

# Notes on Quantum Mechanics

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# Part I

## History



# Chapter 1

## A Historical Overview

Rishi's article + JP sir's slides

### 1.1 Blackbody Radiation

### 1.2 Premise

We can consider a black body to consist of electromagnetic radiation in thermal equilibrium with the walls of the cavity. When they are in thermal equilibrium, the average rate of emission of radiation equals their average rate of absorption of radiation.

The Rayleigh Jeans theory was constructed on the notion that when the walls of an object is in thermal equilibrium, in other words, the temperature of the walls is equal to the "temperature" of radiation. We will see what we mean by the "temperature" of an electromagnetic wave.

If we take the walls of a cavity to consist of oscillating charged particles (about its equilibrium) coupled to a standing-wave mode of an electromagnetic field. This can be seen from Maxwell's theory of electromagnetic waves, which states that a moving charged particle radiates an electromagnetic wave. A point to be noted is that the frequency of the oscillating charge is equal to the frequency of its coupled electromagnetic wave. So then, it is safe to say that in thermal equilibrium, the average energy of the oscillating charge is equal to the average energy of the coupled standing-wave mode of that electromagnetic field.

Now we can see that the oscillating particle has a quadratic potential energy,

$H_{pot}$  of  $\frac{1}{2}aq^2$  and a kinetic energy  $H_{kin}$  of  $\frac{p^2}{2m}$ , so according to the equipartition theorem, in thermal equilibrium the average energy is,

$$\langle H|H\rangle = \langle H_{pot}|H_{pot}\rangle + \langle H_{kin}|H_{kin}\rangle = \frac{1}{2}k_B T + \frac{1}{2}k_B T = k_B T \quad (1.1)$$

Hence the energy of the wave is also taken to be  $k_B T$ , and can be thought to have a "temperature" of  $T$ .

This forms the foundation of the Rayleigh Jeans theory, following which we will derive the Rayleigh-Jeans formula.

## 1.3 Deriving the Rayleigh-Jeans Formula

We start off with the axiom that the energy distribution of a black-body radiation does not depend on the shape of the cavity (which can be proven experimentally). For ease of calculations, we take the shape of the cavity to be a cube. We also assume that the waves vanish at the walls, or in other words, do not pass through them.

The number of standing electromagnetic waves in a cube of length  $L$  needs to be calculated.

Let us take the wave equation for the standing electromagnetic wave,

$$\frac{\partial^2 E_x}{\partial x^2} + \frac{\partial^2 E_x}{\partial y^2} + \frac{\partial^2 E_x}{\partial z^2} + k^2 E_x = 0 \quad (1.2)$$

Where  $E_x = E_x(x, y, z)$  and  $k = \frac{2\pi}{\lambda} = \frac{2\pi f}{c}$ . Assuming that  $E_x = u(x)v(y)w(z)$  (by variable separable method), we can separate Equation (2) into three ordinary differential equations of the type,

$$\frac{d^2 u}{dx^2} + k_x^2 u = 0 \quad (1.3)$$

Where  $k^2 = k_x^2 + k_y^2 + k_z^2$ . By inspection, we can see that Equation (3) is an equation for a simple harmonic oscillator and has the solution,

$$u(x) = B \cos k_x x + C \sin k_x x \quad (1.4)$$

Applying necessary boundary conditions so that  $E_x$  or  $u$  is 0 at  $x = 0$  and at  $x = L$  leads to  $B = 0$  and  $k_x L = n_x \pi$  where  $n_x = 1, 2, 3, \dots$ , (since we are considering standing electromagnetic waves and look at only the positive region of the  $k$ -space) similar solutions are obtained for  $v(y)$  and  $w(z)$ , giving the solution,

$$E_x(x, y, z) = A \sin(k_x x) \sin(k_y y) \sin(k_z z) \quad (1.5)$$

Where,

$$k^2 = \frac{\pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2) \quad (1.6)$$

and  $n_x, n_y$  and  $n_z$  are positive integers.

Now, we take Equation (6) to give us the distance from the origin to a point in  $k$ -space, or often called the "Reciprocal" space (due to the units of  $k$  being  $(length)^{-1}$ ).

Let us take a coordinate system corresponding to the  $k$ -space (as shown in Figure 1), with the axes being  $k_x, k_y$  and  $k_z$ . And we know that  $k_x = n_x \pi / L$ ,  $k_y = n_y \pi / L$ , and  $k_z = n_z \pi / L$ , so the points in  $k$ -space are separated by

$\pi/L$  along each axis, and there is one standing wave in  $k$ -space per  $(\pi/L)^3$  of volume. The number of standing waves,  $N(k)$  having wavenumbers between  $k$  and  $k+dk$  is then simply the volume between  $k$  and  $k+dk$  divided by  $(\pi/L)^3$ . The volume between  $k$  and  $k+dk$  is simply the volume of a spherical shell of thickness  $dk$  multiplied by  $1/8$  (since we need only the positive quadrant of the  $k$ -space, hence  $1/4$  of the volume of sphere), so that

$$N(k)dk = \frac{\frac{1}{2}\pi k^2 dk}{(\pi/L)^3} = \frac{V k^2 dk}{2\pi^2} \quad (1.7)$$

Where  $V = L^3$  is the volume of the cavity.

For any electromagnetic wave, there are two perpendicular polarisations for each mode, so Equation (6) should be increased by a factor of 2, becoming,

$$\frac{N(k)dk}{V} = \frac{k^2 dk}{\pi^2} \quad (1.8)$$

From using the expression  $k = 2\pi f/c$  to obtain  $k$  and  $dk$  and substituting in Equation (8) gives us  $N(f)$ ,

$$N(f)df = \frac{8\pi f^2}{c^3} df \quad (1.9)$$

And from this, the number of modes per unit volume between  $\lambda$  and  $\lambda + d\lambda$  can be derived from Equation (9) by using the expression  $f = c/\lambda$  to get  $\lambda$  and  $d\lambda$  to get,

$$N(\lambda)d\lambda = \frac{8\pi}{\lambda^4} d\lambda \quad (1.10)$$

Now, each mode of oscillation has energy of  $k_B T$ , so the energy in the range  $\lambda$  to  $\lambda + d\lambda$  is  $k_B T N(\lambda) d\lambda$ . Hence the energy density in this region is,

$$u(\lambda)d\lambda = k_B T N(\lambda) = \frac{8\pi k_B T}{\lambda^4} d\lambda \quad (1.11)$$

This is the Rayleigh Jeans expression for spectral density in the range  $\lambda$  to  $d\lambda$ . Considering the energy to be a continuous variable, then the average energy per oscillator is  $k_B T$  and the Rayleigh Jeans formula for  $u(\lambda)$  holds true. The Rayleigh Jeans formula also behaves perfectly well for long wavelengths in the electromagnetic spectrum. It also agrees with the Wien's scaling formula,

$$u(\lambda) = \frac{8\pi k_B T}{\lambda^4} = \frac{f(\lambda T)}{\lambda^5} \quad (1.12)$$

However, we will see in the next section why this is not a correct scaling function.



Figure 1.1: Visualising the k-space

## 1.4 Failure of the Rayleigh Jeans theory in explaining the Stefan-Boltzmann Law

### 1.4.1 Incorrect Scaling function

From the previous equation for the scaling function, we can see that  $f(\lambda T) = 8k_B T$ . So from this, we can notice that as  $\lambda$  decreases, the  $u(\lambda)$  also increases. This means that higher the temperature, more lower wavelength waves are emitted, for example, a campfire emits a large amount of short wavelength microwaves (which is very deadly, but thankfully that isn't how things work in nature) according to this law. Hence, the law fails in this regard.

### 1.4.2 The Ultraviolet Catastrophe

Inspecting the Rayleigh-Jeans formula, and attempting to find the total energy density (by integrating with appropriate limits) of the black body gives us an interesting result,

$$u = \int_{\infty}^0 = u(\lambda)d\lambda = \int_{\infty}^0 \frac{8\pi k_B T}{\lambda^4} d\lambda = \infty \quad (1.13)$$

Here we see that the energy density is infinite, which is easy to figure out that this is nonsensical. It implies that if a cavity filled with radiation radiates infinite amount of energy. This was named by Paul Ehrenfest as the "Ultraviolet Catastrophe". However, Stefan found out that the energy radiated is proportional to  $T^4$ , hence, trying to explain the Stefan-Boltzmann Law using the Rayleigh-Jeans formula for energy density will end in vain.

### 1.4.3 Consequences

As the Rayleigh-Jeans formula failed to address shorter wavelengths, Planck decided to use a different approach to explain the black body radiation curve. He decided not to assume that the average energy of an oscillator in the wall to be  $k_B T$ . He knew how  $u(\lambda)$  varies for short wavelengths, using the Wien's formula and wanted  $u(\lambda)$  to be proportional to  $T$  for longer wavelengths. This led to the formulation of the Planck's formula, which perfectly described the radiation curve.

## 1.5 Planck's Law

## 1.6 The de Broglie Hypothesis

In 1924, the French physicist de Broglie proposed that this wave like structure applies to electrons too and follows the equation:

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda} \quad (1.14)$$

## 1.7 Davidsson-Germer Experiment

# Part II

## Tools



# Chapter 2

## Mathematical Preliminaries

This chapter is a discussion of all the mathematical tools and tricks one would require to master Quantum mechanics. Knowledge of basic matrix manipulation and calculus is assumed.

### 2.1 Vector Calculus

### 2.2 Complex Numbers

A complex number is an order pair  $z \in \mathbb{C}$  where  $a, b \in \mathbb{R}$  where we can denote it as  $z = a + ib$  where  $i = \sqrt{-1}$

#### 2.2.1 Addition

$$z_1 = a_1 + ib_1, \quad z_2 = a_2 + ib_2$$

$$z_1 + z_2 = (a_1 + a_2) + i(b_1 + b_2)$$

#### 2.2.2 Multiplication

$$z_1 = a_1 + ib_1, \quad z_2 = a_2 + ib_2$$

$$z_1 z_2 = (a_1 + ib_1)(a_2 + ib_2) = (a_1 a_2 - b_1 b_2) + i(a_1 b_2 + a_2 b_1)$$

#### 2.2.3 Properties

Where,  $\mathcal{W}, \mathcal{Z}, \lambda \in \mathbb{C}$

**Commutativity**

$$\mathcal{W} + \mathcal{Z} = \mathcal{Z} + \mathcal{W}$$

$$\mathcal{W}\mathcal{Z} = \mathcal{Z}\mathcal{W}$$

**Associativity**

$$(\mathcal{Z}_1 + \mathcal{Z}_2) + \mathcal{Z}_3 = \mathcal{Z}_1 + (\mathcal{Z}_2 + \mathcal{Z}_3)$$

$$(\mathcal{Z}_1\mathcal{Z}_2)\mathcal{Z}_3 = \mathcal{Z}_1(\mathcal{Z}_2\mathcal{Z}_3)$$

**Identities**

$$\mathcal{Z} + 0 = \mathcal{Z}$$

$$\mathcal{Z}1 = \mathcal{Z}$$

**Additive Inverse**

$$\forall \mathcal{Z} \exists \mathcal{Z}^{-1} \mid \mathcal{Z} + \mathcal{Z}^{-1} = 0$$

**Multiplicative Inverse**

$$\forall \mathcal{Z} \neq 0 \exists \mathcal{W} \mid \mathcal{Z}\mathcal{W} = 1$$

**Distributive Property**

$$\lambda(\mathcal{W} + \mathcal{Z}) = \lambda\mathcal{W} + \lambda\mathcal{Z}$$

**2.2.4 Notation**

***$n$ -tuple*** refers to an ordered set of  $n$  numbers over a field  $\mathcal{F}$ .<sup>1</sup>

**2.2.5 Wessel Plane**

Complex numbers can be represented on a 2-dimentional space similar to  $\mathbb{R}^2$

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<sup>1</sup>For our case  $\mathcal{F}$  simply refers to  $\mathbb{C}$

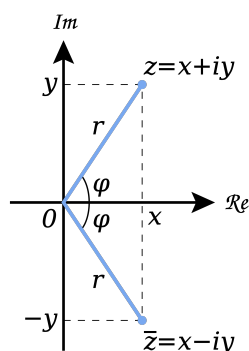


Figure 2.1: Wessel Plane Plot: (Complex conjugate picture.svg from Wikimedia Commons)

## 2.3 Vector Analysis

## 2.4 Solving PDEs

What we'll review here is called the variable separable method,

## 2.5 Linear Vector Spaces

A linear vector space or simply a vector space  $\mathbb{V}$  is a set along with the regular multiplication and addition operations over a field  $\mathcal{F}$ , such that the following axioms hold: <sup>2</sup>

### 2.5.1 Commutativity

$$\mathcal{U} + \mathcal{V} = \mathcal{V} + \mathcal{U}$$

### 2.5.2 Associativity

$$(\mathcal{U} + \mathcal{V}) + \mathcal{W} = \mathcal{V} + (\mathcal{U} + \mathcal{W})$$

$$(\alpha\beta)\mathcal{V} = \alpha(\beta\mathcal{V})$$

### 2.5.3 Additive Identity

$$\exists 0 \in \mathbb{V} \mid \mathcal{V} + 0 = 0 + \mathcal{V} = \mathcal{V}$$

---

<sup>2</sup>Here,  $\alpha, \beta \in \mathcal{F}$  and  $\mathcal{U}, \mathcal{V}$  and  $\mathcal{W} \in \mathbb{V}$

### 2.5.4 Additive Inverse

$$\forall \mathcal{V} \exists \mathcal{V}^{-1} \mid \mathcal{V} + \mathcal{V} = 0$$

### 2.5.5 Multiplicative identity

$$\exists 1 \in \mathbb{V} \mid 1\mathcal{V} = \mathcal{V}$$

### 2.5.6 Distributive properties

$$\alpha(\mathcal{U} + \mathcal{V}) = \alpha\mathcal{U} + \alpha\mathcal{V}$$

$$(\alpha + \beta)\mathcal{U} = \alpha\mathcal{U} + \beta\mathcal{U}$$

## 2.6 Inner Product Spaces

An inner product is simply an operation that takes a Dual  $|\psi\rangle$  and it's corresponding vector  $\langle\psi|$  and maps them to  $\mathbb{R}$ :

$$\langle expression1 | expression2 \rangle$$

## 2.7 Dual Spaces

## 2.8 Dirac Notation

Operators are represented with respect to a particular basis (in this case  $\{e_m, e_n\}$ ) by their matrix elements

$$\langle e_m | \hat{O} | e_n \rangle = \hat{O}_{mn} \quad (2.1)$$

## 2.9 Subspaces

Given a vector space  $\mathbb{V}$ , a subset of its elements that form a vector space among themselves is called a subspace. We will denote a particular subspace  $i$  of dimensionality  $n_i$  by  $\mathbb{V}_i^{n_i}$ .

