Lecture Notes on Modern Physics

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Chapter 1

Schroedinger Equation in One Dimension

1.1 Notes on Feynman’s Quantum Mechanics

The material presented in these notes is adapted from the book Quantum Mechanics and Path Integrals by R.P. Feynman and A.R. Hibbs.

1.1.1 Introduction to Quantum Mechanics

Electron interference experiment and probability concept in QM

As a way of introducing quantum mechanics, let us consider the following experiment. A collimated monoenergetic electron beam is propagating horizontally towards a vertical screen (labeled $\sigma$) which has two holes (labeled 1 and 2); we assume that the beam spot size is larger than the distance $d$ between the two holes. Behind screen $\sigma$, there is a backstop screen (labeled B) at a distance $L$ from screen $\sigma$ (both screens are parallel to each other), on which a detector can be moved vertically. Our goal here is to understand the outcome of this experiment based on various models for the electron.

The classical model of the electron is that it is a particle and, consequently, we expect that a single electron beign detected on the screen B at the location $x$ ($x = 0$ representing the symmetry axis of the system) either passed through hole 1 or hole 2 on screen $\sigma$. Our prediction of the outcome of this experiment, based on this classical picture of the electron, is that the probability $P$ of detection at location $x$ on screen B is the sum of $P_1$, the probability that the electron passed through hole 1 on screen $\sigma$, plus $P_2$, the probability that the electron passed through hole 2 on screen $\sigma$. Thus, we predict that

$$ P = P_1 + P_2. \quad (1.1) $$
Each probability $P_1$ and $P_2$ can be independently determined as follows. By closing hole 2 on screen $\sigma$, for example, we can measure directly the probability $P_1$ as a function of $x$. Typically, $P_1$ and $P_2$ look like Gaussian distributions centered at $x = \pm d/2$, respectively, on screen B. Assuming that the distance $a$ between the two holes is small enough, the sum of these two Gaussians exhibits a maximum at $x = 0$.

The experimental outcome is very different. Instead of the classically expected sum of two Gaussians, we observe an interference pattern similar to that obtained when waves are used (instead of electrons) in the two-slit experiment. Hence, we are forced to change our model for the electron: in this particular experiment, the electron behaves as a wave! Based on this wave picture of the electron, we say that the total probability $P$ is given as the square of a probability amplitude $\phi$:

$$ P \equiv |\phi|^2 \text{ where } \phi = \phi_1 + \phi_2, \quad (1.2) $$

where $\phi_1$ and $\phi_2$ are the partial probability amplitudes associated with the electron passing through hole 1 and hole 2 on screen $\sigma$, respectively. Because these amplitudes are complex-valued, we find, after defining $P_i \equiv |\phi_i|^2 \ (i = 1 \ or \ 2)$:

$$
\begin{align*}
P &= \phi^* \phi = (\phi_1^* + \phi_2^*) (\phi_1 + \phi_2) \\
&= P_1 + P_2 + 2 \text{Re}(\phi_1^* \phi_2), \quad (1.3)
\end{align*}
$$

where $\text{Re}(\cdots)$ denotes the real part of its argument. Hence, we see from (1.3) that $P \neq P_1 + P_2$, in agreement with the experimental observation, and that the difference is indeed associated with interference effects.

**The effect of observation and the Uncertainty Principle**

It is further observed that any attempts to determine which hole a single electron passed through before being detected will completely destroy the interference pattern and the outcome of this modified experiment will exhibit the classical result $P = P_1 + P_2$.

This experimental fact is expressed in terms of the Uncertainty Principle, which is stated as follows: Any determination of the alternative path taken by a process capable of following more than one alternative path destroys the interference between the alternative paths. In the original experiment described above, there were two alternative paths by which an electron could reach screen B and be detected: alternative path I corresponded to the electron passing through hole 1 on screen $\sigma$, while alternative path II corresponded to the electron passing through hole 2 on screen $\sigma$.

Let us now idealize our original experiment by considering the propagation of a single electron from point $a$ (the source) to point $b$ (the detector) through an intermediate screen $\sigma$ with two holes. The total probability amplitude that the electron, having started at point $a$ reaches point $b$ is defined as

$$ K(b|a) \equiv K(b|1) K(1|a) + K(b|2) K(2|a), \quad (1.4) $$
where, for example, \( K(1|a) \) denotes the conditional probability amplitude that the electron began at point \( a \) and reached hole 1 on screen \( \sigma \). Hence, in terms of our previous notation for the partial probability amplitude \( \phi_i \), we have \( \phi_i \equiv K(b|i) K(i|a) \).

Let us now generalize this idealized two-hole experiment by inserting \( N-1 \) additional screens \( \sigma_2, \sigma_3, ..., \sigma_N \) (also with two holes) between the screen \( \sigma_1 \) and point \( b \). We shall also introduce the following useful notation: \( (i, J_i) \) denotes hole \( J_i \) on screen \( \sigma_i \), where \( i = 1, ..., N \) and \( J_i = 1 \) or 2. The total probability amplitude that a single electron propagated from point \( a \) to point \( b \) is now

\[
K(b|a) \equiv \sum_{J} [ \, K(b|N,J_N) \cdots K(2,J_2|1,J_1) K(1,J_1|a) \, ],
\]

where \( \sum_{J} \equiv \sum_{J_1=1,2} \cdots \sum_{J_{N-1}=1,2} \). By taking the limit where \( N \) goes to infinity, we arrive at the concept of an integration over all possible paths linking points \( a \) and \( b \). A simple way to represent this path integration is to choose an intermediate point (say point \( c \)) between \( a \) and \( b \) and consider all paths going from \( a \) to \( c \) and then all paths going from \( c \) to \( b \). By summing over all such intermediate points, we write \( K(b|a) \) as

\[
K(b|a) \equiv \sum_{\text{All intermediate points } c} K(b|c) K(c|a),
\]

where \( K(b|c) \) and \( K(c|a) \) denote the conditional probability amplitudes associated with going from \( c \) to \( b \) and \( a \) to \( c \), respectively.

### 1.1.2 Derivation of the Schroedinger Equation

#### Classical Action and the Principle of Least Action

Before proceeding with the derivation of the Schroedinger equation, we must first introduce the concept of the classical action associated with a path. For the sake of simplicity, we shall focus our attention on particle motion with one degree of freedom. Hence, \( x \) is used to denote the position of a particle. A path is, thus, defined by giving \( x(t) \) as a function of time \( t \) and, at each time \( t \), we may define the instantaneous velocity \( v(t) \equiv \dot{x}(t) \).

According to the laws of classical (Newtonian) mechanics, a particle of mass \( m \) moving in a potential \( U(x) \) satisfies the equation of motion

\[
m \frac{d^2 x}{dt^2} \equiv m \ddot{x} = - \frac{dU}{dx}.
\]

The solution of this equation is \( x(t; z_0) \), where \( z_0 = (x_0, v_0) \) denotes the initial position and velocity of the particle at time \( t = 0 \). For each pair \( z_0 \), we obtain a unique solution of (1.7). A remarkable property associated with the physical path is that it minimizes a quantity called the action, denoted \( S \). A similar property is observed in the case of the

\[\text{(1.5)}\]

\[\text{(1.6)}\]
propagation of light between two points. For light propagation, Fermat’s principle (also known as the principle of least time) states that, when travelling between two points, light follows a path which minimizes the elapsed time \( \tau \equiv \int dx/v \). From Fermat’s principle, we recover well-known relations in geometric optics (e.g., the laws of reflection and refraction).

The principle of least action states that the physical path \( x(t; z_1) \) minimizes the action, defined as
\[
S[X] \equiv \int_{t_1}^{t_2} \left[ \frac{m}{2} \dot{X}^2(t) - U(X(t)) \right] dt,
\]
where the path \( X(t) \) is arbitrary (i.e., it does not correspond to the physical path). To find the equation which the action-minimizing path \( x(t) \) must satisfy, let us substitute the path \( X(t) = x(t) + \epsilon y(t) \) into (1.41), where \( \epsilon \) is a parameter and \( y(t) \) is an arbitrary function which satisfies the conditions:
\[
y(t_1) = 0 = y(t_2).
\] (1.9)

Upon substitution, (1.41) becomes
\[
S[x + \epsilon y] = \int_{t_1}^{t_2} \left[ \frac{m}{2} \left( \dot{x}^2 + 2\epsilon \dot{x} \dot{y} + \epsilon^2 \dot{y}^2 \right) - U(x + \epsilon y) \right] dt.
\] (1.10)

To determine the path \( x(t) \) for which the action \( S[x] \) is a minimum, it is reasonable to require
\[
\lim_{\epsilon \to 0} \frac{1}{\epsilon} \left( S[x + \epsilon y] - S[x] \right),
\] (1.11)
for all functions \( y(t) \) satisfying the boundary conditions (1.9). Carrying out this limit explicitly using (1.10), we find
\[
0 = \int_{t_1}^{t_2} dt \left( \dot{m} \dot{x} \dot{y} - y \frac{dU}{dx} \right) = (m \dot{x} y)_{t_1}^{t_2} - \int_{t_1}^{t_2} y(t) \left( m \ddot{x} + \frac{dU}{dx} \right) dt,
\] (1.12)

where integration by parts was performed on \( m \dot{x} \dot{y} \). Using the fact that \( y \) satisfies the boundary conditions (1.9), (1.12) becomes
\[
0 = \int_{t_1}^{t_2} y(t) \left( m \ddot{x} + \frac{dU}{dx} \right) dt.
\] (1.13)

Lastly, by requiring that (1.13) be true for all functions \( y \), we recover the equation of motion (1.7) whose solution yields the physical path. Hence, the physical path \( x(t) \) is indeed the path of least action, denoted \( S_{cl} \equiv S[x] \).

We remark that the principle of least action is somewhat mysterious in the following sense. It would appear that, as a particle moves from one point to another, a decision is made at each time step (i.e., \( \text{locally} \)) about choosing a path which will minimize the action, a quantity which is defined only \( \text{globally} \) (i.e., it is evaluated as an integral). As we shall see below, the resolution of this mystery, according to quantum mechanics, is that the particle does in fact move by following all the possible paths between \( x_1 \) at time \( t_1 \).
and $x_2$ at time $t_2$. Indeed, according to quantum mechanics, each path is given a partial probability amplitude and all paths must be included in order to have the correct total quantum probability amplitude [see (1.6) above]. In the classical limit (where $\hbar \to 0$), we find that only the physical path has a nonvanishing partial probability amplitude. This is a version of the Corresponding principle, which states that classical mechanics must be recovered from quantum mechanics in the limit $\hbar \to 0$. This situation is similar to the connection between nonrelativistic mechanics and relativistic mechanics, where the former is obtained from the latter in the limit $c \to \infty$.

**Feynman postulates and quantum wave function**

Feynman proceeds with the derivation of the Schrödinger equation by, first, introducing the following postulates.

**Postulate I**: The conditional probability amplitude $K(b|a)$ is expressed as

$$K(b|a) \equiv \sum_{\text{All paths } X(t)} \phi[X], \quad (1.14)$$

where the summation is over all paths $X(t)$ from $a$ to $b$ and the partial conditional probability amplitude associated with path $X(t)$ is

$$\phi[X] \propto \exp \left(\frac{i}{\hbar} S[X]\right), \quad (1.15)$$

with $S[X]$ corresponding to the action for this path. From (1.14)-(1.15), whenever the points $a \equiv x_a$ (at time $t_a$) and $b \equiv x_b$ (at time $t_a + \Delta t$) are infinitesimally close, we have

$$K(x_b, t_a + \Delta t|x_a, t_a) = \frac{1}{A} \exp \left(\frac{i}{\hbar} \frac{m(x_b - x_a)^2}{2\Delta t} - \Delta t U \left(\frac{x_a + x_b}{2}, t_a + \frac{\Delta t}{2}\right)\right), \quad (1.16)$$

where $A$ is a normalization constant.

This postulate provides the appropriate explanation for the mystery behind the principle of least action. Indeed, in the classical limit ($\hbar \to 0$), we find that the variations $\delta X$ around the paths $X(t)$ which are far away from the physical path $x(t)$ yield changes $\delta S$ for which $\delta S/\hbar$ is large. Consequently, such contributions tend to average out to zero because of the corresponding wild oscillations in $\phi[X]$. On the other hand, for variations $\delta X$ near the physical path $x(t)$, we get $\delta S \sim 0$ (to first order) and, consequently, paths $X(t)$ for which $S[X]$ is within $\hbar$ of $S_{cl}$ will contribute strongly. The resulting effect is that only paths in the neighborhood of the physical path $x(t)$ have a nonvanishing probability amplitude. In the strict limit $\hbar \to 0$, the only such path with a nonvanishing probability amplitude is the physical path.

**Postulate II**: The quantum wave function $\psi(x, t)$ is defined as the probability amplitude for the particle to be at the location $x$ at time $t$, i.e., $\psi(x, t) \equiv K(x, t|\bullet)$, where we are
not interested in the previous history of the particle (its previous location is denoted by •) but only on its future time evolution. Using (1.6), we know that the integral equation relating the wave function $\psi(x_2, t_2)$ to the wave function $\psi(x_1, t_1)$ is given as

$$\psi(x_2, t_2) \equiv \int_{-\infty}^{\infty} dx_1 \ K(x_2, t_2|x_1, t_1) \ \psi(x_1, t_1).$$

(1.17)

If we set in (1.18): $t_1 = t$ and $t_2 = t + \epsilon$, $x_2 = x$ and $x_1 = x + \eta$, then for small enough values of $\epsilon$, the conditional probability amplitude (1.16) can be used in (1.18) to yield

$$\psi(x, t + \epsilon) \equiv \int_{-\infty}^{\infty} d\eta \ K(x, t + \epsilon|x + \eta, t) \ \psi(x + \eta, t)
= \int_{-\infty}^{\infty} \frac{d\eta}{A} \ \exp \left[ \frac{i}{\hbar} \left( \frac{m\eta^2}{2\epsilon} - \epsilon U(x + \eta/2, t + \epsilon/2) \right) \right] \psi(x + \eta, t).$$

(1.18)

where a time-dependent potential $U(x, t)$ is considered.

1.1.3 Derivation of the Schroedinger equation

We will now consider the expansion of both sides of (1.18), up to first order in $\epsilon$ (and neglect all higher powers). Hence, on the left side of (1.18), we have

$$\psi(x, t + \epsilon) = \psi(x, t) + \epsilon \frac{\partial \psi(x, t)}{\partial t}.$$ 

(1.19)

On the right side of (1.18), on the other hand, we note that the exponential

$$\exp \left[ \frac{(im)}{2\hbar} \frac{\eta^2}{\epsilon} \right]$$

oscillates wildly as $\epsilon \to 0$ for all values of $\eta$ except those for which $m\eta^2/(2\hbar\epsilon) \sim 1$. We therefore conclude that the contribution from the integral in (1.18) will come from values $\eta = O(\epsilon^{1/2})$ and, consequently, we may expand the remaining functions appearing on the right side of (1.18) up to $\eta^2$. Thus, we may write

$$\psi(x + \eta, t) = \psi(x, t) + \eta \frac{\partial \psi(x, t)}{\partial x} + \frac{\eta^2}{2} \frac{\partial^2 \psi(x, t)}{\partial x^2},$$

while

$$\exp \left[ -\frac{i\epsilon}{\hbar} U(x + \eta/2, t + \epsilon/2) \right] = 1 - \frac{i\epsilon}{\hbar} U(x, t).$$

Expanding the right side of (1.18) to first order in $\epsilon$, therefore, yields

$$\left[ 1 - \frac{i\epsilon}{\hbar} U(x, t) \right] \psi(x, t) + \left( \frac{I_1}{I_0} \right) \frac{\partial \psi(x, t)}{\partial x} + \left( \frac{I_2}{2I_0} \right) \frac{\partial^2 \psi(x, t)}{\partial x^2},$$

(1.20)
where \( a \equiv m/(2i\hbar\epsilon) \) and
\[
I_n \equiv \int_{-\infty}^{\infty} d\eta \, \eta^n \, e^{-\alpha \eta^2},
\]
with \( I_0 = \sqrt{\pi/a}, I_1 = 0, \) and \( I_2 = 1/2a = (\hbar/m)\epsilon. \) Hence, we find that the terms of first order in \( \epsilon \) in (1.19) and (1.20) must also be equal, and we obtain
\[
\frac{\partial \psi(x,t)}{\partial t} = -\frac{i}{\hbar} U(x,t) \psi(x,t) + \frac{i\hbar}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2},
\]
or
\[
i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + U(x,t) \psi(x,t). \tag{1.21}
\]
This equation is known as the Schroedinger equation and it describes the time evolution of the wave function \( \psi(x,t). \)

### 1.1.4 Interpretation of the Schroedinger equation

As expected from the previous discussion, the physical interpretation of the wave function \( \psi(x,t) \) is that \( P(x,t) \equiv |\psi(x,t)|^2 \) corresponds to the probability that a particle finds itself at the location \( x \) at time \( t. \)

Making use of the Schroedinger equation (1.39), we may obtain the evolution for \( P(x,t) \) as follows. For this purpose, we need the evolution equation for \( \psi(x,t) \), given by (1.39), and the evolution equation for the complex-conjugate wave function \( \psi^*(x,t) \), obtained from (1.39) as
\[
-\frac{i\hbar}{\partial t} \frac{\partial \psi^*(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi^*(x,t)}{\partial x^2} + U(x,t) \psi^*(x,t). \tag{1.22}
\]
If we now multiply (1.39) with \( \psi^* \) and (1.22) with \( \psi, \) and subtract these two equations, we obtain (dividing by \( i\hbar \))
\[
\left( \psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} \right) = \frac{i\hbar}{2m} \left( \psi^* \frac{\partial^2 \psi}{\partial x^2} - \psi \frac{\partial^2 \psi^*}{\partial x^2} \right),
\]
where the terms involving the potential \( U \) cancel out. By defining the probability current
\[
J(x,t) \equiv \frac{i\hbar}{2m} \left( \psi \frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial \psi}{\partial x} \right),
\]
we obtain the conservation equation
\[
\frac{\partial P(x,t)}{\partial t} + \frac{\partial J(x,t)}{\partial x} = 0. \tag{1.23}
\]
Based on the interpretation of \( P(x,t), \) we require that
\[
1 \equiv \int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx.
\]
1.1.5 Schroedinger Equation: Summary

\[ \frac{d^2 \psi(x)}{dx^2} + \left[ \pm \frac{k^2}{\hbar^2} - \frac{2mV(x)}{\hbar^2} \right] \psi(x) = 0, \]

where \( k = \sqrt{2m|E|/\hbar^2} \) and the \((\pm)\)-sign applies to \( E > 0 \) or \( E < 0 \).

Types of Problems

- **Bound States** ⇒ Normalized wave function
- **Scattering States** ⇒ Reflection (\( R \)) and transmission (\( T \)) coefficients \((R^2 + T^2 = 1)\)

Discontinuities in \( V(x) \)

- **YES** ⇒ Impose continuity conditions:
  
  \[ \bullet \text{ Infinite discontinuity } V(x) = \infty \ (x > a): \quad \psi(x) \text{ alone must be continuous} \]
  
  \[ \bullet \text{ Delta Function } V(x) = \Omega \ \delta(x - a): \quad \psi'(a^+) - \psi'(a^-) = 2\Omega \ \psi(a) \]
  
  \[ \bullet \text{ Finite discontinuity } V(a^+) - V(a^-) < \infty: \quad \psi(x) \text{ and } \psi'(x) \text{ must be continuous} \]

- **NO** ⇒ Impose solvability conditions:
  
  \[ \bullet \lim_{x \to \pm\infty} \psi(x) = 0 \]
  
  \[ \bullet \psi(x) \text{ must be finite for all } x \]

1.2 Dynamics of Observables in Quantum Mechanics

The expectation value of the \( x^j \)-th coordinate of a particle of mass \( m \) is defined as

\[ \langle x^j \rangle_t \equiv \int d^3x \, \psi^*(x, t) \, x^j \, \psi(x, t), \]

where \( \psi(x, t) \) describes the quantum state of the particle at position \( x \) and at time \( t \). The wave function \( \psi(x, t) \) and its complex-conjugate \( \psi^*(x, t) \) satisfy the respective Schroedinger equations:

\[ \frac{\partial \psi}{\partial t} = \frac{i\hbar}{2m} \nabla^2 \psi - \frac{iV(x, t)}{\hbar} \psi, \]

\[ \frac{\partial \psi^*}{\partial t} = -\frac{i\hbar}{2m} \nabla^2 \psi^* + \frac{iV(x, t)}{\hbar} \psi^*, \]
where \( V(x, t) \) is the potential (possibly time-dependent) affecting the motion of the particle. The expectation value of the particle’s momentum \( \mathbf{p} \), on the other hand, is expressed as

\[
\langle p_j \rangle_t = -\frac{i}{2} \hbar \int d^3x \left[ \psi^*(x, t) \frac{\partial \psi(x, t)}{\partial x^j} - \frac{\partial \psi^*(x, t)}{\partial x^j} \psi(x, t) \right].
\]

We now take the time derivatives of \( \langle x^j \rangle_t \) and \( \langle p_j \rangle_t \), and show that we recover the standard Hamilton equations of classical mechanics. First, we evaluate

\[
\frac{d\langle x^j \rangle_t}{dt} = \int d^3x \left( \frac{\partial \psi^*}{\partial t} x^j \psi + \psi^* x^j \frac{\partial \psi}{\partial t} \right)
= \int d^3x \left( -\frac{i}{2m} \nabla^2 \psi^* + \frac{iV}{\hbar} \psi^* \right) x^j \psi + \psi^* x^j \left( \frac{i}{2m} \nabla^2 \psi - \frac{iV}{\hbar} \psi \right)
= \frac{i}{2m} \int d^3x \left( \psi^* x^j \nabla^2 \psi - \nabla^2 \psi^* x^j \psi \right)
= -\frac{i}{2m} \int d^3x \left[ \nabla(\psi^* x^j) \cdot \nabla \psi - \nabla \psi^* \cdot \nabla(\psi x^j) \right] \equiv \frac{\delta^j_k}{m} \langle p_k \rangle_t.
\]

Next, we evaluate

\[
\frac{d\langle p_j \rangle_t}{dt} = -i\hbar \int d^3x \left( \frac{\partial \psi^*}{\partial t} \frac{\partial \psi}{\partial x^j} - \frac{\partial \psi^*}{\partial x^j} \frac{\partial \psi}{\partial t} \right)
= -i\hbar \int d^3x \left( -\frac{i}{2m} \nabla^2 \psi^* + \frac{iV}{\hbar} \psi^* \right) \frac{\partial \psi}{\partial x^j} - \frac{\partial \psi^*}{\partial x^j} \left( \frac{i}{2m} \nabla^2 \psi - \frac{iV}{\hbar} \psi \right)
= -\int d^3x \psi^*(x, t) \left( \frac{\partial V(r, t)}{\partial x^j} \right) \psi(x, t) \equiv -\left( \frac{\partial V(x, t)}{\partial x^j} \right) \psi(x, t).
\]

An observable \( \mathcal{A}(t) \) is defined as the expectation value of a certain function \( A(x, t) \):

\[
\mathcal{A}(t) \equiv \langle \mathcal{A} \rangle_t = \int d^3x \psi^*(x, t) A(x, t) \psi(x, t).
\]

