{\frac{2b}{\pi}}.$$

The expectation value of the Hamiltonian is

$$\langle H \rangle = \frac{\hbar^2 b}{2m} - \alpha\sqrt{\frac{2b}{\pi}}.$$

Minimizing this expectation value,

$$\frac{d}{db}\langle H \rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0 \quad \Longrightarrow \quad b = \frac{2m^2\alpha^4}{\pi\hbar^4}.$$

Plugging this b into $\langle H \rangle$, we get

$$\langle H \rangle_{\text{min}} = -\frac{m\alpha^2}{\pi\hbar^2},$$

which is somewhat higher than $E_{\text{gs}} = -m\alpha^2/2\hbar^2$.

The variational principle is a powerful and easy way to get the upper bound for the ground state energy. Even for complicated molecules while the trial wave function has nothing to do with the true function, you often get a close energy to the true value. There is also a corollary to the variational principle (see Corollary B.1) to find the upper bound on the first excited state.

7.2   The Ground State of Helium

A helium atom has a nucleus with two protons ($Z = 2$) and two orbiting electrons. It has the Hamiltonian

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right). \tag{7.1}$$

We want to calculate the ground state energy E_{gs}, or the ionization energy for two electrons in helium. The experimental measurement of E_{gs} is about $-78.975\,\text{eV}$. The Schrödinger equation $H\psi = E\psi$ does not have an exact solution because of the electron-electron repulsion term,

$$V_{ee} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{7.2}$$

If we ignore this, the Hamiltonian is separable into two decoupled equations, one for $\psi(\mathbf{r}_1)$ and the other for $\psi(\mathbf{r}_2)$. The wave function is just the product of two hydrogenic wave functions $\psi_{100}(\mathbf{r})$ with the Bohr radius a replaced by a/Z. (See Section 4.2.2 for more information.) The energy for one electron is $E_n(Z) \to Z^2 E_n$. There are two electrons in helium, so the exact solution has the ground state energy $E_{1,\text{He}} = 8E_1 = -109\,\text{eV}$ with the wave function

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2). = \frac{8}{\pi a^3}e^{-2(r_1+r_2)/a},$$

Now we apply the variational principle, using ψ_0 as the trial function because ψ_0 is an eigenfunction of *most* of the Hamiltonian:

$$H\psi_0 = (8E_1 + V_{ee})\psi_0 \quad \Longrightarrow \quad \langle H \rangle = 8E_1 + \langle V_{ee} \rangle,$$

where

$$\langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{8}{\pi a^3}\right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{|\mathbf{r}_1 - \mathbf{r}_2|}d^3\mathbf{r}_1 d^3\mathbf{r}_2 = \frac{5}{4a}\left(\frac{e^2}{4\pi\epsilon_0}\right) = -\frac{5}{2}E_1 = 34\text{ eV}.$$

(See Appendix B.9.2 for how to calculate this integral.) Hence

$$\langle H \rangle = -109\text{ eV} + 34\text{ eV} = -75\text{ eV}.$$

This is close to the experimental value but we can still improve this. Instead of completely ignoring the electron-electron repulsion, we see one electron shielding the nucleus from another electron. The second electron will then see the nucleus having an effective nuclear charge of $Z < 2$. The trial function is of the form

$$\psi_1(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi a^3}e^{-Z(r_1+r_2)/a}.$$

Remember each a is replaced by a/Z. By treating Z as a variational parameter, we can then minimize $\langle H \rangle$. Note that the Hamiltonian is unchanged, we are just varying the trial state. This wave function is an eigenstate of the Hamiltonian neglecting electron repulsion and with Z replacing the 2. Rewrite the original Hamiltonian (7.1) as

$$H = \left[-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)\right] + \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right).$$

The expectation value of H is

$$\langle H \rangle = 2Z^2 E_1 + 2(Z-2)\left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \langle V_{ee} \rangle,$$

where $\langle 1/r \rangle$ is the expectation value of $1/r$ in the one-particle hydrogenic ground state ψ_{100} with nuclear charge Z,

$$\left\langle\frac{1}{r}\right\rangle = \frac{1}{n^2 a} \to \frac{Z}{n^2 a} \quad \Longrightarrow \quad \left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle = \frac{Ze^2}{4\pi\epsilon_0 a} = 2ZE_1.$$

where we used $\langle 1/r \rangle = Z/a$ for ground state and (4.14) $E_1 = e^2/8\pi\epsilon_0 a$. The expectation value of V_{ee} is obtained by replacing 2 by Z, or change $a/2 \to a/Z$ in (7.2):

$$V_{ee} = \frac{5Z}{8a}\left(\frac{e^2}{4\pi\epsilon_0}\right) = -\frac{5Z}{4}E_1.$$

Gathering all terms together,

$$\langle H \rangle = \left[2Z^2 - 4Z(Z-2) - \frac{5}{4}Z\right]E_1 = \left[-2Z^2 + \frac{27}{4}Z\right]E_1.$$

Minimizing $\langle H \rangle$ gives $Z = 27/16$. Putting this value back to $\langle H \rangle$ yields $\langle H \rangle = 729E_1/128 = -77.5$ eV, which is very close to the experimental value.

7.3   The Hydrogen Molecule Ion

The hydrogen molecule ion H_2^+ consists of a single electron in the field of two protons with separation distance R. The Hamiltonian of the electron 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 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 bringing the second proton in from infinity to a distance R. Assume that $R \gg a$ (or else the electron's wave function isn't changed much), and the electron has the same probabilit of being with either proton. This suggests a trial function

$$\psi = A[\psi_0(r_1) + \psi_0(r_2)].$$

The first step is to normalize this function, with some complicated integration,

$$|A|^2 = \frac{1}{2(1+I)}, \quad \text{where} \quad I = e^{-R/a}\left[1 + \left(\frac{R}{a}\right) + \frac{1}{3}\left(\frac{R}{a}\right)^2\right].$$

I is called an **overlap** integral which measus the amount by which $\psi_0(r_1)$ overlaps $\psi_0(r_2)$. The second step is to calculate $\langle H \rangle$ in the trial state ψ. Since

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_1}\right)\psi_0(r_1) = E_1\psi_0(r_1),$$

(and same with r_2), we have

$$H\psi = A\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_2} + \frac{1}{r_2}\right)\right][\psi_0(r_1) + \psi_0(r_2)]$$

$$= E_1\psi - A\left(\frac{e^2}{4\pi\epsilon_0}\right)\left[\frac{1}{r_2}\psi_0(r_1) + \frac{1}{r_1}\psi_0(r_2)\right].$$

It follows that

$$\langle H \rangle = E_1 - 2|A|^2\left(\frac{e^2}{4\pi\epsilon_0}\right)\left[\left\langle\psi_0(r_1)\left|\frac{1}{r_2}\right|\psi_0(r_1)\right\rangle + \left\langle\psi_0(r_1)\left|\frac{1}{r_1}\right|\psi_0(r_2)\right\rangle\right].$$

This expression involves two integrals: the **direct integral**

$$D = a\left\langle\psi_0(r_1)\left|\frac{1}{r_2}\right|\psi_0(r_1)\right\rangle = \frac{a}{R} - \left(1 + \frac{a}{R}\right)e^{-2R/a},$$

and the **exchange integral**

$$X = \left\langle\psi_0(r_1)\left|\frac{1}{r_1}\right|\psi_0(r_2)\right\rangle = \left(1 + \frac{R}{a}\right)e^{-R/a}.$$

Recall that $E_1 = -(e^2/4\pi\epsilon_0)(1/2a)$,

$$\langle H \rangle = \left[1 + 2\frac{D+X}{1+I}\right]E_1.$$

There is also proton-proton repulsion potential energy in the system:

$$V_{pp} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{R} = -\frac{2a}{R}E_1.$$

Hence the total energy of the system is (in the units of $-E_1$):

$$F(x) = -1 + \frac{2}{x}\left\{\frac{[1-(2/3)x^2]e^{-x} + (1+x)e^{-2x}}{1 + [1+x+(1/3)x^2]e^{-x}}\right\},$$

where $x = R/a$.

This is a bounded system if you plot the graph of $F(x)$. The energy of the system at equilibrium (the negative of binding energy) is -1.8 eV, whereas the experimental value is -2.8 eV.

8 THE WKB APPROXIMATION

The **WKB approximation** method (named after Wentzel, Kramers, Brillouin) can be used to solve the time-independent Schrödinger equation in one dimension. It is a powerful method that helps find all approximate allowed energies of a Hamiltonian without solving any particular differential equations. The key idea is as the following: consider a particle with energy E in a constant potential $V(x)$. If $E > V$, then the wave function is of the form

$$\psi(x) = Ae^{\pm ikx}, \quad k = \frac{\sqrt{2m(E-V)}}{\hbar}.$$

This wave function is oscillatory with constant wavelength $\lambda = 2\pi/k$ and amplitude A. Now suppose $V(x)$ is not constant, but varies slowly comparing to λ. The wave function remains practically sinusoidal, with its wavelength and amplitude changing slowly with x. Similarly, if $E < V$,

$$\psi(x) = Ae^{\pm \kappa x}, \quad \kappa = \frac{\sqrt{2m(V-E)}}{\hbar}.$$

If $V(x)$ is not constant, but varies slowly comparing to $1/\kappa$, then the wave function remains practically exponential. The WKB approximation will be difficult to handle only at the turning point, where $E \approx V$ and λ or $1/\kappa$ blows up.

8.1   The Classical Region

The Schrödinger equation can be rewritten as

$$\frac{d^2\psi}{dx^2} = -\frac{p^2}{\hbar^2}\psi, \quad \text{where} \quad p(x) = \sqrt{2m(E-V)} \tag{8.1}$$

is the classical formula for the momentum of a particle with total energy E and potential energy V. In the classical region, assume that $E > V$ so that p is real. We can express $\psi(x)$ in terms of its amplitude $A(x)$ and its phase $\phi(x)$:

$$\psi(x) = A(x)e^{i\phi(x)}.$$

Taking the first and second derivative:

$$\frac{d\psi}{dx} = (A' + iA\phi')e^{i\phi}, \quad \frac{d^2\psi}{dx^2} = [A'' + 2iA'\phi' + iA\phi'' - A\phi'^2]e^{i\phi}.$$

Substitute into (8.1):

$$A'' + 2iA'\phi' + iA\phi'' - A\phi'^2 = -\frac{p^2}{\hbar^2}A.$$

This requires

$$A'' - A\phi'^2 = -\frac{p^2}{\hbar^2}A \quad \Longrightarrow \quad A'' = A\left(\phi'^2 - \frac{p^2}{\hbar^2}\right),$$

and

$$2A'\phi' + A\phi'' = 0 \quad \Longrightarrow \quad \left(A^2\phi'\right)' = 0.$$

The second equation gives $A = C/\sqrt{\phi'}$. The first equation needs the approximation, assuming that the amplitude A varies slowly, i.e. A'' is negligible. In this case

$$(\phi')^2 = \frac{p^2}{\hbar^2} \quad \text{or} \quad \phi(x) = \pm\frac{1}{\hbar}\int p(x)\,dx.$$

The approximated wave function would be

$$\boxed{\psi(x) \simeq \frac{C}{\sqrt{p(x)}}\, e^{\pm \frac{i}{\hbar}\int p(x)\,dx},} \tag{8.2}$$

where $\sqrt{\hbar}$ is absorbed into C. The probability density is

$$|\psi(x)|^2 \simeq \frac{|C|^2}{p(x)}.$$

This indicates that the probability of finding a particle at x is inversely proportional to the momentum at that point. This is expected classically because it is more difficult to catch a particle with high speed at a certain point.

Example 8.1. An infinite square well with bumps

Consider an infinite square well with bumps specified by $f(x)$ and assume $E > V(x)$ inside the well:

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

The wave function inside the well according to (8.2) is

$$\psi(x) \simeq \frac{1}{\sqrt{p(x)}} \left[C_+ e^{i\phi(x)} + C_- e^{-i\phi(x)} \right] = \frac{1}{\sqrt{p(x)}} \left[C_1 \sin \phi(x) + C_2 \cos \phi(x) \right].$$

The phase can be computed by the integral

$$\phi(x) = \frac{1}{\hbar} \int_0^x p(x') \, dx'.$$

The boundary condition is $\psi(0) = \psi(a) = 0$, which gives $C_2 = 0$ and $\phi(a) = n\pi$ for $n = 1, 2, 3, \ldots$. The final result is

$$\int_0^a p(x) \, dx = n\pi\hbar.$$

If $f(x) = 0$, this should give the allowed energies of the ordinary infinite square well. Indeed, in this case $p(x) = \sqrt{2mE}$ and $pa = n\pi\hbar$, so $E_n = n^2\pi^2\hbar^2/2ma^2$.

When Can the WKB Approximation be Used?

WKB approximation is a semi-classical treatment of quantum mechanics. We will see why in this discussion. In general, when we say something is negligible, we always want to compare it with other quantities. In the above derivation, we make the assumption that A'' is negligible. The comparison is

$$|A''| \ll A\phi'^2 \approx \frac{p^2}{\hbar^2} A = k^2 A \quad \Longrightarrow \quad \left| \frac{A''}{A} \right| \ll k^2. \tag{8.3}$$

We know that $A = C/\sqrt{\phi'} = C/\sqrt{k}$. The derivatives of A are

$$A' = -\frac{1}{2}Ck^{-3/2}k', \quad \frac{A''}{A} = \frac{\sqrt{k}}{C}\left(\frac{3}{4}Ck^{-5/2}k'^2 - \frac{1}{2}Ck^{-3/2}k'' \right) = \frac{3}{4}\frac{k'^2}{k^2} - \frac{1}{2}\frac{k''}{k}.$$

To satisfy the condition (8.3), we just require both terms of A''/A to be much smaller than k^2, so

$$|k'| \ll k^2 \quad \text{and} \quad |k''| \ll |k^3|. \tag{8.4}$$

The condition $|k'| \ll k^2$ has many interpretations:

- **The scale of $\hbar$**: we can write $k = p/\hbar$ so that $\hbar|p'| \ll p^2$. To satisfy this, one can choose a system in which $\hbar$ is small enough. Since $\hbar$ sets the scale of quantum mechanics, setting $\hbar \to 0$ treats quantum mechanics classically.

- **The change of momentum**: the condition $\hbar|p'| \ll p^2$ is equivalent to

$$\frac{\hbar|p'|}{|p|} \sim \lambda|p'| \ll |p|,$$

where λ is the de Broglie wavelength. The change local momentum over a distance comparable to the local de Broglie wavelength is small compared to the momentum itself.

- **The change of wavelength**: the third way to write the condition is

$$\left|\frac{\hbar p'}{p^2}\right| = \left|\frac{d}{dx}\left(\frac{\hbar}{p}\right)\right| \ll 1 \quad \implies \quad \lambda' \ll 1.$$

In other words, the de Broglie wavelength varies slowly in space.

- **The change of potential**: recall that $p(x) = \sqrt{2m[E - V(x)]}$. We have

$$|pp'| = \left|\frac{2mV'\sqrt{2m[E - V(x)]}}{2\sqrt{2m[E - V(x)]}}\right| = m|V'| \quad \implies \quad \lambda|V'| = \frac{h}{p}\frac{|pp'|}{m} = \frac{h}{m}|p'| \ll \frac{p^2}{m},$$

where in the last step we used $\hbar|p'| \ll p^2$. This means the change in potential over a distance of order the de Broglie wavelength is much smaller than the kinetic energy.

As mentioned previously, the WKB approximation breaks down when $E \approx V$, or $k \approx 0$, because there is no way to satisfy $|k'| \ll k^2$. Before we solve this, let's first write out the WKB approximation for non-classical region.

8.2   Tunneling

We can write down the corresponding result in the non-classical region ($E < V$). Just change $p(x) \to i|p(x)|$ with $p(x)$ now imaginary:

$$\boxed{\psi(x) \simeq \frac{C}{\sqrt{|p(x)|}} e^{\pm \frac{1}{\hbar} \int |p(x)| \, dx}.} \tag{8.5}$$

Example 8.2. Scattering state with a barrier

Consider a scattering state and let there be a barrier $f(x) > 0$

$$V = \begin{cases} f(x), & 0 \le x \le a, \\ 0, & \text{otherwise.} \end{cases}$$

To the left of the barrier with $x < 0$, $\psi(x) = Ae^{ikx} + Be^{-ikx}$, where A is the incident amplitude, B is the reflected amplitude, and $k = \sqrt{2mE}/\hbar$. To the right ($x > a$), $\psi(x) = Fe^{ikx}$, where F is the transmitted amplitude. The transmission probability is $T = |F|^2/|A|^2$. In $0 \le x \le a$, the WKB approximation (8.5) says

$$\psi(x) \simeq \frac{C}{\sqrt{|p(x)|}} e^{\frac{1}{\hbar} \int_0^x |p(x')| \, dx'} + \frac{D}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar} \int_0^x |p(x')| \, dx'}.$$

When the barrier is high/wide, the coefficient C must approach to 0 (otherwise the wave function will blows up). For a more rigorous derivation, see Example 8.7. The relative amplitudes of the incident and transmitted waves is connected by $\psi(x)$ in the region of the barrier,

$$\frac{|F|}{|A|} \sim e^{-\frac{1}{\hbar} \int_0^a |p(x)| \, dx}.$$

Hence the transmission probability is

$$T = \frac{|F|^2}{|A|^2} \simeq e^{-2\gamma} \quad \text{where} \quad \gamma \equiv \frac{1}{\hbar} \int_0^a |p(x)| \, dx. \tag{8.6}$$

8.3   The Connection Formulas

The WKB approximation breaks down when the classical region meets the non-classical one. For simplicity, assume that the turning

point occurs at $x = 0$, and $V(x) > E$ for $x > 0$. The WKB approximation gives

$$\psi(x) \simeq \begin{cases} \dfrac{1}{\sqrt{p(x)}} \left[B e^{\frac{i}{\hbar} \int_x^0 p(x')\,dx'} + C e^{-\frac{i}{\hbar} \int_x^0 p(x')\,dx'} \right], & x < 0, \\ \dfrac{1}{\sqrt{|p(x)|}} D e^{-\frac{1}{\hbar} \int_0^x |p(x')|\,dx'}, & x > 0. \end{cases} \tag{8.7}$$

(Since we let $V(x) > E$ for all $x > 0$, the positive exponential in (8.5) is excluded.) The usual way to connect two wave functions is to impose boundary conditions such as continuity of ψ and $d\psi/dx$. This will not work in the WKB approximation, because ψ goes to infinity at the turning point as $p(x) \to 0$.

Since we are only fixing the behavior near the turning point (at origin), we can approximate the potential by a straight line:

$$V(x) \simeq E + V'(0)x.$$

Let the patching wave function be ψ_p. We need to solve the Schrödinger equation exactly,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_p}{dx^2} + [E + V'(0)x]\psi_p = E\psi_p \quad \Longrightarrow \quad \frac{\hbar^2}{2m} \frac{d^2\psi_p}{dx^2} = V'(0)x\psi_p.$$

Define $z \equiv \alpha x$ so that the Schrödinger equation becomes

$$\frac{d^2\psi_p}{dz^2} = z\psi_p, \quad \text{where} \quad \alpha = \left[\frac{2m}{\hbar^2} V'(0) \right]^{1/3} \tag{8.8}$$

(8.8) is called **Airy's equation** and the solutions are **Airy functions**. Properties of the Airy functions include:

- Integral representation of the 2 linearly independent solutions:

$$\mathrm{Ai}(z) = \frac{1}{\pi} \int_0^\infty \cos\left(\frac{s^3}{3} + sz \right) ds, \quad \mathrm{Bi}(z) = \frac{1}{\pi} \int_0^\infty \left[e^{-\frac{s^3}{3} + sz} + \sin\left(\frac{s^3}{3} + sz \right) \right] ds. \tag{8.9}$$

- Asymptotic behavior:

$$\left. \begin{array}{l} \mathrm{Ai}(z) \sim \dfrac{1}{2\sqrt{\pi} z^{1/4}} e^{-\frac{2}{3} z^{3/2}} \\[2ex] \mathrm{Bi}(z) \sim \dfrac{1}{\sqrt{\pi} z^{1/4}} e^{\frac{2}{3} z^{3/2}} \end{array} \right\} z \gg 0, \qquad \left. \begin{array}{l} \mathrm{Ai}(z) \sim \dfrac{1}{\sqrt{\pi}(-z)^{1/4}} \sin\left[\dfrac{2}{3}(-z)^{3/2} + \dfrac{\pi}{4} \right] \\[2ex] \mathrm{Bi}(z) \sim \dfrac{1}{\sqrt{\pi}(-z)^{1/4}} \cos\left[\dfrac{2}{3}(-z)^{3/2} + \dfrac{\pi}{4} \right] \end{array} \right\} z \ll 0.$$
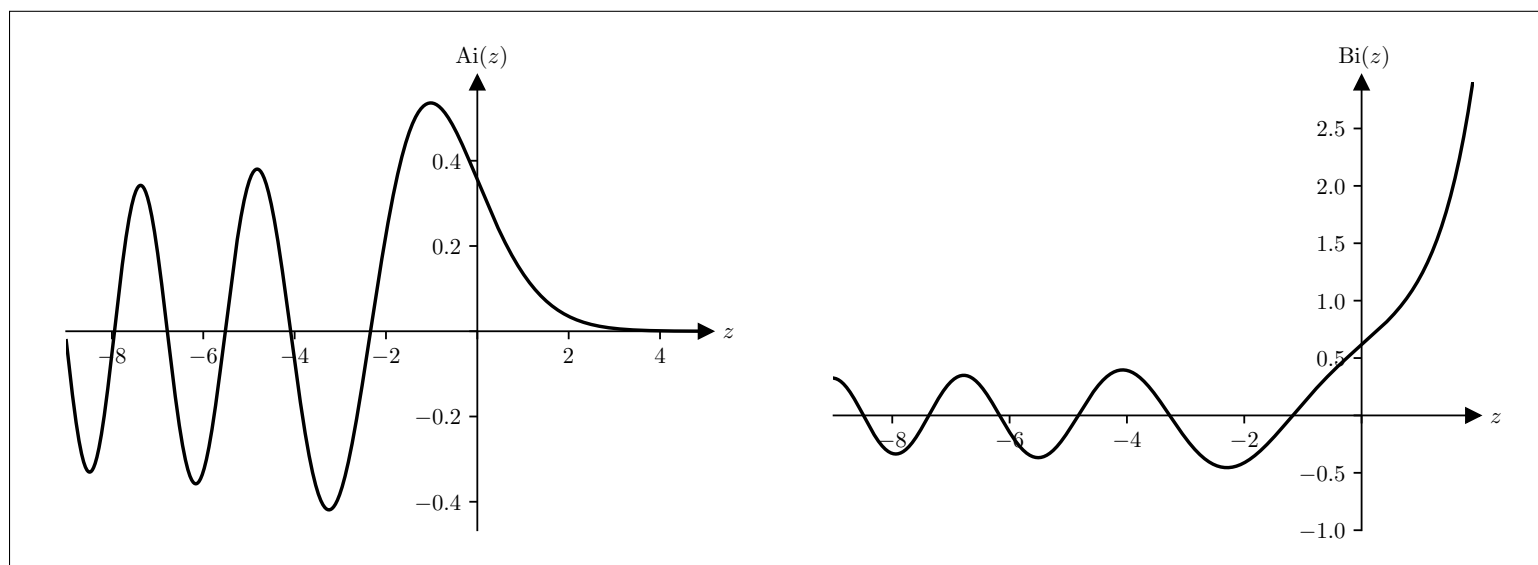
The patching wave function is the linear combination of Airy functions:

$$\psi_p(x) = a\mathrm{Ai}(\alpha x) + b\mathrm{Bi}(\alpha x)$$

for some constants a and b. Our goal is to match ψ_p to the WKB solutions in two *overlap regions*, one for $x > 0$ and another for $x < 0$ because the WKB solutions have different behaviors depending on x. Such regions should satisfy two constraints: 1. they are close enough to the turning point so that a linear potential is about accurate; 2. they are far enough away from the turning point so that WKB approximate well *and* we can apply large-$|z|$ approximation to the Airy functions. For problems involving the WKB approximation, we assume these overlap regions exist.
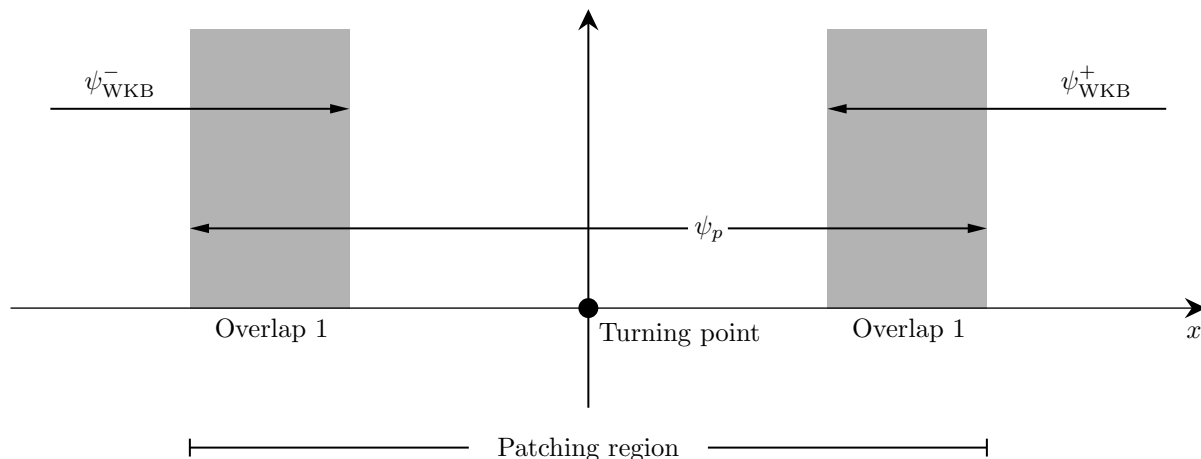
Figure 8.1: Patching region and the two overlap zones.

In the overlap regions, $V(x) \simeq E + V'(0)x$ holds, so

$$p(x) \simeq \sqrt{2m[E - E - V'(0)x]} = \hbar\alpha^{3/2}\sqrt{-x}. \tag{8.10}$$

We first look at the overlap region on the right side of the turning point,

$$\int_0^x |p(x')|\, dx' \simeq \hbar\alpha^{3/2} \int_0^x \sqrt{x'}\, dx' = \frac{2}{3}\hbar(\alpha x)^{3/2}.$$

Referring to (8.7), for $x > 0$, the WKB wave function gives

$$\psi_{\text{WKB}}^+(x) \simeq \frac{D}{\sqrt{\hbar}\alpha^{3/4}x^{1/4}}\, e^{-\frac{2}{3}(\alpha x)^{3/2}}.$$

Then we use the large-z asymptotic forms mentioned in the properties of Airy functions. The patching wave function at overlap region with $z \gg 0$ is

$$\psi_p^+(x) \simeq \frac{a}{2\sqrt{\pi}(\alpha x)^{1/4}}\, e^{-\frac{2}{3}(\alpha x)^{3/2}} + \frac{b}{\sqrt{\pi}(\alpha x)^{1/4}}\, e^{\frac{2}{3}(\alpha x)^{3/2}}.$$

(Note: it seems unreasonable that we can use large-z asymptotics here if we want the linear potential to be close to $z = 0$. This is why we assume there exist a region such that $z = \alpha x$ is large while the linear $V(x)$ is also accurate.) Now compare the WKB wave function ψ_{WKB}^+ with the patching wave function ψ_p^+. It follows that

$$a = \sqrt{\frac{4\pi}{\alpha\hbar}}D \quad \text{and} \quad b = 0.$$

This is what we get from positive overlap region. Repeating the procedure for negative overlap region: similar to (8.10),

$$p(x) \simeq \hbar\alpha^{3/2}\sqrt{-x} \quad \Longrightarrow \quad \int_x^0 p(x')\, dx' \simeq \frac{2}{3}\hbar(-\alpha x)^{3/2}, \tag{8.11}$$

Note that this time p is real as $x < 0$, no absolute sign needed. The WKB wave function is

$$\psi_{\text{WKB}}^-(x) \simeq \frac{1}{\sqrt{\hbar}\alpha^{3/4}(-x)^{1/4}}\left[Be^{i\frac{2}{3}(-\alpha x)^{3/2}} + Ce^{-i\frac{2}{3}(-\alpha x)^{3/2}}\right].$$

The asymptotic form of Airy functions for $z \ll 0$ says

$$\psi_p^-(x) \simeq \frac{a}{\sqrt{\pi}(-\alpha x)^{1/4}}\sin\left[\frac{2}{3}(-\alpha x)^{3/2} + \frac{\pi}{4}\right] = \frac{a}{\sqrt{\pi}(-\alpha x)^{1/4}}\frac{1}{2i}\left[e^{i\pi/4}e^{i\frac{2}{3}(-\alpha x)^{3/2}} - e^{-i\pi/4}e^{-i\frac{2}{3}(-\alpha x)^{3/2}}\right],$$

where we have used $b = 0$ from positive overlap region. Compare it to the WKB wave function ψ_{WKB}^-, we have

$$\frac{a}{2i\sqrt{\pi}}\, e^{i\pi/4} = \frac{B}{\sqrt{\hbar\alpha}} \quad \text{and} \quad -\frac{a}{2i\sqrt{\pi}}\, e^{-i\pi/4} = \frac{C}{\sqrt{\hbar\alpha}}.$$

Writing $a = \sqrt{4\pi/\alpha\hbar}\, D$,

$$B = -ie^{i\pi/4}D \quad \text{and} \quad C = ie^{-i\pi/4}D,$$

and substituting B and C back to ψ_{WKB}^-,

$$\psi_{\mathrm{WKB}}^- \simeq \frac{D}{\sqrt{\hbar}\alpha^{3/4}(-x)^{1/4}}\left[-ie^{i\pi/4}e^{i\frac{2}{3}(-\alpha x)^{3/2}} + ie^{-i\pi/4}e^{-i\frac{2}{3}(-\alpha x)^{3/2}}\right] = \frac{2D}{\sqrt{\hbar}\alpha^{3/4}(-x)^{1/4}}\sin\left[\frac{2}{3}(-\alpha x)^{3/2} + \frac{\pi}{4}\right].$$

Now we get ψ_{WKB}^+ and ψ_{WKB}^- in terms of α. Work back to express $\psi_{\mathrm{WKB}}^\pm$ in terms of $|p(x)|$ using (8.10) and $p(x)$ using (8.11),

$$\psi_{\mathrm{WKB}}^-(x) \simeq \frac{2D}{\sqrt{p(x)}}\sin\left[\frac{1}{\hbar}\int_x^0 p(x')\,dx' + \frac{\pi}{4}\right], \qquad \psi_{\mathrm{WKB}}^+(x) \simeq \frac{D}{\sqrt{p(x)}}\exp\left[-\frac{1}{\hbar}\int_0^x |p(x')|\,dx'\right].$$

These are called the **connection formulas**. We can generalize the turning point to arbitrary point x_t, and the connection formulas are

$$\psi(x) \simeq \begin{cases} \dfrac{2D}{\sqrt{p(x)}}\sin\left[\dfrac{1}{\hbar}\displaystyle\int_x^{x_t} p(x')\,dx' + \dfrac{\pi}{4}\right], & x < x_t, \\[3mm] \dfrac{D}{\sqrt{|p(x)|}}\exp\left[-\dfrac{1}{\hbar}\displaystyle\int_{x_t}^x |p(x')|\,dx'\right], & x > x_t. \end{cases} \tag{8.12}$$

These are the connection formulas for an upward-sloping potential ($V > E$ for $x > 0$). Similarly, we can also work out the connection formulas for a downward-sloping potential ($V > E$ for $x < 0$). See Appendix B.10.1.

$$\psi(x) \simeq \begin{cases} \dfrac{D'}{\sqrt{|p(x)|}}\exp\left[-\dfrac{1}{\hbar}\displaystyle\int_x^{x_t} |p(x')|\,dx'\right], & x < x_t, \\[3mm] \dfrac{2D'}{\sqrt{p(x)}}\sin\left[\dfrac{1}{\hbar}\displaystyle\int_{x_t}^x p(x')\,dx' + \dfrac{\pi}{4}\right], & x > x_t. \end{cases} \tag{8.13}$$

Note the limits of the integrals inside the exponential. We are always keeping the term that is exponentially suppressed for normalizable solutions. Even though $p \to 0$ and $\psi \to \infty$ at turning points, the wave functions are still normalizable (for bound states at least). This is because $\psi_{\mathrm{WKB}}^\pm \propto (\pm x)^{-1/4}$ near the turning points with the assumption that $V(x)$ can be approximated as linear. The purpose of the patching wave function ψ_p is to help connect ψ_{WKB}^+ and ψ_{WKB}^- near turning points, not to eliminate infinities. If we really needs a wave function without infinities, we can replace the patching region with Airy functions directly. Figure 8.2 is a comparison between $\psi_{\mathrm{WKB}}(x)$ and $\mathrm{Ai}(x)$.
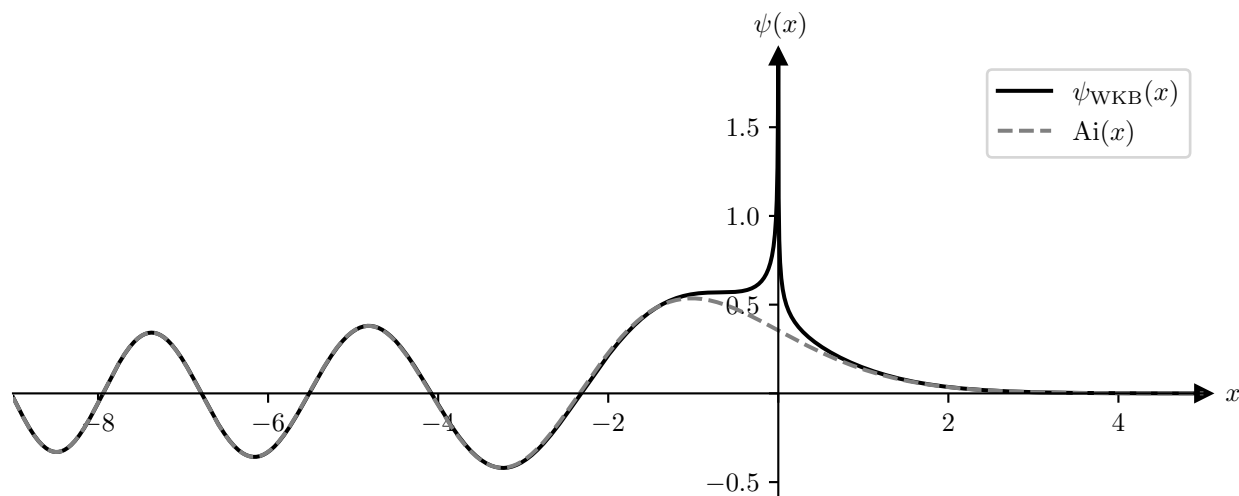
Figure 8.2: $\psi_{\mathrm{WKB}}(x)$ and $\mathrm{Ai}(x)$ near the turning point (not normalized). Though ψ_{WKB} goes to infinity at $x = 0$, it is normalizable as seen from the plot.

Example 8.3. Potential well with one vertical wall

Consider the following potential with one wall and a monotonically increasing function $f(x)$ on the other side:

$$V(x) = \begin{cases} f(x), & x > 0, \\ \infty, & x \leq 0. \end{cases}$$

Suppose the turning point is at $x_t > 0$. In the region $0 < x < x_t$, (8.12) says that

$$\psi(x) \simeq \frac{2D}{\sqrt{p(x)}} \sin\left[\frac{1}{\hbar}\int_x^{x_t} p(x')\,dx' + \frac{\pi}{4}\right].$$

The only boundary condition is $\psi(0) = 0$, which means

$$\frac{1}{\hbar}\int_0^{x_t} p(x)\,dx + \frac{\pi}{4} = n\pi \quad \Longrightarrow \quad \int_0^{x_t} p(x)\,dx = \left(n - \frac{1}{4}\right)\pi\hbar. \tag{8.14}$$

As expected, the energy (or momentum) is quantized for a bound state.

Example 8.4. The half-harmonic oscillator

We can apply the result of Example 8.3 to some particular potential. Consider the half-harmonic oscillator,

$$V(x) = \begin{cases} \frac{1}{2}m\omega^2 x^2, & x > 0, \\ \infty, & x \leq 0. \end{cases}$$

The momentum is of a particle in this potential is

$$p(x) = \sqrt{2m\left(E - \frac{1}{2}m\omega^2 x^2\right)} = m\omega\sqrt{x_t^2 - x^2} \quad \text{where} \quad x_t = \frac{1}{\omega}\sqrt{\frac{2E}{m}}$$

is the turning point. Applying (8.14),

$$\int_0^{x_t} p(x)\,dx = m\omega\int_0^{x_t}\sqrt{x_t^2 - x^2}\,dx = \frac{\pi}{4}m\omega x_t^2 = \frac{\pi E}{2\omega} = \left(n - \frac{1}{4}\right)\pi\hbar.$$

This gives the allowed energies of the half-harmonic oscillator,

$$E_n = \left(2n - \frac{1}{2}\right)\hbar\omega = \frac{1}{2}\hbar\omega[3, 7, 11, \dots].$$

The WKB approximation gives the exact energy because the eigenstates of the half-harmonic oscillator are the odd solutions of the full harmonic oscillator.

Example 8.5. Potential well with no vertical walls

A potential can go to infinity at both $x = \pm\infty$ without having a vertical wall. Let's avoid tunneling for the moment and let there be only two turning points where $E = V(x)$. Let these two turning points be x_1 and x_2, with $V'(x_1) < 0$ and $V'(x_2) > 0$. The solution can be fully described by the connection formulas (8.12) and (8.13). Within the region $x_1 < x < x_2$, both connection formulas should describe the wave function,

$$\psi(x) \simeq \frac{2D}{\sqrt{p(x)}}\sin\left[\frac{1}{\hbar}\int_x^{x_2} p(x')\,dx' + \frac{\pi}{4}\right], \quad \psi(x) \simeq \frac{2D'}{\sqrt{p(x)}}\sin\left[\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' + \frac{\pi}{4}\right] = -\frac{2D'}{\sqrt{p(x)}}\sin\left[-\frac{1}{\hbar}\int_x^{x_1} p(x')\,dx - \frac{\pi}{4}\right].$$

(The negative signs are convenient for steps below.) To let this be true for any x, the argument of sine must be equal mod π,

$$\frac{1}{\hbar} \int_x^{x_2} p(x')\, dx' + \frac{\pi}{4} = -\frac{1}{\hbar} \int_{x_1}^x p(x')\, dx' - \frac{\pi}{4} + n\pi$$

for $n = 1, 2, 3, \ldots$. (It is not mod 2π because $\sin(x + \pi) = -\sin x$, while the negative sign can be absorbed into normalization constant D'.) Move all the integrals to one side,

$$\frac{1}{\hbar} \left(\int_{x_1}^x + \int_x^{x_2} \right) p(x')\, dx = n\pi - \frac{\pi}{2} \quad \implies \quad \int_{x_1}^{x_2} p(x')\, dx' = \left(n - \frac{1}{2} \right) \pi\hbar. \tag{8.15}$$

Example 8.6. Allowed energies of the harmonic oscillator

The full harmonic oscillator is a potential that goes to infinity at both ends. Each energy will intersect with the potential at only two turning points x_1 and x_2, and additionally, $x_1 = -x_2$. We can apply the result of Example 8.5. The momentum of a particle in the harmonic oscillator is

$$p(x) = \sqrt{2m \left(E - \frac{1}{2} m\omega^2 x^2 \right)} = m\omega \sqrt{x_2^2 - x^2} \quad \text{where} \quad x_2 = -x_1 = \frac{1}{\omega} \sqrt{\frac{2E}{m}}.$$

Integrate over $p(x)$ and apply (8.15),

$$\int_{x_1}^{x_2} p(x')\, dx' = 2m\omega \int_0^{x_2} \sqrt{x_2^2 - x^2}\, dx = \frac{\pi}{2} m\omega x_2^2 = \frac{\pi E}{\omega} = \left(n - \frac{1}{2} \right) \pi\hbar.$$

The allowed energies predicted by the WKB approximation are

$$E_n = \left(n - \frac{1}{2} \right) \hbar\omega, \quad n = 1, 2, 3, \ldots \quad \Longleftrightarrow \quad E_n = \left(n + \frac{1}{2} \right) \hbar\omega, \quad n = 0, 1, 2, 3 \ldots.$$

Again, the WKB approximation produces exact results of the harmonic oscillator.

Example 8.7. Tunneling

Consider a barrier with sloping walls. A particle with energy E has two intersections with the potential $V(x)$ at x_1 ($V'(x_1) > 0$) and x_2 ($V'(x_2) < 0$). The full WKB wave function should look like

$$\psi(x) \simeq \begin{cases} \dfrac{1}{\sqrt{p(x)}} \left[A e^{-\frac{i}{\hbar} \int_x^{x_1} p(x')\, dx'} + B e^{\frac{i}{\hbar} \int_x^{x_1} p(x')\, dx'} \right], & x < x_1, \\[2mm] \dfrac{1}{\sqrt{|p(x)|}} \left[C e^{\frac{1}{\hbar} \int_{x_1}^x |p(x')|\, dx'} + D e^{-\frac{1}{\hbar} \int_{x_1}^x |p(x')|\, dx'} \right], & x_1 < x < x_2, \\[2mm] \dfrac{1}{\sqrt{p(x)}} \left[F e^{\frac{i}{\hbar} \int_{x_2}^x p(x')\, dx'} \right], & x > x_2. \end{cases}$$

We assume that there is no incident waves from the right. In Section 8.2, we analyzed a scattering state with broad and high barrier, in which case C is set to zero. In this example, we do not assume that $C = 0$, but we will reproduce the limit in Section 8.2 where the barrier is broad and high.

At the turning point x_1, $V'(x_1) > 0$. As usual, shift the origin to x_1, the WKB wave function around this point is

$$\psi_{\text{WKB}} = \begin{cases} \dfrac{1}{\sqrt{p(x)}} \left[A e^{-\frac{i}{\hbar} \int_x^0 p(x')\, dx'} + B e^{\frac{i}{\hbar} \int_x^0 p(x')\, dx'} \right], & x < 0, \\[2mm] \dfrac{1}{\sqrt{|p(x)|}} \left[C e^{\frac{1}{\hbar} \int_0^x |p(x')|\, dx'} + D e^{-\frac{1}{\hbar} \int_0^x |p(x')|\, dx'} \right], & x > 0. \end{cases}$$

Make the assumption that $V(x)$ is linear around the turning point. For $x > 0$ (overlap region 2),

$$p(x) \simeq \hbar \alpha^{3/2} \sqrt{-x} \quad \text{and} \quad \int_0^x |p(x')|\, dx \simeq \frac{2}{3}\hbar(\alpha x)^{3/2} \quad \text{where} \quad \alpha = \left[\frac{2m}{\hbar^2} V'(0)\right]^{1/3}.$$

The WKB wave function at $x > 0$ is

$$\psi_{\text{WKB}}^+(x) \simeq \frac{1}{\sqrt{\hbar}\alpha^{3/4} x^{1/4}}\left[C e^{\frac{3}{2}(\alpha x)^{3/2}} + D e^{-\frac{3}{2}(\alpha x)^{3/2}}\right].$$

The patching wave function is still

$$\psi_p^+(x) \simeq \frac{a}{2\sqrt{\pi}(\alpha x)^{1/4}} e^{-\frac{2}{3}(\alpha x)^{3/2}} + \frac{b}{\sqrt{\pi}(\alpha x)^{1/4}} e^{\frac{2}{3}(\alpha x)^{3/2}}.$$

Comparing ψ_{WKB}^+ and ψ_p^+, we find that $a = 2D\sqrt{\pi/\alpha\hbar}$ and $b = C\sqrt{\pi/\alpha\hbar}$. (Note that b is now nonzero.) For $x < 0$ (overlap region 1), The WKB wave function is

$$\psi_{\text{WKB}}^-(x) \simeq \frac{1}{\sqrt{\hbar}\alpha^{3/4}(-x)^{1/4}}\left[A e^{-i\frac{2}{3}(-\alpha x)^{3/2}} + B e^{i\frac{2}{3}(-\alpha x)^{3/2}}\right].$$

The patching wave function, with $b \neq 0$, becomes more complicated,

$$\psi_p^-(x) \simeq \frac{a}{\sqrt{\pi}(-\alpha x)^{1/4}} \sin\left[\frac{2}{3}(-\alpha x)^{3/2} + \frac{\pi}{4}\right] + \frac{b}{\sqrt{\pi}(-\alpha x)^{1/4}} \cos\left[\frac{3}{2}(-\alpha x)^{3/2} + \frac{\pi}{4}\right]$$

$$= \frac{1}{2\sqrt{\pi}(-\alpha x)^{1/4}}\left[(-ia + b)e^{i\frac{3}{2}(-\alpha x)^{3/2}} e^{i\pi/4} + (ia + b)e^{-i\frac{2}{3}(-\alpha x)^{3/2}} e^{-i\pi/4}\right].$$

Comparing ψ_{WKB}^- and ψ_p^-, we have

$$A = \sqrt{\frac{\hbar\alpha}{\pi}}\left(\frac{ia + b}{2}\right)e^{-i\pi/4} = \left(\frac{C}{2} + iD\right)e^{-i\pi/4}, \quad B = \sqrt{\frac{\hbar\alpha}{\pi}}\left(\frac{-ia + b}{2}\right)e^{i\pi/4} = \left(\frac{C}{2} - iD\right)e^{i\pi/4}.$$

This concludes the connection formulas at x_1.

At x_2 is a downward-sloping potential $V'(x_2) < 0$. Rewrite ψ_{WKB} between x_1 and x_2 as

$$\psi_{\text{WKB}} = \frac{1}{\sqrt{|p(x)|}}\left[C e^{\frac{1}{\hbar}\int_{x_1}^{x_2}|p(x)|\,dx + \frac{1}{\hbar}\int_{x_2}^{x}|p(x')|\,dx'} + D e^{-\frac{1}{\hbar}\int_{x_1}^{x_2}|p(x)|\,dx - \frac{1}{\hbar}\int_{x_2}^{x}|p(x')|\,dx'}\right].$$

Since the first integral in each exponential is a constant, let $\gamma \equiv \frac{1}{\hbar}\int_{x_1}^{x_2}|p(x)|\,dx$. Let $C' \equiv D e^{-\gamma}$ and $D' \equiv C e^{\gamma}$ and shift the origin to x_2. The WKB wave function around this point is (note the flip in limits of integrals)

$$\psi_{\text{WKB}} = \begin{cases} \dfrac{1}{\sqrt{|p(x)|}}\left[C' e^{\frac{1}{\hbar}\int_x^0 |p(x')|\,dx'} + D' e^{-\frac{1}{\hbar}\int_x^0 |p(x')|\,dx'}\right], & x < 0, \\[3mm] \dfrac{1}{\sqrt{p(x)}}\left[F e^{\frac{i}{\hbar}\int_0^x p(x')\,dx'}\right], & x > 0. \end{cases}$$

The patching wave function is $\psi_p(x) = a\text{Ai}(-\alpha x) + b\text{Bi}(-\alpha x)$, where $\alpha \equiv (2m|V'(0)|/\hbar^2)^{1/3}$. For $x < 0$ (overlap region 1),

$$p(x) \simeq \hbar\alpha^{3/2}\sqrt{x} \quad \text{and} \quad \int_x^0 |p(x')|\,dx' = \frac{2}{3}\hbar(-\alpha x)^{3/2}.$$

The WKB wave function and patching wave function are

$$\psi_{\text{WKB}}^- \simeq \frac{1}{\sqrt{\hbar}\alpha^{3/4}(-x)^{1/4}}\left[C' e^{\frac{2}{3}(-\alpha x)^{3/2}} + D' e^{-\frac{2}{3}(-\alpha x)^{3/2}}\right],$$

$$\psi_p^- \simeq \frac{a}{2\sqrt{\pi}(-\alpha x)^{1/4}} e^{-\frac{2}{3}(-\alpha x)^{3/2}} + \frac{b}{\sqrt{\pi}(-\alpha x)^{1/4}} e^{\frac{2}{3}(-\alpha x)^{3/2}}.$$

Comparing ψ_{WKB}^- and ψ_p^-, we again get $a = 2D'\sqrt{\pi/\hbar\alpha}$ and $b = C'\sqrt{\pi/\hbar\alpha}$. For $x > 0$ (overlap region 2),

$$\psi_{\mathrm{WKB}}^+ \simeq \frac{1}{\sqrt{\hbar}\alpha^{3/4}x^{1/4}} F e^{i\frac{2}{3}(\alpha x)^{3/2}},$$

$$\psi_p^+ \simeq \frac{a}{\sqrt{\pi}(\alpha x)^{1/4}} \sin\left[\frac{2}{3}(\alpha x)^{3/2} + \frac{\pi}{4}\right] + \frac{b}{\sqrt{\pi}(\alpha x)^{1/4}} \cos\left[\frac{2}{3}(\alpha x)^{3/2} + \frac{\pi}{4}\right]$$

$$= \frac{1}{2\sqrt{\pi}(\alpha x)^{1/4}} \left[(-ia + b)e^{i\frac{2}{3}(\alpha x)^{3/2}}e^{i\pi/4} + (ia + b)e^{-i\frac{2}{3}(\alpha x)^{3/2}}e^{-i\pi/4}\right].$$

Comparing ψ_{WKB}^+ and ψ_p^+, there is no $e^{-i\frac{2}{3}(\alpha x)^{3/2}}$, so $b = -ia$. Then

$$F = \sqrt{\frac{\hbar\alpha}{\pi}}\left(\frac{-ia + b}{2}\right)e^{i\pi/4} = b\sqrt{\frac{\hbar\alpha}{\pi}}e^{i\pi/4} \quad\Longrightarrow\quad b = \sqrt{\frac{\pi}{\hbar\alpha}}e^{-i\pi/4}F, \quad a = i\sqrt{\frac{\pi}{\hbar\alpha}}e^{-i\pi/4}F.$$

Express everything in terms of F,

$$C' = \sqrt{\frac{\hbar\alpha}{\pi}}b = e^{-i\pi/4}F, \quad D' = \frac{1}{2}\sqrt{\frac{\hbar\alpha}{\pi}}a = \frac{i}{2}e^{-i\pi/4}F, \quad C = \frac{i}{2}e^{-\gamma-i\pi/4}F, \quad D = e^{\gamma-i\pi/4}F.$$

This concludes the connection formulas at x_2.