Given two subspaces, and , we define their sum  $\mathbb{V}_i^{n_i} \oplus \mathbb{V}_i^{m_i} = \mathbb{V}_i^{l_i}$ <sup>3</sup> as the set containing:

1. All the elements of  $\mathbb{V}_i^{n_i}$

---

<sup>3</sup>Here  $\oplus$  is the direct sum defined as:



2. All the elements of  $\mathbb{V}_j^{m_j}$
3. And all possible linear combinations of the above

However for the elements of (3), closure is lost. The dimensionality of such a subspace is  $n + m$ .

## 2.10 Hilbert Spaces

A Hilbert space  $H$  is simply a normed vector space (a Banach space), whose norm is defined as:

$$\|V\| := \sqrt{\langle V|V \rangle} \quad (2.2)$$

This is an axiomatic definition of a Hilbert space, but we are more concerned with the corollaries of it. All the Cauchy sequences<sup>4</sup> of functions in a Hilbert space always converge to a function that is also a member of the space i.e. it is said to be **complete** which implies that the integral of the absolute square of a function must converge<sup>5</sup>

$$\int_a^b |f(x)|^2 dx < \infty \quad (2.3)$$

Moreover this means that, any function in Hilbert space can be expressed as a linear combination of other functions i.e. it is closed/complete

$$f(x) = \sum_{n=1}^{\infty} c_n f_n(x) \quad (2.4)$$

Where,  $c_n \in \mathbb{C}$

## 2.11 Linear Operators

## 2.12 Eigenvalue Problem

## 2.13 Eigenfunctions of a Hermitian Operator

## 2.14 Transformations

### 2.14.1 Active Transformation

In a loose sense this can be thought of as,

---

<sup>4</sup>Definition

<sup>5</sup>we simply state this but a proof can be found in

### 2.14.2 Passive Transformation

From our discussion before it is also clear that the same transformation can be implemented as,

$$\hat{O} \rightarrow U^\dagger \hat{O} U \quad (2.5)$$

This is a very different viewpoint, we can understand this by visualizing it to be a

### 2.14.3 Equivalence of Transformation types

It's pretty simple to see that both types of transformation constitute the same physical picture. Thus, we can take both viewpoints to mean the same physical transformation in each case, and later on we will see how this leads us two different pictures of Quantum Mechanics and how they are related.

## 2.15 Functions of Operators

## 2.16 Generalization to Infinite Dimensions

## 2.17 Probability

### 2.17.1 Discrete Variables

Suppose we have a frequency distribution

$$N = \sum_{j=0}^{\infty} N(j) \quad (2.6)$$

The probability of an event  $N_j$  is defined as,

$$P(j) = \frac{N(j)}{N} \quad (2.7)$$

In probability theory, the sum of all probabilities is 1,

$$\sum_{j=0}^{\infty} P(j) = \sum_{j=0}^{\infty} \frac{N(j)}{N} = 1 \quad (2.8)$$

The average/mean/expectation value of a value  $j$  is given by the formula:

$$\langle j \rangle = \frac{\sum j N(j)}{N} = \sum_{j=0}^{\infty} j P(j) \quad (2.9)$$

and in general, the average of some function of  $j$ , is given by,

$$\langle f(j) \rangle = \sum_{j=0}^{\infty} f(j)P(j) \quad (2.10)$$

The spread of a variable's value from it's mean is called it's variance, written as

$$\sigma^2 = \langle (\Delta j)^2 \rangle \quad (2.11)$$

where,

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

It's square root is called the standard deviation,

$$\sigma = \sqrt{\langle (\Delta j)^2 \rangle} = \sqrt{\langle j^2 \rangle - \langle j \rangle^2} \quad (2.12)$$

Which comes from a theorem on variances that we'll find useful later on:

$$\begin{aligned} \sigma^2 &= \langle (\Delta j)^2 \rangle = \sum (\Delta j)^2 P(j) = \sum (j - \langle j \rangle)^2 P(j) \\ &= \sum (j^2 - 2j \langle j \rangle + \langle j \rangle^2) P(j) \\ &= \sum j^2 P(j) - 2 \langle j \rangle \sum j P(j) + \langle j \rangle^2 \sum P(j) \\ &= \langle j^2 \rangle - 2 \langle j \rangle \langle j \rangle + \langle j \rangle^2 = \langle j^2 \rangle - \langle j \rangle^2 \end{aligned}$$

### 2.17.2 Continuous Variables

We now move to a continuous probability distribution, we'll create continuous analogs of all the quantities we just introduced. Let's start with probability, the probability of that  $x$  lies between  $a$  and  $b$

$$P_{ab} = \int_a^b \rho(x) dx \quad (2.13)$$

where  $\rho(x)$  is the called the probability density i.e. the probability of getting  $x$ , or more concretely,

$\rho(x)dx$  = Probability that an individual is chosen at random lies between  $x$  and  $x+dx$

Now supposing the rules we held for discrete variables hold, the continuous analogs look like this:

$$1 = \int_{-\infty}^{\infty} \rho(x) dx \quad (2.14)$$

$$\langle x \rangle = \int_{-\infty}^{\infty} x \rho(x) dx \quad (2.15)$$

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x) \rho(x) dx \quad (2.16)$$

$$\sigma^2 := \langle (\Delta x)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 \quad (2.17)$$

## 2.18 Expectation Values

In this section we'll explore how we express the expectation values of a few operators. Let's start with the position operator in the position representation (i.e. position basis):

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi(\vec{x}, t)|^2 dx \quad (2.18)$$

We can differentiate 2.18 with respect to time to find the expectation value for "velocity":

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

Throwing away

$$\langle v \rangle = \frac{d \langle x \rangle}{dt} = -\frac{i\hbar}{m} \int \psi^* \frac{\partial \psi}{\partial x} dx \quad (2.19)$$

Therefore we can write the expectation value of momentum as,

$$\langle p \rangle = m \frac{d \langle x \rangle}{dt} = -i\hbar \int \left( \psi^* \frac{\partial \psi}{\partial x} \right) dx \quad (2.20)$$

In general, every observable is a function of position and momentum, thus for an observable  $\hat{O}(x, p)$ , the expectation value is given by,

$$\langle \hat{O}(x, p) \rangle = \int \psi^* \hat{O}(x, -i\hbar \nabla) \psi dx \quad (2.21)$$

For example, the expectation value of kinetic energy is,

$$\langle T \rangle = -\frac{\hbar^2}{2m} \int \psi^* \frac{\partial^2 \psi}{\partial x^2} dx \quad (2.22)$$

Or to sum it up in Dirac notation,

$$\langle \hat{O} \rangle = \langle \psi | \hat{O} | \psi \rangle \quad (2.23)$$

## 2.19 Fourier Analysis

### 2.19.1 Dirichelet's Theorem

### 2.19.2 Fourier Transform

## 2.20 Delta Function

### 2.20.1 The Divergence of $\frac{\hat{r}}{r^2}$

We can see why the divergence is,

$$\nabla \cdot \frac{\hat{r}}{r^2} = 0 \quad (2.24)$$

But if we calculate this using the Divergence theorem, we find that ,

$$\oint v \cdot da = \int \left( \frac{\hat{r}}{r^2} \right) \cdot (r^2 \sin(\theta) d\theta d\phi \hat{r}) = \left( \int_0^\pi \sin(\theta) d\theta \right) \left( \int_0^{2\pi} d\phi \right) = 4\pi \quad (2.25)$$

This is paradoxical. The issue is that it blows up at  $r = 0$  but is negligible everywhere else. How do we fix this? The Dirac Delta functional!

### 2.20.2 The One-Dimensional Dirac Delta Functional

The Dirac Delta is a functional <sup>6</sup> which we define as,

$$\delta(x - a) = \begin{cases} 0, & \text{if } x \neq a \\ \infty, & \text{if } x = a \end{cases} \quad (2.26)$$

$$\int_{-\infty}^{+\infty} \delta(x - a) dx = 1 \quad (2.27)$$

$\forall a \in \mathbb{R}$  We can visualize it as a sharp peak at  $a$ , We can interpret 2.27 as saying "the area of the delta distribution is always 1".

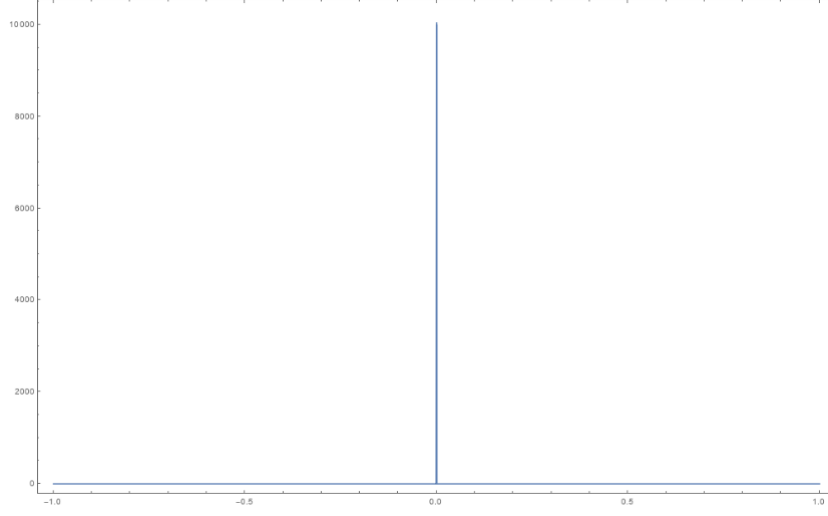
$$f(x)\delta(x - a) = f(a) \quad (2.28)$$

We can combine these to get,

$$\int_{-\infty}^{+\infty} \delta(x - a) f(x) dx = f(a) \quad (2.29)$$

---

<sup>6</sup>An object that is a map between functions

Figure 2.2: A Plot of  $\delta(x)$ 

**A few interesting properties**

$$\delta(kx) = \frac{1}{|k|} \delta(x) \quad (2.30)$$

$$\frac{d}{dx}(\delta(x)) = -\delta(x) \quad (2.31)$$

where  $k$  is a constant

$$\frac{d\theta}{dx} = \delta(x) \quad (2.32)$$

Where  $\theta$  is the step function defined as,

$$\theta(x) = \begin{cases} 1, & \text{if } x > 0 \\ 0, & \text{if } x \leq 0 \end{cases} \quad (2.33)$$

### 2.20.3 The Three-Dimensional Dirac Delta Function

We generalize (2.26) to three dimensions,

$$\delta^3(\vec{r} - \vec{a}) = \delta(x - a_x) \delta(y - a_y) \delta(z - a_z) \quad (2.34)$$

$$\int_{-\infty}^{+\infty} \delta^3(\vec{r} - \vec{a}) dV = 1 \quad (2.35)$$

We can also define the three-dimensional delta function as

$$\delta^3(\mathbf{z}) = \frac{1}{4\pi} \left[ \nabla \cdot \left( \frac{\hat{\mathbf{z}}}{z^2} \right) \right] \quad (2.36)$$

Since,

$$\nabla \left( \frac{1}{\boldsymbol{z}} \right) = -\frac{\hat{\boldsymbol{z}}}{\boldsymbol{z}^2}$$

We can rewrite as,

$$\delta^3(\boldsymbol{z}) = -\frac{1}{4\pi} \left[ \nabla^2 \left( \frac{1}{\boldsymbol{z}} \right) \right] \quad (2.37)$$

#### 2.20.4 Integral representation

We have the relationship for the Fourier transform,

$$F(x) = \int f(t) e^{-ixt} dt \quad (2.38)$$

and it's inverse

$$f(t) = \frac{1}{2\pi} \int F(x) e^{ixt} dx \quad (2.39)$$

Plugging in Eq. into Eq. we find that

$$F(y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(x) dx \int_{-\infty}^{\infty} e^{i(x-y)t} dt \quad (2.40)$$

Now, invoking the defining property of the Delta function,

$$F(y) = \int_{-\infty}^{\infty} F(x) \delta(x-y) dx \quad (2.41)$$

Comparing and we find that,

$$\delta(x-y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(x-y)t} dt \quad (2.42)$$

## 2.21 Complex Analysis

### 2.21.1 Analytic Function

### 2.21.2 A few important relations

Cauchy-Riemann Equations

Laplace Equation

## 2.22 Gaussian Integrals

In this section we'll try to solve integrals of the form

$$I_0(\alpha) = \int_{-\infty}^{\infty} e^{-\alpha x^2} dx \quad \forall \alpha > 0 \quad (2.43)$$

We can't directly integrate it, so we consider

$$I_0^2(\alpha) = \int_{-\infty}^{\infty} e^{-\alpha y^2} dy \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\alpha(x^2+y^2)} dx dy \quad (2.44)$$

Switching to polar coordinates in the x-y plane,

$$I_0^2(\alpha) = \int_0^{\infty} \int_0^{2\pi} e^{-\alpha \rho^2} d\rho d\phi = \frac{\pi}{\alpha} \quad (2.45)$$

Therefore,

$$I_0(\alpha) = \sqrt{\frac{\pi}{\alpha}} \quad (2.46)$$

### 2.22.1 Special Cases

By differentiating w.r.t  $\alpha$  we can get all integrals of the form:

$$I_{2n}(\alpha) = \int_{-\infty}^{\infty} x^{2n} e^{-\alpha x^2} dx \quad (2.47)$$

For example,

$$I_2(\alpha) = \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = -\frac{\partial}{\partial \alpha} \int_{-\infty}^{\infty} e^{-\alpha x^2} dx$$

$$I_2(\alpha) = \frac{\partial}{\partial \alpha} I_0(\alpha) = \frac{1}{2\alpha} \sqrt{\frac{\pi}{\alpha}}$$



The integrals  $I_{2n+1}(\alpha)$  vanish because they are integrals of odd functions over an even interval  $(-\infty$  to  $\infty)$ .