The time derivative of \( \mathcal{A}(t) \) is

\[
\frac{d\mathcal{A}(t)}{dt} = \int d^3x \left( \frac{\partial \psi^*}{\partial t} A \psi + \psi^* \frac{\partial A}{\partial t} \psi + \psi^* A \frac{\partial \psi}{\partial t} \right)
= \left\langle \frac{\partial \mathcal{A}}{\partial t} \right\rangle_t + \int d^3x \left[ \frac{i}{2m} \nabla \psi^* \cdot \nabla (A \psi) - \frac{i}{2m} \nabla (\psi^* A) \cdot \nabla \psi \right]
= \left\langle \left( \frac{\partial \mathcal{A}}{\partial t} + \frac{\mathbf{p} \cdot \nabla A}{m} \right) \right\rangle_t.
\]
1.3 Particle in a Finite Well

1.3.1 Part I: Even-parity Bound States

The even-parity global solution for the finite square-well potential problem is

\[
\psi(x) = B \begin{cases} 
  (e^\beta \cos \alpha) e^{Kx} & x \leq -a/2 \ (\text{region I}) \\
  \cos kx & |x| < a/2 \ (\text{region II}) \\
  (e^\beta \cos \alpha) e^{-Kx} & x \geq a/2 \ (\text{region III}) 
\end{cases}
\]

The normalization constant \(B\) can now evaluated from the condition \(\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1\), or

\[
\frac{1}{B^2} = \int_{-\infty}^{-a/2} e^{K(\alpha + 2x)} \cos^2 \alpha \, dx + \int_{-a/2}^{a/2} \cos^2 kx \, dx + \int_{a/2}^{\infty} e^{K(\alpha - 2x)} \cos^2 \alpha \, dx
\]

\[
= \frac{1}{2K} \cos^2 \alpha + \left( \frac{a}{2} + \frac{1}{2k} \sin 2\alpha \right) + \frac{1}{2K} \cos^2 \alpha
\]

\[
\equiv \frac{a}{2} + \left[ \frac{1}{K} \cos^2 \alpha + \frac{1}{k} \sin \alpha \cos \alpha \right].
\]

The requirement that \(\psi'(x)\) be also continuous at the boundaries \(x = \pm a/2\) yields the energy equation \(K \cos \alpha = k \sin \alpha\) or

\[
\sqrt{\frac{\varepsilon}{V_0 - \varepsilon}} = \tan \left( \alpha_0 \sqrt{\frac{V_0 - \varepsilon}{V_0}} \right),
\]

where \(\alpha_0 \equiv a \sqrt{mV_0/2\hbar^2}\). When this condition is substituted into the normalization condition for \(B\), we find

\[
\frac{1}{B^2} = \frac{1}{k} (\alpha + \cot \alpha).
\]

The roots (solutions) to the energy equation are given in terms of allowed energies \(\varepsilon\). By defining \(\xi \equiv \varepsilon/V_0 < 1\), the energy condition becomes

\[
\sqrt{\xi} = \sqrt{1 - \xi} \tan \left( \alpha_0 \sqrt{1 - \xi} \right)
\]

The right-hand side of this condition is a function of \(\xi\) which exhibits zeros and infinities at certain values of \(\xi\). The zeroes of \(\tan(\alpha_0 \sqrt{1 - \xi})\) are located at \(\xi_n^0\) \((n = 0, 1, \ldots)\), where

\[
0 \leq \xi_n^0 \equiv 1 - \left( \frac{n \pi}{\alpha_0} \right)^2 \equiv 1 - \frac{V_0^{(n)}}{V_0} \leq 1,
\]
where
\[ V_0^{(n)} = \frac{n^2 \hbar^2}{2ma^2} = n^2 W, \]
while the infinities of \( \tan(\alpha_0 \sqrt{1 - \xi}) \) are located at \( \xi_n^\infty \) (for \( n = 1, 2, ... \)), where
\[ 0 \leq \xi_n^\infty \equiv 1 - \left( \frac{(2n - 1)\pi}{2\alpha_0} \right)^2 < 1. \]

(See Figure below for \( \alpha_0 = 5 \))

Note that
\[ 1 = \xi_0^0 > \xi_1^\infty > \xi_1^0 > \xi_2^\infty > \cdots > 0, \]
and that each root \( \Xi_n \) (for \( n = 1, 2, ... \)) satisfies the relation
\[ 0 < \xi_n^\infty < \Xi_n < \xi_{n-1}^0 \leq 1. \]

The first root \( \Xi_1 \) thus always satisfies the condition \( \xi_1^\infty < \Xi_1 < 1 \), i.e., there exists at least one root for all values of \( V_0 \). If \( \xi_1^0 < 0 \) (i.e., if \( V_0 < W \)), however, there exists only one root and a bound particle in such a shallow well only has a single energy level for even-parity modes. A second root appears as soon as \( \xi_1^0 > 0 \) and only two roots exist as long as \( \xi_2^0 < 0 \) (i.e., \( V_0 < 4W \)). In general, we find that \( n \) roots \( \Xi_1 > \Xi_2 > \cdots > \Xi_n \) exist when \( (n - 1)^2 W < V_0 < n^2 W \) (\( n = 1, 2, ... \)). For an electron, the well-depth scale \( W \) is
\[ W(\text{eV}) = \frac{(hc)^2/2mc^2}{a^2} = 150 \ a^{-2}(\text{Å}). \]

Hence, a 5-Åwide square potential well has a depth scale of \( W = (150/25) \text{eV} = 6 \text{eV} \). The number of energy levels for even-parity bound states is \( n \) if \( 6(n - 1)^2 < V_0(\text{eV}) < 6n^2 \); for example, three roots exist for \( V_0 = 40 \text{eV} \), since \( 24 \text{eV} < 40 \text{eV} < 54 \text{eV} \).
1.3.2 Part II: Odd-parity Bound States

The odd-parity global solution for the finite square-well potential problem is

\[ \psi(x) = B \begin{cases} 
- \left( e^\beta \sin \alpha \right) e^{Kx} & x \leq -a/2 \quad \text{(region I)} \\
\sin kx & |x| < a/2 \quad \text{(region II)} \\
\left( e^\beta \sin \alpha \right) e^{-Kx} & x \geq a/2 \quad \text{(region III)}
\end{cases} \]

The normalization constant \( B \) can now be evaluated from the condition \( \int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1 \), or

\[
\frac{1}{B^2} = \frac{1}{2K} \sin^2 \alpha + \left( \frac{a}{2} - \frac{1}{2k} \sin 2\alpha \right) + \frac{1}{2K} \sin^2 \alpha
\]

\[ = \frac{a}{2} + \left[ \frac{1}{K} \sin^2 \alpha - \frac{1}{k} \sin \alpha \cos \alpha \right]. \]

The requirement that \( \psi'(x) \) be also continuous at the boundaries \( x = \pm a/2 \) yields the energy equation \(-K \sin \alpha = k \cos \alpha\) or

\[ -\sqrt{\chi} = \sqrt{1-\chi} \cot \left( \alpha_0 \sqrt{1-\chi} \right) \]

where \( \alpha_0 \equiv a \sqrt{mV_0/2\hbar^2} \) and \( \chi \equiv \varepsilon/V_0 \). When this condition is substituted into the normalization condition for \( B \), we find

\[ \frac{1}{B^2} = \frac{1}{k} \left( \alpha - \tan \alpha \right). \]

The roots (solutions) to the energy equation are given in terms of allowed energies \( X_n < 1 \). The right-hand side of this equation is a function of \( \chi \) which exhibits zeros and infinities at certain values of \( \chi \). The zeros of \( \sqrt{1-\chi} \cot(\alpha_0 \sqrt{1-\chi}) \) are located at \( \chi_n^0 \quad (n = 0, 1, \ldots) \), where

\[ 0 \leq \chi_n^0 \equiv 1 - \left( \frac{2n-1}{2\alpha_0} \right)^2 \equiv 1 - (2n-1)^2 \frac{W_o}{V_0} \leq 1, \]

where

\[ W_o \equiv \frac{(\pi \hbar)^2}{8ma^2}. \]
while the infinities of \( \cot(\alpha_0 \sqrt{1 - \chi}) \) are located at \( \chi_n^\infty \) (for \( n = 1, 2, \ldots \)), where
\[
0 \leq \chi_n^\infty \equiv 1 - \left( \frac{n\pi}{\alpha_0} \right)^2 < 1.
\]

(See Figure below for \( \alpha_0 = 5 \))

Note that
\[
1 = \chi_0^\infty > \chi_1^0 > \chi_1^\infty > \chi_2^0 > \cdots > 0,
\]
and that each root \( X_n \) (for \( n = 1, 2, \ldots \)) satisfies the relation
\[
0 < \chi_n^\infty < X_n < \chi_n^0 \leq 1.
\]

The first odd-parity root \( X_1 > 0 \) exists only if the condition \( \chi_1^0 > 0 \) is satisfied. If \( \chi_1^0 < 0 \) (i.e., if \( V_0 < W_o \)), however, an odd-parity state in such a shallow well is impossible. A second odd-parity root appears as soon as \( \chi_2^0 > 0 \) (i.e., if \( V_0 < 9 W_o \)) and only two roots exist as long as \( \chi_3^0 < 0 \) (i.e., \( V_0 < 25 W_o \)). In general, we find that \( n \) roots \( X_1 > X_2 > \cdots > X_n \) exist when \( (2n - 1)^2 W_o < V_0 < (2n + 1)^2 W_o \) (\( n = 1, 2, \ldots \)). For an electron, the well-depth scale \( W_o \) is
\[
W_o(\text{eV}) = \frac{(\pi \hbar)^2}{8ma^2} = 9.40 \ a^{-2}(\text{Å}).
\]

Hence, a 3-Å-wide square potential well has a depth scale of \( W_o \simeq 1 \text{ eV} \).

### 1.3.3 Part III: Potential Scattering

In the second part of this work, we consider the case where the total particle energy \( E \) is positive. In particular, we investigate what happens when an incoming particle coming
from the left of the square-well potential is scattered by the potential. Scattering theory
tells us that reflection and transmission occurs as will be shown below.

To simplify the calculations, we redefine the square-well potential to be

\[
V(x) = \begin{cases} 
0 & x \leq 0 \quad \text{(region I)} \\
-V_0 & 0 < x < a \quad \text{(region II)} \\
0 & x \geq a \quad \text{(region III)}
\end{cases}
\]

The global solution to the Schrödinger equation for the case of this square-well potential is

\[
\psi(x) = \begin{cases} 
e^{ikx} + A_r e^{-ikx} & x \leq 0 \\
B e^{iKx} + C e^{-iKx} & 0 < x < a \\
A_t e^{i(k(x-a))} & x \geq a
\end{cases}
\]

where \( k = \sqrt{2mE/\hbar^2} \) and \( K = \sqrt{2m(E + V_0)/\hbar^2} \). Here, the amplitude of the incident wave is set at one whereas the wave amplitudes for the reflected (r) wave and the transmitted (t) wave are denoted \( A_r \) and \( A_t \), respectively, while \( B \) and \( C \) are wave amplitudes associated with the particle being above the square well.

Continuity in \( \psi(x) \) at the boundaries \( x = 0 \) and \( x = a \) yields

\[
1 + A_r = B + C \\
A_t = B e^{i\beta} + C e^{-i\beta}
\]

where \( \beta \equiv Ka \). We can thus solve for \( B \) and \( C \) in terms of \( A_r \) and \( A_t \) as

\[
B = \frac{i}{2 \sin \beta} \left[ e^{-i\beta} (1 + A_r) - A_t \right], \\
C = \frac{-i}{2 \sin \beta} \left[ e^{i\beta} (1 + A_r) - A_t \right].
\]

Continuity in \( \psi'(x) \), on the other hand, yields

\[
k (1 - A_r) = K (B - C) \\
k A_t = K (B e^{i\beta} - C e^{-i\beta})
\]

which becomes upon substitution of the expressions for \( B \) and \( C \):

\[
\begin{pmatrix} b & -ic \\ -ic & b \end{pmatrix} \begin{pmatrix} A_r \\ A_t \end{pmatrix} = \begin{pmatrix} b^* \\ ic \end{pmatrix},
\]
where
\[ b \equiv k + iK \cot \beta \quad \text{and} \quad c \equiv \frac{K}{\sin \beta}. \]

These equations can easily be solved and we find the following expressions for the reflected-wave amplitude \( A_r \) and the transmitted-wave amplitude \( A_t \):

\[ A_r = \frac{1}{\Delta} \left( |b|^2 - c^2 \right), \]
\[ A_t = \frac{1}{\Delta} [ic (b^* + b)] = 2i \frac{k c}{\Delta}, \]

where
\[ \Delta \equiv b^2 + c^2 = 2kB - \left( |b|^2 - c^2 \right) = \left( k^2 + K^2 \right) + 2i kK \cot \beta. \]

We note that
\[ |A_r|^2 = \frac{1}{|\Delta|^2} (2kb^* - \Delta^*) (2kb - \Delta) \]
\[ = \frac{1}{|\Delta|^2} \left[ 4k^2 |b|^2 + |\Delta|^2 - 2k(\Delta^* + b^* \Delta) \right] \]
\[ = 1 - \frac{4k^2 c^2}{|\Delta|^2} \equiv 1 - |A_t|^2. \]

Hence, the reflected and transmitted waves satisfy the following conservation law:
\[ 1 = |A_r|^2 + |A_t|^2. \]

In particular, the transmission coefficient \( T \equiv |A_t|^2 \) can be explicitly evaluated as

\[ T = \frac{4k^2 K^2 / \sin^2 \beta}{(k^2 + K^2)^2 + 4k^2 K^2 \cot^2 \beta} = \left[ 1 + \frac{V_0^2}{4E(E + V_0)} \sin^2 \beta \right]^{-1}, \]

where \( \beta \equiv a \sqrt{2m(E + V_0)/\hbar^2} \). The Figure below shows the transmission coefficient \( T(E) \)
as a function of $E/V_0$ for $a \sqrt{2mV_0/\hbar^2} = 20$.

Hence, for certain values of energy $E$, where $\beta(E) \equiv n\pi \ (n = 1, 2, \ldots)$, we find $T \equiv 1$ (i.e., the well is perfectly transparent). For all other values of energy $E$, we find $T < 1$ (i.e., waves are reflected at the well).

### 1.4 Tunneling Effect

Consider the following barrier potential

$$V(x) = \begin{cases} 
0 & x \leq 0 \quad \text{(region I)} \\
V_0 & 0 < x < a \quad \text{(region II)} \\
0 & x \geq a \quad \text{(region III)}
\end{cases}$$

In this work we consider the case where the total energy $E$ of the particle is less than the barrier height $V_0$.

In regions I and III (i.e., outside of the barrier), the Schroedinger equation is written as

$$E \psi_{\text{out}}(x) + \frac{\hbar^2}{2m} \psi''_{\text{out}}(x) = 0,$$

which has the following solutions: in region I ($x \leq 0$), we find

$$\psi_I(x) = e^{ikx} + A_r e^{-ikx} \quad \text{with} \quad k \equiv \sqrt{\frac{2mE}{\hbar^2}};$$
while in region III \((x \geq a)\), we find
\[
\psi_{III}(x) = A_t e^{ik(x-a)},
\]
where \(A_r\) and \(A_t\) denote the amplitudes of the reflected (r) and transmitted (t) wave functions, respectively. In region II, the Schrödinger equation is written as
\[
-(V_0 - E) \psi_{II}(x) + \frac{\hbar^2}{2m} \psi''_{II}(x) = 0
\]
whose solution is
\[
\psi_{II}(x) = Be^{-Kx} + Ce^{Kx} \quad \text{with} \quad K \equiv \sqrt[2m]{\frac{2m}{\hbar^2}(V_0 - E)}.
\]
Here, \(A_r, A_t, B, \) and \(C\) are constants determined from boundary conditions.

The requirements on the global solution \(\psi(x)\) is that \(\psi(x)\) and its first derivative \(\psi'(x)\) shall be continuous at \(x = 0\) and \(x = a\). Continuity in \(\psi(x)\) yields the two equations
\[
1 + A_r = B + C \quad \text{and} \quad A_t = Be^{-\beta} + C e^{\beta},
\]
where \(\beta = K a\). We can thus solve for \(B\) and \(C\) in terms of \(A_r\) and \(A_t\) as
\[
B = \frac{1}{2 \sinh \beta} \left[ e^\beta (1 + A_r) - A_t \right],
\]
\[
C = \frac{-1}{2 \sin \beta} \left[ e^{-\beta} (1 + A_r) - A_t \right],
\]
where \(\sinh \beta = (e^\beta - e^{-\beta})/2\). Continuity in \(\psi'(x)\), on the other hand, yields
\[
\begin{align*}
&ik (1 - A_r) = K (C - B) \\
&ik A_t = K \left( C e^\beta - B e^{-\beta} \right),
\end{align*}
\]
which becomes upon substitution of the expressions for \(B\) and \(C\):
\[
\begin{pmatrix} b & c \\ c & b \end{pmatrix} \begin{pmatrix} A_r \\ A_t \end{pmatrix} = \begin{pmatrix} -b^* \\ -c \end{pmatrix},
\]
where
\[
b \equiv ik - K \coth \beta \quad \text{and} \quad c \equiv \frac{K}{\sinh \beta}.
\]
This matrix equation can easily be solved and we find the following expressions for the reflected-wave amplitude \(A_r\) and the transmitted-wave amplitude \(A_t\):
\[
A_r = \frac{1}{\Delta} \left( c^2 - |b|^2 \right),
\]
\[
A_t = \frac{1}{\Delta} \left[ c (b^* - b) \right] = -2i \frac{kc}{\Delta},
\]
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where
\[ \Delta \equiv b^2 - c^2 = 2ikb + (|b|^2 - c^2). \]

We note that
\[
|A_r|^2 = \frac{1}{|\Delta|^2} \left( 2ikb - \Delta \right) \left( -2ikb^* - \Delta^* \right)
= \frac{1}{|\Delta|^2} \left( 4k^2 |b|^2 + |\Delta|^2 + 2ik \left( b^* \Delta - b \Delta^* \right) \right)
= \left| 1 - \frac{4k^2c^2}{|\Delta|^2} \right| \equiv 1 - |A_t|^2.
\]

Hence, the reflected and transmitted waves satisfy the following conservation law:
\[ 1 = |A_r|^2 + |A_t|^2. \]

A surprising result is that the transmission probability \( T \equiv |A_t|^2 \) is not zero as one might expect classically. This is called the tunneling effect, i.e., the finite probability of a quantum particle for penetrating a potential barrier and escaping on the other side of the barrier. We now derive an explicit formula for the transmission probability:
\[
T = \frac{4E(V_0 - E)/\sinh^2 \beta}{|(2E - V_0) + 2i \sqrt{E(V_0 - E)} \coth \beta|^2}
= \frac{4E(V_0 - E)/\sinh^2 \beta}{(2E - V_0)^2 + 4E(V_0 - E) \coth^2 \beta}
= \left[ \frac{1 + \sinh^2 \beta}{\cosh^2 \beta} + \frac{(2E - V_0)^2}{4E(V_0 - E) \sinh^2 \beta} \right]^{-1}
= \left[ 1 + \frac{V_0^2}{4E(V_0 - E)} \sinh^2 \left( a\sqrt{\frac{2m}{\hbar^2} V_0 - E} \right) \right]^{-1}.
\]

Note that in the classical limit of \( \hbar \to 0 \), we find
\[ T \approx 16 \frac{E}{V_0} \left( 1 - \frac{E}{V_0} \right) \exp \left( -\frac{2a}{\hbar} \sqrt{2m(V_0 - E)} \right) \to 0. \]

Furthermore, the transmission probability \( T \) is also vanishingly small when the barrier width \( a \) is much larger than the quantum width
\[
a_Q = \frac{\hbar}{\sqrt{2mV_0}} = \frac{\hbar c/mc^2}{\sqrt{2V_0/mc^2}} = \frac{2.73 \times 10^{-3} \text{ Å}}{\sqrt{V_0/mc^2}}.
\]
For an electron hitting a 10-eV barrier \((V_0 = 10 \text{ eV}, mc^2 = 511 \text{ keV})\), the quantum width is \(a_Q = 0.6 \text{ Å}\).

By defining the dimensionless energy parameter \(\xi \equiv E/V_0\), the transmission coefficient becomes

\[
T \equiv \left[ 1 + \frac{1}{4\xi (1 - \xi)} \sinh^2 \left( \frac{a}{a_Q \sqrt{1 - \xi}} \right) \right]^{-1}.
\]

Note that by using the electron wavenumber \(k_e \equiv 2\pi/\lambda_e = \sqrt{2mE}/\hbar\), we find

\[
k_e a \equiv \frac{a\sqrt{\xi}}{a_Q} < \frac{a}{a_Q}.
\]

Hence, we expect significant tunneling to occur only when the de Broglie wavelength of the electron is comparable to the barrier’s width, i.e., when \(k_e a\) is not too large.

