

Notes on Quantum Mechanics

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Chapter 1

A Historical Overview

Rishi's article + JP sir's slides

1.0.1 Blackbody Radiation

1.0.2 The de Broglie Hypothesis

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

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda} \quad (1.1)$$

Chapter 2

Mathematical Preliminaries

This chapter is a discussion of all the mathematical tools and tricks one would require to master Quantum mechanics. We assume that the reader has a lucid understanding of matrices and vector calculus. If not the reader may refer to:

•

to refresh themselves or learn those concepts before

2.1 Matrix Inversion

2.2 Complex Numbers

A complex number is an order pair $\in \mathbb{C}$ 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} .¹

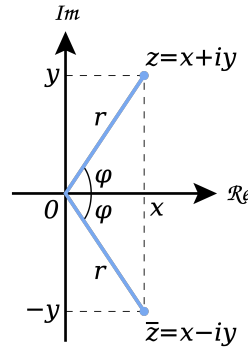


Figure 2.1: Wessel Plane Plot: (Complex conjugate picture.svg from Wikimedia Commons)

2.2.5 Wessel Plane

2.3 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: ²

2.3.1 Commutativity

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

2.3.2 Associativity

$$\begin{aligned} (\mathcal{U} + \mathcal{V}) + \mathcal{W} &= \mathcal{V} + (\mathcal{U} + \mathcal{W}) \\ (\alpha\beta)\mathcal{V} &= \alpha(\beta\mathcal{V}) \end{aligned}$$

2.3.3 Additive Identity

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

2.3.4 Additive Inverse

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

¹For our case \mathcal{F} simply refers to \mathbb{C}

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

2.3.5 Multiplicative identity

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

2.3.6 Distributive properties

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

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

2.4 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} :

$$\langle expression1 | expression2 \rangle$$

2.5 Dual Spaces

2.6 Dirac Notation

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

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

2.7 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 $\mathbb{V}_i^{n_i} \oplus \mathbb{V}_i^{m_i} = \mathbb{V}_i^{l_i}$ ³ as the set containing:

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

³Here \oplus is the direct sum defined as:

2.8 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 sequences⁴ 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 converge⁵

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

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, $c_n \in \mathbb{C}$

2.9 Linear Operators

2.10 Eigenvalue Problem

2.11 Eigenfunctions of a Hermitian Operator

2.12 Transformations

2.12.1 Active Transformation

In a loose sense this can be thought of as,

2.12.2 Passive Transformation

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

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

⁴Definition

⁵we simply state this but a proof can be found in

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

2.12.3 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.

2.13 Functions of Operators

2.14 Generalization to Infinite Dimensions

2.15 Probability

2.15.1 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:

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

2.15.2 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 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:

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

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

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

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

2.16 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,

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

2.17 Fourier Analysis

2.17.1 Dirichelet's Theorem

2.17.2 Fourier Transform

2.18 Delta Function

2.18.1 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!

2.18.2 The One-Dimensional Dirac Delta Functional

The Dirac Delta is a functional ⁶ which we define as,

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

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

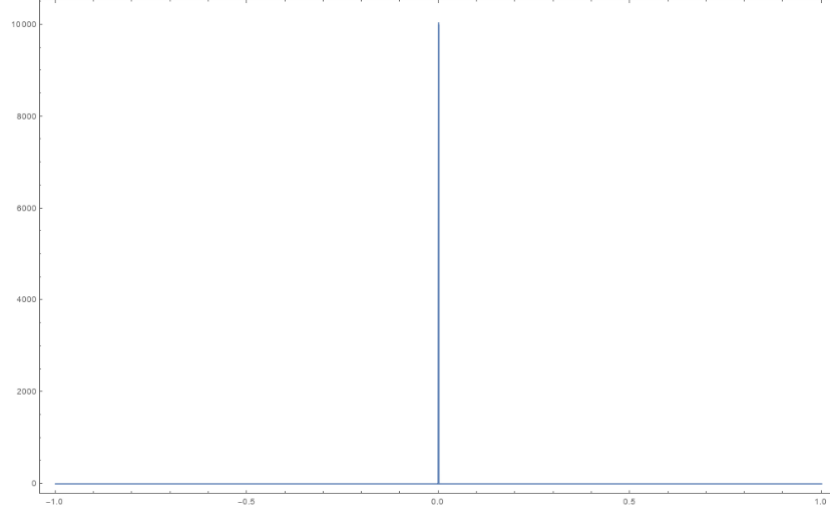
$\forall a \in \mathbb{R}$ We can visualize it as a sharp peak at a , We can interpret 2.27 as saying "the area of the delta distribution is always 1".