**Note:** The integrals discussed so far are valid even if  $\alpha \in \mathbb{C}$ . Next we'll consider,

$$I_0(\alpha, \beta) = \int_{-\infty}^{\infty} e^{-\alpha x^2 + \beta x} dx \quad (2.48)$$

We can simplify this to be,

$$I_0(\alpha, \beta) = e^{\beta^2/4\alpha} \int_{-\infty}^{\infty} e^{\alpha(x-\beta/2\alpha)^2} dx = e^{\beta^2/4\alpha} \sqrt{\frac{\pi}{\alpha}}$$

This holds even if  $\alpha, \beta \in \mathbb{C} : \operatorname{Re}(\alpha) > 0$ . A corollary of the previous equation,

$$\int_0^{\infty} e^{-\alpha r} dr = \frac{1}{\alpha}$$

if we operate on this with,  $(-d/d\alpha)^n$ , we get:

$$\int_0^{\infty} r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}}$$

### 2.22.2 Gamma function

If we consider this integral with  $\alpha = 1$  and  $n$  replaced with  $z - 1$ , where  $z$  is an arbitrary complex number. This leads us to the Gamma function, which is defined as:

$$\Gamma(z) = \int_0^{\infty} r^{z-1} e^{-r} dr = (z-1)! \quad \forall z > 0 \in \mathbb{R} \quad (2.49)$$

## 2.23 The $i\epsilon$ Prescription

We will now derive and interpret the formula:

$$\frac{1}{x \mp i\epsilon} = \mathcal{P} \frac{1}{x} \pm \pi \delta(x) \quad (2.50)$$

where  $\epsilon \rightarrow 0$  is a positive infinitesimally small quantity. Now we'll consider the integral

$$I = \lim_{\epsilon \rightarrow 0} \int_{-\infty}^{\infty} \frac{f(x)}{x - i\epsilon} dx \quad (2.51)$$

$$I = \lim_{\epsilon' \rightarrow 0} \left[ \int_{-\infty}^{\epsilon'} \frac{f(x)}{x} dx + \int_{-\infty}^{\epsilon'} \frac{f(x)}{x} dx + i\pi f(0) \right] \quad (2.52)$$

$$a \quad (2.53)$$

$$asdfkjh$$

## 2.24 Permutation Functions

### 2.24.1 Kronecker delta

It simply has the ‘function’ of ‘renaming’ an index:

$$\delta^\mu_\nu x^\nu = x^\mu$$

it is in a sense simply the identity matrix. Or it is sometimes defined as:

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \quad (2.54)$$

### 2.24.2 Levi-Civita Pseudotensor

The Levi-Civita Pseudotensor i.e. Tensor density is a completely anti-symmetric i.e.  $\epsilon_{ijk} = -\epsilon_{jik} = -\epsilon_{ikj} = -\epsilon_{kji}$ , we define it as:

$$\epsilon_{ijk} = \begin{cases} 1 & \text{if } ijk \text{ is an even permutation of } 123 \\ -1 & \text{if } ijk \text{ is an odd permutation of } 123 \\ 0 & \text{if two indices are equal} \end{cases} \quad (2.55)$$

#### Identities

$$\epsilon_{\alpha\beta\nu}\epsilon_{\alpha\beta\sigma} = \delta_{\mu\rho}\delta_{\nu\sigma} - \delta_{\mu\sigma}\delta_{\nu\rho} \quad (2.56)$$

From this it follows that,

$$\epsilon_{\alpha\beta\nu}\epsilon_{\alpha\beta\sigma} = 2\delta_{\nu\sigma} \quad (2.57)$$

and

$$\epsilon_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma} = 6 \quad (2.58)$$

## 2.25 Tensors

### 2.25.1 Vector Transformation Rules

The rules:

- For basis vectors forward transformations brings us from old to new coordinate systems and backward brings us from new to old.
- However, with vector components it's the opposite.

Suppose we have a vector  $\vec{v}$  in a basis  $\vec{e}_j$ . We now transform it to a basis  $\tilde{\vec{e}}_i$  where it becomes  $\tilde{v}$ . We call the forward transformation as  $F_{ij}$  and the backward as  $B_{ij}$  which we define as:

$$\begin{aligned}\tilde{\vec{e}}_j &= \sum_{i=1}^n F_{ij} \vec{e}_i \\ \vec{e}_j &= \sum_{i=1}^n B_{ij} \tilde{\vec{e}}_i\end{aligned}$$

We can try to derive the statements made previously,

$$\begin{aligned}\vec{v} &= \sum_{j=1}^n v_j \vec{e}_j = \sum_{i=1}^n \tilde{v}_i \tilde{\vec{e}}_i \\ \vec{v} &= \sum_{j=1}^n v_j \vec{e}_j = \sum_{j=1}^n v_j \left( \sum_{i=1}^n B_{ij} \tilde{\vec{e}}_i \right) = \sum_{i=1}^n \sum_{j=1}^n (B_{ij} v_j) \tilde{\vec{e}}_i\end{aligned}$$

Thus,

$$\tilde{v}_i = \sum_{j=1}^n B_{ij} v_j \quad (2.59)$$

Similarly,

$$\begin{aligned}\vec{v} &= \sum_{j=1}^n v_j \vec{e}_j = \sum_{i=1}^n \tilde{v}_i \tilde{\vec{e}}_i \\ \vec{v} &= \sum_{j=1}^n \tilde{v}_j \tilde{\vec{e}}_j = \sum_{j=1}^n \tilde{v}_j \left( \sum_{i=1}^n F_{ij} \vec{e}_i \right) = \sum_{i=1}^n \sum_{j=1}^n (F_{ij} \tilde{v}_j) \vec{e}_i\end{aligned}$$

Thus,

$$v_i = \sum_{j=1}^n F_{ij} \tilde{v}_j \quad (2.60)$$

Now because vector components behave contrary to the basis vectors, they are said to be "***Contravariant***"

## 2.25.2 Index Notation

### Einstein Notation i.e. Summing convention

Let us consider the sum<sup>7</sup>,

$$x_i = \sum_j^n \Lambda_{ij} \mathcal{X}^j$$

---

<sup>7</sup>Mind you there are no exponents there.

Is the same as,

$$x_i = \Lambda_{ij} \mathcal{X}^j$$

Here, we define  $i$  to be the free index and  $j$  to be the summing index or the dummy index that is repeated to signify so.

### Index Convention

When we sum from 1 to 3 we use the symbols  $i, j$  and  $k$  i.e. the English alphabet to signify that we are only considering dimensions that are spatial/that are not a time dimension. However, when we use the symbols  $\nu$  and  $\mu$  i.e. Greek alphabets we are summing from 0 to 3, we also include the temporal dimension according to the tradition of special relativity in which we name components as  $\{x^0, x^1, x^2, x^3\} = \{t, x, y, z\}$  in the Cartesian framework.

### 2.25.3 Covectors

- Covectors can be thought of as row vector or as functions that act on Vectors such that any covector  $\alpha : \mathbb{V} \rightarrow \mathbb{R}$
- Covectors are linear maps i.e.  $\beta(\alpha)\vec{v} = \beta\alpha\vec{v}$  and  $(\beta + \alpha)\vec{v} = \alpha\vec{v} + \beta\vec{v}$
- Covectors are elements of a Dual vector space  $\mathbb{V}^*$  which has different rules for addition and scaling i.e. scalar multiplication
- You visualize covectors to be some sort of gridline on your vector space such that applying a covector to a vector is equivalent to projecting the vector along the gridline
- Covectors are invariant but their components are not
- The covectors that form the basis for the set of all covectors is called the **"Dual Basis"**, because they are a basis for the Dual Space  $\mathbb{V}^*$  i.e. any covector can be expressed as the linear combination of the dual basis
- However we are free to choose a dual basis
- For covector components, forward transformation brings us from old to new and backwards vice versa
- We can flip between row and column vectors for an orthonormal basis

- Vector components are measured by counting how many are used in the construction of a vector, but covector components are measured by counting the number of covector lines that the basis vector pierces
- The covector basis transforms contravariantly compared to the basis and it's components transform covariantly according to the basis

### Contravariant Components

We denote contravariant components using the symbols

$$A^i$$

and their basis like

$$\vec{e}_i$$

### Covariant Components

We denote covariant components using the symbols

$$A_i$$

and their basis like

$$\vec{e}^i$$

### Relationship Between the Two Types of Components

$$|\vec{e}^1| = \frac{1}{|\vec{e}_1| \cos(\theta_1)}$$

and,

$$|\vec{e}_1| = \frac{1}{|\vec{e}^1| \cos(\theta_1)}$$

Or with 3 components we have: Since both types of components represent the same vector (as in same magnitude) only in different bases, we can write

$$\vec{A} = A^i \vec{e}_i = A_i \vec{e}^i$$

### Using Cramer's Method to find Components

#### 2.25.4 Linear Maps

Linear maps to put it naively, Linear Maps transform input vectors but not the basis. Geometrically speaking, Linear Maps:

- Keep gridlines parallel
- Keep gridlines evenly spaced
- Keep the origin stationary

To put it more abstractly, Linear Maps:

- Maps vectors to vectors,  $\mathbb{L} : \mathbb{V} \rightarrow \mathbb{V}$
- Adds inputs or outputs,  $\mathbb{L}(\vec{V} + \vec{W}) = \mathbb{L}(\vec{V}) + \mathbb{L}(\vec{W})$
- Scale the inputs or outputs,  $\mathbb{L}(\alpha \vec{V}) = \alpha \mathbb{L}(\vec{V})$
- i.e. They are Linear/Linearity

When I transform the basis using a forward transformation, the transformed Linear map  $\tilde{\mathbb{L}}_i^l$  can be written as:

$$\tilde{\mathbb{L}}_i^l = \mathbb{B}_k^l \mathbb{L}_j^k \mathbb{F}_i^j \quad (2.61)$$

### 2.25.5 Metric Tensor

- Pythagoras' theorem is a lie for non-orthonormal bases
- The metric Tensor is Tensor that helps us compute lengths and angles
- For two dimensions it can be written as:

$$g_{ij} = \begin{bmatrix} e_1 e_1 & e_1 e_2 \\ e_2 e_1 & e_2 e_2 \end{bmatrix}$$

- Or more abstractly

$$g_{ij} = e_i e_j$$

- The dot product between two vectors can be written as

$$||\vec{v}|| ||\vec{w}|| \cos \theta = v^i w^j g_{ij}$$

- we can see how this allows us to compute angles as well
- To transform the components of the Metric Tensor we have to apply the transformation twice i.e.  $\tilde{g}_{\rho\sigma} = \mathbb{F}_\rho^\mu \mathbb{F}_\sigma^\nu \tilde{g}_{\mu\nu}$  or  $g_{\rho\sigma} = \mathbb{B}_\rho^\mu \mathbb{B}_\sigma^\nu \tilde{g}_{\mu\nu}$

**2.25.6 Bilinear Forms****2.25.7 Tensor Products****2.25.8 Definition of a Tensor****2.25.9 Raising and Lowering Indices****2.26 Covariant Quantities****2.26.1 Contravariant Quantities****2.26.2 Clearer Definitions****2.26.3 Covariant Differentiation****2.27 Variational Calculus**

The basic problem of this subject is to determine the function  $y(x)$ , such that the integral

$$J = \int_{x_1}^{x_2} f\{y(x), y'(x); x\} dx \quad (2.62)$$

•

**2.27.1 The Euler-Lagrangian Equation****2.27.2 The "Second Form" of the Euler Equation****2.27.3 The " $\delta$ " Notation****2.27.4 Special Cases**

*F* Does Not Contain  $y$  Explicitly

*F* Does Not Contain  $x$  Explicitly

**2.27.5 Some extensions**

Several Dependent Variables

Several Independent Variables

Higher-Order Derivatives

Variable End-Points

**2.27.6 Constrained Variation****2.27.7 Physical Variational Principles**

Fermat's Principle in Optics

Hamilton's Principle in Mechanics

**2.27.8 General Eigenvalue Problem****2.27.9 Estimation of Eigenvalues and Eigenfunctions****2.27.10 Adjustment of Parameters**



# Part III

## Rules



# Chapter 3

## Formalism

### 3.1 State Vector

In Quantum Mechanics, we start with an object called the state vector  $|\psi\rangle$ . All the information about the system is contained in it. The position basis representation of the state vector is called the wavefunction  $\psi(\vec{x}, t)$ .

If we wish to know about a particular physical measurable such as an object's position or momentum, we can extract this information from the State vector by means of acting on it with an Operator that corresponds to the measurable quantity.

### 3.2 Observables

To get down to even more specifics if I consider an observable  $\hat{O}$ , then in general I have the form:

$$\hat{O} |\psi\rangle = o |\psi\rangle \quad (3.1)$$

Where,  $o$  is an Eigenvalue. The only types of operators that are constrained in such a fashion are "Hermitian Operators", they are identified with the condition:

$$\text{content...} \quad (3.2)$$

### 3.3 Time Evolution

#### 3.3.1 Schrodinger Picture

Where

If we consider the Schrodinger picture i.e. the State vector evolves with time whereas the Observables are in a loose sense eternal. The time evolution of the state vector is given by the Schrodinger equation:

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H} |\psi\rangle \quad (3.3)$$

Or,

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \quad (3.4)$$

in terms of the Wavefunction. Where,  $\hat{H}$  is the Hamiltonian operator, which can be expressed as:

$$\hat{H} = -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{x}) \quad (3.5)$$

for a free particle.