1.5 Simple Harmonic Oscillator

1.5.1 Series Solution of the Schroedinger Equation

Consider solving the Schroedinger equation

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

with the potential \(V(x)\) given by the simple harmonic oscillator potential

\[
V(x) = \frac{1}{2} \kappa x^2,
\]

where \(\kappa\) is the so-called spring constant. Using the definitions

\[
E \equiv \hbar \omega_0 \quad \text{and} \quad x \equiv s a,
\]

where \(\omega_0 \equiv \sqrt{\kappa/m}\) and \(a \equiv \sqrt{\hbar/(2m\omega_0)}\), the Schroedinger equation becomes

\[
\frac{d^2\psi(s)}{ds^2} + \left( E - \frac{s^2}{4} \right) \psi(s) = 0.
\]

In the asymptotic limit where \(s \gg 2\sqrt{E}\), this equation becomes \(\psi'' \sim \psi s^2/4\), whose bounded solution at \(s = \pm \infty\) is \(\psi(s) \sim \exp(-s^2/4)\). Hence, we express the wavefunction \(\psi(s)\) as

\[
\psi(s) \equiv e^{-s^2/4} \varphi(s),
\]

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where \( \varphi(s) \) satisfies the equation

\[
\varphi''(s) - s \varphi'(s) + \left( \mathcal{E} - \frac{1}{2} \right) \varphi(s) = 0.
\]

The series solution of this equation, of the form \( \varphi(s) = \sum_{k=0}^\infty c_k s^k \), yields

\[
0 = \sum_{k=0}^\infty s^k \left[ (k+2)(k+1) c_{k+2} + \left( \mathcal{E} - k - \frac{1}{2} \right) c_k \right],
\]

which implies that the coefficients \( c_k \) are governed by the recursion relation

\[
c_{k+2} = - \frac{\left( \mathcal{E} - k - \frac{1}{2} \right)}{(k+2)(k+1)} c_k.
\]

This recursion relation leads to an unbounded solution at \( s = \pm \infty \) unless the series truncates at a finite value of \( k = n \geq 0 \), i.e., \( c_k = 0 \) for all \( k \geq n + 2 \) if

\[
\mathcal{E}_n \equiv n + \frac{1}{2} \quad \text{or} \quad E_n = \left( n + \frac{1}{2} \right) \hbar \omega_0.
\]

Thus, the solution of the Schroedinger equation for the simple harmonic oscillator potential is

\[
\psi_n(x) = A_n e^{-x^2/4a^2} \sum_{k=0}^n c_k x^k,
\]

where

\[
c_{k+2} = - \frac{(n-k)}{(k+2)(k+1)} c_k.
\]

### 1.5.2 Normalization of the General Solution

The general solution can be written in terms of the polynomial \( H_n(s) \) (of order \( n \)) defined as

\[
H_n(s) \equiv (-1)^n e^{s^2/2} \frac{d^n}{ds^n} \left( e^{-s^2/2} \right) \equiv s^n - \frac{n!}{2(n-2)!} s^{n-2} + \frac{n!}{8(n-4)!} s^{n-4} - \cdots,
\]

so that

\[
\psi_n(x) = A_n H_n(x/a) e^{-x^2/4a^2},
\]

where \( A_n \) is a normalization constant. We note that \( \psi_n(x) \) is an even(odd) function of \( x \) if \( n \) is even(odd). The normalization condition \( \int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = 1 \) can be written as

\[
\frac{1}{A_n^2} = \int_{-\infty}^{\infty} H_n(x/a) e^{-x^2/2a^2} H_n(x/a) dx = a \int_{-\infty}^{\infty} H_n(s) e^{-s^2/2} H_n(s) ds = a \int_{-\infty}^{\infty} H_n(s) \left( -1 \right)^n \frac{d^n}{ds^n} \left( e^{-s^2/2} \right) ds
\]

\[
= a \left[ \frac{d^n}{ds^n} H_n(s) \right]_{s = \pm \sqrt{\pi}} \left[ \int_{-\infty}^{\infty} e^{-s^2/2} ds \right] = a \sqrt{2\pi} n!,
\]

so that

\[
A_n = \sqrt{\frac{\sqrt{2\pi} n!}{\int_{-\infty}^{\infty} H_n(s) e^{-s^2/2} H_n(s) ds}} = \sqrt{\frac{\sqrt{2\pi} n!}{\sqrt{\frac{\sqrt{2\pi} n!}{\int_{-\infty}^{\infty} e^{-s^2/2} ds}}}} = \sqrt{\frac{\sqrt{2\pi} n!}{\sqrt{\frac{\sqrt{2\pi} n!}{2\pi}}}} = \sqrt{\frac{2\pi n!}{\sqrt{2\pi} n!}} = \sqrt{\frac{2\pi}{\sqrt{2\pi}}} = \sqrt{\frac{2\pi}{\sqrt{2\pi}}} = 1.
\]
so that the general normalized solution is

\[ \psi_n(x) = \frac{1}{\sqrt{a \sqrt{2\pi} n!}} H_n(x/a) e^{-x^2/4a^2}. \]

### 1.5.3 Expectations Values and Uncertainty Principle

The expectation value of \( x \) in the state \( n \), denoted \( \langle x \rangle_n \), is zero. The expectation value of \( x^2 \) on the other hand is

\[ \langle x^2 \rangle_n = \frac{a^2}{\sqrt{2\pi} n!} \int_{-\infty}^\infty H_n(s) s^2 e^{-s^2/2} H_n(s) \, ds = \frac{a^2}{\sqrt{2\pi} n!} \int_{-\infty}^\infty \frac{d^n}{ds^n} \left( s^2 H_n(s) \right) e^{-s^2/2} \, ds \]

\[ = \frac{a^2}{\sqrt{2\pi} n!} \int_{-\infty}^\infty \left( s^2 \cdot \frac{d^n H_n}{ds^n} + n \cdot 2s \cdot \frac{d^{n-1} H_n}{ds^{n-1}} + \frac{n(n-1)}{2} \cdot 2 \cdot \frac{d^{n-1} H_n}{ds^{n-1}} \right) e^{-s^2/2} \, ds \]

\[ = \frac{a^2}{\sqrt{2\pi}} \int_{-\infty}^\infty \left[ s^2 (2n+1) + \frac{n(n-1)}{2} (s^2 - 1) \right] e^{-s^2/2} \, ds. \]

We now use the following definition

\[ \int_{-\infty}^\infty s^{2\ell} e^{-s^2/2} \, ds \equiv (\sqrt{2})^{2\ell+1} \Gamma(\ell + 1/2), \]

where \( \Gamma(1/2) = \sqrt{\pi} \) and \( \Gamma(\ell + 1/2) = (\ell - 1/2) \Gamma(\ell - 1/2) \), to obtain

\[ \langle x^2 \rangle_n \equiv (2n+1) a^2 = \left( n + \frac{1}{2} \right) \frac{\hbar}{m\omega_0}. \]

This results implies that the expectation value of the potential energy is

\[ \langle V(x) \rangle_n = \frac{\kappa}{2} \langle x^2 \rangle_n = \left( n + \frac{1}{2} \right) \kappa a^2 = \left( n + \frac{1}{2} \right) \frac{\hbar \omega_0}{2} = \frac{E_n}{2}, \]

as expected from the virial theorem for simple harmonic oscillators. This implies that the total energy \( E_n \) is evenly split between the kinetic and potential energies of the particle. We therefore immediately find

\[ \langle p^2 \rangle = 2m \frac{E_n}{2} = \left( n + \frac{1}{2} \right) m\hbar \omega_0, \]

while \( \langle p \rangle_n \equiv 0 \) by symmetry.

We now define the uncertainties

\[ \Delta x_n \equiv \sqrt{\langle x^2 \rangle_n - \langle x \rangle_n^2} = \sqrt{\langle x^2 \rangle_n}, \]

\[ \Delta p_n \equiv \sqrt{\langle p^2 \rangle_n - \langle p \rangle_n^2} = \sqrt{\langle p^2 \rangle_n}. \]
and use these definitions to write the uncertainty relation

\[ \Delta x_n \cdot \Delta p_n = \left( n + \frac{1}{2} \right) \hbar, \]

for a simple harmonic oscillator in the \( n \)th energy state \( E_n = (n + 1/2) \hbar \omega_0 \). Hence, we find that \( \Delta x_n \cdot \Delta p_n \geq \hbar/2 \) for all \( n \geq 0 \), with the equality holding for \( n = 0 \) (this state is known as the state of minimum uncertainty).

### 1.6 Problems

**Problem 1**

Consider the scattering problem involving the potential

\[ V(x) = \frac{\hbar^2 \kappa}{m} \delta(x), \quad (1.24) \]

where the \textit{delta} function \( \delta(x) \) is defined as

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

such that for an arbitrary smooth function \( f(x) \) we have

\[ \int_{-\infty}^{\infty} \delta(x-a) \ f(x) = f(a) \quad \text{for any } a. \quad (1.25) \]

The solution for the Schrödinger equation for positive energy \( E \) is of the form

\[
\Psi(x) = \begin{cases} 
e^{ikx} + A_r \ e^{-ikx} & \text{for } x \leq 0 \\
A_t \ e^{ikx} & \text{for } x > 0
\end{cases} \quad (1.26)
\]

where \( k \equiv \sqrt{2mE/\hbar^2} \) while \( A_r \) and \( A_t \) are the amplitudes for the reflected and transmitted waves, respectively.

- Whereas \( \Psi(x) \) must be continuous at \( x = 0 \), i.e., \( \Psi(0^+) = \Psi(0^-) \), its first derivative \( \Psi'(x) \) cannot be continuous since the potential \( V(x) \) has an infinite discontinuity at \( x = 0 \).

The condition on \( \Psi'(x) \) can be obtained from the integration of the Schrödinger equation between \(-\epsilon\) and \(+\epsilon\) and taking the limit \( \epsilon \to 0 \):

\[
\frac{\hbar^2}{2m} \int_{-\epsilon}^{+\epsilon} \frac{d^2 \Psi}{dx^2} \ dx + E \int_{-\epsilon}^{+\epsilon} \Psi(x) \ dx = \frac{\hbar^2 \kappa}{m} \int_{-\epsilon}^{+\epsilon} \delta(x) \ \Psi(x). \quad (1.27)
\]
Using the property (1.35) on the right side and taking the limit $\epsilon \to 0$ on the left side of (1.37) – noting that the second term vanishes – we obtain the jump condition

$$\Psi'(0^+) - \Psi'(0^-) = 2\kappa \Psi(0). \tag{1.28}$$

By using the continuity condition on $\Psi(x)$ and the jump condition (1.38) on $\Psi'(x)$ at $x = 0$, show that the amplitudes $A_r$ and $A_t$ are

$$A_t = \frac{k}{k + i\kappa} \quad \text{and} \quad A_r = -\frac{i\kappa}{k + i\kappa}.$$

**Problem 2**

Consider the following quantum operators

$$\hat{b}_\pm \equiv \frac{1}{\sqrt{2m}} (\hat{p} \pm i m\omega x) = \frac{1}{\sqrt{2m}} \left( -i\hbar \frac{d}{dx} \pm i m\omega x \right), \tag{1.29}$$

where $\omega \equiv \sqrt{\kappa/m}$ is the angular frequency of a particle of mass $m$ undergoing simple harmonic motion on a spring of constant $\kappa$.

(a) The commutator $[\hat{A}, \hat{B}]$ corresponding to two arbitrary operators $\hat{A}$ and $\hat{B}$ is defined as

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

Show that the commutator $[\hat{b}_-, \hat{b}_+]$ satisfies the relation

$$[\hat{b}_-, \hat{b}_+] f(x) \equiv \hat{b}_- \left( \hat{b}_+ f(x) \right) - \hat{b}_+ \left( \hat{b}_- f(x) \right) = \hbar \omega f(x),$$

for any function $f(x)$.

(b) Show that the Hamiltonian $H = p^2/2m + \kappa x^2/2$ for the particle can be written in operator form as

$$\hat{H} = \left( \hat{b}_+ \hat{b}_- + \frac{\hbar \omega}{2} \right) = \left( \hat{b}_- \hat{b}_+ - \frac{\hbar \omega}{2} \right). \tag{1.30}$$

(c) Using the dimensionless variable $s \equiv x/a$, where $a = \sqrt{\hbar/(2m\omega)}$ is the scale-length factor, the operators (1.29) become

$$\hat{b}_\pm = \sqrt{\hbar \omega} \left( -i \frac{d}{ds} \pm i \frac{s}{2} \right).$$

The solution of the Schroedinger equation for the harmonic oscillator is given by the normalized wavefunction

$$\psi_n(x) = \frac{1}{\sqrt{a \, n! \sqrt{2\pi}}} H_n(s) e^{-s^2/4}, \tag{1.31}$$
where the \( n \)-th order polynomial

\[
H_n(s) \equiv (-1)^n e^{s^2/2} \frac{d^n e^{-s^2/2}}{ds^n} = s^n - \frac{n(n-1)}{2} s^{n-2} + \ldots ,
\]
satisfies the following relations

\[
H_n'(s) = s \cdot H_n(s) - H_{n+1}(s) = n H_{n-1}(s). \tag{1.32}
\]

Using these relations show that

\[
\hat{b}_+ \psi_n(x) = i \sqrt{\hbar \omega} (n + 1) \psi_{n+1}(x), \tag{1.33}
\]
i.e., the operator \( \hat{b}_+ \) acts as a \textit{raising} operator \((n \rightarrow n + 1)\). Next, using (1.33), show that

\[
\psi_n(x) \equiv \frac{(-i)^n}{(\sqrt{\hbar \omega})^n} \frac{1}{\sqrt{n!}} \psi_0(x). \]

(d) If the quantum operator \( \hat{b}_+ \) acts a raising operator, the quantum operator \( \hat{b}_- \) must act as a \textit{lowering} operator \((n \rightarrow n - 1)\), with \( \hat{b}_- \psi_0 = 0 \). Using the relations (1.32), obtain an expression for \( \hat{b}_- \psi_n(x) \).

(e) From the eigenvalue equation

\[
\hat{H} \psi_n(x) = E_n \psi_n(x), \quad \text{where} \quad E_n = \left( n + \frac{1}{2} \right) \hbar \omega,
\]
find an expression for \( \hat{b}_- \hat{b}_+ \psi_n(x) \) and \( \hat{b}_+ \hat{b}_- \psi_n(x) \).

\textbf{Problem 3}

Consider the scattering problem involving the potential

\[
V(x) = \frac{\hbar^2 \kappa}{m} \delta(x), \tag{1.34}
\]
where the \textit{delta} function \( \delta(x) \) is defined as

\[
\delta(x) = \begin{cases} 
0 & \text{if } x \neq 0 \\
\infty & \text{if } x = 0
\end{cases}
\]
such that for an arbitrary smooth function \( f(x) \) we have

\[
\int_{-\infty}^{\infty} \delta(x-a) f(x) = f(a) \quad \text{for any } a. \tag{1.35}
\]
The solution for the Schrödinger equation for positive energy $E$ is of the form

$$\psi(x) = \begin{cases} e^{ikx} + A_r e^{-ikx} & \text{for } x \leq 0 \\ A_t e^{ikx} & \text{for } x > 0 \end{cases} \quad (1.36)$$

where $k \equiv \sqrt{2mE/\hbar^2}$ while $A_r$ and $A_t$ are the amplitudes for the reflected and transmitted waves, respectively.

Whereas $\psi(x)$ must be continuous at $x = 0$, i.e., $\psi(0^+) = \psi(0^-)$, its first derivative $\psi'(x)$ cannot be continuous since the potential $V(x)$ has an infinite discontinuity at $x = 0$. The condition on $\psi'(x)$ can be obtained from the integration of the Schrödinger equation between $-\epsilon$ and $+\epsilon$ and taking the limit $\epsilon \to 0$:

$$\frac{\hbar^2}{2m} \int_{-\epsilon}^{+\epsilon} d^2\psi \frac{d^2\psi}{dx^2} dx + E \int_{-\epsilon}^{+\epsilon} \psi(x) dx = \frac{\hbar^2 \kappa}{m} \int_{-\epsilon}^{+\epsilon} \delta(x) \psi(x). \quad (1.37)$$

Using the property (1.35) on the right side and taking the limit $\epsilon \to 0$ on the left side of (1.37) – noting that the second term vanishes – we obtain the jump condition

$$\psi'(0^+) - \psi'(0^-) = 2\kappa \psi(0). \quad (1.38)$$

By using the continuity condition on $\psi(x)$ and the jump condition (1.38) on $\psi'(x)$ at $x = 0$, show that the amplitudes $A_r$ and $A_t$ are

$$A_t = \frac{k}{k + i\kappa} \quad \text{and} \quad A_r = -\frac{i\kappa}{k + i\kappa}.$$

**Problem 4**

The Schrödinger equation for a particle of mass $m$ moving under the influence of a potential function $V(x)$ can be written as

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0, \quad (1.39)$$

where $\psi(x)$ denotes the wavefunction. In the limit $\hbar \to 0$ (i.e., in the classical limit), the wavefunction $\psi(x)$ behaves as

$$\psi(x) = \varphi(x) \exp\left(\frac{i}{\hbar} S(x)\right), \quad (1.40)$$

where $\varphi(x)$ and $S(x)$ are functions of $x$ determined at various orders in the expansion of the Schrödinger equation (1.39) in powers of $\hbar$. 29
(a) By substituting (1.40) into the Schroedinger equation (1.39), show that at order $\hbar^{-2}$ we find

$$S(x) \equiv \int_{x_0}^{x} \sqrt{2m \left[ E - V(y) \right]} \, dy,$$

where $x_0$ defines a definite phase factor such that $\psi(x_0) \equiv \varphi(x_0)$.

(b) The function $\varphi(x)$ is determined at order $\hbar^{-1}$. Obtain the differential equation for $\varphi(x)$ at order $\hbar^{-1}$ and show that

$$\varphi(x) = \frac{A}{p(x)},$$

where $A$ is a constant (in the limit $\hbar \to 0$). The semi-classical solution of the Schroedinger equation (1.39) is therefore expressed as

$$\psi_{s-cl}(x) = \frac{A}{p(x)} \exp \left( \frac{i}{\hbar} \int_{x_0}^{x} p(y) \, dy \right).$$

We note that this solution is valid only if $x$ is far enough away from the classical turning points $x_{t1}$ and $x_{t2}$ where $p(x) \equiv 0$ or $E = V(x)$.

**Problem 5**

The even-parity solution of the Schroedinger equation for the infinite potential well problem $V(x) = 0$ for $|x| < a$ and $\infty$ for $|x| \geq a$ is

$$\Psi(x) = \begin{cases} 
A \cos kx & |x| < a \\
0 & |x| < a 
\end{cases}$$

where $k = \sqrt{2mE/\hbar^2}$ and $A$ denotes the amplitude of the wave function.

(a) Find an expression for the wave function amplitude $A$ in Eq. (1.42) so that the normalization condition $\int_{-\infty}^{\infty} |\Psi(x)|^2 \, dx = 1$ is satisfied.

(b) Find the energy eigenvalue $E_n$ $(n = 0, 1, ...)$ as a function of $m$, $a$, and $\hbar$.

(c) Calculate the expectation values $\langle x \rangle_n$, $\langle \hat{p} \rangle_n$, $\langle x^2 \rangle_n$, and $\langle \hat{p}^2 \rangle_n$ for the quantum number $n$, where $\hat{p} = -i\hbar d/dx$ denotes the momentum operator.

(d) Construct the position and momentum uncertainties

$$\Delta x_n = \sqrt{\langle x^2 \rangle_n - (\langle x \rangle_n)^2} \quad \text{and} \quad \Delta p_n = \sqrt{\langle \hat{p}^2 \rangle_n - (\langle \hat{p} \rangle_n)^2},$$

respectively, and show that the Uncertainty Principle holds:

$$\Delta x_n \cdot \Delta p_n > \frac{\hbar}{2}.$$
For which value of $n$ is $\Delta x_n \cdot \Delta p_n$ the smallest?

**Problem 6**

Consider the scattering problem of a particle of mass $m$ and energy $E$ moving in a two-dimensional potential is given as

$$V(x, y) = \begin{cases} 
0 & x < 0 \ (I) \\
V_0 & x \geq 0 \ (II)
\end{cases}$$

where $E > V_0$. The particle is described in terms of the wave function

$$\begin{align*}
\Psi_I(x, y) &= \exp(ik \cdot r) + R \exp(ik' \cdot r) \\
\Psi_{II}(x, y) &= T \exp(iq \cdot r)
\end{align*}$$

(1.43)

where $R$ and $T$ are the reflection and transmission coefficients, respectively, and (see Figure below) $k = k (\cos \alpha \hat{x} + \sin \alpha \hat{y})$, $k' = k' (-\cos \alpha' \hat{x} + \sin \alpha' \hat{y})$, and $q = q (\cos \beta \hat{x} + \sin \beta \hat{y})$.

(a) Verify that Eqs. (1.43) are solutions of the two-dimensional Schrödinger equation

$$- \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \Psi(x, y) + V(x, y) \Psi(x, y) = E \Psi(x, y),$$

and obtain expressions for the magnitudes $k, k'$, and $q$.

(b) The law of reflection states that $\alpha' = \alpha$, while the law of refraction states that $k \sin \alpha = q \sin \beta$, or that the particle moves from a medium with refractive index 1 (medium I) to a medium with refractive index $n = q/k$ (medium II). Find an expression for the refractive index $n$ as a function of $V_0$ and $E$. 

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Chapter 2

Schroedinger Equation in Three Dimensions

2.1 Laplacian operator $\nabla^2$ in three dimensions

2.1.1 Arbitrary spatial coordinates

Let us consider arbitrary coordinates $\sigma^i = (\sigma^1, \sigma^2, \sigma^3)$ for an arbitrary point $r(\sigma^1, \sigma^2, \sigma^3)$ in three-dimensional space. We construct the following basis vectors $e_i \equiv \partial r / \partial \sigma^i$ and the matrix $g_{ij}$ with components $g_{ij} \equiv e_i \cdot e_j$. We also construct the dual basis vectors $e^i \equiv \nabla \sigma^i$, such that the orthogonality conditions $e^i \cdot e_j \equiv \delta^i_j$ (i.e., $\delta^i_i = 1$ and $\delta^i_j = 0$ for $i \neq j$), and the dual matrix $\hat{g}$ with components $g^{ij} \equiv e^i \cdot e^j$. We note that the Jacobian $\mathcal{J}$ for the transformation $(x, y, z) \rightarrow (\sigma^1, \sigma^2, \sigma^3)$ is

$$\mathcal{J} \equiv \sqrt{\det g} = \frac{1}{\sqrt{\det \hat{g}}}.$$

The expression for the Laplacian operator $\nabla^2$ is

$$\nabla^2 f(\sigma^1, \sigma^2, \sigma^3) = \frac{1}{\mathcal{J}} \frac{\partial}{\partial \sigma^i} \left( \mathcal{J} g^{ij} \frac{\partial f}{\partial \sigma^j} \right).$$

2.1.2 Spherical Coordinates $(r, \theta, \phi)$

An arbitrary point $r$ is expressed in terms of spherical coordinates $(r, \theta, \phi)$ as

$$r(r, \theta, \phi) = r \sin \theta (\cos \phi \, \hat{x} + \sin \phi \, \hat{y}) + r \cos \theta \, \hat{z}.$$
The matrices \( g^\wedge \) and \( g \) are
\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1/r^2 & 0 \\
0 & 0 & 1/(r^2 \sin^2 \theta)
\end{pmatrix}
\] and
\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & r^2 & 0 \\
0 & 0 & r^2 \sin^2 \theta
\end{pmatrix},
\]
so that the Jacobian is \( J \equiv r^2 \sin \theta \). Finally the Laplacian operator in spherical coordinates is
\[
\nabla^2 f(r, \theta, \phi) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 f}{\partial \phi^2} \right].
\]

### 2.2 Angular Momentum Operator in Quantum Mechanics

The angular momentum \( L \equiv \mathbf{p} \times \mathbf{r} \) can be written as a differential operator in quantum mechanics (with \( \mathbf{p}_{\text{op}} \equiv -i\hbar \nabla \)) as
\[
\mathbf{L}_{\text{op}} f \equiv i\hbar \mathbf{r} \times \nabla f = i\hbar \left( \hat{\phi} \frac{\partial f}{\partial \theta} - \frac{\hat{\theta}}{\sin \theta} \frac{\partial f}{\partial \phi} \right)
\]
where \( \hat{\phi} \equiv (- \sin \phi \mathbf{\hat{x}} + \cos \phi \mathbf{\hat{y}}) \) and \( \hat{\theta} \equiv (\cos \phi \mathbf{\hat{x}} + \sin \phi \mathbf{\hat{y}}) \cos \theta - \sin \theta \mathbf{\hat{z}} \). An important operator in quantum mechanics is \( \mathbf{L}_{\text{op}}^2 \equiv \mathbf{L}_{\text{op}} \cdot \mathbf{L}_{\text{op}} \) expressed as
\[
\mathbf{L}_{\text{op}}^2 f \equiv -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 f}{\partial \phi^2} \right].
\]

Hence, the Schroedinger equation in three dimensions
\[
-\frac{\hbar^2}{2M} \nabla^2 \Psi(r) = [E - V(r)] \Psi(r)
\]
can be written in spherical coordinates as
\[
-\frac{\hbar^2}{2Mr^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi(r)}{\partial r} \right) = \left( E - V(r) - \frac{L_{\text{op}}^2}{2Mr^2} \right) \Psi(r).
\]

### 2.3 Schroedinger Equation for Central Potential Problems

If the potential function \( V(r) \) depends only on the radial position \( r \) (this is known as a central potential), the Schroedinger wave function \( \Psi(r) \) can be expressed as
\[
\Psi(r, \theta, \phi) \equiv R_\ell(r) Y_\ell(\theta, \phi)
\]

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such that the angular function $Y_\ell(\theta, \phi)$ satisfies
\begin{equation}
    L^2_{\text{op}} Y_\ell(\theta, \phi) \equiv \hbar^2 \ell (\ell + 1) Y_\ell(\theta, \phi)
\end{equation}
where $\ell = 0, 1, 2, \ldots$, and the Schroedinger equation becomes
\begin{equation}
    -\frac{\hbar^2}{2M r^2} \frac{d}{dr} \left( r^2 \frac{d\mathcal{R}_\ell(r)}{dr} \right) = \left( E - V(r) - \frac{\hbar^2 \ell (\ell + 1)}{2M r^2} \right) \mathcal{R}_\ell(r).
\end{equation}
A particle in a central potential is therefore subjected to an effective potential
\begin{equation}
    V_{\text{eff}}(r) \equiv V(r) + \frac{\hbar^2 \ell (\ell + 1)}{2M r^2}.
\end{equation}

### 2.3.1 Solution of the Angular Equation

Since the operator $L^2_{\text{op}}$ is itself independent of the azimuthal angle $\phi$, we may write
\begin{equation}
    Y_\ell(\theta, \phi) \equiv \Theta_{\ell m}(\theta) e^{im\phi}
\end{equation}
where $m = 0, \pm 1, \pm 2, \ldots$, and
\begin{equation}
    \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta_{\ell m}(\theta)}{d\theta} \right) + \left[ \ell (\ell + 1) - \frac{m^2 \sin^2 \theta}{\sin^2 \theta} \right] \Theta_{\ell m}(\theta) = 0.
\end{equation}
The solution for this equation has the form
\begin{equation}
    \Theta_{\ell m}(\theta) = A_{\ell m} P_{\ell}^{m}(\cos \theta),
\end{equation}
where $A_{\ell m}$ is a normalization constant and $P_{\ell}^{m}(x)$ is the associated Legendre function defined as
\begin{equation}
    P_{\ell}^{m}(x) \equiv (1 - x^2)^{|m|/2} \left( \frac{d}{dx} \right)^{|m|} P_{\ell}(x)
\end{equation}
and $P_{\ell}(x)$ is the Legendre polynomial (of order $\ell$) defined as
\begin{equation}
    P_{\ell}(x) \equiv \frac{1}{2^\ell \ell!} \left( \frac{d}{dx} \right)^\ell (x^2 - 1)^\ell.
\end{equation}
For example, $P_0(x) = 1$, $P_1(x) = x$, $P_2(x) = \frac{1}{2} (3x^2 - 1)$, while $P_1^1(x) = \sqrt{1 - x^2}$, $P_2^1(x) = 3x\sqrt{1 - x^2}$, and $P_2^2(x) = 3(1 - x^2)$. We note that for $|m| > \ell$ we find $P_{\ell}^{m} = 0$ and consequently for each integer value $\ell$, we have
\begin{equation}
    m = -\ell, -\ell + 1, \ldots, 0, \ldots, \ell - 1, \ell
\end{equation}
and $P_{\ell}^{-m}(x) \equiv (-1)^m P_{\ell}^m(x)$. The normalization constant $A_{\ell m}$ is chosen so that

$$1 = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \left| Y_{\ell m}(\theta, \phi) \right|^2 = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \left| A_{\ell m} \right|^2 \left[ P_{\ell}^m(\cos \theta) \right]^2,$$

and thus

$$A_{\ell m} \equiv \pm \left( \frac{(2\ell + 1)(\ell - |m|)!}{4\pi(\ell + |m|)!} \right)^{1/2},$$

where the (+)-sign is associated with $m \leq 0$ and even positive values of $m$ (i.e., $m = 2, 4, \ldots$) whereas the (−)-sign is associated with odd positive values of $m$ (i.e., $m = 1, 3, \ldots$).