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

We can combine these to get,

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

⁶An 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 θ is the step function defined as,

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

2.18.3 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,

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

We can rewrite as,

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

2.19 Gaussian Integrals

2.20 The $i\epsilon$ Prescription

We will now derive and interpret the formula:

$$\frac{1}{x \mp i\epsilon} = \mathcal{P} \frac{1}{x} \pm \pi \delta(x) \quad (2.38)$$

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

$$\text{content...} \quad (2.39)$$

$$a \quad (2.40)$$

$$\text{asdfkjh} \quad (2.41)$$

2.21 Permutation Functions

2.21.1 Kronecker delta

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

$$\delta_{\nu}^{\mu} x^{\nu} = x^{\mu}$$

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

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \quad (2.42)$$

2.21.2 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:

$$\epsilon_{ijk} = \begin{cases} 1 & \text{if } ijk \text{ is an even permutation of } 123 \\ -1 & \text{if } ijk \text{ is an odd permutation of } 123 \\ 0 & \text{if two indices are equal} \end{cases} \quad (2.43)$$

Identities

$$\epsilon_{\alpha\beta\nu}\epsilon_{\alpha\beta\sigma} = \delta_{\mu\rho}\delta_{\nu\sigma} - \delta_{\mu\sigma}\delta_{\nu\rho} \quad (2.44)$$

From this it follows that,

$$\epsilon_{\alpha\beta\nu}\epsilon_{\alpha\beta\sigma} = 2\delta_{\nu\sigma} \quad (2.45)$$

and

$$\epsilon_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma} = 6 \quad (2.46)$$

Chapter 3

Formalism

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.

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:

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

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. 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).

3.1 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,

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

But ψ 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.

3.2 Summary of Postulates

3.3 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), $2\sqrt{\langle\psi|A^2|\psi\rangle\langle\psi|-B^2|\psi\rangle} \geq |\langle X|Y\rangle + \langle Y|X\rangle|$
 Taking the -1 outside, $2i\sqrt{\langle\psi|A^2|\psi\rangle\langle\psi|B^2|\psi\rangle} \geq |\langle X|Y\rangle + \langle Y|X\rangle|$ We now
 substitute in the right hand of the equation $2i\sqrt{\langle\psi|A^2|\psi\rangle\langle\psi|B^2|\psi\rangle} \geq |\langle\psi|\hat{A}\hat{B}|\psi\rangle -$
 $\langle\psi|\hat{B}\hat{A}|\psi\rangle|$ The negative sign is due to the i , this also seems to represent
 the commutator, so we substitute $2i\sqrt{\langle\psi|A^2|\psi\rangle\langle\psi|B^2|\psi\rangle} \geq |\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle|$
 Again, the right hand side looks like the expectation value of a quantity,
 so $2i\sqrt{\langle A^2\rangle\langle B^2\rangle} \geq |\langle[\hat{A}, \hat{B}]\rangle|$ $\sqrt{\langle A^2\rangle\langle B^2\rangle} \geq \frac{1}{2i}|\langle[\hat{A}, \hat{B}]\rangle|$ 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 $[\hat{x}, \hat{p}]|\psi\rangle = -ix\hbar\frac{\partial}{\partial x}|\psi\rangle + i\hbar\frac{\partial x|\psi\rangle}{\partial x}$

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

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

3.4 Generalized Statistical Interpretation

If you measure an observable \hat{O} on a particle in the state $\psi()$, you will
 certainly get an

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Chapter 9

Perturbation Theory

9.1 Non-Degenerate Perturbation Theory

9.1.1 General Formulation

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

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 \quad (9.1)$$

and obtaining a complete set of orthonormal eigenfunctions ψ_n^0 ,

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \quad (9.2)$$

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,

$$H \psi_n = E_n \psi_n \quad (9.3)$$

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,

$$H = H^0 + \lambda H' \quad (9.4)$$

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

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots \quad (9.5)$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \quad (9.6)$$

Here E_n^1 is the first-order correction to the n^{th} eigenvalue, and ψ_n^1 is the first-order correction to the n^{th} eigenfunction. E_n^2 and ψ_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,

$$(H^0 + \lambda H')[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] \quad (9.7)$$

We can rewrite Equation (7) by collecting like powers of λ 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 (λ^1) equation from Equation (7),

$$H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0 \quad (9.8)$$

And the second order (λ^2),

$$H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0 \quad (9.9)$$

And this can be done for higher powers of λ as well.

