

Lecture Notes for Quantum Physics 3C26E

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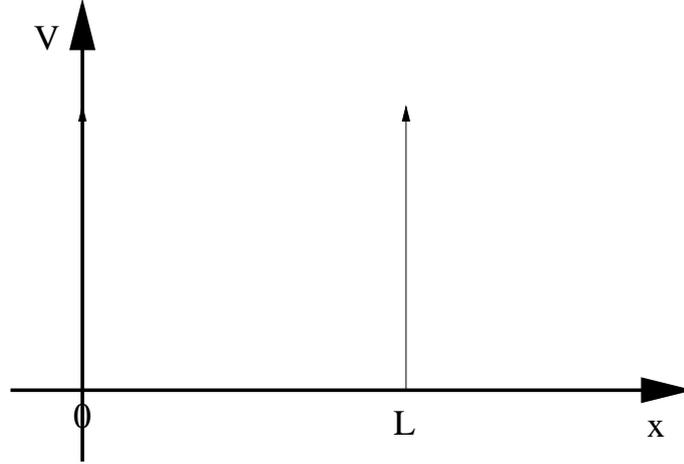
Chapter 1

Formal Aspects of Quantum Theory

1.1 The Wave Function

- Consider a set of N particles with positions $\vec{r}_1 \cdots \vec{r}_N$
- The wave function $\Psi(\vec{r}_1 \cdots \vec{r}_N, t)$ is a complex function (it has both a real and an imaginary part) of the coordinates of the particles (and time). It contains all the information about the particles at time t .
- The fundamental property of the wave function is that it gives the probability of finding the particles in a given configuration. That is $|\Psi(\vec{r}_1 \cdots \vec{r}_N, t)|^2 d\vec{r}_1 \cdots d\vec{r}_N$ is the probability of finding particle 1 in volume $d\vec{r}_1$ centred about \vec{r}_1 and particle 2 in volume $d\vec{r}_2$ centred about \vec{r}_2 etc., at a particular time t .
- We have used the notation $|\Psi|^2 = \Psi^* \Psi = \text{Re}\{\Psi\}^2 + \text{Im}\{\Psi\}^2$
- $d\vec{r} = dx dy dz = r^2 dr \sin \theta d\theta d\phi$
- This interpretation in terms of probability leads to the normalisation of the wave function defined by $\int |\Psi(\vec{r}_1 \cdots \vec{r}_N, t)|^2 d\vec{r}_1 \cdots d\vec{r}_N = 1$. This just means that the probability of finding the system in one of the allowed configurations is one.
- Note that because it is the modulus squared of the wave function which defines the physically observable properties, we can multiply the wave function by a phase factor $\exp(i\phi)$ without changing any of the results.
- Note that normalisation imposes a condition on allowed wave functions. One particularly important wave function is not normalisable, namely a plane wave ($\exp(i\vec{k} \cdot \vec{r})$). We can get around this problem by working with a wave packet, in which the plane wave is multiplied by another function which decays rapidly to zero for large distances, or we can use box normalisation with periodic boundaries.

Figure 1.1: Infinite square well



- Other average properties of the particles are found by taking expectation values. Consider the position of a particle:

$$\langle x_i \rangle = \int |\Psi(\vec{r}_1 \cdots \vec{r}_N, t)|^2 x_i d\vec{r}_1 \cdots d\vec{r}_N \quad (1.1)$$

- We will see later that in general we can write

$$\int \Psi(\vec{r}_1 \cdots \vec{r}_N, t)^* \hat{Q} \Psi(\vec{r}_1 \cdots \vec{r}_N, t) d\vec{r}_1 \cdots d\vec{r}_N = \langle Q \rangle \quad (1.2)$$

- where $\langle Q \rangle$ is the average measured quantity, and \hat{Q} is the corresponding operator.

Example

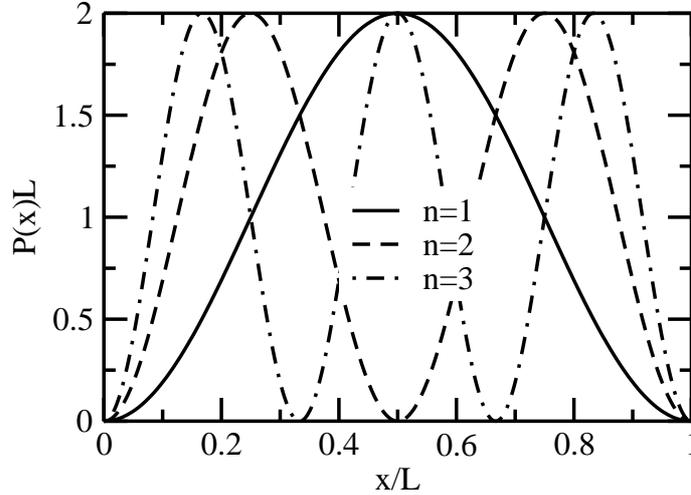
- Consider an electron in a box with infinitely hard walls:
- Allowed wave functions are

$$\Psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) & 0 \leq x \leq L \\ 0 & \text{Otherwise} \end{cases} \quad (1.3)$$