We are interested in $T = |F|^2/|A|^2$, so put B aside and calculate A in terms of F,

$$A = \left(\frac{C}{2} + iD\right)e^{-i\pi/4} = \left(\frac{i}{4}e^{-\gamma-i\pi/4}F + ie^{\gamma-i\pi/4}F\right)e^{-i\pi/4} = \left(\frac{e^{-\gamma}}{4} + e^{\gamma}\right)F,$$

where we used $i = e^{i\pi/2}$ and canceled it with 2 factors of $e^{-i\pi/4}$. The transmission probability is

$$T = \frac{|F|^2}{|A|^2} = \frac{1}{(e^{\gamma} + e^{-\gamma}/4)^2} = \frac{e^{-2\gamma}}{[1 + (e^{-2\gamma}/4)]^2}. \tag{8.16}$$

Now we return to the case where the barrier is broad and high. The integral $\gamma = \frac{1}{\hbar}\int_{x_1}^{x_2}|p(x)|\,dx \gg 1$, and the denominator of (8.16) goes to 1. In this way we can recover (8.6), $T \simeq e^{-2\gamma}$.

9 Time-Dependent Perturbation Theory

So far the all we have discussed has the potential energy function independent of time. It allow us to use separation of variables, and construct time dependent wave function in linear combinations of separable solutions,

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

Even if the wave function is time dependent, the possible values of energy of the system and their respective probability are constant.

In the subject of **quantum dynamics**, there can be time-dependent potentials that allow transitions of energy from one level to another. There are few exact solutions to the Schrödinger equation with time-dependent potential. Nonetheless, we can treat the time-dependent part as a perturbation if it is small compared to the time-independent part. This chapter is about the time-dependent perturbation theory, and its most important application—the emission and absorption of radiation by an atom.

9.1 General Formulation

The full, time-dependent Schrödinger equation is

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

We start by writing down the Hamiltonian $H(t) = H^0 + H'(t)$, where H^0 is the Hamiltonian of some known system, while $H'(t)$ contains the time dependence. The Schrödinger equation becomes

$$(H^0 + H')\Psi = i\hbar \frac{\partial \Psi}{\partial t}. \tag{9.1}$$

This can happen, for example, when $V(\mathbf{r}) \to V(\mathbf{r}, t)$. For now, the time-dependent Hamiltonian $H'(t)$ need not be small. The most general solution to the Schrödinger equation will be

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

where ψ_n are the eigenstates of H^0, and E_n are the eigenvalues of H^0. We can write all the states in this form because ψ_n forms a complete basis. Now the coefficients c_n depend on time as well. At any given time, the linear combination will be different. The goal is to determine their time dependence using the (time-dependent) Schrödinger equation.

The first step is to plug the general solution back into the Schrödinger equation,

$$(H^0 + H')\left[\sum_n c_n(t) \psi_n e^{-iE_n t/\hbar}\right] = i\hbar \frac{\partial}{\partial t}\left[\sum_n c_n(t) \psi_n e^{-iE_n t/\hbar}\right].$$

Using the fact that $H^0 \psi_n = E_n \psi_n$,

$$\sum_n c_n E_n \psi_n e^{-iE_n t/\hbar} + \sum_n c_n H' \psi_n e^{-iE_n t/\hbar} = i\hbar \sum_n \dot{c}_n \psi_n e^{-iE_n t/\hbar} + i\hbar \sum_n c_n \left(-\frac{iE_n}{\hbar}\right) \psi_n e^{-iE_n t/\hbar}.$$

Here $\dot{c}_n$ means the time-derivative of c_n. The first term on the LHS cancels with the second term on the RHS, so

$$\sum_n c_n H' \psi_n e^{-iE_n t/\hbar} = i\hbar \sum_n \dot{c}_n \psi_n e^{-iE_n t/\hbar}.$$

The eigenstates of H^0 are orthonormal, $\langle \psi_m | \psi_n \rangle = \delta_{mn}$. Taking the inner product with $\langle \psi_m |$ and invoke orthonormality,

$$\sum_n c_n \langle \psi_m | H' | \psi_n \rangle \, e^{-iE_n t/\hbar} = i\hbar \sum_n \dot{c}_n \delta_{mn} e^{-iE_n t/\hbar} \quad \implies \quad \sum_n c_n H'_{mn} e^{-iE_n t/\hbar} = i\hbar \dot{c}_m e^{-iE_m t/\hbar},$$

where $H'_{mn} \equiv \langle \psi_m | H' | \psi_n \rangle$ is the matrix element of H'_{mn} in the ψ_n basis. Rearrange some terms, we get the most general equations of the coefficients:

$$\dot{c}_m = -\frac{i}{\hbar} \sum_n c_n H'_{mn} e^{i(E_m - E_n)t/\hbar}. \tag{9.2}$$

Until now, all results are exact. We have not made any approximation yet. (9.2) is a set of coupled, first-order differential equations. Practically, this set of equations are hard to solve unless n is small. We need to rely on perturbation theory again.

9.1.1 Time-Dependent Perturbation Theory

The idea is essentially the same: write the full Hamiltonian as $H = H^0 + \lambda H'$ and expand quantities in different powers of λ. Let

$$\Psi(t, \lambda) = \sum_n \dot{c}_n(t, \lambda) \psi_n e^{-iE_n t/\hbar} \quad \text{where} \quad c_n(t, \lambda) = c_n^0 + \lambda c_n^1 + \lambda^2 c_n^2 + \cdots$$

The energies E_n and eigenstates ψ_n are unchanged. All the changes are embedded in c_n's. Substituting $c_n(\lambda, t)$ into (9.2),

$$\frac{d}{dt}(c_m^0 + \lambda c_m^1 + \lambda^2 c_m^2 + \cdots) = -\frac{i}{\hbar} \sum_n \lambda H'_{mn}(c_n^0 + \lambda c_n^1 + \lambda^2 c_n^2 + \cdots) e^{i(E_m - E_n)t/\hbar}. \tag{9.3}$$

This equation holds true for each power of λ, so the coefficients before each power are the same. Note that there is no zeroth-order of λ on the RHS, so the zeroth-order equation is just

$$\frac{d}{dt} c_m^0 = 0.$$

This just means when there is no time-dependent perturbation, the state stays where it is. The simplest but most useful initial condition is to set $c_n^0 = \delta_{ni}$, which means the initial state is the eigenstate ψ_n of H^0. The first-order equation in (9.3) is

$$\frac{d}{dt} c_m^1 = -\frac{i}{\hbar} \sum_n H'_{mn} c_n^0 e^{i(E_m - E_n)t/\hbar}.$$

The initial condition $c_n^0 = \delta_{ni}$ eliminates the sum, giving the first-order equation

$$\dot{c}_m = -\frac{i}{\hbar} H_{mi} e^{i(E_m - E_i)t/\hbar} \quad \Longleftrightarrow \quad c_f^1(t) = -\frac{i}{\hbar} \int_0^t H'_{fi} e^{i(E_f - E_i)t'/\hbar} \, dt',$$

where the index m is changed to f in the integral equation to give some physical meaning: E_i stands for the initial-state energy, while E_f stands for the final-state energy. Now we can absorb λ into H' and set H' to be small. (Again, λ is only a parameter that tracks the order of perturbation). Combining the zeroth- and first-order results, the time-dependent coefficients are

$$\boxed{c_f^1(t) = \delta_{fi} - \frac{i}{\hbar} \int_0^t H'_{fi} e^{i(E_f - E_i)t'/\hbar} \, dt'.} \tag{9.4}$$

In general, one can plug in (9.4) into (9.3) to obtain $\dot{c}_m^2$ and solve for it, and then plug in c_m^2 into (9.3) and obtain $\dot{c}_m^3$, and so on. We will not go further than the first-order perturbation theory. Physically, if we start out with an initial state ψ_i, the probability of ending up in a different final state ψ_f is give by (9.4) squared. It is proportional to the integral of the matrix element H'_{fi}, weighted by an energy-dependent phase. In many cases, H'_{fi} are zero, as an initial state can only transition to a certain final state under some conditions. These conditions are called selection rules, usually related to the symmetry of the problem.

Example 9.1. A two-level system

Consider a two-level system with the Hamiltonian $H = H^0 + H'$, where

$$H^0 = \begin{bmatrix} E & 0 \\ 0 & -E \end{bmatrix}, \quad H' = \begin{bmatrix} 0 & v(t) \\ v(t) & 0 \end{bmatrix}, \quad |1\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad |2\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

Assume $E \geq 0$ and $v(t) \to 0$ as $t \to \pm\infty$. Now we specify $v(t)$ to have Gaussian time dependence:

$$v(t) = \frac{v}{\sqrt{\pi \tau^2}} e^{-t^2/\tau^2},$$

where τ is some positive number. Let the initial state be $|2\rangle$ at $t \to -\infty$. We want to know the probability that the system is in state $|1\rangle$ at $t \to \infty$. Essentially, we need to calculate $c_1^1(t)$ using (9.4),

$$c_1^1(t) = \delta_{12} - \frac{i}{\hbar} \int_{-\infty}^t H'_{12}(t') e^{i(E_2 - E_1)t/\hbar} \, dt' = -\frac{iv}{\hbar\sqrt{\pi\tau^2}} \int_{-\infty}^t e^{-t'^2/\tau^2 + i\omega_0 t'} \, dt',$$

where $\omega_0 = (E_2 - E_1)/\hbar = -2E/\hbar$. We want the probability at $t \to \infty$, so the integral becomes a Gaussian integral. The result is

$$c_1^1(t) = -\frac{iv}{\hbar\sqrt{\pi\tau^2}} \int_{-\infty}^\infty e^{-t'^2/\tau^2 + i\omega_0 t'} \, dt' = -\frac{iv}{\hbar} e^{-(\omega_0 \tau/2)^2} \quad \Longrightarrow \quad P_1(\infty) = \frac{v^2}{\hbar^2} e^{-(\omega_0\tau)^2/2}.$$

9.1.2 Periodic Perturbation

A periodic perturbation is probably the most useful and important time-dependent perturbation. It has the form

$$H'(\mathbf{r}, t) = V(\mathbf{r}) \cos \omega t, \tag{9.5}$$

where ω is the frequency of the perturbation. It is important because of its application in absorption and emission of electromagnetic waves. Moreover, any well-behaved perturbation can be expressed as a linear combination of periodic perturbations with different frequencies by Fourier analysis.

The matrix element of H' is $H'_{mn} = V_{mn} \cos \omega t$, where $V_{mn} \equiv \langle \psi_m | V | \psi_n \rangle$. Define $\omega_{mn} = (E_m - E_n)/\hbar$. For a different final state $f \neq i$, the first-order coefficients $c_f^1(t)$ is given by (9.4),

$$c_f^1(t) = -\frac{i}{\hbar} \int_0^t dt' \, H'_{fi} e^{i(E_f - E_i)t'/\hbar} = -\frac{i}{\hbar} V_{fi} \int_0^t dt' \, e^{i\omega_{fi}t'} \cos(\omega t').$$

Express $\cos \omega t = (e^{i\omega t} + e^{-i\omega t})/2$,

$$c_f^1(t) = -\frac{i}{2\hbar} V_{fi} \int_0^t dt' \left[e^{i(\omega_{fi}+\omega)t'} + e^{i(\omega_{fi}-\omega)t'} \right] = -\frac{1}{2\hbar} V_{fi} \left[\frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi} + \omega} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega} \right].$$

Rewrite

$$\frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi} + \omega} = e^{i(\omega_{fi}+\omega)t/2} \left[\frac{e^{i(\omega_{fi}+\omega)t/2} - e^{-i(\omega_{fi}+\omega)t/2}}{\omega_{fi} + \omega} \right] = 2i e^{i(\omega_{fi}+\omega)t/2} \sin[(\omega_{fi} + \omega)t/2]$$

and a similar term with $\omega_{fi} - \omega$. The coefficient becomes

$$c_f^1(t) = -\frac{i}{\hbar} V_{fi} \left\{ e^{i(\omega_{fi}+\omega)t/2} \sin[(\omega_{fi} + \omega)t/2] + e^{i(\omega_{fi}-\omega)t/2} \sin[(\omega_{fi} - \omega)t/2] \right\}.$$

The squared amplitude of $c_f(t)$ is the **transition probability** from ψ_i to ψ_f,

$$P_{fi}(t) \simeq \left| c_f^1(t) \right|^2 = \left| -\frac{i}{\hbar} V_{fi} \left\{ e^{i(\omega_{fi}+\omega)t/2} \sin[(\omega_{fi} + \omega)t/2] + e^{i(\omega_{fi}-\omega)t/2} \sin[(\omega_{fi} - \omega)t/2] \right\} \right|^2$$

$$= \frac{|V_{fi}|^2}{\hbar^2} \left\{ \frac{\sin^2[(\omega_{fi} + \omega)t/2]}{(\omega_{fi} + \omega)^2} + \frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2} + \frac{2\sin[(\omega_{fi} - \omega)t/2]\sin[(\omega_{fi} + \omega)t/2]}{\omega_{fi}^2 - \omega^2} \cos\omega t \right\}. \tag{9.6}$$

If the driving frequency ω is very close to the transition frequency ω_{fi} (near resonance), we can make further approximation (see

Figure 9.1). For example, when $\omega \approx \omega_{fi}$, the second term dominates over others. The transition probability is approximately

$$P_{fi}(t) \simeq \frac{|V_{fi}|^2}{\hbar^2} \frac{\sin[(\omega_0 - \omega)t/2]^2}{(\omega_0 - \omega)^2}. \tag{9.7}$$

A key feature of this transition probability is that it oscillates as time evolves (except at $\omega = \omega_{fi}$). The period of this oscillation is $T = 2\pi/|\omega_0 - \omega|$. Only at $\omega = \omega_{fi}$, the probability grows linearly with time and blows up at time goes on. This indicates a break down of the perturbation theory at large t, so (9.6) is only valid for small t. However, the oscillatory behavior of the probability at $\omega \neq \omega_{fi}$ is presented also in exact transition probability—it is not an artifact of the perturbation theory. This effect is known as **Rabi oscillation**.
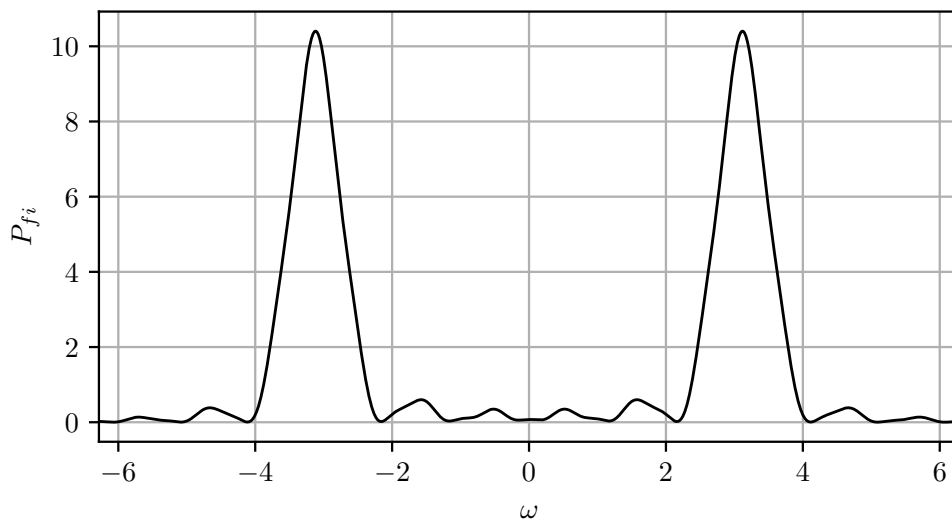
Figure 9.1: Transition probability from first order perturbation, with $\omega_{fi} = 5$ and at $t = 2\pi$. The vertical scale is off by a constant.

Example 9.2. Rabi Oscillation

If we keep only the second term in (9.6), this is equivalent to write $H' = V e^{-i\omega t}/2$ because the second term comes from the $e^{-i\omega t}$ part of $\cos \omega t$. For a two-level system $|\psi_a\rangle$ and $|\psi_b\rangle$ $(E_b > E_a)$, the relevant matrix elements of H' are

$$H'_{ba} = \frac{V_{ba}}{2} e^{-i\omega t}, \quad H'_{ab} = \frac{V_{ab}}{2} e^{i\omega t}.$$

Rabi suggested the **rotating wave approximation**, in which we set $H' = V e^{-i\omega t}/2$ at the beginning and solve (9.2). Since (9.2) is exact, the perturbation theory and any assumption on the field strength are unnecessary. Basically, we need to solve the following coupled equations

$$\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b, \quad \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a, \quad \text{where} \quad \omega_0 \equiv \frac{E_b - E_a}{\hbar}.$$

Using the rotating wave approximation, the equations become

$$\dot{c}_a = -\frac{i}{2\hbar} V_{ab} e^{i(\omega - \omega_0)t} c_b, \quad \dot{c}_b = -\frac{i}{2\hbar} V_{ba} e^{-i(\omega - \omega_0)t} c_a.$$

With the initial conditions $c_a(0) = 1$ and $c_b(0) = 0$, the solutions are

$$c_a = e^{i(\omega - \omega_0)t/2} \left[\cos \omega_r t - \frac{i(\omega - \omega_0)}{2\omega_r} \sin \omega_r t \right], \quad c_b = -\frac{iV_{ba}}{2\hbar\omega_r} e^{-i(\omega - \omega_0)t/2} \sin \omega_r t,$$

where

$$\omega_r \equiv \frac{1}{2} \sqrt{(\omega - \omega_0)^2 + \left(\frac{|V_{ab}|}{\hbar} \right)^2} \tag{9.8}$$

is called the **Rabi flopping frequency**. The derivation is in Appendix B.11.1. The transition probability is given by

$$P_{ba} = |c_b(t)|^2 = \left(\frac{|V_{ab}|}{2\hbar\omega_r}\right)^2 \sin^2\omega_r t.$$

If we take the perturbation to be small, $(|V_{ab}/\hbar|)^2/(\omega-\omega_0)^2 \ll 1$, or $|V_{ab}| \ll \hbar(\omega-\omega_0)$, then

$$\omega_r = \frac{1}{2}\sqrt{(\omega-\omega_0)^2 + \left(\frac{|V_{ab}|}{\hbar}\right)^2} = \frac{1}{2}(\omega-\omega_0)\sqrt{1 + \frac{|V_{ab}|^2}{\hbar^2(\omega-\omega_0)^2}} \simeq \frac{1}{2}(\omega-\omega_0).$$

The transition probability can be approximated as

$$P_{ba} = \frac{|V_{ab}|^2}{4\hbar^2\omega_r^2}\sin^2\omega_r t = \frac{|V_{ab}|^2}{\hbar^2(\omega-\omega_0)^2}\sin^2\left[(\omega-\omega_0)t/2\right],$$

consistent with (9.7). The maximum (exact) probability does not exceed 1 in this exact solution: when $\sin^2\omega_r t = 1$,

$$P_{ba} = \frac{|V_{ab}|^2/\hbar^2}{4\omega_r^2} = \frac{(|V_{ab}|/\hbar)^2}{(\omega-\omega_0)^2 + (|V_{ab}|/\hbar)^2} \leq 1,$$

and it is equal to 1 when $\omega = \omega_0$. As expected, the transition probability is the largest at resonance. It is also straightforward to confirm the normalization condition $|c_a|^2 + |c_b|^2 = 1$. In this exact solution, we see that the probability is oscillatory for a periodic perturbation $H' = Ve^{-i\omega t}/2$.

9.2 Emission and Absorption of Radiation

9.2.1 Electromagnetic Waves

An atom responds *primarily* to the electric component of an electromagnetic wave. For example, consider the hydrogen atom interacting with both static electric field and magnetic field. There are two extra terms added to the Hamiltonian of the hydrogen atom, $\boldsymbol{\mu}\cdot\mathbf{B}$ and $\boldsymbol{\mu}_e\cdot\mathbf{E}$. Assume that the magnitude of $\mathbf{B}$ is 1 Tesla (a relatively strong magnetic field). The energy contribution from the magnetic field is about

$$\boldsymbol{\mu}\cdot\mathbf{B} \sim \mu_{\mathrm{B}}B \approx 58.8\,\mu\mathrm{eV},$$

where μ_{B} is the Bohr magneton. The energy contribution from the electric field is about

$$\boldsymbol{\mu}_e\cdot\mathbf{E} \sim (ea_0)E = (ea_0)(cB) \sim 15\,\mathrm{meV}.$$

Here $\mu_e = ea_0$ is approximately the dipole moment of the hydrogen atom, and we used the speed of light $c = E/B$ from electromagnetism. The perturbation from the magnetic field is therefore negligible, which is true to atoms and many solids.

Another approximation we will make is called the **dipole approximation**. For linearly polarized light, the electric field is given by

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0\cos(\mathbf{k}\cdot\mathbf{r} - \omega t),$$

where $\mathbf{k}$ is the wave vector of light, with $|\mathbf{k}| = 2\pi/\lambda$. It specifies the direction of propagation of light, not the direction of the electric field. In fact, Maxwell's equations say that $\mathbf{k}\cdot\mathbf{E} = 0$, i.e. they are perpendicular. The energy scale of hydrogen is $E_1 = -13.6\,\mathrm{eV}$. An energy level transition corresponds to a light with wavelength of the order 10^2 nm, near the range of visible spectrum. The size of the atom is only $a_0 \approx 0.05$ nm. The phase difference $\mathbf{k}\cdot\mathbf{r}$ is negligible in this case. To the hydrogen atom (and many other atoms), the electric field is effectively uniform in space. Hence we can write

$$\mathbf{E}(t) = \mathbf{E}_0\cos\omega t.$$

Assume that the electric field is in the z-direction, $\mathbf{E} = E_0\cos(\omega t)\hat{\mathbf{z}}$. Then the perturbation in the Hamiltonian is

$$H' = -eE_0 z\cos(\omega t). \tag{9.9}$$

The matrix elements of H' are

$$H'_{mn} = -eE_0 z_{mn} \cos \omega t,$$

where $z_{mn} = \langle \psi_m | z | \psi_n \rangle$. In this case the potential energy matrix is simply $V_{mn} = eE_0 z_{mn}$. Since the electromagnetic wave provides a periodic perturbation, the transition probability (near resonance) is given by (9.7),

$$P_{fi}(t) \simeq \frac{|V_{fi}|^2}{\hbar^2} \frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2} = \frac{2e^2|z_{fi}|^2}{\epsilon_0 \hbar^2} \frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2} u, \tag{9.10}$$

where $u \equiv \epsilon_0 E_0^2 / 2$ is the energy density of the electric field.

9.2.2 Coherent Radiation

There are essentially three types of transition that can happen with coherent radiation, meaning that there is a **monochromatic** light shining on the atom.

1. Suppose initially an atom is in a lower state ψ_i. If a light shines on it, the probability of transition to an upper state ψ_f with $E_f > E_i$ is

$$P_{fi}(t) = \frac{2e^2|z_{fi}|^2}{\epsilon_0 \hbar^2} \frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_0 - \omega)^2} u.$$

   The atoms absorbs the energy $E_f - E_i = \hbar \omega_{fi}$. This process is called **absorption**, and it is said that "the atom absorbed a photon".

2. If the initial state has a higher energy than the final state, the transition probability is exactly the same. Returning back to the original transition probability (9.6),

$$P_{fi}(t) \simeq \frac{|V_{fi}|^2}{\hbar^2} \left\{ \frac{\sin^2[(\omega_{fi} + \omega)t/2]}{(\omega_{fi} + \omega)^2} + \frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2} + \frac{2\sin[(\omega_{fi} - \omega)t/2]\sin[(\omega_{fi} + \omega)t/2]}{\omega_{fi}^2 - \omega^2} \cos \omega t \right\}.$$

   If $\omega \approx -\omega_{fi}$, then the first term dominates. The transition probability is

$$P_{fi}(t) \simeq \frac{|V_{fi}|^2}{\hbar^2} \frac{\sin^2[(\omega_{fi} + \omega)t/2]}{(\omega_{fi} + \omega)^2}.$$

   Swapping the label of the initial and final state gives

$$P_{if}(t) \simeq \frac{|V_{if}|^2}{\hbar^2} \frac{\sin^2[(\omega_{if} + \omega)t/2]}{(\omega_{if} + \omega)^2} = \frac{|V_{fi}|^2}{\hbar^2} \frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2} = P_{fi}(t),$$

   where we used $|V_{if}|^2 = |V_{if}|^2$ and $\omega_{fi} = -\omega_{if}$. Since all quantities are squared, the minus signs do not matter. The electromagnetic field gains energy $\hbar \omega_{if}$. This process is called **stimulated emission**, and it is said that "one photon comes in, with two photons out." This is the principle behind **laser** (light amplification by stimulated emission of radiation). If there is a container with all excited atoms, and we trigger it with a single incident photon, a chain reaction will occur. This reaction will product large number of photons with all the same frequency at nearly the same instant.

3. It turns out that without any electromagnetic field applied, an excited atom can still release a photon and return to its lower state. This is called **spontaneous emission**. In general, only the ground state does not undergo spontaneous emission because it is the lowest energy state possible. The process of spontaneous emission seems unreasonable at first glance: an atom in any stationary state with no external perturbation should remain in that state forever, with time evolution governed by $e^{iEt/\hbar}$. When computing the probability $\langle \psi(t) | \psi(t) \rangle$, the imaginary phase is eliminated. This can only be explained using relativistic quantum mechanics and quantum field theory in which spontaneous decay transitions are allowed, but Section 9.3 discussed some of the implications of spontaneous emissions using Einstein coefficients.

9.2.3 Incoherent Perturbations

So far we have discussed the transition probability between states caused by a monochromatic light. In daily life, almost all lights are incoherent. We want the system exposed to electromagnetc waves at large range of frequencies, so the energy density becomes

$u \to \rho(\omega)\, d\omega$, where $\rho(\omega)$ is the energy density per unit frequency. The net transition probability is an integral:

$$P_{fi}(t) \simeq \frac{2e^2|z_{fi}|^2}{\epsilon_0\hbar^2} \int_0^\infty \rho(\omega) \left\{ \frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2} \right\} d\omega.$$

In fact, we are calculating the time-averaged probability here. Note that we are directly summing up the probability per unit frequency, not summing up $c_f^1(t)$ and then squaring it. We are justified to do this only in incoherent cases. For example, if $E_1(t) = E_0 \cos(\omega t + \phi_1)$ and $E_2(t) = E_0 \cos(\omega t + \phi_2)$ (coherent), the time-averaged intensity is

$$I = \overline{|E_1 + E_2|^2} = E_0^2 \overline{[\cos(\omega t + \phi_1) + \cos(\omega t + \phi_2)]^2} = E_0^2 \overline{\left[4\cos^2\left(\frac{2\omega t + \phi_1 + \phi_2}{2}\right) \cos^2\left(\frac{\phi_1 - \phi_2}{2}\right)\right]}.$$

The average of $\cos(\omega t + \phi)$ over a period $2\pi/\omega$ periods is $1/2$, so

$$I = 2E_0^2 \cos^2\left(\frac{\phi_1 - \phi_2}{2}\right) = E_0^2[1 + \cos(\phi_1 - \phi_2)].$$

All we need to know is that the time-averaged total intensity $I \neq \overline{(E_1^2 + E_2^2)} = E_0^2$. It depends on the phase of two coherent fields. On the contrary, if $E_1(t) = E_1' \cos(\omega_1 t + \phi_1)$ and $E_2(t) = E_2' \cos(\omega_2 t + \phi_2)$ (incoherent for $\omega_1 \neq \omega_2$), the time-averaged total intensity is $I = \overline{(E_1^2 + E_2^2)}$:

$$I = \overline{|E_1 + E_2|^2} = \overline{[E_1'^2 \cos(\omega_1 t + \phi_1) + E_2'^2 \cos^2(\omega_2 t + \phi_2) + 2E_1' E_2' \cos(\omega_1 t + \phi_1)\cos(\omega_2 t + \phi_2)]}.$$

Both cosine squared average to $1/2$, and the cross term average to zero (for some period) as they are not squared. Hence $I = \overline{E_1^2 + E_2^2} = I_1 + I_2$ in the incoherent case.

Now return to the integral, the term in the curly brackets is sharply peaked about ω_{fi}, while $\rho(\omega)$ is typically broad, so we can replace $\rho(\omega)$ by $\rho(\omega_{fi})$,

$$P_{fi} \simeq \frac{2e^2|z_{fi}|^2}{\epsilon_0\hbar^2}\rho(\omega_{fi}) \int_0^\infty \frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2}\, d\omega = \frac{2e^2|z_{fi}|^2}{\epsilon_0\hbar^2}\rho(\omega_{fi}) \int_{-\infty}^\infty \frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2}\, d\omega.$$

We can change the lower bound from 0 to $-\infty$ because the value ω_0 is typically an extremely large value, so these two integral are no different. (For now, we are consider only absorption, $\omega_{fi} > 0$, so do not worry about the other peak at $-\omega_{fi}$.) Changing the variable to $x \equiv (\omega_0 - \omega)t/2$, and using the definite integral

$$\int_{-\infty}^\infty \frac{\sin^2 x}{x^2}\, dx = \pi,$$

the probability becomes

$$P_{fi}(t) \simeq \frac{e^2|z_{fi}|^2}{\epsilon_0\hbar^2}\rho(\omega_{fi})t \int_{-\infty}^\infty \frac{\sin^2 x}{x^2}\, dx = \frac{\pi e^2}{\epsilon_0\hbar^2}|z_{fi}|^2\rho(\omega_{fi})t.$$

Note that the **transition rate** $R \equiv dP/dt$ is now a constant. Essentially, the oscillatory time-evolution in (9.7) is averaged out in the incoherent case. The width of the peak in $\sin^2[(\omega_{fi} - \omega)t/2]/(\omega_{fi} - \omega)$ is characterized by $\Delta\omega = 2\pi/t$. Thus, this probability is valid when the frequency range much larger than $\Delta\omega$. Alternatively, the timescale t should be much larger than the coherence time $\tau \sim 1/\Delta\omega$.

If we want further perturbation from all directions and the energy density $\rho(\omega)$ is shared equally among these modes, we need the average of $|\wp \cdot \hat{\mathbf{n}}|^2$, where

$$\wp \equiv -e\,\langle\psi_f|\mathbf{r}|\psi_i\rangle,$$

and $\hat{\mathbf{n}}$ is the direction of net polarization. We set the direction of propagation $\hat{\mathbf{z}}$ is along x, $\hat{n}$ along z, and the vector $\wp$ defines the spherical angles θ and ϕ. Then

$$\wp \cdot \hat{\mathbf{n}} = \wp\cos\theta,$$

and

$$|\wp \cdot \hat{\mathbf{n}}|_{\text{ave}}^2 = \frac{1}{4\pi r^2} \int |\wp|^2 \cos^2\theta (r^2 \sin\theta\, d\theta\, d\phi) = \frac{|\wp|^2}{4\pi}\left(-\frac{\cos^3\theta}{3}\right)\Bigg|_0^\pi (2\pi) = \frac{1}{3}|\wp|^2.$$

The conclusion is: the transition rate for stimulated emission from state i to state f, under the influence of incoherent, unpolarized light incident from all direction, is

$$\boxed{R_{fi} = \frac{\pi}{3\epsilon_0\hbar^2}|\wp|^2\rho(\omega_{fi}).}$$ (9.11)

9.3   Spontaneous Emission

9.3.1   Einstein's A and B Coefficients

At the time of the investigation on spontaneous emission processes, there was no quantum field theory. Einstein came up with a method to calculate the spontaneous emission rate with the idea of equilibrium. At a given temperature at which some atoms are in thermal equilibrium, it is known from statistical mechanics that a high energy state is less probable. This distribution is called **Boltzmann distribution**, $P \propto e^{-E/k_{\mathrm{B}}T}$, where k_{B} is the Boltzmann constant. Thus, it is reasonable to think that spontaneous emission is responsible for achieving a thermal equilibrium.

Consider a container of atoms with N_a of them in ψ_a, and N_b of them in ψ_b, with $E_b > E_a$ so that ψ_b can spontaneously transition to ψ_a. There are three contributions to the transition rate.

- Let A be the spontaneous emission rate such that the number of particles leaving ψ_b by this process, per unit time, is $N_b A$.

- According to (9.11), the stimulated emission rate is proportional to the energy density per frequency of the field: $B_{ba}\rho(\omega_{ba})$, where $B_{ba} = \pi|\wp|^2/3\epsilon_0\hbar^2$. Then $N_b B_{ba}\rho(\omega_{ba})$ is the number of particles leaving ψ_b by this process, per unit time.

- Likewise, the absorption rate is $B_{ab}\rho(\omega_{ba})$, and the particle joining ψ_b per unit time is $N_b B_{ab}\rho(\omega_{ba})$.

Adding all these rates together gives the total rate of change of number of particles in ψ_b,

$$\dot{N}_b = -N_b A - N_b B_{ba}\rho(\omega_{ba}) + N_a B_{ab}\rho(\omega_{ba}).$$

Consider an equilibrium state such that $\dot{N}_b = 0$. Then

$$\rho(\omega_{ba}) = \frac{A}{(N_a/N_b)B_{ab} - B_{ba}}.$$

From statistical mechanics, the number of particles with energy E in thermal equilibrium at temperature T, is proportional to the **Boltzmann factor**, $e^{-E/k_{\mathrm{B}}T}$, so

$$\frac{N_a}{N_b} = \frac{e^{-E_a/k_{\mathrm{B}}T}}{e^{-E_b/k_{\mathrm{B}}T}} = e^{\hbar\omega_{ba}/k_{\mathrm{B}}T} \quad \Longrightarrow \quad \rho(\omega_{ba}) = \frac{A}{e^{\hbar\omega_{ba}/k_{\mathrm{B}}T}B_{ab} - B_{ba}}.$$

Planck's blackbody spectrum tells the energy density per unit frequency of thermal radiation:

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/k_{\mathrm{B}}T} - 1}.$$

Comparing these two expressions gives

$$B_{ab} = B_{ba} \quad \text{and} \quad A = \frac{\omega_{ba}^3 \hbar}{\pi^2 c^3}B_{ba}.$$

$B_{ab} = B_{ba}$ is expected, because we already know that the probability of transition from ψ_a to ψ_b by absorption is the same as that from ψ_b to ψ_a by stimulated emission. From (9.11), we can substitute $B_{ba} = \pi|\wp|^2/3\epsilon_0\hbar^2$ to get the spontaneous emission rate:

$$\boxed{A = \frac{\omega_{ba}^3 |\wp|^2}{3\pi\epsilon_0\hbar c^3}.} \tag{9.12}$$

The coefficients A and B are known as **Einstein's A and B coefficients**.

9.3.2   The Lifetime of an Excited State

Suppose now we suddenly make a large number of atoms to ψ_b so that these atoms are out of equilibrium. In a time interval dt, the number of spontaneous emission is

$$dN_b = -A N_b\, dt \quad \Longrightarrow \quad N_b(t) = N_b(0)e^{-At}.$$

The number remaining in ψ_b decreases exponentially with a time constant

$$\tau = \frac{1}{A},$$

the **lifetime** of the state. Typically, there are more than two states for the system. An excited atom has many different **decay modes**. The transition rates add, and the net lifetime is

$$\tau = \frac{1}{A_1 + A_2 + A_3 + \dots}.$$

9.4   Selection Rules

The key to calculate the spontaneous emission rates now becomes the evaluation of matrix elements

$$\langle \psi_f | \mathbf{r} | \psi_i \rangle .$$

These quantities are very often zero, and it is better to know in advance when they vanish. Suppose the Hamiltonian is spherically symmetric (like the hydrogen atom). We can specify the states using quantum numbers n, ℓ, and m. The matrix elements are

$$\langle n' \ell' m' | \mathbf{r} | n\ell m \rangle .$$

9.4.1   Magnetic Quantum Number

Consider the commutators of L_z with x, y, and z:

$$[L_z, x] = i\hbar y, \quad [L_z, y] = -i\hbar x, \quad [L_z, z] = 0.$$

The third commutation relation $[L_z, z] = 0$ gives

$$0 = \langle n' \ell' m' | (L_z z - z L_z) | n\ell m \rangle = \langle n' \ell' m' | [(m'\hbar)z - z(m\hbar)] | n\ell m \rangle = (m' - m)\hbar \langle n' \ell' m' | z | n\ell m \rangle .$$

This means that unless $m = m'$, the matrix elements of z are always zero. The first commutation relation $[L_z, x] = i\hbar y$ gives

$$\langle n' \ell' m' | (L_z x - x L_z) | n\ell m \rangle = (m' - m)\hbar \langle n' \ell' m' | x | n\ell m \rangle = i\hbar \langle n' \ell' m' | y | n\ell m \rangle .$$

$$(m' - m) \langle n' \ell' m' | x | n\ell m \rangle = i \langle n' \ell' m' | y | n\ell m \rangle .$$

This means that the matrix elements of y can always derive from the corresponding matrix elements of x. Similarly, the second commutation relation gives

$$(m' - m) \langle n' \ell' m' | y | n\ell m \rangle = -i \langle n' \ell' m' | x | n\ell m \rangle .$$

Combining this with the result from the first relation,

$$(m' - m)^2 \langle n' \ell' m' | x | n\ell m \rangle = \langle n' \ell' m' | x | n\ell m \rangle .$$

This means that $\langle n' \ell' m' | x | n\ell m \rangle = \langle n' \ell' m' | y | n\ell m \rangle = 0$ unless $(m' - m)^2 = 1$. In conclusion, the **selection rule** for m is

$$\boxed{\text{No transitions occur unless } \Delta m = \pm 1 \text{ or } 0.}$$

This is expected because the (emitted) photon carries spin 1, so its m can be 1, 0, or -1. Conservation of angular momentum restricts the value of Δm.

9.4.2   Azimuthal Quantum Number

There exists a commutation relation (see derivation in Appendix B.11.2) that

$$\left[L^2, [L^2, \mathbf{r}] \right] = 2\hbar^2 (L^2 \mathbf{r} + \mathbf{r} L^2).$$

Recall that $L^2 |n\ell m\rangle = \hbar^2 \ell(\ell+1) |n\ell m\rangle$. Then

$$\langle n'\ell'm'|[L^2,[L^2,\mathbf{r}]]|n\ell m\rangle = 2\hbar^2 \langle n'\ell'm'|(L^2\mathbf{r}+\mathbf{r}L^2)|n\ell m\rangle = 2\hbar^4[\ell'(\ell'+1)+\ell(\ell+1)] \langle n'\ell'm'|\mathbf{r}|n\ell m\rangle.$$

Meanwhile, if we expand the commutator

$$\begin{aligned} \langle n'\ell'm'|[L^2,[L^2,\mathbf{r}]]|n\ell m\rangle &= \langle n'\ell'm'|(L^2[L^2,\mathbf{r}]-[L^2,\mathbf{r}]L^2)|n\ell m\rangle \\ &= \hbar^2[\ell'(\ell'+1)-\ell(\ell+1)] \langle n'\ell'm'|[L^2,\mathbf{r}]|n\ell m\rangle \\ &= \hbar^2[\ell'(\ell'+1)-\ell(\ell+1)] \langle n'\ell'm'|(L^2\mathbf{r}-\mathbf{r}L^2)|n\ell m\rangle \\ &= \hbar^4[\ell'(\ell'+1)-\ell(\ell+1)]^2 \langle n'\ell'm'|\mathbf{r}|n\ell m\rangle. \end{aligned}$$

This means that either

$$2[\ell'(\ell'+1)+\ell(\ell+1)] = [\ell'(\ell'+1)-\ell(\ell+1)]^2 \quad \text{or} \quad \langle n'\ell'm'|\mathbf{r}|n\ell m\rangle = 0. \tag{9.13}$$

Observing both sides of the equation. The LHS is

$$2[\ell'(\ell'+1)+\ell(\ell+1)] = (\ell'+\ell+1)^2 + (\ell'-\ell)^2 - 1.$$

The RHS is

$$[\ell'(\ell'+1)-\ell(\ell+1)]^2 = [(\ell'+\ell+1)(\ell'-\ell)]^2.$$

Hence (9.13) can be written in the form

$$[(\ell'+\ell+1)^2 - 1][(\ell'-\ell)^2 - 1] = 0.$$

The first square bracket cannot be zero unless $\ell' = \ell = 0$, and if this happens, $\langle n'00|\mathbf{r}|n00\rangle$ is zero trivially. The second square bracket being zero gives $\ell' = \ell \pm 1$. In conclusion, the selection rule for ℓ is

$$\boxed{\text{No transitions occur unless } \Delta\ell = \pm 1.}$$

9.5 Fermi's Golden Rule

In previous sections we talked about transition between discrete states, from ψ_i to ψ_f. In reality, the initial state can also transition to a continuum of states, specified by a continuous spectrum. For example, if a photon is energetic enough to ionize an electron, then the final state of the electron is a scattering state. This is the famous **photoelectric effect**.

If the final state is in an continuum, then we can only say about the probability of the electron transitioning to a range of states with energy range ΔE about E_f. The probability is then

$$P = \int_{E_f-\Delta E/2}^{E_f+\Delta E/2} \frac{|V_{fi}|^2}{\hbar^2} \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2} g(E)\,dE,$$

where $\omega_0 = (E-E_i)/\hbar$, and the integrand except $g(E)$ comes from (9.10). The quantity $g(E)\,dE$ is called the **density of states**. It describes the number of states between energy E and $E+dE$. At large t, the integrand is sharply peaked at $\omega_0 = \omega$, or $E_f = E_i + \hbar\omega$, with a width of $4\pi\hbar/t$. Then the integral can be approximated as

$$P = \frac{|V_{fi}|}{\hbar^2} g(E_f) \int_{-\infty}^{\infty} \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}\,dE = \frac{\pi|V_{fi}|^2}{2\hbar} g(E_f)t.$$

The transition rate is

$$\boxed{R = \frac{\pi|V_{fi}|^2}{2\hbar} g(E_f).} \tag{9.14}$$

Equation (9.14) is known as **Fermi's Golden Rule**. The transition rate is proportional to the square of V_{fi} and the density of states, or the number of final states available. We can see that Fermi's Golden Rule is essentially the same as the transition rate of incoherent EM perturbation, where we sum over frequencies of light instead of density of states.

Example 9.3. The photoelectric effect

The photoelectric effect results from the ionization of electrons by energetic photons, or electromagnetic radiation. Consider a hydrogen atom in the ground state ψ_{100}. To ionize this atom, the minimum photon energy required is the ground state energy of hydrogen, $E_{\min} = \alpha^2 m_e c^2/2$, where $\alpha = e^2/4\pi\epsilon_0\hbar c$ is the fine structure constant. Suppose we want a scattering state with a wave function $\psi_f \sim e^{i\mathbf{k}\cdot\mathbf{r}}$, it is better to have $E \gg \alpha^2 m_e c^2/2$. On the other hand, the energy of the photon should not be too high because the dipole approximation requires the wavelength λ of the photon to be much larger than the size of the atom. The characteristic length scale of the hydrogen atom is the Bohr radius, $a = \hbar/m_e c\alpha$, so

$$\lambda = \frac{2\pi\hbar c}{E} \gg \frac{\hbar}{m_e c\alpha} \quad \Longrightarrow \quad E \ll \frac{\alpha m_e c^2}{2\pi}.$$

Combining the two approximations,

$$\frac{1}{2}\alpha^2 m_e c^2 \ll E \ll \frac{1}{2\pi}\alpha m_e c^2.$$

The photon energy needs to be $E \sim \alpha^{3/2} m_e c^2/2$. Let the perturbation be $H'(t) = eE_0(\hat{\mathbf{e}}_z \cdot \mathbf{r})\cos(\omega t)$, where E_0 is the amplitude of the electric field. The potential matrix is $V_{fi} = eE_0\hat{\mathbf{e}}_z \cdot \langle\psi_f|\mathbf{r}|\psi_i\rangle$. By Fermi's Golden Rule (9.14), the transition rate from the ground state of hydrogen to a free electron is

$$R_{i\to d\Omega} = \frac{\pi e^2 E_0^2}{2\hbar}|\hat{\mathbf{e}}_z \cdot \langle\psi_f|\mathbf{r}|\psi_i\rangle|^2 g(E),$$

where $d\Omega = \sin\theta\,d\theta\,d\phi$ is a differential solid angle in which the final-state electron is traveling. To compute the density of states $g(E)$, we use a common technique called **box normalization**. We see the final "free particle" confined in a very large box of size L with periodic boundary conditions. The normalized final states are

$$\psi_f = \frac{1}{\sqrt{L^3}}e^{i\mathbf{k}\cdot\mathbf{r}},$$

where $\mathbf{k} = (k_x, k_y, k_z)$ is the wave vector of the electron. Since the final-state electron is now in a 3D box, the allowed wave vector $\mathbf{k}$ are given by the 3D infinite square well,

$$k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}, \quad \text{where} \quad n_x, n_y, n_z = 1, 2, 3, \dots$$

This means the volume of each specified $\mathbf{k}$ is $(2\pi/L)^3$. In k-space, the volume occupied by all states with wave vector $k \to k+dk$ inside $d\Omega$ is $k^2 dk\,d\Omega$, so we obtain the density of states as a function of k:

$$g(k)\,dk = \frac{k^2 dk\,d\Omega}{(2\pi/L)^3} = \left(\frac{L}{2\pi}\right)^3 k^2 dk\,d\Omega.$$

To convert it into energy, we use $k = \sqrt{2mE}/\hbar$ for free particles,

$$g(E)\,dE = \left(\frac{L}{2\pi}\right)^3 k^2 dk\,d\Omega = \left(\frac{L}{2\pi}\right)^3 \frac{2mE}{\hbar^2}\frac{1}{\hbar}\sqrt{\frac{m}{2E}}\,dE\,d\Omega = \left(\frac{L}{2\pi\hbar}\right)^3 \sqrt{2m^3 E}\,d\Omega\,dE.$$

The density of states of the final-state electron is

$$g(E) = \left(\frac{L}{2\pi\hbar}\right)^3 \sqrt{2m^3 E}\,d\Omega. \tag{9.15}$$

We also need to find $\langle \psi_f | \mathbf{r} | \psi_i \rangle$. Because $\mathbf{k}$ is arbitrary, we can choose it to be in the z-direction so $\mathbf{k} = \hat{\mathbf{z}}k$ (this is just a convenient way to evaluate the integral, the actual $\mathbf{k}$ can be in any direction):

$$
\begin{aligned}
\langle \psi_f | \mathbf{r} | \psi_i \rangle &= \int \left(\frac{1}{\sqrt{L^3}} e^{-i\mathbf{k}\cdot\mathbf{r}} \right) \mathbf{r} \left(\frac{1}{\sqrt{\pi a^3}} e^{-r/a} \right) d^3\mathbf{r} \\
&= \frac{i}{\sqrt{\pi a^3 L^3}} \nabla_k \left[\int e^{-i\mathbf{k}\cdot\mathbf{r}} e^{-r/a} \, d^3\mathbf{r} \right] \\
&= \frac{i}{\sqrt{\pi a^3 L^3}} \nabla_k \left[\int e^{-ikr\cos\theta} e^{-r/a} r^2 d(\cos\theta) \, d\phi \right] \\
&= \frac{i}{\sqrt{\pi a^3 L^3}} \nabla_k \left[\frac{8\pi a^3}{(1 + k^2 a^2)^2} \right] \\
&= -i\sqrt{\frac{\pi a^3}{L^3}} \frac{32 a^2}{(1 + k^2 a^2)^3} \mathbf{k}.
\end{aligned}
$$

Putting all of these elements together,

$$
\begin{aligned}
R_{i \to d\Omega} &= \frac{\pi e^2 E_0^2}{2\hbar} |\hat{\mathbf{e}}_z \cdot \langle \psi_f | \mathbf{r} | \psi_i \rangle|^2 g(E) \\
&= \frac{\pi e^2 E_0^2}{2\hbar} \left| -i\hat{\mathbf{e}}_z \sqrt{\frac{\pi a^3}{L^3}} \frac{32 a^2}{(1 + k^2 a^2)^3} \mathbf{k} \right|^2 \left(\frac{L}{2\pi\hbar} \right)^3 \sqrt{2m^3 E} \, d\Omega \\
&= \frac{\pi e^2 E_0^2}{2\hbar} \frac{\pi a^3}{L^3} \frac{1024 a^4 k_z^2}{(1 + k^2 a^2)^6} \frac{L^3}{8\pi^3 \hbar^3} \sqrt{2m^3 E} \, d\Omega \\
&= \frac{64 a^7 e^2 E_0^2}{(1 + k^2 a^2)^6 \pi \hbar^4} k^2 \cos^2\theta \sqrt{2m^3 E} \, d\Omega \\
&= \frac{64 a^7 m e^2 E_0^2}{(1 + k^2 a^2)^6 \pi \hbar^3} k^3 \cos^2\theta \, \sin\theta \, d\theta \, d\phi.
\end{aligned}
$$

Note that our result does not depend on L, as it is just a tool to obtain the density of states. Integrating over all angles gives the transition rate of the electron scattering into all angles:

$$
R_{i \to \text{all}} = \int_0^\pi d\theta \int_0^{2\pi} d\phi \, \frac{64 a^7 m e^2 E_0^2}{(1 + k^2 a^2)^6 \pi \hbar^3} k^3 \cos^2\theta \sin\theta = \frac{64 a^7 m e^2 E_0^2}{(1 + k^2 a^2)^6 \pi \hbar^3} k^3 \left(\frac{4\pi}{3} \right) = \frac{256 a^7 m e^2 E_0^2}{3(1 + a^2 k^2)^6 \hbar^3} k^3.
$$

10 THE ADIABATIC APPROXIMATION

10.1   The Adiabatic Theorem

An **adiabatic** process is defined as a process undergoing a gradual change of the external conditions. (In thermodynamics, an adiabatic process is a process with no heat transfer between the system and its environment. We are not referring to this adiabatic process in quantum mechanics.) Consider a perfect pendulum for example. An adiabatic process can be moving the support gently and steadily. There are two characteristic times involved: T_i, the internal time (the period), and T_e, the external time (the period of support motion). The adiabatic process requires that $T_e \gg T_i$. Usually, we will solve the problem with external parameters held constant, and finally replace a parameter with a changing one. For example, the period of a pendulum with length L is $2\pi\sqrt{L/g}$. If the length is gradually changing, the period will be $2\pi\sqrt{L(t)/g}$. In quantum mechanics, the **adiabatic approximation** is in the form of a theorem called the **adiabatic theorem**.