9.1.2 First order perturbation theory

If we take the inner product of Equation (8), with ψ_n^0 ,

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle \quad (9.10)$$

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

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle = \langle H^0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle = \langle E_n^0 \psi_n^0 | \psi_n^1 \rangle \quad (9.11)$$

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

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle \quad (9.12)$$

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),

$$(H^0 - E_n^0) \psi_n^1 = -(H' E_n^1) \psi_n^0 \quad (9.13)$$

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

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0 \quad (9.14)$$

We know that ψ_m^0 satisfies the unperturbed Schrodinger wave equation, so we have,

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = -(H' - E_n^1) \psi_n^0 \quad (9.15)$$

Taking the inner product with ψ_l^0 ,

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_l^0 | \psi_m^0 \rangle = -\langle \psi_l^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle \quad (9.16)$$

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

$$(E_m^0 - E_n^0) c_l^{(n)} = -\langle \psi_l^0 | H' | \psi_n^0 \rangle \quad (9.17)$$

Or that,

$$c_n^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \quad (9.18)$$

So,

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0 \quad (9.19)$$

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

9.1.3 Second order perturbation theory

We take the inner product of the second-order equation with ψ_n^0 ,

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle \quad (9.20)$$

We exploit the Hermiticity of H^0 ,

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle = \langle H^0 \psi_n^2 | \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle \quad (9.21)$$

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,

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle \quad (9.22)$$

But,

$$\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0 \quad (9.23)$$

so,

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = \sum_{m \neq n} c_m^{(n)} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \quad (9.24)$$

Therefore,

$$E_n^2 = \sum_{m \neq n} c_m^{(n)} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \quad (9.25)$$

This is the fundamental result of second order perturbation theory.

9.2 Degenerate Perturbation Theory

9.2.1 Motivation

If two or more distinct states, take ψ_a^0 and ψ_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.

9.2.2 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,

$$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0 \quad (9.26)$$

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

$$H^0 \psi^0 = E^0 \psi^0 \quad (9.27)$$

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

perturbation, the upper state reduces to one linear combination of ψ_a^0 and ψ_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 α and β adjustable and solving the Schrodinger equation,

$$H\psi = E\psi \quad (9.28)$$

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

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \dots \quad (9.29)$$

$$\psi = \psi^0 + \lambda \psi^1 + \lambda^2 \psi^2 + \dots \quad (9.30)$$

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

$$H^0\psi^0 + \lambda(H\psi^0 + H^0\psi^1) + \dots = E^0\psi^0 + \lambda(E^1\psi^0 + E^0\psi^1) + \dots \quad (9.31)$$

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

$$H\psi^0 + H^0\psi^1 = E^1\psi^0 + E^0\psi^1 \quad (9.32)$$

Taking inner product with ψ_a^0 ,

$$\langle \psi_a^0 | H^0 | \psi^1 \rangle + \langle \psi_a^0 | H' | \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle + E^1 \langle \psi_a^0 | \psi^0 \rangle \quad (9.33)$$

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

$$\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle = \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = \alpha E^1 \quad (9.34)$$

Or in a more compact form,

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1 \quad (9.35)$$

Where,

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

Similarly, the inner product with ψ_b^0 gives us,

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1 \quad (9.36)$$

Now using Equation (35) and (36),

$$\alpha[W_{ab}W_{ba} - (E^1 - W_{aa})(E^1 - W_{bb})] = 0 \quad (9.37)$$

When $\alpha \neq 0$,

$$(E^1)^2 - E^1(W_{aa} + W_{bb}) + (W_{aa}W_{bb} - W_{ab}W_{ba}) = 0 \quad (9.38)$$

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

$$E_{\pm}^1 = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right] \quad (9.39)$$

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 $\beta = 1$).

9.2.3 Higher-Order Degeneracy

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

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (9.40)$$

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,

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle \quad (9.41)$$

9.2.4 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,

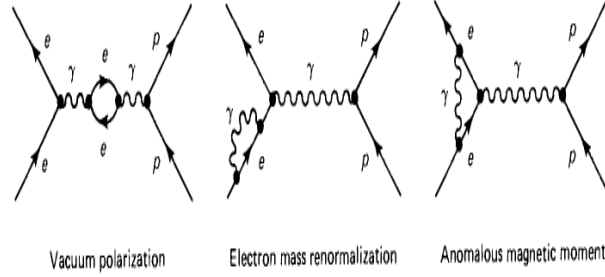


Figure 9.1: Different kinds of radiative corrections

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 $l = 0$,

$$\Delta E_{Lamb} = \alpha^5 mc^2 \frac{1}{4n^3} [k(n, 0)] \quad (9.42)$$

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

$$\Delta E_{Lamb} = \alpha^5 mc^2 \frac{1}{4n^3} \left[k(n, 0) \pm \frac{1}{\pi(l + \frac{1}{2})(l + \frac{1}{2})} \right] \quad (9.43)$$

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 $2P_{1/2}$.

