Notes on Quantum Mechanics

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Contents

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 Brogile proposed that this wave like structure applies to electrons too and follows the equation:

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda} \tag{1.1}$$

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:

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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

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

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

2.2.2 Multiplication

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

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

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

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

Multiplicative Inverse

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

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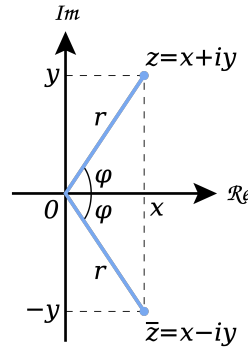
Figure 2.1: Wessel Plane Plot: (Complex conjugate picture.svg from Wikimedia Commons)

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

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

2.3.3 Additive Identity

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

2.3.4 Additive Inverse

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

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

[2] Here, $\alpha, \beta \in \mathcal{F}$ 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

$$\langle e_m | \hat{O} | e_n \rangle = \hat{O}_{mn} \tag{2.1}$$

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 $n + m$.

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[3] Here $\oplus$ 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:

$$\|V\| := \sqrt{\langle V|V \rangle} \tag{2.2}$$

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

$$\int_a^b |f(x)|^2 dx < \infty \tag{2.3}$$

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

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

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 Tranformation

In a loose sense this can be thought of as,

2.12.2   Passive Tranformation

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

$$\hat{O} \rightarrow U^\dagger \hat{O} U \tag{2.5}$$

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[4]Defintion

[5]we 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

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

The probability of an event N_j is defined as,

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

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

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

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

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

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

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

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

$$\sigma^2 = \left\langle (\Delta j)^2 \right\rangle \tag{2.11}$$

where,

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

It's square root is called the standard deviation,

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

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

$$\sigma^2 = \left\langle (\Delta j)^2 \right\rangle = \sum (\Delta j)^2 P(j) = \sum (j - \langle j \rangle)^2 P(j)$$

$$= \sum (j^2 - 2j \langle j \rangle + \langle j \rangle^2) P(j)$$

$$= \sum j^2 P(j) - 2 \langle j \rangle \sum j P(j) + \langle j \rangle^2 \sum P(j)$$

$$= \langle j^2 \rangle - 2 \langle j \rangle \langle j \rangle + \langle j \rangle^2 = \langle j^2 \rangle - \langle j \rangle^2$$

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

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

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 chosend at random lies between x and $x+dx$

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

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

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

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

$$\sigma^2 := \left\langle (\Delta x)^2 \right\rangle = \langle x^2 \rangle - \langle x \rangle^2 \tag{2.17}$$

2.16   Expectation Values

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

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

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

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

Throwing away

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

Therefore we can write the expectation value of momentum as,

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

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,

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

For example, the expectation value of kinetic energy is,

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

Or to sum it up in Dirac notation,

$$\left\langle \hat{O} \right\rangle = \langle \psi|\hat{O}|\psi \rangle \qquad (2.23)$$

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,

$$\nabla . \frac{\hat{r}}{r^2} = 0 \tag{2.24}$$

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

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

This is paradoxical. The issue is that it blows up at $r = 0$ but is is neglible 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,

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

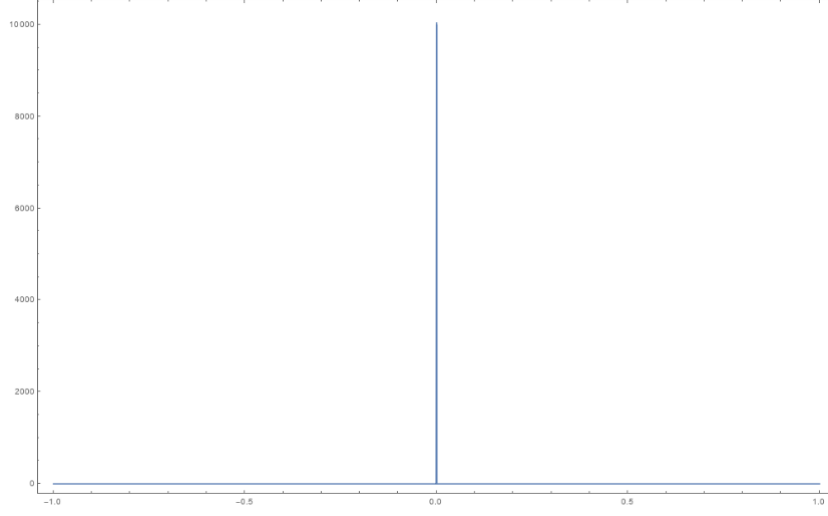$$\int_{-\infty}^{+\infty} \delta(x - a) dx = 1 \tag{2.27}$$