- Normalisation leads to the following

$$\begin{aligned} \int_{-\infty}^{\infty} |\Psi_n(x)|^2 dx &= \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx \\ &= \frac{2}{L} \int_0^L \frac{1}{2} (1 - \cos\left(\frac{n2\pi x}{L}\right)) dx \\ &= 1 \end{aligned}$$

Figure 1.2: Probability distribution



- The probability of finding a particle near x depends on the state

$$P_n(x) dx = \begin{cases} \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) dx & 0 \leq x \leq L \\ 0 & \text{Otherwise} \end{cases} \quad (1.4)$$

1.2 Principle of Superposition

- In optics in the two slit experiment we have waves emanating from two separate states that have a constant phase relationship, and thus produce an interference pattern.
- In quantum mechanics we have the same effect. It is possible to have two coherent sources of particles (for example electrons) that can interfere with one another.
- This interference effect in both cases is produced by the superposition of two coherent waves.
- In general to combine several wave functions for the same particle to produce a total wave function we must add the wave functions together.
- Consider our particle in a box

$$\begin{aligned} \Psi_n &= \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \exp\left(\frac{E_n t}{i\hbar}\right) \\ &= \sqrt{\frac{2}{L}} \frac{1}{2i} \left[\exp\left(\frac{in\pi x}{L}\right) - \exp\left(\frac{-in\pi x}{L}\right) \right] \exp\left(\frac{E_n t}{i\hbar}\right) \\ &= -\frac{i}{\sqrt{2L}} \exp\left(\frac{in\pi x}{L}\right) \exp\left(\frac{E_n t}{i\hbar}\right) + \frac{i}{\sqrt{2L}} \exp\left(-\frac{in\pi x}{L}\right) \exp\left(\frac{E_n t}{i\hbar}\right) \\ &= \Psi_+(x) - \Psi_-(x) \end{aligned}$$

- The wave function for a particle in free space is

$$\Psi_{free}(x) = N \exp(ikx)$$

- When $k > 0$ the particle is moving to the right, and when $k < 0$ the particle is moving to the left.
- Thus we can interpret our particle in a box as being in a state that is a superposition of a left travelling and right travelling states, as you might expect for a particle bouncing between two walls.
- This superposition produces interference effects

$$|\Psi|^2 = |\Psi_1 + \Psi_2|^2 = |\Psi_1|^2 + |\Psi_2|^2 + (\Psi_1^* \Psi_2 + \Psi_2^* \Psi_1)$$

- If we define the phase angles ϕ_1 and ϕ_2 by the equations $\Psi_1 = |\Psi_1| \exp(i\phi_1)$ and $\Psi_2 = |\Psi_2| \exp(i\phi_2)$ then we get the following interference expression

$$|\Psi|^2 = |\Psi_1|^2 + |\Psi_2|^2 + 2|\Psi_1||\Psi_2| \cos(\phi_1 - \phi_2)$$

- This produces the standing wave pattern for the particles in the box.

1.3 Time Dependent Schroedinger Equation

- From the photoelectric effect we have $E = h\nu$ and $p = h/\lambda$.
- De Broglie postulated that these expressions apply to all particles.
- If we write $k = 2\pi/\lambda$, $\omega = 2\pi\nu$ and $\hbar = h/2\pi$ then we can re-express these as $E = \hbar\omega$ and $p = \hbar k$.
- We use plane waves ($\exp(i(kx - \omega t))$) to describe the propagation of electromagnetic waves in free space. We would like to identify this with the wave function of the photon and hence of all free particles ($\Psi(xt) = N \exp[i(kx - \omega t)]$).
- This function satisfies the following equations

$$\begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} &= \hbar\omega \Psi = E\Psi \\ -i\hbar \frac{\partial \Psi}{\partial x} &= \hbar k \Psi = p\Psi \end{aligned}$$

- These equations provide the basic structure of quantum mechanics
 - Observables are represented by operators

$$\begin{aligned} E &\rightarrow i\hbar \frac{\partial}{\partial t} \\ p_x &\rightarrow -i\hbar \frac{\partial}{\partial x} \end{aligned}$$

- The state of the system is described by the wave function.