#### 3.3.2 Heisenberg Picture

### 3.4 Measurement

Measurement is defined as a form of time-evolution that is non-unitary and non-deterministic. According to Born's rule

$$\int_a^b |\psi(\vec{x}, t)|^2 dx = \text{Probability of finding the particle at a time } t \text{ between positions } a \text{ and } b \quad (3.6)$$

Thus, . Physically speaking this lends a kind of indeterminacy to the wavefunction. We can only speak of probabilities. Therefore, we can only , this brings to the measurement hypothesis, that is the State vector evolves to the state corresponding to the measurement being made. And unlike the Schrodinger equation, this evolution is non-deterministic. This tension is often called the "measurement problem", i.e. why is the measurement of an observable a special process distinct from others? Several theories and models claim to have resolved this, but we shall save that discussion for another time. We will fully focus on understanding the theory of Quantum Mechanics in a pragmatic lens before we question its foundations (although the converse isn't necessarily a bad thing, it isn't the purpose of this manuscript).

## 3.5 Normalization

Normalization is a process through which we ensure that,

$$\int_{-\infty}^{\infty} |\psi(\vec{x}, t)|^2 dx = 1 \quad (3.7)$$

This is a natural consequence of Born's rule, we simply want all the probabilities to add up to 1. Thus, to rule out any other absurd scenarios, we make a ruling that non-Normalizable and non-square integrable Wavefunctions are unphysical.

We can also prove that once normalized, the wavefunction always remains normalized, we start by differentiating 3.7 with respect to time

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

Dealing with the term inside the integral,

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

Now the Schrodinger equation for a free particle reads as,

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

Conjugating this we can see that,

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

Thus, ( ) becomes,

$$\frac{\partial}{\partial t} |\psi(\vec{x}, t)|^2 = \frac{i\hbar}{2m} \left( \psi^* \frac{\partial^2 \psi}{\partial x^2} - \psi \frac{\partial^2 \psi^*}{\partial x^2} \right) = \frac{\partial}{\partial x} \left[ \frac{i\hbar}{2m} \left( \psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) \right]$$

Now we evaluate the integral,

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

But  $\psi$  must go to zero as goes to infinity, otherwise the wave function would not be normalizable. Thus it follows that.

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\psi(\vec{x}, t)|^2 dx = 0 \quad (3.8)$$

And hence, the integral is constant i.e. independent of time. Therefore if is normalized at a time  $t = 0$ , it remains normalized for all future.

### 3.6 Summary of Postulates

### 3.7 Generalized Uncertainty Principle

Suppose we have a ket  $|\psi\rangle$  and two operators  $\hat{A}$  and  $\hat{B}$ , we define two new vectors

,

,

We use the Cauchy-Schwarz inequality,

$$2|X||Y| \geq |\langle X|Y\rangle + \langle Y|X\rangle|$$

Substituting in the left-hand side,  $2\sqrt{\langle X|X\rangle\langle Y|Y\rangle} \geq |\langle X|Y\rangle + \langle Y|X\rangle|$   
 Plugging in Eqs. (4) and (5),  $2\sqrt{\langle\psi|\hat{A}^2|\psi\rangle\langle\psi|\hat{B}^2|\psi\rangle} \geq |\langle X|Y\rangle + \langle Y|X\rangle|$   
 Taking the  $-1$  outside,  $2i\sqrt{\langle\psi|\hat{A}^2|\psi\rangle\langle\psi|\hat{B}^2|\psi\rangle} \geq |\langle X|Y\rangle + \langle Y|X\rangle|$  We now  
 substitute in the right hand of the equation  $2i\sqrt{\langle\psi|\hat{A}^2|\psi\rangle\langle\psi|\hat{B}^2|\psi\rangle} \geq |\langle\psi|\hat{A}\hat{B}|\psi\rangle -$   
 $\langle\psi|\hat{B}\hat{A}|\psi\rangle|$  The negative sign is due to the  $i$ , this also seems to represent  
 the commutator, so we substitute  $2i\sqrt{\langle\psi|\hat{A}^2|\psi\rangle\langle\psi|\hat{B}^2|\psi\rangle} \geq |\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle|$   
 Again, the right hand side looks like the expectation value of a quantity,  
 so  $2i\sqrt{\langle\hat{A}^2\rangle\langle\hat{B}^2\rangle} \geq |\langle[\hat{A}, \hat{B}]\rangle|$   $\sqrt{\langle\hat{A}^2\rangle\langle\hat{B}^2\rangle} \geq \frac{1}{2i}|\langle[\hat{A}, \hat{B}]\rangle|$  We use Eq. (2),

$\sqrt{\sigma_A^2\sigma_B^2} \geq \frac{1}{2i}|\langle[\hat{A}, \hat{B}]\rangle|$  Removing the square root we get the expression:  
 $\sigma_A\sigma_B \geq \frac{1}{2i}|\langle[\hat{A}, \hat{B}]\rangle|$

This is called the generalized uncertainty principle. This basically states that two variables that do not commute cannot be measured with precision simultaneously.

Talking about position and momentum

We know that observable properties can be represented using operators, here we'll

$\hat{x} = x$   $\hat{p} = -i\hbar\frac{\partial}{\partial x}$  So we now try to find the commutator now  $[\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x}$   $[\hat{x}, \hat{p}] = -ix\hbar\frac{\partial}{\partial x} + i\hbar\frac{\partial}{\partial x}$  Now let's apply this to state vector to obtain the expectation value  $[\hat{x}, \hat{p}]|\psi\rangle = -ix\hbar\frac{\partial}{\partial x}|\psi\rangle + i\hbar\frac{\partial}{\partial x}|\psi\rangle$

$$[\hat{x}, \hat{p}]|\psi\rangle = -ix\hbar\frac{\partial}{\partial x}|\psi\rangle + i\hbar\frac{\partial}{\partial x}|\psi\rangle + i\hbar$$

$[\hat{x}, \hat{p}]|\psi\rangle = i\hbar$  Substituting this into Eq.(.),  $\sigma_x\sigma_p \geq \frac{1}{2i}i\hbar \sigma_x\sigma_p \geq \frac{\hbar}{2} \sigma_x\sigma_p \geq \frac{\hbar}{4\pi}$

## 3.8 Generalized Statistical Interpretation

If you measure an observable  $\hat{O}$  on a particle in the state  $\psi()$ , you will certainly get one of the eigenvalues of the observable. If the spectra is discrete, the probability of getting the particular eigenvalue  $q_n$  associated with the orthonormalized eigenfunction  $f_n(x)$  is

$$P(q_n) = |c_n|^2 = |\langle f_n | \psi \rangle|^2 \quad (3.9)$$

### 3.8.1 Position Measurements

### 3.8.2 Momentum Measurements

## 3.9 Stationary State





# Part IV

## Toy Models



# Chapter 4

## Toy Models

- 4.1 Time-Dependent Schrodinger Equation
- 4.2 Time-Independent Schrodinger Equation
- 4.3 Stationary States
- 4.4 The Infinite Square Well
- 4.5 Harmonic Oscillator
- 4.6 Free Particle
- 4.7 Delta-Function Potential
- 4.8 Finite Square Well
- 4.9 Wave-Packets



# Part V

## Applications



# Chapter 5

## Systems with $N$ degrees of freedom

- 5.1 Schrodinger Equation in Spherical Coordinates
- 5.2 The Hydrogen Atom
- 5.3  $N$  Particles in One Dimension
- 5.4 More Particles in More Dimensions
- 5.5 Identical Particles
- 5.6 Two-Particle Systems
- 5.7 Atoms
- 5.8 Solids
- 5.9 Quantum Statistical Mechanics







## Chapter 6

# Symmetries and their Consequences

- 6.1 What is a Symmetry?
- 6.2 Translational Invariance in Quantum Mechanics
- 6.3 Time Translational Invariance
- 6.4 Parity Invariance
- 6.5 Time-Reversal Symmetry
- 6.6 Translations in Two Dimensions
- 6.7 Rotations in Two Dimensions
- 6.8 The Eigenvalue Problem of  $L_Z$
- 6.9 Angular Momentum in 3-Dimensions
- 6.10 The Eigenvalue Problem of  $L^2$  and  $L_Z$
- 6.11 Solution to Rotationally Invariant Problems

**6.12 What is Spin?**

**6.13 Kinematics of Spin**

**6.14 Spin Dynamics**

**6.15 Return of Orbital Degrees of Freedom**

**6.16 Addition of Angular Momentum**

**6.16.1 The General Problem**

**6.16.2 Irreducible Tensor Operators**

**6.16.3 Explaining some "Accidental" Degeneracies**



# Chapter 7

## Approximations

- 7.1 Variational Theory
- 7.2 Ground State of Helium
- 7.3 The Hydrogen Molecule Ion
- 7.4 The "Classical" Region
- 7.5 Tunneling
- 7.6 The Connection Formulae
- 7.7 The Adiabatic Theorem
- 7.8 Berry's Phase



# Chapter 8

## Perturbation Theory

### 8.1 Non-Degenerate Perturbation Theory

#### 8.1.1 General Formulation

Suppose we have solved the time-independent Schrodinger wave equation for a given potential (in this case, an infinite potential square well)

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 \quad (8.1)$$

and obtaining a complete set of orthonormal eigenfunctions  $\psi_n^0$ ,

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \quad (8.2)$$

and the corresponding eigenvalues  $E_n^0$ . If we perturb the potential slightly in the potential well and try to solve for the new eigenvalues and eigenfunctions,

$$H \psi_n = E_n \psi_n \quad (8.3)$$

Here, we use perturbation theory to get approximate solutions to the perturbed problem by building on the exact solutions of the unperturbed case. To begin with, we write the perturbed/new Hamiltonian as the sum of two terms,

$$H = H^0 + \lambda H' \quad (8.4)$$

Where  $H'$  is the perturbation. We take  $\lambda$  to be a small number, and the  $H$  will be the true, exact Hamiltonian. Writing  $\psi_n$  and  $E_n$  as a power series in  $\lambda$ , we get,

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots \quad (8.5)$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \quad (8.6)$$

Here  $E_n^1$  is the first-order correction to the  $n^{\text{th}}$  eigenvalue, and  $\psi_n^1$  is the first-order correction to the  $n^{\text{th}}$  eigenfunction.  $E_n^2$  and  $\psi_n^2$  are the second-order corrections to the eigenvalues and eigenfunctions, and so on. Plugging in Equations (4),(5) and (6) in Equation (3) gives us,

$$(H^0 + \lambda H')[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] \quad (8.7)$$

We can rewrite Equation (7) by collecting like powers of  $\lambda$  in the form,

$$H^0 \psi_n^0 + \lambda(H^0 \psi_n^1 + H' \psi_n^0) + \lambda^2(H^0 \psi_n^2 + H' \psi_n^1) + \dots \\ E_n^0 \psi_n^0 + \lambda(E_n^0 \psi_n^1 + E_n^1 \psi_n^0) + \lambda^2(E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0) + \dots$$

We can get the first order ( $\lambda^1$ ) equation from Equation (7),

$$H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0 \quad (8.8)$$

And the second order ( $\lambda^2$ ),

$$H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0 \quad (8.9)$$

And this can be done for higher powers of  $\lambda$  as well.

### 8.1.2 First order perturbation theory

If we take the inner product of Equation (8), with  $\psi_n^0$ ,

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle \quad (8.10)$$

Because of the useful property of  $H^0$  to be Hermitian, hence Equation (10) becomes,

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle = \langle H^0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle = \langle E_n^0 \psi_n^0 | \psi_n^1 \rangle \quad (8.11)$$

And hence the terms in Equation (10) cancel out and the property  $\langle \psi_n^0 | \psi_n^0 \rangle = 1$  give the equation,

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle \quad (8.12)$$

This is a fundamental result in first-order perturbation theory, and it states that first-order correction to energy is the expectation value of the perturbation in the unperturbed state.

Now to get the first-order correction to the wave function, we rewrite Equation (8),

$$(H^0 - E_n^0) \psi_n^1 = -(H' E_n^1) \psi_n^0 \quad (8.13)$$



The right side is a known function, so this amounts to an inhomogeneous differential equation for  $\psi_n^1$ . The unperturbed wave functions constitute a complete set, so  $\psi_n^1$  can be written as a linear combination of them,

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0 \quad (8.14)$$

We know that  $\psi_m^0$  satisfies the unperturbed Schrodinger wave equation, so we have,

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = -(H' - E_n^1) \psi_n^0 \quad (8.15)$$

Taking the inner product with  $\psi_l^0$ ,

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_l^0 | \psi_m^0 \rangle = -\langle \psi_l^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle \quad (8.16)$$

If  $l = n$ , is zero, we then get,

$$(E_m^0 - E_n^0) c_l^{(n)} = -\langle \psi_l^0 | H' | \psi_n^0 \rangle \quad (8.17)$$

Or that,

$$c_n^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \quad (8.18)$$

So,

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0 \quad (8.19)$$

Note that the perturbed energies are surprisingly accurate, while the wave functions are of poor accuracy.

### 8.1.3 Second order perturbation theory

We take the inner product of the second-order equation with  $\psi_n^0$ ,

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle \quad (8.20)$$

We exploit the Hermiticity of  $H^0$ ,

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle = \langle H^0 \psi_n^2 | \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle \quad (8.21)$$

So the first term on the left cancels the first term on the right. Hence we get the formula for  $E_n^2$  to be,

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle \quad (8.22)$$

But,

$$\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0 \quad (8.23)$$

so,

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = \sum_{m \neq n} c_m^{(n)} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \quad (8.24)$$

Therefore,

$$E_n^2 = \sum_{m \neq n} c_m^{(n)} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \quad (8.25)$$

This is the fundamental result of second order perturbation theory.