$\forall \, a \in \mathbb{R}$ 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".

$$f(x)\delta(x - a) = f(a) \tag{2.28}$$

We can combine these to get,

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

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[6]An object that is a map between functions

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

A few interesting properties

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

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

where k is a constant

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

Where θ is the step function defined as,

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

2.18.3   The Three-Dimensional Dirac Delta Function

We generalize (2.26) to three dimensions,

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

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

We can also define the three-dimensional delta function as

$$\delta^3(\boldsymbol{\imath}) = \frac{1}{4\pi}\left[\nabla \cdot \left(\frac{\hat{\boldsymbol{\imath}}}{\boldsymbol{\imath}^2}\right)\right] \tag{2.36}$$

Since,

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

We can rewrite as,

$$\delta^3(\pmb{\imath}) = -\frac{1}{4\pi}\left[\nabla^2\left(\frac{1}{\imath}\right)\right] \tag{2.37}$$

2.19   Gaussian Integrals

2.20   The $i\epsilon$ Prescription

We will now derive and interpret the formula:

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

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

$$content... \tag{2.39}$$

$$a \tag{2.40}$$

$$asdfkjh \tag{2.41}$$

2.21   Permutation Functions

2.21.1   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:

$$\delta_{ij} = \begin{cases} 1 \text{ if } i = j \\ 0 \text{ if } i \neq j \end{cases} \tag{2.42}$$

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:

$$\epsilon_{ijk} = \begin{cases} 1 \text{ if } ijk \text{ is an even permuation of } 123 \\ -1 \text{ if } ijk \text{ is an odd permuation of } 123 \\ 0 \text{ if two indices are equal} \end{cases} \tag{2.43}$$

Identities

$$\epsilon_{\alpha\beta\nu}\epsilon_{\alpha\beta\sigma} = \delta_{\mu\rho}\delta_{\nu\sigma} - \delta_{\mu\sigma}\delta_{\nu\rho} \tag{2.44}$$

From this it follows that,

$$\epsilon_{\alpha\beta\nu}\epsilon_{\alpha\beta\sigma} = 2\delta_{\nu\sigma} \tag{2.45}$$

and

$$\epsilon_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma} = 6 \tag{2.46}$$

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 of momentum, we can extract this information from the State vector by means of acting on 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:

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

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:

$$content... \qquad (3.2)$$

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

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

Or,

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

in terms of the Wavefunction. Where, $\hat{H}$ is the Hamiltonian operator, which

can be expressed as:

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

for a free particle. According to Born's rule

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

Thus, . Physically speaking this lends a kind of indeterminancy 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,

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

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,

$$|\psi(\vec{x}, t)|^2 =$$

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

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

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

3.4 Generalized Statistical Interpretation

Chapter 4

Toy Models

Chapter 5

Systems with N degrees of freedom

Chapter 6

Symmetries and their Consequences

Shankar chapters 11,12 13, 14 ,15

Chapter 7

Hydrogen Atom

7.1 Fine Structure

7.1.1 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 potrayed below. Naively,
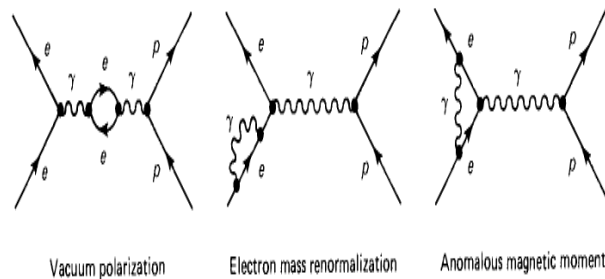

Figure 7.1: Different kinds of radiative corrections

1. the first diagram describes pair-production in the neighbhorhood 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 $l = 0$,

$$\Delta E_{Lamb} = \alpha^5 mc^2 \frac{1}{4n^3} [k(n,0)] \tag{7.1}$$

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

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

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

$$\Delta E_{Lamb} = \alpha^5 mc^2 \frac{1}{4n^3} \left[k(n,0) \pm \frac{1}{\pi(l+\frac{1}{2})(l+\frac{1}{2})} \right] \tag{7.2}$$

Here, $k(n,l)$ is a very small number (< 0.05) which varies a little with it's 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 $2P_{1/2}$.