### 2.3.2 Radial Wave Equation

The normalization of $Y_{\ell m}(\theta, \phi)$ implies that the radial function $R_{\ell}(r)$ has the following normalization condition $\int_0^\infty r^2 |R_{\ell}(r)|^2 = 1$. In fact, if we define the function

$$u_{\ell}(r) \equiv r R_{\ell}(r)$$

which satisfies the radial wave equation

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

### 2.4 Hydrogen Atom

We now consider the central potential problem associated with the Schrödinger equation for an electron subjected to the Coulomb potential of a positively-charged nucleus ($Z > 0$):

$$V(r) = -\frac{\kappa Z}{r}, \quad \text{where} \quad \kappa = \frac{e^2}{4\pi\epsilon_0} = 14.4 \text{ eV} \cdot \text{Å}.$$  

For a bound electron, the total energy $E$ is negative and consequently, after defining the scale length $a \equiv \hbar^2/(M\kappa Z)$, we introduce the expression

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

where both the scale $a$ and the expression for $E$ are motivated by the Bohr model of the Hydrogen atom. The radial wave equation for the Hydrogen-atom problem becomes

$$\frac{d^2 u_{\ell}(s)}{ds^2} = \left[ \alpha^2 - \frac{2}{s} + \frac{\ell(\ell + 1)}{s^2} \right] u_{\ell}(s),$$

where $s \equiv r/a$.  


2.4.1 Asymptotic behavior

We now note that as $s \to \infty$, a proper solution for $u_\ell(s)$ must vanish and hence we find that the dominant behavior for $u_\ell(s)$ involves the exponential $e^{-\alpha s}$. Hence, we write

$$u_\ell(s) \equiv S_\ell(s) e^{-\alpha s},$$

so that the function $S_\ell(s)$ now satisfies

$$S''_\ell(s) - 2\alpha S'_\ell(s) + \left( \frac{2}{s} - \ell(\ell+1) \right) S_\ell(s) = 0.$$

Let us now look at the opposite behavior as $s \to 0$, where $S_\ell(s)$ must be finite. The dominant behavior for $S_\ell(s)$ is either $s^{\ell+1}$ or $s^{-\ell}$. Since the behavior $s^{-\ell}$ is not finite as $s \to 0$, we thus choose

$$S_\ell(s) \equiv s^{\ell+1} \chi_\ell(s),$$

where the new function $\chi_\ell(s)$ now satisfies

$$s \chi''_\ell(s) + 2(\ell + 1 - \alpha s) \chi'_\ell(s) + 2 \left[ 1 - \alpha(\ell + 1) \right] \chi_\ell(s) = 0.$$

The series solution for this equation has the form

$$\chi_\ell(s) \equiv \sum_{k=0}^{\infty} c_k s^k,$$

which when substituted into the equation for $\chi_\ell(s)$ yields

$$0 = \sum_{k=0}^{\infty} s^k \left\{ (k + 1)(k + 2\ell + 2) c_{k+1} - 2[\alpha(k + \ell + 1) - 1] c_k \right\}$$

which implies that

$$c_{k+1} = 2 \left[ \frac{\alpha(k + \ell + 1) - 1}{(k + 1)(k + 2\ell + 2)} \right] c_k.$$

For large values of $k$, we find $c_{k+1} \sim (2\alpha/k) c_k$ or $\chi_\ell(s) \sim e^{+2\alpha s}$ unless for a special value of $k = K \geq 0$, we find $c_{K+1} \equiv 0$ or

$$\alpha = \frac{1}{K + \ell + 1} \equiv \frac{1}{n},$$

where $n \equiv K + \ell + 1 = 1, 2, \ldots$ is a new positive integer. Thus the solution for $\chi_\ell(s)$ is the polynomial

$$\chi_{n\ell}(s) \equiv \sum_{k=0}^{n-(\ell+1)} c_k s^k \quad \text{where} \quad c_{k+1} = -\frac{2}{n} \left[ \frac{n - (\ell + 1) - k}{(k + 1)(k + 2\ell + 2)} \right] c_k.$$

From this polynomial solution we easily check that for each value of $n$ we find that

$$\ell = 0, 1, \ldots, n - 1.$$
2.4.2 Summary

The radial wave function \( R_{n\ell}(r) = s^{\ell+1} \chi_{n\ell}(s) \) \( e^{-r/na} / r \) has the form

\[
R_{n\ell}(r) \equiv \frac{e^{-r/na}}{r} \sum_{k=(\ell+1)}^{n} c_{n, k-(\ell+1)} \left( \frac{r}{a} \right)^k = \frac{e^{-r/na}}{r} \left( c_{n, n-(\ell+1)} \frac{r^n}{a^n} + \cdots + c_{n0} \frac{r^{\ell+1}}{a^{\ell+1}} \right)
\]

where \( a = \hbar^2/(M\kappa Z) \). For example, we find

\[
R_{10}(r) \equiv \rho_{10} e^{-r/a}, \\
R_{20}(r) \equiv \rho_{20} \left( 1 - \frac{r}{2a} \right) e^{-r/2a}, \\
R_{21}(r) \equiv \rho_{21} \frac{r}{a} e^{-r/2a},
\]

where the constants \( \rho_{n\ell} \) are chosen so that \( \int_0^\infty r^2 |R_{n\ell}(r)|^2 \ dr = 1 \), i.e., \( \rho_{10} = 2a^{-3/2}, \rho_{20} = (1/\sqrt{2}) a^{-3/2}, \rho_{21} = (1/\sqrt{24}) a^{-3/2} \). The total wave function is now of the form

\[
\Psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) A_{m\ell} P^m_\ell(\cos \theta) e^{im\phi}.
\]

For example,

\[
\Psi_{100}(r, \theta, \phi) = \frac{2}{a^{3/2}} e^{-r/a} \cdot \sqrt{\frac{1}{4\pi}} \\
\Psi_{200}(r, \theta, \phi) = \frac{1}{\sqrt{2} a^{3/2}} e^{-r/a} \left( 1 - \frac{r}{2a} \right) \cdot \sqrt{\frac{1}{4\pi}} \\
\Psi_{210}(r, \theta, \phi) = \frac{1}{\sqrt{24} a^{3/2}} e^{-r/a} \frac{r}{a} \cdot \sqrt{\frac{3}{8\pi}} \cos \theta \\
\Psi_{21\pm1}(r, \theta, \phi) = \mp \frac{1}{\sqrt{24} a^{3/2}} e^{-r/a} \frac{r}{a} \cdot \sqrt{\frac{3}{8\pi}} \sin \theta \ e^{\pm i\phi}.
\]

Lastly, the total energy of the electron is

\[
E = - \frac{\hbar^2}{2Mn^2a^2} = - \frac{M\kappa^2Z^2}{2n^2\hbar^2},
\]

which is exactly the Bohr-model result. We note that the total energy depends only on the principal quantum number \( n \).
2.5 Problems

Problem 1

The angular momentum vector \( \mathbf{L} = \mathbf{r} \times \mathbf{p} \) of classical mechanics becomes an operator \( \hat{\mathbf{L}} \) in quantum mechanics:

\[
\hat{L}^x = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \\
\hat{L}^y = -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \\
\hat{L}^z = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right).
\]

Verify the following commutation relations

\[
\left[ \hat{L}^x, y \right] = i\hbar z, 
\]

\[
\left[ \hat{L}^x, \hat{p}^y \right] = i\hbar \hat{p}^z, 
\]

\[
\left[ \hat{L}^x, \hat{L}^y \right] = i\hbar \hat{L}^z.
\]

Problem 2

The spin (intrinsic) angular momentum vector \( \mathbf{S} \equiv S_x \hat{x} + S_y \hat{y} + S_z \hat{z} \) satisfies the same quantum-operator relations as ordinary (orbital) angular momentum: for a given eigenstate \( |sm\rangle \), where \( s = 0, \frac{1}{2}, 1, \ldots \) and \( m = -s, -s + 1, \ldots, s - 1, s \) are the quantum numbers associated with each eigenstate, we find

\[
\hat{S}^2 |sm\rangle = \hbar^2 s(s + 1) |sm\rangle \\
\hat{S}_z |sm\rangle = \hbar m |sm\rangle \\
\hat{S}_\pm |sm\rangle = \hbar \sqrt{s(s + 1) - m(m \pm 1)} |s(m \pm 1)\rangle,
\]

where \( S_\pm \equiv S_x \pm i S_y \).

For spin-\( \frac{1}{2} \) particles \( (s = \frac{1}{2} \) and \( m = -\frac{1}{2}, +\frac{1}{2} \)\), we have two eigenstates

\[
\left| \frac{1}{2}, +\frac{1}{2} \right\rangle \equiv | \uparrow \rangle \quad \text{and} \quad \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \equiv | \downarrow \rangle
\]
Using matrix notation, we write
\[ |\uparrow\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |\downarrow\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \] (2.4)
\[ \langle\uparrow| \equiv (1, 0) \quad \text{and} \quad \langle\downarrow| \equiv (0, 1) \] (2.5)
so that
\[ \langle\uparrow|\uparrow\rangle = 1 = \langle\downarrow|\downarrow\rangle \quad \text{and} \quad \langle\uparrow|\downarrow\rangle = 0 \]
and
\[ \hat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \]
\[ \hat{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \]
\[ \hat{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]

(a) Show that the spin operators \( \hat{S}_j \) satisfy the commutation relations
\[ [\hat{S}_j, \hat{S}_k] = i\hbar \epsilon_{jkl} \hat{S}_l, \]
where \( \epsilon_{xyz} = +1 \) and \( \epsilon_{jkl} \) is anti-symmetric under permutation of two of its indices (i.e., \( \epsilon_{yxz} = -1 \)).

(b) Consider the Hamiltonian \( H \equiv -\boldsymbol{\mu} \cdot \boldsymbol{B} \), where \( \boldsymbol{\mu} \equiv \gamma \boldsymbol{S} \) represents the magnetic moment associated with \( \boldsymbol{S} \). Assuming that the magnetic field \( \boldsymbol{B} \) points in the \( \hat{z} \)-direction, we find the Hamiltonian operator
\[ \hat{H} \equiv -\gamma B \hat{S}_z = -\frac{\gamma \hbar B}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \] (2.6)
Show that the eigenvalues of \( \hat{H} \) for \( |\uparrow\rangle \) and \( |\downarrow\rangle \) are
\[ \hat{H} |\uparrow\rangle = -\frac{\hbar \gamma B}{2} |\uparrow\rangle \quad \text{and} \quad \hat{H} |\downarrow\rangle = \frac{\hbar \gamma B}{2} |\downarrow\rangle. \]

(c) Show that the general solution of the time-dependent Schroedinger equation
\[ i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \]
is of the form
\[ |\Psi(t)\rangle \equiv a e^{-i\omega_0 t/2} |\downarrow\rangle + b e^{i\omega_0 t/2} |\uparrow\rangle, \] (2.7)
where $a$ and $b$ are constants and $\omega_0 \equiv \gamma B$. Without loss of generality, we may write $a = \cos \frac{\theta}{2}$ and $b = \sin \frac{\theta}{2}$, since $|a|^2 + |b|^2 \equiv 1$.

(d) Show that the expectation value of the $x$-component of the spin vector

$$\langle S_x(t) \rangle \equiv \langle \Psi(t) | \hat{S}_x | \Psi(t) \rangle$$

is expressed as

$$\langle S_x(t) \rangle = \frac{\hbar}{2} \sin \theta \cos(\omega_0 t).$$
Chapter 3

Perturbation Theory

3.1 Time-Independent Perturbation Theory

Consider an unperturbed Hamiltonian $H_0$ with eigenfunctions $\{|n\rangle^0; n = 0, 1, 2, \ldots\}$ and (non-degenerate) energy eigenvalues $E_n^0$, i.e.,

$$H_0 |n\rangle^0 = E_n^0 |n\rangle^0.$$  \hspace{0.5cm} (3.1)

The eigenfunctions $|n\rangle^0$ form a complete and orthonormal set, i.e.,

$$^0\langle n|m\rangle^0 = \delta_{nm}$$ \hspace{0.5cm} (3.2)

and any wavefunction $|a\rangle$ in wavefunction space $\mathcal{W}$ can be expressed as a superposition

$$|a\rangle \equiv \sum_n c_{na} |n\rangle^0$$ \hspace{0.5cm} where $c_{na} \equiv ^0\langle n|a\rangle$.

We note that this expression can also be written as $|a\rangle = \sum_n \hat{P}_n |a\rangle$, where $\hat{P}_n \equiv |n\rangle^0 \langle n|$ plays the role of a projection operator in wavefunction space $\mathcal{W}$.

We now add a perturbation $V$ to $H_0$ to construct a perturbed Hamiltonian $H = H_0 + \epsilon V$, where $\epsilon$ denotes the strength of the perturbation. As expected, each energy eigenvalue gets changed by this perturbation and is thus expressed as

$$E_n = E_n^0 + \epsilon E_n^1 + \epsilon^2 E_n^2 + \cdots.$$ \hspace{0.5cm} (3.3)

The eigenfunction $|n\rangle$ is also expanded in powers of $\epsilon$:

$$|n\rangle = |n\rangle^0 + \epsilon |n\rangle^1 + \epsilon^2 |n\rangle^2 + \cdots.$$ \hspace{0.5cm} (3.4)

Each term in the previous two expansions is linked to others by the eigenvalue equation

$$H |n\rangle = E_n |n\rangle.$$ \hspace{0.5cm} (3.5)

In the present notes, we shall consider two separate cases: (a) the case in which the energy eigenvalues are non-degenerate (i.e., $E_n^0 \neq E_k^0$ for all $k \neq n$); and (b) the case in which it is possible to find two states $k \neq n$ for which $E_n^0 = E_k^0$. 

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3.1.1 Non-degenerate Energy Eigenvalues

We now begin our analysis of time-independent perturbation theory in quantum mechanics by treating the non-degenerate case. When (3.5) is expanded in powers of $\epsilon$, the first and second order terms are, respectively:

$$H_0|n\rangle^1 + V|n\rangle^0 = E_n^0|n\rangle^1 + E_n^1|n\rangle^0,$$

(3.6)

$$H_0|n\rangle^2 + V|n\rangle^1 = E_n^0|n\rangle^2 + E_n^1|n\rangle^1 + E_n^2|n\rangle^0.$$

(3.7)

**First-order Analysis**

We now operate with $^0\langle k|\, on the first-order equation (3.6) to obtain

$$^0\langle k|H_0|n\rangle^1 + ^0\langle k|V|n\rangle^0 = E_n^0^0\langle k|n\rangle^1 + E_n^1^0\langle k|n\rangle^0,$$

where the unperturbed eigenvalue equation (3.1) was used in the first term on the left side and the orthonormality condition was invoked in the last term on the right side. This equation can be re-arranged to yield

$$E_n^1 \delta_{kn} + (E_n^0 - E_k^0) \, ^0\langle k|n\rangle^1 = ^0\langle k|V|n\rangle^0.$$

(3.8)

Two possibilities arise for the non-degenerate case: either $k = n$ or $k \neq n$, which means that either the second term or the first term on the left side in (3.10) vanish, respectively. First, when $k = n$, we have

$$E_n^1 = ^0\langle n|V|n\rangle^0,$$

(3.9)

i.e., the first-order energy term associated with the perturbation of a non-degenerate state is given by the expectation value of the perturbation potential in that state.

Next, for $k \neq n$, we find instead

$$\left(E_n^0 - E_k^0\right) \, ^0\langle k|n\rangle^1 = ^0\langle k|V|n\rangle^0.$$

(3.10)

We now note that since $|n\rangle^1$ belongs in wavefunction space $\mathcal{W}$, it can be decomposed as a superposition of the complete set of unperturbed eigenfunctions $\{|n\rangle^0\}$ as $|n\rangle^1 = \sum_{k \neq n} c_{kn}^1 |k\rangle^0$, where $c_{kn}^1 \equiv ^0\langle k|n\rangle^1$. Hence, (3.10) yields

$$c_{kn}^1 \equiv \frac{^0\langle k|V|n\rangle^0}{E_n^0 - E_k^0}.$$

(3.11)

We note that the coefficient $c_{nn}^1$ is not needed in the analysis and can consequently be set to zero.
Second-order Analysis

We again operate with \(0\langle k|\) on the second-order equation (3.7) to obtain

\[
\begin{align*}
\left[\left(0\langle k|H_0\right)|n\rangle^2\right] + 0\langle k|V|n\rangle^1 &= E_n^0 0\langle k|n\rangle^2 + E_n^1 0\langle k|n\rangle^1 + E_n^2 0\langle k|n\rangle^0, \\
&= E_n^0 0\langle k|n\rangle^2
\end{align*}
\]

where the unperturbed eigenvalue equation (3.1) was used in the first term on the left side and the orthonormality condition was invoked in the last term on the right side. This equation can be re-arranged to yield

\[
E_n^2 \delta_{kn} + \left(E_n^0 - E_k^0\right) 0\langle k|n\rangle^2 = 0\langle k|V|n\rangle^1 - E_n^1 0\langle k|n\rangle^1.
\]

(3.12)

At this order, we shall only be interested in the second-order energy term \(E_n^2\). Consequently, we set \(k = n\) in the equation above and obtain (note that \(0\langle n|n\rangle^1 \equiv 0\) by choice)

\[
E_n^2 = 0\langle n|V|n\rangle^1 \equiv \sum_{l \neq n} c_l^1 0\langle n|V|l\rangle^0
\]

\[
= \sum_{l \neq n} 0\langle l|V|n\rangle^0 0\langle n|V|l\rangle^0 \equiv \sum_{l \neq n} \frac{0\langle l|V|n\rangle^0}{E_n^0 - E_l^0},
\]

(3.13)

where we used the fact that \(0\langle n|V|l\rangle^0 \equiv (0\langle l|V|n\rangle^0)^*\).

### 3.1.2 Degenerate Energy Eigenvalues

It is quite clear from (3.11) that the degenerate case already leads to difficulties at first order. Let us now look at how the degenerate case \((E_k^0 = E_n^0 \text{ for } k \neq n)\) might be handled. To simplify our analysis, let us consider the case of double-degeneracy, i.e., only two unperturbed eigenstates (denoted \(|a\rangle^0 \text{ and } |b\rangle^0\)) share the same unperturbed eigenvalue \(E_0^0\):

\[
H_0|a\rangle^0 \equiv E_0^0 |a\rangle^0 \text{ and } H_0|b\rangle^0 \equiv E_0^0 |b\rangle^0,
\]

with \(0\langle a|b\rangle^0 = 0\).