9.3 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:

$$H'_Z = -(\mu_l + \mu_s).B_{Ext.} \quad (9.44)$$

Where,

$$\mu_s = -\frac{e}{m_e}S \quad (9.45)$$

is the magnetic dipole moment associated with electron spin, and

$$\mu_l = -\frac{e}{2m_e}L \quad (9.46)$$

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 (9.44) as:

$$H'_Z = \frac{e}{2m_e}(L + 2S).B_{Ext.} \quad (9.47)$$

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.

9.3.1 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,

$$E_Z^1 = \langle nlm_j | H'_Z | nlm_j \rangle = \frac{e}{2m} B_{Ext.} \langle L + 2S \rangle \quad (9.48)$$

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 :

$$S_{Ave} = \frac{(S \cdot J)}{J} J \quad (9.49)$$

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

$$S \cdot J = \frac{1}{2}(J^2 + S^2 - 2J \cdot S) = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - l(l+1)] \quad (9.50)$$

from which it follows that,

$$\langle L + 2S \rangle = \left\langle \left(1 + \frac{S \cdot J}{J^2} J \right) \right\rangle = \left[1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right] \langle J \rangle \quad (9.51)$$

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:

$$E_Z^1 = \mu_B g_j B_{Ext.} m_j \quad (9.52)$$

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:

$$-13.6 \text{ eV} (1 + \alpha^2/4) \pm \mu_B B_{Ext.} \quad (9.53)$$

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

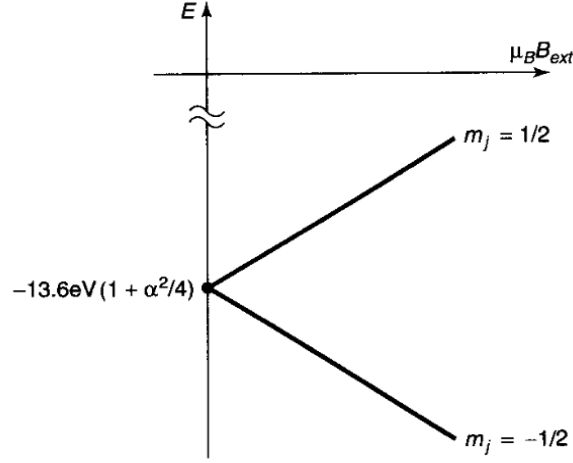


Figure 9.2: Weak-field Zeeman splitting of the ground state of hydrogen; the upper line has a slope of 1 and the lower line a slope of -1

9.3.2 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,

$$H'_Z = \frac{e}{2m} B_{Ext.} (L_z + 2S_z) \quad (9.54)$$

and the unperturbed energies are:

$$E_{nm_l m_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{Ext.} (m_l + 2m_s) \quad (9.55)$$

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:

$$E_{fs}^1 = \langle n \ l \ m_l \ m_s | H'_r + H'_{so} | n \ l \ m_l \ m_s \rangle \quad (9.56)$$

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

$$\langle S.L \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle = \hbar^2 m_l m_s \quad (9.57)$$

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:

$$E_{fs}^1 = \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left(\frac{3}{4n} - \left[\frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right] \right) \quad (9.58)$$

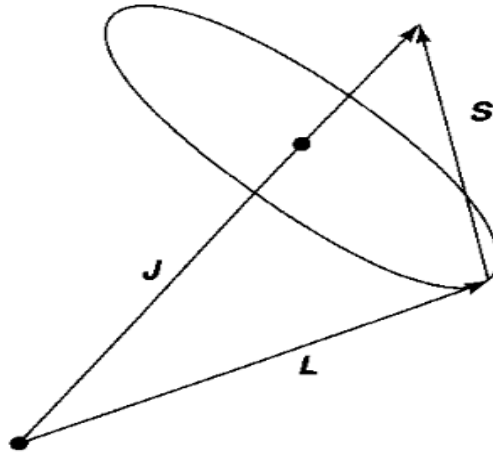


Figure 9.3: In the presence of spin-orbit coupling, L and S are not separately conserved, they precess about the fixed total angular momentum J

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.