7.2 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:

$$H'_Z = -(\mu_l + \mu_s).B_{Ext.} \tag{7.3}$$

Where,

$$\mu_s = -\frac{e}{m_e} S \tag{7.4}$$

is the magnetic dipole moment associated with electron spin, and

$$\mu_l = -\frac{e}{2m_e}L \qquad (7.5)$$

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 (7.3) as:

$$H'_Z = \frac{e}{2m_e}(L + 2S).B_{Ext.} \qquad (7.6)$$

The nature of the Zeeman splitting depnds 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 peturbation theory and will need to diagonlize the necessary portion of the Hamiltonian "by hand"

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

7.2.1 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,

$$E_Z^1 = \langle nljm_j|H_Z'|nljm_j \rangle = \frac{e}{2m}B_{Ext.}\langle L + 2S \rangle \qquad (7.7)$$

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:

$$S_{Ave} = \frac{(S.J)}{J}J \qquad (7.8)$$

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

$$S.J = \frac{1}{2}(J^2 + S^2 - 2J.S) = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - l(l+1)] \qquad (7.9)$$

from which it follows that,

$$\langle L + 2S \rangle = \left\langle \left(1 + \frac{S.J}{J^2}J\right) \right\rangle = \left[1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)}\right]\langle J \rangle \quad (7.10)$$

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:

$$E_Z^1 = \mu_B g_j B_{Ext.}m_j \qquad (7.11)$$

where,

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

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:

$$- 13.6 \ eV(1 + \alpha^2/4) \pm \mu_B B_{Ext.} \qquad (7.12)$$

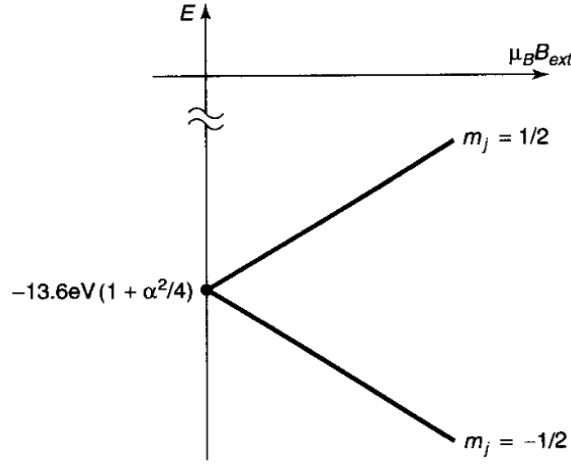with different signs for different m_j's this is plotted below.

Figure 7.2: 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

7.2.2   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,

$$H'_Z = \frac{e}{2m} B_{Ext.} (L_z + 2S_z) \tag{7.13}$$

and the unperturbed energies are:

$$E_{nm_l m_s} = -\frac{13.6\ eV}{n^2} + \mu_B B_{Ext.}(m_l + 2m_s) \tag{7.14}$$

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:

$$E^1_{fs} = \langle n\ l\ m_l\ m_s | H'_r + H'_{so} | n\ l\ m_l\ m_s \rangle \tag{7.15}$$

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

$$\langle S.L \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle = \hbar^2 m_l m_s \tag{7.16}$$

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:

$$E^1_{fs} = \frac{13.6\ eV}{n^3} \alpha^2 \left(\frac{3}{4n} - \left[\frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right] \right) \tag{7.17}$$
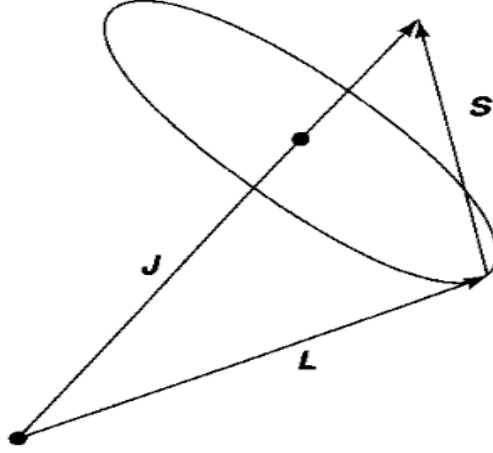
Figure 7.3: In the presence of spin-orbit coupling, L and S are not separately conserved, they precess about the fixed total angular momentum J

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

7.2.3   Intermediate Zeeman Effect

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

$$H^{'} = H^{'}_{Z} + H^{'}_{fs} \tag{7.18}$$

In section we'll discuss the case $n = 2$, and use it as the basis for degerate 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 $|j m_j\rangle$ as a linear combination of $|l m_l\rangle |s m_s\rangle$ we have:

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

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

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.

$$\begin{pmatrix} 5\gamma - \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5\gamma + \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma - 2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma + 2\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma - \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma - \frac{1}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \gamma + \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma + \frac{1}{3}\beta \end{pmatrix}$$
$$(7.19)$$

Where,

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

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:

$$\lambda^2 - \lambda(6\gamma - \beta) + \left(5\gamma^2 - \frac{11}{3}\gamma\beta\right) = 0 \qquad (7.20)$$

and the quadratic formula gives the eigenvalues:

$$\lambda_\pm = 3\gamma - (\beta/2) \pm \sqrt{4\gamma^2 + (2/3)\gamma\beta + (\beta^2/4)} \qquad (7.21)$$

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.

