Quantum Mechanics
from the context of the courses
PHY 471-472: Quantum Mechanics

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Contents

0.1 The SI System

In physics it's often important to have precisely defined units for the purposes of making very accurate measurements or simply having a coherent unit system. It's possible to derive all necessary units from five measurements of **length, mass, time, current, and temperature**. The standard SI units for these properties are listed bellow:

Type	Unit	Definition
Length	Meter(m)	Length of distance light in a vacuum travels in $\frac{1}{299792458}$ seconds
Mass	Kilogram(kg)	Defined by fixing the Planck's constant $h = 6.62607015 \times 10^{-34} kg\ m^2 s^{-1}$
Time	Second(s)	Defined by fixing the ground-state hyperfine transition frequency of the caesium-133 atom, to be $9192631770 s^{-1}$
Current	Ampere(A)	Defined by fixing the charge of an electron as $1.602176634 \times 10^{-19} A \cdot s$
Temperature	Kelvin(K)	Defined by fixing the value of the Boltzmann constant k to $1.380649 \times 10^{-23} kg \cdot m^2 s^{-2} K^{-1}$

Common prefixes are listed bellow:

Prefix	Symbol	Definition
mega	M	10^6
kilo	k	10^3
milli	m	10^{-3}
micro	μ	10^{-6}
nano	n	10^{-9}
pico	p	10^{-12}
femto	f	10^{-15}

Additionally, the following are defined constants:

Symbol	Definition
$\hbar$	$\hbar = \frac{h}{2\pi} \approx 1.0546 \times 10^{-34} kg\ m^2 s^{-1}$

0.2   What's Wrong with Classical Mechanics?

As we have come to discover our universe behaves differently on extremely small scales. While the average or expected outcomes of these small interactions follow classical mechanics, classical mechanics fails to predict our world in the very small. This is what quantum mechanics hopes to explain. The classic example of this is the double slit experiment with electrons. Classically, waves traveling through a double slit will interfere with each other producing a wavy interference pattern. Again classically, fire individual particles through a double slit experiment would not be expected to produce an interference pattern. However, running this experiment with electrons produces an interference pattern. Somehow individual electrons are interfering with themselves. This would hint at the idea that electrons are waves. However if you add detectors to determine if the electron when through both slits, it will only ever pass through one and the interference is destroyed. Simply by observing the path of electrons we fundamentally changed how they behave.

0.3   Postulates of Quantum Mechanics

Towards representing these physical systems with mathematics we need to define some assumptions. Postulates are necessary statements that are assumed to be true. These postulate might not make much sense now, but it will be clear later in this book. Here are the postulates of quantum mechanics:

Postulate 1. Any quantum state can be represented with by a normalized linear combination of the basis vectors. Let $\{|1\rangle, |2\rangle, \ldots, |n\rangle\}$ be the basis vectors and let $|\psi\rangle$ be any quantum state.

$$|\psi\rangle = \psi_1 |1\rangle + \psi_2 |2\rangle + \cdots + \psi_n |n\rangle$$

$$\langle \psi | \psi \rangle = 1$$

Postulate 2. A physical observable is represented by an operator that acts on kets.

Postulate 3. The only possible result of a measurement of an observable is one of the eigenvalues a_n of the corresponding operator A.

Postulate 4. The probability obtaining the eigenvalue ϕ with eigenvector $|\phi\rangle$ from a measurement of an observable on a system in the state of $|\psi\rangle$ is given by

$$P_\phi = |\langle \phi | \psi \rangle|^2$$

Postulate 5. After a measurement of an eigenvalue ϕ with corresponding eigenvector $|\phi\rangle$, the quantum system is in the normalized projection of the original state onto the result of the measurement:

$$|\psi'\rangle = \frac{|\phi\rangle \langle \phi | \psi \rangle}{|\langle \phi | \psi \rangle|^2}$$

Postulate 6. A quantum system evolves through time as described by the Schrödinger equation and the Hamiltonian operator $H(t)$ for the system.

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

Chapter 1

Quantum Systems and States

1.1 Stern-Gerlach Experiments

Definition 1.1.1. Recall from classical mechanics that **Classical Magnetic Moment** is defined using the following formula given some angular momentum **L**

$$\mu = \frac{q}{2m}\mathbf{L}$$

$$\mathbf{L} = rmv$$

where r is radius, m is mass of particle, v is tangential velocity, q is charge, **L** is the angular momentum, and μ is the magnetic moment.

It is reasonable to expect that some classical physics also applies in quantum as classical physics must emerge from quantum physics.

Definition 1.1.2. Electron, Protons, and Neutrons all have an **intrinsic angular momentum** called **spin** denoted **S**.

Definition 1.1.3. Electrons, Protons, and Neutrons also have an **intrinsic magnetic moment** defined by

$$\mu = g\frac{q}{2m}\mathbf{S}$$

where g is the dimensionless gyroscopic ratio or g-factor with the following values:
Electron: $g_e = 2.00231930436256$
Proton: $g_p = 5.5856946893$
Neutron: $g_n = -3.82608545$
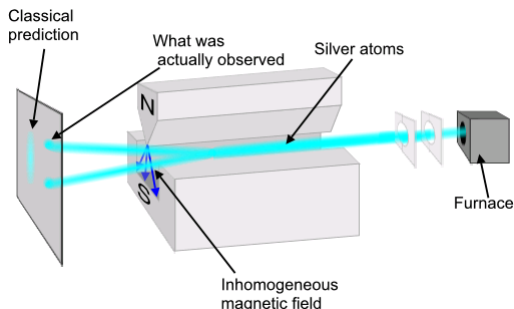
Figure 1.1: Diagram of the Stern-Gerlach experiment

The first Stern-Gerlach experiment seeks to measure the magnetic moment of the valence electron. A silver atom has 47 electrons and 47 protons. The magnetic moments depends on the inverse of mass, so we can neglect heavy protons and neutrons. Silver has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^{10} 5s^1$, so the only electron that contributes to the magnetic moment is the valence electron $5s^1$. Knowing this we expect the magnetic moment of the silver atom to be

$$\mu = -g_e \frac{e}{2m_e}\mathbf{S}$$

Following the laws of electromagnetism the force in the z direction is

$$F_z = -g_e \frac{e}{2m_e} S_z \frac{\partial B_z}{\partial z}$$

The deflection of the beam is therefore a measurement of the spin of the valence electron of the silver atoms in the z-direction. Classically, we would expect the magnetic moment to be aligned in random directive and to observe a continuous range of deflection. Instead we observe two distinct magnetic moments. The magnitudes of these deflections are consistent with the spins of

$$S_z = \pm \frac{\hbar}{2}$$

This is called **quantization** of the electron's spin angular momentum component. The factor $\frac{1}{2}$ in the equation is why we refer to electrons as having **spin-1/2**.

Definition 1.1.4. quantization of a property or material is an effect that constrains the property or material to a discrete set of values.

1.1.5 Additional Stern-Gerlach Experiments

As we alluded to in the introduction the act of observing a quantum property may effect how the system behaves. By stacking multiple Stern-Gerlach experiments back to back we can observe that spin in the x direction and spin in the z direction are incompatible observables. To simplify the diagrams we will use the following simplified schematic:
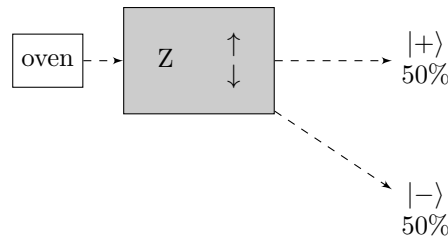
Figure 1.2: Simple schematic of the Stern-Gerlach experiment

Here we represent spin-up states with $|+\rangle$ and spin-down states with $|-\rangle$. More specifically, if a particle has a spin z-component S_z In this first example 50% of the particles are measured with spin-up and 50% of the particles are measured with spin-down. Now consider the following diagram:
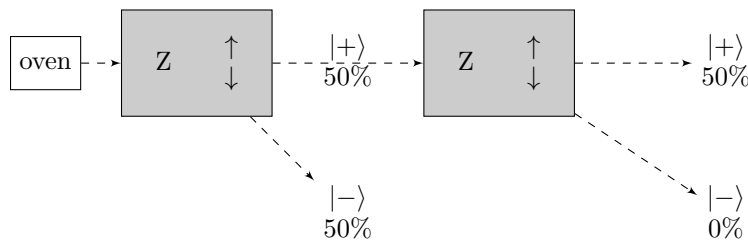
Figure 1.3: This setup measures along the z-axis twice.

As expected, after the first measurement all the remaining particles are spin-z.
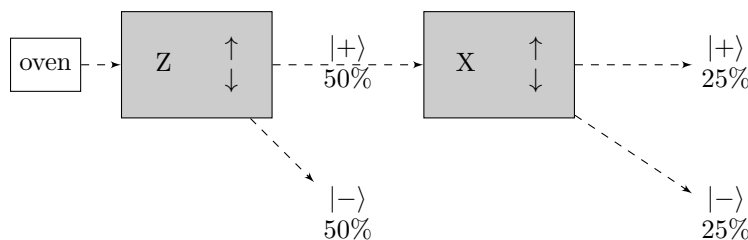
Figure 1.4: This setup measures along the z-axis followed by the x-axis.

If we instead measure along the x axis the result is random and half of the particles are measured to have spin-up or spin-down in the x direction.

Figure 1.5: This demonstrates that Spin-z and Spin-x are incompatible observables.

After measuring in the x-direction, if we again measure in the z-direction the atoms "forget" about the earlier measurement and we observe and random spin in the z direction. Measuring the spin in the x direction destroyed the measured spin in the z direction.

Definition 1.1.6. Incompatible observables are two properties that cannot be simultaneously measured.

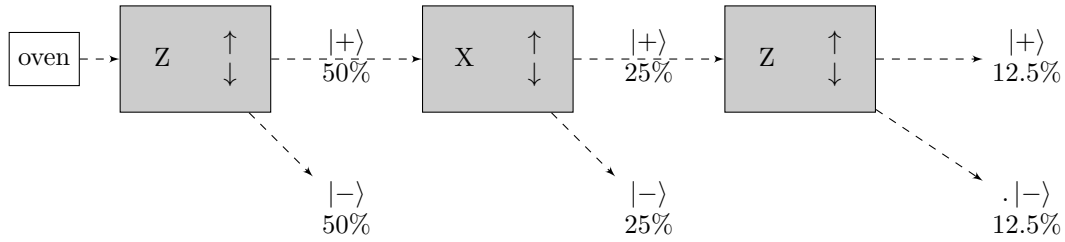**Definition 1.1.7. Compatible observables** are two properties that can be simultaneously measured.

1.2 Quantum State Vectors

To describe quantum states such as the spin in the spin-$\frac{1}{2}$ systems that we've explored so far, we use bra-ket notation. For spin-$\frac{1}{2}$ systems we will use the basis vectors $|+\rangle$ and $|-\rangle$, where $|+\rangle$ represents the spin-up in the z-direction and $|-\rangle$ represents spin-down in the z-direction.

Definition 1.2.1. A **bra** is the row vector that represents the operator that measures a quantum state denoted $\langle\psi|$

Definition 1.2.2. A **ket** is the column vector that represents a particular quantum state denoted $|\psi\rangle$.

Definition 1.2.3. For any matrix/vector A the **hermitian conjugate** or **adjoint** denoted $A^\dagger$ is the conjugate transpose of A.

$$A^\dagger = (A^*)^T$$

Definition 1.2.4. We convert between bras and kets using the hermitian conjugate.

$$|\psi\rangle^\dagger = \langle\psi|$$
$$\langle\psi|^\dagger = |\psi\rangle$$

Corollary 1.2.5.

$$\langle\phi|\psi\rangle = \langle\psi|\phi\rangle$$

Definition 1.2.6. A **basis** is a set of quantum state vectors with the following properties:

1. **Normalization** - For every basis vector $|v\rangle$ we have $\langle v|v\rangle = 1$.