9.3.3 Intermediate Zeeman Effect

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

$$H' = H'_Z + H'_{fs} \quad (9.59)$$

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.

$$\begin{pmatrix} 5\gamma - \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5\gamma + \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma - 2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma + 2\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma - \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma - \frac{1}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \gamma + \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma + \frac{1}{3}\beta \end{pmatrix} \quad (9.60)$$

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 2×2 blocks. The characteristic equation for the first one is given as:

$$\lambda^2 - \lambda(6\gamma - \beta) + \left(5\gamma^2 - \frac{11}{3}\gamma\beta\right) = 0 \quad (9.61)$$

and the quadratic formula gives the eigenvalues:

$$\lambda_{\pm} = 3\gamma - (\beta/2) \pm \sqrt{4\gamma^2 + (2/3)\gamma\beta + (\beta^2/4)} \quad (9.62)$$

The eigenvalues of the second block are the same but with the sign of β 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.

ϵ_1	$=$	$E_2 - 5\gamma + \beta$
ϵ_2	$=$	$E_2 - 5\gamma - \beta$
ϵ_3	$=$	$E_2 - \gamma + 2\beta$
ϵ_4	$=$	$E_2 - \gamma - 2\beta$
ϵ_5	$=$	$E_2 - 3\gamma + \beta/2 + \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$
ϵ_6	$=$	$E_2 - 3\gamma + \beta/2 - \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$
ϵ_7	$=$	$E_2 - 3\gamma - \beta/2 + \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$
ϵ_8	$=$	$E_2 - 3\gamma - \beta/2 - \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}$

Figure 9.4: Energy levels for the $n = 2$ states of hydrogen, with fine structure and Zeeman splitting

9.4 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,

$$\mu_p = \frac{g_p e}{2m_p} S_p \quad (9.63)$$

And the magnetic dipole moment of the electron,

$$\mu_e = -\frac{e}{m_e} S_e \quad (9.64)$$

Classically speaking, the dipole μ sets up a magnetic field:

$$B = \frac{\mu_0}{4\pi r^3} [3(\mu \cdot \hat{r})\hat{r} - \mu] + \frac{2\mu_0}{3} \mu \delta^3(r) \quad (9.65)$$

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

$$H'_{hf} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \frac{[3(S_p \cdot \hat{r})(S_e \cdot \hat{r}) - S_p \cdot S_e]}{r^3} + \frac{\mu_0 g_p e^2}{3m_p m_e} S_p \cdot S_e \delta^3(r) \quad (9.66)$$

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

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \left\langle \frac{3(S_p \cdot \hat{r})(S_e \cdot \hat{r}) - S_p \cdot S_e}{r^3} \right\rangle + \frac{\mu_0 g_p e^2}{3m_p m_e} \langle S_p \cdot S_e \rangle |\psi(0)|^2 \quad (9.67)$$

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

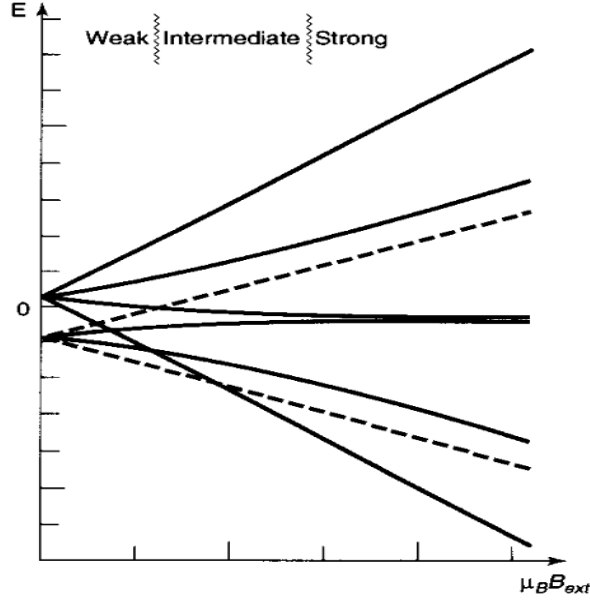


Figure 9.5: Zeeman splitting of the $n = 2$ states of hydrogen, in the weak, intermediate and strong field regimes

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

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3} \langle S_p \cdot S_e \rangle \quad (9.68)$$

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 $S.L$. 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:

$$S = S_e + S_p \quad (9.69)$$

We square this out to get,

$$S_p \cdot S_e = \frac{1}{2}(S^2 - S_e^2 - S_p^2) \quad (9.70)$$

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,

$$E_{hf}^1 = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 \alpha^4} \begin{cases} +1/4, & \text{(triplet);} \\ -3/4, & \text{(singlet)} \end{cases} \quad (9.71)$$