First, we construct the following (normalized) eigenfunction

\[
|ab\rangle^0 \equiv \alpha |a\rangle^0 + \beta |b\rangle^0,
\]

(3.14)

which obviously satisfies the eigenvalue equation \(H_0|ab\rangle^0 = E_0^0 |ab\rangle^0\). Next, we introduce the perturbation potential \(\epsilon V\) and easily derive the first-order eigenvalue equation

\[
H_0|ab\rangle^1 + V|ab\rangle^0 = E_0^0 |ab\rangle^1 + E_1^0 |ab\rangle^0,
\]

(3.15)
where $E^1$ is the first-order energy eigenvalue. Lastly, by operating with $|a\rangle$ and $|b\rangle$ on (3.15), we obtain two coupled equations

$$\begin{align*}
\alpha W_{aa} + \beta W_{ab} &= \alpha E^1 \\
\alpha W_{ba} + \beta W_{bb} &= \beta E^1
\end{align*}$$

(3.16)

where $W_{ij} \equiv 0 \langle i | V | j \rangle^0$ is the component of a $2 \times 2$ perturbation matrix $W$. These two equations can also be written in matrix form as

$$\begin{pmatrix}
W_{aa} - E^1 & W_{ab} \\
W_{ba} & W_{bb} - E^1
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix} = 0.
$$

A non-trivial solution for $\alpha$ and $\beta$ requires that the determinant of the $2 \times 2$ matrix $(W - E^1 I)$ vanishes, which yields the following quadratic equation in $E^1$:

$$(E^1)^2 - E^1 \left( W_{aa} + W_{bb} \right) + \frac{\tau_W W_{aa} W_{bb} - W_{ab} W_{ba}}{2} = 0,$$

where $\tau_W$ and $\Delta_W$ denote the trace and the determinant of the $W$ matrix, respectively. The solution of this quadratic equation is written in standard form as

$$E^1_{\pm} = \frac{\tau_W}{2} \pm \frac{1}{2} \sqrt{\tau_W^2 - 4 \Delta_W}.$$

(3.17)

Hence, we see that the degeneracy of the unperturbed energy level is lifted by the perturbation ($E^1_{\pm} \neq E^1_{-}$) provided $\tau_W^2 \neq 4 \Delta_W$. We may also write $E^1_{\pm}$ as

$$E^1_{\pm} = \frac{1}{2} \left[ (W_{aa} + W_{bb}) \pm \sqrt{(W_{aa} - W_{bb})^2 + 4 |W_{ab}|^2} \right].$$

(3.18)

### 3.2 Applications of Time-independent Perturbation Theory

#### 3.2.1 Non-degenerate Case: Harmonic Oscillator Problem

The harmonic oscillator problem is an ideal example of a non-degenerate problem. Each unperturbed eigensate $|n\rangle^0$ has a unique energy eigenvalue $E^0_n$, where

$$E^0_n = \hbar \omega_0 \left( n + \frac{1}{2} \right) \quad \text{and} \quad |n\rangle^0 = \frac{1}{\sqrt{a \pi n!}} H_n(s) \ e^{-s^2/4},$$

with $\omega_0 \equiv \sqrt{\kappa/m}$ denotes the angular frequency associated with the unperturbed (simple) harmonic motion and $a \equiv \sqrt{\hbar/(2m\omega_0)}$ denotes the characteristic length scale (i.e., $s \equiv x/a$).
We now consider the following potential

\[ V_\epsilon(s) = \frac{V_0}{\epsilon} \left[ 1 - \cos \left( \sqrt{\frac{\hbar \omega_0}{2V_0}} \right) \right], \quad (3.19) \]

where \( V_0 \) denotes the height of the trapping well (see Figure below).

When the potential (3.19) is expanded in powers of \( \epsilon \), we obtain

\[ V_\epsilon(s) = \hbar \omega_0 \left[ \frac{s^2}{4} - \epsilon \left( \frac{\hbar \omega_0}{V_0} \right) \frac{s^4}{96} + \mathcal{O}(\epsilon^2) \right], \]

where the first term denotes the standard harmonic-oscillator potential \( (V_0 = \hbar \omega_0 s^2/4) \) and the second term shall denote the perturbation potential \( V(s) \equiv -[(\hbar \omega_0)^2/V_0] s^4/96 \).

According to (3.9), the first-order term in the energy eigenvalue for the \( n \)th-state is

\[ E_n^1 = -\frac{(\hbar \omega_0)^2}{96 V_0} \langle 0 | s^4 | n \rangle^0 \]

where

\[ I_n = \frac{1}{n!} \int_{-\infty}^{\infty} \frac{ds}{\sqrt{2\pi}} s^4 [H_n(s)]^2 e^{-s^2/2}. \]

Using the identity

\[ \int_{-\infty}^{\infty} \frac{ds}{\sqrt{2\pi}} s^{2\ell} e^{-s^2/2} = (2\ell - 1)!! \equiv (2\ell - 1) \cdot (2\ell - 3) \cdot \cdots \cdot 1, \]

we find that

\[ I_0 = \int_{-\infty}^{\infty} \frac{ds}{\sqrt{2\pi}} s^4 e^{-s^2/2} = 3, \]
and thus

\[ E_0^1 = - \frac{(\hbar \omega_0)^2}{32V_0} = - \left( \frac{\hbar \omega_0}{16V_0} \right) E_0^0. \]

**Exercise I:** Calculate \( E_1^1 \) and \( E_2^1 \).

### 3.2.2 Degenerate Case: Stark Effect in Hydrogen Atom

The eigenstate labeled with the principle quantum number \( n = 2 \) for the hydrogen atom has four-fold degeneracy in Schroedinger theory (without spin-orbit \( \mathbf{L} \cdot \mathbf{S} \) coupling). Indeed, each of the four eigenstates

\[ \{|200\rangle, |210\rangle, |21(+1)\rangle, |21(-1)\rangle \} \]

(we use the notation \(|n\ell m_l\rangle\) and omit the superscript zero to denote unperturbed eigenstates) has the same energy eigenvalue \( E_0^2 = -3.4 \text{ eV} \).

In the presence of an external constant electric field in the \( \hat{z} \) direction (i.e., \( \mathbf{E} = E \hat{z} \)), the degeneracy is partially lifted between the two states \(|200\rangle \equiv |\text{even}\rangle \) and \(|210\rangle \equiv |\text{odd}\rangle \), where the eigenstates are now labeled according to their parity \([(-1)\ell]\). Thus, the two degenerate eigenstates are

\[ |\text{even}\rangle = \frac{1}{4a^{3/2}\sqrt{2\pi}} (2-s) e^{-s/2}, \]
\[ |\text{odd}\rangle = \frac{1}{4a^{3/2}\sqrt{2\pi}} s e^{-s/2} \cos \theta, \]

where \( s = r/a \) and \( a \equiv \hbar^2 e^2/(4\pi \varepsilon_0 m) \) denotes the Bohr radius. The perturbation potential in the present case is

\[ V(s) = eaE s \cos \theta \equiv V_0 s \cos \theta. \]

It is quite easy to verify that

\[ \langle \text{even} | V_0 s \cos \theta | \text{even} \rangle = 0 = \langle \text{odd} | V_0 s \cos \theta | \text{odd} \rangle. \]

**Exercise II:** Verify the identities in (5.40).

On the other hand, we find

\[ \langle \text{even} | V_0 s \cos \theta | \text{odd} \rangle = \frac{V_0}{16} \int_0^\infty \frac{s^2 ds}{2} (2-s)^2 s^2 e^{-s} \int_0^{\pi} \sin \theta d\theta \cos^2 \theta = -3 V_0. \]

Hence the trace \( \tau_W \) of the perturbation matrix \( W \) is identically zero while its determinant is \( \Delta_W = -(3V_0)^2 \). Substituting these expressions into (3.17), we find

\[ E_{2(\pm)}^1 = \pm 3 V_0, \]

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i.e., the constant external electric field lifts the degeneracy of the eigenstates $|\text{even}\rangle$ and $|\text{odd}\rangle$.

**Exercise III**: We can construct the following (normalized) eigenstates

$$|+\rangle \equiv \frac{1}{\sqrt{2}} \left( |\text{even}\rangle + |\text{odd}\rangle \right) \quad \text{and} \quad |-\rangle \equiv \frac{1}{\sqrt{2}} \left( |\text{even}\rangle - |\text{odd}\rangle \right).$$

Note that each state is still an eigenstate with eigenvalue $E_0^2$. Verify that

$$\langle +|V_0 s \cos \theta + \rangle = -3 V_0 \quad \text{and} \quad \langle -|V_0 s \cos \theta | - \rangle = +3 V_0,$$

i.e., the perturbed state with the lowest energy $(E_0^2 - 3\epsilon V_0)$ is a **symmetric** superposition of the even and odd eigenstates, while the perturbed state with the highest energy $(E_0^2 + 3\epsilon V_0)$ is an **anti-symmetric** superposition of the even and odd eigenstates.

### 3.3 Time-Dependent Perturbation Theory

Consider a time-independent Hamiltonian system represented by the Hamiltonian function $H_0(x)$, the orthonormal eigenfunctions $|\psi_j\rangle$ (with $\langle \psi_j | \psi_k \rangle \equiv \delta_{jk}$), and the eigenfrequencies $\omega_j$, such that $\hat{H}_0 |\psi_j\rangle \equiv \hbar \omega_j |\psi_j\rangle$.

We now perturb this system with a time-dependent potential $\epsilon V(x,t)$, where $\epsilon$ is an ordering parameter representing the strength of the perturbation. The general solution $|\Psi(t)\rangle$ of the perturbed Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \left( \hat{H}_0 + \epsilon V \right) |\Psi\rangle,$$  \hspace{1cm} (3.21)

is of the form

$$|\Psi(t)\rangle \equiv \sum_j a_j(t) e^{-i\omega_j t} |\psi_j\rangle,$$  \hspace{1cm} (3.22)

where the coefficients $a_j(t)$ are functions of time only and satisfy the condition $\sum_j |a_j|^2 = 1$ to ensure that $\langle \Psi | \Psi \rangle = 1$. By substituting (3.30) into (3.21), we obtain

$$i\hbar \sum_j \dot{a}_j(t) e^{-i\omega_j t} |\psi_j\rangle = \epsilon \sum_j a_j(t) e^{-i\omega_j t} V |\psi_j\rangle.$$

If we now operate on both sides of this equation with $|\psi_k\rangle$ (using the orthonormality condition $\langle \psi_j | \psi_k \rangle \equiv \delta_{jk}$), we obtain

$$i\hbar \dot{a}_k(t) = \epsilon \sum_j a_j(t) W_{kj}(t),$$  \hspace{1cm} (3.23)

where $W_{kj}(t)$ denotes the matrix element

$$W_{kj}(t) \equiv e^{i\Omega_{kj}} \langle \psi_k | V | \psi_j \rangle,$$  \hspace{1cm} (3.24)
and $\Omega_{kj} \equiv \omega_k - \omega_j$. (Note: we assume that the unperturbed system is non-degenerate.)

The formal solution of (3.23) is of the form

$$a_k(t) = a_k(0) - \frac{i\epsilon}{\hbar} \sum_j \int_0^t a_j(s) W_{kj}(s) \, ds.$$  

We can repeat this substitution inside the integral to yield the infinite expansion

$$a_k(t) = a_k(0) - \frac{i\epsilon}{\hbar} \sum_j \left[ a_j(0) - \frac{i\epsilon}{\hbar} \sum_{\ell} \int_0^s \left( a_{\ell}(0) - \cdots \right) W_{j\ell}(q) \, dq \right] W_{kj}(s) \, ds.$$  

Keeping terms up to order $\epsilon$ only (this is called the Born approximation), we find

$$a_k(t) = a_k(0) - \frac{i\epsilon}{\hbar} \sum_j \int_0^t W_{kj}(s) \, ds.$$  

(3.25)

An important application of this perturbation theory is to consider what happens when the system is originally in a pure state represented by the quantum number $n$, i.e., $a_n(0) = 1$ and $a_{j\neq n}(0) = 0$. In this case, (3.25) becomes

$$a_k(t) = -\frac{i\epsilon}{\hbar} \int_0^t W_{kn}(s) \, ds.$$  

If in addition the perturbation potential is time independent, i.e., $W_{kn}(t) = e^{i\Omega_{kn}t} w_{kn}$, we find, using

$$\int_0^t e^{i\Omega_{kn}s} \, ds \equiv \frac{1}{i\Omega_{kn}} \left( 1 - e^{i\Omega_{kn}t} \right),$$

$$a_k(t) = -\frac{\epsilon w_{kn}}{\hbar \Omega_{kn}} \left( 1 - e^{i\Omega_{kn}t} \right),$$  

(3.26)

where $w_{kn}$ is now just a (complex-valued) number.

The probability $P_k(t) \equiv |a_k(t)|^2$ that a state $k \neq n$ becomes populated at a time $t > 0$ is expressed as

$$P_k(t) = \epsilon^2 \frac{|w_{kn}|^2}{(\hbar \Omega_{kn})^2} \sin^2 \left( \frac{\Omega_{kn}t}{2} \right).$$  

(3.27)

If we sum over all states $k \neq n$, we obtain the total probability that the initial state $n$ becomes depleted for $t > 0$:

$$P(t) \equiv \sum_{k \neq n} P_k(t) = 4\epsilon^2 \sum_{k \neq n} \frac{|w_{kn}|^2}{(\hbar \Omega_{kn})^2} \sin^2 \left( \frac{\Omega_{kn}t}{2} \right).$$

Let us now assume that the final states $k$ are so closely packed that we may replace the summation with $\rho(E_f) \int_{-\infty}^\infty dE$, where $\hbar \Omega_{kn} \to E$ and $\rho \equiv dN/dE$ is the energy density in
the final state (which turns out to be independent of $E$); we also assume that the matrix elements $w_{kn}$ can be replace by $w$. Hence, we find

$$P(t) = 4\varepsilon^2 |w|^2 \rho \int_{-\infty}^{\infty} \frac{\sin^2(Et/2\hbar)}{E^2} = \varepsilon^2 t \frac{2\pi |w|^2 \rho}{\hbar}.$$ 

Although $P(t)$ grows linearly with time, we should remember that $t \ll \varepsilon^{-2}$. The probability transition rate $P(t)/t \equiv \lambda$ defines the transition rate constant

$$\lambda \equiv \frac{2\pi |w|^2 \rho}{\hbar},$$

(this expression is known as Fermi’s Golden Rule #2). This formula means that the likelihood that the initial state be depleted increases as the density of final states increases (i.e., $\lambda \propto \rho$) and/or the strength of the interaction increases (i.e., $\lambda \propto |w|^2$).

We note that Fermi’s Golden Rule $\lambda = (2\pi \rho/\hbar) |w|^2$ clearly separates dynamics (i.e., physical interactions hidden in $|w|^2$) from kinematics (hidden in $2\pi \rho/\hbar$). An important example in particle physics involves the Yukawa potential

$$V(r) \equiv -\frac{g^2}{4\pi} \frac{e^{-r/R}}{r},$$

where $g$ denotes the fundamental charge of the Yukawa interaction and $R \equiv \hbar/M_Xc$. According to the Feynman picture for this interaction, two particles feel the Yukawa interaction through the exchange of virtual X particle (with mass $M_X$) only if the two particles are closer than the interaction distance $R$. Assuming that the particles are freely propagating before and after the interaction (i.e., $H_0 = |p|^2/2m$ for each particle), then the matrix element $w$ becomes

$$w(q) = \int d^3x V(r) e^{iq \cdot r/\hbar},$$

where $q$ is the net momentum transfer between the two particles. Since the Yukawa potential is spherically symmetric, we can write $q \cdot r \equiv qr \cos \theta$ and $d^3x = 2\pi r^2 \sin \theta dr d\theta$, so that

$$w(q) = -\frac{g^2}{2} \int_0^\infty r^2 dr \frac{e^{-r/R}}{r} \int_0^\pi d\theta \sin \theta e^{-iqr \cos \theta/\hbar} \equiv \frac{(2\hbar/qr) \sin q r/\hbar}{(2\hbar/qr) \sin q r/\hbar} \int_0^{(a^2+1)^{-1}} e^{-ax} \sin x dx$$

$$= -\frac{g^2\hbar}{q} \int_0^\infty e^{-r/R} \sin \left(\frac{qr}{\hbar}\right) dr = -\frac{g^2\hbar^2}{q^2} \int_0^\infty e^{-ax} \sin x dx$$

$$= -\frac{g^2\hbar^2}{q^2 + M_X^2 c^2}.$$ 

(3.29)
In the limit of small momentum transfer \((q \ll M_X c)\), we find that \(w\) is a constant independent of \(q\)
\[
w = -\frac{g^2 \hbar^2}{M_X^2 c^2} \equiv -G_X \rightarrow \frac{G_X}{(\hbar c)^3} = \frac{g^2/\hbar c}{(M_X c)^2}.
\]
For weak interactions, for example, the X particle is either the \(W^\pm\) \((M_W c^2 = 80.3 \text{ GeV})\) or \(Z^0\) \((M_Z c^2 = 91.2 \text{ GeV})\) spin-1 vector bosons with an effective range \(R_W \approx R_Z \approx 2 \times 10^{-3}\) fm (i.e., much smaller than the size of the nucleus); here the strength of the weak interactions is expressed in terms of the Fermi weak-interaction constant
\[
\frac{G_F}{(\hbar c)^3} = (1.16639 \pm 0.00001) \times 10^{-5} \text{ GeV}^{-2}.
\]

### 3.4 Problems

**Problem 1**

Consider a two-level system labeled by the two non-degenerate orthonormal eigenstates \(|\pm\rangle\) with eigenvalues \(E_{\pm}\) (i.e., \(\hat{H}_0|\pm\rangle \equiv E_{\pm}|\pm\rangle\)), where
\[
E_{\pm} \equiv E_0 \pm \frac{\hbar \omega_0}{2}
\]
such that \(E_+ - E_- \equiv \hbar \omega_0\). Let us now assume that the system is exposed to a time-dependent perturbation potential \(W\) such that
\[
\langle \pm|W|\pm\rangle = 0 \quad \text{and} \quad \langle -|W|+\rangle \equiv \frac{w}{2} e^{i\omega t}.
\]
The time-dependent Schrödinger wavefunction \(|\Psi(t)\rangle\) can thus be expressed as
\[
|\Psi(t)\rangle \equiv a_-(t) e^{-iE_- t/\hbar}|-\rangle + a_+(t) e^{-iE_+ t/\hbar}|+\rangle,
\]
where the time-dependent coefficients \(a_{\pm}(t)\) satisfy the evolution equations
\[
i\hbar \dot{a}_-(t) = \frac{w}{2} e^{i\Delta \omega t} a_+(t), \quad (3.31)
i\hbar \dot{a}_+(t) = \frac{w^*}{2} e^{-i\Delta \omega t} a_-(t), \quad (3.32)
\]
with \(\Delta \omega \equiv \omega - \omega_0\). At time \(t = 0\), we write \(a_-(0) = \cos \frac{\theta}{2}\) and \(a_+(0) = \sin \frac{\theta}{2}\) and thus
\[
|\Psi(0)\rangle = a_-(0) |-\rangle + a_+(0) |+\rangle \equiv \cos \frac{\theta}{2} |-\rangle + \sin \frac{\theta}{2} |+\rangle.
\]
(a) If the two-level system is initially in thermal equilibrium at temperature $T$, the ratio $\frac{P_+(0)}{P_-(0)} \equiv \tan^2 \frac{\theta}{2}$ satisfies the Maxwell-Boltzmann relation

$$\frac{P_+(0)}{P_-(0)} = e^{-\hbar \omega_0 / T} \equiv e^{-\chi}.$$ 

Show that $\cos \theta = \tanh \frac{\chi}{2}$.

(b) The general solutions of (3.31) and (3.32) have the form

$$a_{\pm}(t) = e^{\pm i \frac{\Delta \omega}{2} t} \left( \alpha_{\pm} e^{i \Omega t} + \beta_{\pm} e^{-i \Omega t} \right), \quad (3.33)$$

where $\alpha_{\pm}$ and $\beta_{\pm}$ are constants and $\Omega$ is known as the Rabi frequency. Show that

$$\Omega \equiv \frac{1}{2} \sqrt{\left( \Delta \omega \right)^2 + \frac{|w|^2}{\hbar^2}}. \quad (3.34)$$

(c) Using the relation $4\Omega^2 = (\Delta \omega)^2 + |w|^2 / \hbar^2$, let us write $\Delta \omega \equiv 2\Omega \sin \varphi$ and $w \equiv 2\hbar \Omega \cos \varphi$ (i.e., $|w| = 2\hbar \Omega \cos \varphi$). Show that

$$\begin{align*}
\alpha_+ &\equiv \frac{1}{2} \left[ (1 + \sin \varphi) \sin \frac{\theta}{2} - e^{-i \delta} \cos \varphi \cos \frac{\theta}{2} \right], \\
\alpha_- &\equiv \frac{1}{2} \left[ (1 - \sin \varphi) \cos \frac{\theta}{2} - e^{i \delta} \cos \varphi \sin \frac{\theta}{2} \right], \\
\beta_+ &\equiv \frac{1}{2} \left[ (1 - \sin \varphi) \sin \frac{\theta}{2} + e^{-i \delta} \cos \varphi \cos \frac{\theta}{2} \right], \\
\beta_- &\equiv \frac{1}{2} \left[ (1 + \sin \varphi) \cos \frac{\theta}{2} + e^{i \delta} \cos \varphi \cos \frac{\theta}{2} \right],
\end{align*}$$

and verify that

$$\begin{align*}
a_-(t) &= e^{i \frac{\Delta \omega}{2} t} \left( \alpha_- e^{i \Omega t} + \beta_- e^{-i \Omega t} \right) \\
&= e^{i \frac{\Delta \omega}{2} t} \left[ \cos \frac{\theta}{2} \cos \Omega t - i \sin \Omega t \left( \sin \varphi \cos \frac{\theta}{2} + e^{i \delta} \cos \varphi \sin \frac{\theta}{2} \right) \right], \quad (3.35) \\
a_+(t) &= e^{-i \frac{\Delta \omega}{2} t} \left( \alpha_+ e^{i \Omega t} + \beta_+ e^{-i \Omega t} \right) \\
&= e^{-i \frac{\Delta \omega}{2} t} \left[ \sin \frac{\theta}{2} \cos \Omega t + i \sin \Omega t \left( \sin \varphi \sin \frac{\theta}{2} - e^{-i \delta} \cos \varphi \cos \frac{\theta}{2} \right) \right]. \quad (3.36)
\end{align*}$$

(d) Show that the probability that the eigenstate $|+\rangle$ is occupied at time $t$ is

$$P_+(t) \equiv |a_+(t)|^2 = \sin^2 \theta + \sin^2 \Omega t \left( \cos^2 \varphi \cos 2\theta - \cos \delta \cos \varphi \sin \varphi \sin 2\theta \right) - (\sin \delta \cos \varphi \sin \theta) \cos \Omega t \sin \Omega t. \quad (3.37)$$
(e) At resonance $\Delta \omega \equiv 0$ (or $\varphi \equiv 0$), we find

$$P_+(t) = \sin^2 \frac{\theta}{2} + \sin \Omega t \left( \cos \theta \sin \Omega t - \sin \delta \sin \theta \cos \Omega t \right).$$

Show that $P_+(t)$ reaches a maximum

$$P_+|_{\text{max}} = \frac{1}{2} \left( 1 + \sqrt{1 - \cos^2 \delta \sin^2 \theta} \right)$$

at regular intervals determined by

$$\cos 2\Omega t \equiv -\frac{\cos \theta}{\sqrt{1 - \cos^2 \delta \sin^2 \theta}}.$$
Chapter 4

Nuclear Theory

4.1 Alpha Decay

4.1.1 Kinematics of Alpha Decay

The $\alpha$-decay reaction is expressed as

$$^{A+4}_{Z+2}X \rightarrow ^{A}_{Z}Y + ^{4}_{2}\text{He} + Q,$$

where $Z$ and $A$ denote the atomic number and mass number, respectively, $^{A+4}_{Z+2}X$ is called the parent nucleus, $^{A}_{Z}Y$ is the daughter nucleus, and $^{4}_{2}\text{He}$ denotes the $\alpha$ particle. The reaction energy $Q$ is defined as

$$Q \equiv [m(\frac{A+4}{Z+2}X) - m(\frac{A}{Z}Y) - m_{\alpha}] c^2 \geq 0, \quad (4.1)$$

i.e., the nucleus $^{A+4}_{Z+2}X$ is unstable to $\alpha$ decay if $Q$ is positive.

By conservation of momentum, we find $p_{Y} = p_{\alpha}$ but since the kinetic energy is $K_{j} \equiv p_{j}^2/2m_{j}$, we easily find $K_{Y} = (m_{\alpha}/m_{Y}) K_{\alpha} \ll K_{\alpha}$ and $K_{\alpha} = Q/(1 + m_{\alpha}/m_{Y}) \simeq Q$, i.e., the kinetic energy of the escaping $\alpha$ particle is almost entirely $Q$ (since $m_{\alpha}/m_{Y} \simeq 4/A \ll 1$).