> **Theorem 10.1. The Adiabatic theorem**
>
> Suppose the Hamiltonian changes gradually from H^i to H^f. Then if the particle was initially in the nth eigenstate of H^i, it will be carried under the Schrödinger equation into the nth eigenstate of H^f.

Proof. If the Hamiltonian changes with time, its eigenfunctions and eigenvalues are time-dependent:

$$H(t)\psi_n(t) = E_n(t)\psi_n(t), \tag{10.1}$$

but they still form a complete orthonormal set: $\langle \psi_m(t)|\psi_n(t)\rangle = \delta_{mn}$. Thus, the general solution to the time-dependent Schrödinger equation

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

can be expressed as a linear combination of them:

$$\Psi(t) = \sum_n c_n(t)\psi_n(t)e^{i\theta_n(t)} \quad \text{where} \quad \theta_n(t) = -\frac{1}{\hbar}\int_0^t E_n(t')\,dt'. \tag{10.2}$$

The θ_n is the phase factor to the case where E_n varies with time. Substituting (10.2) to the time-dependent Schrödinger equation gives

$$i\hbar \sum_n [\dot{c}_n\psi_n + c_n\dot{\psi}_n + ic_n\psi_n\dot{\theta}_n]e^{i\theta_n} = \sum_n c_n(H\psi_n)e^{i\theta_n}.$$

With (10.1) and the fact that $\dot{\theta}_n = -E_n/\hbar$, the last term on the LHS cancels with the RHS, leaving

$$\sum_n \dot{c}_n\psi_n e^{i\theta_n} = -\sum_n c_n\dot{\psi}_n e^{i\theta_n}.$$

Taking the inner product with $\langle \psi_m|$,

$$\sum_n \dot{c}_n\delta_{mn}e^{i\theta_n} = -\sum_n c_n\langle\psi_m|\dot{\psi}_n\rangle e^{i\theta_n},$$

or

$$\dot{c}_m(t) = -\sum_n c_n\langle\psi_m|\dot{\psi}_n\rangle e^{i(\theta_n-\theta_m)}. \tag{10.3}$$

Differentiating (10.1) with respect to time yields $\dot{H}\psi_n + H\dot{\psi}_n = \dot{E}_n\psi_n + E_n\dot{\psi}_n$, and taking the inner product with $\langle\psi_m|$,

$$\langle\psi_m|\dot{H}|\psi_n\rangle + \langle\psi_m|H|\dot{\psi}_n\rangle = \dot{E}_n\delta_{mn} + E_n\langle\psi_m|\dot{\psi}_n\rangle.$$

Exploiting the Hermiticity of H such that $\langle\psi_m|H|\dot\psi_n\rangle = E_m\langle\psi_m|\dot\psi_n\rangle$, then for $n \neq m$,

$$\langle\psi_m|\dot H|\psi_n\rangle = (E_n - E_m)\,\langle\psi_m|\dot\psi_n\rangle\,.$$

Substituting this into (10.3),

$$\dot c_m = -c_m\langle\psi_m|\dot\psi_m\rangle - \sum_{n\neq m} c_n \frac{\langle\psi_m|\dot H|\psi_n\rangle}{E_n - E_m} e^{-\frac{i}{\hbar}\int_0^t[E_n(t')-E_m(t')]dt'}\,.$$

So far everything is exact. Using the adiabatic approximation that $\dot H$ is extremely small, we can drop the second term,

$$\dot c_m(t) = -c_m\langle\psi_m|\dot\psi_m\rangle\,.$$

This differential equation has solution (where the dummy index m is changed to n)

$$c_n(t) = c_n(0)e^{i\gamma_n(t)} \quad \text{where} \quad \gamma_n(t) = i\int_0^t \left\langle \psi_n(t')\left|\frac{\partial}{\partial t'}\psi_n(t')\right.\right\rangle dt'\,.$$

If the particle starts out in the nth eigenstate ($c_n(0) = 1$, and $c_m(0) = 0$ for $m \neq n$), then from (10.2),

$$\boxed{\Psi_n(t) = e^{i\theta_n(t)}e^{i\gamma_n(t)}\psi_n(t).} \tag{10.4}$$

It remains in the nth eigenstate with some phase factors. Note that $e^{i\gamma_n(t)}$ is a phase factor because $\gamma_n(t)$ is in fact real. The normalization condition $\langle\psi_n|\psi_n\rangle$ requires that

$$0 = \frac{d}{dt}\langle\psi_n|\psi_n\rangle = \langle\psi_n|\dot\psi_n\rangle + \langle\dot\psi_n|\psi_n\rangle = 2\,\mathrm{Re}[\langle\psi_n|\dot\psi_n\rangle].$$

In other words, the integrand of $\gamma_n(t)$ is pure imaginary, so $\gamma_n(t)$ is real. Moreover, if ψ_n is real, then $\mathrm{Re}[\langle\psi_n|\dot\psi_n\rangle] = 0$ means $\langle\psi_n|\dot\psi_n\rangle = 0$ and $\gamma_n(t)$ vanishes. □

Example 10.1. An expanding well

Consider a particle in the ground state of the infinite square well with walls separated by a:

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

If the wall is gradually expanded to $2a$, the particle will end up in

$$\psi_f(x) = \sqrt{\frac{1}{a}}\sin\left(\frac{\pi x}{2a}\right),$$

up to a phase factor, because ψ_f is the ground state of an infinite square well twice as wide.

Note that in adiabatic approximation, there need not be a small change in the Hamiltonian as in perturbation theory, but it needs to be a gradual one so that $|\dot H_{mn}/H_{mn}| \ll |\omega_{mn}|$. Here $\omega_{mn} = (E_m - E_n)/\hbar$ is the intrinsic timescale of the system. The adiabatic approximation requires the timescale of the change in Hamiltonian is large compared to the intrinsic timescale of the system.

10.2   Berry's Phase

10.2.1   Nonholonomic Processes

Consider again the classical pendulum. We already know that as long as the motion of the support is very slow compared to the period of the pendulum, it will continue swing in the same plane and with the same amplitude. However, if the pendulum is carried around a closed loop, it may not return to its original state. For example, suppose the pendulum is initially at the North pole,

swinging in the north and south direction. When it is carried south along the longitude line, and then carried along the equator, it is still swinging in the NS direction. Then the pendulum is carried back to the North Pole, it will certainly make an angle with the initial direction because the Earth is not a flat space. A system such as this, which does not return to its original state when transported around a closed loop, is said to be **nonholonomic**.
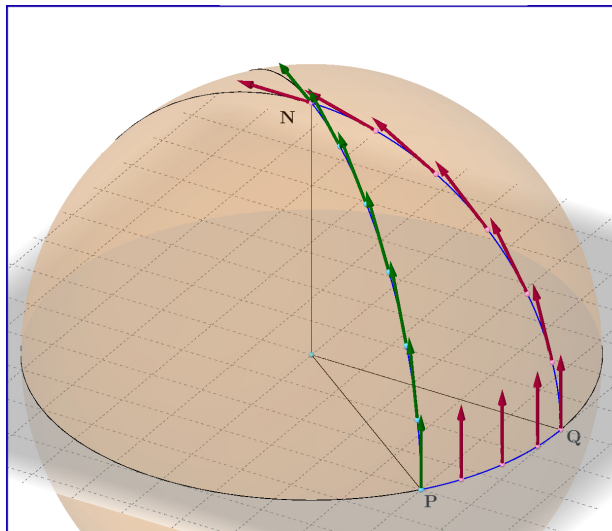
Figure 10.1: Nonholonomic system.

10.2.2 Geometric Phase

In the proof of the adiabatic theorem, a particle which starts out in the nth eigenstate of $H(0)$ remains in the nth eigenstate of $H(t)$ under adiabatic conditions. Specifically, the wave function is

$$\Psi_n(t) = e^{i[\theta_n(t) + \gamma_n(t)]}\psi_n(t),$$

where

$$\theta_n(t) \equiv -\frac{1}{\hbar}\int_0^t E_n(t')\,dt' \quad \text{and} \quad \gamma_n(t) \equiv i\int_0^t \left\langle \psi_n(t') \left| \frac{\partial}{\partial t'}\psi_n(t') \right. \right\rangle dt'.$$

The former is called the **dynamic phase**, while the latter is called the **geometric phase**.

$\psi(t)$ depends on time because there is some parameter $R(t)$ in the Hamiltonian depending on t. Thus

$$\frac{\partial \psi_n}{\partial t} = \frac{\partial \psi_n}{\partial R}\frac{dR}{dt},$$

and the geometric phase is then

$$\gamma_n(t) = i\int_0^t \left\langle \psi_n \left| \frac{\partial \psi_n}{\partial R} \right. \right\rangle \frac{dR}{dt'}\,dt' = i\int_{R_i}^{R_f} \left\langle \psi_n \left| \frac{\partial \psi_n}{\partial R} \right. \right\rangle dR,$$

where R_i and R_f are the initial and final values of $R(t)$. If the Hamiltonian returns to its orginal form after time T such that $R_f = R_i$, then $\gamma_n(T) = 0$.

However, if there are N parameters in the Hamiltonian that is changing with time: $R_1(t)$, $R_2(t)$,..., $R_N(t)$, then

$$\frac{\partial \psi_n}{\partial t} = \frac{\partial \psi_n}{\partial R_1}\frac{dR_1}{dt} + \frac{\partial \psi_n}{\partial R_2}\frac{dR_2}{dt} + \cdots + \frac{\partial \psi_n}{\partial R_N}\frac{dR_N}{dt} = (\nabla_R\psi_n)\cdot\frac{d\mathbf{R}}{dt},$$

where $\mathbf{R} \equiv (R_1, R_2, \ldots, R_N)$ is the position in R-space, and ∇_R is the gradient with respect to these parameters. This time

$$\gamma_n(t) = i\int_{\mathbf{R}_i}^{\mathbf{R}_f} \langle \psi_n | \nabla_R \psi_n \rangle \cdot d\mathbf{R}.$$

If the Hamiltonian returns to its original form after time T, the net geometric phase change is

$$\gamma_n(T) = i \oint \langle \psi_n | \nabla_R \psi_n \rangle \cdot d\mathbf{R}. \tag{10.5}$$

This is a line integral around a closed loop in parameter-space and it is not zero in general. $\gamma_n(T)$ is called Berry's phase, which depends only on the path taken, but not on how fast that path is traversed. On the contrary, the dynamic phase $\theta_n(T)$ clearly depends on the elapsed time.

Particularly, if the parameter space is three dimensional, $\mathbf{R} = (R_1, R_2, R_3)$, we can rewrite Berry's phase in a surface integral using Stokes' theorem:

$$\gamma_n(T) = i \int_S [\nabla_R \times \langle \psi_n | \nabla_R \psi_n \rangle] \cdot d\mathbf{S}.$$

Example 10.2. A constantly expanding well

Consider expanding infinite square well in a constant rate v:

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t), \quad \text{where} \quad V(x,t) = \begin{cases} 0, & 0 \leq x \leq w, \\ \infty, & \text{otherwise.} \end{cases}$$

The parameter $w \equiv a + vt$ is the width of the well at time t, a is the initial size. Before we go into the adiabatic approximation, it is important to know that the Schrödinger equation $H\Psi = i\hbar\partial_t\Psi$ with this Hamiltonian can be solved exactly. The complete set of solutions is

$$\phi_n(x,t) = \sqrt{\frac{2}{w}} \sin\left(\frac{n\pi x}{w}\right) e^{i(mvx^2 - 2E_n^i at)/2\hbar w},$$

where $E_n^i = n^2\pi^2\hbar^2/2ma^2$ is the nth allowed energy of the original well. The general solution to the Schrödinger equation is

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \phi_n(x,t),$$

where c_n are independent of t. At the time dependence are in $\phi(x,t)$ themselves. To check that ϕ_n satisfies the Schrödinger equation, see Appendix B.11.3. Suppose the initial state $\Psi(x,0) = \psi_0$ starts out in the ground state of the infinite square well with width a. Because ϕ_n form a complete set, we can expand $\Psi(x,0)$ in the ϕ_n basis. The expansion coefficients are

$$c_n = \int_0^a \phi_n^*(x,0)\Psi(x,0)\,dx$$

$$= \int_0^a \sqrt{\frac{2}{w}} \sin\left(\frac{n\pi x}{w}\right) e^{-i(mvx^2 - 2E_n^i at)/2\hbar w}\bigg|_{t=0} \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) dx$$

$$= \frac{2}{a} \int_0^a e^{-imvx^2/2\hbar a} \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{\pi x}{a}\right) dx$$

Let $z = \pi x/a$, $dx = a\,dz/\pi$, and $\alpha = mva/2\pi^2\hbar$,

$$c_n = \frac{2}{a}\frac{a}{\pi} \int_0^{\pi} e^{-i(mva/2\pi^2\hbar)(\pi^2 x^2/a^2)} \sin(nz)\sin(z)\,dz = \frac{2}{\pi} \int_0^{\pi} e^{-i\alpha z^2} \sin(nz)\sin(z)\,dz.$$

This integral cannot be written in terms of elementary functions, so now we return to the adiabatic approximation. Define the external time T_e to be the time for the well to expand to $w = 2a$, so $T_e = a/v$. Define the internal time T_i to be the period of one oscillation of the phase factor in ϕ_n, $e^{iE_n^i at/\hbar w}$. The frequency and period in the initial ground state is

$$\omega_i = \frac{E_0^i a}{\hbar w(0)} = \frac{\pi^2\hbar}{2ma^2} \quad \Longrightarrow \quad T_i = \frac{2\pi}{\omega_i} = \frac{4ma^2}{\pi\hbar}.$$

The adiabatic approximation requires $T_i/T_e \ll 1$, or

$$1 \gg \frac{T_i}{T_e} = \frac{v}{a}\frac{4ma^2}{\pi\hbar} = \frac{4mva}{\pi\hbar} = 8\pi\alpha \quad \Longrightarrow \quad \alpha \ll 1.$$

This means we can approximate $e^{-i\alpha z^2} \approx 1$ in the adiabatic approximation. The coefficients can now be calculated:

$$c_n = \frac{2}{\pi} \int_0^\pi e^{-i\alpha z^2} \sin(nz) \sin(z)\, dz \simeq \frac{2}{\pi} \int_0^\pi \sin(nz) \sin(z)\, dz.$$

This integral is zero for $n \neq 1$, and is 1 for $n = 1$. In other words, the probability of the final state to be in the ground state ϕ_1 is 100%, consistent with the adiabatic theorem.

The phase factor in time in $\Psi(x, t)$ is $e^{-2iE_n^i at/2\hbar w}$. Differentiating the exponent,

$$\frac{d}{dt}\left[-\frac{E_n^i at}{\hbar(a + vt)}\right] = -\frac{E_n^i a}{\hbar}\frac{a}{(a + vt)^2} = -\frac{n^2\pi^2\hbar^2}{2ma^2}\frac{a^2}{\hbar w^2} = -\frac{1}{\hbar}\frac{n^2\pi^2\hbar^2}{2mw^2} = -\frac{1}{\hbar}E_n(t),$$

where $E_n(t) = n^2\pi^2\hbar^2/2mw^2$ is the nth instantaneous eigenvalue of the Hamiltonian. If we let $e^{-2iE_n^i at/2\hbar w} = e^{i\theta}$, where $\theta_n = -E_n^i at/\hbar w$, the above differentiation is equivalent to saying

$$\frac{d\theta_n}{dt} = -\frac{E_n}{\hbar} \iff \theta_n(t) = -\frac{1}{\hbar}\int_0^t E_n(t')\, dt'.$$

In other words, the entire phase factor is in the dynamic phase, there is no geometric phase at any time.

10.2.3   The Aharonov-Bohm Effect Revisited

In classical electrodynamics, the potentials ϕ and $\mathbf{A}$ are not directly measureable, but are related to EM fields,

$$\mathbf{E} = -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}.$$

There are no electromagnetic influence in regions where $\mathbf{E}$ and $\mathbf{B}$ are zero. In quantum mechanics, potentials are more important, as the Hamiltonian is expressed in terms of ϕ and $\mathbf{A}$:

$$H = \frac{1}{2m}\left(-i\hbar\nabla - q\mathbf{A}\right)^2 + q\phi.$$

In 1959 Aharonov and Bohm showed that the vector potential can affect the quantum behavior of a charged partice even when it is moving through a region with zero fields.

Consider a particle constrained on a wire ring with radius b. A solenoid of radius $a < b$ runs along the axis of the ring with a steady current I. Assuming the solenoid to be infinitely long, the magnetic field inside is uniform, while the field outside is zero. The vector potential (using gauge condition $\nabla \cdot \mathbf{A} = 0$) outside the solenoid is not zero,

$$\mathbf{A} = \frac{\Phi}{2\pi r}\hat{\phi} \quad (r > a), \tag{10.6}$$

where $\Phi = \pi a^2 B$ is the magnetic flux through the solenoid. The solenoid is not charged ($\phi = 0$), so the Hamiltonian becomes

$$H = \frac{1}{2m}\left[-\hbar^2\nabla^2 + q^2\mathbf{A}^2 + 2i\hbar q\mathbf{A} \cdot \nabla\right].$$

Obviously the wave function depends only on the azimuthal angle ϕ because of the constraints ($\theta = \pi/2$ and $r = b$). Thus $\nabla \to (\hat{\phi}/b)(d/d\phi)$, and the Schrödinger equation reads

$$\frac{1}{2m}\left[-\frac{\hbar^2}{b^2}\frac{d^2}{d\phi^2} + \left(\frac{q\Phi}{2\pi b}\right)^2 + i\frac{\hbar q\Phi}{\pi b^2}\frac{d}{d\phi}\right]\psi(\phi) = E\psi(\phi).$$

It is a second-order linear differential equation

$$\frac{d^2\psi}{d\phi^2} - 2i\beta\frac{d\psi}{d\phi} + \epsilon\psi = 0, \quad \text{where} \quad \beta \equiv \frac{q\Phi}{2\pi\hbar} \quad \text{and} \quad \epsilon \equiv \frac{2mb^2 E}{\hbar^2} - \beta^2.$$

The solutions are

$$\psi = Ae^{i\lambda\phi}, \quad \text{where} \quad \lambda = \beta \pm \sqrt{\beta^2 + \epsilon} = \beta \pm \frac{b}{\hbar}\sqrt{2mE}.$$

The continuity of $\psi(\phi)$ at $\phi = 2\pi$ requires that $\beta \pm \sqrt{2mE}/\hbar = n$. Then we can get the energy

$$E_n = \frac{\hbar^2}{2mb^2}\left(n - \frac{q\Phi}{2\pi\hbar}\right)^2, \quad (n = 0, \pm 1, \pm 2, \dots).$$

If q is positive, the particle traveling in the same direction as the current (positive n) has lower energy. The allowed energy clearly depends on the field inside the solenoid even though the particle is in a region with zero field.

Suppose the particle moves through a region where $\mathbf{B} = \nabla \times \mathbf{A} = 0$, but with nonzero $\mathbf{A}$. The more general Schrödinger equation is

$$\left[\frac{1}{2m}\left(-i\hbar\nabla - q\mathbf{A}\right)^2 + V\right]\Psi = i\hbar\frac{\partial\Psi}{\partial t}.$$

We can solve for Ψ by letting

$$\Psi = e^{ig}\Psi' \quad \text{where} \quad g(\mathbf{r}) = \frac{q}{\hbar}\int_{\mathcal{O}}^{\mathbf{r}} \mathbf{A}(\mathbf{r}') \cdot d\mathbf{r}'.$$

$\mathcal{O}$ is some arbitrary reference point. This definition makes sense only when $\nabla \times \mathbf{A} = 0$. Otherwise, the line integral depends on the path from $\mathcal{O}$ to $\mathbf{r}$, and $g(\mathbf{r})$ is undefined. The gradient of Ψ is

$$\nabla\Psi = e^{ig}(i\nabla g)\Psi' + e^{ig}(\nabla\Psi').$$

With $\nabla g = (q/\hbar)\mathbf{A}$,

$$\left(-i\hbar\nabla - q\mathbf{A}\right)\Psi = -i\hbar e^{ig}\nabla\Psi' \quad \Longrightarrow \quad \left(-i\hbar\nabla - q\mathbf{A}\right)^2\Psi = -\hbar^2 e^{ig}\nabla^2\Psi'.$$

Putting this into Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\Psi' + V\Psi' = i\hbar\frac{\partial\Psi'}{\partial t}.$$

Ψ' satisfies the Schrödinger equation without $\mathbf{A}$. We can solve this equation first and then get Ψ with the phase factor e^{ig}.

Aharonov and Bohm proposed an experiment with a beam of electrons is split in two, and passed either side of a solenoid and combined into one. The two beams arrive with different phases:

$$g = \frac{q}{\hbar}\int \mathbf{A} \cdot d\mathbf{r} = \frac{q\Phi}{2\pi\hbar}\int \left(\frac{1}{r}\hat{\boldsymbol{\phi}}\right) \cdot (r\hat{\boldsymbol{\phi}}\, d\phi) = \pm\frac{q\Phi}{2\hbar}.$$

We can measure the interference created by this phase difference.
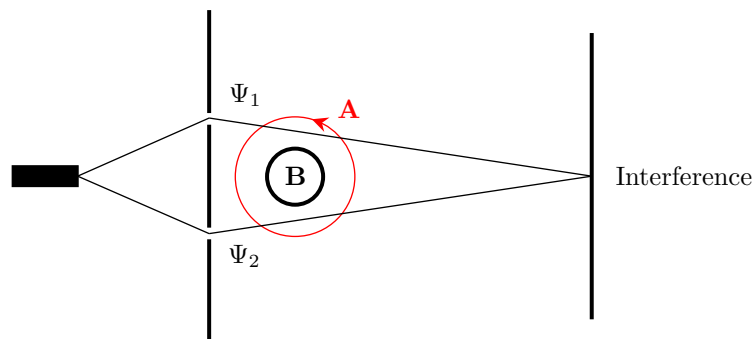
The phase difference is obviously $q\Phi/\hbar$. Berry pointed out that the Aharonov-Bohm effect is an example of geometric phase. Suppose the particle is confined (i.e. bounded) to a box that is centered at $\mathbf{R}$ outside the solenoid by a potential $V(\mathbf{r} - \mathbf{R})$. The eigenfuntions of the Hamiltonian can be determined by

$$\left\{\frac{1}{2m}\left[-i\hbar\nabla - q\mathbf{A}(\mathbf{r})\right]^2 + V(\mathbf{r} - \mathbf{R})\right\}\psi_n = E_n\psi_n.$$

We use the same method: let

$$\psi_n = e^{ig}\psi_n', \quad \text{where} \quad g \equiv \frac{q}{\hbar}\int_{\mathbf{R}}^{\mathbf{r}} \mathbf{A}(\mathbf{r}') \cdot d\mathbf{r}'.$$

With $\nabla \times \mathbf{A} = 0$, $\psi'(\mathbf{r} - \mathbf{R})$ satisfies

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r} - \mathbf{R})\right]\psi_n' = E_n\psi_n'.$$

Now carry the box around the solenoid (for one revolution). We shall first get $\langle \psi_n | \nabla_R \psi_n \rangle$ to evaluate Berry's phase,

$$\nabla_R \psi_n = \nabla_R \left[e^{ig} \psi'_n(\mathbf{r} - \mathbf{R}) \right] = -i\frac{q}{\hbar} \mathbf{A}(\mathbf{R}) e^{ig} \psi'(\mathbf{r} - \mathbf{R}) + e^{ig} \nabla_R \psi'_n(\mathbf{r} - \mathbf{R}).$$

Then

$$\langle \psi_n | \nabla_R \psi_n \rangle = \int e^{-ig} [\psi'_n(\mathbf{r} - \mathbf{R})]^* e^{ig} \left[-i\frac{q}{\hbar} \mathbf{A}(\mathbf{R}) \psi'_n(\mathbf{r} - \mathbf{R}) + \nabla_R \psi'_n(\mathbf{r} - \mathbf{R}) \right] d^3\mathbf{r}$$

$$= -i\frac{q}{\hbar} \mathbf{A}(\mathbf{R}) - \int [\psi'_n(\mathbf{r} - \mathbf{R})]^* \nabla \psi'_n(\mathbf{r} - \mathbf{R}) \, d^3\mathbf{r}.$$

Note: ∇ with no subscript is with respect to $\mathbf{r}$, and $\nabla_R = -\nabla$ when acting on a function of $(\mathbf{r} - \mathbf{R})$. The last integral is $i/\hbar$ times the expectation value of momentum. It vanishes because the expectation value of momentum in a bounded eigenstate of the Hamiltonian is always zero. This gives a simple form

$$\langle \psi_n | \nabla_R \psi_n \rangle = -i\frac{q}{\hbar} \mathbf{A}(\mathbf{R}).$$

Putting this into Eq. 10.5,

$$\gamma_n(T) = \frac{q}{\hbar} \oint \mathbf{A}(\mathbf{R}) \cdot d\mathbf{R} = \frac{q}{\hbar} \int_S (\nabla \times \mathbf{A}) \cdot d\mathbf{S} = \frac{q\Phi}{\hbar},$$

which is exactly the Aharonov-Bohm result.

10.3 Diabatic Processes

To be written.

Example 10.3. A sudden expansion of an infinite square well

Consider an infinite square well with walls at $x = 0$ and $x = a$. Suddenly, the right wall expands to $x = 2a$. We would like to know the probability of getting certain energies if we measure it immediately after the sudden expansion. First, the wave function immediately after the expansion is still $\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$. We need to expand it in terms of the eigenstates of an infinite square well with width $2a$,

$$\psi = \sum_n c_n \psi_n \quad \text{where} \quad \psi_n = \sqrt{\frac{1}{a}} \sin\left(\frac{n\pi x}{2a}\right), \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2m(2a)^2} = \frac{n^2 \pi^2 \hbar^2}{8ma^2}.$$

The coefficients are

$$c_n = \langle \psi_n | \psi \rangle = \int_0^{2a} \psi_n^* \psi \, dx = \frac{\sqrt{2}}{a} \int_0^a \sin\left(\frac{n\pi x}{2a}\right) \sin\left(\frac{\pi x}{a}\right) dx = \frac{4\sqrt{2} \sin(n\pi/2)}{4\pi - n^2 \pi}.$$

This works for $n \neq 2$. When $n = 2$, $c_2 = \langle \psi_2 | \psi \rangle = \frac{1}{\sqrt{2}} \langle \psi | \psi \rangle = \frac{1}{\sqrt{2}}$. The most probable result is

$$E_2 = \frac{\pi^2 \hbar^2}{2ma^2} \quad \text{with probability} \quad P_2 = \left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{2},$$

the ground state energy of the orignial well, but the first-excited state energy of the expanded well. The second most probable energy is the ground state energy of the expanded well,

$$E_1 = \frac{\pi^2 \hbar^2}{8ma^2} \quad \text{with probability} \quad P_1 = \left(\frac{4\sqrt{2}}{3}\right)^2 \approx 0.36.$$

The expectation value of the energy immediately after the expansion is the original ground state energy $\langle H \rangle = \pi^2 \hbar^2 / 2ma^2$ because the system has no time to react,

$$\langle H \rangle = \int \psi^* H \psi \, dx = \frac{2}{a} \int_0^a \sin\left(\frac{\pi x}{a}\right) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\right) \sin\left(\frac{\pi x}{a}\right) dx = \frac{\pi^2 \hbar^2}{2ma^2}.$$

This result tells us that in the sudden expansion case, the energy is conserved. If one wants to calculate the expectation value of the energy by the infinite series $\langle H \rangle = \sum_n |c_n|^2 E_n$ (the definition of the expectation value), check Appendix B.11.4.

11 SCATTERING

11.1 Introduction

11.1.1 Classical Scattering Theory

The basic problem of classical scattering theory is: for a particle incident on some scattering center, given the **impact parameter** b, calculate the **scattering angle** θ. The scattering center is azimuthal symmetrical so that the trajectory is in one plane. The impact parameter b is the perpendicular distance between the initial trajectory of the particle and the scattering center. The scattering angle θ is the angle of the particle's final velocity deviated from the initial velocity. For example, $\theta = 0$ indicates no direction change, while $\theta = \pi$ means the particle bounces back.

To simplify a problem, there are several assumptions to make:

- We are interested in the scattering problem of the form $A + B \rightarrow A + B$: the initial particles and final particles are the same.

- The scattering is elastic: the internal structure of particles are unchanged. For example, the ground state atom does not become an excited state after scattering, and the spin is unchanged.

- The interaction potential depends only on the relative position between A and B, $V(\mathbf{r}_A, \mathbf{r}_B) = V(\mathbf{r}_A - \mathbf{r}_B) = V(\mathbf{r})$.

- The potential goes to zero as $r \rightarrow \infty$ and goes at or faster than $1/r$.

If we have multiple non-interacting particles within an infinitesimal of cross-sectional area $d\sigma$, they will scatter into a corresponding infinitesimal solid angle $d\Omega$. The proportionality factor $D(\theta) \equiv d\sigma/d\Omega$ is called the **differential (scattering) cross-section**.
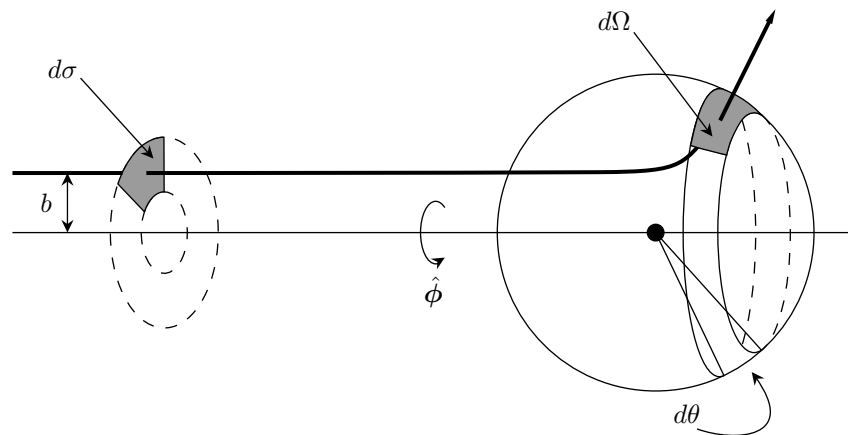
In terms of the impact paramter and the azimuthal angle ϕ, $d\sigma = b \, db \, d\phi$ and $d\Omega = \sin\theta \, d\theta \, d\phi$.. We get that

$$D(\theta) = \frac{b}{\sin\theta}\left|\frac{db}{d\theta}\right|.$$

There is an absolute value because θ is typically a decreasing function of b. The **total cross-section** is defined as

$$\sigma \equiv \int D(\theta) \, d\Omega = \int_0^\pi d\theta \int_0^{2\pi} d\phi \, D(\theta) \sin\theta. \tag{11.1}$$

A classic classical scattering process is **Rutherford scattering** (see Appendix B.12.1), which has infinite total cross-section. Suppose now we have a beam of particles with uniform intensity or **luminosity** $\mathcal{L}$, the number of incident particles per unit area, per unit

time. The number of particles entering $d\sigma$ per unit time is $dN = \mathcal{L}\, d\sigma = \mathcal{L} D(\theta)\, d\Omega$. Then in terms of luminosity,

$$D(\theta) = \frac{1}{\mathcal{L}} \frac{dN}{d\Omega}.$$

11.1.2 Quantum Scattering Theory

Consider an incident plane wave in the z-direction, $\psi(z) = Ae^{ikz}$, where $k \equiv \sqrt{2mE}/\hbar$. It encounters a scattering potential and produces an spherical wave, $\sim e^{ikr}$, along the radial direction. The solutions to the Schrödinger equation is in the general form (assuming azimuthal symmetry)

$$\psi(r,\theta) \simeq A\left[e^{ikz} + f(\theta)\frac{e^{ikr}}{r}\right], \quad \text{for large } r. \tag{11.2}$$

The factor of $1/r$ is because this portion of $|\psi|^2$ goes like $1/r^2$ so that probability is conserved when integrated over space. Think of it classically: suppose there are N particles coming out at a solid angle $\delta\Omega$, so $|\psi_s|^2 \propto |f(\theta)|^2 \delta\Omega$, where ψ_s is the scattering portion of the wave function. Meanwhile, $|\psi_s|^2$ should also go like $1/r^2$ at large r because the particle is in an area $r^2\delta\Omega$ spanned by the same solid angle. Thus, to conserve probability (or particle number),

$$|\psi_s|^2 \propto \frac{|f(\theta)|^2}{r^2} \quad \Longrightarrow \quad \psi_s \propto \frac{f(\theta)}{r}e^{ikr}.$$

The quantum scattering problem is to determine the **scattering amplitude** $f(\theta)$, which gives the probability of scattering in θ direction. The scattering amplitude is directly related to observable quantities. The probability of the incident particles with speed v that passes through area $d\sigma$ in time dt is

$$dP = |\psi_i|^2 dV = |A|^2(v\, dt)\, d\sigma,$$

which is equal to the scattering probability in to the corresponding solid angle $d\Omega$,

$$dP = |\psi_s|^2 dV = \frac{|A|^2|f|^2}{r^2}(v\, dt)r^2 d\Omega = |f|^2(v\, dt)\, d\Omega.$$

This is because the particle number/probability is conserved: the number/amplitude of incident particles should be equal to that of the scattered particles. The two speeds are equal because the scattering is elastic so that there is no energy loss. Comparing the two dP's gives $d\sigma = |f|^2 d\Omega$, and

$$D(\theta) = \frac{d\sigma}{d\Omega} = |f(\theta)|^2. \tag{11.3}$$

Once we know $f(\theta)$, we know the differential cross-section. The following sections discuss the techniques to find the scattering amplitude $f(\theta)$. They are **partial wave analysis** and the **Born approximation**.

11.2 Partial Wave Analysis

In Chapter 4, the Schrödinger equation for a spherically symmetric potential has solutions

$$\psi(r,\theta,\phi) = R(r)Y_\ell^m(\theta,\phi).$$

$u(r) = rR(r)$ satisfies the radial equation

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

At very large r the potential goes to zero, and the centrifugal term is negligible:

$$\frac{d^2u}{dr^2} \approx -k^2u \quad \Longrightarrow \quad u(r) = Ce^{ikr} + De^{-ikr}.$$

The first term is an outgoing wave while the second is an incoming one. Physically, for scattering problems, we want $D = 0$. Hence at very large r (more precisely $kr \gg 1$ at which it is called the **radiation zone**),

$$R(r) \sim \frac{e^{ikr}}{r}.$$

In the intermediate region where V is ignored but centrifugal term is not, the radial equation is

$$\frac{d^2 u}{dr^2} - \frac{\ell(\ell+1)}{r^2}u = -k^2 u.$$

It has the general solution

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

where j_ℓ and n_ℓ are spherical Bessel functions. However, they do not represent outgoing or incoming waves, but their linear combination known as the **spherical Hankel functions** do,

$$h_\ell^{(1)}(r) = j_\ell(r) + in_\ell(r), \quad h_\ell^{(2)}(r) = j_\ell(r) - in_\ell(r).$$

Particularly, the functions $h_\ell^{(1)}$ represents an outgoing wave at large r,

$$h_\ell^{(1)} \to \frac{1}{r}(-i)^{\ell+1}e^{ir} \quad \Longrightarrow \quad R(r) \sim h_\ell^{(1)}(kr).$$

Hence, the wave function is

$$\psi(r,\theta,\phi) = A\left[e^{ikz} + \sum_{\ell,m} C_{\ell,m}h_\ell^{(1)}(kr)Y_\ell^m(\theta,\phi)\right],$$

where $C_{\ell,m}$ is the expansion coefficients. Now, we assumed the potential to be azimuthally symmetric, so the wave function cannot depend of ϕ. Recall that the spherical harmonics $Y_\ell^m \sim e^{im\phi}$, so $m = 0$. Then from Eq. 4.7,

$$Y_\ell^0(\theta,\phi) = \sqrt{\frac{2\ell+1}{4\pi}}P_\ell(\cos\theta),$$

where P_ℓ is the ℓth Legendre polynomial. It is convenient to let $C_{\ell,0} \equiv i^{\ell+1}k\sqrt{4\pi(2\ell+1)}a_\ell$, where a_ℓ is called the ℓth **partial wave amplitude**, so that

$$\psi(r,\theta) = A\left[e^{ikz} + k\sum_\ell i^{\ell+1}(2\ell+1)a_\ell h_\ell^{(1)}(kr)P_\ell(\cos\theta)\right]. \tag{11.4}$$

At large r, the Hankel function behaves like $(-i)^{\ell+1}e^{ikr}/kr$, so

$$f(\theta) = \sum_{\ell=0}^{\infty}(2\ell+1)a_\ell P_\ell(\cos\theta).$$

The differential cross-section is

$$D(\theta) = |f(\theta)|^2 = \sum_{\ell,\ell'}(2\ell+1)(2\ell'+1)a_\ell^* a_{\ell'}P_\ell(\cos\theta)P_{\ell'}(\cos\theta).$$

The total cross section is

$$\sigma = \int D(\theta)\,d\Omega = 4\pi\sum_{\ell=0}^{\infty}(2\ell+1)|a_\ell|^2.$$

where we use the orthonormality of Legendre polynomials,

$$\int_{-1}^{1} P_\ell(x)P_{\ell'}(x)\,dx = \left(\frac{2}{2\ell+1}\right)\delta_{\ell\ell'}.$$

The partial wave amplitudes a_ℓ is obtained by solving the Schrödinger equation in the region where $V(r) \neq 0$ with some boundary conditions. One more problem is that e^{ikz} is not in the spherical coordinates. We use **Rayleigh's formula** (with $m = 0$) to express this,

$$e^{ikz} = \sum_{\ell=0}^{\infty} i^\ell(2\ell+1)j_\ell(kr)P_\ell(\cos\theta).$$

Hence the wave function in the exterior region is entirely in terms of r and θ,

$$\psi(r,\theta) = A\sum_{\ell=0}^{\infty} i^\ell(2\ell+1)\left[j_\ell(kr) + ika_\ell h_\ell^{(1)}(kr)\right]P_\ell(\cos\theta).$$

11.3 The Born Approximation

11.3.1 Integral Form of the Schrödinger equation

The time-independent Schrödinger equation can be written as

$$(\nabla^2 + k^2)\psi = Q, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar} \quad \text{and} \quad Q \equiv \frac{2m}{\hbar^2}V\psi. \tag{11.5}$$

This is in the form of the **Helmholtz equation** but with the "source" term Q depending on ψ. A common and very powerful technique to handle the inhomogeneous term/sourse term on the RHS is to use **Green's functions**. Basically, we replace Q by a delta function $\delta^3(\mathbf{r})$ and ψ by a function named $G(\mathbf{r})$ in (11.5). Then once we solve for $G(\mathbf{r})$, we can find $\psi(\mathbf{r})$:

$$(\nabla^2 + k^2)G(\mathbf{r}) = \delta^3(\mathbf{r}) \implies \psi(\mathbf{r}) = \int G(\mathbf{r} - \mathbf{r}')Q(\mathbf{r}')\,d^3\mathbf{r}'.$$

(In general, there is a Green's function associated with a linear differential equation. The above Green's function is for the Helmholtz equation.) It is straightforward to show that $\psi(\mathbf{r})$ satisfies (11.5):

$$(\nabla^2 + k^2)\psi = \int [(\nabla^2 + k^2)G(\mathbf{r} - \mathbf{r}')]Q(\mathbf{r}')\,d^3\mathbf{r}' = \int \delta(\mathbf{r} - \mathbf{r}')Q(\mathbf{r}')\,d^3\mathbf{r}' = Q(\mathbf{r}).$$

Note that ∇^2 is the derivatives with respect to $\mathbf{r}$ coordinates, not $\mathbf{r}'$. It directly shows the power of the Green's function: once we know $G(\mathbf{r})$ of a certain linear operator ($\nabla^2 + k^2$ in our case), the solution ψ is merely an integral with *any* source term $Q(\mathbf{r})$. Now the goal is to solve for $G(\mathbf{r})$ in

$$(\nabla^2 + k^2)G(\mathbf{r}) = \delta^3(\mathbf{r}).$$

It is not an easy equation to solve, but the answer is pretty simple:

$$G(\mathbf{r}) = -\frac{e^{ikr}}{4\pi r}.$$

One can just plug this solution into the differential equation and verify. Appendix B.12.2 has a detailed derivation. It requires some knowledge of complex analysis and familiarity with vector calculus (especially integral theorems). With the Green's function for the Helmholtz equation, we can put this back into $\psi(\mathbf{r})$,

$$\psi(\mathbf{r}) = -\frac{m}{2\pi\hbar^2} \int \frac{e^{ik|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}')\psi(\mathbf{r}')\,d^3\mathbf{r}'.$$

In fact, we can always add a $\psi_0(\mathbf{r})$ that satisfies the free-particle Schrödinger equation $(\nabla^2 + k^2)\psi_0 = 0$ (i.e. this is the homogeneous solution to the Helmholtz equation). It also tells us that the Green's function is not unique, since $G' = G + \psi_0$ is also a Green's function that solves $(\nabla^2 + k^2)G'(\mathbf{r}) = \delta^3(\mathbf{r})$. Finally, we arrive at

$$\boxed{\psi(\mathbf{r}) = \psi_0(\mathbf{r}) - \frac{m}{2\pi\hbar^2} \int \frac{e^{ik|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}')\psi(\mathbf{r}')\,d^3\mathbf{r}'.} \tag{11.6}$$

This equation is called the **integral form of the Schrödinger equation**. It is an *equation* rather than a solution because there is also a ψ in the integral, which cannot be solved unless the solution ψ is known. It seems like we have done nothing but turning a differential equation into an integral equation.

11.3.2 The First Born Approximation

Suppose $V(\mathbf{r}')$ is zero outside some finite region about $\mathbf{r}' = 0$. Then for the integral in (11.6), only $|\mathbf{r}'| \ll |\mathbf{r}|$ contributes. Hence we get

$$|\mathbf{r} - \mathbf{r}'|^2 = r^2 + r'^2 - 2\mathbf{r}\cdot\mathbf{r}' \simeq r^2\left(1 - 2\frac{\mathbf{r}\cdot\mathbf{r}'}{r^2}\right) \implies |\mathbf{r} - \mathbf{r}'| \simeq \left[r^2\left(1 - 2\frac{\mathbf{r}\cdot\mathbf{r}'}{r^2}\right)\right]^{1/2} \simeq r - \hat{\mathbf{r}}\cdot\mathbf{r}'.$$

Let $\mathbf{k} \equiv k\hat{\mathbf{r}}$. Then the exponential

$$e^{ik|\mathbf{r} - \mathbf{r}'|} \simeq e^{ik(r - \hat{\mathbf{r}}\cdot\mathbf{r}')} = e^{ikr}e^{-i\mathbf{k}\cdot\mathbf{r}'},$$

and to leading order in r'/r,

$$\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \simeq (r - \hat{\mathbf{r}} \cdot \mathbf{r}')^{-1} e^{ikr} e^{-i\mathbf{k}\cdot\mathbf{r}'} \simeq \frac{1}{r}\left(1 + \hat{\mathbf{r}} \cdot \frac{\mathbf{r}'}{r}\right) e^{ikr} e^{-i\mathbf{k}\cdot\mathbf{r}'} \simeq \frac{e^{ikr}}{r} e^{-i\mathbf{k}\cdot\mathbf{r}'}.$$

The incident plane wave for large r is $\psi_0(\mathbf{r}) = Ae^{ikz}$. The total wave function (11.6) is

$$\psi(\mathbf{r}) \simeq Ae^{ikz} - \frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r} \int e^{-i\mathbf{k}\cdot\mathbf{r}'} V(\mathbf{r}')\psi(\mathbf{r}')\, d^3\mathbf{r}'.$$

Comparing it to (11.2), the scattering amplitude indicated by this wave function is

$$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2 A} \int e^{-i\mathbf{k}\cdot\mathbf{r}'} V(\mathbf{r}')\psi(\mathbf{r}')\, d^3\mathbf{r}'.$$

Here comes the **Born approximation**. Suppose the incoming plane wave is not substantially altered by the potential. (The Born approximation is for particles is much larger than the potential, opposite to partial wave analysis.) Then

$$\psi(\mathbf{r}') \simeq \psi_0(\mathbf{r}') = Ae^{ikz'} = Ae^{i\mathbf{k}'\cdot\mathbf{r}'}, \quad \text{where} \quad \mathbf{k}' \equiv k\hat{\mathbf{z}}.$$

Note that $\mathbf{k}'$ is the initial beam direction, while $\mathbf{k}$ is the final (radial) beam direction. They have the same amplitude because the scattering is elastic (no energy loss). The scattering amplitude is now

$$f(\theta, \phi) \simeq -\frac{m}{2\pi\hbar^2} \int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}'} V(\mathbf{r}')\, d^3\mathbf{r}' \tag{11.7}$$

If the energy is not extremely high, the exponential wiggle factor is essentially constant over the scattering region. That is, $|\mathbf{k} - \mathbf{k}'| \sim 1/\lambda \gg$ (scattering region), essentially the dipole approximation. The integral can be further approximated as

$$f(\theta, \phi) \simeq -\frac{m}{2\pi\hbar^2} \int V(\mathbf{r})\, d^3\mathbf{r}.$$

For a spherically symmetric potential $V(\mathbf{r}) = V(r)$, we can define $\boldsymbol{\kappa} \equiv \mathbf{k}' - \mathbf{k}$, and let the polar axis for $\mathbf{r}'$ coordinates lie along $\boldsymbol{\kappa}$ so that $\boldsymbol{\kappa} \cdot \mathbf{r}' = \kappa r' \cos\theta'$. Then

$$f(\theta) \simeq -\frac{m}{2\pi\hbar^2} \int e^{i\kappa r'\cos\theta'} V(r')(r')^2 \sin\theta'\, dr'd\theta'd\phi' = -\frac{2m}{\hbar^2\kappa} \int_0^\infty rV(r)\sin(\kappa r)\, dr.$$

The parameter κ is a function of θ. The incident wave is specified by $\mathbf{k}'$ and the final wave is specified by $\mathbf{k}$ and $k = k'$. They differ by the scattering angle θ. Because $\boldsymbol{\kappa} \equiv \mathbf{k}' - \mathbf{k}$, its magnitude can be determined,

$$\kappa = |\mathbf{k}' - \mathbf{k}| = \sqrt{k'^2 + k^2 - 2\mathbf{k}'\cdot\mathbf{k}} = k\sqrt{2 - 2\cos\theta} = k\sqrt{4\sin^2(\theta/2)} = 2k\sin(\theta/2).$$

Appendix B.12.3 discusses the Born approximation of the one-dimensional Schrödinger equation. The steps are simiar to the 3-dimensional case, but are simpler. We will find Green's function for the one-dimensional Schrödinger equation, its integral form, and its applications. Eventually, we shall find that the Born approximation agrees with the results derived from the delta potential well (Section 1.6) and the finite square well (Section 1.7) in the high energy limit.