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:

$$\Delta E = \frac{4g_p\hbar^4}{3m_pm_e^2c^2\alpha^4} = 5.88 \times 10^{-6} \text{ eV} \quad (9.72)$$

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

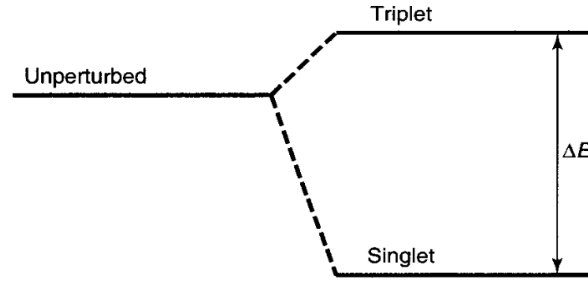


Figure 9.6: Hyperfine splitting in the ground state of Hydrogen

state is:

$$\nu = \frac{\Delta E}{h} = 1420 \text{ MHz} \quad (9.73)$$

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 10

Scattering

10.1 Introduction

10.2 Partial Wave Analysis

10.3 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,

$$\psi_i(x) = Ae^{ikx} \quad (10.1)$$

is entirely reflected,

$$\psi_r(x) = Be^{-ikx} \quad (10.2)$$

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

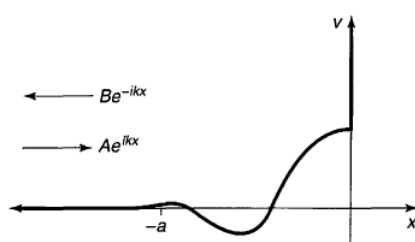


Figure 10.1: 1D scattering from a localized potential bounded on the right by an infinite wall

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,

$$\psi_0 = A(e^{ikx} - e^{-ikx}) \quad (10.3)$$

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

$$\psi = A(e^{ikx} - e^{i(2\delta - kx)}) \quad (10.4)$$

Thus, the whole scattering problem reduces to the problem of calculating the phase shift δ as a function of k and hence of the Energy $E = \hbar^2 k^2 / 2m$. Yes there's a factor of 2, before δ , 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 δ we mean the one-way phase shift and 2δ 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 δ 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

$$\psi_0^l = Ai^l(2l+1)j_l(kr)P_l(\cos(\theta)) \quad (10.5)$$

But from our previous considerations,

$$j_l(x) = \frac{1}{2} [h^{(1)}(x) + h_l^{(2)}(x)] \approx \frac{1}{2x} [(-i)^{l+1}e^{ix} + i^{l+1}e^{-ix}] \quad (10.6)$$

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

$$\psi_0^{(l)} \approx A \frac{2l+1}{2ikr} [e^{ikr} - (-1)^l e^{-ikr}] P_l(\cos(\theta)) \quad (10.7)$$

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 δ_l :

$$\psi^{(l)} \approx A \frac{2l+1}{2ikr} \left[e^{i(kr+2\delta_l)} - (-1)^l e^{-ikr} \right] P_l(\cos(\theta)) \quad (10.8)$$

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 δ_l . There must be a connection between the two. Well if we take the asymptotic i.e. large r limit of eq. (10.8):

$$\psi^{(l)} \approx A \left(\frac{(2l+1)}{2ikr} \left[e^{i(kr+2\delta_l)} - (-1)^l e^{-ikr} \right] + \frac{(2l+1)}{r} a_l e^{ikr} \right) P_l(\cos(\theta)) \quad (10.9)$$

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

$$a = \frac{1}{2ik} (e^{2i\delta_l} - 1) = \frac{1}{k} e^{i\delta_l} \sin(\delta_l) \quad (10.10)$$

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 δ_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,

$$f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin(\delta_l) P_l(\cos(\theta)) \quad (10.11)$$

and,

$$\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2(\delta_l) \quad (10.12)$$

Voila!

10.4 Born Approximation

10.4.1 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

$$\frac{\hbar^2 k^2}{2m} \psi + V\psi = E\psi \quad (10.13)$$

We can rewrite this as,

$$(\nabla^2 + k^2)\psi = Q \quad (10.14)$$

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 ψ . Suppose we could find a function that solves the Helmholtz equation with a delta function source:

$$\nabla^2 G(\vec{r}) = -\delta(\vec{r} - \vec{r}_0) \quad (10.15)$$

We can then express ψ as an integral:

$$\psi(\vec{r}) = \int G(\vec{r} - \vec{r}_0) Q(\vec{r}_0) d^3r_0 \quad (10.16)$$

$G(\vec{r})$ 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. Note that $G + G_0$ still satisfies Equation (10.15). This is simply due to the multivalued nature of the holomorphic function. Thus, the integral form of the Schrodinger equation can be written as,

$$\psi(\vec{r}) = \psi_0(\vec{r}) - \frac{m}{2\pi\hbar^2} \int \frac{e^{ik|\vec{r}-\vec{r}_0|}}{|\vec{r}-\vec{r}_0|} V(\vec{r}_0) \psi(\vec{r}_0) d^3r_0 \quad (10.17)$$

Let's see how this helps us.