2. **Orthogonalization** - For any two basis vectors $|v\rangle$ and $|w\rangle$ where $|v\rangle \neq |w\rangle$ we have $\langle v|w\rangle = 0$.

3. **Completeness** - Any $|\psi\rangle$ can be represented as a linear combination of the bases vectors $|\psi\rangle = \psi_1 |v_1\rangle + \cdots + \psi_2 |v_n\rangle$.

Definition 1.2.7. The **z-spin-$\frac{1}{2}$ basis** represented with the basis vectors $|+\rangle$ and $|-\rangle$ represents the quantum state with the spin up or down respectively in the z-direction. We will write all **spin-$\frac{1}{2}$** quantum states with this basis.

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Definition 1.2.8. Under these definitions we can define a bases for the X and Y directions. It must be orthogonal to the z direction so we chose the following values:

$$|+\rangle_X = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, |-\rangle_X = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$|+\rangle_Y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}, |-\rangle_Y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$$

Now consider postulate 1, we can understand the Stern-Gerlach experiments mathematically. Consider the two following example from earlier.
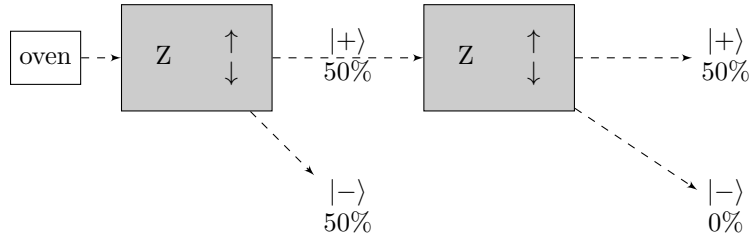
Figure 1.6: This setup measures along the z-axis twice.

The first Stern-Gerlach will serve to purpose of preparing the quantum states for the following Stern-Gerlach. So to calculate the probability of $|+\rangle$ in the z-direction we find that

$$P = |\langle +|+\rangle|^2 = |1|^2 = 1$$

As expected, 100% of the particles that make it to the second detector are measured as $|+\rangle$.
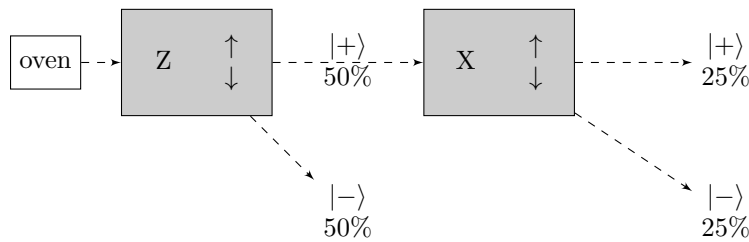
Figure 1.7: This setup measures along the z-axis followed by the x-axis.

Again the first detector on serves the purpose of preparing the state for the second detector. To calculate the probability of $|+\rangle_X$ we have

$$P = |_X\langle +|+\rangle|^2 = \left| \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right|^2 = \frac{1}{2}$$

So the probability of measuring spin up in the x-direction is 50%.

1.3   General Quantum Systems

Up until this point, we've been working in the Spin-$\frac{1}{2}$ quantum system with only two basis vectors. More generally we can represent a quantum system with more that two basis vectors. A quantum system can have any number of basis vectors.

Definition 1.3.1. A **General Quantum System** is a set of quantum states represented using a set of basis states.

$$|\psi\rangle = v_1 |v_1\rangle + v_2 |v_2\rangle + \cdots + v_n |v_n\rangle$$

Example. The spin-1 system is another quantum system similar to the spin-$\frac{1}{2}$ system. It has three basis vectors representing spin up $|+\rangle$, spin down $|-\rangle$, and no spin $|0\rangle$. In spin-1 systems we observe a spin values of $S_z = \hbar, 0, -\hbar$.

$$|\psi\rangle = a |+\rangle + b |0\rangle + c |-\rangle$$

where the basis vectors are for spin in the z direction are:

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, |0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, |-\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

Figure 1.8: Diagram of a spin-1 observable

Chapter 2

Operators and Observables

Definition 2.0.1. An **operator** is a complex matrix that represents an operation that acts on a ket to produce a new ket.

$$A \left| \phi \right\rangle = \left| \varphi \right\rangle$$

The use of Dirac notation allow for the elements of the matrix to be denoted using the basis vectors of a quantum system.

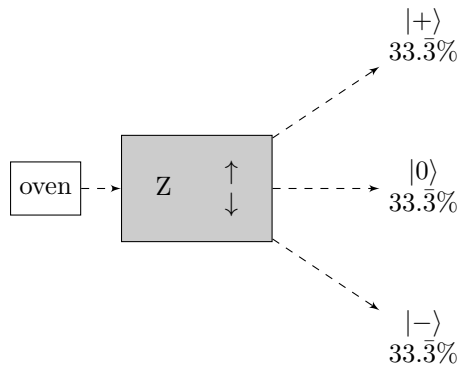**Proposition 2.0.2.** For an operator $\hat{A}$ in a quantum system with n basis vectors $\{\left| 1 \right\rangle, \left| 2 \right\rangle, \ldots, \left| n \right\rangle\}$. The ith row and jth column entry of the matrix representation of $\hat{A}$ can be written as

$$\hat{A}_{ij} = \left\langle i \right| \hat{A} \left| j \right\rangle$$

Definition 2.0.3. An operator $\hat{A}$ is **hermitian** if

$$\hat{A} = \hat{A}^\dagger$$

Using postulate 2 and 3, we can write the operator for spin in the z-direction. The possible results are $\pm \frac{\hbar}{2}$ and the eigenvectors are the spin-up and spin-down states in the z-direction.

Proposition 2.0.4. The operator for spin-1/2 in the z-direction can be derived from the following properties

$$S_z \left| + \right\rangle = \frac{\hbar}{2} \left| + \right\rangle$$

$$S_z \left| - \right\rangle = \frac{\hbar}{2} \left| - \right\rangle$$

Therefore, the matrix representation of the spin-1/2 in the z-direction is

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Similarly, for the x-direction and y-directions we can derive the following matrices.

Proposition 2.0.5. The operator for spin-1/2 in the x-direction can be derived from the following properties

$$S_x \left| + \right\rangle_x = \frac{\hbar}{2} \left| + \right\rangle_x$$

$$S_x \left| - \right\rangle_x = \frac{\hbar}{2} \left| - \right\rangle_x$$

Therefore, the matrix representation of the spin-1/2 in the x-direction is

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Proposition 2.0.6. The operator for spin-1/2 in the y-direction can be derived from the following properties

$$S_y \left| + \right\rangle_y = \frac{\hbar}{2} \left| + \right\rangle_y$$
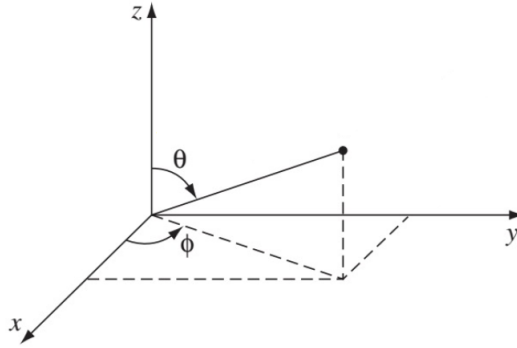
$$S_y \left| - \right\rangle_y = \frac{\hbar}{2} \left| - \right\rangle_y$$

Therefore, the matrix representation of the spin-1/2 in the y-direction is

$$S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Now that we have the operators for the spin components along all three axes, we can construct the general operator for spin-$\frac{1}{2}$ systems. We will represent the direction of this operator in spherical coordinates describing the vector $\hat{\mathbf{n}}$ with

$$\hat{\mathbf{n}} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$$

To find the operator associated with measuring in this spin direction we simply project this the spin operators for the three axes onto this unit vector.

$$S_n = S_x \sin\theta\cos\phi + S_y \sin\theta\sin\phi + S_z \cos\theta$$

Proposition 2.0.7. The operator for measuring spin-$\frac{1}{2}$ at an arbitrary direction (ϕ, θ) is given by

$$S_n = \begin{pmatrix} \cos\theta & \sin\theta e^{-i\phi} \\ \sin\theta e^{-\phi} & -\cos\theta \end{pmatrix}$$

Diagonalizing this matrix yields use the values for spin up and spin down in this arbitrary direction:

$$\left|+\right\rangle_n = \cos\frac{\theta}{2}\left|+\right\rangle + \sin\frac{\theta}{2}e^{i\phi}\left|-\right\rangle$$

$$\left|-\right\rangle_n = \sin\frac{\theta}{2}\left|+\right\rangle - \cos\frac{\theta}{2}e^{i\phi}\left|-\right\rangle$$

2.1 Projection Operators

Definition 2.1.1. A **projection operator** projects a quantum state to another quantum state. The projection operator for a vector $\left|\phi\right\rangle$ is given by

$$P_\phi = \left|\phi\right\rangle\left\langle\phi\right|$$

Example. Consider a quantum state $\left|\psi\right\rangle$ in a spin-$\frac{1}{2}$ system, and the projection operator P_+ for the spin up state $\left|+\right\rangle$. If $\left|\psi\right\rangle = a\left|+\right\rangle + b\left|-\right\rangle$, then we have

$$P_+\left|\psi\right\rangle = \left|+\right\rangle\left\langle+|\psi\right\rangle = a\left|+\right\rangle$$

Proposition 2.1.2. The projection operator for spin-1/2 up in the z-direction can be derived fro m the following

$$\left|\psi\right\rangle = a\left|+\right\rangle + b\left|-\right\rangle$$

$$\hat{P}_+\left|\psi\right\rangle = a\left|+\right\rangle$$

Therefore, the projection operator for spin-1/2 up in the z-direction is

$$\hat{P}_+ = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

Similarly, for spin-1/2 down in the z-direction we have

$$\left|\psi\right\rangle = a\left|+\right\rangle + b\left|-\right\rangle$$

$$\hat{P}_-\left|\psi\right\rangle = b\left|-\right\rangle$$

Therefore, the projection operator for spin-1/2 down in the z-direction is

$$\hat{P}_+ = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

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Theorem 2.1.3. These projection operators can be used to write the probability of a particular measurement. Recall, from postulate 4 that the probability of measuring a quantum state $|\phi\rangle$ is given by

$$P(|\phi\rangle) = |\langle\phi|\psi\rangle|^2$$

We can rewrite this in terms of the projection operator for $|\phi\rangle$:

$$P(|\phi\rangle) = \langle\psi|\hat{P}_\phi|\psi\rangle$$

We now have the notation necessary to understand postulate 5. So, after a measurement of an eigenvalue ϕ with corresponding eigenvector $|\phi\rangle$, the quantum system is in the normalized projection of the original state onto the result of the measurement:

$$|\psi'\rangle = \frac{P_{|\phi\rangle}|\psi\rangle}{\langle\psi|P_{|\phi\rangle}|\psi\rangle} = \frac{|\phi\rangle\langle\phi|\psi\rangle}{|\langle\phi|\psi\rangle|^2}$$

2.2 Measurement

Since all possible measurements are represented by a hermitian operator we can prove a few useful properties of measurements.

Proposition 2.2.1. The eigenvalues of a hermitian operator are real.