4.1.2 Tunneling Theory of $\alpha$ Emission

A very successful model for $\alpha$ decay assumes that the $\alpha$ particle actually exists as a whole particle inside the daughter nucleus $^{A}_{Z}Y$ under the influence of the potential

$$V_{\alpha}(r) = \begin{cases} 
-V_{0} & r < R \\
2Z \kappa r^{-1} & r \geq R 
\end{cases}$$
where $V_0$ denotes the depth of the nuclear well ($V_0 \simeq 45$ MeV), $R(A) \equiv R_0 A^{1/3}$ is the nuclear radius ($R_0 = 1.2$ fm $\equiv 1.2 \times 10^{-15}$ m), and $2Z \kappa r^{-1}$ denotes the electrostatic potential associated with the repulsive interaction between the positively-charged $\alpha$ particle (with charge $+2$) and the positively-charged $Y$ nucleus (with charge $+Z$) (where $\kappa \equiv e^2/4\pi\varepsilon_0 = 1.440$ MeV·fm).

In general, the reaction energy $Q$ is less than the maximum potential energy $V_\alpha(R) \equiv 2Z\kappa R^{-1}$, i.e.,

\[
X(A, Z, Q) \equiv \frac{2Z \kappa}{QR(A)} = \frac{\rho(Z, Q)}{R(A)} > 1,
\]

where $\rho(Z, Q) \equiv 2Z \kappa Q^{-1}$ is the outer radius from which the $\alpha$ particle comes out of the Coulomb barrier.

Using the quantum theory of barrier tunneling, we find that the transmission probability for a particle of mass $m$ and energy $E$ crossing through a barrier of height $V(x) > E$ and infinitesimal width $\Delta x$ is

\[
T(\Delta x) \propto \exp \left( -\frac{2\Delta x}{\hbar} \sqrt{2m \left[ V(x) - E \right]} \right).
\]

The total transition probability $T$ for the particle crossing the barrier from $x = x_{in}$ to $x = x_{out}$ is obtained by multiplying the infinitesimal transitions to yield

\[
T \propto \exp (-2 \mathcal{G}),
\]

where

\[
\mathcal{G}(A, Z, Q) = \frac{1}{\hbar} \int_{R(A)}^{\rho(Z, Q)} \sqrt{\frac{2}{M} \left( \frac{2\kappa Z}{r} - Q \right)} \, dr
\]

\[
= \sqrt{\frac{2MQ}{\hbar^2}} \frac{R(A)}{R}(A) \int_{1}^{X(A, Z, Q)} \sqrt{\frac{X(A, Z, Q)}{x}} \, dx
\]

is called the Gamow function, with the reduced mass $M \equiv m_\alpha/(1 + m_\alpha/m_Y) \simeq m_\alpha$. Using the substitution $x = X \cos^2 \theta$, the integral is simply evaluated as

\[
\int_{1}^{X} \sqrt{\frac{X}{x}} - 1 \, dx = X \left[ \arccos \left( \frac{1}{\sqrt{X}} \right) - \sqrt{\frac{1}{X} \left( 1 - \frac{1}{X} \right)} \right],
\]

so that the Gamow function becomes

\[
\mathcal{G}(A, Z, Q) = \sqrt{\frac{2M Q}{\hbar^2}} \rho \left[ \arccos \left( \frac{R}{\rho} \right) - \sqrt{\frac{R}{\rho} \left( 1 - \frac{R}{\rho} \right)} \right].
\]

In general, $\alpha$ decay is likely to occur for $A > 200$, $Z > 90$ and, hence, using $Q < 10$ MeV, we find $X = 2.4 \left( Z/Q \right) A^{1/3} > 3$, where $Q$ is henceforth evaluated in MeV. In the limit $X = \rho/R \gg 1$ (i.e., when the barrier is thick), we can use the approximate expansion

\[
\arccos \epsilon \simeq \frac{\pi}{2} - \epsilon \quad \text{(for $\epsilon \ll 1$)},
\]

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so that
\[
\arccos\left(\sqrt{\frac{R}{\rho}}\right) - \sqrt{\frac{R}{\rho}} \left(1 - \frac{R}{\rho}\right) \simeq \frac{\pi}{2} - 2\sqrt{\frac{R}{\rho}}.
\]

Hence, we obtain the approximate expression for the Gamow function
\[
G(A, Z, Q) \equiv c_1 \frac{Z}{Q^{\frac{1}{2}}} - c_2 \sqrt{Z} A^{\frac{1}{3}},
\]
(4.3)

where \(Q\) is evaluated in MeV units, and the constants \(c_1\) and \(c_2\) are defined as
\[
c_1 = \frac{\pi \sqrt{2} \kappa}{\hbar c} \sqrt{m_\alpha c^2} = 1.98,
\]
\[
c_2 = \frac{4\kappa}{\hbar c} \sqrt{m_\alpha c^2} \frac{R_0}{\kappa} = 1.63
\]
with \(Mc^2 \simeq m_\alpha c^2 = 3,728\) MeV, \(\hbar c = 197.4\) MeV·fm, and \(\kappa = 1.440\) MeV·fm.

The half-life \(t_{1/2}(A, Z, Q)\) for \(\alpha\)-decay is therefore expressed as
\[
t_{1/2}(A, Z, Q) = (\ln 2) \times \tau(A, Z, Q) \times \exp\left[2G(A, Z, Q)\right],
\]
where \((\ln 2)\) appears as a result of the definition of half-life and \(\tau(A, Z, Q)\) is the collision time scale associated with the \(\alpha\) particle hitting the inner wall of the potential well (of effective depth \(Q + V_0\))
\[
\tau = \frac{2R}{v_\alpha} = \frac{\sqrt{R_0}}{\sqrt{\sqrt{2} m_\alpha c^2(\text{MeV})}} \left(\frac{A^{1/3}}{\sqrt{Q + V_0}}\right) = 3.45 \times 10^{-22} \text{sec}.
\]
We thus find the useful expression
\[
\ln\left(\frac{t_{1/2}}{\tau_0}\right) = \frac{1}{3} \ln A - \frac{1}{2} \ln(Q + V_0) + \frac{2c_1 Z}{Q^{1/2}} - 2c_2 \sqrt{Z} A^{1/3},
\]
where
\[
\tau_0 = \ln 2 \frac{R_0}{\sqrt{2} m_\alpha c^2(\text{MeV})} = 2.4 \times 10^{-22} \text{sec}.
\]
Under normal conditions \((Z > 90\) and \(A > 200)\), we find
\[
\frac{\partial}{\partial A} \ln\left(\frac{t_{1/2}}{\tau_0}\right) < 0, \quad \frac{\partial}{\partial Z} \ln\left(\frac{t_{1/2}}{\tau_0}\right) > 0, \quad \text{and} \quad \frac{\partial}{\partial Q} \ln\left(\frac{t_{1/2}}{\tau_0}\right) < 0.
\]
The last inequality implies that the half-life \(t_{1/2}\) decreases as \(Q\) increases, which makes sense since tunneling becomes easier as the thickness of the barrier
\[
\Delta(A, Z, Q)/R_0 = 2.4 \frac{Z}{Q} - A^{1/3}
\]
decreases. Likewise, the first and second inequalities also make sense since the barrier thickness \(\Delta(A, Z, Q)\) increases with \(Z\) and decreases with \(A\).
4.2 Fermi Theory of Beta Decay

The reaction equation for β-decay is expressed as

$$A_{Z \pm 1}X \rightarrow A_{Z}Y + e^{\pm} + \left( \nu_e \right),$$

which combines the two basic β-decay processes $p^+ \rightarrow n^0 + e^+ + \nu_e$ and $n^0 \rightarrow p^+ + e^- + \bar{\nu}_e$ describing the β-decays of the proton and neutron, respectively. The reaction energy for β-decay is therefore

$$Q = \left[ m_A \left( A_{Z \pm 1}X \right) - m_A \left( A_{Z}Y \right) - m_e - m_{\nu} \right] c^2 \equiv \left[ m_I \left( A_{Z \pm 1}X \right) - m_I \left( A_{Z}Y \right) \right] c^2.$$

**Important Note:** Isotopic masses $m_I$ are given for neutral atoms and thus include the total electronic masses and $m_{\nu} \equiv 0$ is often used. Note that for the neutron β-decay reaction, we find $Q > 0$ (since $m_n > m_p + m_e$), and thus a free neutron is unstable to β-decay (its lifetime is approximately $10^3$ sec). For the proton β-decay reaction, however, we find $Q < 0$, and thus a free proton is stable to β-decay (or its lifetime is believed to be greater than $10^{33}$ years!).

Since the products of a β-decay reaction involves the daughter nucleus $A_Z Y$ and the much lighter electron and neutrino, the latter two particles virtually carry all of the reaction energy $Q$ between them. Hence, we can consider the parent and daughter nuclei to be at rest in the laboratory frame and consider the production of an electron (or positron) of mass $m_e = 0.51098$ MeV/c² and an electron anti-neutrino (or electron neutrino) of mass $m_{\nu} \ll m_e$. In fact, for all pratical purposes, although the electron-neutrino mass has recently been shown to be finite, we shall here assume that its mass is zero. Consequently, keeping in mind that in general $Q > m_e c^2$, we shall treat both the electron and the neutrino relativistically:

$$E_e \equiv \sqrt{m_e^2 c^4 + p_e^2 c^2} \quad \text{and} \quad E_\nu \equiv p_\nu c.$$

We therefore note that energy conservation is expressed as

$$Q \equiv p_\nu c + \left( \sqrt{m_e^2 c^4 + p_e^2 c^2} - m_e c^2 \right). \quad (4.4)$$

We further note that momentum conservation between the electron and the neutrino does not apply here since the daughter nucleus plays an important role in momentum conservation. Lastly, we note that the electron escapes with a momentum ranging from $p_e = 0$ (when the entire reaction energy is taken by the neutrino) to a maximum value $p_e = \overline{p}_e$ (when the neutrino gets no energy at all!) defined as

$$\overline{p}_e c \equiv \sqrt{m_e^2 c^4 + Q^2} - m_e c^2. \quad (4.5)$$
4.2.1 Phase-Space Density of Final States

The final states of a $\beta$-decay reactions are therefore represented by a freely propagating electron (with momentum $p_e$) and a freely propagating neutrino (with momentum $p_\nu$). The infinitesimal number of final states in volume $V$ is

$$dN = \left(\frac{4\pi V}{(2\pi \hbar)^3} p_e^2 \, dp_e\right) \left(\frac{4\pi V}{(2\pi \hbar)^3} p_\nu^2 \, dp_\nu\right) \equiv \left(\frac{4\pi V}{(2\pi \hbar)^3} \right)^2 p_e^2 \, dp_e \, p_\nu^2 \, dp_\nu.$$  

Because of (4.4), however, the neutrino momentum $p_\nu$ is actually not independent of the electron momentum $p_e$. Hence, we can replace $dp_e \, dp_\nu$ with $dp_e \, dQ/c$, where

$$p_\nu c \equiv \left(\sqrt{m^2 c^4 + \bar{p}^2 c^2} - \sqrt{m^2 c^4 + p^2 c^2}\right),$$

where we shall henceforth omit the subscript $e$. We finally arrive at the expression for the density $dN/dQ \equiv d\rho$ of final states as

$$\rho = \frac{1}{c^3} \left(\frac{4\pi V}{(2\pi \hbar)^3}\right)^2 \int_0^{\bar{p}} \left(\sqrt{m^2 c^4 + \bar{p}^2 c^2} - \sqrt{m^2 c^4 + p^2 c^2}\right)^2 p^2 \, dp.$$  \hspace{1cm}(4.6)

If we now set $p \equiv mc \eta$ and $\bar{p} \equiv mc \bar{\eta}$, the integral becomes

$$\int_0^{\bar{p}} \left(\sqrt{m^2 c^4 + \bar{p}^2 c^2} - \sqrt{m^2 c^4 + p^2 c^2}\right)^2 p^2 \, dp \equiv m^5 c^7 F(\bar{\eta}),$$

where

$$F(\eta) \equiv \int_0^\eta \left(\sqrt{1 + \eta^2} - \sqrt{1 + \bar{\eta}^2}\right)^2 \eta^2 \, d\eta.$$  \hspace{1cm}(4.7)

The integral can be evaluated explicitly and we obtain

$$F(\bar{\eta}) = \frac{1}{30} \bar{\eta}^5 - \frac{1}{12} \bar{\eta}^4 - \frac{1}{4} \bar{\eta}^3 + \frac{1}{4} \sqrt{1 + \bar{\eta}^2} \sinh^{-1} \bar{\eta}.$$  

where $\sinh^{-1} \bar{\eta} \equiv \ln(\bar{\eta} + \sqrt{1 + \bar{\eta}^2})$. As the Table and graph show below, this function is a rapid function of its argument:

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<th>$\bar{\eta}$</th>
<th>$F(\bar{\eta})$</th>
</tr>
</thead>
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</tr>
<tr>
<td>1</td>
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</tr>
<tr>
<td>2</td>
<td>0.7070</td>
</tr>
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<td>3</td>
<td>6.537</td>
</tr>
<tr>
<td>4</td>
<td>29.95</td>
</tr>
</tbody>
</table>

The final expression for the density of final states for $\beta$-decay is therefore

$$\rho = \frac{m^5 c^4}{4\pi^4 \hbar^6} V^2 F(\bar{\eta}).$$  \hspace{1cm}(4.8)
4.2.2 Fermi’s Golden Rule

The formula for the lifetime $\tau \equiv 1/\lambda$ of a $\beta$-unstable nucleus is given in terms of Fermi’s Golden Rule

$$\lambda \equiv \frac{2\pi}{\hbar} |w|^2 \rho = \frac{mc^2}{2\pi^3\hbar} \left( \frac{m^2c^4 |V w|}{(\hbar c)^3} \right)^2 F(\overline{\eta}),$$

(4.9)

where $mc^2/(2\pi^3\hbar) = 1.25 \times 10^{19}$ s$^{-1}$. For weak interactions, the wavefunctions of the free electron and neutrino are of the form

$$\psi_a(r) \equiv \frac{1}{\sqrt{V}} e^{i p_a \cdot r / \hbar},$$

so that

$$\frac{|V w|}{(\hbar c)^3} \equiv \frac{G_F}{(\hbar c)^3} = 1.16 \times 10^{-5} \text{ GeV}^{-2} \quad \text{and} \quad \frac{m^2c^4 G_F}{(\hbar c)^3} = 3 \times 10^{-12}.$$

Combining these results yields the following simple relation for the lifetime $\tau$ of $\beta$-decay reactions:

$$F\tau = \frac{2\pi^3\hbar}{mc^2} \left( \frac{(\hbar c)^3}{m^2c^4 G_F} \right)^2 = 8.9 \times 10^3 \text{ sec}.$$

Hence, when the Fermi factor $F$ is small (large), the lifetime $\tau$ is large (small).

4.2.3 Additional Physical Effects in $\beta$ decay

The analysis presented above ignores very important physical effects observed in $\beta$ decay. For example, during $\beta^+$ decay, the escaping positron ($e^+$) feels a repulsive electrostatic interaction with the daughter nucleus and thus escapes with greater kinetic energy compared to the attractive electrostatic interaction felt by an escaping electron ($e^-$) during $\beta^-$ decay. There is therefore a difference between $F^+(Z, \overline{\eta})$ and $F^-(Z, \overline{\eta})$.

In addition, the escaping electron-neutrino pair can either carry no total angular momentum (orbital + spin) or can carry net total angular momentum. A Fermi transition is associated with the scenario in which the electron-neutrino pair have opposite spins (i.e., they carry zero spin), while a Gamow-Teller transition is associated with the scenario in which the electron-neutrino pair have parallel spins (i.e., they carry one unit of spin). For a Fermi transition ($\Delta s = 0$), if $\Delta j = 0$ for the parent-daughter nuclei we then find $\Delta \ell = 0$ (i.e., parity did not change). For a Gamow-Teller transition ($\Delta s = 1$), on the other hand, we find either $\Delta j = 0$ (and hence parity changes $\Delta \ell = 1$) or $\Delta j = 1$ (and hence parity does not change $\Delta \ell = 0$). Fermi and Gamow-Teller $\beta$ decays have different $F\tau$ values; for values $3 < \log F\tau < 4$, the transitions are said to be superallowed, for values $4 < \log F\tau < 6$, the transitions are said to be allowed, and whenever $\log F\tau \geq 7$, the transitions are said to be forbidden.
Chapter 5

Quantum Statistics

5.1 Example: A Simple Two-Particle System

Let us consider the partition of two particles (A and B) in three possible energy states (1, 2, or 3). According to the classical Maxwell-Boltzmann (MB) distribution, the two particles are distinguishable (A ≠ B) and both particles can occupy the same energy state. We also consider two quantum distributions: the Bose-Einstein (BE) distribution and the Fermi-Dirac (FD) distributions. According to the quantum BE distribution, particle A is indistinguishable from particle B (i.e., B = A) and both particles can occupy the same energy state, while according to the quantum FD distribution, particle A is indistinguishable from particle B (i.e., B = A) and no more than one particle can occupy the same energy state (this is the Pauli Exclusion principle).

Here are now the possible configurations involving two particles in three possible energy states according to each distributions. According to the classical Maxwell-Boltzmann (MB) distribution, there are 9 possible configurations:

<table>
<thead>
<tr>
<th>Configuration</th>
<th>State 1</th>
<th>State 2</th>
<th>State 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AB</td>
<td>·</td>
<td>·</td>
</tr>
<tr>
<td>2</td>
<td>·</td>
<td>AB</td>
<td>·</td>
</tr>
<tr>
<td>3</td>
<td>·</td>
<td>·</td>
<td>AB</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>B</td>
<td>·</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>A</td>
<td>·</td>
</tr>
<tr>
<td>6</td>
<td>A</td>
<td>·</td>
<td>B</td>
</tr>
<tr>
<td>7</td>
<td>B</td>
<td>·</td>
<td>A</td>
</tr>
<tr>
<td>8</td>
<td>·</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>9</td>
<td>·</td>
<td>B</td>
<td>A</td>
</tr>
</tbody>
</table>

According to the quantum Bose-Einstein (BE) distribution, there are 6 possible configurations:
Lastly, according to the quantum Fermi-Dirac (FD) distribution, there are only 3 possible configurations:

<table>
<thead>
<tr>
<th>Configuration</th>
<th>State 1</th>
<th>State 2</th>
<th>State 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AA</td>
<td>·</td>
<td>·</td>
</tr>
<tr>
<td>2</td>
<td>·</td>
<td>AA</td>
<td>·</td>
</tr>
<tr>
<td>3</td>
<td>·</td>
<td>·</td>
<td>AA</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>A</td>
<td>·</td>
</tr>
<tr>
<td>5</td>
<td>A</td>
<td>·</td>
<td>A</td>
</tr>
<tr>
<td>6</td>
<td>·</td>
<td>A</td>
<td>A</td>
</tr>
</tbody>
</table>

5.2 Partition Functions

We now introduce the following notation:
- $s$ denotes a state label ($s = 1, 2, ...$),
- $\epsilon_s$ denotes the energy of state $s$ (assume that $\epsilon_1 < \epsilon_2 < \cdots$),
- $n_s$ denotes the occupation number of state $s$
  - $n_s = 0, 1, 2, \cdots$ for MB and BE distributions and
  - $n_s = 0$ or 1 for FD distribution,
- $N = n_1 + n_2 + \cdots$ denotes the total number of particles to be partitioned,
- $\mathcal{R}$ denotes a particular configuration allowed by a distribution,
- $E_{\mathcal{R}} \equiv (n_1)_{\mathcal{R}}\epsilon_1 + (n_2)_{\mathcal{R}}\epsilon_2 + \cdots$ denotes the total energy of configuration $\mathcal{R}$.

Consider a system of $N$ particles in thermal equilibrium (at temperature $T$) and partitioned among a set of energy states ($s = 1, 2, \ldots$). Using the notation introduced above, we now define the partition function $Z$ for each distribution (MB, BE, or FD) as a sum over all possible configurations:

$$Z(N) \equiv \sum_{\mathcal{R}} e^{-\beta E_{\mathcal{R}}}, \quad (5.1)$$

where $\beta \equiv 1/kT$ ($k$ denotes the Boltzmann constant). For example, for the two-particle system, we find the following expressions for the partition functions:

$$Z^{MB}(2) \equiv e^{-\beta(2\epsilon_1)} + e^{-\beta(2\epsilon_2)} + e^{-\beta(2\epsilon_3)} + 2 e^{-\beta(\epsilon_1+\epsilon_2)} + 2 e^{-\beta(\epsilon_1+\epsilon_3)} + 2 e^{-\beta(\epsilon_2+\epsilon_3)},$$

$$Z^{BE}(2) \equiv e^{-\beta(2\epsilon_1)} + e^{-\beta(2\epsilon_2)} + e^{-\beta(2\epsilon_3)} + e^{-\beta(\epsilon_1+\epsilon_2)} + e^{-\beta(\epsilon_1+\epsilon_3)} + e^{-\beta(\epsilon_2+\epsilon_3)},$$

$$Z^{FD}(2) \equiv e^{-\beta(\epsilon_1+\epsilon_2)} + e^{-\beta(\epsilon_1+\epsilon_3)} + e^{-\beta(\epsilon_2+\epsilon_3)}.$$
Because the state energies are not equal ($\epsilon_1 < \epsilon_2 < \epsilon_3$), the probability of finding the system in a given configuration is not equal to the inverse of the total number of configurations.