10.4.2 The First Born Approximation

Suppose $V(\vec{r}_0)$ is localized about $\vec{r} = 0$, 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,

$$|\vec{r} - \vec{r}_0| = \sqrt{r^2 + r_0^2 - 2\vec{r} \cdot \vec{r}_0} \cong r \left(1 - 2\frac{\vec{r} \cdot \vec{r}_0}{r^2} \right) \quad (10.18)$$

and hence,

$$|\vec{r} - \vec{r}_0| \cong r - \hat{r} \cdot \vec{r}_0 \quad (10.19)$$

Let,

$$\vec{K} = k\hat{z} \quad (10.20)$$

then

$$e^{-i\vec{K}|\vec{r}-\vec{r}_0|} \approx e^{ikr} e^{-i\vec{K} \cdot \vec{r}_0} \quad (10.21)$$

and therefore,

$$\frac{e^{-i\vec{K}|\vec{r}-\vec{r}_0|}}{|\vec{r} - \vec{r}_0|} \approx \frac{e^{ikr}}{r} e^{-i\vec{K} \cdot \vec{r}_0} \quad (10.22)$$

In the case of scattering, we want:

$$\psi_o(\vec{r}) = Ae^{ikz} \quad (10.23)$$

to represent an incident plane wave. For large r ,

$$\psi \cong Ae^{ikz} - \frac{m}{2\pi\hbar^2 A} \int e^{-i\vec{K} \cdot \vec{r}_0} V(\vec{r}_0) \psi(\vec{r}_0) d^3\vec{r}_0 \quad (10.24)$$

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

$$f(\theta, \phi) = \frac{m}{2\pi\hbar^2 A} \int e^{-i\vec{K} \cdot \vec{r}_0} V(\vec{r}_0) \psi(\vec{r}_0) d^3\vec{r}_0 \quad (10.25)$$

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

$$\psi(\vec{r}_0) \cong \psi_o(\vec{r}_0) = Ae^{ikz_o} = Ae^{i\vec{K}' \cdot \vec{r}_o} \quad (10.26)$$

where

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

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,

$$f(\theta, \phi) \cong -\frac{m}{2\pi\hbar^2} \int e^{i(\vec{K}' - \vec{k}) \cdot \vec{r}_0} V(\vec{r}_0) d^3\vec{r}_0 \quad (10.27)$$

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

$$f(\theta, \phi) \cong -\frac{m}{2\pi\hbar^2} \int V(\vec{r}) d^3r \quad (10.28)$$

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:

$$\mathcal{K} = k' - k \quad (10.29)$$

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

$$(k' - k) \cdot r_0 = \mathcal{K} r_0 \cos(\theta_0) \quad (10.30)$$

Then,

$$f(\theta) \cong -\frac{m}{2\pi\hbar^2} \int e^{i\mathcal{K}r_0 \cos(\theta_0)} V(\theta_0) r_0^2 \sin(\theta_0) dr_0 d\theta_0 d\phi_0 \quad (10.31)$$

The integral is trivial, 2π , and the integral θ_0 is on we have encountered before in equation (). Dropping the subscript on r , we are left with

$$f(\theta) \cong -\frac{2m}{\hbar^2 \mathcal{K}} \int_0^\infty r V(r) \sin(\mathcal{K}r) dr \quad (10.32)$$

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

$$\mathcal{K} = 2k \sin(\theta/2) \quad (10.33)$$

10.4.3 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,

$$V(\vec{r}) = \begin{cases} V_0, & \text{if } r \leq a \\ 0, & \text{if } r > a \end{cases} \quad (10.34)$$

In this case the low-energy scattering amplitude is,

$$f(\theta, \phi) \cong -\frac{m}{2\pi\hbar^2} V_0 \left(\frac{4}{3} \pi a^3 \right) \quad (10.35)$$