11.3.3 The Born Series

The integral form of the Schrödinger equation is

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \int g(\mathbf{r} - \mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}')\, d^3\mathbf{r}'.$$

In short,

$$\psi = \psi_0 + \int gV\psi.$$

If this ψ is taken under the integral,

$$\psi = \psi_0 + \int gV\psi_0 + \iint gVgV\psi.$$

By interating this process, we can get a series for ψ:

$$\psi = \psi_0 + \int gV\psi_0 + \iint gVgV\psi_0 + \iiint gVgVgV\psi_0 + \cdots.$$

12 OTHER TOPICS

12.1 Bell's Inequality

12.1.1 Quantum Entanglement and the EPR Paradox

We will focus on the singlet state of two spin-1/2 particles for now,

$$|0,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle).$$

This state may be produced by the neutral pion decay into an electron and a positron,

$$\pi^0 \longrightarrow e^- + e^+.$$

If the pion is initially at rest, the electron and positron will travel oppositely due to the conservation of momentum. The pion has zero spin, so the combined spin state of the electron and positron must be the singlet state, $s = 0$, $m = 0$. Here comes the **quantum entanglement**: one cannot really know which state the electron is in without making a measurement, but one can tell that the electron and positron are correlated. There are 1/2 chance that the electron has spin up, and 1/2 chance spin down. Once you measure the electron to be spin up, you *immediately* know that someone measuring the proton will get spin down, and vice versa. It does not matter whether the distance between the two particles is 10 meters, or 10 light years.

In general, two systems are entangled if their combined states cannot be written as a product of one-particle state. For a two-level system (such as a spin-1/2 particle) $|\phi_a\rangle$ and $|\phi_b\rangle$ with $\langle\phi_i|\phi_j\rangle = \delta_{ij}$, the two-particle state

$$\alpha|\phi_a(1)\rangle|\phi_b(2)\rangle + \beta|\phi_b(1)\rangle|\phi_b(2)\rangle\,, \quad \alpha, \beta \neq 0$$

cannot be expressed as a product of one-particle states $|\psi_r(1)\rangle|\psi_s(2)\rangle$.

Proof. Suppose the two-particle state can be written as a product of one-particle states,

$$\alpha|\phi_a(1)\rangle|\phi_b(2)\rangle + \beta|\phi_b(1)\rangle|\phi_a(2)\rangle = |\psi_r(1)\rangle|\psi_s(2)\rangle\,.$$

Since it is a two level system, $|\phi_a\rangle$ and $|\phi_b\rangle$ for a complete basis. Thus, any other one-particle state can be written as a linear combination of them,

$$|\psi_r\rangle = A\,|\phi_a\rangle + B\,|\phi_b\rangle\,, \quad |\psi_s\rangle = C\,|\phi_a\rangle + D\,|\phi_b\rangle\,,$$

for some constants A, B, C, and D. Then

$$
\begin{aligned}
&\alpha|\phi_a(1)\rangle|\phi_b(2)\rangle + \beta|\phi_b(1)\rangle|\phi_a(2)\rangle \\
&= [A\,|\phi_a(1)\rangle + B\,|\phi_b(1)\rangle][C\,|\phi_a(2)\rangle + D\,|\phi_b(2)\rangle] \\
&= AC\,|\phi_a(1)\rangle|\phi_a(2)\rangle + AD\,|\phi_a(1)\rangle|\phi_b(2)\rangle + BC\,|\phi_b(1)\rangle|\phi_a(2)\rangle + BD\,|\phi_b(1)\rangle|\phi_b(2)\rangle\,.
\end{aligned}
$$

Now take some inner products:
1. with $\langle\phi_a(1)|\,\langle\phi_b(2)| \implies \alpha = AD$,
2. with $\langle\phi_a(1)|\,\langle\phi_a(2)| \implies 0 = AC$,
3. with $\langle\phi_b(1)|\,\langle\phi_a(2)| \implies \beta = BC$,
4. with $\langle\phi_b(1)|\,\langle\phi_b(2)| \implies 0 = BD$.

The second line means that either $A = 0$ or $C = 0$, which cannot be true because both α and β are not zero by assumption. $\qquad\square$

It seems like quantum mechanics, particularly the entanglement, has violated the principle of **locality**—no influence can propagate faster than the speed of light. This is the **EPR paradox** (Einstein, Podolsky, and Rosen paradox). Einstein, Podolsky, and Rosen

believed that the electron and positron must have well-defined spins immediately after they are produced by the pion decay. That is, their spins are determined prior to the measurement. It is just we don't know the exact way to characterize them fully. Thus, Einstein, Podolsky, and Rosen think that the quantum mechanics is certainly correct, but it is just an *incomplete* theory to describe physical really. They believed that there was some **hidden variable** λ needed to describe the system in addition to the wave function. Indeed, there appeared many hidden variable theory over years until 1964. That year J. S. Bell proved that any local hidden variable theory is incompatible with quantum mechanics, namely **Bell's theorem**.

12.1.2   Bell's Theorem

Bell thought of an experiment, where two detectors can measure the electron's and positron's spin along any direction. For example, the electron detector can measure the electron spin in the direction of a unit vector $\mathbf{a}$; the positron detector can measure proton electron spin along $\mathbf{b}$. Of course, each detector should measure either spin up or spin down. For convenience, let the detectors record the spin in units of $\hbar/2$, so they will get a value of $+1$ or -1. Bell suggested to compute the average value of the product of the spins, $P(\mathbf{a}, \mathbf{b})$, where we do many pion decay measurements. If $\mathbf{a} = \mathbf{b}$, then we already know the measurements should always disagree, so

$$P(\mathbf{a}, \mathbf{a}) = -1.$$

If $\mathbf{a} = -\mathbf{b}$ (anti-parallel), then the measurements always agree,

$$P(\mathbf{a}, -\mathbf{a}) = +1.$$

For arbitrary orientations, quantum mechanics would predict (see Appendix B.6.4)

$$P(\mathbf{a}, \mathbf{b}) = -\mathbf{a} \cdot \mathbf{b}.$$

Now suppose we can know the "complete" state of the electron-proton system through the wave function and the hidden variable(s) λ. We also assume that the outcome of the electron measurement is independent of $\mathbf{b}$ of the positron detector (the locality assumption). With all the information, there must be a function $A(\mathbf{a}, \lambda)$ that determines (based on theory) the result of the electron measurement. Likewise, some function $B(\mathbf{b}, \lambda)$ determines the proton spin measurement. The two functions will follow only two (already experimentally verified) restrictions:

1. They can only produce ± 1,
$$A(\mathbf{a}, \lambda) = \pm 1, \quad B(\mathbf{b}, \lambda) = \pm 1.$$

2. When the detectors are aligned, they should obey
$$A(\mathbf{a}, \lambda) = -B(\mathbf{a}, \lambda), \quad \forall \lambda.$$

The average of the product of measurements is

$$P(\mathbf{a}, \mathbf{b}) = \int \rho(\lambda) A(\mathbf{a}, \lambda) B(\mathbf{b}, \lambda) \, d\lambda,$$

where $\rho(\lambda)$ is the probability density for λ. It is real, non-negative, and normalized, $\int \rho(\lambda) \lambda = 1$, like any probability density. There are no additional assumptions of $\rho(\lambda)$. Using $A(\mathbf{a}, \lambda) = -B(\mathbf{a}, \lambda)$, we have

$$P(\mathbf{a}, \mathbf{b}) = -\int \rho(\lambda) A(\mathbf{a}, \lambda) A(\mathbf{b}, \lambda) \, d\lambda.$$

If $\mathbf{c}$ is any other unit vector,
$$P(\mathbf{a}, \mathbf{b}) - P(\mathbf{a}, \mathbf{c}) = -\int \rho(\lambda)[A(\mathbf{a}, \lambda) A(\mathbf{b}, \lambda) - A(\mathbf{a}, \lambda) A(\mathbf{c}, \lambda)] \, d\lambda.$$

Since $[A(\mathbf{b}, \lambda)]^2 = 1$, we can insert it in the second term and get

$$P(\mathbf{a}, \mathbf{b}) - P(\mathbf{a}, \mathbf{c}) = -\int \rho(\lambda)[1 - A(\mathbf{b}, \lambda) A(\mathbf{c}, \lambda)] A(\mathbf{a}, \lambda) A(\mathbf{b}, \lambda) \, d\lambda.$$

With $|A(\mathbf{a}, \lambda)A(\mathbf{b}, \lambda)| = 1$ and $\rho(\lambda)[1 - A(\mathbf{b}, \lambda)A(\mathbf{c}, \lambda)] \geq 0$,

$$|P(\mathbf{a}, \mathbf{b}) - P(\mathbf{a}, \mathbf{c})| = \left| \int \rho(\lambda)[1 - A(\mathbf{b}, \lambda)A(\mathbf{c}, \lambda)]A(\mathbf{a}, \lambda)A(\mathbf{b}, \lambda) \, d\lambda \right| \leq \int \rho(\lambda)[1 - A(\mathbf{b}, \lambda)A(\mathbf{c}, \lambda)] \, d\lambda.$$

We arrive at **Bell inequality**:

$$\boxed{|P(\mathbf{a}, \mathbf{b}) - P(\mathbf{a}, \mathbf{c})| \leq 1 + P(\mathbf{b}, \mathbf{c}).} \tag{12.1}$$

This works for any local hidden variable theory. But Bell inequality certainly contradicts with quantum mechanics prediction, $P(\mathbf{a}, \mathbf{b}) = -\mathbf{a} \cdot \mathbf{b}$. For example, let $\mathbf{a}, \mathbf{b}, \mathbf{c}$ lie in a plane, with $\mathbf{a}$ perpendicular to $\mathbf{b}$, and $\mathbf{c}$ is their bisector. Quantum mechanics would predict

$$P(\mathbf{a}, \mathbf{b}) = 0, \quad P(\mathbf{a}, \mathbf{c}) = P(\mathbf{b}, \mathbf{c}) = -\frac{\sqrt{2}}{2} \approx -0.707.$$

This is inconsistent with Bell inequality,

$$0.707 \nleq 1 - 0.707 = 0.293.$$

Now let's conclude the whole story. Einstein, Podolsky, and Rosen said that quantum mechanics should be correct but incomplete, as there needs local hidden variables to fully describe a system. But Bell proved that if there exists some local hidden variables, then quantum mechanics is *wrong*. In other words, if quantum mechanics is right, then there is no local hidden variable theory—quantum mechanics is fundamentally nonlocal.

What happens if something violates the principle of locality? For *causal* influence, it means that in some reference frame, the effect comes before the cause, or simply, the time runs backwards. Then is quantum entanglement a *causal* influence? That is, is the measurement of electron *cause* the outcome of the positron measurement? They certainly are correlated with each other, but we are considering whether one causes the other. Imagine you are the positron detector and have produced a list of $+1$ and -1. It is impossible for you to observe/tell the list that the electron detector would produce once you make the positron measurement, since the electron detector can decide whether to make a measurement at all. You do not know whether it is the electron being spin up causes the positron being spin down, or it is just you measure the positron first and get spin down. The only way to show the entanglement correlations is to compare the two lists after the measurement. Therefore, quantum entanglement is not a causal influence.

12.2 Quantum Zeno Effect

12.2.1 Version 1: Transition Probability

Consider a system in an excited state ψ_b. Its transition probability to the ground state ψ_a is

$$P_a(t) \propto \int_0^\infty \rho(\omega)\frac{\sin^2[(\omega_{ba} - \omega)t/2]}{(\omega_{ba} - \omega)^2} \, d\omega,$$

where $\omega_{ba} = (E_b - E_a)/\hbar$ and ω is the frequency of the emitted photon. For extremely short time, the probability is

$$P_a(t) \propto \frac{t^2}{4} \int_0^\infty \rho(\omega) \, d\omega = \alpha t^2,$$

where α is some constants. This means the probability in to remain in ψ_b after a time t is $P_b(t) = 1 - \alpha t^2$ if we measure the state of the system. Now suppose we do find the system in ψ_b after time t, and the wave function collapse to ψ_b. After another time interval t, we measure the system again. The probability to remain in ψ_b is still $P_b(t) = 1 - \alpha t^2$. Together with our first measurement, the probability for the two subsequent measurement both in ψ_b is thus

$$P_b(t)^2 = (1 - \alpha t)^2 \simeq 1 - 2\alpha t^2.$$

However, if we make only one measurement at $2t$, the probability of the system still in ψ_b is instead

$$P_b(2t) = 1 - \alpha(2t)^2 = 1 - 4\alpha t^2 \neq P_b(t)^2.$$

Let's generalize this to a time interval $[0, T]$. Divide T into n equal time intervals, each with $t = T/n$. After each T/n, we measure the state of the system (i.e. we measure the system at T/n, $2T/n$, $3T/n$, and so on). After n measurements, the probability that the system is still in ψ_b is

$$P_b(t)^n = \left[1 - \alpha \left(\frac{T}{n} \right)^2 \right]^n.$$

We can expand this probability by the binonial expansion,

$$P_b(t)^n = \left[1 - \alpha \left(\frac{T}{n} \right) \right]^n = 1 - n\alpha \left(\frac{T}{n} \right)^2 + \frac{n(n-1)}{2} \alpha^2 \left(\frac{T}{n} \right)^4 + \cdots = 1 - \frac{1}{n} \alpha T^2 + \frac{n-1}{2n^3} \alpha^2 T^4 + \cdots.$$

In the limit $n \to \infty$, it is easy to see that

$$\lim_{n \to \infty} P_b(t)^n = 1.$$

That is, if we *continuously* measure the state of a system, it does not evolve at all.

12.2.2 Version 2: Spin Agreement

Consider a spin-1/2 particle with the initial state in χ_+. In other words, you measure the spin of this spin-1/2 particle and find $S_z = \hbar/2$, and the particle is now spin-up. If we measure S_x, the probability to get $S_x = \hbar/2$ is the projection of the initial state χ_+ on the eigenstate of S_x with eigenvalue $\hbar/2$, squared:

$$P(\hbar/2) = |\langle \chi_+^{(x)} | \chi_+ \rangle|^2 = \left| \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \right|^2 = \frac{1}{2}.$$

In the second experiment, we measure the spin in two steps: we first measure the spin along the direction $\mathbf{n} = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}} + \hat{\mathbf{z}})$ (45° between x and z), and then measure S_x. We would like to know the probability that both results are $\hbar/2$. The initial state is still prepared in χ_+ ($S_z = \hbar/2$). In Appendix A.3.3, we find the eigenspinors of S_r where $\hat{\mathbf{r}} = \hat{\mathbf{x}} \sin\theta \cos\phi + \hat{\mathbf{y}} \sin\theta \sin\phi + \hat{\mathbf{z}} \cos\theta$ to be

$$\chi_+^{(r)} = \begin{bmatrix} \cos(\theta/2) \\ e^{i\phi} \sin(\theta/2) \end{bmatrix}, \quad \chi_-^{(r)} = \begin{bmatrix} \sin(\theta/2) \\ -e^{i\phi} \cos(\theta/2) \end{bmatrix}.$$

If $\hat{\mathbf{r}} = \hat{\mathbf{n}}$, the eigenspinors are

$$\chi_+^{(n)} = \begin{bmatrix} \cos(\pi/8) \\ \sin(\pi/8) \end{bmatrix}, \quad \chi_-^{(r)} = \begin{bmatrix} \sin(\pi/8) \\ -\cos(\pi/8) \end{bmatrix}.$$

The probability of getting $\hbar/2$ when we measure S_n is

$$P(\hbar/2) = |\langle \chi_+^{(n)} | \chi_+ \rangle|^2 = \cos^2 \left(\frac{\pi}{8} \right).$$

If we get $S_n = 1/2$, subsequently measuring S_x to be $\hbar/2$ will also have a probability of $\cos^2(\pi/8)$. This is because we can define $\hat{\mathbf{n}}$ to be the new z-axis, and the original x-axis would be like $\hat{\mathbf{n}}$ in the new coordinate. The probability of getting both $\hbar/2$ is

$$P(\hbar/2)^2 = \cos^4 \left(\frac{\pi}{8} \right) \approx 0.729 > \frac{1}{2}.$$

In the third experiment, we measure the spin n times, starting from the z-axis, each time tilting the angle of measurement by $\pi/2n$ until reaching the x-axis. That is, the state is initially prepared in χ_+, and measure the spin along $\pi/2n$ from the z-axis, then π/n from the z-axis, then $3\pi/2n$, and so on. Following the step in the second experiment, first calculate the probability of yielding $\hbar/2$ along the direction $\pi/2n$ from the z-axis:

$$P(\hbar/2) = |\langle \chi_+^{(\pi/2n)} | \chi_+ \rangle|^2 = \cos^2 \left(\frac{\pi}{4n} \right).$$

If we get $\hbar/2$, the state is now in $\chi_+^{(\pi/2n)}$. Then measure along the direction π/n from the z-axis, or $\pi/2n$ from the $\pi/2n$ axis. The probability of getting $\hbar/2$ is the same, $\cos^2(\pi/4n)$, with the same reasoning as in the second experiment. In total there are n steps, so the probability of getting $\hbar/2$ in all the n measurements is

$$P(\hbar/2)^n = \cos^{2n} \left(\frac{\pi}{4n} \right).$$

In the limit $n \to \infty$, this probability will be

$$\lim_{n\to\infty} \cos^{2n}\left(\frac{\pi}{4n}\right) = \lim_{n\to\infty}\left[1 - \frac{1}{2}\left(\frac{\pi}{4n}\right)^2 + \cdots\right]^{2n} = \lim_{n\to\infty}\left[1 - n\left(\frac{\pi}{4n}\right)^2 + \cdots\right] = 1.$$

Again, continuouly measuring the state of a system does not change the state.

12.3   Quantum Information

12.3.1   No-Go Theorems

There are many no-go theorems in quantum world. We will use **qubits**, or simply two-level quantum systems, to make our arguments. For example, $|0\rangle$ and $|1\rangle$ may represent $|\uparrow\rangle$ and $|\downarrow\rangle$, respectively, of a spin-1/2 particle such as an electron. Here are some theorems:

1. Given a system in an arbitrary state $|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$, one cannot determine α and β.

2. The **no-clone theorem**: given an arbitrary state $|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$, one cannot make a copy of it. That is, there is no machine that takes in $|\psi\rangle$ and $|X\rangle$ and spits out $|\psi\rangle|\psi\rangle$:
$$|\psi\rangle|X\rangle \nrightarrow |\psi\rangle|\psi\rangle\,.$$

   This is not to be confused with "preparing same states" like having many electrons with $|\uparrow\rangle$. You can always prepare as many same states as you want, but you cannot copy a given state. (It is the difference between a printing machine and a copy machine.)

3. The **no-deleting theorem**: there is no machine that can delete an arbitrary state to $|0\rangle$ without doing anything else. This is like a time-reversal theorem of the no-clone theorem.

4. This is what one can do: one can teleport a state $|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$ through some clever tricks, without knowing what α and β are. However, there must be a classical information sent from the sender to receiver, so quantum teleportation is not faster than the speed of light.

We will not prove them here, but there will be an example of how to do quantum teleportation.

12.3.2   Quantum Gates

Quantum gates unitary (and reversible) operations on qubits. For a given basis, quantum gates can be represented by matrices. The most common basis for two-qubit systems is the **computational basis**:

$$|00\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad |01\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \quad |10\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}, \quad |11\rangle = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}.$$

There are many gates that can act on a two-qubit system:

1. SWAP gate that swap the two qubits, not entangling:

$$|00\rangle \to |00\rangle$$
$$|01\rangle \to |10\rangle$$
$$|10\rangle \to |01\rangle$$
$$|11\rangle \to |11\rangle$$

$$\text{SWAP} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}.$$

2. Square-root of SWAP gate, entangling two qubits:

$$|00\rangle \rightarrow |00\rangle$$
$$|01\rangle \rightarrow \tfrac{1}{2}[(1+i)|01\rangle + (1-i)|10\rangle]$$
$$|10\rangle \rightarrow \tfrac{1}{2}[(1-i)|01\rangle + (1+i)|10\rangle]$$
$$|11\rangle \rightarrow |11\rangle$$

$$\sqrt{\text{SWAP}} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \tfrac{1}{2}(1+i) & \tfrac{1}{2}(1-i) & 0 \\ 0 & \tfrac{1}{2}(1-i) & \tfrac{1}{2}(1+i) & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}.$$

3. Controlled Not gate (CNOT or CX), entangling (if the state is in some superposition of two basis vectors):

$$|00\rangle \rightarrow |00\rangle$$
$$|01\rangle \rightarrow |01\rangle$$
$$|10\rangle \rightarrow |11\rangle$$
$$|11\rangle \rightarrow |10\rangle$$

$$\text{CNOT} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}.$$

4. There can also be one-qubit gates such as $X = \sigma_x$, $Y = \sigma_y$, and $Z = \sigma_z$. They are just Pauli-spin matrices that rotates a state. If the basis is $|0\rangle = |\uparrow\rangle$ and $|1\rangle = |\downarrow\rangle$, then

$$X = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad Y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad Z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

For example, applying X to $|0\rangle$ gives $|1\rangle$, and to $|1\rangle$ gives $|0\rangle$, which is a rotation about x by π. How do we do this physically? We need magnetic fields. Recall that the Hamiltonian of a particle with spin in a magnetic field is

$$H = \gamma(\sigma_x B_x + \sigma_y B_y + \sigma_z B_z).$$

Assume that $B_y = B_z = 0$ and $B_x \neq 0$. We turn on B_x for a small amount of time $t = \pi\hbar/\gamma B_x$. (Actually we can rotate the state by any degree by controlling t.) The final state is the evolution operator acting on the initial state

$$|\psi(t)\rangle = e^{-iHt/\hbar}|\psi_0\rangle = U(t)|\psi_0\rangle.$$

Plugging in $t = \pi\hbar/\gamma B_x$ and $H = \gamma\sigma_x B_x$,

$$U = e^{-i\pi\sigma_x/2} = 1 + \left(-\frac{i\pi}{2}\right)\sigma_x + \left(-\frac{i\pi}{2}\right)^2 \sigma_x^2 + \left(-\frac{i\pi}{2}\right)^3 \sigma_x^3 + \dots$$

Since $\sigma_x^2 = I$, this operator can be simplified as

$$U = \cos\left(\frac{\pi}{2}\right) I - i\sin\left(\frac{\pi}{2}\right)\sigma_x = -i\sigma_x.$$

Therefore, applying a B_x for $t = \pi\hbar/\gamma B_x$ is the same as acting an X gate to the qubit. (The factor of i is unimportant because it only add a phase factor to the state, which has no physical significance). Similar results can be derived for Y and Z gates.

5. The final one-qubit gate is the Hadamard gate:

$$|0\rangle \rightarrow \tfrac{1}{\sqrt{2}}(|0\rangle + |1\rangle) = |+\rangle$$
$$|1\rangle \rightarrow \tfrac{1}{\sqrt{2}}(|0\rangle - |1\rangle) = |-\rangle$$

$$H = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}.$$

This can be seen as a rotation about $(\hat{\mathbf{x}} + \hat{\mathbf{z}})/\sqrt{2}$ by π.

Another common basis is the **Bell basis**, which we will not use in this notes:

$$\left|\Phi^+\right\rangle = \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle)$$

$$\left|\Phi^-\right\rangle = \frac{1}{\sqrt{2}}(|00\rangle - |11\rangle)$$

$$\left|\Psi^+\right\rangle = \frac{1}{\sqrt{2}}(|01\rangle + |10\rangle)$$

$$\left|\Psi^-\right\rangle = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle).$$

12.3.3 Quantum Teleportation

Consider the following scenario: Alice has a qubit $|\psi_1\rangle = \alpha|0\rangle + \beta|1\rangle$, and she does not know α and β. She also shares (or entangles) another qubit with Bob,

$$|\psi_{23}\rangle = \frac{1}{\sqrt{2}}(|0\rangle_2|1\rangle_3 - |1\rangle_2|0\rangle_3) = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle),$$

where Alice can measure qubit 2 and Bob can measure qubit 3. The goal for Alice is to teleport $|\psi_1\rangle$ to Bob with the help of some classical information and some gate operations. Both Alice and Bob can apply gates to their qubits.

The procedure is the following. First, Alice entangles qubit 1 with qubit 2, producing the whole states:

$$|\psi\rangle = \frac{1}{2}(\alpha|001\rangle - \alpha|010\rangle + \beta|101\rangle - \beta|110\rangle).$$

Next, Alice apply the Hadamard gate on her qubit 1, making

$$|0\rangle \to \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle), \quad |1\rangle \to \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle).$$

The whole state is now

$$|\psi\rangle = \frac{1}{2\sqrt{2}}(\alpha|001\rangle + \alpha|101\rangle - \alpha|010\rangle - \alpha|110\rangle + \beta|011\rangle - \beta|111\rangle + \beta|100\rangle - \beta|000\rangle).$$

We should remember that the first two qubits (numbers) belong to Alice and the third belongs to Bob. Now is the crucial part. Alice will *measure* her two qubits (1 and 2) and collapse the state, so after the measurement, she no longer have her $|\psi_1\rangle$. She will also tell Bob via a classical information (such as a message) what result she gets. There are four possible states she can get, and we will see how Bob can get $\frac{1}{\sqrt{2}}(\alpha|0\rangle + \beta|1\rangle)$ in each case:

1. If Alice gets $|00\rangle$ from measurement, then the state collapse to

$$|\psi\rangle = \frac{1}{\sqrt{2}}(\alpha|001\rangle - \beta|000\rangle) = \frac{1}{\sqrt{2}}|00\rangle\,(\alpha|1\rangle - \beta|0\rangle).$$

   After she tells Bob she gets $|00\rangle$), Bob will know that his qubit now must be $\frac{1}{\sqrt{2}}(\alpha|1\rangle - \beta|0\rangle)$ because their states are entangled. Bob will applies a Y gate to his qubit, yielding

$$|\psi_3\rangle = Y\left[\frac{1}{\sqrt{2}}(\alpha|1\rangle - \beta|0\rangle)\right] = \frac{i}{\sqrt{2}}\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}\left(\alpha\begin{bmatrix} 0 \\ 1 \end{bmatrix} - \beta\begin{bmatrix} 1 \\ 0 \end{bmatrix}\right) = \frac{i}{\sqrt{2}}\left(\alpha\begin{bmatrix} -1 \\ 0 \end{bmatrix} - \beta\begin{bmatrix} 0 \\ 1 \end{bmatrix}\right).$$

   The final qubit Bob gets is

$$|\psi_3\rangle = -\frac{i}{\sqrt{2}}(\alpha|0\rangle + \beta|1\rangle).$$

   Again, the $-i$ factor is a phase factor which does not have a physical meaning. Bob gets the state teleported from Alice, while both of them do not know α or β.

2. If Alice gets $|01\rangle$ from measurement, the state collapse to

$$|\psi\rangle = \frac{1}{\sqrt{2}}(-\alpha|010\rangle + \beta|011\rangle) = \frac{1}{\sqrt{2}}|01\rangle\,(-\alpha|0\rangle + \beta|1\rangle).$$

   Bob applies a Z gate to his qubit,

$$|\psi_3\rangle = \frac{1}{\sqrt{2}}Z(-\alpha|0\rangle + \beta|1\rangle) = -\frac{1}{2}(\alpha|0\rangle + \beta|1\rangle).$$

3. If Alice gets $|10\rangle$ from measurement, the state collapse to

$$|\psi\rangle = \frac{1}{\sqrt{2}}(\alpha|101\rangle + \beta|100\rangle) = \frac{1}{\sqrt{2}}|10\rangle\,(\alpha|1\rangle + \beta|0\rangle).$$

   Bob applies a X gate to his qubit,

$$|\psi_3\rangle = \frac{1}{\sqrt{2}}X(\alpha|1\rangle + \beta|0\rangle) = \frac{1}{\sqrt{2}}(\alpha|0\rangle + \beta|1\rangle).$$

4. If Alice gets $|11\rangle$, the state collapse to

$$|\psi\rangle = \frac{1}{\sqrt{2}}(-\alpha|110\rangle - \beta|111\rangle) = -\frac{1}{\sqrt{2}}|11\rangle\,(\alpha|0\rangle + \beta|1\rangle).$$

Bob does nothing because the state is already in

$$|\psi_3\rangle = -\frac{1}{\sqrt{2}}(\alpha|0\rangle + \beta|1\rangle).$$

Acknowledgements

Reference:

Introduction to Quantum Mechanics. 3rd ed. (Griffiths).
Modern Quantum Mechanics. 2nd ed. (Sakurai).
Elementary Quantum Mechanics. (Saxon).

Part III

Appendix

A Commutators, States, Matrices, and Others

A.1   Commutators

Commutator identities:

$$[A+B,C] = [A,C] + [B,C], \quad [AB,C] = A[B,C] + [A,C]B, \quad [A,BC] = [A,B]C + B[A,C].$$

$$[A,B] = 0 \quad \Longrightarrow \quad [A^n, B] = 0.$$

Canonical commutation relations:

$$[r_i, p_j] = -[p_i, r_j] = i\hbar\delta_{ij}, \quad [r_i, r_j] = [p_i, p_j] = 0.$$

Harmonic oscillator:

$$[a, a^\dagger] = 1, \quad [H, a_\pm] = \pm\hbar\omega a_\pm.$$

Angular momentum:

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y, \quad \text{or} \quad [L_i, L_j] = i\hbar\epsilon_{ijk}L_k.$$

$$[L^2, \mathbf{L}] = 0, \quad [L^2, L_\pm] = 0, \quad [L_z, L_\pm] = \pm\hbar L_\pm.$$

$$[L_i, r_j] = i\hbar\epsilon_{ijk}r_k, \quad [L_i, p_j] = i\hbar\epsilon_{ijk}p_k.$$

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

$$[L^2, r] = 0, \quad [L^2, r^2] = 0, \quad [L^2, p^2] = 0.$$

$$[H, \mathbf{L}] = 0 \quad \text{if } V(\mathbf{r}) = V(r).$$

Spin:

$$[S_x, S_y] = i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y, \quad \text{or} \quad [S_i, S_j] = i\hbar\epsilon_{ijk}S_k.$$

$$[S^2, \mathbf{S}] = 0, \quad [S^2, S_\pm] = 0, \quad [S_z, S_\pm] = \pm\hbar S_\pm.$$

Spin-orbit coupling: $\mathbf{J} = \mathbf{L} + \mathbf{S}$, $J^2 = L^2 + S^2 + 2\mathbf{L}\cdot\mathbf{S}$,

$$[\mathbf{L}\cdot\mathbf{S}, \mathbf{L}] = i\hbar(\mathbf{L}\times\mathbf{S}), \quad [\mathbf{L}\cdot\mathbf{S}, \mathbf{S}] = i\hbar(\mathbf{S}\times\mathbf{L}), \quad [\mathbf{L}\cdot\mathbf{S}, \mathbf{J}] = 0.$$

$$[\mathbf{L}\cdot\mathbf{S}, L^2] = 0, \quad [\mathbf{L}\cdot\mathbf{S}, S^2] = 0, \quad [\mathbf{L}\cdot\mathbf{S}, J^2] = 0.$$

Electromagnetism:

$$[\Pi_i, \Pi_j] = i\hbar q\epsilon_{ijk}B_k, \quad \text{where} \quad \mathbf{\Pi} = \mathbf{p} - q\mathbf{A}, \quad \mathbf{B} = \nabla\times\mathbf{A}.$$

Other commutators:

$$[f(\mathbf{r}), p_i] = i\hbar\frac{\partial f}{\partial x_i}, \quad [x_i, f(\mathbf{p})] = i\hbar\frac{\partial f}{\partial p_i}.$$

$$[H, \mathbf{r}] = -\frac{i\hbar}{m}\mathbf{p}, \quad [H, \mathbf{p}] = i\hbar\nabla V \quad \text{for} \quad H = \frac{p^2}{2m} + V(\mathbf{r})$$

A.2 Polynomials and States

A.2.1 Hermite Polynomials $H_n(x)$

The normalization convention for Hermite polynomials $H_n(x)$ is that the highest power of x has the coefficient 2^n.

- Rodrigues formula:
$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}.$$

- Coefficients:
$$H_n(x) = \sum_j^n a_j x^j, \quad a_{j+2} = \frac{-2(n-j)}{(j+1)(j+2)} a_j.$$

- Generating function:
$$\Phi(x,t) = e^{2xt - t^2} = \sum_{n=0}^{\infty} H_n(x) \frac{t^n}{n!}.$$

- Inner product and orthogonality:
$$\int_{-\infty}^{\infty} e^{-x^2} H_m(x) H_n(x) \, dx = 2^n n! \sqrt{\pi} \delta_{mn}.$$

- Hermite polynomials satisfy Hermite equation:
$$\left(\frac{d^2}{dx^2} - 2x \frac{d}{dx} + 2n \right) H_n = 0.$$

The first few Hermite polynomials and their plot are shown below. For visual purposes, the leading coefficient of $H_n(x)$ is set to 1 in the plot.

$$H_0 = 1,$$
$$H_1 = 2x,$$
$$H_2 = 4x^2 - 2,$$
$$H_3 = 8x^3 - 12x,$$
$$H_4 = 16x^4 - 48x^2 + 12,$$
$$H_5 = 32x^5 - 160x^3 + 120x.$$
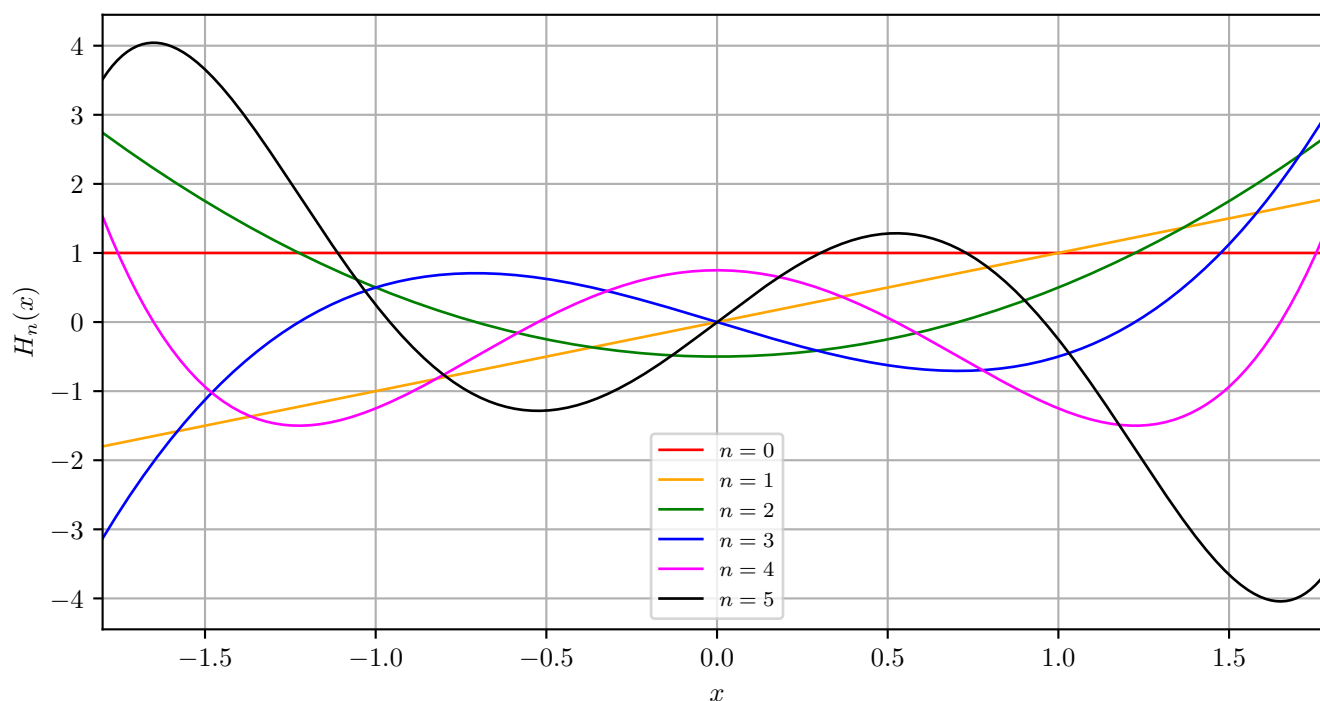
A.2.2 The Harmonic Oscillator Wave Functions

The normalized harmonic oscillator wave functions follow the general formula

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}, \quad \xi = \sqrt{\frac{m\omega}{\hbar}} x.$$

The first few harmonic oscillator wave functions and their plot are shown below. For convenience, we set $m = 1$, $\omega = 1$, and $\hbar = 1$.

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

$$\psi_1 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{2}\,\xi e^{-\xi^2/2}$$

$$\psi_2 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2}}(2\xi^2 - 1)e^{-\xi^2/2}$$

$$\psi_3 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{3}}(2\xi^3 - 3\xi)e^{-\xi^2/2}$$

$$\psi_4 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{2\sqrt{6}}(4\xi^4 - 12\xi^3 + 3)e^{-\xi^2/2}$$

$$\psi_5 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{2\sqrt{15}}(4\xi^5 - 20\xi^3 + 15\xi)e^{-\xi^2/2}.$$
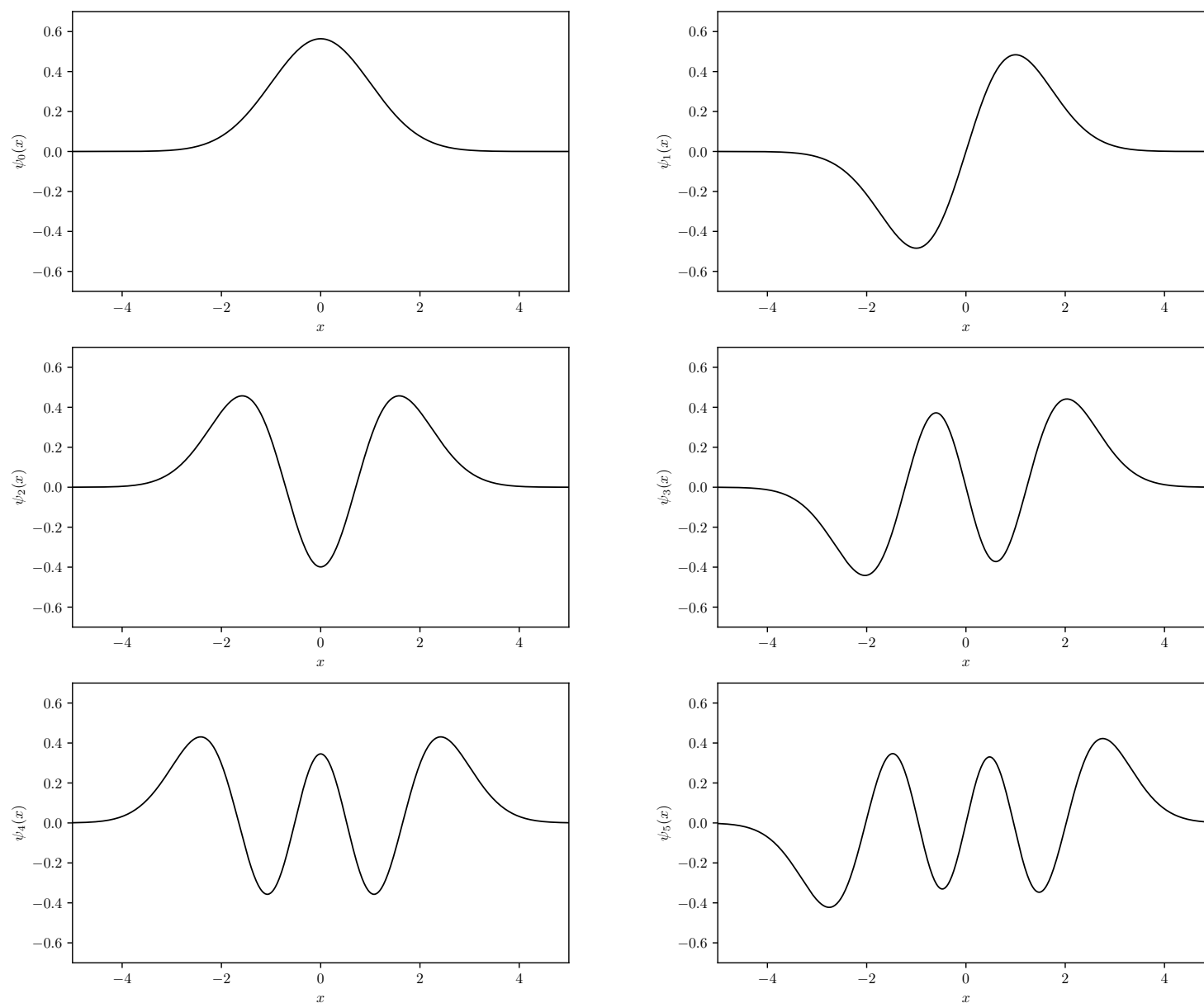
A.2.3 Legendre Polynomials $P_\ell(x)$

The normalization convention for Legendre polynomials $P_\ell(x)$ is $P_\ell(1) = 1$.

- Rodrigues formula:

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

- Coefficients:

$$P_\ell(x) = \sum_n^\ell a_n x^n, \quad a_{n+2} = -\frac{(\ell - n)(\ell + n + 1)}{(n+2)(n+1)} a_n.$$

- Generating function:

$$\Phi(x, t) = \frac{1}{\sqrt{1 - 2xt + t^2}} = \sum_{\ell=0}^\infty P_\ell(x) t^\ell, \quad |t| < 1.$$

- Inner product and orthogonality:

$$\int_{-1}^1 P_\ell(x) P_{\ell'}(x) \, dx = \frac{2}{2\ell + 1} \delta_{\ell\ell'}.$$

- Legendre polynomials satisfy Legendre differential equation:

$$\left[(1 - x^2) \frac{d^2}{dx^2} - 2x \frac{d}{dx} + \ell(\ell + 1) \right] P_\ell(x) = 0.$$

The first few Legendre polynomials and their plot are shown below.

$$P_0 = 1,$$
$$P_1 = x,$$
$$P_2 = \frac{1}{2}(3x^2 - 1),$$
$$P_3 = \frac{1}{2}(5x^3 - 3x),$$
$$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3),$$
$$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x).$$
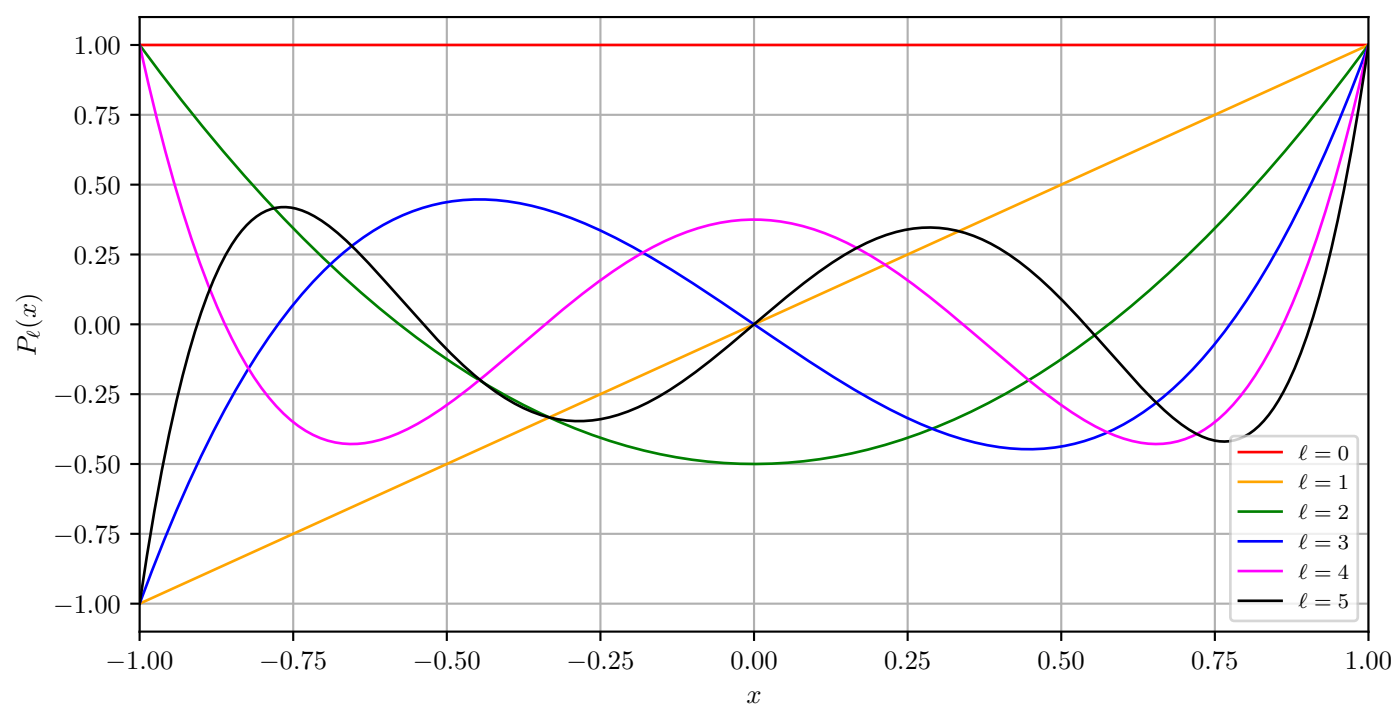
A.2.4 Associated Legendre Polynomials $P_\ell^m(x)$

The associated Legendre polynomials $P_\ell^m(x)$ satisfy the associated Legendre equation:

$$\left[(1-x^2)\frac{d^2}{dx^2} - 2x\frac{d}{dx} + \ell(\ell+1) - \frac{m^2}{1-x^2}\right]P_\ell^m(x) = 0.$$

Making a change of variable $x = \cos\theta$, this is equivalent to the θ-equation (4.3):

$$\left[\frac{d}{d\theta}\left(\sin^2\theta\frac{d}{d\theta}\right) + \ell(\ell+1)\sin^2\theta - m^2\right]P_\ell^m(\cos\theta) = 0.$$

P_ℓ^m can be derived from Legendre polynomials P_ℓ by

$$P_\ell^m = (-1)^m(1-x^2)^{m/2}\frac{d^m}{dx^m}P_\ell(x), \quad P_\ell^{-m} = (-1)^m\frac{(\ell-m)!}{(\ell+m)!}P_\ell^m, \quad \text{for } \ell \geq 0,\ -\ell \leq m \leq \ell.$$

The orthogonality condition for the associated Legendre polynomials for fixed m is

$$\int_{-1}^{1} P_\ell^m(x)P_{\ell'}^m(x)\,dx = \int_0^\pi P_\ell^m(\cos\theta)P_{\ell'}^m(\cos\theta)\sin\theta\,d\theta = \frac{2(\ell+m)!}{(2\ell+1)(\ell-m)!}\delta_{\ell\ell'}.$$

For fixed ℓ, it is

$$\int_{-1}^{1} \frac{P_\ell^m(x)P_\ell^n(x)}{1-x^2}\,dx = \int_0^\pi P_\ell^m(\cos\theta)P_\ell^n(\cos\theta)\csc\theta\,d\theta = \begin{cases} \infty, & m = n = 0, \\ \dfrac{(\ell+m)!}{m(\ell-m)!}\delta_{mn}, & \text{otherwise.} \end{cases}$$

The first few associated Legendre polynomials (with arguments $\cos\theta$) are shown below.

$$
\begin{aligned}
&P_0^0 = 1, \\
&P_1^0 = \cos\theta, && P_1^1 = -\sin\theta, \\
&P_2^0 = \tfrac{1}{2}(3\cos^2\theta - 1), && P_2^1 = -3\cos\theta\sin\theta, && P_2^2 = 3\sin^2\theta, \\
&P_3^0 = \tfrac{1}{2}(5\cos^3\theta - 3\cos\theta), && P_3^1 = -\tfrac{3}{2}(5\cos^2\theta - 1)\sin\theta, && P_3^2 = 15\cos\theta\sin^2\theta, && P_3^3 = -15\sin^3\theta.
\end{aligned}
$$

A.2.5 Spherical Harmonics $Y_\ell^m(\theta,\phi)$

Spherical harmonics are given by

$$Y_\ell^m(\theta,\phi) = \epsilon\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\,e^{im\phi}P_\ell^m(\cos\theta),$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. They form an orthonormal and complete basis for angular wave functions. The orthogonality condition is

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

The first few spherical harmonics are listed below.

$$
\begin{aligned}
&Y_0^0 = \sqrt{\frac{1}{4\pi}}, && Y_2^{\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\,e^{\pm 2i\phi}, \\
&Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta, && Y_3^0 = \sqrt{\frac{7}{16\pi}}(5\cos^3\theta - 3\cos\theta), \\
&Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\,e^{\pm i\phi}, && Y_3^{\pm1} = \mp\sqrt{\frac{21}{64\pi}}\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}, \\
&Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1), && Y_3^{\pm2} = \sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta\,e^{\pm 2i\phi}, \\
&Y_2^{\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\,e^{\pm i\phi}, && Y_3^{\pm3} = \mp\sqrt{\frac{35}{64\pi}}\sin^3\theta\,e^{\pm 3i\phi}.
\end{aligned}
$$

A.2.6 Laguerre Polynomials $L_q(x)$

The normalization convention for Laguerre polynomials $L_q(x)$ is $L_q(0) = 1$.