Proof. Let $|a_n\rangle$ be eigenstates of a hermitian operator $\hat{A}$, with eigenvalues a_n. For any $|\varphi\rangle$ we have

$$\langle\varphi|a_n\rangle = \langle a_n|\varphi\rangle^*$$

Now, let $|\varphi\rangle = \hat{A}|a_n\rangle$ we have

$$\langle\varphi| = \langle a_n|\hat{A}^\dagger = \langle a_n|\hat{A}$$
$$\langle a_n|\hat{A}|a_n\rangle = \langle a_n|\hat{A}|a_n\rangle^*$$
$$a_n = a_n^*$$

$\square$

Proposition 2.2.2. The eigenvectors of a hermitian operator with different eigenvalues are orthogonal. That is for two eigenvectors $|a\rangle$ and $|b\rangle$ with eigenvalues $a \neq b$ we have

$$\langle a|b\rangle = 0$$

Proposition 2.2.3. Eigenstates of an hermitian operator form a basis for a complete Hilbert space.

We know from the Stern-Gerlach experiments that measurements in quantum mechanics are statistical. This section will discuss how to calculate common statistical quantities such as average value and standard deviation for measurements.

Example. Measuring $\hat{S}_z$ we have two possible results $\pm\frac{\hbar}{2}$ with probabilities determined by postulate 4. So the average value is given by

$$\langle\hat{S}_z\rangle = \frac{\hbar}{2}|\langle+|\psi\rangle|^2 - \frac{\hbar}{2}|\langle-|\psi\rangle|^2$$

Definition 2.2.4. The **average value** or **expected value** of a measurement with operator $\hat{A}$ denoted $\langle\hat{A}\rangle$ is given by

$$\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle$$

For the standard deviation there is a similar derivation from standard statistics:

$$\Delta A = \sqrt{\langle(\hat{A} - \langle\hat{A}\rangle)^2\rangle} = \sqrt{\langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2}$$

Definition 2.2.5. The **standard deviation** of a measurement with operator $\hat{A}$ denoted $\Delta\hat{A}$ is given by

$$\Delta\hat{A} = \sqrt{\langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2}$$

2.3   Uncertainty Principle

As determined in the Stern-Gerlach examples, two observations can be incompatible observables. Incompatible observables cannot be simultaniously measured. We can represent this property mathematically by defining a commutator of both matrices.

Definition 2.3.1. The **commutator** of two operators A, B denoted $[A, B]$ is given by

$$[A, B] = AB - BA$$

When the commutator is zero, the operators are commutative with each other. Otherwise, the operators represent incompatible observables that cannot be simultaniously measured. This property my be familiar to you as the uncertainty principle.

Proposition 2.3.2. If the operators representing two observables A, B have a zero commutator that is $[A, B] = 0$, then the observables are compatible observables.

Proposition 2.3.3. If the operators representing two observables A, B have a zero commutator that is $[A, B] = 0$, then the observables share eigenstates.

Theorem 2.3.4. The Uncertainty Principle states that the minimum product of the standard deviation of two observables is determined by the commutator of the operators representing the observables.

$$\Delta A \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle|$$

2.4 S^2 Operator

Consider the operator that measures the magnitude of the spin vector without measuring the direction. This is represented by the S^2 operator defined by

$$S^2 = S_x^2 + S_y^2 + S_z^2$$

Calculating the matrix representation gives you

$$S^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Since this is propotional to the identity matrix S^2 is compatable with all operators. Therefore every vector is an eignevector, with the corresponding eigenvalue $\frac{3}{4} \hbar^2$. So the expected value of the S^2 operator is

$$\langle S^2 \rangle = \frac{3}{4} \hbar^2$$

Since this is larger than $\frac{\hbar}{2}$ the spin is never perfectly aligned in with the direction. One can think of this a the spin rotating around the axis that it is pointing in.

Chapter 3

Schrödinger Equation

As stated in postulate 6 quantum state evolve with time under the Scrödinger equation.

$$i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle = \hat{\mathcal{H}}\left|\psi(t)\right\rangle$$

Definition 3.0.1. $\hat{\mathcal{H}}$ is the **Hamiltonian** which is a hermitian operator that represents the total energy of a system.

Proposition 3.0.2. $\hat{\mathcal{H}}$ is an observable so the eigenstates of $\hat{\mathcal{H}}$ form a complete basis. We will denote these eigenstate and there corresponding eigenvalues with $\left|E_n\right\rangle$ an E_N such that for $1,\ldots,n$ we have

$$\hat{\mathcal{H}}\left|E_n\right\rangle = E_n\left|E_n\right\rangle$$

3.1 Time Independent Hamiltonian

If $\hat{\mathcal{H}}$ is independent of time then energy is conserved within the system. We will assume that $\hat{\mathcal{H}}$ is energy conserving. Lets consider a simple case, for some $1 \leq k \leq n$:

$$\left|\psi(0)\right\rangle = \left|E_k\right\rangle$$

$$\left|\psi(t)\right\rangle = c(t)\left|E_k\right\rangle$$

From the Schrödinger Equation we have

$$i\hbar\frac{\partial}{\partial t}c(t)\left|E_k\right\rangle = \hat{\mathcal{H}}c(t)\left|E_k\right\rangle$$

$$i\hbar\frac{\partial c(t)}{\partial t}\left|E_k\right\rangle = c(t)\hat{\mathcal{H}}\left|E_k\right\rangle$$

$$i\hbar\frac{\partial c(t)}{\partial t}\left|E_k\right\rangle = c(t)E_k\left|E_k\right\rangle$$

$$i\hbar\frac{\partial c(t)}{\partial t} = c(t)E_k$$

$$\frac{\partial c(t)}{\partial t} = \frac{-ic(t)E_k}{\hbar}$$

$$c(t) = e^{-iE_k t/\hbar}$$

Since multiplying by a phase factor does not change probabilities of measurement. This system does not change in an observable way in time.

Definition 3.1.1. Stationary States are eigenstates that don't change in time.

Now, lets generalize this case to any quantum system $\left|\psi(t)\right\rangle$ again assuming that $\hat{\mathcal{H}}$ is energy conserving. Since, $\{\left|E_1\right\rangle,\ldots,\left|E_n\right\rangle\}$ forms a basis we can write:

$$\left|\psi(t)\right\rangle = \sum_{i=1}^{n} c_i(t)\left|E_i\right\rangle$$

Applying the Schrödinger Equation we have

$$i\hbar\frac{\partial}{\partial t}\sum_{i=1}^{n} c_i(t)\left|E_i\right\rangle = \hat{\mathcal{H}}\sum_{i=1}^{n} c_i(t)\left|E_i\right\rangle$$

$$\sum_{i=1}^{n} i\hbar \frac{\partial}{\partial t} c_i(t) \left| E_i \right\rangle = \sum_{i=1}^{n} c_i(t) \hat{\mathcal{H}} \left| E_i \right\rangle$$

$$\sum_{i=1}^{n} i\hbar \frac{\partial}{\partial t} c_i(t) \left| E_i \right\rangle = \sum_{i=1}^{n} c_i(t) E_i \left| E_i \right\rangle$$

$$\frac{\partial}{\partial t} c_i(t) \left| E_i \right\rangle = \frac{-i c_i(t) E_i}{\hbar} \left| E_i \right\rangle$$

$$c_i(t) = c_i(0) e^{-iE_i t/\hbar}$$

$$\left| \psi(t) \right\rangle = \sum_{i=1}^{n} c_i(0) e^{-iE_i t/\hbar} \left| E_i \right\rangle$$

Proposition 3.1.2. Time Independent Solution - The solution to any quantum system with a time-independent Hamiltonian is

$$\left| \psi(t) \right\rangle = \sum_{i=1}^{n} c_i e^{-iE_i t/\hbar} \left| E_i \right\rangle$$

where $\left| E_i \right\rangle$ are the eigenstates of the Hamiltonian with eigenvalues E_i and c_i are the initial conditions in the basis determined by the Hamiltonian.

Example. Consider a Hamiltonian with two eigenstates $\left| E_1 \right\rangle$ and $\left| E_2 \right\rangle$

$$\left| \psi(t) \right\rangle = c_1 e^{-iE_1 t/\hbar} \left| E_1 \right\rangle + c_2 e^{-iE_2 t/\hbar} \left| E_2 \right\rangle$$

Consider an incompatible observable $\hat{A}$ with eigenstates $\left| a_1 \right\rangle$ and $\left| a_2 \right\rangle$ with corresponding eigenvalues a_1 and a_2. The probability of measuring a_1 is given by

$$\left| \langle a_1 | \psi(t) \rangle \right|^2 = \left| \begin{pmatrix} a_1^* & a_2^* \end{pmatrix} \begin{pmatrix} c_1 e^{-iE_1 t/\hbar} \\ c_2 e^{-iE_2 t/\hbar} \end{pmatrix} \right|^2 = \left| a_1^* c_1 e^{-iE_1 t/\hbar} + a_2^* c_2 e^{-iE_2 t/\hbar} \right|^2 = |a_1|^2 |c_1|^2 + |a_2|^2 |c_2|^2 + 2 a_1 a_2^* c_1^* c_2 \cos\left(\frac{E_2 - E_1}{\hbar} t \right)$$

So independent of the operator we chose it will oscillate with a frequency $\frac{E_2 - E_1}{\hbar}$.

Definition 3.1.3. The **Bohr Frequency** is the frequency $\omega = \frac{E_2 - E_1}{\hbar}$ which is the frequency of oscillation for a quantum system with two energy eigenstates $\left| E_1 \right\rangle$ and $\left| E_2 \right\rangle$.

3.2 Spin-$\frac{1}{2}$ in a Magnetic Field

Let's consider a spin-$\frac{1}{2}$ system in a uniform magnetic field. A magnetic dipole of an electron is given by

$$\mu = -g_e \frac{e}{2m_e} \mathbf{S}$$

the Hamiltonian represents the potential energy of the system. So, for a magnetic dipole in a magnetic field $\mathbf{B}$ we have

$$\hat{\mathcal{H}} = -\mu \cdot \mathbf{B} = g_e \frac{e}{2m_e} \mathbf{S} \cdot \mathbf{B}$$

Let θ be the angle of the magnetic field from the z axis and for simplicity assume it is in the $x - z$ plane. We could simply rotate our coordinate system to reflect this. So we have

$$\mathbf{B} = B \cos\theta \hat{\mathbf{z}} + B \sin\theta \hat{\mathbf{x}}$$

Now, apply this to find our hamiltonian. Note that $g_e \approx 2$.

$$\hat{\mathcal{H}} = \frac{e}{m_e} \mathbf{S} \cdot \mathbf{B} = \frac{e}{m_e} \hat{S}(B \cos\theta \hat{\mathbf{z}} + B \sin\theta \hat{\mathbf{x}}) = \frac{eB}{m_e} \left(\cos\theta \hat{S}_z + \sin\theta \hat{S}_x \right) = \frac{e\hbar B}{2m_e} \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}$$

Determining the eigenvalues of the Hamiltonian are $E_1 = \frac{e\hbar B}{2m_e}$ and $E_2 = -\frac{e\hbar B}{2m_e}$ with corresponding eigenstates

$$\left| E_1 \right\rangle = \cos\frac{\theta}{2} \left| + \right\rangle + \sin\frac{\theta}{2} \left| - \right\rangle$$

$$\left| E_2 \right\rangle = \sin\frac{\theta}{2} \left| + \right\rangle - \cos\frac{\theta}{2} \left| - \right\rangle$$

Since the Hamiltonian is time independent we can apply Proposition 3.1.2 to show that

$$|\psi(t)\rangle = c_1 e^{-iE_1 t/\hbar} |E_1\rangle + c_2 e^{-iE_2 t/\hbar} |E_2\rangle$$