## 8.2 Degenerate Perturbation Theory

### 8.2.1 Motivation

If two or more distinct states, take  $\psi_a^0$  and  $\psi_b^0$  share the same energy, ordinary perturbation theory fails since Equation (25) blows up. So hence we need to obtain a different way to handle the problem.

### 8.2.2 Twofold Degeneracy

Suppose,

$$\begin{aligned} H^0 \psi_a^0 &= E^0 \psi_a^0 \\ H^0 \psi_b^0 &= E^0 \psi_b^0 \\ \langle \psi_a^0 | \psi_b^0 \rangle &= 0 \end{aligned}$$

And note that any of linear combinations of these states,

$$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0 \quad (8.26)$$

is still an eigenstate of  $H^0$ , with the same eigenvalue  $E^0$ ,

$$H^0 \psi^0 = E^0 \psi^0 \quad (8.27)$$

When  $H$  is perturbed, it breaks the degeneracy. When we increase  $\lambda$ , the common unperturbed energy  $E^0$  splits into two. When we take away the

perturbation, the upper state reduces to one linear combination of  $\psi_a^0$  and  $\psi_b^0$ , and the lower state reduces to some other linear combination. We need to figure out the good linear combinations.

Now writing the good unperturbed states in general form, keeping  $\alpha$  and  $\beta$  adjustable and solving the Schrodinger equation,

$$H\psi = E\psi \quad (8.28)$$

With  $H = H^0 + \lambda H'$  and,

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \dots \quad (8.29)$$

$$\psi = \psi^0 + \lambda \psi^1 + \lambda^2 \psi^2 + \dots \quad (8.30)$$

Plugging these into Equation (28) and collecting like powers of  $\lambda$ , as before, we find,

$$H^0\psi^0 + \lambda(H\psi^0 + H^0\psi^1) + \dots = E^0\psi^0 + \lambda(E^1\psi^0 + E^0\psi^1) + \dots \quad (8.31)$$

But  $H^0\psi^0 = E^0\psi^0$ , so the first term cancel; at order  $\lambda^1$  we have,

$$H\psi^0 + H^0\psi^1 = E^1\psi^0 + E^0\psi^1 \quad (8.32)$$

Taking inner product with  $\psi_a^0$ ,

$$\langle \psi_a^0 | H^0 | \psi^1 \rangle + \langle \psi_a^0 | H' | \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle + E^1 \langle \psi_a^0 | \psi^0 \rangle \quad (8.33)$$

Because  $H^0$  is Hermitian, the first term on the left cancels the term on the right. Putting this in Equation (26), we get,

$$\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle = \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = \alpha E^1 \quad (8.34)$$

Or in a more compact form,

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1 \quad (8.35)$$

Where,

$$W_{ab} = \langle \psi_a^0 | H' | \psi_b^0 \rangle$$

Similarly, the inner product with  $\psi_b^0$  gives us,

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1 \quad (8.36)$$

Now using Equation (35) and (36),

$$\alpha [W_{ab}W_{ba} - (E^1 - W_{aa})(E^1 - W_{bb})] = 0 \quad (8.37)$$

When  $\alpha \neq 0$ ,

$$(E^1)^2 - E^1(W_{aa} + W_{bb}) + (W_{aa}W_{bb} - W_{ab}W_{ba}) = 0 \quad (8.38)$$

Using the quadratic formula and knowing that  $W_{ba} = W_{ab}^*$ ,

$$E_{\pm}^1 = \frac{1}{2} \left[ W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right] \quad (8.39)$$

This is the fundamental result of degenerate perturbation theory, the two roots correspond to the two perturbed energies.

Note that when  $\alpha = 0$ , we get the nondegenerate perturbation theory (since  $\beta = 1$ ).

### 8.2.3 Higher-Order Degeneracy

We start by rewriting Equations (35) and (36) in matrix form,

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (8.40)$$

The  $E^1$ s are the eigenvalues of the  $W$ -matrix, Equation (38) being the characteristic equation for this matrix and the good linear combinations of the unperturbed states are the eigenvectors of  $W$ . For  $n$ -fold degeneracy, we look for the eigenvalues of the  $n \times n$  matrix,

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle \quad (8.41)$$

### 8.2.4 Lamb Shift

An interesting feature of the fine structure formula is that it depends only on  $j$  and not  $l$ , moreover in general two different values of  $l$  share the same energy. For example, the  $2S_{1/2}()$  and  $2P_{1/2}()$  states should remain perfectly degenerate. However in 1947 Lamb and Retherford performed an experiment that displayed something to the contrary. The  $S$  state is slightly higher in energy than the  $p$  state. The explanation of this "Lamb" shift was later explained by Bethe, Feynman, Schwinger and Tomonaga (the founders of QED) as a corollary of the electromagnetic field itself being quantised. Sharply in contrast to the hyperfine structure of Hydrogen, the Lamb shift is a completely novel i.e. non-classical (as the hyperfine structure is explained through Coulomb's law and the Biot-Savart Law) phenomena. It arises from a radiative correction in Quantum Electrodynamics to which classical theories are mute. In Feynman lingo, this arises from loop corrections as portrayed below. Naively,

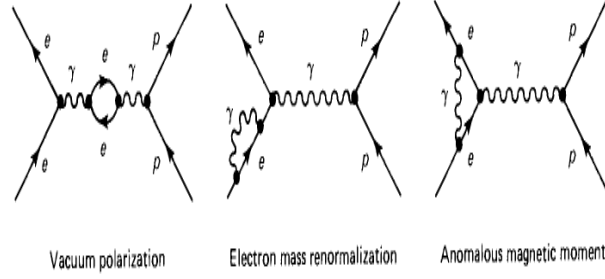


Figure 8.1: Different kinds of radiative corrections

1. the first diagram describes pair-production in the neighborhood of a nucleus, leading to a partial screening effect of the proton's charge;
2. the second diagram reflects the fact that the electromagnetic field has a non-zero ground state
3. the third diagram leads to a tiny modification of the electron's magnetic dipole moment (an addition of  $a + \alpha/2\pi = 1.00116$ )

We shall not discuss the results in depth but rather consider two exemplary cases:

For  $l = 0$ ,

$$\Delta E_{Lamb} = \alpha^5 mc^2 \frac{1}{4n^3} [k(n, 0)] \quad (8.42)$$

Where  $k(n, 0)$  is a numerical factor defined as:

$$k(n, 0) = \begin{cases} 12.7, & \text{if } n = 1 \\ 13.2, & \text{if } n \rightarrow \infty \end{cases}$$

For  $l = 0$  and  $j = l \pm \frac{1}{2}$ ,

$$\Delta E_{Lamb} = \alpha^5 mc^2 \frac{1}{4n^3} \left[ k(n, 0) \pm \frac{1}{\pi(l + \frac{1}{2})(l + \frac{1}{2})} \right] \quad (8.43)$$

Here,  $k(n, l)$  is a very small number ( $< 0.05$ ) which varies a little with its arguments.

The Lamb shift is tiny except for the case  $l = 0$ , for which it amounts to about 10% of the fine structure. However, since it depends on  $l$ , it lifts the degeneracy of the pairs of states with common  $n$  and  $j$  and in particular it splits  $2S_{1/2}$  and  $2P_{1/2}$ .

### 8.3 The Zeeman Effect

When an atom is placed in a uniform magnetic field  $B_{Ext.}$ , the energy levels are shifted, this is known as the Zeeman effect. For the case of a single electron, the shift is:

$$H'_Z = -(\mu_l + \mu_s).B_{Ext.} \quad (8.44)$$

Where,

$$\mu_s = -\frac{e}{m_e}S \quad (8.45)$$

is the magnetic dipole moment associated with electron spin, and

$$\mu_l = -\frac{e}{2m_e}L \quad (8.46)$$

is the dipole moment associated with orbital motion. The gyromagnetic ratio in this case is simply classical i.e.  $q/2m$ , it is only for spin that we have an extra factor of 2. We now rewrite (8.44) as:

$$H'_Z = \frac{e}{2m_e}(L + 2S).B_{Ext.} \quad (8.47)$$

The nature of the Zeeman splitting depends on the strength of the external field vs. the internal one that gives rise to spin-orbit/spin-spin coupling. This table provides a short review of the different cases:

Case	Name	Comments
$B_{Ext.} \gg B_{Int.}$	Strong-Field Zeeman Effect	Zeeman effect dominates; fine structure becomes the perturbation
$B_{Ext.} \ll B_{Int.}$	Weak-Field Zeeman Effect	Fine structure dominates; $H'_Z$ can be treated as a small perturbation
$B_{Ext.} = B_{Int.}$	Intermediate Zeeman Effect	Both the fields are equal in strength thus we would need elements of degenerate perturbation theory and will need to diagonalize the necessary portion of the Hamiltonian "by hand"

In the next few sections we'll explore all of them in depth.

### 8.3.1 Weak-Field Zeeman Effect

Here the fine structure dominates, thus the conserved quantum numbers are  $n, l, j$  and  $m_j$ , but not  $m_l$  and  $m_s$  due to the spin-orbit coupling  $L$  and  $S$  are not separately conserved. Generally speaking, in this problem we have a perturbation pile on top of a perturbation. Thus, the conserved quantum number are those appropriate to the dominant . In first order perturbation theory, the Zeeman correction to energy is,

$$E_Z^1 = \langle nljm_j | H'_Z | nljm_j \rangle = \frac{e}{2m} B_{Ext.} \langle L + 2S \rangle \quad (8.48)$$

Now to figure out  $\langle L + 2S \rangle$ , we know that  $L + 2S = J + S$ , this doesn't immediately tell us the expectation value of  $S$  but we can figure it out as by understanding that  $J = L + S$  is conserved and that the time average of  $S$  is simply it's projection along  $J$ :

$$S_{Ave} = \frac{(S \cdot J)}{J} J \quad (8.49)$$

But,  $L = J - S$ , so  $L^2 = J^2 + S^2 - 2J \cdot S$ , hence:

$$S \cdot J = \frac{1}{2}(J^2 + S^2 - 2J \cdot S) = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - l(l+1)] \quad (8.50)$$

from which it follows that,

$$\langle L + 2S \rangle = \left\langle \left( 1 + \frac{S \cdot J}{J^2} J \right) \right\rangle = \left[ 1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right] \langle J \rangle \quad (8.51)$$

The term in the square brackets is called the Lande g-factor, denoted by  $g_j$ . Now, if we choose  $B_z$  to lie along  $B_{Ext.}$ , then:

$$E_Z^1 = \mu_B g_j B_{Ext.} m_j \quad (8.52)$$

where,

$$\mu_B = \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \text{ eV} T^{-1}$$

is the so called Bohr magneton. The total energy is the sum of the fine-structure part and the Zeeman contribution, in the ground state i.e.  $n = 1, l = 0, j = 1/2$  and therefore,  $g_J = 2$ , it splits into two levels:

$$-13.6 \text{ eV} (1 + \alpha^2/4) \pm \mu_B B_{Ext.} \quad (8.53)$$

with different signs for different  $m_j$ 's this is plotted below.

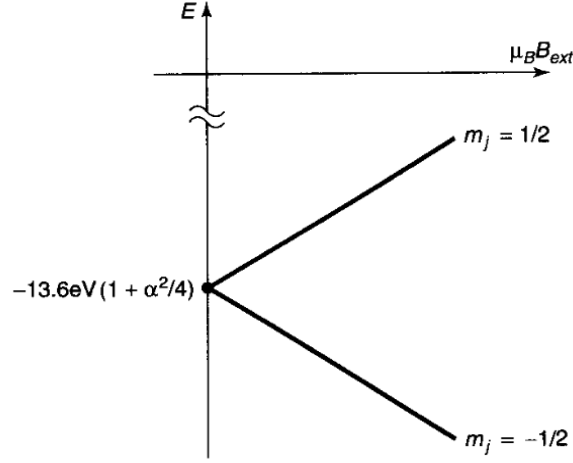


Figure 8.2: Weak-field Zeeman splitting of the ground state of hydrogen; the upper line has a slope of 1 and the lower line a slope of  $-1$

### 8.3.2 Strong-Field Zeeman Effect

In this case, the Zeeman effect is often referred to as the "Paschen-Back" effect. The conserved quantum numbers are now but and because in the presence of an external torque, the total angular momentum is not conserved but the it's individual components are. The Zeeman Hamiltonian is,

$$H'_Z = \frac{e}{2m} B_{Ext.} (L_z + 2S_z) \quad (8.54)$$

and the unperturbed energies are:

$$E_{nm_l m_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{Ext.} (m_l + 2m_s) \quad (8.55)$$

This would be our result if we ignore the fine structure completely. However, we need to take that into account as well. In first-order perturbation theory, the fine structure correction to these levels is:

$$E_{fs}^1 = \langle n \ l \ m_l \ m_s | H'_r + H'_{so} | n \ l \ m_l \ m_s \rangle \quad (8.56)$$

The relativistic contribution is the same as before for the spin-orbit term, we need

$$\langle S.L \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle = \hbar^2 m_l m_s \quad (8.57)$$

Here  $\langle S_x \rangle = \langle S_y \rangle = \langle L_x \rangle = \langle L_y \rangle = 0$  for the eigenstates of  $S_z$  and  $L_z$ . Putting it all together:

$$E_{fs}^1 = \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left( \frac{3}{4n} - \left[ \frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right] \right) \quad (8.58)$$



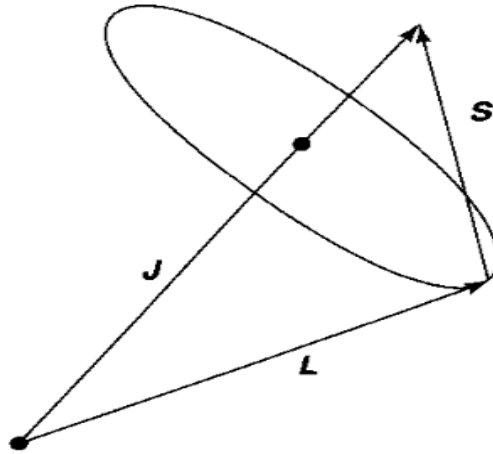


Figure 8.3: In the presence of spin-orbit coupling,  $L$  and  $S$  are not separately conserved, they precess about the fixed total angular momentum  $J$

The term in the square brackets is indeterminate for  $l = 0$ , its correct value in this case is 1. The total energy here is the sum of the Zeeman part and the fine structure contribution.