This is independent of θ and ϕ ! Thus, the differential cross-section is:

$$\frac{d\sigma}{d\Omega} = |f|^2 \cong \left[\frac{2mV_0a^3}{3\hbar^2} \right]^2 \quad (10.36)$$

and the total cross-section:

$$\sigma \cong 4\pi \left(\frac{2mV_0a^3}{3\hbar^2} \right)^2 \quad (10.37)$$

Yukawa Scattering

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

$$V(r) = \beta \frac{e^{-\mu r}}{r} \quad (10.38)$$

where β and μ are constants. The Born approximation gives,

$$f(\theta) \cong -\frac{2m\beta}{\hbar^2 k} \int_0^\infty e^{-\mu r} \sin(kr) dr = -\frac{2m\beta}{\hbar^2(\mu^2 + k^2)} \quad (10.39)$$

Rutherford Scattering

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

$$f(\theta) \cong -\frac{2mq_1q_2}{4\pi\epsilon_0\hbar^2k^2} \quad (10.40)$$

or,

$$f(\theta) \cong -\frac{q_1q_2}{16\pi\epsilon_0 E \sin^2(\theta/2)} \quad (10.41)$$

The differential cross-section is the square of this:

$$\frac{d\sigma}{d\Omega} = \left[\frac{q_1q_2}{16\pi\epsilon_0 E \sin^2(\theta/2)} \right]^2 \quad (10.42)$$

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

$$I = \int F_\perp dt \quad (10.43)$$

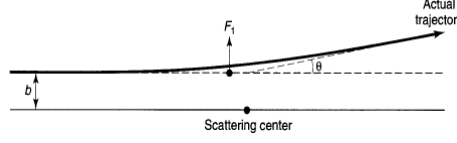


Figure 10.2: An example of the impulse approximation: the particle continues undeflected

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:

$$\theta = \arctan(I/p) \quad (10.44)$$

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:

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int g(\vec{r} - \vec{r}_0) V(\vec{r}_0) \psi(\vec{r}_0) d^3 r_0 \quad (10.45)$$

where ψ_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 ψ and plug it back into (10.45),

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

Iterating this we obtain the series expansion for ψ ,

$$\psi = \psi_0 + \int gV\psi_0 + \int \int gVgV\psi_0 + \int \int \int gVgVgV\psi_0 \dots \quad (10.46)$$

We notice the following from (10.46):

- The first Born approximation truncates the series after the Next to Leading Order (NLO) term

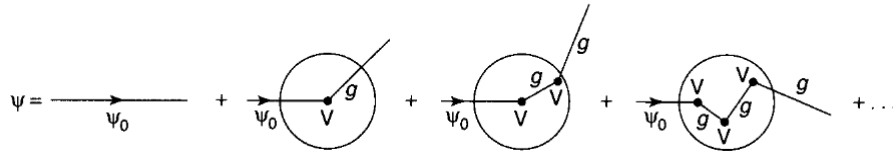


Figure 10.3: A diagram representing the Born series

- In the Leading Order ψ 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 ¹
- This was in fact the inspiration for Feynman diagrams which is expressed in terms of vertex factors (V) and propagators (g)

Figure (10.4.4) might look familiar, because it closely represents Feynman diagrams.

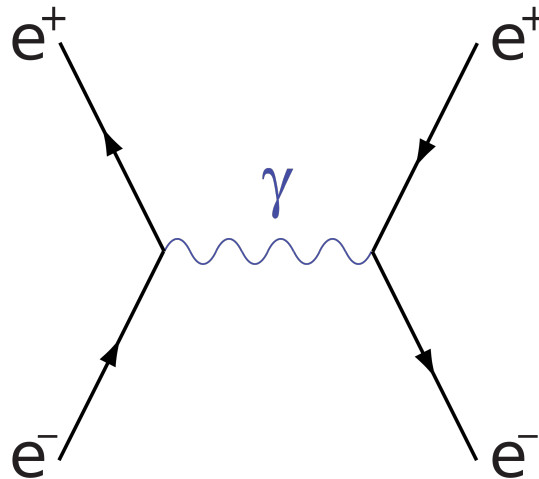


Figure 10.4: Bhabha scattering: Annihilation

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

Chapter 11

Path Integral Formulation

11.1 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)

11.2 An Approximation to $U(t)$ for a Free Particle

11.3 Path Integral Evaluation of the Free-Particle Propagator

11.4 Equivalence to the Schrodinger Equation

11.5 Potentials of the form $V = a + bx + cx^2 + dx + ex$

Chapter 12

Dirac Equation

Chapter 13

The Heisenberg Picture/Theorems that connect to classical mech

Copy paste assignment here lol

Chapter 14

Epilogue: What lies ahead