This solution can be used to predict how any spin-$\frac{1}{2}$ quantum system would develop in a constant magnetic field. It is often important to consider the probability of a spin-flip event. That is the probability that a quantum system starting in spin up would be measured spin down. To calculate this we need to find c_1 and c_2 that represents spin up, that is

$$|+\rangle = c_1 |E_1\rangle + c_2 |E_2\rangle$$

Consider

$$\langle E_1|+\rangle = c_1 \langle E_1|E_1\rangle + c_2 \langle E_1|E_2\rangle = c_1$$
$$\langle E_2|+\rangle = c_1 \langle E_2|E_1\rangle + c_2 \langle E_2|E_2\rangle = c_2$$

So, since we have the representations of $|E_1\rangle$ and $|E_2\rangle$ in terms of $|+\rangle$ and $|-\rangle$ we have

$$c_1 = \cos\frac{\theta}{2}, c_2 = \sin\frac{\theta}{2}$$

Therefore, a system starting in the spin up state will evolve with time as described by

$$|\psi(t)\rangle = \cos\frac{\theta}{2} e^{-iE_1 t/\hbar} |E_1\rangle + \sin\frac{\theta}{2} e^{-iE_2 t/\hbar} |E_2\rangle$$

Let's consider the probability of measuring the spin down state

$$|\langle -|\psi(t)\rangle|^2 = \left| \cos\frac{\theta}{2} e^{-iE_1 t/\hbar} \sin\frac{\theta}{2} - \sin\frac{\theta}{2} e^{-iE_2 t/\hbar} \cos\frac{\theta}{2} \right|^2 = \sin^2\frac{\theta}{2}\cos^2\frac{\theta}{2} \left| e^{-iE_1 t/\hbar} - e^{-iE_2 t/\hbar} \right|^2$$

$$= \sin^2\frac{\theta}{2}\cos^2\frac{\theta}{2} \left(2 - 2\cos\left(\frac{(E_1 - E_2)t}{\hbar}\right)\right) = \sin^2\theta \sin^2\left(\frac{(E_1 - E_2)t}{2\hbar}\right)$$

In many applications it is reasonable to write the $\omega_0 = \frac{eB}{m_e}\cos\theta$ and $\omega_1 = \frac{eB}{m_e}\sin\theta$. This allows for the simplification of the Hamiltonian but more importantly we can write

$$\sin^2\theta = \frac{\omega_1^2}{\omega_0^2 + \omega_1^2}$$

$$E_1 - E_2 = \frac{e\hbar B}{m_e} = \hbar\sqrt{\omega_0^2 + \omega_1^2}$$

Therefore, we have

$$|\langle -|\psi(t)\rangle|^2 = \frac{\omega_1^2}{\omega_0^2 + \omega_1^2} \sin^2\left(\sqrt{\omega_0^2 + \omega_1^2}t/2\right)$$

Definition 3.2.1. The **Rabi Formula** predicts the probability of a spin flip caused by a magnetic field.

$$P = \frac{\omega_1^2}{\omega_0^2 + \omega_1^2} \sin^2\left(\sqrt{\omega_0^2 + \omega_1^2}t/2\right)$$

Lets consider some limiting cases of the Rabi Formula.

1. If $\omega_1 = 0$ then the magnetic field points entirely in the z direction and the probability is

$$P = \frac{0^2}{\omega_0^2} \sin^2\left(\omega_0 t/2\right) = 0$$

2. If $\omega_0 = 0$ then the field points entirely in the x direction and the probability is

$$P = \frac{\omega_1^2}{\omega_1^2} \sin^2\left(\omega_1 t/2\right) = \sin^2\left(\omega_1 t/2\right)$$
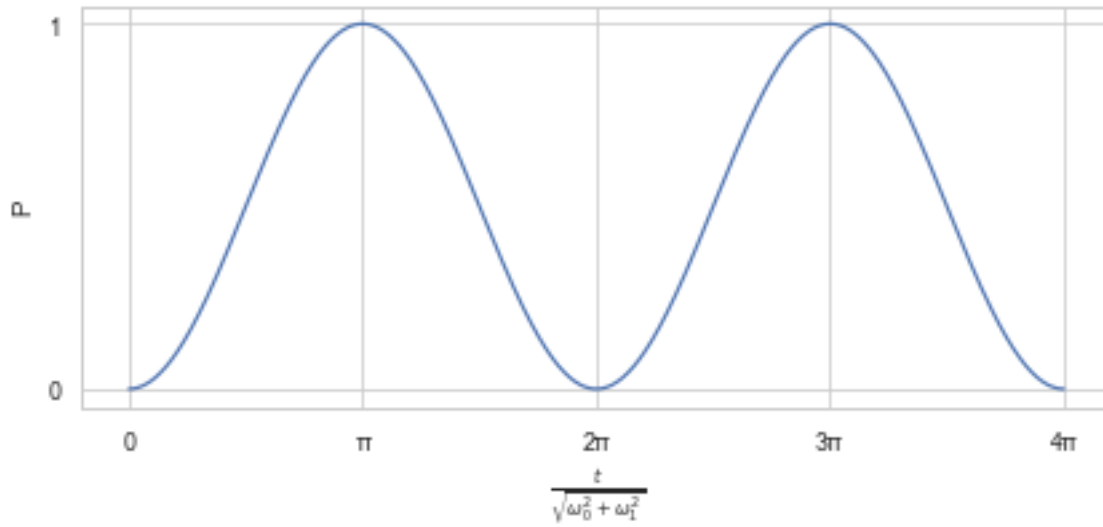
Figure 3.1: Plot of probability verses time.

3. If both $\omega_1 \neq 0$ and $\omega_1 \neq 0$ then the probability will oscillate between zero and $\frac{\omega_1^2}{\omega_0^2 + \omega_1^2}$.
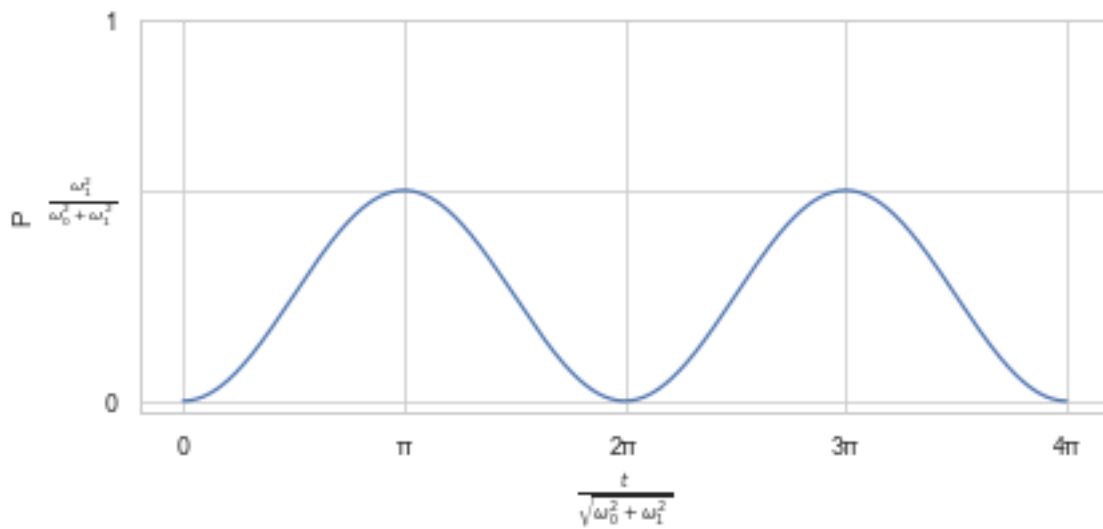

Figure 3.2: Plot of probability verses time.

Chapter 4

Entanglement

Up until this point we've worked with quantum system that consist of only one particle. However systems consisting on multiple particles do not necessarily act like the sum of there parts. The Einstein-Poltololsky-Rosen paradox is the famous example of this. Using quantum mechanics we can set up an experiment where two particles appear to be communicating faster than light to match there states. This can only be explained through quantum entanglement.

Theorem 4.0.1. Bell's Theorem Any explaination based on entrinsic properties of the particles will predict a probability greater than 5/9.

Therefore, quantum mechanics is the only explanation that models the experiment. To model this we need to define multi particles systems.

4.1 Multiparticle System

The state of a system of two particles is conveniently written with the direct product.

Definition 4.1.1. The **direct product** of two states $|a\rangle = \begin{pmatrix} a_1 \\ \dots \\ a_n \end{pmatrix}$ and $|b\rangle = \begin{pmatrix} b_1 \\ \dots \\ b_m \end{pmatrix}$ is defined as

$$|a\rangle\,|b\rangle = \begin{pmatrix} a_1 \\ \dots \\ a_n \end{pmatrix} \begin{pmatrix} b_1 \\ \dots \\ b_m \end{pmatrix} = \begin{pmatrix} a_1 b_1 \\ \dots \\ a_n b_m \\ \dots \\ a_n b_1 \\ \dots \\ a_n b_m \end{pmatrix}$$

Definition 4.1.2. The **multiparticle system** consisting of two systems with bases vectors $|E_1\rangle_1, \dots, |E_n\rangle_1$ and $|E_1\rangle_2, \dots, |E_m\rangle_2$ is a four dimensional Hilbert space with bases vectors

$$|E_1\rangle_1 |E_1\rangle_2, \dots, |E_1\rangle_1 |E_m\rangle_2, \dots, |E_n\rangle_1 |E_1\rangle_2, \dots, |E_n\rangle_1 |E_m\rangle_2$$

Example. Consider a two particle system of spin-1/2 system constructed from $|+\rangle_1, |-\rangle_1$ and $|+\rangle_2, |-\rangle_2$. The basis vectors are

$$|+\rangle_1 |+\rangle_2, |+\rangle_1 |-\rangle_2, |-\rangle_1 |+\rangle_2, |-\rangle_1 |-\rangle_2$$

Consider the state $|\psi\rangle = \frac{1}{\sqrt{2}} (|+\rangle_1 |-\rangle_2 + |-\rangle_1 |+\rangle_2) \hat{S_{1z}}$. Now, suppose we measure $\hat{S_{1z}}$ as observe $+\hbar/2$ where $\hat{S_{1z}}$ measures the spin of particle 1. Applying **postulate** 5 the quantum system is now in the state

$$|\psi'\rangle = |+\rangle_1 |-\rangle_2$$

So we know the outcome of a measurement of the second particle. This is the concept of entanglement. By measuring one particle we instantly know the state of the other particle.

Definition 4.1.3. A **spin singlet** is the fully entangled quantum state of a two particle spin-1/2 system written

$$\frac{1}{\sqrt{2}} (|+\rangle_1 |-\rangle_2 + |-\rangle_1 |+\rangle_2)$$

Definition 4.1.4. A multiparticle system is **entangled** if measurements of one particle are correlated with measurements of another particle.

Proposition 4.1.5. A multiparticle system is not entangled if it can be represented by one of the basis vectors.

Chapter 5

Position Representation

Definition 5.0.1. The **position representation** is an infinite dimensional vector space where each basis state $\mathbf{r}$ is a particular point in space.