- To determine wave functions for more general systems we need to extend our ideas. The constraints we have are
 - The equations need to be linear in Ψ so that we can make use of superposition.
 - They need to be linear in $\frac{\partial}{\partial t}$ so that we do not need to define any derivatives of the wave function as part of our initial conditions ($t = 0$) since we wish to have the system completely defined by the wave function.
 - They should reproduce the results of classical mechanics in the limit of large systems.
- We also have the quantum mechanical postulates. One way to put all this together is the following

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{E}_{op} \Psi$$

- Here \hat{E}_{op} is an energy operator motivated by classical mechanics and has the form $\hat{E}_{op} = \hat{T}_{op} + \hat{V}_{op}$ where \hat{T}_{op} is the kinetic energy operator and \hat{V}_{op} is the potential energy operator. But from classical mechanics we know that $T = p^2/2M$, and we already have an expression for the momentum operator ($\hat{p}_{op} = -i\hbar \frac{\partial}{\partial x}$). Thus we propose the following equations of motion for the wave function

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} + V(x) \right] \Psi$$

- This forms the heart of quantum dynamics. It is the quantum mechanical equivalent of Newton's second law of motion. It is, of course, Schroedinger's equation.
- The more precise, if abstract, form of the equation is $\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$ where \hat{H} is the Hamiltonian operator. The Hamiltonian is a version of the total energy borrowed from classical mechanics which has the property that it is constant throughout the motion of a system in the absence of external time varying forces. Often it just equals the total energy, which is what we assume here.
- In three dimensions, but still for one particle, the Schroedinger equation becomes

$$i\hbar \frac{\partial \Psi(x, y, z, t)}{\partial t} = \left[-\frac{\hbar^2}{2M} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z) \right] \Psi(x, y, z, t)$$

- This can be written in a more compact form using the following notation

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = \left[-\frac{\hbar^2}{2M} \nabla^2 + V(\vec{r}) \right] \Psi(\vec{r}, t)$$

- When the potential is independent of time we can make the following very useful separation $\Psi(\vec{r}, t) = \Phi(\vec{r})\Theta(t)$. If we substitute this product into Schroedinger's equation we obtain the following

$$\frac{1}{\Theta(t)} i\hbar \frac{\partial \Theta(t)}{\partial t} = \frac{1}{\Phi(\vec{r})} \left[-\frac{\hbar^2}{2M} \nabla^2 + V(\vec{r}) \right] \Phi(\vec{r})$$

- Since the left-hand side depends only on time, and the right-hand side depends only on position, both sides must be equal to a constant which we shall call E . We can then separate our one equation into two equations.

$$\begin{aligned} \left[-\frac{\hbar^2}{2M} \nabla^2 + V(\vec{r}) \right] \Phi(\vec{r}) &= E\Phi(\vec{r}) \\ i\hbar \frac{\partial \Theta(t)}{\partial t} &= E\Theta(t) \end{aligned}$$

- The first of these equations is the time independent Schroedinger equation.
- The second of these equations we can solve immediately $\Theta(t) = \exp(Et/i\hbar)$.
- We can now form a general solution to the time dependent Schroedinger equation by using the principle of superposition.
- Let us index the allowed values of E by n ($E \in \{E_n\}$). Then we have the following expansion $\Psi(\vec{r}, t) = \sum_n C_n \Phi_n(\vec{r}) \exp(E_n t/i\hbar)$. C_n is a constant coefficient.
- The coefficients C_n are determined from the wave function at time $t = 0$ ($\Psi(\vec{r}, 0) = \sum_n C_n \Phi_n(\vec{r})$). As we will prove later we have the following condition $\int \Phi_m^*(\vec{r}) \Phi_n(\vec{r}) d\vec{r} = \delta_{nm}$ where δ_{nm} is the Kroenecker δ -function given by

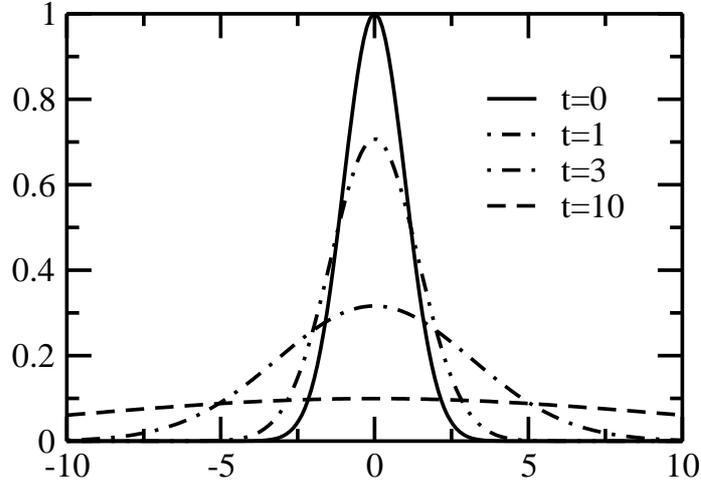
$$\delta_{nm} = \begin{cases} 0 & n \neq m \\ 1 & n = m \end{cases}$$