Let us now define the following subpartition function

$$Z_s(N) \equiv \sum_{\mathcal{R}_s} e^{-\beta E_{Rs}}$$

as the partition function associated with $N$ particles partitioned into all states other than state $s$ ($\mathcal{R}_s$ denotes all configurations for which $n_s = 0$). Going back to our two-particle system, we find

$$Z_1^{MB}(2) \equiv e^{-\beta(2\epsilon_2)} + e^{-\beta(2\epsilon_3)} + 2 e^{-\beta(\epsilon_2 + \epsilon_3)},$$
$$Z_1^{BE}(2) \equiv e^{-\beta(2\epsilon_2)} + e^{-\beta(2\epsilon_3)} + e^{-\beta(\epsilon_2 + \epsilon_3)},$$
$$Z_1^{FD}(2) \equiv e^{-\beta(\epsilon_2 + \epsilon_3)}.$$

We also define the subpartition function $Z_s(N - 1)$ as the partition function associated with one particle being in state $s$ and $N - 1$ particles partitioned into all states other than state $s$. For our two-particle system, we find

$$Z_1^{MB}(1) \equiv 2 e^{-\beta\epsilon_2} + 2 e^{-\beta\epsilon_3},$$
$$Z_1^{BE}(1) \equiv e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3},$$
$$Z_1^{FD}(1) \equiv e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3}.$$

We now obtain the following formula for the partition function $Z$ in terms of the subpartition functions $Z_s(N)$, $Z_s(N - 1)$, ..., $Z_s(0)$ \(\equiv 1\):

$$Z(N) \equiv Z_s(N) + e^{-\beta\epsilon_s} Z_s(N - 1) + e^{-\beta(2\epsilon_3)} Z_s(N - 2) + \cdots + e^{-\beta(N\epsilon_s)}.$$  \hspace{1cm} (5.3)

We note that the subpartition functions $Z_s(N)$, $Z_s(N - 1)$, ..., $Z_s(0)$ are all independent of the energy $\epsilon_s$. From our two-particle system, for example, we find the MB formula

$$Z_1^{MB}(2) = Z_1^{MB}(2) + e^{-\beta\epsilon_1} Z_1^{MB}(1) + e^{-\beta(2\epsilon_1)}$$
$$= \left( e^{-\beta(2\epsilon_2)} + e^{-\beta(2\epsilon_3)} + 2 e^{-\beta(\epsilon_2 + \epsilon_3)} \right) + e^{-\beta\epsilon_1} \left( 2 e^{-\beta\epsilon_2} + 2 e^{-\beta\epsilon_3} \right) + e^{-\beta(2\epsilon_1)},$$

the BE formula

$$Z_1^{BE}(2) = Z_1^{BE}(2) + e^{-\beta\epsilon_1} Z_1^{BE}(1) + e^{-\beta(2\epsilon_1)}$$
$$= \left( e^{-\beta(2\epsilon_2)} + e^{-\beta(2\epsilon_3)} + e^{-\beta(\epsilon_2 + \epsilon_3)} \right) + e^{-\beta\epsilon_1} \left( e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3} \right) + e^{-\beta(2\epsilon_1)},$$

and the FD formula (where $n_s = 0$ or 1 only)

$$Z_1^{FD}(2) = Z_1^{FD}(2) + e^{-\beta\epsilon_1} Z_1^{FD}(1)$$
$$= \left( e^{-\beta(\epsilon_2 + \epsilon_3)} \right) + e^{-\beta\epsilon_1} \left( e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3} \right).$$
To simplify the expression (5.54) for the partition function $Z(N)$, we consider the expansion formula for the generic subpartition function $Z_s(N)$:

$$Z_s(N - \Delta N) = Z_s(N) - \Delta N \frac{\partial Z_s(N)}{\partial N} + \frac{(\Delta N)^2}{2!} \frac{\partial^2 Z_s(N)}{\partial N^2} - \cdots,$$

where we assume that $\Delta N \ll N$. Next, we define

$$\frac{\partial Z_s(N)}{\partial N} \equiv \alpha_s Z_s(N),$$

where $\alpha_s(T)$ is independent of $N$, so that

$$Z_s(N - \Delta N) \equiv Z_s(N) \left[ 1 - \alpha_s \Delta N + \frac{(\alpha_s \Delta N)^2}{2!} - \cdots \right] = Z_s(N) e^{-\alpha_s \Delta N}. \quad (5.4)$$

Hence, when the number of particles is large ($N \gg 1$), the Fermi-Dirac partition function becomes

$$Z^{FD}(N) = Z_s^{FD}(N) \left[ 1 + e^{-(\alpha_s + \beta \epsilon_s)} \right], \quad (5.5)$$

whereas the Bose-Einstein partition function

$$Z^{BE}(N) = Z_s^{BE}(N) \left[ 1 + e^{-(\alpha_s + \beta \epsilon_s)} + e^{-2(\alpha_s + \beta \epsilon_s)} + \cdots \right] \xrightarrow{N \to \infty} \frac{Z_s^{BE}(N)}{1 - e^{-(\alpha_s + \beta \epsilon_s)}}. \quad (5.6)$$

A useful expression for the Maxwell-Boltzmann partition function $Z^{MB}(N)$ can be given as

$$Z^{MB}(N) \equiv \sum_{R} e^{-\beta E_R},$$

where $C_R \equiv N!/(n_1! \, n_2! \cdots)$ denotes the number of permutations associated with a single equivalent configurations (i.e., two configurations are equivalent if their configuration energies are equal). Hence, the Maxwell-Boltzmann partition function is

$$Z^{MB}(N) \equiv \left( \sum_s e^{-\beta \epsilon_s} \right)^N. \quad (5.7)$$

From our two-particle system, for example, we indeed find

$$Z^{MB}(2) = \left( e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + e^{-\beta \epsilon_3} \right)^2.$$

### 5.3 Mean Occupation Number

The probability of finding $n$ particles in state $s$ and $N - n$ particles in all states other than state $s$ must be

$$P_s^{(n)} \equiv e^{-\beta (n \epsilon_s)} \frac{Z_s(N-n)}{Z}, \quad (5.8)$$
with \( P_s^{(N)} \equiv Z^{-1} e^{-\beta(N\epsilon_s)} \) and
\[
\sum_{n=0}^{N} P_s^{(n)} \equiv 1.
\]

We can now compute the mean occupation number for state \( s \):
\[
\bar{n}_s \equiv \sum_{n=0}^{N} n P_s^{(n)} = \sum_{n=0}^{N} n e^{-\beta(n\epsilon_s)} \frac{Z_s(N-n)}{Z} \equiv -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s}.
\]  
(5.9)

### 5.3.1 Fermi-Dirac Distribution

Let us look at the Fermi-Dirac case first. Using (5.5), the mean occupation number for the FD case is
\[
\bar{n}_s \equiv -\frac{1}{\beta} \frac{\partial \ln Z^{FD}}{\partial \epsilon_s} = \frac{e^{-(\alpha_s+\beta\epsilon_s)}}{1 + e^{-(\alpha_s+\beta\epsilon_s)}},
\]
In general, the constant \( \alpha_s(T) \) is also independent of the state label \( s \) (i.e., \( \alpha_s \equiv \alpha \)); indeed, from \( \ln Z^{FD}(N) = \ln Z_s^{FD}(N) + \ln[1 + e^{-(\alpha_s+\beta\epsilon_s)}] \), we find \( \alpha(N) = \alpha_s(N) + \bar{n}_s^{FD} \partial \alpha_s/\partial N \), so that if \( |\partial \alpha_s/\partial N| \ll \alpha_s \) (note that \( \bar{n}_s^{FD} < 1 \)), we find \( \alpha \equiv \alpha_s \). Defining the chemical potential
\[
\mu(T) \equiv -\alpha(T) kT \quad \text{(or } \alpha = -\beta \mu),
\]
the final expression for the mean occupation number for the Fermi-Dirac case is therefore
\[
\bar{n}_s^{FD} = \frac{1}{e^{\beta(\epsilon_s-\mu)} + 1}.
\]  
(5.10)

We note that as expected, we find \( 0 < \bar{n}_s^{FD} < 1 \). At \( \epsilon_s = 0 \), we find
\[
\bar{n}_s^{FD}(\epsilon_s = 0) = \frac{1}{e^{-\beta\mu} + 1};
\]
at \( \epsilon_s = \mu \), we find
\[
\bar{n}_s^{FD}(\epsilon_s = \mu) = \frac{1}{2};
\]
and as \( \epsilon_s \to \infty \), we find
\[
\bar{n}_s^{FD} \to e^{-\beta(\epsilon_s-\mu)}.
\]

### 5.3.2 Bose-Einstein Distribution

We now consider the Bose-Einstein case (for massive bosons in thermal equilibrium at temperature \( T \)). Using (5.6), the mean occupation number for the BE case is
\[
\bar{n}_s^{BE} = -\frac{1}{\beta} \frac{\partial \ln Z^{BE}}{\partial \epsilon_s} = \frac{e^{-\beta(\epsilon_s-\mu)}}{1 - e^{-\beta(\epsilon_s-\mu)}},
\]
or
\[ \bar{n}^{BE}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1}. \] (5.11)

The special case of the massless photons (with spin 1) is dealt by setting their chemical potential \( \mu \equiv 0 \) and therefore the mean occupation photon number in state \( \epsilon = h\nu \) is
\[ \bar{n}'(\nu, T) = \frac{1}{e^{h
u/kT} - 1}; \] (5.12)
this is the so-called Planck distribution.

We now note that since \( \bar{n}^{BE}_s \geq 0 \), we must have \( \epsilon_s > \mu(T) \). When \( \epsilon_s \to \mu \) we find \( \bar{n}^{BE}_s \to \infty \); and as \( \epsilon_s \to \infty \), we find
\[ \bar{n}^{BE}_s \to e^{-\beta(\epsilon_s - \mu)}. \]

Since there is no longer any distinction between the FD and BE mean occupation numbers at high energies, we shall call this limit \( \epsilon_s \gg \mu \) the classical limit.

### 5.3.3 Maxwell-Boltzmann Distribution

Using (5.7), the mean occupation number in state \( s \) for the MB case is
\[ \bar{n}^{MB}_s \equiv -\frac{1}{\beta} \frac{\partial \ln Z^{MB}}{\partial \epsilon_s} = N \frac{e^{-\beta \epsilon_s}}{\sum_r e^{-\beta \epsilon_r}}. \]

We easily verify that the condition \( \sum_s \bar{n}^{MB}_s = N \) holds. If we now use the definition
\[ \alpha \equiv \frac{\partial \ln Z^{MB}(N)}{\partial N} = \ln \left( \sum_s e^{-\beta \epsilon_s} \right), \]
then we find
\[ \sum_s e^{-\beta \epsilon_s} \equiv e^{\alpha}, \]
and the mean occupation number for the MB case becomes
\[ \bar{n}^{MB}_s = N e^{-(\alpha + \beta \epsilon_s)}. \] (5.13)

### 5.4 Thermodynamics of a Bose-Einstein Gas

We now turn our attention to a non-relativistic Bose-Einstein gas of spin-0 bosons. The infinitesimal number of particles \( dN \) contained in the infinitesimal phase-space volume \( V d^3p/(2\pi\hbar)^3 \) is
\[ dN \equiv \frac{a}{2} VT^{3/2} \frac{z^{1/2} dz}{\alpha e^z - 1}. \] (5.14)
where \( a \equiv \sqrt{2} m^{3/2}/(\pi^2 \hbar^3) \) is a constant while \( z \equiv E/T \) and \( \alpha \equiv e^{-\mu(T)/T} \). Here, we note that \( \alpha \geq 1 \) since \( \mu \leq 0 \) for a Bose-Einstein gas. The total number of particles enclosed in volume \( V \) is therefore

\[
N(V, T; \alpha) = \frac{a}{2} V T^{3/2} \int_0^\infty \frac{z^{1/2} \, dz}{\alpha \ e^z - 1}. \tag{5.15}
\]

The integral can be evaluated explicitly as

\[
\int_0^\infty \frac{z^{1/2} \, dz}{\alpha \ e^z - 1} = \frac{1}{\alpha} \int_0^\infty z^{1/2} e^{-z} \, dz + \frac{1}{\alpha^2} \int_0^\infty z^{1/2} e^{-2z} \, dz + \cdots \equiv \Gamma(3/2) \zeta_2^\alpha(\alpha^{-1}),
\]

where \( \Gamma(3/2) = \sqrt{\pi}/2 \) and \( \zeta_x(\alpha^{-1}) \equiv \sum_{n=1}^\infty \alpha^{-n}/n^x \) is the Riemann zeta function. The number of particles \( N \) in a non-relativistic Bose-Einstein gas in thermal equilibrium at temperature \( T \) is

\[
N(T, V, \mu) = \frac{\sqrt{\pi} a}{4} V T^{3/2} \zeta_2^\alpha(\alpha^{-1}) = \frac{V}{\lambda^3} \zeta_2^\alpha(\alpha^{-1}), \tag{5.16}
\]

where \( \lambda \equiv (2\pi \hbar^2/mT)^{\frac{1}{2}} \). The chemical potential \( \mu(N, V, T) \) can be obtained by inverting \( \lambda^3 N/V = \zeta_2^\alpha(\alpha^{-1}) \).

### 5.4.1 Degeneracy Parameter

The chemical potential \( \mu \) can be easily obtained in the limit of large temperatures (and/or small number densities). For this purpose, we now define the degeneracy parameter

\[
D(n, T) \equiv \lambda^3 \frac{N}{V} = \lambda^3 n
\]

so that (5.51) becomes

\[
D(n, T) = \zeta_2^\alpha(\alpha^{-1}). \tag{5.17}
\]

In the limit where \( \alpha \) is very large (i.e., \( \mu < 0 \) and \(-\mu/T \gg 1\)), we can approximate \( \zeta_2^\alpha(\alpha^{-1}) \) as \( \zeta_2^\alpha(\alpha^{-1}) = \alpha^{-1} + \alpha^{-2}/2^\frac{3}{2} \). Hence, (5.17) becomes the quadratic equation \( \alpha^2 D - \alpha - 2^{-\frac{3}{2}} = 0 \), whose solution (for \( \alpha > 0 \)) is

\[
\alpha = \frac{1}{2D} \left( 1 + \sqrt{1 + 2^\frac{1}{2} D} \right).
\]

The limit \( \alpha \gg 1 \) is therefore equivalent to the limit \( D \ll 1 \) and thus

\[
\alpha = \frac{1}{D} \left( 1 + \frac{D}{2^\frac{3}{2}} + \cdots \right). \tag{5.18}
\]

By definition, the chemical potential \( \mu \) is defined as \( \mu \equiv -T \ln \alpha \) or, using (5.18), we find

\[
\mu(T, n) = T \ln D = T \left[ \ln \left( \frac{m}{2\pi \hbar^2} \right)^{\frac{3}{2}} + \ln n - \frac{3}{2} \ln T \right].
\]

The chemical potential of spin-0 bosons at large temperatures (or small number densities) is therefore negative.
5.4.2 Critical Temperature for a Bose-Einstein Gas

It is quite clear that the expansion used to derive (5.51) [or (5.17)] becomes invalid as $\mu$ becomes positive (or as $\alpha$ decreases below 1). The value $\mu = 0$ (or $\alpha = 1$) corresponds to a critical temperature $T_c$ defined as

$$T_c \equiv \frac{2\pi \hbar^2}{m} \left( \frac{n}{\zeta_2(1)} \right)^\frac{1}{3}. \quad (5.19)$$

Hence, the solution presented in (5.51) is valid when $T > T_c$, so that

$$\mu = T \left[ \ln \zeta_2(1) - \frac{3}{2} \ln \left( \frac{T}{T_c} \right) \right].$$

We note that this expression is valid only when $T \gg T_c$.

When $T < T_c$, the formula (5.31) itself is suspect and we must go back to the original formula for the mean occupation number $N_s$ of a Bose-Einstein gas in thermal equilibrium associated with the quantum state $s$ (with energy $E_s$) given previously as

$$N_s = \frac{1}{\alpha e^{E_s/T} - 1}. \quad (5.20)$$

Assuming that the quantum states $s = 0, 1, \ldots$ have ordered energy levels ($E_0 < E_1 < \ldots$), it is quite clear that we must focus our attention on the lowest-energy (ground) state $s = 0$ (for which we can set $E_0 \equiv 0$), i.e.,

$$N_0 = \frac{1}{\alpha - 1}. \quad (5.21)$$

Hence, the mean occupation number $N_0$ of the ground state appears to become arbitrarily large as $\alpha \to 1$ (or as $T \to T_c$). To study this phenomenon more closely, we now look at the total mean occupation number $N_s$ for all excited states ($s \neq 0$):

$$N_s = \sum_{s \neq 0} N_s \equiv N - N_0, \quad (5.22)$$

where the second expression comes from the identity $N \equiv \sum_{s \geq 0} N_s$. Since we are interested in the limit $T \to T_c$ (or $\mu \to 0$), we can safely set $\alpha = 1$ in the sum in (5.22) and, replace the sum by the integral:

$$N_s \equiv \lambda^{-3} V \int_0^\infty \frac{z^\frac{1}{2} dz}{e^z - 1} = \lambda^{-3} V \zeta_2(1). \quad (5.23)$$

Using the definition (5.19) for the critical temperature $T_c$, the total mean occupation number $N_s$ for all excited states ($s \neq 0$) becomes (for $T \leq T_c$)

$$N_s = N \left( \frac{T}{T_c} \right)^\frac{3}{2}, \quad (5.24)$$

66
so that the mean occupation number \( \overline{N}_0 \) for the ground state becomes (for \( T \leq T_c \))

\[
\overline{N}_0 = N \left[ 1 - \left( \frac{T}{T_c} \right)^{\frac{3}{2}} \right].
\]  

We therefore find that as \( T \) decreases below \( T_c \), the number of bosons occupying the ground state increases.

### 5.4.3 Bose-Einstein Condensation

To study further the transition occurring at \( T = T_c \), we consider the change in behavior in the internal energy of a Bose-Einstein gas in thermal equilibrium at temperature \( T \). First, we look at the case when \( T > T_c \), for which the internal energy, denoted \( U > \) i.e.,

\[
U > (V, T; \alpha) = \frac{a}{2} VT^{5/2} \int_0^\infty \frac{z^{3/2} \, dz}{\alpha \, e^z - 1} \equiv \frac{3 \, TV}{2\lambda^3} \zeta_{\frac{5}{2}} (\alpha^{-1}),
\]

or, using (5.51), we find

\[
U > (V, T; \alpha) \equiv \frac{3}{2} N > \, T \frac{\zeta_{\frac{5}{2}} (\alpha^{-1})}{\zeta_{\frac{3}{2}} (\alpha^{-1})}.
\]

We note that in the limit \( \alpha \to \infty \), we find \( \zeta_{\frac{5}{2}} (\alpha^{-1})/\zeta_{\frac{3}{2}} (\alpha^{-1}) \to 1 \) and \( U \to \frac{3}{2} N T \), which is the classical result (note that \( U \) in this limit is independent of the volume \( V \)).

Next, we look at the case when \( T < T_c \), for which the internal energy, denoted \( U < \), is now

\[
U < (V, T; \alpha \equiv 1) = \frac{3 \, TV}{2\lambda^3} \zeta_{\frac{3}{2}} (1) \equiv \frac{3 \, \zeta_{\frac{3}{2}} (1)}{2 \zeta_{\frac{3}{2}} (1)} \overline{N} \, T,
\]

where we have used (5.23); it is clear that the ground state does not contribute to the mean energy since \( E_0 \equiv 0 \). If we now substitute (5.24), we finally obtain

\[
U < (V, T; \alpha \equiv 1) \equiv \frac{3 \, \zeta_{\frac{3}{2}} (1)}{2 \zeta_{\frac{3}{2}} (1)} N T \left( \frac{T}{T_c} \right)^{\frac{3}{2}}.
\]

That a phase transition occurs at \( T = T_c \) is most easily shown by studying the behavior of the specific heat capacity at constant volume \( C_V \equiv \partial U/\partial T \mid _V,N \). For \( T < T_c \), we easily find from (5.28)

\[
C_V^<(T) \equiv \frac{15}{4} \zeta_{\frac{3}{2}} (1) N \left( \frac{T}{T_c} \right)^{\frac{3}{2}}.
\]

We note that as \( T \to 0 \), \( C_V^<(T) \) scales as \( T^3 \) (in contrast to the photon case for which \( C_V^\gamma \) scales as \( T^3 \) as a result of the fact that photons are massless spin-1 bosons with \( \mu_\gamma \equiv 0 \)).
Lastly, at $T = T_c$, we find
\[ C_V^<(T_c) = \frac{15 \zeta_\frac{3}{2}(1)}{4 \zeta_\frac{1}{2}(1)} N. \]

Here, we note that $C_V^<(T_c)$ is finite.

For $T > T_c$, on the other hand, we use (5.26) to obtain
\[ C_V^>(T) = \frac{3}{2} \frac{V}{2\lambda^3 \zeta_\frac{3}{2}(\alpha^{-1})} \left[ \frac{5}{2} + \left( \frac{\partial \ln \alpha^{-1}}{\partial \ln T} \right) \frac{\zeta_\frac{3}{2}(\alpha^{-1})}{\zeta_\frac{1}{2}(\alpha^{-1})} \right]. \]

We shall use the property that
\[ \frac{d\zeta_\frac{3}{2}(y)}{dy} = \sum_{n=1}^{\infty} \frac{y^{n-1}}{n^{x-1}} \equiv y^{-x} \zeta_{x-1}(y) \]
to find
\[ C_V^>(T) = \frac{3 V}{2\lambda^3} \frac{\zeta_\frac{3}{2}(\alpha^{-1})}{\alpha^{-1}} \left[ \frac{5}{2} + \left( \frac{\partial \ln \alpha^{-1}}{\partial \ln T} \right) \frac{\zeta_\frac{3}{2}(\alpha^{-1})}{\zeta_\frac{1}{2}(\alpha^{-1})} \right] \]
\[ = \frac{3 N}{2} \left[ \frac{5}{2} \frac{\zeta_\frac{3}{2}(\alpha^{-1})}{\zeta_\frac{1}{2}(\alpha^{-1})} + \frac{\partial \ln \alpha^{-1}}{\partial \ln T} \right]. \]

The derivative $\partial \ln \alpha^{-1}/\partial \ln T|_{V,N}$ can be evaluated from $n \equiv \lambda^{-3} \zeta_\frac{3}{2}(\alpha^{-1})$ as
\[ \left. \frac{\partial \ln \alpha^{-1}}{\partial \ln T} \right|_{n} = -\frac{3 \zeta_\frac{3}{2}(\alpha^{-1})}{2 \zeta_\frac{1}{2}(\alpha^{-1})}. \]

Hence, the specific heat capacity at constant volume for $T > T_c$ is
\[ C_V^>(T) = \frac{3 N}{2} \left[ \frac{5}{2} \frac{\zeta_\frac{3}{2}(\alpha^{-1})}{\zeta_\frac{1}{2}(\alpha^{-1})} - \frac{3 \zeta_\frac{3}{2}(\alpha^{-1})}{2 \zeta_\frac{1}{2}(\alpha^{-1})} \right]. \]
(5.30)

When (5.30) is evaluated at $T = T_c$ (or $\alpha = 1$), we find
\[ C_V^>(T_c) = C_V^<(T_c) - \frac{9 N}{4} \lim_{\alpha \to 1} \frac{\zeta_\frac{3}{2}(\alpha^{-1})}{\zeta_\frac{1}{2}(\alpha^{-1})} \equiv C_V^<(T_c), \]

since
\[ \lim_{\alpha \to 1} \zeta_\frac{1}{2}(\alpha^{-1}) = \sum_{n=1}^{\infty} \frac{1}{n^{\frac{1}{2}}} = \infty. \]

Even though $C_V(T)$ is continuous at $T = T_c$, it has a discontinuity in its first derivative, i.e., $\partial TC_V^>(T_c) \neq \partial TC_V^<(T_c)$. The Bose-Einstein condensation is known to be a first-order phase transition, defined as a phase transition with a finite latent heat (examples
of first-order transitions include the solid-liquid-gas transitions); higher-order transitions are associated with zero latent heat and include the transition from the conducting phase to the superconducting phase of some metals (a second-order phase transition) and the transition from the paramagnetic (disordered) state to the ferromagnetic (ordered) state in non-magnetic metals.

5.4.4 Problems

Problem 1. The mass of \( ^4\text{He} \) is \( 6.65 \times 10^{-24} \, \text{g} \) and the density of liquid Helium-4 is 0.15 \( \text{g cm}^{-3} \). Calculate the critical temperature \( T_c \) at which liquid Helium-4 theoretically undergoes Bose-Einstein condensation (Note: the boiling point of Helium-4 is 4.2 K and the superfluid phase transition in Helium-4 is experimentally observed to occur at 2.17 K.)

Problem 2. Derive Equation (11-53) in your textbook by using (5.27).

Problem 3. The thermodynamic potential \( \Omega(T, V, \mu) \) for a non-relativistic Bose-Einstein gas is

\[
\Omega(T, V, \mu) = \frac{m^{3/2} V}{\sqrt{2\pi \hbar^3}} T^{5/2} \int_0^{\infty} z^{1/2} \ln \left(1 - \frac{\alpha^{-1}}{e^z - 1}\right) \, dz
\]

\[
= -\frac{\sqrt{2} m^{3/2} V}{3\pi \hbar^3} T^{5/2} \int_0^{\infty} \frac{z^{3/2} \, dz}{\alpha e^z - 1} = -\frac{V T}{\lambda^3} \zeta_2(\alpha^{-1}),
\]

where \( \lambda \equiv \left(2\pi^2 \hbar^2 / m T\right)^{1/2} \) and \( \Gamma(5/2) = 3\sqrt{\pi}/4 \).