Definition 5.0.2. A **position space wave function** is a function represented a state in position representation formed by taking the inner product of the position and the state.

$$\psi(\mathbf{r}) = \langle \mathbf{r}|\psi \rangle$$

Proposition 5.0.3. The inner product in position space is evaluated with an integral of the wave functions across all of space

$$\langle \phi(\mathbf{r})|\psi(\mathbf{r}) \rangle = \int \phi^*(\mathbf{r})\psi(\mathbf{r})\partial\mathbf{r}$$

Definition 5.0.4. The **probability density function** is function that can be used to calculate the probability of finding a particle in a particular region of space

$$\mathcal{P}(\mathbf{r}) = |\psi(\mathbf{r})|^2$$

$$\mathcal{P}_R = \int_R |\psi(\mathbf{r})|^2 d\mathbf{r}$$

Proposition 5.0.5. The expected value of an operator in position space is evaluated with the following integral

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle = \int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})\partial\mathbf{r}$$

Proposition 5.0.6. The standard deviation of an operator in position space is evaluated with the following integral

$$\Delta\hat{A} = \sqrt{\langle \psi | \hat{A}^2 | \psi \rangle - \langle \psi | \hat{A} | \psi \rangle^2} = \sqrt{\left(\int \psi^*(\mathbf{r})\hat{A}\psi^2(s\mathbf{r})\partial\mathbf{r} \right) - \left(\int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})\partial\mathbf{r} \right)^2}$$

5.1 Position and Momentum Operators

Position and momentum operators can be derived from classical laws.

Definition 5.1.1. The **position operator** in position representation is

$$\hat{r} = \mathbf{r}$$

Definition 5.1.2. The **momentum operator** is position representation is

$$\hat{p} = -i\hbar\frac{\partial}{\partial\mathbf{r}}$$

Proposition 5.1.3. The **free particle hamiltonian** is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{r})$$

Proposition 5.1.4. The **free particle energy eigenvalue equation** is given by

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2} + V(\mathbf{r}) \right)\varphi_E(\mathbf{r}) = E\varphi_E(\mathbf{r})$$

5.2   Infinite Square Well

Consider the one dimension potential defined by

$$V(x) = \begin{cases} \infty & x \leq 0 \\ 0 & 0 < x < L \\ \infty & x \geq L \end{cases}$$

Towards solving this equation we split it up intro the three sections they must be continuously differentiable across the boundaries so we aquire boundary conditions

$$\psi(x) = 0 \quad x \leq 0$$
$$\psi(x) = 0 \quad x \geq L$$
$$\psi(0) = 0, \psi(L) = 0$$

Thus we only need to solve the equation inside the well.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\varphi_E(x) = E\varphi_E(x)$$

$$\frac{d^2}{dx^2}\varphi_E(x) = -\frac{2mE}{\hbar^2}\varphi_E(x)$$

This is a standard differential equation. So the solution inside the box is given by

$$\varphi_E(x) = A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) + B\cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right)$$

We can apply our boundary conditions to find the energy eigenvalues.

Proposition 5.2.1. Infinite Square Well Energy Eigenvalues - The energy eigenvalues of the infinite square well are

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad n = 1, 2, 3, \ldots$$

Now we just need to normalize the equation to find the A coefficient.

Proposition 5.2.2. Infinite Square Well Energy Eigenstates - The energy eigenstates of the infinite square well are

$$\varphi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \quad n = 1, 2, 3, \ldots$$

Now we can apply Proposition 3.1.2 to model this system.

$$\psi(x,t) = \sum_{n=1}^{\infty} c_n e^{-iE_n t/\hbar}\varphi_n(x)$$

5.3   Finite Square Well

Consider the one dimension potential defined by

$$V(x) = \begin{cases} V_0 & x \leq -\frac{L}{2} \\ 0 & -\frac{L}{2} < x < \frac{L}{2} \\ V_0 & x \geq \frac{L}{2} \end{cases}$$

Proposition 5.3.1. Finite Square Well Energy Eigenvalues - The energies must be split up by even and odd solutions. There is no simple formula for the energies they must be solved for based on the height of the well.
Allowed Even Energies satisfy this equation:

$$\sqrt{\frac{2mE}{\hbar^2}}\tan\left(\frac{L}{2}\sqrt{\frac{2mE}{\hbar^2}}\right) = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$$

Allowed Odd Energies satisfy this equation:

$$-\sqrt{\frac{2mE}{\hbar^2}}\cot\left(\frac{L}{2}\sqrt{\frac{2mE}{\hbar^2}}\right) = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$$

Proposition 5.3.2. Finite Square Well Energy Eigenstates - The energy eigenstates of the infinite square well must also be split up by even and odd solution. And since the number of energies varies they must also be normalized for each case. **Even Energy Eigenstates** are given by

$$\varphi_E(x) = \begin{cases} Ae^{\sqrt{\frac{2m}{\hbar^2}(V_0-E)}x} & x \leq -\frac{L}{2} \\ B\cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) & -\frac{L}{2} < x < \frac{L}{2} \\ Ae^{-\sqrt{\frac{2m}{\hbar^2}(V_0-E)}x} & x \geq \frac{L}{2} \end{cases}$$

Odd Energy Eigenstates are given by

$$\varphi_E(x) = \begin{cases} Ae^{\sqrt{\frac{2m}{\hbar^2}(V_0-E)}x} & x \leq -\frac{L}{2} \\ C\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) & -\frac{L}{2} < x < \frac{L}{2} \\ -Ae^{-\sqrt{\frac{2m}{\hbar^2}(V_0-E)}x} & x \geq \frac{L}{2} \end{cases}$$

5.4   Infinite Cube Well

The solution for the infinite square well can be easily expanded into three dimensions.

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

$$\psi(x,y,z) = \psi(x)\psi(y)\psi(z)$$

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

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

$$-\frac{\hbar^2}{2m}\left(\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + \frac{1}{\psi(y)}\frac{\partial^2\psi(y)}{\partial y^2} + \frac{1}{\psi(z)}\frac{\partial^2\psi(z)}{\partial z^2}\right) = E$$

$$\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + \frac{1}{\psi(y)}\frac{\partial^2\psi(y)}{\partial y^2} + \frac{1}{\psi(z)}\frac{\partial^2\psi(z)}{\partial z^2} = -\frac{2mE}{\hbar^2}$$

We must split the energy into the contributions from each degree of freedom:

$$E = E_x + E_y + E_z$$

$$\frac{\partial^2\psi(x)}{\partial x^2} = -\frac{2mE_x}{\hbar^2}\psi(x)$$

$$\frac{\partial^2\psi(y)}{\partial y^2} = -\frac{2mE_y}{\hbar^2}\psi(y)$$

$$\frac{\partial^2\psi(z)}{\partial z^2} = -\frac{2mE_z}{\hbar^2}\psi(z)$$

The solution of each of these equations is identical to the one dimensional version.

$$\psi(x) = \sqrt{\frac{2}{a}}\sin\left(n_x\pi^2\frac{x}{a}\right) \quad E_x = \frac{n_x^2\pi^2\hbar^2}{2ma^2}$$

$$\psi(y) = \sqrt{\frac{2}{b}}\sin\left(n_y\pi^2\frac{y}{b}\right) \quad E_y = \frac{n_y^2\pi^2\hbar^2}{2mb^2}$$

$$\psi(z) = \sqrt{\frac{2}{c}}\sin\left(n_z\pi^2\frac{z}{c}\right) \quad E_z = \frac{n_z^2\pi^2\hbar^2}{2mc^2}$$

Therefore, the total energy is given by

$$E(n_x, n_y, n_z) = \frac{n_x^2\pi^2\hbar^2}{2ma^2} + \frac{n_y^2\pi^2\hbar^2}{2mb^2} + \frac{n_z^2\pi^2\hbar^2}{2mc^2}$$

$$E(n_x, n_y, n_z) = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

Chapter 6

Free Particle

We start with the same one dimensional Hamiltonian and energy eigenvalue equation we used in the last chapter.

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

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\varphi_E(x) = E\varphi_E(x)$$

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

Consider a zero potential everywhere.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\varphi_E(x) = E\varphi_E(x)$$

$$\frac{d^2}{dx^2}\varphi_E(x) = -\frac{2mE}{\hbar^2}\varphi_E(x)$$

6.1 Momentum and Position Space

Proposition 6.1.1. Free Particle Energy Eigenstates - The energy eigenstates for a free particle are

$$k^2 = \frac{2mE}{h^2}$$

$$\varphi_E(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{ikx}$$

Note that k can be positive or negative depending on the direction of the particles motion. Since the particle is not bound in space by a potential function so the momentum is not quantized. Also since these energy eigenstates continue out to infinity it is impossible to normalize one of the eigenstates so a free particle is always in a superposition of eigenstates. Consider the momentum of each of these eigenstates

$$\hat{p}\varphi_E(x) = \left(i\hbar\frac{d}{dx}\right)\frac{1}{\sqrt{2\pi\hbar}}e^{ikx} = \hbar k\frac{1}{\sqrt{2\pi\hbar}}e^{ikx}$$

Proposition 6.1.2. Free Particle Momentum Eigenstates - The momentum eigenstates for a free particle are

$$p = \hbar k = \pm\hbar\sqrt{\frac{2mE}{h^2}}$$

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

Definition 6.1.3. The **de Broglie Wavelength** of a particle with momentum p is

$$\lambda = \frac{h}{p}$$

Definition 6.1.4. A **momentum space wave function** is a function representing a state in momentum space formed by taking the inner product across all of space.

$$\phi(p) = \langle p|\psi\rangle$$

We can used the momentum and position operators to derive a formula to convert between momentum and position space.

Proposition 6.1.5. The Fourier transform of a momentum space wave function is the position space wave function.

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p) e^{ipx/\hbar} dp$$

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x) e^{-ipx/\hbar} dx$$

6.2 Wave Packets

Definition 6.2.1. The **Gaussian momentum space wave function** with expected momentum p_0 and uncertainty β is

$$\phi(p) = \left(\frac{1}{2\pi\beta^2}\right)^{1/4} e^{-(p-p_0)^2/4\beta^2}$$

Proposition 6.2.2. The probability distribution of the Gaussian momentum space wave function is a Gaussian distribution.

$$(P)(p) = |\phi(p)|^2 = \frac{e^{-(p-p_0)^2/2\beta^2}}{\beta\sqrt{2\pi}}$$

hence the expected value and standard deviation are

$$\langle p \rangle = p_0$$

$$\Delta p = \beta$$

Definition 6.2.3. The **Gaussian position space wave function** is

$$\psi(x, t) = \frac{\sqrt{2\beta}}{\sqrt{\hbar\gamma\sqrt{2\pi}}} e^{ip_0(x - \frac{p_0}{2m}t)} e^{-(x-\frac{p_0}{m}t)^2\beta^2/\hbar^2\gamma}$$

with parameters

$$\gamma = 1 + \frac{it}{\tau}$$

$$\tau = \frac{m\hbar}{2\beta^2}$$

Proposition 6.2.4. The probability distribution of the Gaussian momentum space wave function is a Gaussian distribution.

$$\mathcal{P}(x) = |\psi(x)|^2 = \frac{e^{-(x-\frac{p_0}{m}t)^2 / \frac{2\hbar^2}{4\beta^2}\left(1 + \left(\frac{2\beta^2 t}{m\hbar}\right)^2\right)}}{\frac{\hbar\sqrt{2\pi}}{2\beta}\sqrt{1 + \left(\frac{2\beta^2 t}{m\hbar}\right)^2}}$$

hence the expected value and standard deviation are

$$\langle x \rangle = \frac{p_0}{m}t$$

$$\Delta x = \frac{\hbar}{2\beta}\sqrt{1 + \left(\frac{2\beta^2 t}{m\hbar}\right)^2}$$

Proposition 6.2.5. The Gaussian wave packet has the minimum possible uncertainty

$$\Delta x \Delta p = \frac{\hbar}{2}\sqrt{1 + \left(\frac{2\beta^2 t}{m\hbar}\right)^2}$$

Proposition 6.2.6. The **uncertainty principle** for position and momentum is

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

6.3 Scattering and Tunneling

6.4 Extension to Three Dimensions

6.5 Two Body Hamiltonian

Definition 6.5.1. The **two body Hamiltonian** is given by

$$\hat{H} = \frac{\mathbf{p}_1}{2m_1} + \frac{\mathbf{p}_2}{2m_2} + V(\mathbf{r}_1, \mathbf{r}_2)$$

This Hamiltonian is similar to the Hamiltonian used for a system of one particle. Assuming that the potential is only dependent of the distance between the two particles $|\mathbf{r}_1 - \mathbf{r}_2|$, we can split the Hamiltonian into center of mass and relative motion as we would do in classical mechanics.