### 8.3.3 Intermediate Zeeman Effect

In this case, we must treat both the effects as perturbations to the Bohr Hamiltonian,

$$H' = H'_Z + H'_{fs} \quad (8.59)$$

In section we'll discuss the case  $n = 2$ , and use it as the basis for degenerate perturbation theory. The states here are characterized by  $l$ ,  $j$  and  $m_j$ . We could use  $l, m_l, m_s$  states but this makes the matrix elements of  $H'_Z$  easier to deal with but that of  $H'_{fs}$  difficult. Using the Clebsch-Gordan coefficients to express  $|jm_j\rangle$  as a linear combination of  $|lm_l\rangle |sm_s\rangle$  we have:

$$l = 0 = \begin{cases} \psi_1 & |\frac{1}{2} \frac{1}{2}\rangle = |0 \ 0\rangle |\frac{1}{2} \frac{1}{2}\rangle \\ \psi_2 & |\frac{1}{2} \frac{-1}{2}\rangle = |0 \ 0\rangle |\frac{1}{2} \frac{-1}{2}\rangle \end{cases}$$

$$l = 1 = \begin{cases} \psi_3 & \left| \frac{3}{2} \frac{3}{2} \right\rangle = |1 \ 1\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle \\ \psi_4 & \left| \frac{3}{2} \frac{-3}{2} \right\rangle = |1 \ -1\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle \\ \psi_5 & \left| \frac{3}{2} \frac{1}{2} \right\rangle = \sqrt{2/3} |1 \ 0\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{1/3} |1 \ 1\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle \\ \psi_6 & \left| \frac{1}{2} \frac{1}{2} \right\rangle = -\sqrt{1/3} |1 \ 0\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{2/3} |1 \ 1\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle \\ \psi_7 & \left| \frac{3}{2} \frac{-1}{2} \right\rangle = \sqrt{1/3} |1 \ -1\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{2/3} |1 \ 0\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle \\ \psi_8 & \left| \frac{1}{2} \frac{-1}{2} \right\rangle = -\sqrt{2/3} |1 \ -1\rangle \left| \frac{1}{2} \frac{1}{2} \right\rangle + \sqrt{1/3} |1 \ 0\rangle \left| \frac{1}{2} \frac{-1}{2} \right\rangle \end{cases}$$

In this basis the matrix the non-zero elements of  $H'_{fs}$  are all on the diagonal and are given by the Bohr model.  $H'_z$  has four off diagonal elements. The complete matrix, W as we will see is more complicated but its eigenvalues are the same since they are independent of the chosen basis.

$$\begin{pmatrix} 5\gamma - \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5\gamma + \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma - 2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma + 2\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma - \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma - \frac{1}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \gamma + \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma + \frac{1}{3}\beta \end{pmatrix} \quad (8.60)$$

Where,

$$\gamma = (\alpha/8)^2 13.6 \text{ eV}$$

and,

$$\beta = \mu_B B_{Ext.}$$

The first four eigenvalues are already displayed along the diagonal. We only need to find the eigenvalues of the two  $2 \times 2$  blocks. The characteristic equation for the first one is given as:

$$\lambda^2 - \lambda(6\gamma - \beta) + \left(5\gamma^2 - \frac{11}{3}\gamma\beta\right) = 0 \quad (8.61)$$

and the quadratic formula gives the eigenvalues:

$$\lambda_{\pm} = 3\gamma - (\beta/2) \pm \sqrt{4\gamma^2 + (2/3)\gamma\beta + (\beta^2/4)} \quad (8.62)$$

The eigenvalues of the second block are the same but with the sign of  $\beta$  reversed. The eight energy levels are listed in the table and are plotted against in the figure (). In the zero field limit they reduce to the fine structure values. For the other cases, the splitting is seen clearly.

---

$\epsilon_1$	=	$E_2 - 5\gamma + \beta$
$\epsilon_2$	=	$E_2 - 5\gamma - \beta$
$\epsilon_3$	=	$E_2 - \gamma + 2\beta$
$\epsilon_4$	=	$E_2 - \gamma - 2\beta$
$\epsilon_5$	=	$E_2 - 3\gamma + \beta/2 + \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$
$\epsilon_6$	=	$E_2 - 3\gamma + \beta/2 - \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$
$\epsilon_7$	=	$E_2 - 3\gamma - \beta/2 + \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$
$\epsilon_8$	=	$E_2 - 3\gamma - \beta/2 - \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$

---

Figure 8.4: Energy levels for the  $n = 2$  states of hydrogen, with fine structure and Zeeman splitting

## 8.4 Hyperfine Splitting in Hydrogen

The proton also has a magnetic dipole moment, however this is much smaller than that of the electron due to the mass of the proton. It is given by,

$$\mu_p = \frac{g_p e}{2m_p} S_p \quad (8.63)$$

And the magnetic dipole moment of the electron,

$$\mu_e = -\frac{e}{m_e} S_e \quad (8.64)$$

Classically speaking, the dipole  $\mu$  sets up a magnetic field:

$$B = \frac{\mu_0}{4\pi r^3} [3(\mu \cdot \hat{r})\hat{r} - \mu] + \frac{2\mu_0}{3} \mu \delta^3(r) \quad (8.65)$$

So the Hamiltonian of the electron, in the magnetic field due to the proton's magnetic dipole moment, is

$$H'_{hf} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \frac{[3(S_p \cdot \hat{r})(S_e \cdot \hat{r}) - S_p \cdot S_e]}{r^3} + \frac{\mu_0 g_p e^2}{3m_p m_e} S_p \cdot S_e \delta^3(r) \quad (8.66)$$

According to perturbation theory, the first-order correction to the energy is the expectation value of the perturbing Hamiltonian:

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \left\langle \frac{3(S_p \cdot \hat{r})(S_e \cdot \hat{r}) - S_p \cdot S_e}{r^3} \right\rangle + \frac{\mu_0 g_p e^2}{3m_p m_e} \langle S_p \cdot S_e \rangle |\psi(0)|^2 \quad (8.67)$$

In the ground state or any other state at which  $l = 0$ , the wavefunction is spherically symmetrical, and the first expectation value vanishes. Meanwhile,

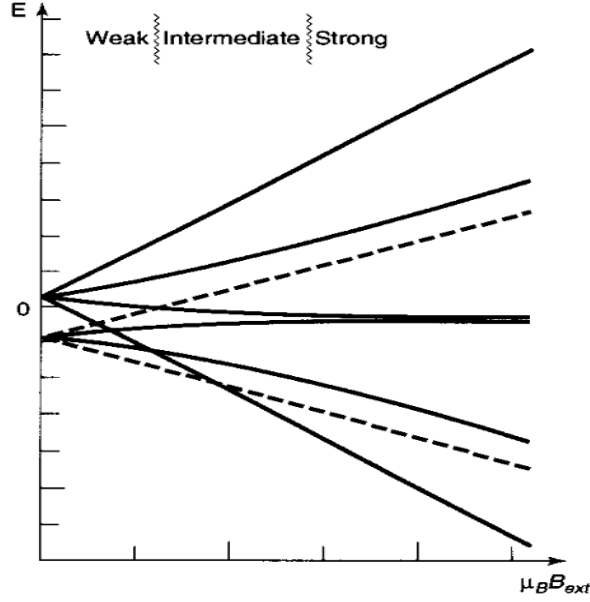


Figure 8.5: Zeeman splitting of the  $n = 2$  states of hydrogen, in the weak, intermediate and strong field regimes

from the Schrodinger equation in three dimensions, we find that  $|\psi(0)|^2 = 1/(\pi a^3)$ , thus,

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3} \langle S_p \cdot S_e \rangle \quad (8.68)$$

in the ground state. This is called Spin-Spin coupling because it involves the dot product of two spins in contrast with spin-orbit coupling which involves  $S \cdot L$ . In the presence of spin-spin coupling, the individual spin angular momenta are no longer conserved. However the eigenvectors of the total spin is conserved:

$$S = S_e + S_p \quad (8.69)$$

We square this out to get,

$$S_p \cdot S_e = \frac{1}{2}(S^2 - S_e^2 - S_p^2) \quad (8.70)$$

But the electron and proton both have spin  $1/2$ , so  $S_e^2 = S_p^2 = (3/4)\hbar^2$ . In the triplet i.e. parallel spin state, the total spin is 1, and hence  $S^2 = 2\hbar^2$ . In the singlet state the total spin is 0, and  $S^2 = 0$ . Thus,

$$E_{hf}^1 = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 \alpha^4} \begin{cases} +1/4, & \text{(triplet);} \\ -3/4, & \text{(singlet)} \end{cases} \quad (8.71)$$

The Spin-Spin coupling breaks the spin degeneracy of the ground state, lifting the triplet and depressing the singlet, leading to an energy gap. The energy gap is given by:

$$\Delta E = \frac{4g_p\hbar^4}{3m_pm_e^2c^2\alpha^4} = 5.88 \times 10^{-6} \text{ eV} \quad (8.72)$$

The frequency of the photon emitted when the triplet transitions to a singlet

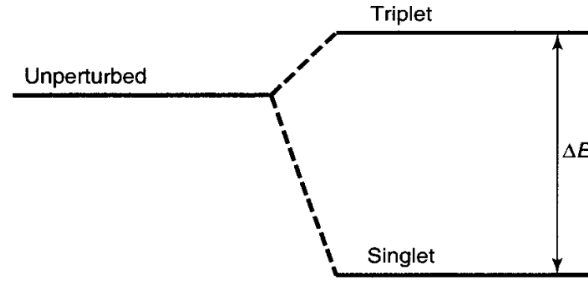


Figure 8.6: Hyperfine splitting in the ground state of Hydrogen

state is:

$$\nu = \frac{\Delta E}{h} = 1420 \text{ MHz} \quad (8.73)$$

The corresponding wavelength is 21 cm which falls in the microwave region. It permeates the universe and is a very important part of Astrophysics.



# Chapter 9

## Scattering

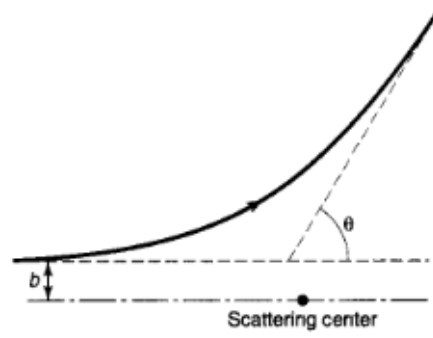
### 9.1 Classical Scattering

#### 9.1.1 Motivation

We can also define the size/radius of the proton is through its rate of interacting with itself or other particles. This is done by us determining the cross-sectional area. The larger this area is, the more likely it is that you will interact with it. The smaller the area, the less likely to interact. This motivates a connection between proton size and scattering probability. In particle physics, a collision or interaction rate is expressed in effective cross-sectional area, typically just called cross section. As an “area,” we can measure scattering cross sections as the square of some relevant length scale.

#### 9.1.2 The problem

Consider a particle incident on some scattering center. It comes in with an energy  $E$  and an impact parameter  $b$ , and it emerges at some scattering angle  $\theta$ . The essential problem of classical scattering theory is this: *Given the impact parameter, calculate the scattering angle.* Ordinarily, of course, the smaller the impact parameter, the greater the scattering angle.





### 9.1.3 Solving for differential cross-section

Particles incident within an infinitesimal patch of cross-sectional area  $d\sigma$  will scatter into a corresponding infinitesimal solid angle  $d\Omega$ . The larger  $d\sigma$  is, the bigger  $d\Omega$  will be; the proportionality factor,  $D(\theta) = d\sigma/d\Omega$ , is called the differential (scattering) cross-section, and is given by,

$$d\sigma = D(\theta)d\Omega \quad (9.1)$$

In terms of the impact parameter and the azimuthal angle  $\phi$ ,  $d\sigma = b.db.d\phi$  and  $d\Omega = \sin(\theta)d\theta d\phi$ , and so,

$$D(\theta) = \frac{b}{\sin \theta} \left| \frac{db}{d\theta} \right| \quad (9.2)$$

And then the total cross-section is the integral of  $D(\theta)$  over all solid angles,

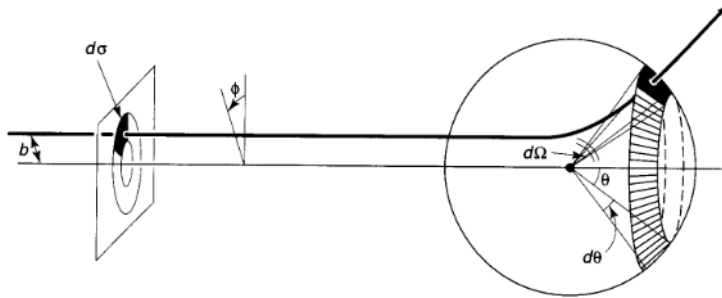
$$\sigma = \int D(\theta)d\Omega \quad (9.3)$$

The differential cross-section is the total area of incident beam that is scattered by the target. Beams incident within this area will hit the target, and those farther out will miss it completely.

If we have a beam of incident particles, with uniform intensity/luminosity ( $\mathcal{L}$ ), the number of particles entering area  $d\sigma$  (and hence scattering into solid angle  $d\Omega$ ), per unit time, is  $dN = \mathcal{L}d\sigma = \mathcal{L}D(\theta)d\Omega$ , then,

$$D(\theta) = \frac{1}{\mathcal{L}} \frac{dN}{d\Omega} \quad (9.4)$$

This is the definition of the differential cross-section.