- Rodrigues formula:

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

- Coefficients:

$$L_q(x) = \sum_{n=0}^{q} \frac{(-1)^n}{n!} \binom{q}{n} x^n, \quad \text{where} \quad \binom{q}{n} = \frac{q!}{n!(q-n)!}.$$

- Generating function:

$$\Phi(x, t) = \frac{e^{-xt/(1-t)}}{1-t} = \sum_{q=0}^{\infty} L_q(x) t^q.$$

- Inner product and orthogonality:

$$\int_0^\infty e^{-x} L_q(x) L_{q'}(x)\, dx = \delta_{qq'}.$$

- Laguerre polynomials satisfy Laguerre differential equation:

$$\left[x \frac{d^2}{dx^2} + (1-x)\frac{d}{dx} + n \right] L_q(x) = 0.$$

The first few Laguerre polynomials and their plot are shown below.

$$L_0 = 1,$$
$$L_1 = -x + 1,$$
$$L_2 = \frac{1}{2}(x^2 - 4x + 2),$$
$$L_3 = \frac{1}{6}(-x^3 + 9x^2 - 18x + 6),$$
$$L_4 = \frac{1}{24}(x^4 - 16x^3 + 72x^2 - 96x + 24),$$
$$L_5 = \frac{1}{120}(-x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120).$$
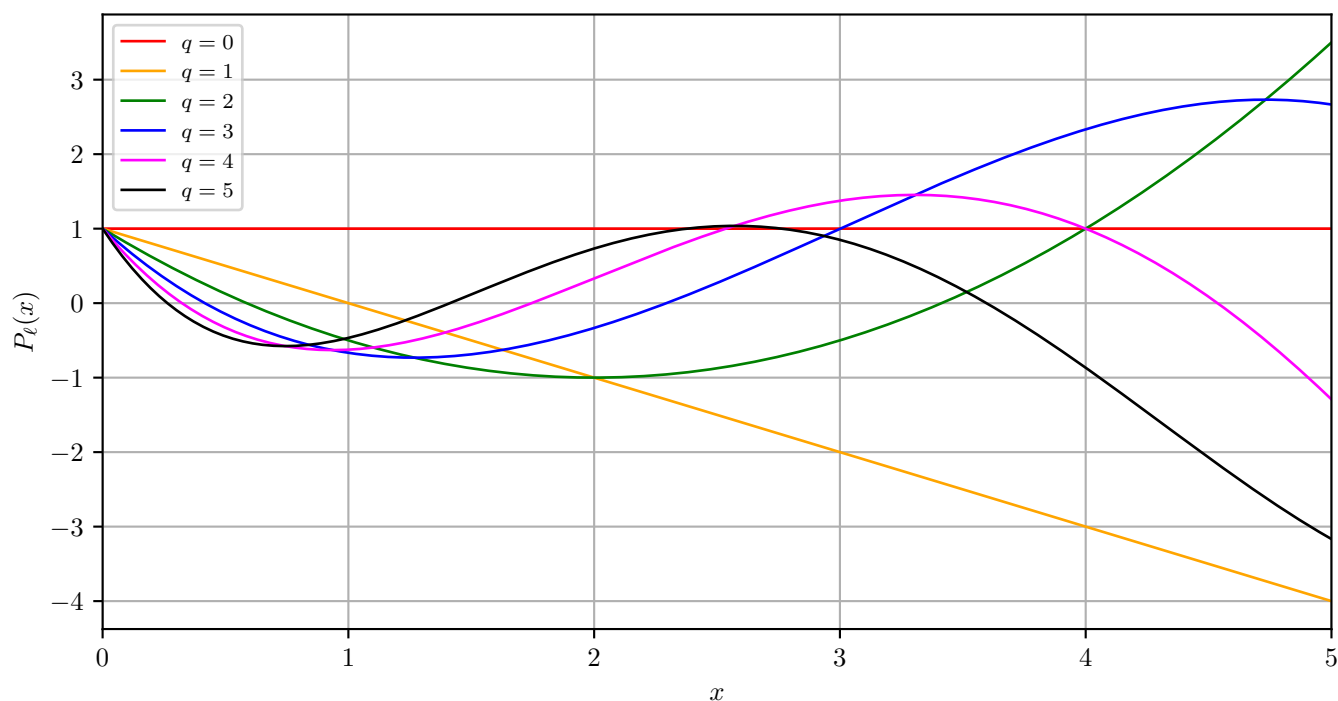
A.2.7 Associated Laguerre Polynomials $L_q^p(x)$

The associated Laguerre polynomials $L_q^p(x)$ satisfy the associated Laguerre equation:

$$\left[x \frac{d^2}{dx^2} + (p+1-x)\frac{d}{dx} + n \right] L_q^p(x) = 0.$$

L_q^p can be derived from Laguerre polynomials L_q by

$$L_q^p(x) = (-1)^p \frac{d^p}{dx^p} L_{q+p}(x),$$

or from the Rodrigues formula

$$L_q^p(x) = \frac{x^{-p}e^x}{q!} \frac{d^q}{dx^q}(x^{q+p}e^{-x}).$$

The orthogonality condition for the associated Laguerre polynomials for fixed p is

$$\int_0^\infty x^p e^{-x} L_q^p(x) L_{q'}^p(x)\, dx = \frac{(p+q)!}{q!} \delta_{qq'}.$$

The normalization integral for the hydrogen atom is essentially

$$\int_0^\infty x^{p+1} e^{-x} \left[L_q^p(x) \right]^2 dx = (2q+p+1)\frac{(q+p)!}{q!}.$$

The first few associated Laguerre polynomials are shown below.

$$L_0^0 = 1,$$
$$L_1^0 = -x + 1, \qquad\qquad L_1^1 = -1,$$
$$L_2^0 = \tfrac{1}{2}(x^2 - 4x + 2), \qquad L_2^1 = -2x + 4, \qquad\qquad L_2^2 = 2,$$
$$L_3^0 = \tfrac{1}{6}(-x^3 + 9x^2 - 18x + 6), \quad L_3^1 = \tfrac{1}{2}(-3x^2 + 18x - 18), \quad L_3^2(x) = -6, \quad L_3^3 = -6.$$

A.2.8 Radial Wave Functions $R_{n\ell}(r)$

The normalized radial wave functions of the hydrogen atom are given by

$$R_{n\ell} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}}\, e^{-r/na} \left(\frac{2r}{na}\right)^\ell \left[L_{n-\ell-1}^{2\ell+1}(2r/na) \right].$$

They form an orthonormal but incomplete basis:

$$\int_0^\infty R_{n\ell}^*(r) R_{n'\ell'}(r) r^2\, dr = \delta_{nn'}\delta_{\ell\ell'}.$$

The first few radial wave functions are listed below.

$$R_{10} = \frac{2}{\sqrt{a^3}} e^{-r/a},$$

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

$$R_{21} = \frac{1}{2\sqrt{6a^3}}\left(\frac{r}{a}\right) e^{-r/2a},$$

$$R_{30} = \frac{2}{81\sqrt{3a^3}}\left[27 - 18\frac{r}{a} + 2\left(\frac{r}{a}\right)^2\right] e^{-r/3a},$$

$$R_{31} = \frac{4}{81\sqrt{6a^3}}\left(6 - \frac{r}{a}\right)\left(\frac{r}{a}\right) e^{-r/3a},$$

$$R_{32} = \frac{4}{81\sqrt{30a^3}}\left(\frac{r}{a}\right)^2 e^{-r/3a},$$

$$R_{40} = \frac{1}{768\sqrt{a^3}}\left[192 - 144\frac{r}{a} + 24\left(\frac{r}{a}\right)^2 - \left(\frac{r}{a}\right)^3\right] e^{-r/4a},$$

$$R_{41} = \frac{1}{256\sqrt{15a^3}}\left[80 - 20\frac{r}{a} + \left(\frac{r}{a}\right)^2\right]\left(\frac{r}{a}\right) e^{-r/4a},$$

$$R_{42} = \frac{1}{768\sqrt{5a^3}}\left(12 - \frac{r}{a}\right)\left(\frac{r}{a}\right)^2 e^{-r/4a},$$

$$R_{43} = \frac{1}{768\sqrt{35a^3}}\left(\frac{r}{a}\right)^3 e^{-r/4a}.$$

A.2.9   The Hydrogen Atom Wave functions $\psi_{n\ell m}(r, \theta, \phi)$

The full hydrogen wave functions are given by

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

Here is a list of the first few states and some density plots of $|n, \ell, m\rangle = \psi_{n\ell m}$ for $n = 1$ to 5.

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a},$$

$$\psi_{200} = \frac{1}{4\sqrt{2\pi a^3}} \left(2 - \frac{r}{a}\right) e^{-r/2a},$$

$$\psi_{210} = \frac{1}{4\sqrt{2\pi a^3}} \left(\frac{r}{a}\right) e^{-r/2a} \cos\theta,$$

$$\psi_{21\pm 1} = \mp \frac{1}{8\sqrt{\pi a^3}} \left(\frac{r}{a}\right) e^{-r/2a} \sin\theta \, e^{\pm i\phi},$$

$$\psi_{300} = \frac{1}{81\sqrt{3\pi a^3}} \left[27 - 18\frac{r}{a} + 2\left(\frac{r}{a}\right)^2\right] e^{-r/3a},$$

$$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi a^3}} \left(6 - \frac{r}{a}\right) \left(\frac{r}{a}\right) e^{-r/3a} \cos\theta,$$

$$\psi_{31\pm 1} = \mp \frac{1}{81\sqrt{\pi a^3}} \left(6 - \frac{r}{a}\right) \left(\frac{r}{a}\right) e^{-r/3a} \sin\theta \, e^{\pm i\phi},$$

$$\psi_{320} = \frac{1}{81\sqrt{6\pi a^3}} \left(\frac{r}{a}\right)^2 e^{-r/3a} (3\cos^2\theta - 1),$$

$$\psi_{32\pm 1} = \mp \frac{1}{81\sqrt{\pi a^3}} \left(\frac{r}{a}\right)^2 e^{-r/3a} \sin\theta \cos\theta \, e^{\pm i\phi},$$

$$\psi_{32\pm 2} = \frac{1}{162\sqrt{\pi a^3}} \left(\frac{r}{a}\right)^2 e^{-r/3a} \sin^2\theta \, e^{\pm 2i\phi}.$$

$|1, 0, 0\rangle$

$|2, 0, 0\rangle$ $|2, 1, 0\rangle$ $|2, 1, 1\rangle$

$|3, 0, 0\rangle$ $|3, 1, 0\rangle$ $|3, 1, 1\rangle$ $|3, 2, 0\rangle$ $|3, 2, 1\rangle$ $|3, 2, 2\rangle$

$|4, 0, 0\rangle$ $|4, 1, 0\rangle$ $|4, 1, 1\rangle$ $|4, 2, 0\rangle$ $|4, 2, 1\rangle$ $|4, 2, 2\rangle$ $|4, 3, 0\rangle$ $|4, 3, 1\rangle$ $|4, 3, 2\rangle$ $|4, 3, 3\rangle$

$|5, 0, 0\rangle$ $|5, 1, 0\rangle$ $|5, 1, 1\rangle$ $|5, 2, 0\rangle$ $|5, 2, 1\rangle$ $|5, 2, 2\rangle$ $|5, 3, 0\rangle$ $|5, 3, 1\rangle$ $|5, 3, 2\rangle$ $|5, 3, 3\rangle$

$|5, 4, 0\rangle$ $|5, 4, 1\rangle$ $|5, 4, 2\rangle$ $|5, 4, 3\rangle$ $|5, 4, 4\rangle$
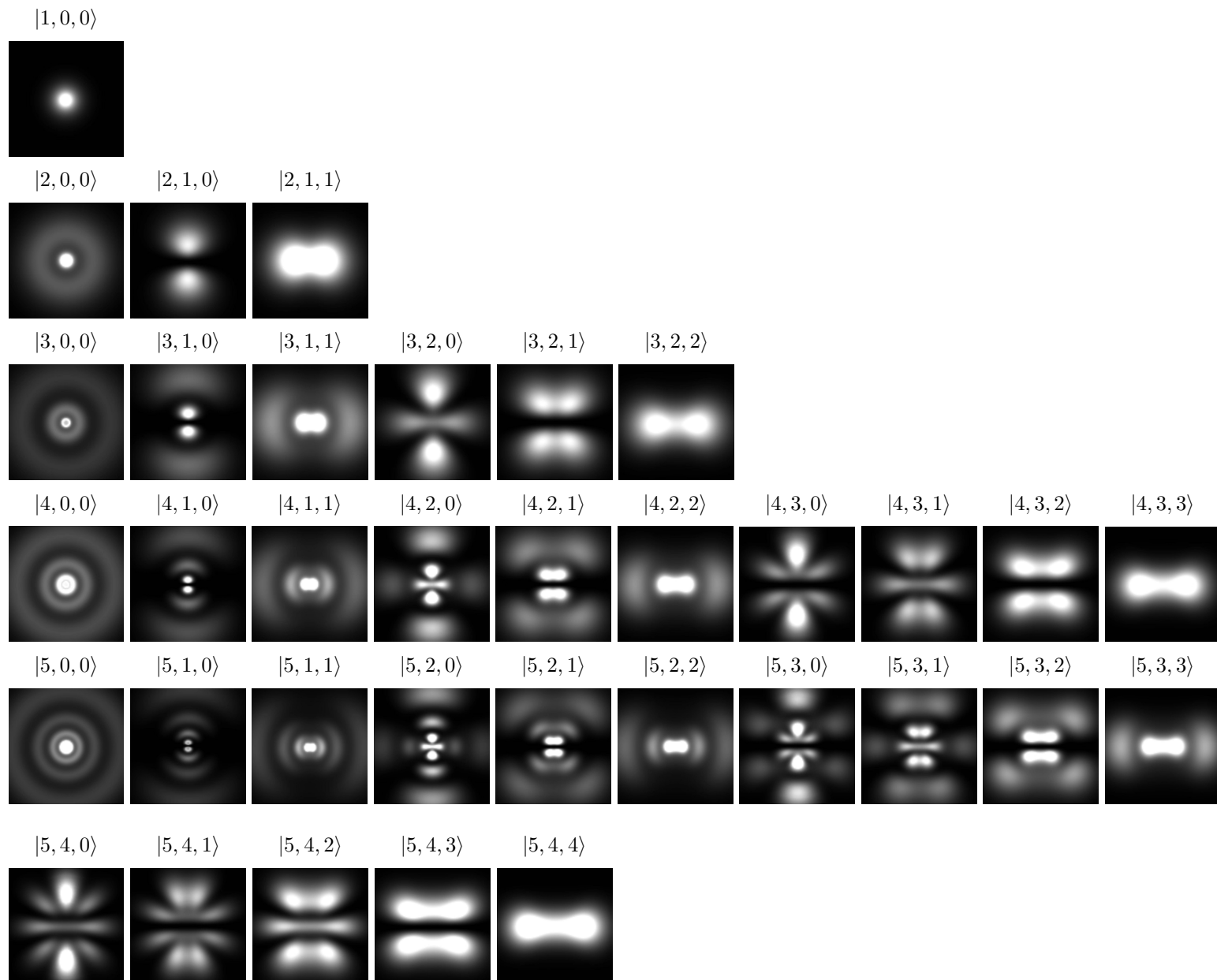
Figure A.1: Probability density $|\psi_{n\ell m}|^2$ plots for the first few hydrogen states $|n, \ell, m\rangle$. Plots are arranged for readers to see patterns easily. These plots are generated by "Atom in a Box" by Dauger Research (see http://dauger.com).

A.3   Matrix Mechanics

In quantum mechanics, states can be represented by vectors $|\psi\rangle$, and operators can be represented by matrices. For a given basis $\{|\psi_i\rangle\}$, the element M_{ij} (ith row and jth column) of a matrix M can be calculated by

$$\langle\psi_i|\hat{M}|\psi_j\rangle,$$

where $\hat{M}$ is the operator form of matrix M. The following sections are useful operators and matrices in different quantum systems (and we will drop the "hat" of the operator for convenience).

A.3.1   1D Harmonic Oscillator

A 1D harmonic oscillator has the Hamiltonian

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

It very complicated stationary states, specified by e^{-x^2} and Hermite polynomials. However, the matrix representation of operators are very clean and elegant. The energy of the state $|n\rangle$ is given by

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, 3\ldots.$$

Choose the basis to be

$$|0\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ \vdots \end{bmatrix}, \quad |1\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ \vdots \end{bmatrix}, \quad |2\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ \vdots \end{bmatrix}, \quad |3\rangle = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ \vdots \end{bmatrix}, \quad \ldots$$

In this basis, the Hamiltonian is

$$H = \hbar\omega \begin{bmatrix} 1/2 & & & & \\ & 3/2 & & & \\ & & 5/2 & & \\ & & & 7/2 & \\ & & & & \ddots \end{bmatrix}.$$

The most useful operators for a harmonic oscillator is the ladder operators, $a^\dagger$ and a. Their matrix representations are constructed by the following relations

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \quad a|n\rangle = \sqrt{n}|n-1\rangle.$$

Explicitly,

$$a = \begin{bmatrix} 0 & \sqrt{1} & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{2} & 0 & \cdots \\ 0 & 0 & 0 & \sqrt{3} & \cdots \\ 0 & 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}. \quad \text{and} \quad a^\dagger = \begin{bmatrix} 0 & 0 & 0 & 0 & \cdots \\ \sqrt{1} & 0 & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}.$$

By the definition $a_\pm = \frac{1}{\sqrt{2\hbar m\omega}}(m\omega x \mp ip)$, we can solve for x and p and construct their matrices,

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a), \quad p = i\sqrt{\frac{\hbar m\omega}{2}}(a^\dagger - a).$$

In matrix form,

$$
x = \sqrt{\frac{\hbar}{2m\omega}}
\begin{bmatrix}
0 & \sqrt{1} & 0 & 0 & \cdots \\
\sqrt{1} & 0 & \sqrt{2} & 0 & \cdots \\
0 & \sqrt{2} & 0 & \sqrt{3} & \cdots \\
0 & 0 & \sqrt{3} & 0 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{bmatrix},
\quad \text{and} \quad
p = i\sqrt{\frac{\hbar m\omega}{2}}
\begin{bmatrix}
0 & -\sqrt{1} & 0 & 0 & \cdots \\
\sqrt{1} & 0 & -\sqrt{2} & 0 & \cdots \\
0 & \sqrt{2} & 0 & -\sqrt{3} & \cdots \\
0 & 0 & \sqrt{3} & 0 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{bmatrix}.
$$

A.3.2   Particle on a Sphere

This in general works for any spherically symmetric potential for a specified ℓ. We will focus on the matrices for the angular parts, namely angular momentum matrices. For a given ℓ, we can define a basis $\{|\ell, m\rangle\}$, where m runs from $-\ell$ to ℓ. For example, a set of basis with $\ell = 1$ is

$$
|1,1\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad
|1,0\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad
|1,-1\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}.
$$

We will work out the general form using this convention with the basis

$$
|\ell, \ell\rangle = \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \\ 0 \end{bmatrix}, \quad
|\ell, \ell - 1\rangle = \begin{bmatrix} 0 \\ 1 \\ \vdots \\ 0 \\ 0 \end{bmatrix}, \quad \cdots \quad
|\ell, -\ell + 1\rangle = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 1 \\ 0 \end{bmatrix}, \quad
|\ell, -\ell\rangle = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix}.
$$

Since these states are eigenstates of L^2 and L_z,

$$
L^2 |\ell, m\rangle = \hbar^2 \ell(\ell+1) |\ell, m\rangle, \quad L_z |\ell, m\rangle = m\hbar |\ell, m\rangle,
$$

their matrices should be diagonal. L^2 has eigenvalues independent of m, so its diagonal entries should all be the same. L_z has eigenvalues $m\hbar$, so its diagonal entries runs from $-\ell$ to ℓ.

$$
L^2 = \hbar^2 \ell(\ell+1)
\begin{bmatrix}
1 & & & & \\
& 1 & & & \\
& & 1 & & \\
& & & \ddots & \\
& & & & 1
\end{bmatrix},
\quad
L_z = \hbar
\begin{bmatrix}
\ell & & & & \\
& \ell - 1 & & & \\
& & \ddots & & \\
& & & -\ell + 1 & \\
& & & & -\ell
\end{bmatrix}.
$$

Next, the matrices for $L_\pm$ can be obtained using

$$
L_+ |\ell, m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m+1)}|\ell, m+1\rangle \quad \text{and} \quad L_- |\ell, m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m-1)}|\ell, m-1\rangle.
$$

By orthonormality of $|\ell, m\rangle$, it is easy to compute matrix elements for $L_\pm$:

$$
[L_+]_{ij} = \langle \ell, m_i | L_+ | \ell, m_j \rangle = \hbar\sqrt{\ell(\ell+1) - m_j(m_j+1)}\, \langle \ell, m_i | \ell, m_j + 1\rangle = \hbar\sqrt{\ell(\ell+1) - m_j(m_j+1)}\delta_{i(j-1)}.
$$

$$
[L_-]_{ij} = \langle \ell, m_i | L_- | \ell, m_j \rangle = \hbar\sqrt{\ell(\ell+1) - m_j(m_j-1)}\, \langle \ell, m_i | \ell, m_j - 1\rangle = \hbar\sqrt{\ell(\ell+1) - m_j(m_j-1)}\delta_{i(j+1)}.
$$

The inner product $\langle \ell, m_1 | \ell, m_j + 1 \rangle = \delta_{i(j-1)}$ seems to be counter-intuitive. *This is because we defined our basis so that $|\ell, \ell\rangle$ is the one with $i = 0$, $|\ell, \ell - 1\rangle$ is $i = 1$, and so on.* Thus, it is very important to specify the basis at first so that the matrix elements make sense. Finally, L_x and L_y can be obtained by the definition of $L_\pm$,

$$
L_\pm = L_x \pm iL_y \quad \Longrightarrow \quad L_x = \frac{1}{2}(L_+ + L_-), \quad L_y = \frac{1}{2i}(L_+ - L_-).
$$

These are the angular momentum matrices. They can also applied to spin angular momentum—just change all the L's to S's and ℓ's to s's. Here is an example for $\ell = 1$.

Case $\ell = 1$:

Basis:

$$|1, 1\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad |1, 0\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad |1, -1\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}.$$

Matrices:

$$L^2 = 2\hbar^2 \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad L_z = \hbar \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad L_x = \frac{\hbar}{2} \begin{bmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix}, \quad L_y = \frac{\hbar}{2i} \begin{bmatrix} 0 & \sqrt{2} & 0 \\ -\sqrt{2} & 0 & \sqrt{2} \\ 0 & -\sqrt{2} & 0 \end{bmatrix}.$$

$$L_+ = \hbar \begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{bmatrix}, \quad L_- = \hbar \begin{bmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix}.$$

A.3.3 Spin 1/2 Matrices along $\hat{\mathbf{r}}$

If we want the matrix S_r along an arbitrary direction $\hat{\mathbf{r}} = \hat{\mathbf{x}} \sin\theta \cos\phi + \hat{\mathbf{y}} \sin\theta \sin\phi + \hat{\mathbf{z}} \cos\theta$, just project S_x, S_y and S_z along $\hat{\mathbf{r}}$ and add them up:

$$S_r = \mathbf{S} \cdot \hat{\mathbf{r}} = S_x \sin\theta \cos\phi + S_y \sin\theta \sin\phi + S_z \cos\theta$$

$$= \frac{\hbar}{2} \left(\begin{bmatrix} 0 & \sin\theta \cos\phi \\ \sin\theta \cos\phi & 0 \end{bmatrix} + \begin{bmatrix} 0 & -i\sin\theta \sin\phi \\ i\sin\theta \sin\phi & 0 \end{bmatrix} + \begin{bmatrix} \cos\theta & 0 \\ 0 & -\cos\theta \end{bmatrix} \right)$$

$$= \frac{\hbar}{2} \begin{bmatrix} \cos\theta & \sin\theta(\cos\phi - i\sin\phi) \\ \sin\theta(\cos\phi + i\sin\phi) & -\cos\theta \end{bmatrix}$$

Using Euler's formula,

$$\boxed{S_r = \frac{\hbar}{2} \begin{bmatrix} \cos\theta & e^{-i\phi} \sin\theta \\ e^{i\phi} \sin\theta & -\cos\theta \end{bmatrix}.}$$

We can determine its eigenvalue and eigenspinors. Let

$$\begin{vmatrix} \frac{\hbar}{2}\cos\theta - \lambda & \frac{\hbar}{2}e^{-i\phi}\sin\theta \\ \frac{\hbar}{2}e^{i\phi}\sin\theta & -\frac{\hbar}{2}\cos\theta - \lambda \end{vmatrix} = -\frac{\hbar^2}{4}\cos^2\theta + \lambda^2 - \frac{\hbar^2}{4}\sin^2\theta = 0.$$

We can easily get $\lambda = \pm\hbar/2$, same as S_i because there is no prefered direction or coordinates. To determine the eigenspinors $\chi_+^{(r)}$ and $\chi_-^{(r)}$, let

$$\frac{\hbar}{2} \begin{bmatrix} \cos\theta & e^{-i\phi}\sin\theta \\ e^{i\phi}\sin\theta & -\cos\theta \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \pm\frac{\hbar}{2} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \quad \Longrightarrow \quad \alpha\cos\theta + \beta e^{-i\phi}\sin\theta = \pm\alpha.$$

We can solve for β,

$$\beta = e^{i\phi} \frac{(\pm 1 - \cos\theta)}{\sin\theta} \alpha.$$

Upper Sign Using trig formulas $1 - \cos\theta = 2\sin^2\frac{\theta}{2}$ and $\sin\theta = 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}$, we can write

$$\beta = e^{i\phi} \frac{\sin(\theta/2)}{\cos(\theta/2)} \alpha.$$

Normalizing the state,

$$1 = |\alpha|^2 + |\beta|^2 = |\alpha|^2 + \frac{\sin^2(\theta/2)}{\cos^2(\theta/2)}|\alpha|^2 = \frac{|\alpha|^2}{\cos^2(\theta/2)}.$$

The result is

$$\alpha = \cos\frac{\theta}{2}, \quad \beta = e^{i\phi}\sin\frac{\theta}{2}.$$

Lower Sign Using $1 + \cos\theta = 2\cos^2\frac{\theta}{2}$ and $\sin\theta = 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}$,

$$\beta = -e^{i\phi}\frac{\cos(\theta/2)}{\sin(\theta/2)}\alpha.$$

After normalization, we have

$$\alpha = \sin(\theta/2), \quad \beta = -e^{i\phi}\cos(\theta/2).$$

Summarizing, the eigenvalues of S_r are $\pm\hbar/2$, with corresponding eigenspinors

$$\chi_+^{(r)} = \begin{bmatrix} \cos(\theta/2) \\ e^{i\phi}\sin(\theta/2) \end{bmatrix}, \quad \chi_-^{(r)} = \begin{bmatrix} \sin(\theta/2) \\ -e^{i\phi}\cos(\theta/2) \end{bmatrix}.$$

Note that because of the normalization, we can always times a phase like $e^{i\phi}$ to the spinors.

A.4 Others

A.4.1 Clebsch-Gordan Coefficients

Legend:

$j_1 \times j_2$	j	j	$\cdots$
	m	m	$\cdots$
m_1 m_2			
m_1 m_2	Coefficients		
$\vdots$ $\vdots$			

$2 \times 1/2$

	5/2			
	5/2	5/2	3/2	
2 1/2	1	3/2	3/2	
2 -1/2	1/5	4/5	5/2	3/2
1 1/2	4/5	-1/5	1/2	1/2
1 -1/2		2/5	3/5	5/2 3/2
0 1/2		3/5	-2/5	-1/2 -1/2
0 -1/2			3/5	2/5	5/2 3/2
-1 1/2			2/5	-3/5	-3/2 -3/2
-1 -1/2				4/5 1/5	5/2
-2 1/2				1/5 -4/5	-5/2
-2 -1/2					1

$1/2 \times 1/2$

	1		
	1	1	0
1/2 1/2	1	0	0
1/2 -1/2	1/2	1/2	1
-1/2 1/2	1/2	-1/2	-1
-1/2 -1/2			1

$3/2 \times 1/2$

	2		
	2	2	1
3/2 1/2	1	1	1
3/2 -1/2	1/4	3/4	2 1
1/2 1/2	3/4	-1/4	0 0
1/2 -1/2		1/2	1/2	2 1
-1/2 1/2		1/2	-1/2	-1 -1
-1/2 -1/2			3/4	1/4	2
-3/2 1/2			1/4	-3/4	-2
-3/2 -1/2				1

$1 \times 1/2$

	3/2		
	3/2	3/2	1/2
1 1/2	1	1/2	1/2
1 -1/2	1/3	2/3	3/2 1/2
0 1/2	2/3	-1/3	-1/2 -1/2
0 -1/2		2/3	1/3	3/2
-1 1/2		1/3	-2/3	-3/2
-1 -1/2			1

$3/2 \times 1$

	5/2		
	5/2	5/2	3/2
3/2 1	1	3/2	3/2
3/2 0	2/5	3/5	5/2 3/2 1/2
1/2 1	3/5	-2/5	1/2 1/2 1/2
3/2 -1	1/10	2/5	1/2
1/2 0	3/5	1/15	-1/3	5/2 3/2 1/2
-1/2 1	3/10	-8/15	1/6	-1/2 -1/2 -1/2
1/2 -1	3/10	8/15	1/6
-1/2 0	3/5	-1/15	-1/3	5/2 3/2
-3/2 1	1/10	-2/5	1/2	-3/2 -3/2
-1/2 -1	3/5	2/5	5/2
-3/2 0	2/5	-3/5	-5/2
-3/2 -1	1

2×1

	3		
	3	3	2
2 1	1	2	2
2 0	1/3	2/3	3 2 1
1 1	2/3	-1/3	1 1 1
2 -1	1/15	1/3	3/5
1 0	8/15	1/6	-3/10	3 2 1
0 1	6/15	-1/2	1/10	0 0 0
1 -1	1/5	1/2	3/10
0 0	3/5	0	-2/5	3 2 1
-1 1	1/5	-1/2	3/10	-1 -1 -1
0 -1	6/15	1/2	1/10
-1 0	8/15	-1/6	-3/10	3 2
-2 1	1/15	-1/3	3/5	-2 -2
-1 -1	2/3	1/3	3
-2 0	1/3	-2/3	-3
-2 -1	1

1×1

	2		
	2	2	1
1 1	1	1	1
1 0	1/2	1/2	2 1 0
0 1	1/2	-1/2	0 0 0
1 -1	1/6	1/2	1/3
0 0	2/3	0	-1/3	2 1
-1 1	1/6	-1/2	1/3	-1 -1
0 -1	1/2	1/2	2
-1 0	1/2	-1/2	-2
-1 -1	1

Figure A.2: Clebsch-Gordan coefficients. A square root is understood on each coefficient, e.g. $-1/3$ means $-\sqrt{1/3}$. If one of the particle has zero angular momentum, then $C^{0j_2j}_{0m_2m} = \delta_{j,j_2}\delta_{m,m_2}$ and $C^{j_10j}_{m_10m} = \delta_{j,j_1}\delta_{m,m_1}$. That is, the total angular momentum must match the angular momentum of the nonzero one.

B Theorems, Proofs, and Derivations

B.1 Theorems

Theorem B.1. Integration by parts for wave functions

This is not a theorem but a useful technique:

$$\int_{-\infty}^{\infty} \frac{\partial^m f}{\partial x^m} \frac{\partial^n g}{\partial x^n} \, dx = -\int_{-\infty}^{\infty} \frac{\partial^{m+1} f}{\partial x^{m+1}} \frac{\partial^{n-1} g}{\partial x^{n-1}} \, dx.$$

Basically, for two normalizable wave functions f and g, one can move one derivative to the other with a cost of a minus sign.

Proof. Integration by parts:

$$\int_{-\infty}^{\infty} \frac{\partial^m f}{\partial x^m} \frac{\partial^n g}{\partial x^n} \, dx = \frac{\partial^m f}{\partial x^m} \frac{\partial^{n-1} g}{\partial x^{n-1}} \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial^{m+1} f}{\partial x^{m+1}} \frac{\partial^{n-1} g}{\partial x^{n-1}} \, dx.$$

$\square$

Theorem B.2. Ehrenfest theorem: Newton's second law

The rate of change in the expectation value of momentum is the expectation value of the negative gradient of potential:

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

Proof. The LHS of the equation is

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

Compute the integrand:

$$\frac{\partial}{\partial t} \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) = \frac{\partial \Psi^*}{\partial t} \frac{\partial \Psi}{\partial x} + \Psi^* \frac{\partial^2 \Psi}{\partial x \partial t} = \left[-\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V \Psi^* \right] \frac{\partial \Psi}{\partial x} + \Psi^* \frac{\partial}{\partial x} \left[\frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V \Psi \right]$$

$$= \frac{i\hbar}{2m} \left[\Psi^* \frac{\partial^3 \Psi}{\partial x^3} - \frac{\partial^2 \Psi^*}{\partial x^2} \frac{\partial \Psi}{\partial x} \right] + \frac{i}{\hbar} \left[V \Psi^* \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial}{\partial x} (V \Psi) \right].$$

Integrating by parts,

$$\frac{d\langle p \rangle}{dt} = -i\hbar \int \left\{ \frac{i\hbar}{2m} \left[\Psi^* \frac{\partial^3 \Psi}{\partial x^3} - \frac{\partial^2 \Psi^*}{\partial x^2} \frac{\partial \Psi}{\partial x} \right] + \frac{i}{\hbar} \left[V \Psi^* \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial}{\partial x} (V \Psi) \right] \right\} dx$$

$$= \frac{\hbar^2}{2m} \int \left[-\frac{\partial \Psi^*}{\partial x} \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial \Psi^*}{\partial x} \frac{\partial^2 \Psi}{\partial x^2} \right] dx + \int \left(V \Psi^* \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial V}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right) dx$$

$$= -\int \Psi^* \frac{\partial V}{\partial x} \Psi \, dx = \left\langle \frac{\partial V}{\partial x} \right\rangle.$$

$\square$

Theorem B.3.

There is no degenerate bound states in one dimension.

Proof. Suppose two normalized stationary states ψ_1 and ψ_2 have the same energy E. They both solve the Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} + V\psi_1 = E\psi_1, \quad -\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + V\psi_2 = E\psi_2.$$

Multiply the first equation by ψ_2 and the second equation by ψ_1,

$$-\frac{\hbar^2\psi_2}{2m}\frac{d^2\psi_1}{dx^2} + V\psi_1\psi_2 = E\psi_1\psi_2, \quad -\frac{\hbar^2\psi_1}{2m}\frac{d^2\psi_2}{dx^2} + V\psi_1\psi_2 = E\psi_1\psi_2.$$

Subtract two equations,

$$-\frac{\hbar^2}{2m}\left(\psi_2\frac{d^2\psi_1}{dx^2} - \psi_1\frac{d^2\psi_2}{dx^2}\right) = 0.$$

Note that the terms in the bracket can be written as a total derivative

$$0 = \psi_2\frac{d^2\psi_1}{dx^2} - \psi_1\frac{d^2\psi_2}{dx^2} = \psi_2\frac{d^2\psi_1}{dx^2} + \frac{d\psi_2}{dx}\frac{d\psi_1}{dx} - \frac{d\psi_1}{dx}\frac{d\psi_2}{dx} - \psi_1\frac{d^2\psi_2}{dx^2} = \frac{d}{dx}\left(\psi_2\frac{d\psi_1}{dx} - \psi_1\frac{d\psi_2}{dx}\right).$$

This means

$$\psi_2\frac{d\psi_1}{dx} - \psi_1\frac{d\psi_2}{dx} = \text{const.}$$

For normalizable solutions, ψ_1, ψ_2 and their derivatives goes to zero at infinities, so this constant must be zero. Hence

$$\psi_2\frac{d\psi_1}{dx} = \psi_1\frac{d\psi_2}{dx} \quad \Longrightarrow \quad \frac{1}{\psi_1}\frac{d\psi_1}{dx} = \frac{1}{\psi_2}\frac{d\psi_2}{dx}.$$

The general solution is

$$\ln\psi_1 = \ln\psi_2 + C \quad \Longrightarrow \quad \psi_1 = A\psi_2$$

for some constant A. Since both ψ_1 and ψ_2 are normalized, the constant of proportionality must be $A = 1$. The two stationary states are the same state. There is no degenerate bound states in one dimension. $\square$

Theorem B.4.

The number of nodes of the stationary states of a one-dimensional potential always increases with energy.

Proof. Consider two real, normalized solutions ψ_n and ψ_m with $E_n > E_m$ to the Schrödinger equation. The Schrödinger equation says that

$$\frac{d^2\psi_n}{dx^2} = -\frac{2m}{\hbar^2}(E_n - V)\psi_n, \quad \frac{d^2\psi_m}{dx^2} = -\frac{2m}{\hbar^2}(E_m - V)\psi_m.$$

Then the total derivative

$$\frac{d}{dx}\left(\frac{d\psi_m}{dx}\psi_n - \psi_m\frac{d\psi_n}{dx}\right) = \frac{d^2\psi_m}{dx^2}\psi_n + \frac{d\psi_m}{dx}\frac{d\psi_n}{dx} - \frac{d\psi_m}{dx}\frac{d\psi_n}{dx} - \psi_m\frac{d^2\psi_m}{dx^2}.$$

By the Schrödinger equation,

$$\frac{d}{dx}\left(\frac{d\psi_m}{dx}\psi_n - \psi_m\frac{d\psi_n}{dx}\right) = -\frac{2m}{\hbar^2}[(E_m - V)\psi_m\psi_n - \psi_m(E_n - V)\psi_n] = \frac{2m}{\hbar^2}(E_n - E_m)\psi_m\psi_n.$$

Let x_1 and x_2 be two adjacent nodes of ψ_m. Integrating from x_1 to x_2,

$$\left(\frac{d\psi_m}{dx}\psi_n - \psi_m\frac{d\psi_n}{dx}\right)\Bigg|_{x_1}^{x_2} = \frac{2m}{\hbar^2}(E_n - E_m)\int_{x_1}^{x_2}\psi_m\psi_n\,dx.$$

Because $\psi_m(x_1) = \psi_m(x_2) = 0$, the second term on the LHS vanishes,

$$\psi'_m(x_2)\psi_n(x_2) - \psi'_m(x_1)\psi_n(x_1) = \frac{2m}{\hbar^2}(E_n - E_m)\int_{x_1}^{x_2}\psi_m\psi_n\,dx.$$

Suppose that ψ_n has no nodes between x_1 and x_2. Then it must be either positive or negative throughout the whole region between x_1 and x_2. The same applies for ψ_m. Assume that $\psi_m, \psi_n > 0$ for $x_1 < x < x_2$ so the RHS is positive. $\psi_m > 0$ requires that $\psi'_m(x_1) > 0$ and $\psi'_m(x_2) < 0$, so the LHS is negative, a contradiction. Hence there is at least one node for ψ_n between x_1 and x_2. The same reasoning works for the case $\psi_m > 0, \psi_n < 0$, case $\psi_m < 0, \psi_n > 0$, and $\psi_m, \psi_n < 0$. In conclusion, for every pair of adjacent nodes of $\psi_m(x)$, $\psi_n(x)$ must have at least one node in between. Because ψ_m is normalized, we can also see $x_1 = -\infty$ and $x_2 = \infty$ as nodes as $\psi_m(\pm\infty) = 0$. Therefore, if ψ_m has N nodes, ψ_n has at least $N+1$ nodes because its energy is higher. □

Theorem B.5. Baker-Campbell-Hausdorff formula

Consider operators A and B that do not commute with each other, $C = [A, B]$ but commute with their commutator: $[A, C] = [B, C] = 0$. Then

$$e^{A+B} = e^A e^B e^{-C/2}. \tag{B.1}$$

Proof. First, we shall show that $[A^n, B] = nA^{n-1}C$. This relation is evidently true for $n = 1$. Prove by induction: assume that this is true for $n - 1$, $[A^{n-1}, B] = (n-1)A^{n-2}C$. Then

$$[A^n, B] = [A(A^{n-1}), B] = A[A^{n-1}, B] + [A, B]A^{n-1} = A(n-1)A^{n-2}C + CA^{n-1} = nA^{n-1}C. \checkmark$$

For any complex number λ, expressing $e^{\lambda A}$ as a power series, we can show that

$$[e^{\lambda A}, B] = \left[\sum_{n=0}^{\infty}\frac{\lambda^n}{n!}A^n, B\right] = \sum_{n=0}^{\infty}\frac{\lambda^n}{n!}[A^n, B] = \sum_{n=0}^{\infty}\frac{\lambda^n}{n!}nA^{n-1}C = \lambda\sum_{n=1}^{\infty}\frac{1}{(n-1)!}\lambda^{n-1}A^{n-1}C = \lambda\sum_{m=0}^{\infty}\frac{1}{m!}\lambda^m A^m C = \lambda e^{\lambda A}C.$$

Define two functions $f(\lambda)$ and $g(\lambda)$,

$$f(\lambda) = e^{\lambda(A+B)}, \quad g(\lambda) = e^{\lambda A}e^{\lambda B}e^{-\lambda^2 C/2}.$$

Note that $f(0) = g(0) = 1$. If they satisfy the same differential equation, then $f(\lambda) = g(\lambda)$ for all λ. Indeed,

$$\frac{df}{d\lambda} = (A+B)f,$$
$$\frac{dg}{d\lambda} = (Ae^{\lambda A})e^{\lambda B}e^{-\lambda^2 C/2} + e^{\lambda A}(Be^{\lambda B})e^{-\lambda^2 C/2} - e^{\lambda A}e^{\lambda B}(\lambda C)e^{-\lambda^2 C/2}$$
$$= Ae^{\lambda A}e^{\lambda B}e^{-\lambda^2 C/2} + (e^{\lambda A}B)e^{\lambda B}e^{-\lambda^2 C/2} - \lambda e^{\lambda A}Ce^{\lambda B}e^{-\lambda^2 C/2}$$
$$= Ae^{\lambda A}e^{\lambda B}e^{-\lambda^2 C/2} + (\lambda e^{\lambda A}C + Be^{\lambda A})e^{\lambda B}e^{-\lambda^2 C/2} - (\lambda e^{\lambda A}C)e^{\lambda B}e^{-\lambda^2 C/2}$$
$$= (A+B)e^{\lambda A}e^{\lambda B}e^{-\lambda^2 C/2}$$
$$= (A+B)g$$

In the second line of $dg/d\lambda$, we use the fact that C commutes with $e^{\lambda B}$. This is because $[B, C] = 0$, $[B^n, C] = 0$; any power series of B commutes with C. Now $f(0) = g(0)$, and they satisfy the same differential equation. When $\lambda = 1$, $f(1) = g(1)$ is the **Baker-Campbell-Hausdorff formula**:

$$e^{A+B} = e^A e^B e^{-C/2}.$$

□

Note: the Baker-Campbell-Hausdorff formula generalizes exponential rules to operators; $e^{A+B} = e^A e^B$ does not hold true for operators. An example of $C = [A, B]$ but $[A, C] = [B, C] = 0$: $i\hbar = [x, p]$ but $[x, i\hbar] = [p, i\hbar] = 0$.

Lemma B.1. Baker-Hausdorff lemma

Consider arbitrary operators A and B.

$$e^{iB\lambda} A e^{-iB\lambda} = A + i\lambda[B, A] + \frac{(i\lambda)^2}{2!}[B, [B, A]] + \cdots + \frac{(i\lambda)^n}{n!}[B, [B, [B, \ldots [B, A]]]] + \cdots .$$

Proof. To be written. $\square$

Theorem B.6. The three-dimensional virial theorem

For stationary states, $2\langle T \rangle = \langle \mathbf{r} \cdot \nabla V \rangle$.

Proof. The commutator $[H, \mathbf{r} \cdot \mathbf{p}]$ is

$$[H, \mathbf{r} \cdot \mathbf{p}] = \sum_{i=1}^{3}[H, r_i p_i] = \sum_{i=1}^{3}([H, r_i]p_i + r_i[H, p_i]) = \sum_{i=1}^{3}\left(\frac{1}{2m}[p^2, r_i]p_i + r_i[V, p_i]\right).$$

The first term is

$$[p^2, r_i] = \sum_{j=1}^{3}[p_j p_j, r_i] = \sum_{j=1}^{3}(p_j[p_j, r_i] + [p_j, r_i]p_j) = \sum_{j=1}^{3}[p_j(-i\hbar\delta_{ij}) + (-i\hbar\delta_{ij})p_j] = -2i\hbar p_i.$$

The second term is just $[V, p_i] = i\hbar \partial V/\partial r_i$. Thus,

$$[H, \mathbf{r} \cdot \mathbf{p}] = \sum_{i=1}^{3}\left[\frac{1}{2m}(-2i\hbar)p_i p_i + r_i\left(i\hbar\frac{\partial V}{\partial r_i}\right)\right] = i\hbar\left(-\frac{p^2}{m} + \mathbf{r} \cdot \nabla V\right).$$

By generalized Ehrenfest theorem (2.10),

$$\frac{d}{dt}\langle \mathbf{r} \cdot \mathbf{p} \rangle = \frac{i}{\hbar}\langle [H, \mathbf{r} \cdot \mathbf{p}] \rangle = \left\langle \frac{p^2}{m} - \mathbf{r} \cdot \nabla V \right\rangle = 2\langle T \rangle - \langle \mathbf{r} \cdot \nabla V \rangle.$$

For stationary states, the time-derivative of all expectation value vanishes, $d\langle \mathbf{r} \cdot \mathbf{p} \rangle/dt = 0$, so $2\langle T \rangle = \langle \mathbf{r} \cdot \nabla V \rangle$. $\square$

Example B.1. The virial theorem on hydrogen and harmonic oscillator

The hydrogen atom has a Coulomb potential,

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad \implies \quad \mathbf{r} \cdot \nabla V = \mathbf{r} \cdot \frac{e^2}{4\pi\epsilon_0 r^2}\hat{\mathbf{r}} = \frac{e^2}{4\pi\epsilon_0 r} = -V,$$

so $2\langle T \rangle = -\langle V \rangle$. This is exactly the classical virial theorem for $1/r$ potential (so it also works for gravity). For stationary states with energy E_n, we have $\langle T \rangle = -E_n$ and $\langle V \rangle = 2E_n$.

For the harmonic oscillator potential,

$$\mathbf{r} \cdot \nabla V = \mathbf{r} \cdot \nabla \left(\frac{1}{2}m\omega^2 r^2\right) = \mathbf{r} \cdot m\omega^2 r\hat{\mathbf{r}} = m\omega^2 r^2 = 2V,$$

so $2\langle T \rangle = 2\langle V \rangle$, or $\langle T \rangle = \langle V \rangle = E_n/2$. This is consistent with Example 1.3. The kinetic energy and potential energy divides the total energy equally for the harmonic oscillator.