Part (a) Show that, for \( T > T_c \) and using \( \alpha^{-1} \equiv e^{\mu / T} \), (5.51) is given as

\[
N(T, V, \mu) \equiv -\frac{\partial \Omega}{\partial \mu}\bigg|_{T,V}.
\]

Part (b) Show that the entropy of a Bose-Einstein gas is

\[
S(T, V, \mu) \equiv -\frac{\partial \Omega}{\partial T}\bigg|_{\mu,V} = \frac{5 V}{2} \frac{T}{\lambda^3} \zeta_2(\alpha^{-1}) - \frac{\mu N}{T}.
\]

Show that this expression for the entropy satisfies the Third Law of Thermodynamics

\[
\lim_{T \to 0} S(T) \equiv 0.
\]

Part (c) Using the identities \( \Omega \equiv -PV \equiv -\frac{2}{3} U \), show that the thermodynamic relation

\[
U = \mu N + T S - PV
\]

is satisfied for a Bose-Einstein gas.
5.5 Thermodynamics of a Fermi-Dirac Gas

The infinitesimal number of particles \(dN\) contained in the infinitesimal phase-space volume \(V \, d^3p/(2\pi\hbar)^3\) is

\[
dN = \frac{g \, 4\pi V}{(2\pi\hbar)^3} \frac{p^2 \, dp}{1 + e^{(E-\mu)/T}}
\]

where \(V\) denotes the volume of the enclosed gas, \(g = (2s+1)\) for a particle of spin \(s\), \(E\) denotes the energy of a particle of momentum \(p\), \(\mu(T)\) is the chemical potential for fermions, and \(T\) is the temperature of the gas (in energy units). The Fermi energy \(E_F\) is defined as the chemical potential at \(T = 0\):

\[
\lim_{T \to 0} \mu(T) \equiv E_F.
\]

The Fermi energy \(E_F(n)\) is a function of the number density \(n \equiv N/V\) of the Fermi gas.

For a non-relativistic particle of mass \(m\), we may substitute \(p\) for \(E = p^2/2m\) to obtain

\[
dN \equiv \frac{a \, VT^{3/2}}{2} \int_0^{\infty} \frac{z^{1/2} \, dz}{1 + e^{z-\eta}}, \quad (5.31)
\]

where \(a \equiv g \, m^{3/2}/(\sqrt{2\pi^2\hbar^3})\) is a constant (\(g = 2\) for electrons) while \(z \equiv E/T\) and \(\eta \equiv \mu(T)/T\) are dimensionless energies. The total number of particles enclosed in volume \(V\) is therefore

\[
N(V,T;\eta) = a \, VT^{3/2} \int_0^{\infty} \frac{z^{1/2} \, dz}{1 + e^{z-\eta}}. \quad (5.32)
\]

5.5.1 Fermi Function

We now define the following function (called the Fermi function)

\[
F_\sigma(\eta) \equiv \int_0^{\infty} \frac{z^{\sigma} \, dz}{1 + e^{z-\eta}}. \quad (5.33)
\]

Here, we note that, for \(\sigma > 0\), its derivative is expressed as

\[
\frac{dF_\sigma}{d\eta} = \int_0^{\infty} \frac{z^{\sigma} \, e^{z-\eta}}{(1 + e^{z-\eta})^2} \, dz = \sigma \int_0^{\infty} \frac{z^{\sigma-1} \, dz}{1 + e^{z-\eta}} \equiv \sigma \, F_{\sigma-1}(\eta). \quad (5.34)
\]

Another useful expression for \(F_\sigma\) is obtained as follows. First, let us write \(F_\sigma(\eta)\) as

\[
F_\sigma(\eta) = \int_{-\infty}^{\infty} \frac{(\eta + t)^\sigma \, dt}{1 + e^{-t}} = \int_0^\eta \frac{(\eta - t)^\sigma \, dt}{1 + e^{-t}} + \int_0^{\infty} \frac{(\eta + t)^\sigma \, dt}{1 + e^{-t}}
\]

\[
= \int_0^\eta \frac{(\eta - t)^\sigma \, dt}{1 + e^{-t}} + \int_0^{\infty} \frac{(\eta + t)^\sigma \, dt}{1 + e^{-t}}
\]

\[
= \int_0^\eta \frac{(\eta - t)^\sigma \, dt}{1 + e^{-t}} + \int_0^{\infty} \frac{(\eta + t)^\sigma \, dt}{1 + e^{-t}}
\]

\[
= \int_0^\eta \frac{(\eta - t)^\sigma \, dt}{1 + e^{-t}} + \int_0^{\infty} \frac{(\eta + t)^\sigma \, dt}{1 + e^{-t}}
\]

\[
= \int_0^\eta \frac{(\eta - t)^\sigma \, dt}{1 + e^{-t}} + \int_0^{\infty} \frac{(\eta + t)^\sigma \, dt}{1 + e^{-t}}
\]
Using the identity
\[
\frac{1}{1 + e^{-t}} = 1 - \frac{1}{e^t + 1},
\]
the Fermi function can be expressed as
\[
F_\sigma(\eta) = \int_0^\eta (\eta - t)\sigma dt + \int_0^\eta \frac{[(\eta + t)^\sigma - (\eta - t)^\sigma]}{1 + e^t} dt + \int_\eta^\infty \frac{(\eta + t)^\sigma dt}{1 + e^t}.
\]
The first term can be integrated explicitly to give
\[
\int_0^\eta (\eta - t)^\sigma dt = \frac{\eta^{\sigma+1}}{\sigma + 1},
\]
while, in the limit \( \eta \to \infty \), the third term vanishes and the second term can be written as
\[
\int_0^\infty \frac{[(\eta + t)^\sigma - (\eta - t)^\sigma]}{1 + e^t} dt \equiv G_\sigma(\eta).
\]
Using the expansions
\[
(\eta \pm t)^\sigma = \eta^\sigma \pm \sigma \eta^{\sigma-1} t + \frac{\sigma(\sigma-1)}{2!} \eta^{\sigma-2} t^2 \pm \frac{\sigma(\sigma-1)(\sigma-2)}{3!} \eta^{\sigma-3} t^3 + \cdots,
\]
we find
\[
G_\sigma(\eta) = 2\sigma \eta^{\sigma-1} \int_0^\infty \frac{t dt}{e^t + 1} + \frac{\sigma(\sigma-1)(\sigma-2)}{3} \eta^{\sigma-3} \int_0^\infty \frac{t^3 dt}{e^t + 1} + \cdots.
\]
In the limit \( \eta \to \infty \), the Fermi function is therefore given as
\[
F_\sigma(\eta) = \frac{\eta^{\sigma+1}}{\sigma + 1} + 2\sigma \eta^{\sigma-1} I_2 + \frac{\sigma(\sigma-1)(\sigma-2)}{3} \eta^{\sigma-3} I_4 + \cdots,
\]
where
\[
I_x = \int_0^\infty \frac{t^{x-1} dt}{e^t + 1} \equiv \left( 1 - 2^{1-x} \right) \Gamma(x) \zeta_x(1),
\]
\( \Gamma(x) \) is the Gamma function [when \( x \) is an integer \( n \geq 1 \), we find \( \Gamma(n) = (n-1)! \)], and \( \zeta_x(\alpha) \equiv \sum_{n=1}^{\infty} \alpha^n/n^x \) is the Riemann zeta-function [when \( \alpha = 1 \), \( \zeta_x(1) \) converges only if \( x > 1 \)]. Here, since \( \zeta_2(1) = \pi^2/6 \) and \( \zeta_4(1) = \pi^4/90 \), we find
\[
I_2 = \left( 1 - 2^{-1} \right) \Gamma(2) \zeta_2(1) = \frac{\pi^2}{12},
\]
\[
I_4 = \left( 1 - 2^{-3} \right) \Gamma(4) \zeta_4(1) = \frac{7\pi^4}{120},
\]
and the Fermi function can now be expanded as
\[
F_\sigma(\eta) = \eta^{\sigma+1} \left[ \frac{1}{\sigma + 1} + \sigma \frac{\pi^2}{6 \mu^2(T)} + \sigma(\sigma-1)(\sigma-2) \frac{7\pi^4}{360 \mu^4(T)} + \cdots \right]. \quad (5.35)
\]
5.5.2 Thermodynamic Functions

The total particle number (5.51) can be written in terms of the Fermi function as

\[ N(V, T; \eta) = aVT^{3/2} F_{1/2}(\eta). \]

We can also calculate the mean energy

\[ U(V, T; \eta) \equiv \int_0^\infty E \, dN = aVT^{5/2} \int_0^\infty \frac{z^{3/2} \, dz}{e^{z-\eta} + 1} \equiv aVT^{5/2} F_{3/2}(\eta). \] (5.36)

Next, we define the free energy

\[ \Omega(V, T; \eta) \equiv -gV \int \ln \left(1 + e^{-(E-\mu)/T}\right) \frac{d^3p}{(2\pi\hbar)^3} \]

\[ = -aVT^{5/2} \int_0^\infty z^{1/2} \ln(1 + e^{\eta-z}) \, dz \]

Integration by parts \( \Rightarrow \)

\[ = -\frac{2}{3} aVT^{5/2} \int_0^\infty \frac{z^{3/2} \, dz}{1 + e^{z-\eta}} \equiv -\frac{2}{3} aVT^{5/2} F_{3/2}(\eta). \] (5.37)

From this expression, we verify that

\[ N \equiv -\frac{\partial \Omega}{\partial \mu} \bigg|_{V,T} = -\frac{1}{T} \frac{\partial \Omega}{\partial \eta} \bigg|_{V,T}. \]

Next, we can obtain an expression for the pressure of a non-relativistic Fermi gas

\[ P \equiv -\frac{\partial \Omega}{\partial V} \bigg|_{T,\mu} = \frac{2}{3} aT^{5/2} F_{3/2}(\eta), \] (5.38)

and the entropy of a non-relativistic Fermi gas

\[ S \equiv -\frac{\partial \Omega}{\partial T} \bigg|_{\mu,V} = \frac{5}{3} aVT^{3/2} F_{1/2}(\eta) + \frac{\eta}{T} \frac{\partial \Omega}{\partial \eta} \bigg|_{V,T} \]

\[ = aVT^{3/2} \left[ \frac{5}{3} F_{1/2}(\eta) - \eta F_{3/2}(\eta) \right]. \] (5.39)

By combining these results, we arrive at the thermodynamic identity

\[ U = N \mu + TS - PV. \] (5.40)

Since \( \Omega \equiv -PV = -\frac{2}{3} U \), we can use the classical result \( U = \frac{3}{2} NT \) to obtain the ideal gas law: \( PV = NT \) from (5.40).
5.5.3 Degenerate Limit

We now investigate the limit of very low temperatures: $T \to 0$. In this limit, $\mu \to E_F$ and $\eta \equiv \mu/T \to \infty$. In the limit $\eta \to \infty$, the Fermi function $F_\sigma(\eta)$ becomes

$$F_\sigma(\eta) \to \frac{E_F^{\sigma+1}}{(\sigma + 1) T^{\sigma+1}},$$

(5.41)

and, hence, the total particle number becomes

$$N = aVT^{3/2} F_2(\eta) \to \frac{2aV}{3} E_F^{3/2}.$$  

(5.42)

Since the number of particles is obviously independent of temperature (i.e., $\partial N/\partial T \equiv 0$), we obtain an expression for the Fermi energy (in the non-relativistic case)

$$E_F = \left( \frac{3N}{2aV} \right)^{2/3} = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 n}{2} \right)^{2/3},$$

(5.43)

where $n \equiv N/V$ is the number density of the Fermi gas and the last expression applies to the case of electrons ($g = 2$). Note that the Fermi energy is a purely quantum-mechanical concept ($\hbar \neq 0$). The limit $T \ll E_F$ is called the degenerate limit; indeed, if we define $N_T \equiv \frac{4\pi}{3} \lambda_T^3 n$ to be the number of fermions inside a sphere of radius $\lambda_T \equiv \hbar/p_{\text{rms}}(T) = \hbar (3mT)^{-1/2}$, we easily find

$$N_T = \frac{32\pi^2}{9} \left( \frac{E_F}{3T/2} \right)^{3/2},$$

and, hence, when $E_F \gg T$ we also have $N_T \gg 1$.

Matter is in a degenerate state when the number density $n$ is large enough (e.g., inside most metals at room temperature). For example, in a cube of Silver metal (density = 10.49 g cm$^{-3}$, atomic mass = 1.809 $\times$ 10$^{-22}$ g, and valence number = 1), the conduction-electron number density is $n = 5.80 \times 10^{22}$ cm$^{-3}$ and the Fermi energy is $E_F = 5.46$ eV. At room temperature (293 K), we find $T = 0.0252$ eV and, since $E_F \gg T$, the electrons in Silver are degenerate.

In the degenerate limit ($T \to 0$), we also find the zero-temperature entropy

$$S \to aVT^{3/2} \left( \frac{5}{3} \frac{\eta^{5/2}}{5/2} - \eta \frac{\eta^{3/2}}{3/2} \right) = 0,$$

in accordance with the Third Law of Thermodynamics. Lastly, the zero-temperature Fermi gas pressure is

$$P = \frac{2}{3} aT^{5/2} F_4(\eta) \to \frac{4a}{15} E_F^{5/2} = \frac{2}{5} nE_F.$$

For the case of conduction electrons in Silver metal, for example, we find a pressure of $p = 2.03 \times 10^{10}$ Pa $\simeq$ 200,000 atm!
5.5.4 Near-degenerate Case

For small but finite temperatures, we may use the first two terms in the expansion (5.52) for the Fermi function. The number of particles is thus expressed as

\[ N = aV \left( \frac{2}{3} \eta^{3/2} + \frac{\eta^{-1/2}}{12} + \cdots \right) \]

\[ = aV \left[ \frac{2}{3} \mu^{3/2}(T) + \frac{\pi^2}{12} \frac{T^2}{\mu^{1/2}(T)} + \cdots \right]. \]

Since \( N \) must be independent of temperature, i.e., \( N = (2aV/3) E_F^{3/2} \), we easily obtain an expression for the chemical potential of a Fermi gas

\[ \mu(T) \equiv E_F \left( 1 - \frac{\pi^2}{12} \frac{T^2}{E_F^2} + \cdots \right). \quad (5.44) \]

We now compute the mean energy

\[ U = aV T^{5/2} \left( \frac{2}{5} \eta^{5/2} + \frac{\eta^{1/2}}{4} + \cdots \right) \]

\[ = aV \left[ \frac{2}{5} \mu^{5/2}(T) + \frac{\pi^2}{4} \mu^{1/2}(T) T^2 + \cdots \right]. \]

Substituting the expression (5.44) for the chemical potential of a Fermi gas, we find

\[ U = aV E_F^{5/2} \left( \frac{2}{5} + \frac{\pi^2}{6} \frac{T^2}{E_F^2} + \cdots \right). \quad (5.45) \]

From this expression, we now find the specific heat capacity at constant volume

\[ C_V \equiv \frac{\partial U}{\partial T}_{V,N} = \frac{\pi^2 aV}{3} E_F^{1/2} T + \cdots \equiv \frac{\pi^2 N}{2} \frac{T}{E_F} + \mathcal{O} \left( \frac{T^3}{E_F^3} \right). \quad (5.46) \]

Experimentally, it is found that a plot of \( C_V/T \) versus \( T^2 \) for metals shows a linear relationship at low temperatures with a \( y \)-axis intercept (i.e., \( C_V/T \) \( \exp \equiv \gamma + AT^2 \); see below). This implies that the low-temperature specific heat capacity of a metal is dominated by its degenerate conduction (valence) electrons.

5.6 Specific Heat of a Crystalline Lattice

The wavelength \( \lambda_n (n \geq 1) \) of a standing wave excited on a string of length \( L \) is \( \lambda_n = 2L/n \) and thus the wave’s angular frequency is \( \omega_n = \pi nv/L \), where \( v \) is the wave speed. For
waves propagating in a lattice (with lattice spacing $a$), the wavelength must be larger than $a$ and thus $\omega_n$ has a maximum value denoted as $\Omega \equiv \pi v/a$.

In a three-dimensional lattice, each lattice point can support 3 standing waves (one along each of three directions) and therefore the total number of vibration modes is $3N$, where $n$ is the number of lattice points. The number of lattice vibrations in a volume $V$ in the range $\omega$ and $\omega + d\omega$ is

$$dN(\omega) = \frac{V}{(2\pi v)^3} 4\pi \omega^2 d\omega,$$

so that the maximum angular frequency $\Omega$ is defined by the integral relation

$$\int_0^\Omega dN(\omega) \equiv 3N \quad \rightarrow \quad \Omega = \left(18\pi^2 n\right)^{\frac{1}{3}} v,$$

(5.47)

where $n \equiv N/V$ is the number density of lattice points.

The internal energy of lattice vibrations in a volume in thermal equilibrium at temperature $T$ is now written as

$$U = \int_0^\Omega \frac{\hbar \omega}{e^{\hbar \omega/T} - 1} dN(\omega) = \frac{4\pi V T^4}{(2\pi \hbar v)^3} \int_0^{\hbar \Omega/T} \frac{x^3 dx}{e^x - 1}.$$ 

By defining the Debye temperature $\Theta$ as

$$\Theta \equiv \hbar \Omega = \left(18\pi^2 n\right)^{\frac{1}{3}} \hbar v,$$

(5.48)

the expression for the internal energy is finally written as

$$U = \frac{9NT^4}{\Theta^3} \int_0^{\Theta/T} \frac{x^3 dx}{e^x - 1}.$$ 

(5.49)

From this expression, the specific heat capacity at constant volume $C_V \equiv \partial U/\partial T|_{V,N}$ is

$$C_V = 9N \left[ \frac{4}{\eta^3} \int_0^\eta \frac{x^3 dx}{e^x - 1} - \frac{\eta}{e^\eta - 1} \right],$$

(5.50)

where $\eta \equiv \Theta/T$. In the limit $T \to 0$ (or $\eta \to \infty$), (5.50) becomes

$$C_V \to 36 \frac{NT^3}{\Theta^3} \int_0^\infty \frac{x^3 dx}{e^x - 1} = 12\pi^4 N \frac{T^3}{5} \left(\frac{T}{\Theta}\right)^3.$$
5.7 Problems

Problem 1

In the Notes on the thermodynamics of a Fermi-Dirac gas, we investigated the case of a non-relativistic electron gas. The infinitesimal number $dN$ of electrons contained in a volume $V$ in thermal equilibrium at temperature $T$ (given in energy units) was given by the Fermi-Dirac formula

$$dN = \frac{V}{\pi^2 \hbar^3} \frac{p^2 \, dp}{e^{(E-\mu)/T} + 1},$$

where $E = p^2/2m$ in the non-relativistic limit and $\mu$ denotes the chemical potential of the electrons. The relativistic formula for the energy of an electron is

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

In the ultra-relativistic limit ($pc \gg mc^2$), we may express the electron momentum as $p \simeq E/c$.

(a) Show that for a gas of ultra-relativistic electrons, we find

$$N \equiv \frac{V T^3}{\pi^2 (\hbar c)^3} F_2(\eta), \quad (5.51)$$

where $\eta \equiv \mu/T$ and

$$F_\sigma(\eta) \equiv \int_0^\infty \frac{z^\sigma \, dz}{e^z - \eta + 1} = \eta^{\sigma+1} \left[ \frac{1}{\sigma + 1} + \sigma \frac{\pi^2 T^2}{6 \, \mu^2(T)} + \sigma (\sigma - 1) (\sigma - 2) \frac{7 \pi^4 T^4}{360 \, \mu^4(T)} + \cdots \right]. \quad (5.52)$$

(b) Show that the mean energy

$$U \equiv \int E \, dN = \frac{V T^4}{\pi^2 (\hbar c)^3} F_3(\eta).$$

(c) In the limit $T \to 0$, the Fermi energy $E_F \simeq p_F c$ is defined for the ultra-relativistic case as

$$E_F \equiv (3 \pi^2 n)^{1/3} \hbar c,$$

where $n \equiv N/V$. Show that in the same limit,

$$U = \frac{3}{4} N E_F.$$
(d) A more accurate formula for $U$ at $T = 0$ is given as

$$U \equiv \frac{V}{\pi^2 \hbar^3} \int_0^{p_F} \sqrt{p^2 c^2 + m^2 c^4} p^2 dp. \quad (5.53)$$

By changing the integration variable from $p$ to $\chi \equiv p/mc$, show that

$$U = \frac{(mc^2)^4 V}{8\pi^2 (hc)^3} \left[ \chi_F (2\chi_F^2 + 1) \sqrt{1 + \chi_F^2} - \sinh^{-1} \chi_F \right],$$

where $\chi_F \equiv p_F/mc$.

(e) Using (5.51) and the fact that $N$ is in fact independent of temperature $T$, show that the chemical potential for an ultra-relativistic Fermi gas is

$$\mu(T) = E_F \left( 1 - \frac{\pi^2 T^2}{3 E_F^2} + \cdots \right).$$

**Problem 2**

The partition function of a monochromatic photon gas ($E_n \equiv n \hbar \omega$) is defined as

$$Z(T, \omega) \equiv \sum_{n=0}^{\infty} e^{-E_n/k_B T} = \sum_{n=0}^{\infty} e^{-n\hbar \omega/k_B T} = \frac{1}{1 - e^{-\hbar \omega/k_B T}}. \quad (5.54)$$

From this definition, we may also define the probability

$$p_n \equiv \frac{1}{Z} e^{-E_n/k_B T} \text{ so that } \sum_{n=0}^{\infty} p_n = 1. \quad (5.55)$$

(a) The average mode number $\bar{n}$ and the average energy $\bar{E}$ are defined as

$$\bar{n} \equiv \sum_{n=0}^{\infty} n p_n \equiv N(T, \omega)$$

$$\bar{E} \equiv \sum_{n=0}^{\infty} E_n p_n \equiv U(T, \omega).$$

Using (5.54) and (5.55), show that

$$N(T, \omega) \equiv - \frac{k_B T}{\hbar} \frac{\partial \ln Z(T, \omega)}{\partial \omega} \quad \text{and} \quad U(T, \omega) \equiv k_B T^2 \frac{\partial \ln Z(T, \omega)}{\partial T},$$

and calculate those expressions using (5.54).

(b) We now introduce the Helmholtz free energy function $F(T, \omega)$ such that the partition function (5.54) is now written as $Z \equiv e^{-F/k_B T}$ or

$$F(T, \omega) \equiv - k_B T \ln Z(T, \omega) = k_B T \ln \left( 1 - e^{-\hbar \omega/k_B T} \right)$$
and the entropy function $S(T, \omega)$

$$S(T, \omega) \equiv -\frac{\partial F(T, \omega)}{\partial T}.$$  

[Note: The functions $U$, $F$, and $S$ are related by the formula $U = F + TS$.] Obtain an explicit expression for the entropy function $S(T, \omega)$. In addition, show that as $T \to 0$, we have

$$\lim_{T \to 0} S(T, \omega) \equiv 0.$$  

This statement is known as the Third Law of Thermodynamics.

(c) Boltzmann’s definition of entropy is given in terms of the expression

$$S \equiv -k_B \sum_{n=0}^{\infty} p_n \ln p_n$$

where

$$p_n = Z^{-1} e^{-E_n/k_B T} \equiv e^{-(E_n - F)/k_B T}.$$  

Show that Boltzmann’s entropy definition is identical to the expression for $S(T, \omega)$ you obtained in part (b).