## 9.2 Quantum Scattering

### 9.2.1 Defining the problem

In the quantum theory of scattering, we imagine an incident plane wave,  $\psi(z) = Ae^{ikz}$ , traveling in the  $z$  direction, which encounters a scattering potential, producing an outgoing spherical wave. That is, we look for solutions to the Schrödinger equation of the generic form,

$$\psi(r, \theta) \approx A \left\{ e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \right\}, \text{ for large } r \quad (9.5)$$

The relation between wave number  $k$  and energy of incident particles are,

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \quad (9.6)$$

### 9.2.2 Determining scattering amplitude

Probability of the incident particle travelling with speed  $v$  passing through infinitesimal area  $d\sigma$  in time  $dt$  is,

$$dP = |\psi_{incident}|^2 dV = |A|^2 (vdt) d\sigma \quad (9.7)$$

This is equal to the probability that the particle later emerges into the corresponding solid angle  $d\Omega$ ,

$$dP = |\psi_{scattered}|^2 dV = \frac{|A|^2 |f|^2}{r^2} (vdt) r^2 d\sigma \quad (9.8)$$

And  $d\sigma = |f|^2 d\Omega$ , so,

$$D(\theta) = \frac{d\sigma}{d\Omega} = |f(\theta)|^2 \quad (9.9)$$

The differential cross-section (which is the quantity of interest to the experimentalist) is equal to the absolute square of the scattering amplitude. Now we look at different methods to determine this scattering amplitude.

## 9.3 Partial Wave Analysis

### 9.3.1 Formalism

We know that the Schrodinger equation for a spherically symmetrical potential  $V(r)$  admits the separable solutions,

$$\psi(r, \theta, \phi) = R(r)Y_l^m(\theta, \phi) \quad (9.10)$$

Where  $Y_l^m$  is a spherical harmonic and  $u(R) = rR(r)$  satisfies the radial equation,

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[ V(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu \quad (9.11)$$

At very large  $r$ , the potential goes to zero, and the centrifugal term is negligible, so,

$$\frac{d^2 u}{dr^2} \approx -k^2 u \quad (9.12)$$

Whose general solution is takes the form,

$$u(r) = Ce^{ikr} + De^{-ikr} \quad (9.13)$$

The first term represents an outgoing spherical wave, and the second an incoming one. For the scattered wave, we want  $D = 0$ . At very large  $r$ , then.

$$R(r) \approx \frac{e^{ikr}}{r} \quad (9.14)$$

The radial equation then becomes,

$$\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} u = -k^2 u \quad (9.15)$$

The general solution for the radial equation is a linear combinations of spherical Bessel functions,

$$u(r) = Arj_l(kr) + Brn_l(kr) \quad (9.16)$$

We need solutions that are linear combinations analogous to  $e^{ikr}$  and  $e^{-ikr}$ , these are called the spherical Hankel functions,

$$h_l^{(1)} \equiv j_l(x) + in_l(x) \quad (9.17)$$

Below we see some examples of Hankel functions,

$$\begin{array}{ll}
 h_0^{(1)} = -i \frac{e^{ix}}{x} & h_0^{(2)} = i \frac{e^{-ix}}{x} \\
 h_1^{(1)} = \left( -\frac{i}{x^2} - \frac{1}{x} \right) e^{ix} & h_1^{(2)} = \left( \frac{i}{x^2} - \frac{1}{x} \right) e^{-ix} \\
 h_2^{(1)} = \left( -\frac{3i}{x^3} - \frac{3}{x^2} + \frac{i}{x} \right) e^{ix} & h_2^{(2)} = \left( \frac{3i}{x^3} - \frac{3}{x^2} - \frac{i}{x} \right) e^{-ix} \\
 \left. \begin{array}{l} h_\ell^{(1)} \rightarrow \frac{1}{x} (-i)^{\ell+1} e^{ix} \\ h_\ell^{(2)} \rightarrow \frac{1}{x} (i)^{\ell+1} e^{-ix} \end{array} \right\} \text{ for } x \gg 1
 \end{array}$$

The Hankel function of the first kind becomes  $e^{-ikr}/r$  for large  $r$ , so we use these to get,

$$R(r) = C j_l^{(1)}(kr) \quad (9.18)$$

### 9.3.2 Exact wavefunction and the partial wave amplitude

The exact wave function in the exterior region where  $V(r) = 0$  is,

$$\psi(r, \theta, \phi) = A \left\{ e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r} \right\} \quad (9.19)$$

Where,

$$f(\theta, \phi) + \frac{1}{k} \sum_{l,m} (-i)^{l+1} C_{l,m} Y_l^m(\theta, \phi) \quad (9.20)$$

The  $C_{l,m}$  are called the partial wave amplitudes. Now the cross section is,

$$D(\theta, \phi) = |f(\theta, \phi)|^2 = \frac{1}{k^2} \sum_{l,m} \sum_{l',m'} (i)^{l-l'} C_{l,m}^* C_{l',m'} (Y_l^m)^* Y_{l'}^{m'} \quad (9.21)$$

And the total cross-section is,

$$\sigma = \frac{1}{k^2} \sum_{l,m} \sum_{l',m'} (i)^{l-l'} C_{l,m}^* C_{l',m'} \int (Y_l^m)^* Y_{l'}^{m'} d\Omega = \frac{1}{k^2} \sum_{l,m} |C_{l,m}|^2 \quad (9.22)$$

We know from the Legendre functions that,

$$Y_l^0(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta) \quad (9.23)$$

where  $P_l$  is the  $l$ th Legendre Polynomial. Now the exact wave function in the exterior region is,

$$\psi(r, \theta) = A \left\{ e^{ikz} + \sum_{l=0}^{\infty} \sqrt{\frac{2l+1}{4\pi}} C_l h_l^{(1)}(kr) P_l(\cos\theta) \right\} \quad (9.24)$$

The scattering amplitude is now given by,

$$f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (-i)^{l+1} \sqrt{\frac{2l+1}{4\pi}} C_l P_l(\cos\theta) \quad (9.25)$$

and the total cross-section is,

$$\sigma = \frac{1}{k^2} \sum_{l=0}^{\infty} |C_l|^2 \quad (9.26)$$

To fix the hybrid notation of the cartesian incoming wave and the spherical outgoing wave, we write it in a more consistent form.

We know that the general solution to the Schrodinger equation with  $V = 0$  can be written in the form,

$$\sum_{l,m} [A_{l,m} j_l(kr) + B_{l,m} n_l(kr)] Y_l^m(\theta, \phi) \quad (9.27)$$

Expanding the plane wave in terms of spherical waves using Rayleigh's formula,

$$e^{ikz} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos\theta) \quad (9.28)$$

Substituting this in Equation (24), the consistent exterior region wave function can be written as,

$$\psi(r, \theta) = A \left[ l(2l+1) j_l(kr) + \sum_{l=0}^{\infty} \sqrt{\frac{2l+1}{4\pi}} C_l h_l^{(1)}(kr) \right] P_l(\cos\theta) \quad (9.29)$$

## 9.4 Phase Shift

Let's begin by considering a one-dimensional scattering problem with a localized potential on the half-line  $x < 0$  and a brick wall at  $x = 0$ . So a wave incident from the left,

$$\psi_i(x) = Ae^{ikx} \quad (9.30)$$

is entirely reflected,

$$\psi_r(x) = Be^{-ikx} \quad (9.31)$$

where  $x < -a$ . No matter what happens in  $-a < x < 0$  (the interaction

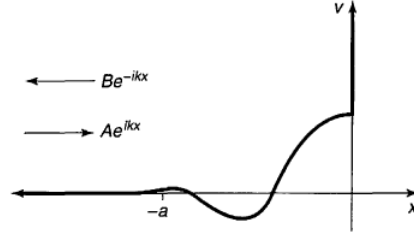


Figure 9.1: 1D scattering from a localized potential bounded on the right by an infinite wall

region), the amplitude (amplitude in the context of waves not probability amplitude) of the reflected wave is the same as the incident wave simply due to conservation of probability. However, the two waves need not have the same phase. If there were no potential at all ( $V(x) = 0$ ), but just at the wall ( $x = 0$ ), then  $B = -A$ , since the total wave function, incident + reflected must vanish at the origin,

$$\psi_0 = A(e^{ikx} - e^{-ikx}) \quad (9.32)$$

If the potential is not zero ( $V(x) \neq 0$ ), then the wave function ( $x < -a$ ) takes the form:

$$\psi = A(e^{ikx} - e^{i(2\delta - kx)}) \quad (9.33)$$

Thus, the whole scattering problem reduces to the problem of calculating the phase shift  $\delta$  as a function of  $k$  and hence of the Energy  $E = \hbar^2 k^2 / 2m$ . Yes there's a factor of 2, before  $\delta$ , but that's only conventional. We think of the incident wave as being phase shifted once on the way in and again on the way out. Thus, by  $\delta$  we mean the one-way phase shift and  $2\delta$  the total phase shift. We go about this by solving the Schrodinger equation in  $-a < x < 0$  along with relevant boundary conditions. Why are we working with  $\delta$  rather than the complex amplitude  $B$ ? It makes the physics and math simpler:

- **Physically:** We only need to think of the conservation of probability. The potential merely shifts the phase
- **Mathematically:** We trade a complex number for a real one

Let's return to the 3D case. The incident plane wave carries no angular momentum in the  $z$  direction. Thus Rayleigh's formula contains no terms with  $m \neq 0$  but instead it contains all values of the total angular momentum ( $l = 0, 1, 2$ ). Since angular momentum is conserved by a spherically symmetric potential each partial wave labelled by a particular  $l$  scatters independently with no change in amplitude (amplitude in this context refer to the amplitude of the wave not the probability amplitude) but differing in phase. If there is no potential then  $\psi_0 = Ae^{ikx}$  and the  $l$ th partial wave is

$$\psi_0^l = Ai^l(2l+1)j_l(kr)P_l(\cos(\theta)) \quad (9.34)$$

But from our previous considerations,

$$j_l(x) = \frac{1}{2} [h^{(1)}(x) + h_l^2(x)] \approx \frac{1}{2x} [(-i)^{l+1}e^{ix} + i^{l+1}e^{-ix}] \quad (9.35)$$

for  $x \gg 1$ . So for large  $r$ ,

$$\psi_0^{(l)} \approx A \frac{2l+1}{2ikr} [e^{ikr} - (-1)^l e^{-ikr}] P_l(\cos(\theta)) \quad (9.36)$$

The second term in square brackets corresponds to an incoming spherical wave. It is unchanged when we introduce the scattering potential. The first term is the outgoing wave. It picks up a phase shift  $\delta_l$ :

$$\psi^{(l)} \approx A \frac{2l+1}{2ikr} [e^{i(kr+2\delta_l)} - (-1)^l e^{-ikr}] P_l(\cos(\theta)) \quad (9.37)$$

Think of it as a converging spherical wave due to the  $h_l^{(2)}$  component in  $e^{ikz}$ , which is phase shifted by  $2\delta_l$  and emerges as an outgoing spherical wave i.e. the  $h_l^l$  part of  $e^{ikz}$  as well as the scattered wave itself. In the previous section the whole theory was expressed in terms of partial wave amplitudes  $a_l$ , now we have formulated it in terms of the phase shifts  $\delta_l$ . There must be a connection between the two. Well if we take the asymptotic i.e. large  $r$  limit of eq. (9.37):

$$\psi^{(l)} \approx A \left( \frac{(2l+1)}{2ikr} [e^{i(kr+2\delta_l)} - (-1)^l e^{-ikr}] + \frac{(2l+1)}{r} a_l e^{ikr} \right) P_l(\cos(\theta)) \quad (9.38)$$

With the generic expression in terms of  $e^{i\delta_l}$  we find

$$a = \frac{1}{2ik}(e^{2i\delta_l} - 1) = \frac{1}{k}e^{i\delta_l} \sin(\delta_l) \quad (9.39)$$

Although we used the asymptotic form of the wave function to find the connection there's nothing approximate about the result. Both of them are constants independent of  $r$  and  $\delta_l$  means the phase shift in the asymptotic region i.e. where the Hankel functions have settled down to  $e^{\pm ikr}/kr$ . It follows in particular that,

$$f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin(\delta_l) P_l(\cos(\theta)) \quad (9.40)$$

and,

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2(\delta_l) \quad (9.41)$$

Voila!

## 9.5 Born Approximation

### 9.5.1 Integral Form of the Schrodinger Equation

Before we even head to deriving the "Integral Form of the Schrodinger Equation". Why you might ask? It will become evident in the upcoming sections. So let's begin by recalling the time-independent Schrodinger equation

$$\frac{\hbar^2 \nabla^2 \psi}{2m} + V\psi = E\psi \quad (9.42)$$

We can rewrite this as,

$$(\nabla^2 + k^2)\psi = Q \quad (9.43)$$

where

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

$$Q = \frac{2m}{\hbar^2} V\psi$$

This looks pretty similar to the Helmholtz equation from electrodynamics. Here however the "inhomogeneous" term  $Q$  itself depends on  $\psi$ . Suppose we could find a function that solves the Helmholtz equation with a delta function source:

$$(\nabla^2 + k^2)G(\vec{r}) = \delta^3(\vec{r}) \quad (9.44)$$



We can then express as an integral:

$$\psi(\vec{r}) = \int G(\vec{r} - \vec{r}_0) Q(\vec{r}_0) d^3 \vec{r}_0 \quad (9.45)$$

$G(\vec{r})$  is called the Green's function for the Helmholtz equation. Moreover, generally speaking the Green's function for a linear differential equation represents the response to a delta function. Our goal now is to solve this differential equation, we start by Fourier transforming it to turn it into an algebraic equation:

$$G(\vec{r}) = \frac{1}{(2\pi)^{3/2}} \int e^{i\vec{s} \cdot \vec{r}} g(\vec{s}) d^3 \vec{s} \quad (9.46)$$

Then,

But,

and

thus,

It follows from Plancherel's theorem that,

Plugging this back, we see that

Text

Thus,

We can rewrite this as,

From Cauchy's integral formula it follows that,

Therefore,

$$\text{content...} \quad (9.47)$$

Note that  $G + G_0$  still satisfies Equation (). This is simply due to the multivalued nature of the holomorphic function. Thus, the integral form of the Schrodinger equation can be written as,

$$\psi(\vec{r}) = \psi_0(\vec{r}) - \frac{m}{2\pi\hbar^2} \int \frac{e^{ik|\vec{r}-\vec{r}_0|}}{|\vec{r}-\vec{r}_0|} V(\vec{r}_0) \psi(\vec{r}_0) d^3\vec{r}_0 \quad (9.48)$$

Let's see how this helps us.