Theorem B.7. The spin-statistics theorem

All particles with integer spin are bosons; all particles with half integer spin are fermions.

Proof. We will not prove this theorem in non-relativistic quantum mechanics. □

Theorem B.8. Wigner-Eckart Theorem

To be written.

Proof. To be written. □

Theorem B.9. Feynman-Hellmann Theorem

Let the Hamiltonian H for a particular quantum system to be a function of some parameter λ. Let $E_n(\lambda)$ and $\psi_n(\lambda)$ be the eigenvalues and normalized eigenfunctions of $H(\lambda)$. (Assume that E_n is non-degenerate. If it is degenerate, then assume ψ_n are good states mentioned in degenerate perturbation theory.) Then

$$\frac{\partial E_n}{\partial \lambda} = \left\langle \psi_n \left| \frac{\partial H}{\partial \lambda} \right| \psi_n \right\rangle.$$

Proof. If $H(\lambda)\,|\psi_n(\lambda)\rangle = E_n(\lambda)\,|\psi_n(\lambda)\rangle$ and $\langle \psi_n(\lambda)|\psi_n(\lambda)\rangle = 1$, then

$$\begin{aligned}
\frac{dE_n}{d\lambda} &= \left\langle \frac{d\psi_n}{d\lambda} \middle| H \middle| \psi_n \right\rangle + \left\langle \psi_n \left| \frac{dH}{d\lambda} \right| \psi_n \right\rangle + \left\langle \psi_n \middle| H \middle| \frac{d\psi_n}{d\lambda} \right\rangle \\
&= E_n \left\langle \frac{d\psi_n}{d\lambda} \middle| \psi_n \right\rangle + E_n \left\langle \psi_n \middle| \frac{d\psi_n}{d\lambda} \right\rangle + \left\langle \psi_n \left| \frac{dH}{d\lambda} \right| \psi_n \right\rangle \\
&= E \frac{d}{d\lambda}\langle\psi_n|\psi_n\rangle + \left\langle \psi_n \left| \frac{dH}{d\lambda} \right| \psi_n \right\rangle \\
&= \left\langle \psi_n \left| \frac{dH}{d\lambda} \right| \psi_n \right\rangle.
\end{aligned}$$

□

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*Note: Suppose $E(\lambda_0)$ is two-fold degenerate with

$$H|\psi_1\rangle = E|\psi_1\rangle \quad \text{and} \quad H|\psi_2\rangle = E|\psi_2\rangle,$$

and $\langle \psi_i|\psi_j\rangle = \delta_{ij}$. Then any linear combination of $|\psi_1\rangle$ and $|\psi_2\rangle$ is also an eigenstate of H. Let this state be $|\psi\rangle = \alpha|\psi_1\rangle + \beta|\psi_2\rangle$ and we have

$$H(\alpha|\psi_1\rangle + \beta|\psi_2\rangle) = E(\alpha|\psi_1\rangle + \beta|\psi_2\rangle).$$

Differentiating with respect to λ on both sides,

$$\frac{dH}{d\lambda}(\alpha|\psi_1\rangle + \beta|\psi_2\rangle) + H\left(\alpha \left|\frac{d\psi_1}{d\lambda}\right\rangle + \beta\left|\frac{d\psi_2}{d\lambda}\right\rangle\right) = \frac{dE}{d\lambda}(\alpha|\psi_1\rangle + \beta|\psi_2\rangle) + E\left(\alpha\left|\frac{d\psi_1}{d\lambda}\right\rangle + \beta\left|\frac{d\psi_2}{d\lambda}\right\rangle\right).$$

Then take the inner product with $|\psi_1\rangle$ on both sides and invoke orthonormality,

$$\alpha\left\langle\psi_1\left|\frac{dH}{d\lambda}\right|\psi_1\right\rangle + \beta\left\langle\psi_1\left|\frac{dH}{d\lambda}\right|\psi_2\right\rangle + E\alpha\left\langle\psi_1\middle|\frac{d\psi_1}{d\lambda}\right\rangle + E\beta\left\langle\psi_1\middle|\frac{d\psi_2}{d\lambda}\right\rangle = \alpha\frac{dE}{d\lambda} + E\alpha\left\langle\psi_1\middle|\frac{d\psi_1}{d\lambda}\right\rangle + E\beta\left\langle\psi_1\middle|\frac{d\psi_2}{d\lambda}\right\rangle.$$

There is an extra term of $\beta\left\langle\psi_1|\frac{dH}{d\lambda}|\psi_2\right\rangle$ that fails the Feynman-Hellmann theorem. The condition to make the theorem hold is

$$\left\langle\psi_1\left|\frac{dH}{d\lambda}\right|\psi_2\right\rangle = 0.$$

This is the same as how do we find good states (to first order of λ): we want to find states such that $\langle\psi_1|H'|\psi_2\rangle = 0$.

Theorem B.10. Kramers' relation

For an electron in the state $\psi_{n\ell m}$,

$$\frac{s+1}{n^2}\langle r^s\rangle - (2s+1)a\langle r^{s-1}\rangle + \frac{s}{4}\left[(2\ell+1)^2 - s^2\right]a^2\langle r^{s-2}\rangle = 0.$$

This relates the expectation values of r to three different powers (s, $s-1$, and $s-2$).

Proof. To be written. □

Corollary B.1. Variational Principle

For any ψ, if $\langle\psi|\psi_{\mathrm{gs}}\rangle = 0$, then $\langle H\rangle \geq E_{\mathrm{fe}}$, where E_{fe} is the energy of the first excited state. In other words, if a trial function is orthogonal to the exact ground state, we can get an upper bound on the first excited state.

Proof. The general trial wave function ψ can be written as

$$\psi = \sum_{n=1}^{\infty} c_n \psi_n,$$

where ψ_1 is the ground state. It is given that $\langle\psi_1|\psi\rangle = 0$, so

$$\langle\psi_1|\psi\rangle = \sum_{n=1}^{\infty} c_n \langle\psi_1|\psi_n\rangle = c_1 = 0.$$

The expectation value of the Hamiltonian is

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

because $E_n \geq E_{\mathrm{fe}}$ for $n \geq 2$. □

It is in general hard to find a trial wave function that is orthogonal to the exact ground state because we don't know the latter. However, if the potential $V(x)$ is an even function of x, then the ground state will also be even. Then any odd trial function will be orthogonal to the ground state. This corollary can be generalized to a way to get an upper bound on the nth excited state, if the trial wave function is orthogonal to all the lower energy states. (The difficulty of finding the trial wave function is also increasing.)

Theorem B.11. Existence of bound states

A potential well in one dimension is a function $V(x)$ that is never positive ($V(x) \leq 0$ for all x), and goes to zero at infinity. If a potential well $V_1(x)$ supports at least one bound state, then any deeper/wider well ($V_2(x) \leq V_1(x)$ for all x) will also support at least one bound state.

Proof. Let $\psi_1(x)$ be the ground state of the Hamiltonian with potential V_1. Use ψ_1 as a variational wave function for the Hamiltonian with potential V_2. By the variational principle, the ground state energy E_2 of the Hamiltonian with V_2 is

$$E_2 \leq \int_{-\infty}^{\infty} \psi_1^*(x)\left[-\frac{\hbar^2}{2m} + V_2(x)\right]\psi_1(x)\,dx$$

$$= \int_{-\infty}^{\infty} \psi_1^*(x)\left[-\frac{\hbar^2}{2m} + V_1(x)\right]\psi_1(x)\,dx + \int_{-\infty}^{\infty} \psi_1^*(x)[V_2(x) - V_1(x)]\psi_1(x)\,dx$$

$$= E_1 + \int_{-\infty}^{\infty} |\psi_1(x)|^2[V_2(x) - V_1(x)]\,dx.$$

Because $V_2(x) \leq V_1(x)$ for all x, the integral is less than or equal to zero, which means $E_2 \leq E_1$. Since $E_1 < 0$ (because it is a bound state), we must have $E_2 < 0$. Thus, V_2 also admits a bound state. $\square$

B.2 The Harmonic Oscillator

B.2.1 Saturated Uncertainty Principle

In this section we will find $\langle x \rangle$, $\langle p \rangle$, $\langle x^2 \rangle$, $\langle p^2 \rangle$, σ_x and σ_p of normalized stationary states ψ_n of the harmonic oscillator. Useful relations (1.23) and (1.21) are listed here for reference,

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a), \quad p = i\sqrt{\frac{\hbar m\omega}{2}}(a^\dagger - a)$$

$$a^\dagger \psi_n = \sqrt{n+1}\psi_n, \quad a\psi_n = \sqrt{n}\psi_{n-1}.$$

1. Expectation of position and momentum:

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^* \, x \, \psi_n \, dx = \sqrt{\frac{\hbar}{2m\omega}} \int_{-\infty}^{\infty} \psi_n^*(a^\dagger + a)\psi_n \, dx$$

$$= \sqrt{\frac{\hbar}{2m\omega}} \left[\int_{-\infty}^{\infty} \psi_n^* \sqrt{n+1} \, \psi_{n+1} \, dx + \int_{-\infty}^{\infty} \psi_n^* \sqrt{n} \, \psi_{n-1} \, dx \right] = 0.$$

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt} = 0.$$

2. Expectation of position and momentum squared:

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_n^* \, x^2 \, \psi_n \, dx = \frac{\hbar}{2m\omega} \int_{-\infty}^{\infty} \psi^*(a^\dagger + a)^2 \psi_n \, dx$$

$$= \frac{\hbar}{2m\omega} \int_{-\infty}^{\infty} \psi_n^*(a^{\dagger 2} + a^\dagger a + aa^\dagger + a^2)\psi_n^* \, dx$$

$$= \frac{\hbar}{2m\omega} \int_{-\infty}^{\infty} \psi_n^* \left[\sqrt{(n+1)(n+2)} \, \psi_{n+2} + n\psi_n + (n+1)\psi_n + \sqrt{n(n+1)}\psi_{n-2} \right] dx$$

$$= \frac{\hbar}{2m\omega}(1 + 2n).$$

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \psi_n^* \, p^2 \, \psi_n \, dx = -\frac{\hbar m\omega}{2} \int_{-\infty}^{\infty} \psi_n^*(a^\dagger - a)^2 \psi_n \, dx$$

$$= -\frac{\hbar m\omega}{2} \int_{-\infty}^{\infty} \psi_n^* \overbrace{(a^{\dagger 2} + a^2)}\psi_n \, dx + \frac{\hbar m\omega}{2} \int_{-\infty}^{\infty} \psi_n^*(a^\dagger a + aa^\dagger)\psi_n \, dx$$

$$= \frac{\hbar m\omega}{2}(1 + 2n).$$

In above calculations we invoke orthonormality of ψ_n multiple times.

3. The uncertainties:

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{\hbar}{2m\omega}(1 + 2n)}, \quad \sigma_p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{\frac{\hbar m\omega}{2}(1 + 2n)}.$$

First let's check that the uncertainty principle is satisfied:

$$\sigma_x \sigma_p = \sqrt{\frac{\hbar}{2m\omega}(1 + 2n)}\sqrt{\frac{\hbar m\omega}{2}(1 + 2n)} = \frac{\hbar}{2}(1 + 2n) \geq \frac{\hbar}{2}.$$

Moreover, when $n = 0$, the uncertainty is saturated, meaning that $\sigma_x \sigma_p = \hbar/2$.

B.2.2 The Coherent States

The **coherent states** are eigenfunctions of the lowering operator a,

$$aS_\alpha = \alpha S_\alpha,$$

for some complex number $\alpha = |\alpha| e^{i\sigma}$. They also saturate the uncertainty principle even though they are not ψ_0 (but obviously ψ_0 is a coherent state with $\alpha = 0$). We assume that the coherent states are normalized. To investigate them, we need the relations

$$a_\pm = \frac{1}{\sqrt{2\hbar m\omega}}(\mp ip + m\omega x), \quad x = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a), \quad p = i\sqrt{\frac{\hbar m\omega}{2}}(a^\dagger - a),$$

and Theorem 1.6,

$$\int f^*(\alpha_\pm g)\, dx = \int (a_\mp f)^* g\, dx.$$

1. Expectation of position and momentum:

$$
\begin{aligned}
\langle x \rangle &= \int S_\alpha^* \, x \, S_\alpha \, dx = \sqrt{\frac{\hbar}{2m\omega}} \int S_\alpha^*(a^\dagger + a)S_\alpha \, dx = \sqrt{\frac{\hbar}{2m\omega}} \left[\int (aS_\alpha)^* S_\alpha \, dx + \int S_\alpha^*(aS_\alpha)\, dx \right] \\
&= \sqrt{\frac{\hbar}{2m\omega}} \left[\alpha^* \int S_\alpha^* S_\alpha \, dx + \alpha \int S_\alpha^* S_\alpha \, dx \right] \\
&= \sqrt{\frac{\hbar}{2m\omega}}(\alpha^* + \alpha). \\
\langle p \rangle &= \int S_\alpha^* \, p \, S_\alpha \, dx = i\sqrt{\frac{\hbar m\omega}{2}} \int S_\alpha^*(a^\dagger - a)S_\alpha \, dx = i\sqrt{\frac{\hbar m\omega}{2}} \left[\int (aS_\alpha)^* S_\alpha \, dx - \int S_\alpha^*(aS_\alpha)\, dx \right] \\
&= i\sqrt{\frac{\hbar m\omega}{2}}(\alpha^* - \alpha).
\end{aligned}
$$

Expectation of position and momentum squared:

$$
\begin{aligned}
\langle x^2 \rangle &= \frac{\hbar}{2m\omega} \int S_\alpha^*(a^\dagger + a)^2 S_\alpha \, dx = \frac{\hbar}{2m\omega} \int S_\alpha^*(a^{\dagger 2} + a^\dagger a + a a^\dagger + a^2)S_\alpha \, dx \\
&= \frac{\hbar}{2m\omega} \int S_\alpha^*(a^{\dagger 2} + 2a^\dagger a + 1 + a^2)S_\alpha \, dx \qquad \longleftarrow \text{using } [a, a^\dagger] = 1 \\
&= \frac{\hbar}{2m\omega}(\alpha^{*2} + 2\alpha^*\alpha + \alpha^2 + 1). \\
\langle p^2 \rangle &= -\frac{\hbar m\omega}{2} \int S_\alpha^*(a^\dagger - a)^2 S_\alpha \, dx = -\frac{\hbar m\omega}{2} \int S_\alpha^*(a^{\dagger 2} - a^\dagger a - a a^\dagger + a^2)S_\alpha \, dx \\
&= -\frac{\hbar m\omega}{2} \int S_\alpha^*(a^{\dagger 2} - 2a^\dagger a - 1 + a^2)S_\alpha \, dx \\
&= -\frac{\hbar m\omega}{2}(\alpha^{*2} - 2\alpha^*\alpha + \alpha^2 - 1).
\end{aligned}
$$

Uncertainty of position and momentum:

$$
\begin{aligned}
\sigma_x &= \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{\hbar}{2m\omega}\left[(\alpha^{*2} + 2\alpha^*\alpha + \alpha^2 + 1) - (\alpha^* + \alpha)^2\right]} = \sqrt{\frac{\hbar}{2m\omega}}, \\
\sigma_p &= \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{\frac{\hbar m\omega}{2}\left[-(\alpha^{*2} - 2\alpha^*\alpha + \alpha^2 - 1) - i^2(\alpha^* - \alpha)^2\right]} = \sqrt{\frac{\hbar m\omega}{2}}.
\end{aligned}
$$

All coherent states saturate the uncertainty principle: $\sigma_x \sigma_p = \hbar/2$.

2. To visualize the dynamics of coherent states, it is better to obtain its series expansion. The coherent state must be an infinite series of ψ_n (unless $S_\alpha = \psi_0$, for which $\alpha = 0$),

$$S_\alpha = \sum_{n=0}^{\infty} c_n \psi_n(x),$$

for some coefficients c_n to be determined. (If it is not an infinite series, but instead terminates at ψ_t, then acting a on S_α makes it terminates at ψ_{t-1}. Then S_α will not be an eigenfunction of a because stationary states are orthogonal.) To determine c_n, we use Fourier's trick and (1.22),

$$c_n = \int \psi_n^* S_\alpha \, dx = \int \left[\frac{1}{\sqrt{n!}}(a^\dagger)^n \psi_0 \right]^* S_\alpha \, dx = \frac{1}{\sqrt{n!}} \int \psi_0^* \left[(a)^n S_\alpha\right] dx = \frac{\alpha^n}{\sqrt{n!}} \int \psi_0^* S_\alpha \, dx = \frac{\alpha^n}{\sqrt{n!}} c_0.$$

Thus, all the coefficients c_n depends on a complex number c_0. To get c_0, we normalize S_α,

$$\int S_\alpha^* S_\alpha \, dx = \int \left(\sum_{m=0}^\infty \frac{\alpha^{*m}}{\sqrt{m!}} c_0^* \psi_m \right) \left(\sum_{n=0}^\infty \frac{\alpha^n}{\sqrt{n!}} c_0 \psi_n \right) dx = \sum_{m=0}^\infty \sum_{n=0}^\infty \frac{\alpha^{*m} \alpha^n}{\sqrt{m!n!}} |c_0|^2 \int \psi_m^* \psi_n \, dx$$

$$= \sum_{m=0}^\infty \sum_{n=0}^\infty \frac{\alpha^{*m} \alpha^n}{\sqrt{m!n!}} |c_0|^2 \delta_{mn} = \sum_{n=0}^\infty \frac{(|\alpha|^2)^n}{n!} |c_0|^2 = e^{|\alpha|^2} |c_0|^2.$$

Setting $e^{|\alpha|^2} |c_0|^2 = 1$ and c_0 to be real, we get

$$c_0 = e^{-|\alpha|^2/2}.$$

In conclusion, the coherent state can be expressed as

$$\boxed{S_\alpha(x) = e^{-|\alpha|^2/2} \sum_{n=0}^\infty \frac{\alpha^n}{\sqrt{n!}} \psi_n.} \tag{B.2}$$

Now add the time dependence $e^{-iE_n t/\hbar} = e^{-i(n+1/2)\hbar\omega t/\hbar} = e^{-in\omega t} e^{-i\omega t/2}$ to each ψ_n,

$$S_\alpha(x,t) = e^{-(|\alpha|^2 + i\omega t)/2} \sum_{n=0}^\infty \frac{\alpha^n}{\sqrt{n!}} e^{-in\omega t} \psi_n \to S_\alpha(x,t) = e^{-|\alpha|^2/2} \sum_{n=0}^\infty \frac{\alpha(t)^n}{\sqrt{n!}} \psi_n.$$

Recall that the overall phase factor $e^{-i\omega t/2}$ has no physical significance, so it is thrown away. We also define the time-dependent parameter $\alpha(t) \equiv \alpha e^{-i\omega t} = |\alpha| e^{i\sigma - i\omega t}$. Note that even though α depends on time, the series form of S_α isn't changing. S_α is still an eigenfunction of a, with a changing eigenvalue $\alpha(t)$. This is to say that coherent states stay coherent forever.

It is also possible to express the coherent states in a closed form by directly solving the equation

$$a S_\alpha = \alpha S_\alpha.$$

By the definition of lowering operator $a = (ip + m\omega x)/\sqrt{2\hbar m\omega}$,

$$\frac{1}{\sqrt{2\hbar m\omega}} \left(-\hbar \frac{\partial}{\partial x} + m\omega x \right) S_\alpha = \alpha S_\alpha \quad \Longrightarrow \quad \frac{\partial S_\alpha}{\partial x} = \left(-\frac{m\omega}{\hbar} x + \sqrt{\frac{2m\omega}{\hbar}} \alpha \right) S_\alpha.$$

Separation of variables:

$$\frac{dS_\alpha}{S_\alpha} = \left(-\frac{m\omega}{\hbar} x + \sqrt{\frac{2m\omega}{\hbar}} \alpha \right) dx.$$

Integrating on both sides gives the final (normalized) solution, also a Gaussian:

$$S_\alpha(x,t) = A e^{-ax^2 - bx}, \quad \text{where} \quad A = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\alpha^2}, \quad a = \frac{m\omega}{2\hbar}, \quad b = -\sqrt{\frac{2m\omega}{\hbar}} \alpha(t).$$

Note that a is a constant, but b is a function of time. That is, the width or shape of the Gaussian remains the same, but its position moves back and forth according to $\alpha(t)$.

3. It turns out that if we stick to $\alpha(t) = |\alpha| e^{i(\sigma - \omega t)}$, and calculate $\langle x \rangle$ and $\langle p \rangle$ using our previous results,

$$\langle x(t) \rangle = \sqrt{\frac{\hbar}{2m\omega}} (\alpha^* + \alpha) = \sqrt{\frac{2\hbar}{m\omega}} \left[\frac{|\alpha| e^{-i(\sigma - \omega t)} + |\alpha| e^{i(\sigma - \omega t)}}{2} \right] = \sqrt{\frac{2\hbar}{m\omega}} |\alpha| \cos(\omega t - \sigma),$$

$$\langle p(t) \rangle = i\sqrt{\frac{\hbar m\omega}{2}} (\alpha^* - \alpha) = -\sqrt{2\hbar m\omega} \left[\frac{|\alpha| e^{-i(\sigma - \omega t)} - |\alpha| e^{i(\sigma - \omega t)}}{2i} \right] = -\sqrt{2\hbar m\omega} |\alpha| \sin(\omega t - \sigma).$$

You may check that $\langle p(t) \rangle = m \, d\langle x(t) \rangle / dt$.

The coherent states have many applications. The name comes from their application in laser, a beam of coherent photons.

B.2.3 Time Evolution of x

Here we present an alternative derivation of 3.10 using the definition of operators in the Heisenberg picture:

$$x(t) = U^\dagger x_0 U = e^{iHt/\hbar} x_0 e^{-iHt/\hbar}.$$

We invoke the **Baker-Hausdorff lemma** (Lemma B.1)

$$e^{iHt/\hbar} x_0 e^{-iHt/\hbar} = x_0 + \frac{it}{\hbar}[H, x_0] + \frac{i^2 t^2}{2!\hbar^2}[H, [H, x_0]] + \cdots .$$

Each term on the RHS can be reduced to x or p by using

$$[H, x_0] = -i\hbar \frac{\partial H}{\partial p}\Big|_{t=0} = -\frac{i\hbar p_0}{m}, \quad [H, p_0] = i\hbar \frac{\partial H}{\partial x}\Big|_{t=0} = i\hbar m \omega^2 x_0.$$

Then

$$e^{iHt/\hbar} x_0 e^{-iHt/\hbar} = x_0 + \frac{p_0 t}{m} - \frac{1}{2!}\omega^2 x_0 t - \frac{1}{3!}\frac{\omega^2 p_0 t^3}{m} + \cdots = x_0 \cos \omega t + \frac{p_0}{m\omega}\sin \omega t.$$

B.2.4 The Creation Space Representation

In B.2.2, we discussed eigenstates (coherent states) of the lowering operator a. Here we will discuss eigenstates of the raising operator $a^\dagger$, satisfying the equation eigenvalue equation

$$\frac{1}{\sqrt{2}}\left(\xi - \frac{d}{d\xi}\right)\psi_{a^\dagger}(\xi) = \beta \psi_{a^\dagger}(\xi), \quad \text{where} \quad \xi = \sqrt{\frac{m\omega}{\hbar}}x.$$

The eigenvalue β can be any complex number. The solution of this equation is

$$\psi_{a^\dagger}(\xi) = A e^{\xi^2/2 - \sqrt{2}\xi a^\dagger}$$

for some constant A. This wave function is definitely not normalizable because of the factor $e^{\xi^2/2}$. Here we will choose the integration constant be $A = e^{\beta^2/2}$ so that the wave function becomes

$$\psi_{a^\dagger}(\xi) = e^{\xi^2/2 - \sqrt{2}\xi a^\dagger + a^{\dagger 2}/2}.$$

Now $\{|\beta\rangle\}$, or $\{\psi_{a^\dagger}(\xi)\}$, is a set of states that *may* be used as a basis. We let $f(a^\dagger)$ to be the $a^\dagger$-space wave function, and define the position-space wave function to be

$$\psi(\xi) = \frac{1}{i\sqrt{2\pi}}\int_{-i\infty}^{i\infty} f(a^\dagger) e^{\xi^2/2 - \sqrt{2}\xi a^\dagger + a^{\dagger 2}/2}\, da^\dagger. \tag{B.3}$$

Because here $a^\dagger$ is complex, we can choose any convenient path of integration for superposition, hence the integration along the imaginary axis. Making a change of variable $a^\dagger = ib$, $\psi(\xi)$ can be expressed as

$$\psi(\xi) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(b) e^{\xi^2/2 - i\sqrt{2}\xi b - b^2/2}\, db \quad \Longrightarrow \quad \psi(\xi)e^{-\xi^2/2} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}[f(b)e^{-b^2/2}]e^{-i\sqrt{2}\xi b}\, db.$$

We see that $\psi(\xi)e^{-\xi^2/2}$ and $f(b)e^{-b^2/2}$ are Fourier transform and inverse Fourier transform of each other, with the inverse being

$$f(b)e^{-b^2/2} = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}[\psi(\xi)e^{-\xi^2/2}]e^{i\sqrt{2}\xi b}\, d\xi \quad \Longrightarrow \quad f(a^\dagger) = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}\psi(\xi)e^{-\xi^2/2 + \sqrt{2}\xi a^\dagger - a^{\dagger 2}/2}\, d\xi.$$

Therefore, in the Fourier integral representation $\psi(\xi)e^{-\xi^2/2}$ and $f(b)e^{-b^2/2}$, the eigenstates of $a^\dagger$ are complete. The wave function $f(a^\dagger)$ are known as the **creation-space representation** of a state.

The lowering operator a is the operator of differentiation in the creation space. In position space, the lowering operator is defined as

$$a\psi(\xi) = \frac{1}{\sqrt{2}}\left(\xi + \frac{d}{d\xi}\right)\psi(\xi), \quad \xi = \sqrt{\frac{m\omega}{\hbar}}x.$$

Expanding $\psi(\xi)$ in the creation space using (B.3),

$$
\begin{aligned}
a\psi(\xi) &= \frac{1}{i\sqrt{2\pi}} \int_{-i\infty}^{i\infty} f(a^\dagger) \frac{1}{\sqrt{2}} \left(\xi + \frac{d}{d\xi} \right) e^{\xi^2/2 - \sqrt{2}\xi a^\dagger + a^{\dagger 2}/2}\, da^\dagger \\
&= \frac{1}{i\sqrt{2\pi}} \int_{-i\infty}^{i\infty} f(a^\dagger)(\sqrt{2}\xi - a^\dagger) e^{\xi^2/2 - \sqrt{2}\xi a^\dagger + a^{\dagger 2}/2}\, da^\dagger \\
&= \frac{1}{i\sqrt{2\pi}} \int_{-i\infty}^{i\infty} f(a^\dagger) \left(-\frac{d}{da^\dagger} e^{\xi^2/2 - \sqrt{2}\xi a^\dagger + a^{\dagger 2}/2} \right) da^\dagger \\
&= -\frac{1}{i\sqrt{2\pi}} \left[\cancel{ \left. f(a^\dagger) e^{\xi^2/2 - \sqrt{2}\xi a^\dagger + a^{\dagger 2}/2} \right|_{-i\infty}^{i\infty} } - \int_{-i\infty}^{i\infty} \frac{d}{da^\dagger} f(a^\dagger) e^{\xi^2/2 - \sqrt{2}\xi a^\dagger + a^{\dagger 2}/2}\, da^\dagger \right] \\
&= \frac{1}{i\sqrt{2\pi}} \int_{-i\infty}^{i\infty} \left[\frac{d}{da^\dagger} f(a^\dagger) \right] e^{\xi^2/2 - \sqrt{2}\xi a^\dagger + a^{\dagger 2}/2}\, da^\dagger .
\end{aligned}
$$

In the fourth line, we used integration by parts and the first term vanishes for normalizable $\psi(\xi)$. Later we will see that eigenfunctions $f_n(a^\dagger)$ of the harmonic oscillator in creation space is suppressed by the factor $e^{a^{\dagger 2}/2}$, where $a^\dagger$ is purely imaginary. In conclusion, $f(a^\dagger)$ in creation space is equivalent to $\psi(\xi)$ in position space, while $df/da^\dagger$ is equivalent to $a\psi$. In this way, we reproduce the commutation relation $[a, a^\dagger] = 1$. (In fact, this is part of the motivation for the creation-space representation.)

The energy eigenstates of the harmonic oscillator in position space involves Hermite polynomials and Gaussians, which are hard to work with. Using the ladder operator, we can write those eigenfunctions as (1.22):

$$
\psi_n(\xi) = \frac{1}{\sqrt{n!}} (a^\dagger)^n \psi_0(\xi), \quad \text{where} \quad a\psi_0(\xi) = 0.
$$

In $a^\dagger$ space, $\psi_n(\xi) \to f_n(a^\dagger)$, $a^\dagger \to a^\dagger$, and $a \to d/da^\dagger$, so

$$
f_n(a^\dagger) = \frac{1}{\sqrt{n!}} a^{\dagger n} f_0(a^\dagger), \quad \text{where} \quad \frac{d}{da^\dagger} f_0(a^\dagger) = 0,
$$

which means $f_0(a^\dagger) = c_0$ is just some constant, and $f_n(a^\dagger)$ is a monomial,

$$
\boxed{ f_n(a^\dagger) = \frac{c_0}{\sqrt{n!}} a^{\dagger n} \quad \Longleftrightarrow \quad \psi_n(\xi) = \frac{c_0}{i\sqrt{2\pi n!}} \int_{-i\infty}^{i\infty} a^{\dagger n} e^{\xi^2/2 - \sqrt{2}\xi a^\dagger + a^{\dagger 2}/2}\, da^\dagger . } \tag{B.4}
$$

We see that $f_n(a^\dagger)$ indeed grows no faster than $e^{a^{\dagger 2}/2}$. To determine c_0, we find $\psi_0(\xi)$ directly from (B.3),

$$
\psi_0(\xi) = \frac{c_0}{i\sqrt{2\pi}} e^{\xi^2/2} \int_{-i\infty}^{i\infty} e^{-\sqrt{2}\xi a^\dagger + a^{\dagger 2}/2}\, da^\dagger = \frac{c_0}{\sqrt{2\pi}} e^{\xi^2/2} \int_{-\infty}^{\infty} e^{-i\sqrt{2}\xi b - b^2/2}\, db = \frac{c_0}{\sqrt{2\pi}} e^{\xi^2/2} (\sqrt{2\pi}\, e^{-\xi^2}) = c_0 e^{-\xi^2/2}
$$

Compare this with (1.27), we find that $c_0 = (m\omega/\pi\hbar)^{1/4}$.

Example B.2. The Propagator

To find the propagator, we use (3.16) directly. Taking $t_0 = 0$ for convenience,

$$
K(x, t; x', 0) = \sum_n \psi_n(x) \psi_n^*(x') e^{-i(n+1/2)\omega t}.
$$

In the creation-space representation, the propagator gas the form (note the integration limit of the second integral because of the complex conjugate in $\psi_n^*(x')$)

$$
K(x, t; x', 0) = \frac{1}{2} \sqrt{\frac{m\omega}{\pi\hbar}} e^{(\xi^2 + \xi'^2 - i\omega t)/2} \sum_n \int_{-i\infty}^{i\infty} da^\dagger \int_{i\infty}^{-i\infty} da^{\dagger'} \frac{(a^\dagger a^{\dagger'})^n e^{-in\omega t}}{n!} e^{-\sqrt{2}(\xi a^\dagger + \xi' a^{\dagger'}) + (a^{\dagger 2} + a^{\dagger' 2})/2}.
$$

Performing the sum over n first,

$$
\sum_n \frac{(a^\dagger a^{\dagger'} e^{-i\omega t})^n}{n!} = e^{a^\dagger a^{\dagger'} e^{-i\omega t}}.
$$

The propagator becomes some combination of Gaussian integrals:

$$K(x,t;x',0) = \frac{1}{2\pi}\sqrt{\frac{m\omega}{\pi\hbar}}e^{(\xi^2+\xi'^2-i\omega t)/2}\int_{-i\infty}^{i\infty}da^\dagger\int_{i\infty}^{-i\infty}da^{\dagger'}e^{-\sqrt{2}(\xi a^\dagger+\xi'a^{\dagger'})+(a^{\dagger 2}+a^{\dagger' 2})/2+a^\dagger a^{\dagger'}e^{-i\omega t}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{m\omega}{\pi\hbar}}e^{(\xi^2+\xi'^2-i\omega t)/2}\int_{-i\infty}^{i\infty}da^\dagger\,e^{-\sqrt{2}\xi a^\dagger+a^{\dagger 2}/2}\int_{i\infty}^{-i\infty}da^{\dagger'}\,e^{-(\sqrt{2}\xi'-a^\dagger e^{i\omega t})a^{\dagger'}+a^{\dagger' 2}/2}.$$

Making the change of variable $a^\dagger = ib$ and $a^{\dagger'} = -ib'$, and frequently using $\int e^{-(Ax^2+Bx)} = \sqrt{\pi/A}\,e^{B^2/4A}$,

$$K(x,t;x',0) = \frac{1}{2\pi}\sqrt{\frac{m\omega e^{-i\omega t}}{\pi\hbar}}e^{(\xi^2+\xi'^2)/2}\int_{-\infty}^{\infty}db\,e^{-i\sqrt{2}\xi b-b^2/2}\int_{-\infty}^{\infty}db'\,e^{i(\sqrt{2}\xi'-ibe^{-i\omega t})b'-b'^2/2}$$

$$= \frac{1}{2\pi}\sqrt{\frac{m\omega e^{-i\omega t}}{\pi\hbar}}e^{(\xi^2+\xi'^2)/2}\int_{-\infty}^{\infty}db\,e^{-i\sqrt{2}\xi b-b^2/2}\left[\sqrt{2\pi}e^{-(\sqrt{2}\xi'-ibe^{-i\omega t})^2/2}\right]$$

$$= \frac{1}{\sqrt{2\pi}}\sqrt{\frac{m\omega e^{-i\omega t}}{\pi\hbar}}e^{(\xi^2-\xi'^2)/2}\int_{-\infty}^{\infty}db\,e^{-(1-e^{-2i\omega t})b^2/2-i\sqrt{2}(\xi-\xi'e^{-i\omega t})b}$$

$$= \frac{1}{\sqrt{2\pi}}\sqrt{\frac{m\omega e^{-i\omega t}}{\pi\hbar}}e^{(\xi^2-\xi'^2)/2}\left[\sqrt{\frac{2\pi}{1-e^{-2i\omega t}}}e^{-2(\xi-\xi'e^{-i\omega t})^2/2(1-e^{-2i\omega t})}\right]$$

$$= \sqrt{\frac{m\omega}{\pi\hbar(e^{i\omega t}-e^{-i\omega t})}}\exp\left[-\frac{\xi^2 e^{i\omega t}-2\xi\xi'+\xi'^2 e^{-i\omega t}}{e^{i\omega t}-e^{-i\omega t}}+\frac{1}{2}\xi^2-\frac{1}{2}\xi'^2\right]$$

$$= \sqrt{\frac{m\omega}{2\pi i\hbar\sin\omega t}}\exp\left[\frac{-\xi^2 e^{i\omega t}/2+2\xi\xi'-\xi'^2 e^{-i\omega t}/2-\xi^2 e^{-i\omega t}/2-\xi'^2 e^{i\omega t}/2}{e^{i\omega t}-e^{-i\omega t}}\right]$$

$$= \sqrt{\frac{m\omega}{2\pi i\hbar\sin\omega t}}\exp\left\{\frac{i}{2\sin\omega t}[(\xi^2+\xi'^2)\cos\omega t-2\xi\xi']\right\}.$$

Changing to the original variable by $\xi = (\sqrt{m\omega/\hbar})x$ and $\xi' = (\sqrt{m\omega/\hbar})x'$ gives the desired result (3.19):

$$K(x,t;x',0) = \sqrt{\frac{m\omega}{2\pi i\hbar\sin\omega t}}\exp\left\{\frac{im\omega}{2\hbar\sin\omega t}[(x^2+x'^2)\cos\omega t-2xx']\right\}.$$

B.2.5 Propagator from the Path Integral Formulation

To be written.

B.2.6 The 3D Harmonic Oscillator in Spherical Coordinates

To be written.

B.3 Dirac Delta Function

B.3.1 Equality Involving Delta Functions

Two expressions $D_1(x)$ and $D_2(x)$ involving delta functions are said to be equal if

$$\int_{-\infty}^{\infty} f(x) D_1(x)\, dx = \int_{-\infty}^{\infty} f(x) D_2(x)\, dx$$

for every ordinary function $f(x)$.

Example B.3.

Consider $D_1(x) = \delta(cx)$, where $c \neq 0$ is a real constant. Assuming $c > 0$, multiply any ordinary function $f(x)$ to $D_1(x)$ and integrate,

$$\int_{-\infty}^{\infty} f(x) \delta(cx)\, dx = \int_{-\infty}^{\infty} \frac{f(y)\delta(y)\, dy}{c} = \frac{f(0)}{c},$$

where we make a change of variable $y = cx$. Consider $D_2(x) = \delta(x)/c$,

$$\int_{-\infty}^{\infty} f(x) \left[\frac{\delta(x)}{c}\right] dx = \frac{f(0)}{c}.$$

Combining the two integral results, we find that

$$\delta(cx) = \frac{1}{c}\delta(x), \quad [c > 0].$$

If $c < 0$,

$$\int_{-\infty}^{\infty} f(x)\delta(cx)\, dx = \int_{\infty}^{-\infty} \frac{f(y)\delta(y)\, dy}{c} = \frac{f(0)}{-c} \quad \Longrightarrow \quad \delta(cx) = \frac{1}{-c}\delta(x), \quad [c < 0].$$

Thus, for any real nonzero c,

$$\delta(cx) = \frac{1}{|c|}\delta(x).$$

Example B.4. Delta function of a function

Let $f(x)$ be a well-behaved function. Then

$$\delta(f(x)) = \sum_i \frac{\delta(x - x_i)}{|f'(x_i)|}, \quad \text{where} \quad f'(x_i) = \left.\frac{df}{dx}\right|_{x_i},$$

and each x_i is a zero of $f(x)$. We prove it by considering another test function and its integral with $\delta(f(x))$. Since $\delta(f(x))$ is nonzero only when $f(x) = 0$, we can divide the domain of $f(x)$ into small intervals around zeros of f, namely $[x_i - \epsilon, x_i + \epsilon]$. Then

$$\int_{-\infty}^{\infty} g(x)\delta(f(x))\, dx = \sum_i \int_{x_i-\epsilon}^{x_i+\epsilon} g(x)\delta(f(x))\, dx.$$

Making a change of variable $u = f(x)$, $x = f^{-1}(u)$. (This requires $f(x)$ to be a well-behaved function such that the inverse exist at least around each x_i.) The integral becomes

$$\int_{-\infty}^{\infty} g(x)\delta(f(x))\, dx = \sum_i \int_{f(x_i-\epsilon)}^{f(x_i+\epsilon)} g(f^{-1}(u))\delta(u)\, d[f^{-1}(u)] = \sum_i \int_{f(x_i-\epsilon)}^{f(x_i+\epsilon)} \frac{g(f^{-1}(u))}{f'(f^{-1}(u))}\delta(u)\, du.$$

There are two cases. If $f'(x_i) > 0$, then $f(x_i + \epsilon) > f(x_i - \epsilon)$, so

$$\int_{f(x_i-\epsilon)}^{f(x_i+\epsilon)} \frac{g(f^{-1}(u))}{f'(f^{-1}(u))}\delta(u)\, du = \frac{g(f^{-1}(f(x_i)))}{f'(f^{-1}(f(x_i)))} = \frac{g(x_i)}{f'(x_i)} = \int_{-\infty}^{\infty} \frac{\delta(x - x_i)}{f'(x_i)} g(x)\, dx.$$

If $f'(x_i) < 0$, then $f(x_i + \epsilon) < f(x_i - \epsilon)$, so switching the limit gives a minus sign,

$$\int_{f(x_i-\epsilon)}^{f(x_i+\epsilon)} \frac{g(f^{-1}(u))}{f'(f^{-1}(u))}\delta(u)\,du = -\frac{g(f^{-1}(f(x_i)))}{f'(f^{-1}(f(x_i)))} = -\frac{g(x_i)}{f'(x_i)} = -\int_{-\infty}^{\infty} \frac{\delta(x-x_i)}{f'(x_i)}g(x)\,dx.$$

The two cases can be combined to a single argument:

$$\int_{-\infty}^{\infty} g(x)\delta(f(x))\,dx = \sum_i \int g(x)\frac{\delta(x-x_i)}{|f'(x_i)|}\,dx \quad \Longrightarrow \quad \delta(f(x)) = \sum_i \frac{\delta(x-x_i)}{|f'(x_i)|}.$$

This general expression reduces to the previous example when $f(x) = cx$.

Example B.5. Relation to the Gaussian

The delta function distribution is a limit of a gaussian distribution: for $\epsilon > 0$,

$$\delta(x) = \lim_{\epsilon \to 0} \frac{1}{\sqrt{\pi\epsilon}} e^{-x^2/\epsilon}. \tag{B.5}$$

To be written.

B.3.2 The Step Function

Consider the **Heaviside step function** $\theta(x)$:

$$\theta(x) \equiv \begin{cases} 1, & x > 0, \\ 0, & x < 0. \end{cases} \tag{B.6}$$

In most cases, the value at $x = 0$ does not matter. Here we let $\theta(0) = 1/2$. The derivative of $\theta(x)$ is the delta function:

$$\frac{d\theta}{dx} = \delta(x). \tag{B.7}$$

Proof. Multiplying the LHS of (B.7) by an ordinary function $f(x)$ and integrating:

$$\int_{-\infty}^{\infty} f(x)\frac{d\theta}{dx}\,dx = f(x)\theta(x)\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \theta(x)\frac{df}{dx}\,dx = f(\infty) - \int_0^{\infty} \frac{df}{dx}\,dx = f(\infty) - [f(\infty) - f(0)] = f(0).$$

Do the same for the RHS of (B.7),

$$\int_{-\infty}^{\infty} f(x)\delta(x)\,dx = f(0).$$

Hence

$$\int_{-\infty}^{\infty} f(x)\frac{d\theta}{dx}\,dx = \int_{-\infty}^{\infty} f(x)\delta(x)\,dx.$$

$\square$

B.3.3 Fourier Transform of the Delta Function

Let $f(x) = \delta(x)$. The Fourier transform of the delta function is

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

An inverse Fourier transform shows that

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

This gives a extremely useful equation:

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx}\, dk. \tag{B.8}$$

If handled with care, (B.8) helps eliminate integrals, just like the Kronecker delta δ_{mn}, which eliminate sums.

B.3.4   Orthogonality of Bound State and Scattering States

The bound state of the delta-function well is orthogonal to the scattering states.

Proof. The bound state is (1.33)

$$\psi_b = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2}.$$

The scattering states are

$$\psi_{sc} = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < 0, \\ Fe^{ikx} + Ge^{-ikx}, & x > 0. \end{cases}$$

The constraints (continuity of ψ_{sc} and discontinuity of $d\psi_{sc}/dx$) are

$$F + G = A + B \quad \text{and} \quad ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A + B).$$

Do the integral:

$$
\begin{aligned}
\int_{-\infty}^{\infty} \psi_b^* \psi_{sc}\, dx &= \frac{\sqrt{m\alpha}}{\hbar} \left[\int_{-\infty}^{0} e^{m\alpha x/\hbar^2}(Ae^{ikx} + Be^{-ikx})\, dx + \int_{0}^{\infty} e^{-m\alpha x/\hbar^2}(Fe^{ikx} + Ge^{-ikx})\, dx \right] \\
&= \frac{\sqrt{m\alpha}}{\hbar} \left[A\int_{-\infty}^{0} e^{(m\alpha/\hbar^2 + ik)x}\, dx + B\int_{-\infty}^{0} e^{(m\alpha/\hbar^2 - ik)x}\, dx + F\int_{0}^{\infty} e^{(-m\alpha/\hbar^2 + ik)x}\, dx + G\int_{0}^{\infty} e^{(-m\alpha/\hbar^2 - ik)x}\, dx \right] \\
&= \frac{\sqrt{m\alpha}}{\hbar} \left[\frac{Ae^{(m\alpha/\hbar^2 + ik)x}}{m\alpha/\hbar^2 + ik} \bigg|_{-\infty}^{0} + \frac{Be^{(m\alpha/\hbar^2 - ik)x}}{m\alpha/\hbar^2 - ik} \bigg|_{-\infty}^{0} + \frac{Fe^{(-m\alpha/\hbar^2 + ik)x}}{-m\alpha/\hbar^2 + ik} \bigg|_{0}^{\infty} + \frac{Ge^{(-m\alpha/\hbar^2 - ik)x}}{-m\alpha/\hbar^2 - ik} \bigg|_{0}^{\infty} \right] \\
&= \frac{\sqrt{m\alpha}}{\hbar} \left(\frac{A}{m\alpha/\hbar^2 + ik} + \frac{B}{m\alpha/\hbar^2 - ik} - \frac{F}{-m\alpha/\hbar^2 + ik} - \frac{G}{-m\alpha/\hbar^2 - ik} \right) \\
&= \frac{\sqrt{m\alpha}}{\hbar} \left(\frac{A + G}{m\alpha/\hbar^2 + ik} + \frac{B + F}{m\alpha/\hbar^2 - ik} \right) \\
&= \frac{\sqrt{m\alpha}}{\hbar} \left[\frac{(m\alpha/\hbar^2 - ik)(A + G) + (m\alpha/\hbar^2 + ik)(B + F)}{(m\alpha/\hbar^2)^2 + k^2} \right] \\
&= \frac{\sqrt{m\alpha}}{\hbar} \left[\frac{(m\alpha/\hbar^2)(A + B + F + G) + ik(B + F - A - G)}{(m\alpha/\hbar^2)^2 + k^2} \right].
\end{aligned}
$$

By the two constraints above,

$$A + B + F + G = 2(A + B) \quad \text{and} \quad ik(B + F - A - G) = -\frac{2m\alpha}{\hbar^2}(A + B),$$

the integral becomes

$$\int_{-\infty}^{\infty} \psi_b^* \psi_{sc}\, dx = \frac{\sqrt{m\alpha}}{\hbar} \left[\frac{(2m\alpha/\hbar^2)(A + B) - (2m\alpha/\hbar^2)(A + B)}{(m\alpha/\hbar^2)^2 + k^2} \right] = 0.$$

The bound state and scattering states are orthogonal. $\square$

B.4 Finite Square Well

B.4.1 Odd Solution of Bound States

Back to the general solution of bound states:

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

If the solution is odd, then

$$\psi(x) = \begin{cases} -Fe^{\kappa x}, & x < -a, \\ C\sin(\ell x), & -a < x < a, \\ Fe^{-\kappa x}, & x > a. \end{cases}$$

Imposing continuity of ψ and $d\psi/dx$ at $x = a$ gives

$$C\sin(\ell a) = Fe^{-\kappa a},$$
$$C\ell\cos(\ell a) = -\kappa Fe^{-\kappa a}.$$

Dividing the second equation by the first,

$$\kappa = -\ell\cot(\ell a).$$

Again define $z \equiv \ell a$ and $z_0 \equiv \frac{a}{\hbar}\sqrt{2mV_0}$. Using $\kappa = \sqrt{-2mE}/\hbar$ and $\ell = \sqrt{2m(E + V_0)}/\hbar$, we can find that

$$\cot z = -\frac{\kappa}{\ell} = -\frac{\sqrt{-2mE}}{\sqrt{2m(E + V_0)}} = -\sqrt{\frac{2mV_0}{2m(E + V_0)} - 1} = -\sqrt{\left(\frac{z_0}{z}\right)^2 - 1}.$$

We need to solve the transcendental equation

$$\boxed{\cot z = -\sqrt{\left(\frac{z_0}{z}\right)^2 - 1}.}$$

Two graphical solutions are shown in Figure B.1.
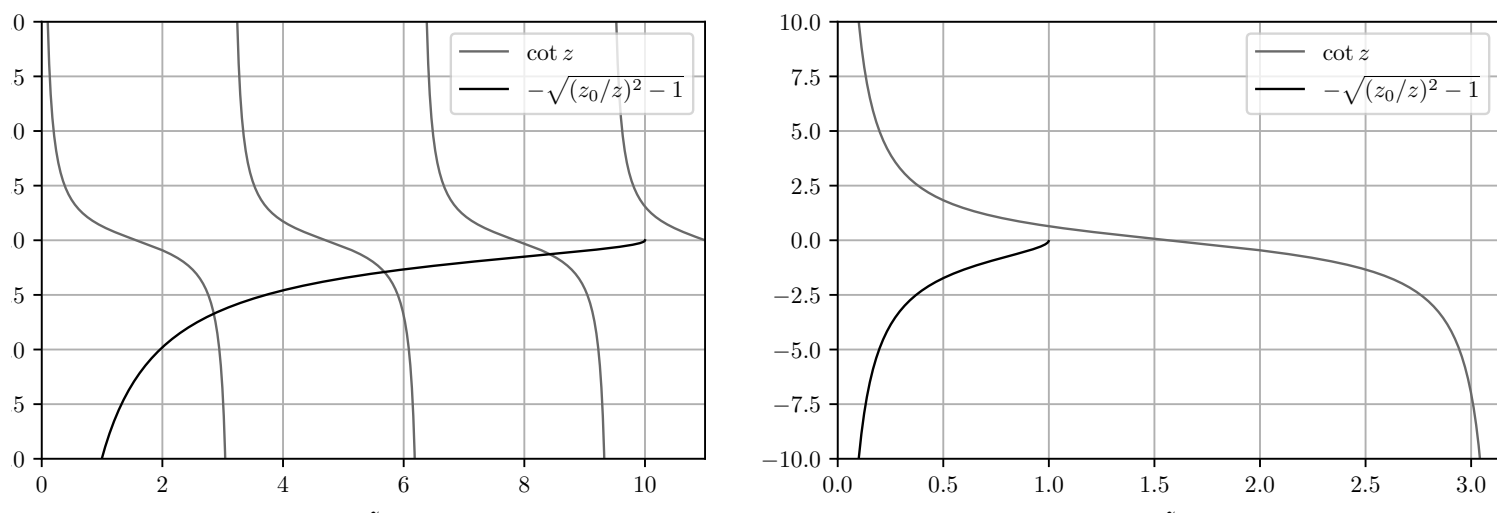

Figure B.1: Graphical solutions to $\cot z = -\sqrt{(z_0/z)^2 - 1}$. The left figure is a wide, deep well with $z_0 = 10$. The right figure is a narrow, shallow well with $z_0 = 1$.