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

Figure 7.4: Energy levels for the $n = 2$ states of hydrogen, with fine structure and Zeeman splitting

7.3   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,

$$
\mu_p = \frac{g_p e}{2m_p} S_p \tag{7.22}
$$

And the magnetic dipole moment of the electron,

$$
\mu_e = -\frac{e}{m_e} S_e \tag{7.23}
$$

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

$$
B = \frac{\mu_0}{4\pi r^3}[3(\mu.\hat{r})\hat{r} - \mu] + \frac{2\mu_0}{3}\mu\delta^3(r) \tag{7.24}
$$

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

$$
H'_{hf} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \frac{[3(S_p.\hat{r})(S_e.\hat{r}) - S_p.S_e]}{r^3} + \frac{\mu_0 g_p e^2}{3m_p m_e} S_p.S_e \delta^3(r) \tag{7.25}
$$

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

$$
E^1_{hf} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e} \left\langle \frac{3(S_p.\hat{r})(S_e.\hat{r}) - S_p.S_e}{r^3} \right\rangle + \frac{\mu_0 g_p e^2}{3m_p m_e} \langle S_p.S_e \rangle |\psi(0)|^2 \tag{7.26}
$$

In the groud state or any other state at which $l = 0$, the wavefunction is spherically symmetrical, and the first expectation value vanishes. Meanwhile,
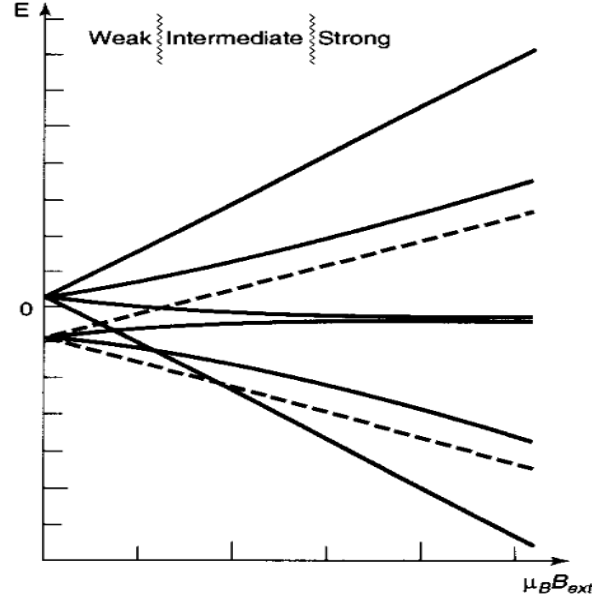
Figure 7.5: Zeeman splitting of the $n = 2$ states of hydrogen, in the weak, intermediate and strong field regimes

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

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3} \langle S_p.S_e \rangle \tag{7.27}$$

in the groud 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:

$$S = S_e + S_p \tag{7.28}$$

We square this out to get,

$$S_p.S_e = \frac{1}{2}(S^2 - S_e^2 - S_p^2) \tag{7.29}$$

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,

$$E_{hf}^1 = \frac{4g_p \hbar^4}{3m_p m_e^2 c^2 \alpha^4} \begin{cases} +1/4, & \text{(triplet)}; \\ -3/4, & \text{(singlet)} \end{cases} \tag{7.30}$$

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

$$\Delta E = \frac{4g_p\hbar^4}{3m_p m_e^2 c^2 \alpha^4} = 5.88 \times 10^{-6} \ eV \tag{7.31}$$

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

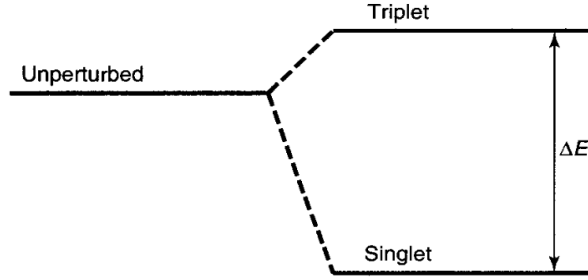
Figure 7.6: Hyperfine splitting in the ground state of Hydrogen

state is:

$$\nu = \frac{\Delta E}{h} = 1420 \ \text{MHz} \tag{7.32}$$

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 8

Approximations

Chapter 9

Pertubation Theory

Chapter 10

Scattering

10.1 Phase Shift

10.2 Born Approximation

Chapter 11

Path Integral Formulation

Chapter 12

Dirac Equation

Chapter 13

The Heisenberg Picture/Theorems that connect to classical mech

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Chapter 14

Epilogue: What lies ahead