Definition 6.5.2. The **center of mass position** is given by

$$\mathbf{R} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}$$

Definition 6.5.3. The **relative position** is given by

$$\mathbf{r} = \mathbf{r_2} - \mathbf{r_1}$$

With these position vectors we can define momentum for the center of mass motion and the relative motion.

Definition 6.5.4. The **total momentum** is simply the sum of the individual momentum.

$$\mathbf{P} = \mathbf{p_1} + \mathbf{p_2}$$

Definition 6.5.5. The **relative momentum** is the weighted difference between the individual momentum.

$$\mathbf{p}_{rel} = \frac{m_1 \mathbf{p_2} - m_2 \mathbf{p_1}}{m_1 + m_2}$$

We will also define the relative mass and total mass

Definition 6.5.6. The **total mass** is simply the sum of the individual masses

$$M = m_1 + m_2$$

Definition 6.5.7. The **relative mass** is the average mass between the two particles

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Proposition 6.5.8. Assuming the potential is only dependent on the distance between the two particles $|\mathbf{r}_1 - \mathbf{r}_2|$, the two body Hamiltonian can be split into the center of mass Hamiltonian $\hat{H}_{CM}$ and the relative motion Hamiltonian $\hat{H}_{rel}$

$$\hat{H} = \hat{H}_{CM} + \hat{H}_{rel}$$

$$\hat{H}_{CM} = \frac{\mathbf{P}^2}{2M}$$

$$\hat{H}_{rel} = \frac{\mathbf{P}_{rel}^2}{2\mu} + V(r)$$

The next chapter will focus on solving the relative motion Hamiltonian towards developing a complete model for the hydrogen atom.

Chapter 7

Angular Momentum

Towards finding a general solution for the two body system we will solve the relative Hamiltonian and the radial Hamiltonian separately.

$$\hat{H}_{rel}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$\left(\frac{\mathbf{P}_{rel}^2}{2\mu} + V(r)\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

The relative motion can be further divided into angular and radial components. To do this we will write the Hamiltonian and the operators for angular momentum in terms of spherical coordinates.

$$x = r\sin\theta\cos\phi$$

$$y = r\sin\theta\sin\phi$$

$$z = r\cos\theta$$

In spherical coordinates, the relative energy eigenvalue equation becomes

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi) + V(r)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

The angular momentum operator for the angular component of this equation is the same as the operators for spin that we discussed in the earlier sections of this book.

Definition 7.0.1. The **angular momentum operators** in spherical coordinates are

$$L_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)$$

$$L_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$L_z\left|\ell, m\right\rangle = m\hbar\left|\ell, m\right\rangle$$

Definition 7.0.2. The **square angular momentum operator** in spherical coordinates is

$$\mathbf{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$\mathbf{L}^2\left|\ell, m\right\rangle = \ell(\ell+1)\hbar^2\left|\ell, m\right\rangle$$

Definition 7.0.3. The **orbital angular momentum quantum number** ℓ measures the magnetud of the angularm momentum vector with the following possible values

$$\ell = 0, 1, 2, 3, 4, \ldots$$

Definition 7.0.4. The **orbital magnetic quantum number** m measures the magnitude of the z-component of the angular momentum with the following possible values

$$m = -\ell, -\ell + 1, \ldots, -1, 0, 1, \ldots, \ell - 1, \ell$$

With these definitions we can rewrite the energy eigenvalue equation.

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\mathbf{L}^2\right]\psi(r,\theta,\phi) + V(r)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

All of the angular components of this energy eigenvalue equation is contained in the $\mathbf{L}^2$ operator. We will assume that the total relative Hamiltonian can be written in terms of it's angular dependence and it's radial dependence.

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

plugging this into the energy eigenvalue equations yields us with

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{dR(r)}{\partial r}\right) - \frac{2\mu}{\hbar^2}(E - V(r))r^2 = \frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\mathbf{L}^2 Y(\theta,\phi)$$

The left hand side of this equation is the radial component and the right hand side is the angular component. We can even further isolate the θ dependence from the ϕ dependence to solve the azimuthal component separately.

$$Y(\theta,\phi) - \Theta(\theta)\Phi(\phi)$$

7.1 Ring Motion

Solving for just the ϕ dependence the eigenvalue equation becomes

$$-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial \phi^2}\Phi(\phi) = E\Phi(\phi)$$

The solution to this energy eigenvalue equation depends only on the quantum number m. And the energy eigenvalues depend on the absolute value of m. The eigenvalues of the energy are also eigenvalues of the L_z operator.

$$L_z\left|m\right\rangle = m\hbar\left|m\right\rangle$$
$$L_z\Phi(\phi) = m\hbar\Phi(\phi)$$

Proposition 7.1.1. Azimuthal Motion Eigenvalues - The energy eigenvalues of a particle on a ring are

$$E_{|m|} = m^2\frac{\hbar^2}{2I}$$

Proposition 7.1.2. Azimuthal Motion Eigenstates - The energy eigenstates of a particle on a ring are

$$\left|m\right\rangle = \Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

7.2 Polar Motion

With the azimuthal solution of the hydrogen atom solved by the last section we can start working towards the polar component of the angular solution. We will start with the Hamiltonian from earlier isolating the angular component $Y(\theta,\phi)$.

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi) = E_{sphere}Y(\theta,\phi)$$

which can be rewritten in terms of the angular momentum operator $\mathbf{L}^2$

$$\frac{\mathbf{L}^2}{2I}Y(\theta,\phi) = E_{sphere}Y(\theta,\phi)$$

Using the quantum numbers from the azimuthal solution we can find solutions to this differential equation. The solution involves Legendre polynomials.

Definition 7.2.1. The **Legendre polynmials** are polynomials of degree ℓ, denoted $P_\ell(z)$ that appear in spherically symmetric systems. They are defined with Rodrigues' formula

$$P_\ell(z) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{d\ell}(z^2 - 1)^\ell$$

Proposition 7.2.2. The Legendre polynomials are normalized to the squared norm $2/(2\ell + 1)$.

$$\int_{-1}^{1} P_k(z)P_\ell(z)dz = \frac{2}{2\ell + 1}\delta_{k\ell}$$

To include the orbital angular momentum, the associated Lagendre polynomials are used.

Definition 7.2.3. The **associated Legendre polynomials** are a set of related polynomials solve from the degree ℓ Legendre polynomial for an integer m.

$$P_\ell^m(z) = P_\ell^{-m}(z) = (1 - z^2)^{m/2}\frac{d^m}{dz^m}P_\ell(z)$$

Proposition 7.2.4. The associated Legendre polynomials are normalized to a term dependent on ℓ and m.

$$\int_{-1}^{1} P_k^m(z)P_\ell^m(z)dz = \frac{2}{2\ell + 1}\frac{(\ell + m)!}{(\ell - m)!}\delta_{k\ell}$$

Proposition 7.2.5. Polar Motion Eigenstates - The energy eigenstates of the polar component of spherical motion are

$$\Theta_\ell^m(\theta) = (-1)^m \frac{2\ell + 1}{2}\frac{(\ell - m)!}{(\ell + m)!}P_\ell^m(\cos\theta)$$

Applying the normalization term to the Legendre polynomials we find the polar solution.

Proposition 7.2.6. Polar Motion Eigenvalues - The energy eigenvalues of the polar component of spherical motion are

$$E_\ell = \frac{\hbar^2}{2I}\ell(\ell + 1)$$

7.3   Spherical Harmonics

Combining the polar and azimuthal solution we can find the total angular solution.

Proposition 7.3.1. Spherical Harmonic Eigenstates - The energy eigenstates of the angular solution $Y(\theta, \phi)$ are

$$Y_\ell^m(\theta, \phi) = (-1)^{(m+|m|)/2}\sqrt{\frac{2\ell + 1}{4\pi}\frac{(\ell - |m|)!}{(\ell + |m|)!}}P_\ell^m(\cos\theta)e^{im\phi}$$

Proposition 7.3.2. Spherical Harmonic Eigenvalues - the energy eigenvalues of the angular solution are

$$E_{sphere} = \frac{\hbar^2}{2I}\ell(\ell + 1)$$

Proposition 7.3.3. The spherical harmonic eigenstates are orthonormal

$$\langle \ell_1, m_1 | \ell_2, m_2 \rangle = \int_0^{2\pi}\int_0^{\pi} Y_{\ell_1}^{m_1*}(\theta, \phi)Y_{\ell_2}^{m_2}(\theta, \phi)\sin\theta d\theta d\phi = \delta_{\ell_1, \ell_2}\delta_{m_1, m_2}$$

Proposition 7.3.4. The spherical harmonic eigenstates form a complete basis for any function $\psi(\theta, \phi)$ on the sphere.

$$\psi(\theta, \phi) = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} c_{\ell m}Y_\ell^m(\theta, \phi)$$

$$c_{\ell m} = \langle \ell m | \psi \rangle = \int_0^{2\pi}\int_0^{\pi} Y_\ell^{m*}(\theta, \phi)\psi(\theta\phi)\sin\theta d\theta d\phi$$

Chapter 8

Hydrogen Atom

The angular solutions we found last chapter are a component of the total solution for a hydrogen atom. Up until this point we haven't specified what potential governs the two particles in our system. The only assumption we made was that is was an attractive potential.

$$\left[-\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + V(r) + \ell(\ell+1)\frac{\hbar^2}{2\mu r^2} \right] R(r) = ER(r)$$

8.1 Radial Motion

We will consider the solution of the Schrödinger for the Coulomb potential. This solution is a model of a hydrogen atom.

Definition 8.1.1. The **Coulomb potential** is the attractive potential responsible for the attraction in an atom with one electron, where Z is the number of protons in the nucleus.

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

Applying our choice of potential to the radial Hamiltonian we find that the radial differential equation is

$$\left[-\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{Ze^2}{4\pi\varepsilon_0 r} + \ell(\ell+1)\frac{\hbar^2}{2\mu r^2} \right] R(r) = ER(r)$$

We can rewrite this as an effective potential problem by introducing the term $u(r) = rR(r)$.

$$\frac{\hbar^2}{2\mu} \frac{d^2 u}{dr^2} + \left[-\frac{Ze^2}{4\pi\varepsilon_0 r} + \ell(\ell+1)\frac{\hbar^2}{2\mu r^2} \right] u = Eu$$

$$V_{eff}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \ell(\ell+1)\frac{\hbar^2}{2\mu r^2}$$

$$\frac{\hbar^2}{2\mu} \frac{d^2 u}{dr^2} + V_{eff}(r)u = Eu$$

Definition 8.1.2. The **Bohr radius** denoted a is the length scale of the hydrogen atom.

$$a = \frac{4\pi\varepsilon_0 \hbar^2}{\mu Z e^2}$$

We will used the Bohr radius to write a dimensionless coordinate ρ.

$$\rho = \frac{r}{a} = \frac{r}{\frac{4\pi\varepsilon_0 \hbar^2}{\mu Z e^2}}$$

$$r = \frac{4\pi\varepsilon_0 \hbar^2}{\mu Z e^2} \rho$$

Definition 8.1.3. The **Rydberg energy** is the first energy level an atom.

$$\mathrm{Ryd} = \frac{\mu}{2\hbar^2} \left(\frac{Ze^2}{4\pi\varepsilon_0} \right)^2$$

We will use the Rydberg energy to write a dimensionless energy γ.

$$E = -\text{Ryd}\gamma^2 = -\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\gamma^2$$

$$\gamma = \sqrt{\frac{-E}{\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2}} = \frac{1}{n}$$

Now with these definition we can rewrite our eigenvalue equation in dimensionless terms.

$$\frac{d^2u(\rho)}{d\rho^2} + \left(\frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2} - \gamma^2\right)u(\rho) = 0$$

We solve this differential equation with a recursion relation to define the polynomial $H(\rho)$.

$$H(\rho) = \sum_{j=0}^{\infty} c_j\rho^j$$

$$u(\rho) = \rho^{\ell+1}\left(\sum_{j=0}^{\infty} c_j\rho^j\right)e^{-\gamma\rho}$$

$$\frac{c_j}{c_{j-1}} = \frac{2\left[\gamma(j+\ell) - 1\right]}{j^2 + j(2\ell+1)}$$

This series must terminate, otherwise H grows to infinity. This only occurs for quantized values $n = 1, 2, 3, 4, \ldots$.