- **Wide, deep well.** If $z_0 \to \infty$, then $\cot z \to \infty$, or $z \simeq n\pi$. By the definition of z,

$$z \equiv \ell a = \frac{\sqrt{2m(E + V_0)}\, a}{\hbar} \simeq n\pi.$$

The allowed energies are

$$E_n + V_0 \simeq \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad n = 1, 2, 3, \ldots$$

or, in terms of energy levels of the infinite square well with width $2a$, the odd solutions to the finite square well admit even n's,

$$E_n + V_0 \simeq \frac{n^2\pi^2\hbar^2}{2m(2a)^2}, \quad n = 2, 4, 6, \ldots$$

This compensates the even solutions, where all n's are odd.

- **Narrow, shallow well.** In contrast with even solutions, an odd solution may not have a bound state. From the Figure B.1 (right), we see that there is no intersections between two functions. In fact, it requires $z_0 > \pi/2$ to have at least one bound state because $\cot z$ becomes negative when $z > \pi/2$. Equivalently, the condition on V_0 is $V_0 > \pi^2\hbar^2/8ma^2$.

B.4.2   Reflected amplitude and Transmitted Amplitude

The equations to use are the boundary conditions:

$$\begin{cases} Ae^{-ika} + Be^{ika} = -C\sin(\ell a) + D\cos\ell a, & \text{[continuity of } \psi \text{ at } -a], \\ ik[Ae^{-ika} - Be^{ika}] = \ell[C\cos(\ell a) + D\sin(\ell a)], & \text{[continuity of } d\psi/dx \text{ at } -a], \\ C\sin(\ell a) + D\cos(\ell a) = Fe^{ika}, & \text{[continuity of } \psi \text{ at } +a], \\ \ell[C\cos(\ell a) - D\sin(\ell a)] = ikFe^{ika}, & \text{[continuity of } d\psi/dx \text{ at } +a]. \end{cases}$$

Multiply the third equation by $\sin(\ell a)$ and the fourth equation by $\frac{1}{\ell}\cos(\ell a)$,

$$\begin{cases} C\sin^2(\ell a) + D\sin(\ell a)\cos(\ell a) = Fe^{ika}\sin(\ell a), \\ C\cos^2(\ell a) - D\sin(\ell a)\cos(\ell a) = \frac{ik}{\ell}Fe^{ika}\cos(\ell a), \end{cases} \implies C = Fe^{ika}\left[\sin(\ell a) + \frac{ik}{\ell}\cos(\ell a)\right].$$

Plug in C into either equation can give

$$D = Fe^{ika}\left[\cos(\ell a) - \frac{ik}{\ell}\sin(\ell a)\right].$$

Substitute C into the first two boundary conditions:

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

$$= -Fe^{ika}\left[\sin(\ell a) + \frac{ik}{\ell}\cos(\ell a)\right]\sin(\ell a) + Fe^{ika}\left[\cos(\ell a) - \frac{ik}{\ell}\sin(\ell a)\right]\cos(\ell a)$$

$$= Fe^{ika}\left[-\sin^2(\ell a) - \frac{ik}{\ell}\sin(\ell a)\cos(\ell a) + \cos^2(\ell a) - \frac{ik}{\ell}\sin(\ell a)\cos(\ell a)\right]$$

$$Ae^{-ika} + Be^{ika} = Fe^{ika}\left[\cos(2\ell a) - \frac{ik}{\ell}\sin(2\ell a)\right],$$

$$Ae^{-ika} - Be^{ika} = -\frac{i\ell}{k}[C\cos(\ell a) + D\sin(\ell a)]$$

$$= -\frac{i\ell}{k}Fe^{ika}\left\{\left[\sin(\ell a) + \frac{ik}{\ell}\cos(\ell a)\right]\cos(\ell a) + \left[\cos(\ell a) - \frac{ik}{\ell}\sin(\ell a)\right]\sin(\ell a)\right\}$$

$$= -\frac{i\ell}{k}Fe^{ika}\left(\sin(\ell a)\cos(\ell a) + \frac{ik}{\ell}\cos^2(\ell a) + \sin(\ell a)\cos(\ell a) - \frac{ik}{\ell}\sin^2(\ell a)\right)$$

$$= -\frac{i\ell}{k}Fe^{ika}\left[\sin(2\ell a) + \frac{ik}{\ell}\cos(2\ell a)\right]$$

$$Ae^{-ika} - Be^{ika} = Fe^{ika}\left[\cos(2\ell a) - \frac{i\ell}{k}\sin(2\ell a)\right].$$

Solving for A and B using the system of equations above: for A,

$$2Ae^{-ika} = Fe^{ika}\left[2\cos(2\ell a) - i\left(\frac{k}{\ell} + \frac{\ell}{k}\right)\sin(2\ell a)\right] \implies F = \frac{e^{-2ika}A}{\cos(2\ell a) - i\frac{k^2+\ell^2}{2k\ell}\sin(2\ell a)}.$$

For B,

$$2Be^{ika} = Fe^{ika}\left[i\left(\frac{\ell}{k} - \frac{k}{\ell}\right)\sin(2\ell a)\right] \quad \Longrightarrow \quad B = i\frac{\ell^2 - k^2}{2k\ell}\sin(2\ell a)F.$$

The inverse of the transmission coefficient is

$$\begin{aligned}
T^{-1} = \frac{|A|^2}{|F|^2} &= \left|\cos(2\ell a) - i\frac{k^2 + \ell^2}{2k\ell}\sin(2\ell a)\right|^2 \\
&= \cos^2(2\ell a) + \frac{(k^2 + \ell^2)^2}{(2k\ell)^2}\sin^2(2\ell a) \\
&= 1 - \sin^2(2\ell a) + \frac{(k^2 + \ell^2)^2}{(2k\ell)^2}\sin^2(2\ell a) \\
&= 1 + \sin^2(2\ell a)\left[\frac{(k^2 + \ell^2)^2}{(2k\ell)^2} - 1\right] \\
&= 1 + \frac{(k^2 - \ell^2)^2}{(2k\ell)^2}\sin^2(2\ell a).
\end{aligned}$$

By the definitions $k \equiv \sqrt{2mE}/\hbar$ and $\ell \equiv \sqrt{2m(E + V_0)}/\hbar$,

$$k^2 - \ell^2 = -\frac{2mV_0}{\hbar^2}, \quad (2k\ell)^2 = 4\left(\frac{2m}{\hbar^2}\right)^2 E(E + V_0).$$

The (inverse of) transmission coefficient in terms of E and V_0 is

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

B.4.3 Transmitted Particles with a Different Wavenumber

Example B.6. A Step Potential

Consider a step potential

$$V(x) = \begin{cases} 0, & x \leq 0, \\ V_0, & x > 0. \end{cases}$$

Assume that $E < V_0$ and there is no incident wave from the right. The wave function is

$$\psi = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < 0, \\ Fe^{-\kappa x}, & x > 0, \end{cases} \quad \text{where} \quad k = \frac{\sqrt{2mE}}{\hbar}, \quad \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}.$$

The continuity of ψ and $d\psi/dx$ provides

$$A + B = F \quad \text{and} \quad ik(A - B) = -\kappa F.$$

Solving for A and B gives

$$B = -\frac{1 + ik/\kappa}{1 - ik/\kappa}A \quad \Longrightarrow \quad R = \frac{|B|^2}{|A|^2} = \frac{|1 + ik/\kappa|^2}{|1 - ik/\kappa|^2} = 1.$$

Interestingly, even though the wave function is nonzero at $x > 0$, the reflection coefficient is 1.

If we assume that $E > V_0$, the wave function is

$$\psi = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < 0, \\ Fe^{i\ell x}, & x > 0, \end{cases} \quad \text{where} \quad k = \frac{\sqrt{2mE}}{\hbar}, \quad \ell = \frac{\sqrt{2m(E - V_0)}}{\hbar}.$$

The continuity of ψ and $d\psi/dx$ provides

$$A + B = F \quad \text{and} \quad ik(A - B) = i\ell F.$$

Solving for B and F in terms of A and the reflection coefficient,

$$B = -\frac{1 - k/\ell}{1 + k/\ell}A, \quad F = \frac{2k}{k + \ell}A, \quad \implies \quad R = \frac{|B|^2}{|A|^2} = \frac{(1 - k/\ell)^2}{(1 + k/\ell)^2} = \frac{(k - \ell)^4}{(k^2 - \ell^2)^2}.$$

Substituting k and ℓ in terms of E and V_0, we find that

$$R = \frac{(\sqrt{E} - \sqrt{E - V_0})^4}{V_0^2}.$$

The problem is to find the transmission coefficient T. Because the free particles e^{ikx} and $e^{i\ell x}$ does not have the same wave number, the transmission coefficient is not simply $|F|^2/|A|^2$. Physically, the transmission coefficient indicates the probability of the particle to transmit through the barrier, so T is related to the probability current J. The incident part of the wave function is $\psi_i = Ae^{ikx}$. Its probability current (using Equation 1.4) is

$$J_i = \frac{i\hbar}{2m}\left(\frac{d\psi_i^*}{dx}\psi_i - \psi_i^*\frac{d\psi_i}{dx}\right) = \frac{i\hbar}{2m}(-ik|A|^2 - ik|A|^2) = \frac{\hbar k}{m}|A|^2.$$

Similarly, the transmitted part of the wave function is $\psi_t = Fe^{i\ell x}$, so its probability current is

$$J_t = \frac{\hbar \ell}{m}|F|^2.$$

It is natural to think that the transmission coefficient, or probability, is the ratio of the transmission probability current J_t and the incident J_i.

$$T = \frac{J_t}{J_i} = \frac{|F|^2}{|A|^2}\frac{\ell}{k} = \left(\frac{2k}{k + \ell}\right)^2\frac{\ell}{k} = \frac{4k\ell}{(k + \ell)^2} = \frac{4\sqrt{E(E - V_0)}(\sqrt{E} - \sqrt{E - V_0})^2}{V_0^2}.$$

To check whether this transmission coefficient derived from probability currents is correct, we add T and R:

$$T + R = \frac{4k\ell}{(k + \ell)^2} + \frac{(k - \ell)^2}{(k + \ell)^2} = \frac{(k + \ell)^2}{(k + \ell)^2} = 1.$$

The probability is indeed conserved.

B.5   The Momentum Space

B.5.1   Normalization

Provided that the position-space wave function $\Psi(x,t)$ is normalized, the momentum-space wave function is also normalized,

$$\int_{-\infty}^{\infty} |\Phi(p,t)|^2 \, dp = 1.$$

Proof. By (2.14), we can write the normalization condition of $\Psi(x,t)$ as

$$\begin{aligned}
1 &= \int |\Psi(x,t)|^2 \, dx = \int \left[\frac{1}{\sqrt{2\pi\hbar}} \int e^{-ip'x/\hbar} \Phi^*(p',t) \, dp' \right] \left[\frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \Phi(p,t) \, dp \right] dx \\
&= \frac{1}{2\pi\hbar} \iiint e^{i(p-p')x/\hbar} \Phi^*(p',t) \Phi(p,t) \, dp' \, dp \, dx \\
&= \iint \delta(p-p') \Phi^*(p',t) \Phi(p,t) \, dp' \, dp \\
&= \int |\Phi(p,t)|^2 \, dp.
\end{aligned}$$

$\square$

B.5.2   Operators

From (2.14), we can write the expectation value of x as

$$\begin{aligned}
\langle x \rangle &= \int \Psi^* x \Psi = \int \left[\frac{1}{\sqrt{2\pi\hbar}} \int e^{-ip'x/\hbar} \Phi^*(p',t) \, dp' \right] (x) \left[\frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \Phi(p,t) \, dp \right] dx \\
&= \frac{1}{2\pi\hbar} \iint e^{-ip'x/\hbar} \Phi^*(p',t) \, dp' \left[\int \left(-i\hbar \frac{\partial}{\partial p} e^{ipx/\hbar} \right) \Phi(p,t) \, dp \right] dx
\end{aligned}$$

Using integration by parts on the last integral,

$$\begin{aligned}
\langle x \rangle &= \frac{1}{2\pi\hbar} \iiint e^{-ip'x/\hbar} \Phi^*(p',t) e^{ipx/\hbar} \left[i\hbar \frac{\partial}{\partial p} \Phi(p,t) \right] dp' \, dp \, dx \\
&= \frac{1}{2\pi\hbar} \iiint e^{i(p-p')x/\hbar} \Phi(p',t) \left[i\hbar \frac{\partial}{\partial p} \Phi(p,t) \right] dp' \, dp \, dx \\
&= \iint \delta(p-p') \Phi(p',t) \left[i\hbar \frac{\partial}{\partial p} \Phi(p,t) \right] dp' \, dp \\
&= \int \Phi^*(p,t) \left(i\hbar \frac{\partial}{\partial p} \right) \Phi(p,t) \, dp.
\end{aligned}$$

Recall that the momentum operator in position space is defined as

$$\langle p \rangle = \int \Psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(x,t) \, dx \quad \implies \quad p = -i\hbar \frac{\partial}{\partial x} \quad \text{[in position space]}.$$

The form of position operator in momentum space is almost identical (with a minus sign difference)

$$\langle x \rangle = \int \Phi^*(p,t) \left(i\hbar \frac{\partial}{\partial p} \right) \Phi(p,t) \, dx \quad \implies \quad x = i\hbar \frac{\partial}{\partial p} \quad \text{[in momentum space]}.$$

Evidently, the momentum operator $\hat{p}$ in momentum space is just p, just like $\hat{x} = x$ in position space:

$$
\begin{aligned}
\langle p \rangle = \int \Psi^* p \Psi &= \int \left[\frac{1}{\sqrt{2\pi\hbar}} \int e^{-ip'x/\hbar} \Phi^*(p',t)\,dp' \right] \left(-i\hbar \frac{\partial}{\partial x} \right) \left[\frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \Phi(p,t)\,dp \right] dx \\
&= \frac{1}{2\pi\hbar} \iiint e^{-ip'x/\hbar} \Phi^*(p',t)(p)e^{ipx/\hbar}\Phi(p,t)\,dp'\,dp\,dx \\
&= \frac{1}{2\pi\hbar} \iiint e^{i(p-p')x/\hbar} \Phi^*(p',t)(p)\Phi(p,t)\,dp'\,dp\,dx \\
&= \iint \delta(p-p')\Phi^*(p',t)(p)\Phi(p,t)\,dp'\,dp \\
&= \int \Phi^*(p,t)(p)\Phi(p,t)\,dp \quad \Longrightarrow \quad \hat{p} = p \quad \text{[in momentum space]}.
\end{aligned}
$$

As a check, we need to find some relation between x and p that does not depend on the space we are in. That relation is their commutator $[x,p] = i\hbar$—note that $i\hbar$ is just a constant, so it must be true in momentum space as well. Consider a test function $f(p)$. In momentum space,

$$
[\hat{x},\hat{p}]f(p) = \hat{x}(\hat{p}f) - \hat{p}(\hat{x}f) = i\hbar \frac{\partial}{\partial p}[pf] - pi\left(\hbar \frac{\partial f}{\partial p} \right) = i\hbar f + i\hbar p \frac{\partial f}{\partial p} - i\hbar p \frac{\partial f}{\partial p} = i\hbar f \quad \Longrightarrow \quad [x,p] = i\hbar.
$$

The commutation relation still holds in momentum space.

In general, the expectation value of a generic observable $Q(x,p,t)$ can be calculated in both position and momentum space because it is just a number,

$$
\langle Q(x,p,t) \rangle = \begin{cases} \displaystyle\int \Psi^* \hat{Q}(x, -i\hbar\partial_x, t)\Psi\,dx, & \text{[position space]}, \\[2ex] \displaystyle\int \Phi^* \hat{Q}(i\hbar\partial_p, p, t)\Phi\,dp, & \text{[momentum space]}. \end{cases}
$$

B.5.3   The Schrödinger Equations

The Harmonic Oscillator.   The Schrödinger equation for the harmonic oscillator is

$$
-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \Psi = i\hbar \frac{\partial \Psi}{\partial t}.
$$

Substitute the Fourier transform of $\Psi(x,t)$,

$$
-\frac{\hbar^2}{2m} \frac{1}{\sqrt{2\pi\hbar}} \int \frac{\partial^2}{\partial x^2} e^{ipx/\hbar}\Phi(p,t)\,dp + \frac{1}{2}m\omega^2 x^2 \frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar}\Phi(p,t)\,dp = \frac{i\hbar}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \frac{\partial \Phi}{\partial t}\,dp.
$$

$$
\frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \left[\frac{p^2}{2m}\Phi(p,t) \right] dp + \frac{1}{\sqrt{2\pi\hbar}} \int \frac{\partial^2}{\partial p^2} e^{ipx/\hbar} \left[-\frac{1}{2}m\hbar^2\omega^2 \Phi(p,t) \right] dp = \frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \left(i\hbar \frac{\partial \Phi}{\partial t} \right) dp.
$$

Do integration by parts for the second term (see Theorem B.1),

$$
\int \frac{\partial^2}{\partial p^2} e^{ipx/\hbar}\Phi(p,t)\,dp = -\int \frac{\partial}{\partial p} e^{ipx/\hbar} \frac{\partial \Phi}{\partial p}\,dp = +\int e^{ipx/\hbar} \frac{\partial^2 \Phi}{\partial p^2}\,dp.
$$

Thus, the Fourier transformed Schrödinger equation is

$$
\frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \left[-\frac{1}{2}m\hbar^2\omega^2 \frac{\partial^2 \Phi}{\partial p^2} + \frac{p^2}{2m}\Phi(p,t) \right] dp = \frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \left(i\hbar \frac{\partial \Phi}{\partial p} \right) dp.
$$

Two functions with the same Fourier transform are equal, so

$$
\boxed{ -\frac{1}{2}m\hbar^2\omega^2 \frac{\partial^2 \Phi}{\partial p^2} + \frac{p^2}{2m}\Phi = i\hbar \frac{\partial \Phi}{\partial t}. }
$$

Alternatively, since we know $p \to p$ and $x \to i\hbar\partial_p$ in momentum space, directly replacing these operators in the Schrödinger equation gives the same result. Note that the harmonic oscillator equation in momentum space has the same form as in position space: second derivatives in momentum as the "kinetic term", and squared momentum as the "potential term". This means we can use exactly the same method to solve this new harmonic oscillator equation.

The time-independent Schrödinger equation is

$$-\frac{1}{2}m\hbar^2\omega^2\frac{\partial^2\phi}{\partial p^2} + \frac{p^2}{2m}\phi = E\phi \quad\Longrightarrow\quad -m\hbar\omega\frac{\partial^2\phi}{\partial p^2} + \frac{p^2}{m\hbar\omega}\phi = \frac{2E}{\hbar\omega}\phi.$$

Define $\chi \equiv p/\sqrt{m\hbar\omega}$ and $K \equiv 2E/\hbar\omega$,

$$\frac{d^2\phi}{d\chi^2} = (\chi^2 - K)\phi.$$

This has the same form as (1.16). Following exactly the same analytic method and normalization, we will get

$$\boxed{\phi_n(p) = \left(\frac{1}{\pi m\hbar\omega}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}H_n(\chi)e^{-\chi^2/2}.}$$

$H_n(\chi)$ are Hermite polynomials with argument χ. Now consider the ground state in position and momentum space, It is expected that the Fourier transform of $\psi_0(x)$ will give $\phi_0(p)$.

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}e^{-m\omega x^2/2\hbar} \quad\Longleftrightarrow\quad \phi_0(p) = \left(\frac{1}{\pi m\hbar\omega}\right)^{1/4}e^{-p^2/2m\hbar\omega}.$$

As a check, we shall compute the Fourier transform

$$\mathcal{F}[\psi_0(x)] = \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\int_{-\infty}^{\infty}e^{-ipx/\hbar}e^{-m\omega x^2/2\hbar}\,dx.$$

Here is a new way to compute it: let $F(p)$ be the integral,

$$\frac{dF}{dp} = \frac{d}{dp}\int_{-\infty}^{\infty}e^{-ipx/\hbar}e^{-m\omega x^2/2\hbar}\,dx = -\frac{ix}{\hbar}\int_{-\infty}^{\infty}e^{-ipx/\hbar}e^{-m\omega x^2/2\hbar} = +\frac{i}{m\omega}\int_{-\infty}^{\infty}e^{-ipx/\hbar}\frac{d}{dx}\left(e^{-m\omega x^2/2\hbar}\right)dx.$$

Using integration by parts,

$$\frac{dF}{dp} = \frac{i}{m\omega}\left[\cancel{e^{-ipx/\hbar}e^{-m\omega x^2/2\hbar}}\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}e^{-m\omega x^2/2\hbar}d\left(e^{-ipx/\hbar}\right)\right] = -\frac{p}{m\hbar\omega}\int e^{-ipx/\hbar}e^{-m\omega x^2/2\hbar}\,dx = -\frac{p}{m\hbar\omega}F.$$

In other words, the general solution to this differential equation is $F = Ae^{-p^2/2m\hbar\omega}$. To determine A, a convenient boundary condition is

$$A = F(0) = \int_{-\infty}^{\infty}e^{-m\omega x^2/2\hbar}\,dx = \sqrt{\frac{2\hbar}{m\omega}}\int_{-\infty}^{\infty}e^{-y^2}\,dy = \sqrt{\frac{2\pi\hbar}{m\omega}}.$$

Thus,

$$F = \int_{-\infty}^{\infty}e^{ipx/\hbar}e^{-m\omega x^2/2\hbar}\,dx = \sqrt{\frac{2\pi\hbar}{m\omega}}e^{-p^2/2m\hbar\omega},$$

and the Fourier transform of $\psi_0(x)$ is indeed $\phi_0(x)$,

$$\mathcal{F}[\psi_0(x)] = \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\sqrt{\frac{2\pi\hbar}{m\omega}}e^{-p^2/2m\hbar\omega} = \left(\frac{1}{\pi m\hbar\omega}\right)^{1/4}e^{-p^2/2m\hbar\omega} = \phi_0(p).$$

The Free Particle. To be written.

The Hydrogen Atom. To be written.

B.6 Quantum Mechanics in Three Dimensions

B.6.1 The Earth-Sun System

The potential of the Earth-Sun system is

$$V(r) = -\frac{GMm}{r},$$

where M and m are the mass of the Sun and Earth, respectively. To find the gravitational analog of the hydrogen atom in the Earth-Sun system, we just replace every $e^2/4\pi\epsilon_0$ by GMm. For example, the "Bohr radius" a_g of the Earth-Sun system is

$$a_g = \frac{\hbar^2}{GMm^2} \quad \Longleftarrow \quad a = \frac{4\pi\epsilon_0\hbar^2}{me^2}.$$

It is approximately $a_g \approx 2.34 \times 10^{-138}$ m. The "allowed energies" of the Earth-Sun system is

$$E_n = -\left[\frac{m}{2\hbar^2}(GMm)^2\right]\frac{1}{n^2} \quad \Longleftarrow \quad E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}.$$

Classically, the Earth-Sun system obeys the virial theorem—the kinetic energy T and potential energy V follows $V = -2T$. Hence the total energy of the system is

$$E_{\text{tot}} = T + V = -\frac{1}{2}V = \frac{-GMm}{2r_0},$$

where we assume that the Earth has a circular orbit of radius r_0 around the Sun. If $E_n = E_{\text{tot}}$, the "principle quantum number" of the Earth follows

$$-\left[\frac{m}{2\hbar^2}(GMm)^2\right]\frac{1}{n^2} = -\frac{GMm}{2r_0} \quad \Longrightarrow \quad n = \sqrt{\frac{GMm^2r_0}{\hbar^2}} = \sqrt{\frac{r_0}{a_g}}.$$

The (average) Earth-Sun distance is $r_0 = 1.496 \times 10^{11}$ m, so the energy level of the Earth is about $n \approx 2.53 \times 10^{74}$. Suppose the energy level of the Earth drops from n to $n-1$. The change in energy is

$$\Delta E = -\frac{G^2M^2m^3}{2\hbar^2}\left[\frac{1}{n^2} - \frac{1}{(n-1)^2}\right] = -\frac{G^2M^2m^3}{2\hbar^2}\left[\frac{1}{n^2} - \frac{1}{n^2(1-1/n)^2}\right] \simeq -\frac{G^2M^2m^3}{2\hbar^2}\left[\frac{1}{n^2} - \frac{1}{n^2}\left(1 + \frac{2}{n}\right)\right] = \frac{G^2M^2m^3}{\hbar^2n^3}.$$

If this energy is carried out by a photon, the wavelength of the photon will be

$$\lambda = \frac{hc}{\Delta E} = (2\pi\hbar c)\frac{\hbar^2n^3}{G^2M^2m^3}.$$

Substituting $n = \sqrt{GMm^2r_0/\hbar^2}$,

$$\lambda = \frac{2\pi\hbar^3 c}{G^2M^2m^3}\left(\frac{GMm^2r_0}{\hbar^2}\right) = 2\pi c\sqrt{\frac{r_0^3}{GM}}.$$

By Kepler's third law, the period of an orbit (for the Earth, 1 year) is given by

$$t^2 = 4\pi^2\frac{r_0^3}{GM} \quad \Longrightarrow \quad t = 2\pi\sqrt{\frac{r_0^3}{GM}}.$$

Thus, we can also write the wavelength of the photon as

$$\lambda = ct.$$

This is a remarkable result. For large n, a photon emitted by a transition in neighboring energy level for the Earth has the wavelength of 1 light year! In fact, a similar result holds true for the hydrogen atom, provided that $n \gg 1$. The emitted photon has a wavelength equal to the distance that light travels in one electron orbital period.

B.6.2 Angular Momentum Ladder Operators

First, we should know $L_\pm$ is the Hermitian conjugate of $L_\pm$, $(L_\pm)^\dagger = L_\mp$, for

$$\langle f|L_\pm g\rangle = \langle f|L_x g\rangle \pm i\langle f|L_y g\rangle = \langle L_x f|g\rangle \pm i\langle L_y f|g\rangle = \langle (L_x \mp iL_y)f|g\rangle = \langle L_\mp f|g\rangle.$$

Then using Eq. (4.23), $L_\mp L_\pm = L^2 - L_z^2 \mp \hbar L_z$, we have

$$\langle Y_\ell^m | L_\mp L_\pm | Y_\ell^m \rangle = \langle Y_\ell^m | (L^2 - L_z^2 \mp \hbar L_z) | Y_\ell^m \rangle = \langle Y_\ell^m | [\hbar^2 \ell(\ell+1) - \hbar^2 m^2 \mp \hbar^2 m] | Y_\ell^m \rangle$$
$$= \hbar^2 [\ell(\ell+1) - m(m\pm 1)] \langle Y_\ell^m | Y_\ell^m \rangle = \hbar^2 [\ell(\ell+1) - m(m\pm 1)] = \langle L_\pm Y_\ell^m | L_\pm Y_\ell^m \rangle .$$

This gives

$$L_+ |Y_\ell^m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m+1)}\,|Y_\ell^{m+1}\rangle \quad \text{and} \quad L_- |Y_\ell^m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m-1)}\,|Y_\ell^{m-1}\rangle .$$

Note that at $m = \ell$, $\hbar\sqrt{\ell(\ell+1) - m(m+1)} = 0$. Similarly, at $m = -\ell$, $\hbar\sqrt{\ell(\ell+1) - m(m-1)} = 0$.

B.6.3 Conservation of Angular Momentum

We start by the x-component of the orbital angular momentum. By (2.10), the time-derivative of $\langle L_x \rangle$ is given by

$$\frac{d\langle L_x \rangle}{dt} = \frac{i}{\hbar} \langle [H, L_x] \rangle,$$

with the commutator $[H, L_x] = \frac{1}{2m}[p^2, L_x] + [V, L_x]$. From A.1, the first term is zero., leaving the second term being

$$[H, L_x] = [V, yp_z - zp_y] = y[V, p_z] - z[V, p_y] = y\left(i\hbar\frac{\partial V}{\partial z}\right) - z\left(i\hbar\frac{\partial V}{\partial y}\right) = i\hbar[\mathbf{r} \times (\nabla V)]_x.$$

Thus,

$$\frac{d\langle L_x \rangle}{dt} = -\langle [\mathbf{r} \times (\nabla V)]_x \rangle.$$

The same works for the other two components, so

$$\frac{d\langle \mathbf{L} \rangle}{dt} = \langle [\mathbf{r} \times (-\nabla V)] \rangle = \langle \boldsymbol{\tau} \rangle.$$

If the force is central, $V(\mathbf{r}) = V(r)$, then $\nabla V = \hat{\mathbf{r}}\,\partial V/\partial r$ and $\mathbf{r} \times \hat{\mathbf{r}} = 0$. This means

$$\frac{d\langle \mathbf{L} \rangle}{dt} = 0 \quad \text{if } V(\mathbf{r}) = V(r).$$

This is the quantum statement of conservation of angular momentum.

B.6.4 Average Product of Measurements along Different Axis

The choice of axis is arbitrary. Let $\mathbf{a}$ be along the z-axis, and $\mathbf{b}$ on the xz-plane. Set the angle between $\mathbf{a}$ and $\mathbf{b}$ to be θ. Then

$$S_a = S_{1z}, \quad \text{and} \quad S_b = S_{2z}\cos\theta + S_{2x}\sin\theta.$$

The average of the product of the spins is

$$P(\mathbf{a}, \mathbf{b}) = \langle 0, 0 | S_a S_b | 0, 0 \rangle .$$

We first calculate

$$S_a S_b |0,0\rangle = \frac{1}{\sqrt{2}} \left[S_{1z}(S_{2z}\cos\theta + S_{2x}\sin\theta) \right] (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$
$$= \frac{1}{\sqrt{2}} \left[(S_z |\uparrow\rangle)(S_z |\downarrow\rangle \cos\theta + S_x |\downarrow\rangle \sin\theta) - (S_z |\downarrow\rangle)(S_z |\uparrow\rangle \cos\theta + S_x |\uparrow\rangle \sin\theta) \right]$$
$$= \frac{1}{\sqrt{2}} \left\{ \left(\frac{\hbar}{2}|\uparrow\rangle\right)\left[\left(-\frac{\hbar}{2}|\downarrow\rangle\right)\cos\theta + \left(\frac{\hbar}{2}|\uparrow\rangle\right)\sin\theta\right] - \left(-\frac{\hbar}{2}|\downarrow\rangle\right)\left[\left(\frac{\hbar}{2}|\uparrow\rangle\right)\cos\theta + \left(\frac{\hbar}{2}|\downarrow\rangle\right)\sin\theta\right] \right\}$$
$$= \frac{\hbar^2}{4} \left[\frac{1}{\sqrt{2}}(-|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)\cos\theta + \frac{1}{\sqrt{2}}(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle)\sin\theta \right]$$
$$= \frac{\hbar^2}{4} \left[|0,0\rangle \cos\theta + \frac{1}{\sqrt{2}}(|1,1\rangle + |1,-1\rangle)\sin\theta \right].$$

Therefore, by orthonormality,

$$\langle 0, 0 | S_a S_b | 0, 0 \rangle = -\frac{\hbar^2}{4} \cos \theta = -\frac{\hbar^2}{4} (\mathbf{a} \cdot \mathbf{b}).$$

In units of $\hbar/2$, we have

$$\boxed{P(\mathbf{a}, \mathbf{b}) = -\mathbf{a} \cdot \mathbf{b}.}$$

B.6.5   Probability Current in Three Dimensions

Taking the time-derivative of the probability density $|\Psi(\mathbf{x}, t)|^2$,

$$-\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial t} |\Psi|^2 = -\left(\frac{\partial \Psi^*}{\partial t} \Psi + \Psi^* \frac{\partial \Psi}{\partial t} \right).$$

The 3D Schrödinger equation is

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

Dividing $i\hbar$ on both sides to obtain $\partial_t \Psi$ and its complex conjugate,

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m} \nabla^2 \Psi - \frac{i}{\hbar} V \Psi \quad \text{and} \quad \frac{\partial \Psi^*}{\partial t} = -\frac{i\hbar}{2m} \nabla^2 \Psi^* + \frac{i}{\hbar} V \Psi^*.$$

Substitute these into $-\partial_t \rho$,

$$-\frac{\partial \rho}{\partial t} = -\frac{i\hbar}{2m} \left(\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^* \right).$$

Using the vector calculus identity $\nabla \cdot (\Psi^* \nabla \Psi) = (\nabla \Psi^*) \cdot (\nabla \Psi) + \Psi^* \nabla^2 \Psi$, we can show that

$$-\frac{\partial \rho}{\partial t} = -\frac{i\hbar}{2m} \left[\nabla \cdot (\Psi^* \nabla \Psi) - \nabla \cdot (\Psi \nabla \Psi^*) \right] = \nabla \cdot \left[-\frac{i\hbar}{2m} \left(\Psi^* \nabla \Psi - \Psi \nabla \Psi^* \right) \right].$$

This gives the probability current in three dimensions, generalizing (1.4)

$$\mathbf{J} \equiv -\frac{i\hbar}{2m} \left(\Psi^* \nabla \Psi - \Psi \nabla \Psi^* \right).$$

Integrating the continuity equation over all space,

$$\int (\nabla \cdot \mathbf{J}) \, d^3 \mathbf{r} = -\int \frac{\partial \rho}{\partial t} \, d^3 \mathbf{r}.$$

By the divergence theorem, we can turn the volume integral into a surface integral, evaluated at infinity,

$$-\int \frac{\partial \rho}{\partial t} \, d^3 \mathbf{r} = \oint \mathbf{J} \cdot d\mathbf{S} = 0.$$

The surface S encloses the whole space while the probability current $\mathbf{J}$ is evaluated at infinity. $\mathbf{J}$ is proportional to Ψ, and Ψ has to vanish at infinity or otherwise it will not be normalizable. Thus, $\mathbf{J}(\infty, t) = 0$, making the whole integral zero. This is just saying that in non-relativistic quantum mechanics, the total probability of a particle is conserved.

B.6.6   Probability Current with Electromagnetic Hamiltonian

To be written.

B.7 Identical Particles

B.7.1 Central Potential between Two Particles

Suppose the potential is only a function of the separation between two particles: $V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r})$, where $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$. In classical two-body problems, another useful coordinate is the center of mass coordinate: $\mathbf{R} \equiv (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1 + m_2)$. It can be shown easily that

$$\mathbf{r}_1 = \mathbf{R} + \frac{\mu}{m_1}\mathbf{r}, \quad \mathbf{r}_2 = \mathbf{R} - \frac{\mu}{m_2}\mathbf{r},$$

where $\mu = m_1 m_2/(m_1 + m_2)$ is the reduced mass. Using the chain rule, we can derive how derivatives transform under the change of coordinates. For example, for the x-component of $\mathbf{r}_1$,

$$\frac{\partial}{\partial r_{1x}} = \frac{\partial R_x}{\partial r_{1x}}\frac{\partial}{\partial R_x} + \frac{\partial r_x}{\partial r_{1x}}\frac{\partial}{\partial r_x} = \left(\frac{m_1}{m_1 + m_2}\right)\frac{\partial}{\partial R_x} + \frac{\partial}{\partial r_x}.$$

Similar for y- and z-components. Combining the three components gives

$$\nabla_1 = \left(\frac{m_1}{m_1 + m_2}\right)\nabla_R + \nabla_r = \frac{\mu}{m_2}\nabla_R + \nabla_r.$$

By the same token, for $\mathbf{r}_2$,

$$\nabla_2 = \left(\frac{m_2}{m_1 + m_2}\right)\nabla_R - \nabla_r = \frac{\mu}{m_1}\nabla_R - \nabla_r.$$

The Hamiltonian is now

$$
\begin{aligned}
H &= -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}) \\
&= -\frac{\hbar^2}{2m_1}\left(\frac{\mu}{m_2}\nabla_R + \nabla_r\right)^2 - \frac{\hbar^2}{2m_2}\left(\frac{\mu}{m_1}\nabla_R - \nabla_r\right)^2 + V(\mathbf{r}) \\
&= -\frac{\hbar^2}{2m_1}\left(\frac{\mu^2}{m_2^2}\nabla_R^2 + \frac{\mu}{m_2}\nabla_R\nabla_r + \frac{\mu}{m_2}\nabla_r\nabla_R + \nabla_r^2\right) - \frac{\hbar^2}{2m_2}\left(\frac{\mu^2}{m_1^2}\nabla_R^2 - \frac{\mu}{m_1}\nabla_R\nabla_r - \frac{\mu}{m_1}\nabla_r\nabla_R + \nabla_r^2\right) + V(\mathbf{r}) \\
&= -\frac{\hbar^2\mu^2}{2m_1m_2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\nabla_R^2 - \frac{\hbar^2}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\nabla_r^2 + V(\mathbf{r}) \\
&= -\frac{\hbar^2}{2(m_1 + m_2)}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(\mathbf{r})
\end{aligned}
$$

so the time-independent Schrödinger equation becomes

$$\boxed{-\frac{\hbar^2}{2(m_1 + m_2)}\nabla_R^2\psi - \frac{\hbar^2}{2\mu}\nabla_r^2\psi + V\psi = E\psi.}$$

Define $M \equiv m_1 + m_2$. Separate the variables, letting $\psi(\mathbf{R}, \mathbf{r}) = \psi_R(\mathbf{R})\psi_r(\mathbf{r})$:

$$-\frac{\hbar^2}{2M}\nabla_R^2(\psi_R\psi_r) - \frac{\hbar^2}{2\mu}\nabla_r^2(\psi_R\psi_r) + V\psi_R\psi_r = E\psi_R\psi_r.$$

$$-\frac{\hbar^2}{2M}\psi_r\nabla_R^2\psi_R - \frac{\hbar^2}{2\mu}\psi_R\nabla_r^2\psi_r + V\psi_R\psi_r = E\psi_R\psi_r.$$

Dividing both sides by $\psi_R\psi_r$ gives

$$\left(-\frac{\hbar^2}{2M}\frac{1}{\psi_R}\nabla_R^2\psi_R\right) + \left(-\frac{\hbar^2}{2\mu}\frac{1}{\psi_r}\nabla_r^2\psi_r\right) = E.$$

The first bracket depends only on $\mathbf{R}$, while the second depends only on $\mathbf{r}$, so each must be a constant. Let these constants be E_R and E_r respectively, and $E_R + E_r = E$. This separates a two-body problem to two one-body problems,

$$
\begin{cases}
-\dfrac{\hbar^2}{2M}\nabla_R^2\psi_R = E_R\psi_R, \\
-\dfrac{\hbar^2}{2\mu}\nabla_r^2\psi_r + V(\mathbf{r})\psi_r = E_r\psi_r.
\end{cases}
$$

The first equation is like a Schrödinger equation of a free particle with mass $m_1 + m_2$ in the center of mass coordinate. This makes sense, because the potential depends only on separation of two particles and there is no external forces. The whole system should have conserved momentum and energy.

B.7.2 Slater Determinant and Permanent

To construct a state of n fermions with single particle states $\psi_a(\mathbf{r}_1)$, $\psi_b(\mathbf{r}_2)$, etc, it is convenient to use the **Slater determinant**:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \begin{vmatrix} \psi_a(\mathbf{r}_1) & \psi_b(\mathbf{r}_1) & \psi_c(\mathbf{r}_1) & \cdots \\ \psi_a(\mathbf{r}_2) & \psi_b(\mathbf{r}_2) & \psi_c(\mathbf{r}_2) & \cdots \\ \psi_a(\mathbf{r}_3) & \psi_b(\mathbf{r}_3) & \psi_c(\mathbf{r}_3) & \cdots \\ \vdots & \vdots & \vdots & \ddots \\ \psi_a(\mathbf{r}_n) & \psi_b(\mathbf{r}_n) & \psi_c(\mathbf{r}_n) & \cdots \end{vmatrix} \tag{B.9}$$

For example, if we have a state with 3 fermions, one in state $\psi_a(\mathbf{r}_1)$, one in state $\psi_b(\mathbf{r}_2)$, and one in state $\psi_c(\mathbf{r}_3)$, then the 3-particle state is

$$\begin{aligned} \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \begin{vmatrix} \psi_a(\mathbf{r}_1) & \psi_b(\mathbf{r}_1) & \psi_c(\mathbf{r}_1) \\ \psi_a(\mathbf{r}_2) & \psi_b(\mathbf{r}_2) & \psi_c(\mathbf{r}_2) \\ \psi_a(\mathbf{r}_3) & \psi_b(\mathbf{r}_3) & \psi_c(\mathbf{r}_3) \end{vmatrix} \\ &= \psi_a(\mathbf{r}_1)[\psi_b(\mathbf{r}_2)\psi_c(\mathbf{r}_3) - \psi_c(\mathbf{r}_2)\psi_b(\mathbf{r}_3)] + \psi_b(\mathbf{r}_1)[\psi_c(\mathbf{r}_2)\psi_a(\mathbf{r}_3) - \psi_a(\mathbf{r}_2)\psi_c(\mathbf{r}_3)] \\ &\quad + \psi_c(\mathbf{r}_1)[\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_3) - \psi_b(\mathbf{r}_2)\psi_a(\mathbf{r}_3)]. \end{aligned}$$

We may check that exchanging *any* pair of $\mathbf{r}_i$ and $\mathbf{r}_j$ for $i \neq j$ let the whole state acquire a minus sign (anti-symmetric). In fact, this is just a property of the determinant in linear algebra: exchanging any two rows in a determinant gives it a minus sign. Since in Slater determinant each row is characterized by $\mathbf{r}_i$, exchanging $\mathbf{r}_i$ and $\mathbf{r}_j$ for $i \neq j$ has the same effect as exchanging rows.

A state of n bosons are much simpler: just replace all minus signs in the Slater determinant with plus signs, making the state symmetric. This is called the **permanent**.

B.7.3 Hund's Rule

The following are three Hund's rules:

1. **Hund's first rule**: the state with the highest total spin (S), consistent with the Pauli exclusion principle, will have the lowest energy.

2. **Hund's second rule**: for a given spin, the state with the highest total orbital angular momentum (L), consistent with overall anti-symmetrization, will have the lowest energy.

3. **Hund's third rule**: if a subshell (n, ℓ) is no more than half filled, then the lowest energy level has $J = |L - S|$; if it is more than half filled, then $J = L + S$ has the lowest energy.

Let's figure out the ground state configuration of carbon as an example. In orbital notation, carbon has $1s^2\, 2s^2\, 2p^2$. There are two electrons in $1s$ orbital, two in $2s$ orbital, and two in $2p$ orbital. Both $1s$ and $2s$ orbitals are filled, and the electrons are in the singlet state (opposite spin orientation) because the spatial wave functions are symmetric. The $2p$ orbital is a bit tricky. First, the two electrons can either choose spin up ($+1/2$) or spin down ($-1/2$) in $m = \pm 1$ or $m = 0$ states as long as they do not violate the Pauli exclusion principle. Thus, the total spin can be 1 or 0 according to addition of angular momenta. Hund's first rule says that highest total spin is preferred, so $S = 1$. Now, if $S = 1$, the two electrons cannot be in the singlet state ($S = 0$), so they will have symmetric spin states, or triplet states. In this case, they must have anti-symmetric spatial wave functions because electrons are fermions. Hund's second rule favors $L = 2$, but all $L = 2$ states are symmetric. You may check this using Clebsch-Gordan table of two particles of spin-1 (which also applies to orbital angular momentum):

$$\text{singlet} : \left\{ |0, 0\rangle = \tfrac{1}{\sqrt{3}} \left(|1, 1\rangle|1, -1\rangle - |1, 0\rangle|1, 0\rangle + |1, -1\rangle|1, 1\rangle \right) \quad \text{(symmetric)}, \right.$$

$$\text{triplet}: \begin{cases} |1,1\rangle = \frac{1}{\sqrt{2}}\left(|1,1\rangle|1,0\rangle - |1,0\rangle|1,1\rangle\right) & \text{(anti-symmetric)}, \\ |1,0\rangle = \frac{1}{\sqrt{2}}\left(|1,1\rangle|1,-1\rangle - |1,-1\rangle|1,1\rangle\right) & \text{(anti-symmetric)}, \\ |1,-1\rangle = \frac{1}{\sqrt{2}}\left(|1,0\rangle|1,-1\rangle - |1,-1\rangle|1,0\rangle\right) & \text{(anti-symmetric)}, \end{cases}$$

$$\text{quintuplet}: \begin{cases} |2,2\rangle = |1,1\rangle|1,1\rangle & \text{(symmetric)}, \\ |2,1\rangle = \frac{1}{\sqrt{2}}\left(|1,1\rangle|1,0\rangle + |1,0\rangle|1,1\rangle\right) & \text{(symmetric)}, \\ |2,0\rangle = \frac{1}{\sqrt{6}}|1,1\rangle|1,-1\rangle + \sqrt{\frac{2}{3}}|1,0\rangle|1,0\rangle + \frac{1}{\sqrt{6}}|1,-1\rangle|1,1\rangle & \text{(symmetric)}, \\ |2,-1\rangle = \frac{1}{\sqrt{2}}\left(|1,0\rangle|1,-1\rangle + |1,-1\rangle|1,0\rangle\right) & \text{(symmetric)}, \\ |2,-2\rangle = |1,-1\rangle|1,-1\rangle & \text{(symmetric)}. \end{cases}$$

To have anti-symmetric spatial wave functions, we need to have $L = 1$. Following the configuration rule $^{2S+1}L_J$, there are three possibilities for ground state carbon: $^3P_2$, $^3P_1$, $^3P_0$. Obviously carbon does not have its p-subshell half filled (it requires at least three electrons to half-fill p). According to Hund's third rule, the lowest energy level should have $J = |L - S| = 0$. In conclusion, the ground state configuration for carbon is

$$\boxed{\text{Carbon}: {}^3P_0.}$$

B.8 Time-Independent Perturbation Theory

B.8.1 Expectation of $1/r$ and $1/r^2$ for Hydrogen

By the Feynman-Hellmann Theorem. The effective Hamiltonian for the radial wave function is (4.9),

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} - \frac{e^2}{4\pi\epsilon_0 r}.$$

Its eigenvalues are given by (4.12) and (4.14),

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = -\frac{e^2}{8\pi\epsilon_0 an^2} = -\frac{e^2}{8\pi\epsilon_0 a(N+\ell)^2},$$

where we replace n by $N + \ell$ and $N = j_{\max} + 1$ (in the derivation of Hydrogen radial wave function) is a fixed integer. The Feynman-Hellmann theorem (B.9) says that

$$\frac{\partial E}{\partial \lambda} = \left\langle \psi \left| \frac{\partial H}{\partial \lambda} \right| \psi \right\rangle.$$

To find $\langle 1/r \rangle$, treat $\lambda = e$. Then

$$\frac{\partial H}{\partial e} = -\frac{e}{2\pi\epsilon_0 r} \quad \text{and} \quad \frac{\partial E}{\partial e} = -\frac{e}{4\pi\epsilon_0 an^2}.$$

By the Feynman-Hellmann theorem,

$$-\frac{e}{4\pi\epsilon_0 an^2} = -\frac{e}{2\pi\epsilon_0}\left\langle \frac{1}{r} \right\rangle \quad \Longrightarrow \quad \boxed{\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a},}$$

To find $\langle 1/r^2 \rangle$, treat $\lambda = \ell$. (Though ℓ is a discrete quantum number, we will still treat it as a continuous variable.)

$$\frac{\partial H}{\partial \ell} = \frac{\hbar^2(2\ell+1)}{2mr^2} \quad \text{and} \quad \frac{\partial E}{\partial \ell} = \frac{e^2}{4\pi\epsilon_0 a(N+\ell)^3}.$$

By the Feynman-Hellmann theorem,

$$\frac{\hbar^2(2\ell+1)}{2m}\left\langle \frac{1}{r^2} \right\rangle = \frac{e^2}{4\pi\epsilon_0 a(N+\ell)^3} \quad \Longrightarrow \quad \boxed{\left\langle \frac{1}{r^2} \right\rangle = \frac{me^2}{4\pi\epsilon_0\hbar^2(\ell+1/2)(N+\ell)^3} = \frac{1}{(\ell+1/2)n^3 a^2},}$$

where we used the Bohr radius $a = 4\pi\epsilon_0\hbar^2/me^2$.