- Hence we can obtain the coefficients $\sum_n C_n \int \Phi_m^*(\vec{r}) \Phi_n(\vec{r}) d\vec{r} = C_m = \int \Phi_m^*(\vec{r}) \Psi(\vec{r}, 0) d\vec{r}$.

Example

- In free space we have no potential. Thus the Hamiltonian contains only the kinetic energy.
- Our one-dimensional Schroedinger equation is thus $i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2M} \frac{\partial^2 \Psi}{\partial x^2}$. If we make a separation of variables we obtain $\frac{1}{\Theta(t)} i\hbar \frac{\partial \Theta(t)}{\partial t} = \frac{1}{\Phi(x)} \left[-\frac{\hbar^2}{2M} \frac{\partial^2 \Phi(x)}{\partial x^2} \right] = E$. If we define $E = \hbar\omega = p^2/2M$, and $p = \hbar k$ then we obtain $\Psi(x, t) = N \exp(-i[\omega t \pm kx])$, which should now all look familiar.
- To produce the general wave function we construct the sum of individual terms. However in this case we have a continuum of energy levels allowed, since the wave vector k can have any real value. Therefore we must replace our sum by an integral. We therefore have $\Psi(x, t) = \int dk c(k) \exp(-i[\omega(k)t - kx])$.
- We obtain the expansion coefficients from the equation $\Psi(x, 0) = \int dk c(k) \exp(ikx)$.

Figure 1.3: Spread of gaussian wavepacket



Example

- There is a second solution to the Schroedinger equation for a free particle which corresponds to what is called a wave packet. To find this solution we will write down its form and show that it satisfies the Schroedinger equation.
- The trial wave function is

$$\Psi(x, t) = N \frac{1}{\sqrt{1 + \alpha t}} f\left(\beta \frac{(x/\sigma)^2}{1 + \alpha t}\right)$$

- In order to substitute this into the Schroedinger equation we need the following derivatives

$$\begin{aligned} \frac{\partial \Psi}{\partial t} &= N \left(\frac{-\alpha/2}{\sqrt{(1 + \alpha t)^3}} f - \frac{\alpha \beta (x/\sigma)^2}{\sqrt{(1 + \alpha t)^3}} f' \right) \\ \frac{\partial^2 \Psi}{\partial x^2} &= N \left(\frac{2\beta/\sigma^2}{\sqrt{(1 + \alpha t)^3}} f' + \frac{4\beta^2 x^2/\sigma^4}{\sqrt{(1 + \alpha t)^5}} f'' \right) \end{aligned}$$

- Schroedinger's equation is satisfied provided the following conditions hold true: $f(y) = f'(y) = f''(y) = \exp(y)$, $\beta = -\frac{1}{4}$ and $\alpha = i\hbar/2M\sigma^2$. If these conditions are satisfied then we have

$$\Psi(x, t) = N \exp \left[-\frac{1}{4} \frac{(x/\sigma)^2}{1 + i\hbar t/2M\sigma^2} \right] \frac{1}{\sqrt{1 + i\hbar t/2M\sigma^2}}$$

- Let us introduce a timescale into this problem $\tau = 2M\sigma^2/\hbar$. For an electron, assuming $\sigma \approx 10^{-10}$ m, this will have a value of about 10^{-16} s.

We can then rewrite our wave function as

$$\Psi(x, t) = N \exp \left[-\frac{1}{4} \frac{(x/\sigma)^2}{1 + it/\tau} \right] \frac{1}{\sqrt{1 + it/\tau}}$$

- From this we are able to calculate the probability density function which is

$$|\Psi(x, t)|^2 = N^2 \exp \left[-\frac{1}{2} \frac{(x/\sigma)^2}{1 + (t/\tau)^2} \right] \frac{1}{\sqrt{1 + (t/\tau)^2}}$$

- When the time is much greater than our timescale ($t \gg \tau$) we get

$$|\Psi(x, t)|^2 \approx N^2 \frac{\tau}{t} \exp \left[-\frac{1}{2} \left(\frac{x}{\sigma t/\tau} \right)^2 \right]$$

- If we define the effective width of our wave packet by $\sigma^*(t) = \sigma t/\tau$, then we see that the wave packet is spreading with a constant speed of about 10^6 m/s.