In summary, the quantum numbers for an atom are

$$n = 1, 2, 3, \ldots$$

$$\ell = 0, 1, 2, \ldots, n-1$$

$$m = -\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell$$

Proposition 8.1.4. Radial Energy Eigenvalues - The radial energy eigenvalues of an atom are

$$E_n = -\frac{\mu}{2\hbar^2 n^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2$$

Proposition 8.1.5. Radial Energy Eigenstates - The radial energy eigenstates of an atom are

$$R_{n\ell}(r) = \left(\frac{r}{a}\right)^{\ell}e^{-r/na}H\left(\frac{r}{a}\right)$$

8.2 Full Atomic Solutions

Now with the radial and angular components solved we can write the complete wave-function and eigenvalues for the atom.

$$|n\ell m\rangle = \psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}Y_\ell^m(\theta, \phi)$$

The three measurable operators are energy H, total angular momentum $\mathbf{L}^2$ and angular momentum in the z direction L_z.

$$H\psi(r, \theta, \phi) = \frac{\mu}{2\hbar^2 n^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\psi(r, \theta, \phi)$$

$$\mathbf{L}^2\psi(r, \theta, \phi) = \ell(\ell+1)\hbar^2\psi(r, \theta, \phi)$$

$$L_z\psi(r, \theta, \phi) = m\hbar\psi(r, \theta, \phi)$$

Proposition 8.2.1. The following are radial expectation values for the hydrogen atom

$$\langle r \rangle = \frac{3a}{2}\left[3n^2 - \ell(\ell+1)\right]$$

$$\langle r^2 \rangle = \frac{a^2 n^2}{2}\left[5n^2 + 1 - 3\ell(\ell+1)\right]$$

$$\langle \frac{1}{r} \rangle = \frac{1}{an^2}$$

$$\langle \frac{1}{r^2} \rangle = \frac{1}{a^2 n^3(\ell + \frac{1}{2})}$$

$$\langle \frac{1}{r^3} \rangle = \frac{1}{a^3 n^3 \ell(\ell + \frac{1}{2})(\ell+1)}$$

Chapter 9

Harmonic Oscillator

The harmonic oscillator is a very common system in classical mechanics. The system consists of an object with mass m and a restoring force:

$$F = -kx$$

Using newtons second law we can derive a differential equation. We will define the fundamental frequency ω

$$\omega = \sqrt{\frac{k}{m}}$$

Definition 9.0.1. The **harmonic oscillator Hamiltonian** is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

Plugging this into the Schrodinger equation we find the following differential equation

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi_E(x)}{dx^2} + \frac{1}{2}m\omega^2 x^2\varphi_E(x) = E\varphi_E(x)$$

While it is possible to solve this differential equation directly. It is much easier to find a solution by introducing raising and lowering operators.

9.1 Raising and Lowering Operators

Definition 9.1.1. The **raising operator** $\hat{a}^\dagger$ and the **lowering operator** $\hat{a}$ are defined as

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - i\frac{\hat{p}}{m\omega}\right)$$

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + i\frac{\hat{p}}{m\omega}\right)$$

Proposition 9.1.2. The following can be used to relate the Hamiltonian to the raising and lowering operators.

$$\hat{a}\hat{a}^\dagger = \hat{a}^\dagger\hat{a} + 1$$

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

$$\hat{H} = \hbar\omega(\hat{a}\hat{a}^\dagger - \frac{1}{2})$$

As the names of these operators implies they can be used to iterate across the energy eigenstates of the harmonic oscillator. if the lowering operator is applied to the ground state then the result is zero.

Proposition 9.1.3. The ground state of the harmonic oscillator has an eigenvalue of $\frac{1}{2}$ and is eliminated by the lowering operator.

$$\hat{a}\left|E_0\right\rangle = 0$$

$$\hat{H}\left|E_0\right\rangle = \frac{1}{2}\left|E_0\right\rangle$$

Proposition 9.1.4. The raising and lowering operators have the following properties when acting on energy eigenstates

$$\hat{a}^\dagger \left| n \right\rangle = \sqrt{n+1} \left| n+1 \right\rangle$$

$$\hat{a} \left| n \right\rangle = \sqrt{n} \left| n-1 \right\rangle$$

$$\left| n \right\rangle = \frac{1}{\sqrt{n!}} (\hat{a}^\dagger)^n \left| 0 \right\rangle$$

Proposition 9.1.5. Harmonic Oscillator Eigenvalues - The harmonic oscillator energy eigenvalues are

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

Proposition 9.1.6. Harmonic Oscillator Eigenstates - The harmonics oscillator energy eigenstates are

$$\varphi_0(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}$$

$$\varphi_n(x) = \frac{1}{\sqrt{n!}} \left[\sqrt{\frac{m\omega}{2\hbar}} \left(x - \frac{\hbar}{m\omega} \frac{d}{dx} \right) \right]^n \varphi_0(x)$$

Proposition 9.1.7. The **position** operator and the **momentum** operator can be represented in terms of the raising and lowering operators.

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

$$\hat{p} = i\sqrt{\frac{\hbar m\omega}{2}} \left(\hat{a}^\dagger - \hat{a} \right)$$

9.2   Harmonic Dirac Notation

The operators used to derive the eigenstates and eigenvalues of the harmonic oscillator can be represented as infinite matrices in the basis defined by the energy eigenstates.

Proposition 9.2.1. Dirac Harmonic Oscillator Hamiltonian - the Hamiltonian for the harmonic oscillator in dirac notation is given by

$$\hat{H} \left| n \right\rangle = E_n \left| n \right\rangle$$

$$\left\langle m \right| \hat{H} \left| n \right\rangle = \left(n + \frac{1}{2} \right) \hbar\omega \left\langle m | n \right\rangle = \left(n + \frac{1}{2} \right) \hbar\omega \delta_{m,n}$$

$$\hat{H} = \begin{pmatrix} \frac{1}{2}\hbar\omega & 0 & 0 & \dots \\ 0 & \frac{3}{2}\hbar\omega & 0 & \dots \\ 0 & 0 & \frac{5}{2}\hbar\omega & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Proposition 9.2.2. Dirac Raising and Lowering Operators - the raising an lowering operators can be written as matrices with the energy eigenstates as a basis.

$$\left\langle m \right| \hat{a}^\dagger \left| n \right\rangle = \sqrt{n+1} \left\langle m | n+1 \right\rangle = \sqrt{n+1} \delta_{m,n+1}$$

$$\left\langle m \right| \hat{a}^\dagger \left| n \right\rangle = \sqrt{n} \left\langle m | n-1 \right\rangle = \sqrt{n} \delta_{m,n-1}$$

$$\hat{a}^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 & \dots \\ \sqrt{1} & 0 & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & 0 & \dots \\ 0 & 0 & \sqrt{3} & 0 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad \hat{a} = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & \dots \\ 0 & 0 & 0 & \sqrt{3} & \dots \\ 0 & 0 & 0 & 0 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Proposition 9.2.3. Dirac Position and Momentum Operators - the position and momentum operators can be written as matrices withe the energy eigenstates as a basis.

$$\langle m| \hat{x} |n\rangle = \sqrt{\frac{\hbar}{2m\omega}} \left(\sqrt{n+1} \langle m|n+1\rangle + \sqrt{n} \langle m|n-1\rangle \right) = \sqrt{\frac{\hbar}{2m\omega}} \left(\sqrt{n+1}\delta_{m,n+1} + \sqrt{n}\delta_{m,n-1} \right)$$

$$\langle m| \hat{p} |n\rangle = i\sqrt{\frac{\hbar m\omega}{2}} \left(\sqrt{n+1} \langle m|n+1\rangle - \sqrt{n} \langle m|n-1\rangle \right) = i\sqrt{\frac{\hbar m\omega}{2}} \left(\sqrt{n+1}\delta_{m,n+1} - \sqrt{n}\delta_{m,n-1} \right)$$

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \cdots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \vdots & \vdots & \vdots & & \ddots \end{pmatrix}, \quad \hat{p} = i\sqrt{\frac{\hbar m\omega}{2}} \begin{pmatrix} 0 & -\sqrt{1} & 0 & 0 & \cdots \\ \sqrt{1} & 0 & -\sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & -\sqrt{3} & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \vdots & \vdots & \vdots & & \ddots \end{pmatrix}$$

Since we know the eigenstates of the hamiltonian finding the time dependence of the harmonic oscillator is very simple. However, if the particle is charged then energy may be radiated via electromagnetic waves. To determine when this occurs we will calculate the expected position of two states.

$$|\psi(t)\rangle = \sum_{n=0}^{\infty} c_n e^{-i(n+\frac{1}{2})\omega t} |n\rangle$$

Consider a superposition of two energy eigenstates $|n\rangle$ and $|m\rangle$.

Theorem 9.2.4. Selection Rule for electric dipole radiation in a harmonic oscillator - The expected position is only nonzero for adjacent states.

$$m \neq n+1 \text{ and } m \neq n-1 \Rightarrow \langle \hat{x} \rangle = 0$$

Chapter 10

Perturbation Theory

Definition 10.0.1. A Hamiltonian is **exactly solved** if an exact representation of the energy eigenvalues and energy eigenvectors can be found.

In some problems we only need to find an approximation of the real solution. One method we can use to go this is the

Definition 10.0.2. A **perturbation** is a system consisting of a small change from a exactly solved system $\hat{H}_0$. $\hat{H}'$ is the small change that is applied. The solution of a perturbation is found with an infinite series.