By Kramers' Relation To be written.

B.8.2 Commutators of Spin-Orbit Coupling

The spin angular momentum and orbital angular momentum are in different spaces, so $\mathbf{S}$ commutes with $\mathbf{L}$. By components:

$$[\mathbf{L}\cdot\mathbf{S}, L_x] = [L_x S_x + L_y S_y + L_z S_z, L_x] = S_x[L_x, L_x] + S_y[L_y, L_x] + S_z[L_z, L_x] = i\hbar(-S_y L_z + L_y S_z) = i\hbar(\mathbf{L}\times\mathbf{S})_x.$$

Similar for y- and z-components, so

$$[\mathbf{L}\cdot\mathbf{S}, \mathbf{L}] = i\hbar(\mathbf{L}\times\mathbf{S}).$$

If we switch $\mathbf{L}$ and $\mathbf{S}$, it gives another commutation relation

$$[\mathbf{L}\cdot\mathbf{S}, \mathbf{S}] = i\hbar(\mathbf{S}\times\mathbf{L}).$$

$\mathbf{L}\cdot\mathbf{S}$ commutes with $\mathbf{J}$ because cross products anticommutes:

$$[\mathbf{L}\cdot\mathbf{S}, \mathbf{J}] = [\mathbf{L}\cdot\mathbf{S}, \mathbf{L}] + [\mathbf{L}\cdot\mathbf{S}, \mathbf{S}] = i\hbar[\mathbf{L}\times\mathbf{S} + \mathbf{S}\times\mathbf{L}] = 0.$$

L^2 commutes with $\mathbf{L}$ and $\mathbf{S}$; S^2 commutes with $\mathbf{S}$ and $\mathbf{L}$, so we have

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

Finally,

$$[\mathbf{L}\cdot\mathbf{S}, J^2] = [\mathbf{L}\cdot\mathbf{S}, L^2] + [\mathbf{L}\cdot\mathbf{S}, S^2] + 2[\mathbf{L}\cdot\mathbf{S}, \mathbf{L}\cdot\mathbf{S}] = 0.$$

B.8.3 First-Order Fine Structure Correction

To derive the complete first-order fine structure correction to the energy (6.17), we need both relativistic correction (6.13) and spin-orbit coupling correction (6.16):

$$E_r^1 = -\frac{(E_n^0)^2}{2mc^2}\left[\frac{4n}{\ell+1/2} - 3\right], \quad E_{\text{so}}^1 = \frac{(E_n^0)^2}{mc^2}\left\{\frac{n\left[j(j+1) - \ell(\ell+1) - 3/4\right]}{\ell(\ell+1/2)(\ell+1)}\right\}.$$

An electron has spin $s = 1/2$, so its total angular momentum can only be $j = \ell \pm 1/2$.

First, let's look at $j = \ell + 1/2$ or $\ell = j - 1/2$,

$$E_r^1 = -\frac{(E_n^0)^2}{2mc^2}\left(\frac{4n}{j} - 3\right),$$

$$E_{\text{so}}^1 = \frac{(E_n^0)^2}{mc^2}\cdot\frac{n\left[j(j+1) - (j-1/2)(j+1/2) - 3/4\right]}{(j-1/2)j(j+1/2)} = \frac{(E_n^0)^2}{mc^2}\cdot\frac{n(j^2 + j - j^2 + 1/4 - 3/4)}{j(j-1/2)(j+1/2)} = \frac{(E_n)^2}{mc^2}\frac{n}{j(j+1/2)}.$$

The fine structure correction is

$$E_{\text{fs}}^1 = E_r^1 + E_{\text{so}}^1 = \frac{(E_n^0)^2}{2mc^2}\left(-\frac{4n}{j} + 3 + \frac{2n}{j(j+1/2)}\right) = \frac{(E_n^0)^2}{2mc^2}\left\{3 + \frac{2n}{j(j+1/2)}\left[1 - 2\left(j + \frac{1}{2}\right)\right]\right\}$$

$$= \frac{(E_n^0)^2}{2mc^2}\left(3 - \frac{4n}{j+1/2}\right).$$

For $j = \ell - 1/2$ or $\ell = j + 1/2$,

$$E_r^1 = -\frac{(E_n^0)}{2mc^2}\left(\frac{4n}{j+1} - 3\right),$$

$$E_{\text{so}}^1 = \frac{(E_n^0)^2}{mc^2}\frac{n\left[j(j+1) - (j+1/2)(j+3/2) - 3/4\right]}{(j+1/2)(j+1)(j+3/2)} = \frac{(E_n^0)^2}{mc^2}\frac{n(j^2 + j - j^2 - 2j - 3/2)}{(j+1/2)(j+1)(j+3/2)} = -\frac{(E_n^0)^2}{mc^2}\frac{n}{(j+1)(j+1/2)}.$$

The fine structure correction is

$$E_{\text{fs}}^1 = E_r^1 + E_{\text{so}}^1 = \frac{(E_n^0)^2}{2mc^2}\left[-\frac{4n}{j+1} + 3 - \frac{2n}{(j+1)(j+1/2)}\right] = \frac{(E_n^0)^2}{2mc^2}\left\{3 - \frac{2n}{(j+1)(j+1/2)}\left[1 + 2\left(j+1/2\right)\right]\right\}$$

$$= \frac{(E_n^0)^2}{2mc^2}\left(3 - \frac{4n}{j+1/2}\right).$$

Either using $j = \ell + 1/2$ or $j = \ell - 1/2$ will produce

$$\boxed{E_{\text{fs}}^1 = \frac{(E_n^0)^2}{2mc^2}\left(3 - \frac{4n}{j+1/2}\right).}$$

B.8.4 Spin Expectation

To be written.

B.8.5 Strong-Field Zeeman Effect

To be written.

B.8.6 The Stark Effect

To be written.

B.9 Variational Principle

B.9.1 A Problem with the Trial Wave Function $e^{-\alpha|x|}$

The Problem. Consider a 1D harmonic oscillator with $V = \frac{1}{2}m\omega^2 x^2$ as an example. Let the trial wave function be $\psi = Ae^{-\alpha|x|}$. First normalize the trial wave function,

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-2\alpha|x|} = 2|A|^2 \int_0^{\infty} e^{-2\alpha x} = \frac{|A|^2}{\alpha} \quad \Longrightarrow \quad \boxed{A = \sqrt{\alpha}.}$$

The expectation value the potential energy V is

$$\langle V \rangle = \langle \psi|V|\psi \rangle = \int_{-\infty}^{\infty} |A|^2 e^{-2\alpha|x|} \left(\frac{1}{2}m\omega^2 x^2 \right) dx = \alpha m\omega^2 \int_0^{\infty} x^2 e^{-2\alpha x}\, dx = \boxed{\frac{m\omega^2}{4\alpha^2}.}$$

So far there is no problem. The problem appears when we compute the expection value of the kinetic energy. We know the kinetic energy is proportional to the second-derivative of x,

$$\langle T \rangle \propto \left\langle \psi \left| \frac{d^2}{dx^2} \right| \psi \right\rangle \propto \int_{-\infty}^{\infty} e^{-\alpha|x|} \frac{d^2}{dx^2} \left(e^{-\alpha|x|} \right) dx.$$

What do we do now? The function $e^{-\alpha|x|}$ has a discontinuous first-derivative at $x = 0$. The second-derivative will diverge. A "careless" way to proceed is to ignore the discontinuity at $x = 0$ and directly do the integral:

$$\langle T \rangle \propto 2 \int_0^{\infty} e^{-\alpha x} \frac{d^2}{dx^2} \left(e^{-\alpha x} \right) dx = 2\alpha^2 \int_0^{\infty} e^{-2\alpha x}\, dx = \alpha.$$

The proportionality constant is $-\frac{\hbar^2}{2m}|A|^2 = -\frac{\hbar^2\alpha}{2m}$. It turns out $\langle T \rangle$ is negative!

$$\langle T \rangle = -\frac{\hbar^2\alpha^2}{2m}.$$

If we keep ignore this fact and try to estimate the energy,

$$\langle H \rangle = \langle T \rangle + \langle V \rangle = -\frac{\hbar^2\alpha^2}{2m} + \frac{m\omega^2}{4\alpha^2}.$$

To find the ground state energy, we minimize $\langle H \rangle$ by taking derivative with respect to α,

$$0 = \frac{d}{d\alpha}\langle H \rangle = -\frac{\hbar^2\alpha}{m} - \frac{m\omega^2}{2\alpha^3} \quad \Longrightarrow \quad \alpha = \left(-\frac{m^2\omega^2}{2\hbar^2} \right)^{1/4}.$$

We are unable to find $\langle H \rangle_{\min}$ because α is imaginary.

Solution 1. There are two solutions. The first one is to write $\langle \psi|p^2|\psi \rangle = \langle p\psi|p\psi \rangle$ because p is Hermitian. This can also be proved from integration by parts,

$$\left\langle \psi \left| \frac{d^2}{dx^2} \right| \psi \right\rangle = \int_{-\infty}^{\infty} \psi \frac{d^2\psi}{dx^2}\, dx = \psi \frac{d\psi}{dx} \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{\infty} \frac{d\psi}{dx} \frac{d\psi}{dx}\, dx = -\left\langle \frac{d\psi}{dx} \Big| \frac{d\psi}{dx} \right\rangle.$$

Using this expression to find $\langle T \rangle$:

$$-\left\langle \frac{d\psi}{dx} \Big| \frac{d\psi}{dx} \right\rangle \propto -\int_{-\infty}^{\infty} \left[\frac{d}{dx} \left(e^{-\alpha|x|} \right) \right]^2 dx = -2\alpha^2 \int_0^{\infty} e^{-2\alpha x}\, dx = -\alpha.$$

The kinetic energy is now positive,

$$\langle T \rangle = -\frac{\hbar^2|A|^2}{2m} \left\langle \psi \left| \frac{d^2}{dx^2} \right| \psi \right\rangle = -\frac{\hbar^2\alpha}{2m}(-\alpha) = \frac{\hbar^2\alpha^2}{2m}.$$

The total expectation value of energy is

$$\langle H \rangle = \langle T \rangle + \langle V \rangle = \frac{\hbar^2\alpha^2}{2m} + \frac{m\omega^2}{4\alpha^2}.$$

Minimizing $\langle H \rangle$ yields the optimized trial wave function,

$$0 = \frac{d}{d\alpha}\langle H \rangle = \frac{\hbar^2 \alpha}{m} - \frac{m\omega^2}{2\alpha^3} \implies \alpha = \left(\frac{m^2\omega^2}{2\hbar^2}\right)^{1/4}.$$

Substitute α into $\langle H \rangle$ to find $\langle H \rangle_{\min}$,

$$\langle H \rangle_{\min} = \frac{\hbar^2}{2m}\frac{m\omega}{\sqrt{2}\hbar} + \frac{m\omega^2}{4}\frac{\sqrt{2}\hbar}{m\omega} = \frac{1}{2\sqrt{2}}\hbar\omega + \frac{1}{2\sqrt{2}}\hbar\omega = \boxed{\frac{1}{\sqrt{2}}\hbar\omega.}$$

This is a bit larger than the true ground state $E_0 = \frac{1}{2}\hbar\omega$ of the harmonic oscillator. This make sense because $e^{-\alpha|x|}$ is not an eigenstate of the harmonic oscillator Hamiltonian.

Solution 2. There is a more mathematical way to solve the problem. We know that the first-derivative is discontinuous and the second-derivative diverge at $x = 0$. Meanwhile, the trial wave function is $e^{-\alpha|x|}$. These information should remind us of the delta function $\delta(x)$. We will also use the Heaviside step function (B.6) defined as

$$\theta(x) = \begin{cases} 1, & x > 0, \\ 0, & x < 0, \end{cases} \quad \text{with} \quad \frac{d}{dx}\theta(x) = \delta(x).$$

The first- and second-derivative of $e^{-\alpha|x|}$ can be written in terms of the Heaviside function and delta function:

$$\frac{d}{dx}\left(e^{-\alpha|x|}\right) = -\alpha\frac{x}{|x|}e^{-\alpha|x|} = -\alpha[2\theta(x) - 1]e^{-\alpha|x|},$$

and

$$\begin{aligned}
\frac{d^2}{dx^2}\left(e^{-\alpha|x|}\right) &= -2\alpha\frac{d}{dx}\left[\theta(x)e^{-\alpha|x|}\right] + \alpha\frac{d}{dx}\left(e^{-\alpha|x|}\right) \\
&= -2\alpha e^{-\alpha|x|}\frac{d\theta}{dx} - 2\alpha\theta\frac{d}{dx}\left(e^{-\alpha|x|}\right) + \alpha\frac{d}{dx}\left(e^{-\alpha|x|}\right) \\
&= -2\alpha\delta(x)e^{-\alpha|x|} + 2\alpha^2\theta[2\theta(x) - 1]e^{-\alpha|x|} - \alpha^2[2\theta(x) - 1]e^{-\alpha|x|} \\
&= -2\alpha\delta(x)e^{-\alpha|x|} + \alpha^2 e^{-\alpha|x|}[2\theta(x) - 1]^2.
\end{aligned}$$

Notice that $[2\theta(x) - 1]^2 = 1$, so

$$\frac{d^2}{dx^2}\left(e^{-\alpha|x|}\right) = -2\alpha\delta(x)e^{-\alpha|x|} + \alpha^2 e^{-\alpha|x|}.$$

Now there is no problem if we do direct integration,

$$\langle T \rangle \propto \int_{-\infty}^{\infty} e^{-\alpha|x|}\frac{d^2}{dx^2}\left(e^{-\alpha|x|}\right)dx = \int_{-\infty}^{\infty}\left[-2\alpha\delta(x)e^{-2\alpha|x|} + \alpha^2 e^{-2\alpha|x|}\right]dx = -2\alpha + 2\alpha^2\int_0^{\infty}e^{-2\alpha x}dx = -2\alpha + \alpha = -\alpha.$$

The proportionality constant is $-\frac{\hbar^2}{2m}|A|^2 = -\frac{\hbar^2\alpha}{2m}$, which gives

$$\langle T \rangle = -\frac{\hbar^2\alpha}{2m}(-\alpha) = \frac{\hbar^2\alpha^2}{2m},$$

positive as desired. The rest of the steps to find $\langle H \rangle_{\min}$ is the same.

In conclusion, the wave function $e^{-\alpha|x|}$ is not a very good trial wave function to evaluate the kinetic energy. This applies to other trial wave functions with discontinuity in first-derivatives. The takeaway lesson is that when using the variational principle, we had better choose a *smooth* trial function. This is why the Gaussian e^{-bx^2} is always a popular trial wave function.

B.9.2 The expectation value of V_{ee}

To be written.

B.10 The WKB Approximation

B.10.1 Downward-Sloping Turning Point

To be written.

B.11 Time-Dependent Perturbation Theory

B.11.1 Rabi Oscillation

The goal is to solve

$$\dot{c}_a = -\frac{i}{2\hbar}V_{ab}e^{i(\omega-\omega_0)t}c_b, \quad \dot{c}_b = -\frac{i}{2\hbar}V_{ba}e^{-i(\omega-\omega_0)t}c_a.$$

It is more convenient to start with the $\dot{c}_b$-equation. (If one tries to start with the $\dot{c}_a$-equation, one will probably run into a messier calculation before getting to the right answer. It seems like $\dot{c}_a$ and $\dot{c}_b$ are kind of symmetric, but their initial conditions will make a big difference.) Differentiating the $\dot{c}_b$ equation,

$$\ddot{c}_b = -i\frac{V_{ba}}{2\hbar}\left[-i(\omega-\omega_0)e^{-i(\omega-\omega_0)t}c_a + e^{-i(\omega-\omega_0)t}\dot{c}_a\right].$$

Substituting $\dot{c}_a$,

$$\ddot{c}_b = -i(\omega-\omega_0)\left[-i\frac{V_{ba}}{2\hbar}e^{-i(\omega-\omega_0)t}c_a\right] - i\frac{V_{ba}}{2\hbar}e^{-i(\omega-\omega_0)t}\left[-i\frac{V_{ab}}{2\hbar}e^{i(\omega-\omega_0)t}c_b\right] = -i(\omega-\omega_0)\dot{c}_b - \frac{|V_{ab}|^2}{(2\hbar)^2}c_b.$$

This gives a second-order linear differential equation,

$$\ddot{c}_b + i(\omega-\omega_0)\dot{c}_b + \frac{|V_{ab}|^2}{4\hbar^2}c_b = 0.$$

If the solution is of the form $c_b = e^{\lambda t}$, this differential equation is equivalent to the characteristic equation

$$\lambda^2 + i(\omega-\omega_0)\lambda + \frac{|V_{ab}|^2}{4\hbar^2} = 0.$$

The solutions of this characteristic equation is

$$\lambda = \frac{1}{2}\left[-i(\omega-\omega_0) \pm \sqrt{-(\omega-\omega_0)^2 - \frac{|V_{ab}|^2}{\hbar^2}}\right] = i\left[-\frac{\omega-\omega_0}{2} \pm \omega_r\right].$$

The general solution of the c_b-equation is the linear combination

$$c_b(t) = Ae^{-i(\omega-\omega_0)t/2+i\omega_r t} + Be^{-i(\omega-\omega_0)t/2-i\omega_r t} = e^{-i(\omega-\omega_0)t/2}[C\cos\omega_r t + D\sin\omega_r t],$$

where C and D are constants fixed by initial conditions. The initial condition for c_b is $c_b(0) = 0$, so $C = 0$. Then we have

$$c_b(t) = De^{-i(\omega-\omega_0)t/2}\sin\omega_r t, \quad \dot{c}_b = D\left[-i\left(\frac{\omega-\omega_0}{2}\right)e^{-i(\omega-\omega_0)t/2}\sin\omega_r t + \omega_r e^{-i(\omega-\omega_0)t/2}\cos\omega_r t\right].$$

Plugging this into the $\dot{c}_b$-equation to solve for c_a:

$$c_a = i\frac{2\hbar}{V_{ba}}e^{i(\omega-\omega_0)t}\dot{c}_b = i\frac{2\hbar}{V_{ba}}e^{i(\omega-\omega_0)t/2}D\left[-i\left(\frac{\omega-\omega_0}{2}\right)\sin\omega_r t + \omega_r\cos\omega_r t\right].$$

The initial condition $c_a(0) = 1$ sets

$$1 = i\frac{2\hbar}{V_{ba}}D\omega_r \quad\Longrightarrow\quad D = -i\frac{V_{ba}}{2\hbar\omega_r}.$$

In conclusion,

$$c_a(t) = e^{i(\omega-\omega_0)t/2}\left[\cos\omega_r t - i\left(\frac{\omega-\omega_0}{2\omega_r}\right)\sin\omega_r t\right], \quad c_b(t) = -\frac{iV_{ba}}{2\hbar\omega_r}e^{-i(\omega-\omega_0)t/2}\sin\omega_r t.$$

B.11.2 Azimuthal Quantum Number Selection Rule

We are to compute the commutation relation $\left[L^2, [L^2, \mathbf{r}]\right]$. Starting with $\left[L^2, [L^2, z]\right]$, it is straightforward to generalize to x and y and then $\mathbf{r}$. We will make use of the commutators listed in A.1 very often. First, $[L_z, z] = 0$,

$$[L^2, z] = [L_x^2, z] + [L_y^2, z] + \cancel{[L_z^2, z]} = L_x[L_x, z] + [L_x, z]L_x + L_y[L_y, z] + [L_y, z]L_y.$$

Because $[L_x, z] = -i\hbar y$ and $[L_y, z] = i\hbar x$,

$$[L^2, z] = L_x(-i\hbar y) + (-i\hbar y)L_x + L_y(i\hbar x) + (i\hbar x)L_y = i\hbar(-L_x y - y L_x + L_y x + x L_y).$$

Then rewrite

$$L_x y = L_x y - y L_x + y L_x = [L_x, y] + y L_x = i\hbar z + y L_x,$$
$$L_y x = L_y x - x L_y + x L_y = [L_y, x] + x L_y = -i\hbar z + x L_y,$$

so

$$[L^2, z] = i\hbar(2x L_y - i\hbar z - 2y L_x - i\hbar z) = 2i\hbar(x L_y - y L_x - i\hbar z).$$

Generalizing to x and y using cyclic permutation, we have

$$[L^2, x] = 2i\hbar(y L_z - z L_y - i\hbar x), \quad [L^2, y] = 2i\hbar(z L_x - x L_z - i\hbar y).$$

Next, compute $\left[L^2, [L^2, z]\right]$,

$$\left[L^2, [L^2, z]\right] = 2i\hbar([L^2, x L_y] - [L^2, y L_x] - i\hbar[L^2, z]) = 2i\hbar\left\{[L^2, x]L_y + x[L^2, L_y] - [L^2, y]L_x - y[L^2, L_x] - i\hbar(L^2 z - z L^2)\right\}.$$

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

$$\left[L^2, [L^2, z]\right] = 2i\hbar[2i\hbar(y L_z - z L_y - i\hbar x)L_y - 2i\hbar(z L_x - x L_z - i\hbar y)L_x - i\hbar(L^2 z - z L^2)]$$
$$= -2\hbar^2(2y L_z L_y \textcolor{magenta}{-2z L_y^2} - 2i\hbar x L_y \textcolor{magenta}{-2z L_x^2} - 2x L_z L_x + 2i\hbar y L_x - L^2 z + z L^2)$$
$$= -2\hbar^2(2y L_z L_y - 2i\hbar x L_y + 2x L_z L_x + 2i\hbar y L_x \textcolor{magenta}{-2z L^2 + 2z L_z^2} - L^2 z + z L^2)$$
$$= 2\hbar^2(z L^2 + L^2 z) - 4\hbar^2[(y L_z - i\hbar x)L_y + (x L_z + i\hbar y)L_x + z L_z^2]$$
$$= 2\hbar^2(z L^2 + L^2 z) - 4\hbar^2(L_z y L_y + L_z x L_x + L_z z L_z)$$
$$= 2\hbar^2(z L^2 + L^2 z) - 4\hbar^2 L_z(\mathbf{r} \cdot \mathbf{L})$$
$$= 2\hbar^2(z L^2 + L^2 z).$$

In the last step, we used the fact that $\mathbf{r} \cdot \mathbf{L} = \mathbf{r} \cdot (\mathbf{r} \times \mathbf{p}) = 0$. Generalizing to x, y, and then $\mathbf{r}$,

$$\left[L^2, [L^2, \mathbf{r}]\right] = 2\hbar^2(\mathbf{r} L^2 + L^2 \mathbf{r}).$$

B.11.3 A Constantly Expanding Well

We would like to check

$$\phi_n(x,t) = \sqrt{\frac{2}{w}} \sin\left(\frac{n\pi x}{w}\right) e^{i(mvx^2 - 2E_n^i at)/2\hbar w}$$

satisfies the time-dependent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\phi_n}{\partial x^2} + V(x,t) = i\hbar\frac{\partial\phi_n}{\partial t}, \quad \text{where} \quad V(x,t) = \begin{cases} 0, & 0 \le x \le w, \\ \infty, & \text{otherwise.} \end{cases}$$

$w = a + vt$ and $E_n^i = n^2\pi^2\hbar^2/2ma^2$. Compute the position-derivatives:

$$\frac{\partial\phi_n}{\partial x} = \sqrt{\frac{2}{w}}\frac{\partial}{\partial x}\left[\sin\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w}\right]$$

$$= \sqrt{\frac{2}{w}}\left[\frac{n\pi}{w}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w} + \frac{imvx}{\hbar w}\sin\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w}\right].$$

$$\frac{\partial^2\phi_n}{\partial x^2} = \sqrt{\frac{2}{w}}\frac{\partial}{\partial x}\left[\frac{n\pi}{w}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w} + \frac{imvx}{\hbar w}\sin\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w}\right]$$

$$= \sqrt{\frac{2}{w}}\left[-\left(\frac{n\pi}{w}\right)^2\sin\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w} + \frac{n\pi}{w}\frac{imvx}{\hbar w}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w} + \frac{n\pi}{w}\frac{imvx}{\hbar w}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w}\right.$$

$$\left. + \frac{imv}{\hbar w}\sin\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w} - \frac{m^2v^2x^2}{\hbar^2w^2}\sin\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w}\right]$$

$$= \left[-\left(\frac{n\pi}{w}\right)^2 + \frac{imv}{\hbar w} - \frac{m^2v^2x^2}{\hbar^2w^2}\right]\phi_n + \sqrt{\frac{2}{w}}\frac{2imvn\pi x}{\hbar w^2}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w}.$$

Inside the well,

$$H\phi_n = -\frac{\hbar^2}{2m}\frac{\partial^2\phi_n}{\partial x^2}$$

$$= -\frac{\hbar^2}{2m}\left[-\left(\frac{n\pi}{w}\right)^2 + \frac{imv}{\hbar w} - \left(\frac{mvx}{\hbar w}\right)^2\right]\phi_n - \sqrt{\frac{2}{w}}\frac{\hbar}{2m}\frac{2imvn\pi x}{\hbar w^2}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w}$$

$$= \left(\frac{n^2\pi^2\hbar^2}{2mw^2} - \frac{i\hbar v}{2w} + \frac{mv^2x^2}{2w^2}\right)\phi_n - \sqrt{\frac{2}{w}}\frac{i\hbar n\pi vx}{w^2}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w}.$$

Compute the time-derivative:

$$\frac{\partial\phi_n}{\partial t} = \frac{\partial}{\partial t}\left[\sqrt{\frac{2}{w}}\sin\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w}\right] = \frac{\partial}{\partial w}\left[\sqrt{\frac{2}{w}}\sin\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i a\frac{w-a}{v})/2\hbar w}\right]\frac{dw}{dt}$$

$$= v\left[-\frac{\sqrt{2}}{2w^{3/2}}\sin\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i a\frac{w-a}{v})/2\hbar w} - \sqrt{\frac{2}{w}}\frac{n\pi x}{w^2}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i a\frac{w-a}{v})/2\hbar w}\right.$$

$$\left. + \sqrt{\frac{2}{w}}\sin\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i a\frac{w-a}{v})/2\hbar w}\frac{\partial}{\partial w}\left(\frac{imvx^2}{2\hbar w} - E_n^i ia\frac{w-a}{v\hbar w}\right)\right]$$

$$= v\left[-\frac{\phi_n}{2w} - \sqrt{\frac{2}{w}}\frac{n\pi x}{w^2}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w} + i\phi_n\left(-\frac{mvx^2}{2\hbar w^2} - E_n^i\frac{a^2}{\hbar vw^2}\right)\right]$$

$$= -\frac{v\phi_n}{2w} - \sqrt{\frac{2}{w}}\frac{n\pi vx}{w^2}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w} - v\left(\frac{imvx^2}{2\hbar w^2} + i\frac{n^2\pi^2\hbar^2}{2ma^2}\frac{a^2}{\hbar vw}\right)\phi_n$$

$$= -\frac{v\phi_n}{2w} - \sqrt{\frac{2}{w}}\frac{n\pi vx}{w^2}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w} - \left(\frac{imv^2x^2}{2\hbar w^2} + \frac{in^2\pi^2\hbar}{2mw}\right)\phi_n$$

$$= \left(-\frac{v}{2w} - \frac{imv^2x^2}{2\hbar w^2} - \frac{in^2\pi^2\hbar}{2mw}\right)\phi_n - \sqrt{\frac{2}{w}}\frac{n\pi vx}{w^2}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w}.$$

Then

$$i\hbar\frac{\partial\phi_n}{\partial t} = \left(-\frac{i\hbar v}{2w} + \frac{mv^2x^2}{2w^2} + \frac{n^2\pi^2\hbar^2}{2mw}\right) - \sqrt{\frac{2}{w}}\frac{i\hbar n\pi vx}{w^2}\cos\left(\frac{n\pi x}{w}\right)e^{i(mvx^2-2E_n^i at)/2\hbar w}.$$

We see that $H\phi_n = i\hbar\partial_t\phi_n$.

B.11.4   A Sudden Expansion

The expectation value of the energy is

$$\sum_n |c_n|^2 E_n = \sum_{n\neq 2} |c_n|^2 E_n + |c_2|^2 E_2,$$

where the nth coefficient and energy are (for $n \neq 2$)

$$c_n = \frac{4\sqrt{2}}{\pi} \sin\left(\frac{n\pi}{2}\right) \frac{1}{4 - n^2}, \quad E_n = \frac{n^2\pi^2\hbar^2}{8ma^2},$$

and (for $n = 2$),

$$c_2 = \frac{1}{\sqrt{2}}, \quad E_2 = \frac{\pi^2\hbar^2}{2ma^2}.$$

The goal is to compute the series

$$\sum_{n\neq 2} \left| \frac{4\sqrt{2}}{\pi} \sin\left(\frac{n\pi}{2}\right) \frac{1}{4 - n^2} \right|^2 \frac{n^2\pi^2\hbar^2}{8ma^2}.$$

Before we compute this infinite series, it is good to know the sum of reciprocals of squares of odd positive integers is

$$\sum_{\text{odd}+} \frac{1}{n^2} = \frac{1}{1^2} + \frac{1}{3^2} + \frac{1}{5^2} + \cdots = \frac{\pi^2}{8}.$$

Now do the calculation:

$$\sum_{n\neq 2} |c_n|^2 E_n = \sum_{n\neq 2} \left| \frac{4\sqrt{2}}{\pi} \sin\left(\frac{n\pi}{2}\right) \frac{1}{4 - n^2} \right|^2 \frac{n^2\pi^2\hbar^2}{8ma^2}$$

$$= \sum_{n\neq 2} \frac{32}{\pi^2} \sin^2\left(\frac{n\pi}{2}\right) \frac{1}{(4 - n^2)^2} \frac{n^2\pi^2\hbar^2}{8ma^2}$$

$$= \frac{4\hbar^2}{ma^2} \sum_{n\neq 2} \sin^2\left(\frac{n\pi}{2}\right) \left[\frac{n}{(n+2)(n-2)} \right]^2$$

$$= \frac{2\hbar^2}{ma^2} \sum_{n\neq 2} [1 - \cos(n\pi)] \left[\frac{1}{2}\left(\frac{1}{n+2} + \frac{1}{n-2} \right) \right]^2$$

$$= \frac{\hbar^2}{2ma^2} \sum_{n\neq 2} [1 + (-1)^{n+1}] \left[\frac{1}{(n+2)^2} + \frac{2}{(n+2)(n-2)} + \frac{1}{(n-2)^2} \right]$$

$$= \frac{\hbar^2}{2ma^2} \sum_{n\neq 2} [1 + (-1)^{n+1}] \left[\frac{1}{(n+2)^2} + \frac{1}{2(n-2)} - \frac{1}{2(n+2)} + \frac{1}{(n-2)^2} \right]$$

$$= \frac{\hbar^2}{ma^2} \sum_{\text{odd}+} \left[\frac{1}{(n+2)^2} + \frac{1}{2(n-2)} - \frac{1}{2(n+2)} + \frac{1}{(n-2)^2} \right].$$

Notice that the terms in the square bracket can pair up:

$$\sum_{\text{odd}+} \left[\frac{1}{(n+2)^2} + \frac{1}{(n-2)^2} \right] = \left(\frac{1}{3^2} + \frac{1}{5^2} + \cdots \right) + \left[\frac{1}{(-1)^2} + \frac{1}{1^2} + \frac{1}{3^2} + \frac{1}{5^2} + \cdots \right] = 2 \sum_{\text{odd}+} \frac{1}{n^2} = 2 \cdot \frac{\pi^2}{8} = \frac{\pi^2}{4}.$$

$$\sum_{\text{odd}+} \left[\frac{1}{2(n-2)} - \frac{1}{2(n+2)} \right] = \frac{1}{2} \left[\left(\frac{1}{-1} + \frac{1}{1} + \frac{1}{3} + \frac{1}{5} + \cdots \right) - \left(\frac{1}{3} + \frac{1}{5} + \cdots \right) \right] = 0.$$

Therefore,

$$\sum_{n\neq 2} |c_n|^2 E_n = \frac{\hbar^2}{ma^2} \sum_{\text{odd}+} \left[\frac{1}{(n+2)^2} + \frac{1}{2(n-2)} - \frac{1}{2(n+2)} + \frac{1}{(n-2)^2} \right] = \frac{\hbar^2}{ma^2} \frac{\pi^2}{4} = \frac{\pi^2\hbar^2}{4ma^2}.$$

the expectation value of the energy is

$$\langle H \rangle = \sum_{n\neq 2} |c_n|^2 E_n + |c_2|^2 E_2 = \frac{\pi^2\hbar^2}{4ma^2} + \frac{\pi^2\hbar^2}{4ma^2} = \boxed{\frac{\pi^2\hbar^2}{2ma^2}},$$

exactly the ground state energy of the original well.

B.12 Scattering

B.12.1 Rutherford Scattering

To be written.

B.12.2 Green's Function of the Helmholtz Equation

We want to solve for $G(\mathbf{r})$ in the equation

$$(\nabla^2 + k^2)G(\mathbf{r}) = \delta^3(\mathbf{r}).$$

A common way to do this is to use Fourier transform to turn a differential equation to an algebraic equation. Let the Fourier transform of $G(\mathbf{r})$ be

$$g(\mathbf{s}) \equiv \mathcal{F}[G(\mathbf{r})] = \int G(\mathbf{r})e^{-i\mathbf{s}\cdot\mathbf{r}}d^3\mathbf{r}.$$

The Fourier transform of $\nabla^2 G(\mathbf{r})$ is

$$
\begin{aligned}
\int e^{-i\mathbf{s}\cdot\mathbf{r}}(\nabla^2 G)\,d^3\mathbf{r} &= \int \nabla\cdot(e^{-i\mathbf{s}\cdot\mathbf{r}}\nabla G)\,d^3\mathbf{r} - \int \nabla(e^{-i\mathbf{s}\cdot\mathbf{r}})\cdot\nabla G\,d^3\mathbf{r} \\
&= \oint_S e^{-i\mathbf{s}\cdot\mathbf{r}}(\nabla G)\,d^3\mathbf{r} + i\mathbf{s}\cdot\int e^{-i\mathbf{s}\cdot\mathbf{r}}(\nabla G)\,d^3\mathbf{r} \\
&= i\mathbf{s}\cdot\int \nabla(e^{-i\mathbf{s}\cdot\mathbf{r}}G)\,d^3\mathbf{r} - i\mathbf{s}\cdot\int \nabla(e^{-i\mathbf{s}\cdot\mathbf{r}})G\,d^3\mathbf{r} \\
&= i\mathbf{s}\cdot\oint_S e^{-i\mathbf{s}\cdot\mathbf{r}}G\,d\mathbf{S} - s^2\int e^{-i\mathbf{s}\cdot\mathbf{r}}G\,d^3\mathbf{r} \\
&= -s^2 g(\mathbf{s}),
\end{aligned}
$$

where we used the fact that $G(\mathbf{r})$ and ∇G vanishes at the boundary (i.e. at infinity) because it needs to inherit the boundary conditions of ψ. The Fourier transform of the delta function is just 1. Thus, taking the Fourier transform of the whole equation $(\nabla^2 + k^2)G(\mathbf{r}) = \delta^3(\mathbf{r})$ reduces this differential equation to an algebraic equation

$$\int \left\{(\nabla^2 + k^2)G(\mathbf{r}) = \delta^3(\mathbf{r})\right\}e^{-i\mathbf{s}\cdot\mathbf{r}}d^3\mathbf{r} \implies (-s^2 + k^2)g(\mathbf{s}) = 1,$$

which gives

$$g(\mathbf{s}) = \frac{1}{k^2 - s^2}.$$

Taking the inverse Fourier transform of $g(\mathbf{s})$ gives back $G(\mathbf{r})$,

$$G(\mathbf{r}) = \frac{1}{(2\pi)^3}\int g(\mathbf{s})e^{i\mathbf{s}\cdot\mathbf{r}}\,d^3\mathbf{s} = \frac{1}{(2\pi)^3}\int \frac{e^{i\mathbf{s}\cdot\mathbf{r}}}{k^2 - s^2}\,d^3\mathbf{s}.$$

To calculate this integral, consider the spherical coordinates (s, θ, ϕ) with $\mathbf{r}$ along the polar axis. Then $\mathbf{s}\cdot\mathbf{r} = sr\cos\theta$, and the integral is

$$
\begin{aligned}
G(\mathbf{r}) &= \frac{1}{(2\pi)^3}\int_0^\infty\int_0^{2\pi}\int_0^\pi \frac{e^{isr\cos\theta}}{k^2 - s^2}s^2\sin\theta\,d\theta\,d\phi\,ds \\
&= \frac{1}{(2\pi)^2}\int_0^\infty \frac{1}{k^2 - s^2}e^{isr\cos\theta}d(\cos\theta)\,ds \\
&= \frac{1}{(2\pi)^2}\int_0^\infty \frac{1}{k^2 - s^2}\left[-\frac{e^{isr\cos\theta}}{isr}\right]_0^\pi ds \\
&= \frac{1}{4\pi^2 r}\int_{-\infty}^\infty \frac{s\sin(sr)}{k^2 - s^2}\,ds.
\end{aligned}
$$

We split the sine into exponentials,

$$G(\mathbf{r}) = \frac{i}{8\pi^2 r}\left[\int_{-\infty}^\infty \frac{se^{isr}}{(s-k)(s+k)}\,ds - \int_{-\infty}^\infty \frac{se^{-isr}}{(s-k)(s+k)}\,ds\right].$$

Each integral can be solved by contour integration (using either Cauchy's integral formula or the residue theorem),

$$G(\mathbf{r}) = \frac{i}{8\pi^2 r}\left[(i\pi e^{ikr}) - (-i\pi e^{ikr})\right] = -\frac{e^{ikr}}{4\pi r}.$$

The actual answer may differ from the one shown here, because the poles $s = k$ and $s = -k$ are on the contour (real lines). Each integral surely has a true answer, independent of the contour, but the results from different contour integrals are essentially the same. We just pick the most useful one $\sim e^{ikr}/r$.

B.12.3 1D Born Approximation

The one-dimensional time-independent Schrödinger equation is

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

Let $k = \sqrt{2mE}/\hbar$, we can write the Schrödinger equation as

$$\left(\frac{d^2}{dx^2} + k^2 \right) \psi(x) = \frac{2m}{\hbar^2}V(x)\psi(x).$$

The LHS are operators that act on ψ, while the RHS is the source (but still containing ψ). The Green's function for this equation satisfies

$$\left(\frac{d^2}{dx^2} + k^2 \right) G(x) = \delta(x). \tag{B.10}$$

We will not use Fourier transform this time. Equation (B.10) should remind us of the delta potential well. When $x \neq 0$, the Green's function satisfies

$$\left(\frac{d^2}{dx^2} + k^2 \right) G(x) = 0 \quad \Longrightarrow \quad G = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x > 0, \\ Ce^{ikx} + De^{-ikx}, & x < 0, \end{cases} \quad \text{and} \quad \frac{dG}{dx} = \begin{cases} ik(Ae^{ikx} - Be^{-ikx}), & x > 0, \\ ik(Ce^{ikx} - De^{-ikx}), & x < 0. \end{cases}$$

Integrate the Green's function equation on both sides from $-\epsilon$ to ϵ, and take the limit $\epsilon \to 0$,

$$\lim_{\epsilon \to 0} \int_{-\epsilon}^{\epsilon} \left(\frac{d^2}{dx^2} + k^2 \right) G(x)\, dx = \lim_{\epsilon \to 0} \int_{-\epsilon}^{\epsilon} \delta(x)\, dx = 1.$$

In the limit $\epsilon \to 0$, the k^2 of the integral vanishes, so we have a boundary condition on the first-derivative,

$$1 = \lim_{\epsilon \to 0} \int_{-\epsilon}^{\epsilon} \frac{d^2}{dx^2} G(x)\, dx = \left. \frac{dG}{dx} \right|_{0^+} - \left. \frac{dG}{dx} \right|_{0^-} = ik(A - B - C + D).$$

Another boundary condition is the continuity at $x = 0$,

$$A + B = C + D.$$

There are only two boundary conditions but four unknowns. But since the Green's function is not unique, we have freedom to set some constants to zero for simplicity. I will set B and C to be zero. Solving for A and D will give $A = D = -i/2k$. The Green's function is

$$G(x) = -\frac{i}{2k}e^{ik|x|}.$$

We can check that this indeed satisfy the Green's function equation (B.10). From Appendix B.9.1, we know the second-derivative of the exponential of absolute value functions,

$$\frac{d^2}{dx^2}e^{\alpha|x|} = 2\alpha\delta(x)e^{\alpha|x|} + \alpha^2 e^{\alpha|x|}.$$

Using this formula,

$$\frac{d^2}{dx^2}e^{ik|x|} = 2ik\delta(x)e^{ik|x|} + (ik)^2 e^{ik|x|} = e^{ik|x|}\left[2ik\delta(x) - k^2 \right].$$

Substituting into the LHS of the Green's function equation (B.10),

$$-\frac{i}{2k}\left(\frac{d^2}{dx^2} + k^2 \right) e^{ik|x|} = -\frac{i}{2k}e^{ik|x|}\left[2ik\delta(x) - k^2 + k^2 \right] = -\frac{i}{2k}e^{ik|x|}[2ik\delta(x)] = e^{ik|x|}\delta(x).$$

But $e^{ik|x|}\delta(x)$ is just $\delta(x)$ because an equality involving the delta function is defined by integrating on both sides,

$$\int_{-\infty}^{\infty} e^{ik|x|}\delta(x)\, dx = \int_{-\infty}^{\infty} \delta(x)\, dx \quad \Longrightarrow \quad e^{ik|x|}\delta(x) = \delta(x).$$

As mentioned above, the Green's function is not unique when there is not enough boundary conditions. You may check that $G(x) = (i/2k)e^{-ik|x|}$ is also a solution to (B.10), and it is linear independent from $-(i/2k)e^{ik|x|}$.

The solution to the Schrödinger equation is

$$\psi(x) = \frac{2m}{\hbar^2} \int_{-\infty}^{\infty} G(x - x')\psi(x')V(x')\,dx'.$$

Again, we can add a homogeneous solution $\psi_0(x)$ that satisfies the free particle equation,

$$\boxed{\psi(x) = \psi_0(x) - \frac{im}{\hbar^2 k} \int_{-\infty}^{\infty} e^{ik|x-x'|}V(x')\psi(x')\,dx'.}$$

In the Born approximation, suppose the scattering wave is not so different from the incident wave, $\psi \simeq \psi_0(x)$. We choose the incident wave to travel to the right, $\psi_0 = Ae^{ikx}$. Then

$$\begin{aligned}
\psi(x) \simeq &Ae^{ikx} - \frac{im}{\hbar^2 k} \int_{-\infty}^{\infty} e^{ik|x-x'|}V(x')Ae^{ikx'}\,dx' \\
= &Ae^{ikx} - \frac{imA}{\hbar^2 k} \left[\int_{-\infty}^{x} e^{ik(x-x')}V(x')e^{ikx'}\,dx' + \int_{x}^{\infty} e^{ik(x'-x)}V(x')e^{ikx'}\,dx' \right] \\
= &Ae^{ikx} - \frac{imA}{\hbar^2 k} \left[e^{ikx} \int_{-\infty}^{x} V(x')\,dx' + e^{-ikx} \int_{x}^{\infty} e^{2ikx'}V(x')\,dx' \right].
\end{aligned}$$

If $V(x)$ is localized, then $|x'| \ll |x|$. Suppose are interested in the reflection coefficient, so we can let $x \to -\infty$,

$$\psi(x) \simeq Ae^{ikx} - \frac{imA}{\hbar^2 k} \left[e^{ikx} \int_{-\infty}^{-\infty} V(x')\,dx' + e^{-ikx} \int_{-\infty}^{\infty} e^{2ikx'}V(x')\,dx' \right] = Ae^{ikx} - \frac{imA}{\hbar^2 k} e^{ikx} \int_{-\infty}^{\infty} e^{2ikx'}V(x')\,dx'$$

Apparently, the first term is the incident wave, so the second therm is the reflecting wave. The reflection coefficient is

$$R \simeq \frac{1}{|A|^2} \left| -\frac{imA}{\hbar^2 k} \int_{-\infty}^{\infty} e^{2ikx'}V(x')\,dx' \right|^2 = \left(\frac{m}{\hbar^2 k} \right)^2 \left| \int_{-\infty}^{\infty} V(x)e^{2ikx}\,dx \right|^2,$$

where the dummy index x' is changed to x in the final result. The transmission coefficient is defined as $T = 1 - R$, or

$$T \simeq 1 - \left(\frac{m}{\hbar^2 k} \right)^2 \left| \int_{-\infty}^{\infty} V(x)e^{2ikx}\,dx \right|^2.$$

We cannot do more without specifying $V(x)$. In Chapter 1, we encounter to potentials that admit scattering states. The first one is the delta well $V(x) = -\alpha\delta(x)$. From the Born approximation,

$$T_{\text{Born}} \simeq 1 - \left(\frac{m}{\hbar^2 k} \right)^2 \left| -\alpha \int_{-\infty}^{\infty} \delta(x)e^{2ikx}\,dx \right|^2 = 1 - \frac{m^2\alpha^2}{\hbar^4 k^2}.$$

Using $k^2 \equiv 2mE/\hbar^2$, this can be simplified to

$$T_{\text{Born}} \simeq 1 - \frac{m^2\alpha^2}{\hbar^4}\frac{\hbar^2}{2mE} = 1 - \frac{m\alpha^2}{2\hbar^2 E}.$$

The exact result of the transmission coefficient of the delta well is known (1.34). In the high energy limit, $E \gg m\alpha^2/2\hbar^2$,

$$T = \frac{1}{1 + m\alpha^2/2\hbar^2 E} = \left(1 + \frac{m\alpha^2}{2\hbar^2 E} \right)^{-1} \simeq 1 - \frac{m\alpha^2}{2\hbar^2 E} = T_{\text{Born}},$$

consistent with the Born approximation.

The second one is the finite square well,

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

From the Born approximation,

$$T_{\text{Born}} \simeq 1 - \left(\frac{m}{\hbar^2 k} \right)^2 \left| -V_0 \int_{-a}^{a} e^{2ikx}\,dx \right|^2 = 1 - \left(\frac{m}{\hbar^2 k} \right)^2 \left| -V_0 \left(\frac{1}{2ik} \right)(e^{2ika} - e^{-2ika}) \right|^2 = 1 - \left(\frac{m}{\hbar^2 k} \right)^2 \frac{V_0^2}{k^2} \sin^2(2ka) = 1 - \frac{m^2 V_0^2}{\hbar^2 k^4} \sin^2(2ka).$$

Substituting $k^2 \equiv 2mE/\hbar^2$,

$$T_{\text{Born}} \simeq 1 - \frac{m^2 V_0^2}{\hbar^2} \frac{\hbar^4}{4m^2 E^2} \sin^2\left(\frac{2a}{\hbar}\sqrt{2mE}\right) = 1 - \frac{\hbar^2 V_0^2}{4E^2} \sin^2\left(\frac{2a}{\hbar}\sqrt{2mE}\right).$$

We also know the exact result (1.37) for the finite square well. In the high energy limit $E \gg V_0$,

$$T = \left[1 + \frac{V_0^2}{4E(E+V_0)} \sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right)\right]^{-1} \simeq 1 - \frac{V_0^2}{4E(E+V_0)} \sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right) \simeq 1 - \frac{V_0^2}{4E_2} \sin^2\left(\frac{2a}{\hbar}\sqrt{2mE}\right) = T_{\text{Born}},$$

also consistent with the Born approximation. Thus, the Born approximation is very suitable to high energy scattering problems.