### 9.5.2 The First Born Approximation

Suppose  $V(\vec{r}_0)$  is localized about  $r = 0$ , that is the potential drops to 0 after a finite region and we want to calculate  $\psi(\vec{r})$  at points distant from the scattering center. Then for all points that contribute to the integral form of the Schrodinger equation. So,

$$|\vec{r} - \vec{r}_0| = r^2 + r_0^2 - 2\vec{r}\vec{r}_0 \cong r^2 \left(1 - 2\frac{\vec{r}\cdot\vec{r}_0}{r^2}\right) \quad (9.49)$$

and hence,

$$|\vec{r} - \vec{r}_0| \cong r - \hat{r}\cdot\vec{r}_0 \quad (9.50)$$

Let,

$$\vec{K} = k\hat{z} \quad (9.51)$$

then

$$e^{-i\vec{K}|\vec{r}-\vec{r}_0|} \approx e^{ikr} e^{-i\vec{K}\cdot\vec{r}_0} \quad (9.52)$$

and therefore,

$$\frac{e^{-i\vec{K}|\vec{r}-\vec{r}_0|}}{|\vec{r}-\vec{r}_0|} \approx \frac{e^{ikr}}{r} e^{-i\vec{K}\cdot\vec{r}_0} \quad (9.53)$$

In the case of scattering, we want:

$$\psi_o(\vec{r}) = Ae^{ikz} \quad (9.54)$$

to represent an incident plane wave. For large  $r$ ,

$$\psi \cong Ae^{ikz} - \frac{m}{2\pi\hbar^2 A} \int e^{-i\vec{K}\cdot\vec{r}_0} V(\vec{r}_0) \psi(\vec{r}_0) d^3\vec{r}_0 \quad (9.55)$$

This is in the standard form. We can read off the scattering amplitude:

$$f(\theta, \phi) = \frac{m}{2\pi\hbar^2 A} \int e^{-i\vec{K}\cdot\vec{r}_0} V(\vec{r}_0) \psi(\vec{r}_0) d^3\vec{r}_0 \quad (9.56)$$

So far this is exact. Now we invoke the Born approximation: "Suppose the incoming plane wave is not substantially altered by the potential; then we can say that

$$\psi(\vec{r}_0) \cong \psi_0(\vec{r}_0) = Ae^{ikz_0} = Ae^{i\vec{K}' \cdot \vec{r}_0} \quad (9.57)$$

where

$$K' = k\hat{z}$$

inside the integral. This would be just the wave function if  $V$  were zero. It is essentially just a weak potential approximation. Generally partial wave analysis is useful when the incident particle has low energy the only the first few terms in the series contribute significantly. The Born approximation applies when the potential is weak when compared to the incident energy, thus the deflection is small. In the Born approximation then,

$$f(\theta, \phi) \cong -\frac{m}{2\pi\hbar^2} \int e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}_0} V(r_0) d^3\vec{r}_0 \quad (9.58)$$

In particular, for low energy scattering, the exponential factor is essentially constant over the scattering region and the Born approximation simplifies to:

$$f(\theta, \phi) \cong -\frac{m}{2\pi\hbar^2} \int V(\vec{r}) d^3r \quad (9.59)$$

For a spherically symmetrical potential,  $V(\vec{r}) = V(r)$  but not necessarily at low energy. The Born approximation reduces to a simpler form. First we define:

$$\mathcal{K} = k' - k \quad (9.60)$$

and let the polar axis for the  $r_0$ , the integral lies along so that;

$$(\vec{k}' - \vec{k}) \cdot \vec{r}_0 = \mathcal{K}r_0 \cos(\theta_0) \quad (9.61)$$

Then,

$$f(\theta) \cong -\frac{m}{2\pi\hbar^2} \int e^{i\mathcal{K}r_0 \cos(\theta_0)} V(\theta_0) r_0^2 \sin(\theta_0) dr_0 d\theta_0 d\phi_0 \quad (9.62)$$

The integral is trivial,  $2\pi$ , and the integral  $\theta_0$  is on we have encountered before in equation ( ). Dropping the subscript on  $r$ , we are left with

$$f(\theta) \cong -\frac{2m}{\hbar^2 \mathcal{K}} \int_0^\infty r V(r) \sin(\mathcal{K}r) dr \quad (9.63)$$

The angular dependence of  $f$  is carried by  $\mathcal{K}$ . From our previous considerations we can see that:

$$\mathcal{K} = 2k \sin(\theta/2) \quad (9.64)$$

### 9.5.3 Examples

#### Low-energy soft-sphere scattering

Note: We can't apply the Born approximation to hard-sphere scattering as the integral blows up due to our assumption (i.e. potential does not affect the wave function) here. Suppose,

$$V(\vec{r}) = \begin{cases} V_0, & \text{if } r \leq a \\ 0, & \text{if } r > a \end{cases} \quad (9.65)$$

In this case the low-energy scattering amplitude is,

$$f(\theta, \phi) \cong -\frac{m}{2\pi\hbar^2} V_0 \left( \frac{4}{3} \pi a^3 \right) \quad (9.66)$$

This is independent of  $\theta$  and  $\phi$  ! Thus, the differential cross-section is:

$$\frac{d\sigma}{d\Omega} = |f|^2 \cong \left[ \frac{2mV_0a^3}{3\hbar^2} \right]^2 \quad (9.67)$$

and the total cross-section:

$$\sigma \cong 4\pi \left( \frac{2mV_0a^3}{3\hbar^2} \right)^2 \quad (9.68)$$

#### Yukawa Scattering

The Yukawa potential is a toy-model for the binding force in the nucleus of an atom. It has the form,

$$V(r) = \beta \frac{e^{-\mu r}}{r} \quad (9.69)$$

where  $\beta$  and  $\mu$  are constants. The Born approximation gives,

$$f(\theta) \cong -\frac{2m\beta}{\hbar^2 k} \int_0^\infty e^{-\mu r} \sin(kr) dr = -\frac{2m\beta}{\hbar^2(\mu^2 + k^2)} \quad (9.70)$$

### Rutherford Scattering

If we substitute  $\beta = q_1 q_2 / 4\pi\epsilon_0$  and  $\mu = 0$ . The scattering amplitude is given by,

$$f(\theta) \cong -\frac{2mq_1q_2}{4\pi\epsilon_0\hbar^2k^2} \quad (9.71)$$

or,

$$f(\theta) \cong -\frac{q_1q_2}{16\pi\epsilon_0E\sin^2(\theta/2)} \quad (9.72)$$

The differential cross-section is the square of this:

$$\frac{d\sigma}{d\Omega} = \left[ \frac{q_1q_2}{16\pi\epsilon_0E\sin^2(\theta/2)} \right]^2 \quad (9.73)$$

#### 9.5.4 The Born series

The Born approximation is very similar to the impulse approximation in the context of classical scattering. In that sector we start by assuming that the

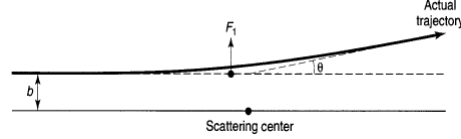


Figure 9.2: An example of the impulse approximation: the particle continues undeflected

particle keeps going in a straight line and compute the transverse impulse that would be delivered to it in that case:

$$I = \int F_{\perp} dt \quad (9.74)$$

If the deflection is small in comparison to the motion, it would then be a good approximation to the transverse momentum supplied to the particle. Thus we express the scattering angle as:

$$\theta = \arctan(I/p) \quad (9.75)$$

where  $p$  is the incident momentum. This is the "first-order" impulse approximation. The zeroth-order is what we started with i.e. no deflection at all. Likewise, in the zeroth-order Born approximation the incident plane wave passes by with no modification and what we saw earlier was just the first

order correction to this. But the same pattern of thought can lead us to a series which then leads us to higher-order corrections. Let's recall the integral form of the Schrodinger equation:

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int g(\vec{r} - \vec{r}_0) V(\vec{r}_0) \psi(\vec{r}_0) d^3 r_0 \quad (9.76)$$

where  $\psi_0$  is the incident wave and,

$$g(\vec{r}) = -\frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r}$$

is the Green's function with a factor  $m/2\pi\hbar^2$  for convenience and  $V$  is the scattering potential. Suppose we take the equation for  $\psi$  and plug it back into (9.74),

$$\psi = \psi_0 + \int gV\psi_0 + \int \int gVgV\psi$$

Iterating this we obtain the series expansion for  $\psi$ ,

$$\psi = \psi_0 + \int gV\psi_0 + \int \int gVgV\psi_0 + \int \int \int gVgVgV\psi_0 \dots \quad (9.77)$$

We notice the following from (9.75):

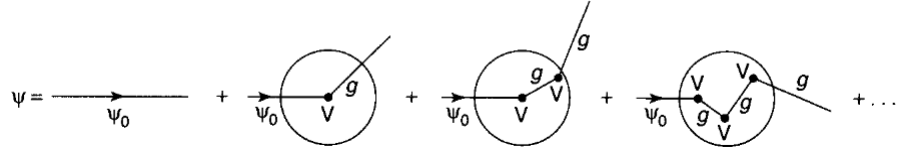


Figure 9.3: A diagram representing the Born series

- The first Born approximation truncates the series after the Next to Leading Order (NLO) term
- In the Leading Order  $\psi$  is untouched by  $V$
- In the first order (Next to Leading Order) it is kicked once
- In the second order it is kicked, propagates to a new location and is kicked again and so on
- In this context the Green's function is essentially just the propagator <sup>1</sup>

<sup>1</sup>In this context it tells us how the disturbance propagates between one interaction and the next

- This was in fact the inspiration for Feynman diagrams which is expressed in terms of vertex factors ( $V$ ) and propagators ( $g$ )

Figure (9.5.4) might look familiar, because it closely represents Feynman diagrams.

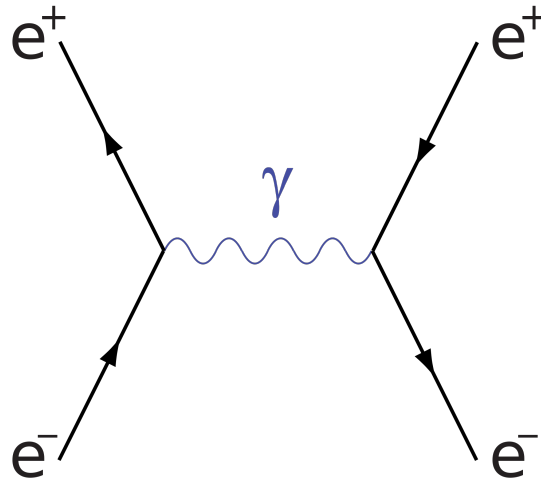


Figure 9.4: Bhabha scattering: Annihilation





# Chapter 10

## Path Integral Formulation

### 10.1 The Path Integral Recipe

So far our strategy has been to find the eigenstates of  $H$  then express the propagator in terms of this. However, the path integral formulation cuts one step and gets to the propagator directly. For a single particle in one dimension we follow the following procedure to find  $U(x, t; x', t')$ :

1. Draw all paths in the  $x - t$  plane connecting  $(x', t')$  and  $(x, t)$ :

- 2.

- 10.2 An Approximation to  $U(t)$  for a Free Particle
- 10.3 Path Integral Evaluation of the Free-Particle Propagator
- 10.4 Equivalence to the Schrodinger Equation
- 10.5 Potentials of the form  $V = a + bx + cx^2 + d\dot{x} + ex\dot{x}$
- 10.6 Derivation of the Path Integral
- 10.7 Imaginary Time Formalism
- 10.8 Spin and Fermion Path Integrals
- 10.9 Summary



# Chapter 11

## Dirac Equation

### 11.1 The Klein-Gordon Equation

### 11.2 The Free-Particle Dirac Equation

### 11.3 Electromagnetic Interaction of the Dirac Particle

### 11.4 More on Relativistic Quantum Mechanics

### 11.5 Covariant Formalism

#### 11.5.1 The Adjoint Spinor and the Covariant Current

### 11.6 Solutions to the Dirac Equation

#### 11.6.1 Particles at Rest

#### 11.6.2 General Free-Particle Solutions

### 11.7 Antiparticles

#### 11.7.1 The Dirac Sea Interpretation

#### 11.7.2 The Feynman-Stueckelberg Interpretation

#### 11.7.3 Antiparticle Spinors

# Chapter 12

## Epilogue: What lies ahead

Quantum foundations rant. Refer to:

- Lee Smolin
- Carlo Rovelli
- Sabine Hosenfelder
- Hooft
- Tong
- Maudlin
- Laloe
- Norsen



# Appendix A

## Analytical Mechanics

### A.1 Lagrangian Mechanics

### A.2 Hamiltonian Mechanics





# Appendix B

## Classical Field Theory

B.1 Potentials and the Helmholtz Theorem

B.2 Electromagnetic Radiation

B.3 Electromagnetic Waves

B.4 Special Relativity

B.5 Electromagnetism in the Language of Tensors and Lagrangians



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<http://www-cs-faculty.stanford.edu/~uno/abcde.html>