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + E_n^{(3)} + \dots$$

$$|n\rangle = \left|n^{(0)}\right\rangle + \left|n^{(1)}\right\rangle + \left|n^{(2)}\right\rangle + \left|n^{(3)}\right\rangle + \dots$$

10.1   Non-degenerate Perturbation Theory

Proposition 10.1.1. First Order Perturbation Eigenvalues - The first order correction for the levels of a perturbation are given by

$$E_n^{(1)} = \left\langle n^{(0)}\right| \hat{H}' \left|n^{(0)}\right\rangle$$

Proposition 10.1.2. First Order Perturbation Eigenstates - The first order correction for the eigenstates of a perturbation is given by

$$\left|n^{(1)}\right\rangle = \sum_{m \neq n} \frac{\left\langle m^{(0)}\right| \hat{H}' \left|n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|m^{(0)}\right\rangle$$

Proposition 10.1.3. Second Order Perturbation Eigenvalues - The second order correction for the eigenstates of a perturbation is given by

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left|\left\langle m^{(0)}\right| \hat{H}' \left|n^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}}$$

Proposition 10.1.4. Second Order Perturbation Eigenstates - The second order correction for the eigenstates of a perturbation is given by

$$\left|n^{(2)}\right\rangle = \sum_{m \neq n} \sum_{k \neq n} \frac{\left\langle m^{(0)}\right| \hat{H}' \left|k^{(0)}\right\rangle \left\langle k^{(0)}\right| \hat{H}' \left|n^{(0)}\right\rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_k^{(0)}\right)} \left|m^{(0)}\right\rangle$$

$$- \sum_{m \neq n} \frac{\left\langle m^{(0)}\right| \hat{H}' \left|n^{(0)}\right\rangle \left\langle n^{(0)}\right| \hat{H}' \left|n^{(0)}\right\rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} \left|m^{(0)}\right\rangle - \frac{1}{2} \sum_{m \neq n} \frac{\left|\left\langle m^{(0)}\right| \hat{H}' \left|n^{(0)}\right\rangle\right|^2}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} \left|n^{(0)}\right\rangle$$

Proposition 10.1.5. The first order correction to the energy eigenvalue of the ground state always exact or an overestimate.

Proposition 10.1.6. The second order correction to the energy eigenvalue of the ground state is always negative.

10.2 Degenerate Perturbation theory

Perturbation theory does not work for degenerate energies. To resolve this issue we will find a new energy eigenbasis of $\hat{H}_0$ such that
$$\left\langle m^{(0)}\hat{H}' \left| n^{(0)} \right\rangle \right| = 0$$

For any two degenerate states m and n. The perturbation Hamiltonian $\hat{H}'$ may split the degeneracy. However, since $\hat{H}'$ is not generally diagonalizable we will consider $\hat{H}'$ in the subspace of each degenerate energy.

Definition 10.2.1. A **conservation law** is an operator $\hat{A}$ such that $[\hat{H}_0, \hat{A}] = [\hat{H}', \hat{A}] = 0$.

Theorem 10.2.2. Degenerate Perturbation Subspace Theorem - If a conservation law exists then perturbation theory can be used by finding an energy eigenbasis of $\hat{H}_0$ such that $\left\langle m^{(0)}\hat{H}' \left| n^{(0)} \right\rangle \right| = 0$ for any two degenerate states m and n. To find such an eigenbasis, apply the following for each degeneracy:

1. Consider the subspace of degenerate eigenstates $|n\rangle$.

2. Find the matrix of $\hat{H}'$ in in this subspace.

3. Diagonalize the matrix to find a new basis $|n'\rangle$.

4. The new basis elements are simultaneous eigenstates of $\hat{H}'$ and $\hat{H}_0$.

5. Repeat this process for each degeneracy.

Chapter 11

Hydrogen Atomic Perturbations

Our current model of the hydrogen atom does not account for relatavistic effects, spin, the size of the nucleous, or magnetism.

Definition 11.0.1. The **fine structure** of an atom is the effects of relativity and spin on an atom.

Definition 11.0.2. The **hyperfine structure** of an atom is the effects of magnetism on an atom

11.1 General Angular Momentum

Definition 11.1.1. General Angular Momentum is an operator denoted $\hat{\mathbf{J}}$ with eigenvalues $|j, m_j\rangle$ for $j = 0, 1, 2, \ldots$ and $m_j = -j, -j + 1, \ldots, 0, \ldots, j - 1, j$ that is used to generalize the properties of angular momentum.

Proposition 11.1.2. $|j, m_j\rangle$ are simultaneous eigenstates of $\hat{J}^2$ and $\hat{J}_z$.

$$[\hat{J}^2, \hat{J}_z] = 0, \quad [\hat{J}^2, \hat{J}_x] = 0, \quad [\hat{J}^2, \hat{J}_y] = 0$$

Proposition 11.1.3. The operators $\hat{J}^2$ and $\hat{J}_z$ have the following eigenvalues

$$\hat{J}^2 |j, m_j\rangle = \hbar^2 j(j + 1) |j, m_j\rangle$$

$$\hat{J}_z |j, m_j\rangle = \hbar m_j |j, m_j\rangle$$

Proposition 11.1.4. The angular momentum components do not commute.

$$[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z, \quad [\hat{J}_y, \hat{J}_z] = i\hbar\hat{J}_x, \quad [\hat{J}_z, \hat{J}_x] = i\hbar\hat{J}_y$$

Definition 11.1.5. The **angular momentum latter operators** are the operators $\hat{J}_+$ and $\hat{J}_-$ defined

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y$$

$$\hat{J}_- = \hat{J}_x - i\hat{J}_y$$

Proposition 11.1.6. The latter operators are Hermitian conjugates.

$$\hat{J}_+^\dagger = \hat{J}_-$$

Proposition 11.1.7. The latter operators commute with $\hat{J}^2$

$$[\hat{J}^2, \hat{J}_\pm] = 0$$

Proposition 11.1.8. The latter operators do not commute with each other

$$[\hat{J}_+, \hat{J}_-] = 2\hbar\hat{J}_z$$

Proposition 11.1.9. The latter operators do not commute with $\hat{J}_z$

$$[\hat{J}_z, \hat{J}_+] = \hbar\hat{J}_+$$

$$[\hat{J}_z, \hat{J}_-] = \hbar\hat{J}_-$$

Proposition 11.1.10. The angular momentum latter operators can be used to raise and lower eigenstates.

$$\hat{J}_+ |j, m_j\rangle = \hbar\sqrt{j(j + 1) - m_j(m_j + 1)} |j, m_j + 1\rangle$$

$$\hat{J}_- |j, m_j\rangle = \hbar\sqrt{j(j + 1) - m_j(m_j - 1)} |j, m_j - 1\rangle$$

$$\hat{J}_+ |j, j\rangle = 0$$

$$\hat{J}_- |j, -j\rangle = 0$$

11.2 Coupling of Angular Momentum

For a system consisting of two angular momentum operators we can find a basis consisting of eigenstates of the combined angular momentum.

Definition 11.2.1. The **total angular momentum** for two angular momentum operators $\mathbf{J}_1$ and $\mathbf{J}_2$ is the operator

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$$

Definition 11.2.2. An **uncoupled basis** is a basis of a system of angular momentum that consists of eigenstates of the original separate momentum operators. For two angular momentum operators $\mathbf{J}_1$ and $\mathbf{J}_2$ the uncoupled basis is written $|j_1, j_2, m_1, m_2\rangle$ in terms of the quantum numbers j_1, m_1, j_2, and m_2.

Definition 11.2.3. An **coupled basis** is a basis of a system of angular momentum that consists of eigenstates of the total angular momentum written $|J, M\rangle$ in terms of to total quantum numbers J and M.

Proposition 11.2.4. The min and max value of J are determined by the values of j_1 and j_2

$$J^{max} = j_1 + j_2$$

$$J^{min} = |j_1 - j_2|$$

$$M = m_1 + m_2$$

Definition 11.2.5. The **Clebsch-Gordan Coefficients** are the terms $C^{j_1,j_2,J}_{m_1,m_2,M}$ that can be used to write the coupled basis in terms of the uncoupled basis.

$$C^{j_1,j_2,J}_{m_1,m_2,M} = \langle j_1, j_2, m_1, m_2 | J, M \rangle$$

$$|J, M\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} C^{j_1,j_2,J}_{m_1,m_2,M} |j_1, j_1, m_1, m_2\rangle$$

$$|j_1, j_2, m_1, m_2\rangle = \sum_{J=|j_1-j_2|}^{j_1+j_2} C^{j_1,j_2,J}_{m_1,m_2,M} |J, M\rangle$$

Proposition 11.2.6. The Clebsch-Gordan Coefficients are always real and $C^{j_1,j_2,J}_{m_1,m_2,M} = 0$ for all $m_1 + m_2 \neq M$.

Theorem 11.2.7. Procedure for Finding an Uncoupled Basis

1. The highest element on the ladder is $|J^{max}, J^{max}\rangle = |j_1, j_2, j_1, j_2\rangle$

2. Apply $\hat{J}_- = \hat{J}_{1-} + \hat{J}_{2-}$ to find $\left|J^{max}, \hat{J}^{max} - 1\right\rangle$.

3. Use orthogonality to find $\left|\hat{J}^{max} - 1, \hat{J}^{max} - 1\right\rangle$.

11.3 Hyperfine Structure

The hyper fine structure is a perturbation of the hydrogen atom. It is defined in terms of the magnetic moments of the electron and proton.

Definition 11.3.1. The **electron magnetic moment** is

$$\mu_e = -\frac{g_e e}{2m_e}\mathbf{S} = -\frac{g_e \mu_B}{\hbar}\mathbf{S}$$

where $\mathbf{S}$ is the electron spin, $g_e \approx 2$ is the gyro-magnetic ratio, and $\mu_B = \frac{e\hbar}{2m_e}$ is the **Bohr magneton**.

Definition 11.3.2. The **nuclear magnetic moment** is

$$\mu_p = -\frac{g_p e}{2m_p}\mathbf{I} = -\frac{g_p \mu_N}{\hbar}\mathbf{I}$$

where $\mathbf{I}$ is the electron spin, $g_p \approx 5.59$ is the gyro-magnetic ratio, and $\mu_N = \frac{e\hbar}{2m_p}$ is the **nuclear magneton**.

Definition 11.3.3. The **Hyperfine perturbation Hamiltonian** is

$$\hat{H}'_{hf} = \mu_{\mathbf{p}}\frac{\mu_0}{4\pi}\frac{e\mathbf{L}}{mr^3} + \frac{\mu_0}{4\pi}\frac{1}{r^3}\left[\mu_{\mathbf{e}} \cdot \mu_{\mathbf{p}} - 3\frac{(\mu_{\mathbf{e}} \cdot \mathbf{r})(\mu_{\mathbf{p}} \cdot \mathbf{r})}{r^2}\right] - \frac{\mu_0}{4\pi}\frac{8\pi}{3}\mu_{\mathbf{e}} \cdot \mu_{\mathbf{p}}\delta(\mathbf{r})$$

Proposition 11.3.4. When $\ell = 0$ the Hyperfine structure simplifies

$$\hat{H}'_{hf} = \frac{A}{\hbar}\hat{S} \cdot \hat{I}, \quad A = \frac{2\mu_0}{3}(g_e\mu_B)(g_p\mu_N)|\psi(\mathbf{r} = 0)|^2$$

Proposition 11.3.5. The coupled basis for the angular momentum of the hydrogen atom is

$$|E_1\rangle = |++\rangle, \quad |E_2\rangle = |--\rangle, \quad |E_3\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle), \quad |E_4\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle)$$

where the first quantum number in the uncoupled basis is for the spin of the electron and the second quantum number is for the spin of the nucleus.

Definition 11.3.6. The **total angular momentum of the hydrogen atom** is defined in terms of the angular momentum of the electron and nucleus.

$$\mathbf{F} = \mathbf{S} + \mathbf{I}$$

Proposition 11.3.7. The hyper-fine perturbation Hamiltonian can be written in terms of total angular momentum

$$\hat{H}'_{hf} = \frac{A}{\hbar^2}\mathbf{S} \cdot \mathbf{I} = \frac{A}{\hbar^2}\frac{1}{2}\left(\hat{F}^2 - \hat{S}^2 - \hat{I}^2\right)$$

Applying this to the coupled basis we find the following eigenvalues

$$E_1 = A/4, \quad E_2 = A/4, \quad E_3 = A/4, \quad E_4 = -3A/4$$