1.4 Expectation Values

- If you perform an experiment many times and measure some quantity which we will call Q (for example position or momentum) each time, then you can find an average value

$$\langle Q \rangle = \frac{1}{N} \sum_{i=1}^N Q_i$$

- $\langle Q \rangle$ can also be calculated from the quantum mechanical operator \hat{Q} (\hat{x} , $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$, etc.) for this observable and the wave function. In this case it is referred to as an expectation value and is given by:

$$\langle Q \rangle = \int \Psi^*(\vec{r}) \hat{Q} \Psi(\vec{r}) d\vec{r}$$

- This will be elaborated upon later.
- Note that this is an average value. What you obtain from any one given experiment will in general differ from this.
- Once again consider a particle in a box with infinitely hard walls for which the wave functions are given by:

$$\Psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) & 0 \leq x \leq L \\ 0 & \text{Otherwise} \end{cases}$$

- The expectation value of position is

$$\begin{aligned}\langle x \rangle_n &= \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) x \sin\left(\frac{n\pi x}{L}\right) dx \\ &= \frac{2}{L} \int_0^L \frac{1}{2} [x - x \cos\left(\frac{2n\pi x}{L}\right)] dx \\ &= \frac{L}{2}\end{aligned}$$

- On average we will find a particle in the middle of the box. The expectation value of the momentum is

$$\begin{aligned}\langle p \rangle_n &= \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) (-i\hbar \frac{\partial}{\partial x}) \sin\left(\frac{n\pi x}{L}\right) dx \\ &= \frac{2}{L} (-i\hbar \frac{n\pi}{L}) \int_0^L \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) dx \\ &= 0\end{aligned}$$

- The particle is equally likely to be travelling to the right or to the left, as it is bouncing between two walls.
- Expectation values can behave like classical variables. The Ehrenfest equations are interesting example

$$\begin{aligned}m \frac{d\langle x \rangle}{dt} &= \langle p \rangle \\ \frac{d\langle p \rangle}{dt} &= -\left\langle \frac{\partial V}{\partial x} \right\rangle\end{aligned}$$

- These results will be proven later.

1.5 Hermitian Operators

- An operator acts on a function to modify that function:

$$\hat{O}f(\vec{r}) = g(\vec{r})$$

- For example, the derivative operator ($\hat{O} = \frac{d}{dx}$) acting on the function $f(x) = \sin x$:

$$\begin{aligned}\hat{O}f(x) &= \frac{d}{dx} \sin x \\ &= \cos x\end{aligned}$$

- Linear operators obey the following relation $\hat{L}(\alpha\psi + \beta\phi) = \alpha\hat{L}\psi + \beta\hat{L}\phi$.
- Operators corresponding to physical observables are hermitian.
- Now consider integrals of the form $\int \Psi^*(\vec{r}) \hat{O} \Phi(\vec{r}) d\vec{r}$. We define the hermitian conjugate of \hat{O} to be \hat{O}^\dagger where

$$\int \Psi^*(\vec{r}) \hat{O}^\dagger \Phi(\vec{r}) d\vec{r} = \int (\hat{O} \Psi(\vec{r}))^* \Phi(\vec{r}) d\vec{r}$$

- Hermitian operator satisfies $\hat{O}^\dagger = \hat{O}$. That is

$$\begin{aligned} \int \Psi^*(\vec{r}) \hat{O}^\dagger \Phi(\vec{r}) d\vec{r} &= \int (\hat{O}\Psi(\vec{r}))^* \Phi(\vec{r}) d\vec{r} \\ &= \int \Psi^*(\vec{r}) (\hat{O}\Phi(\vec{r})) d\vec{r} \end{aligned}$$

The operator can act on either wave function and give the same result.

- Consider two operators

$$\begin{aligned} \int \Psi^*(\vec{r}) (\hat{A}\hat{B})^\dagger \Phi(\vec{r}) d\vec{r} &= \int (\hat{A}\hat{B}\Psi(\vec{r}))^* \Phi(\vec{r}) d\vec{r} \\ &= \int (\hat{B}\Psi(\vec{r}))^* (\hat{A}^\dagger \Phi(\vec{r})) d\vec{r} \\ &= \int \Psi(\vec{r})^* \hat{B}^\dagger (\hat{A}^\dagger \Phi(\vec{r})) d\vec{r} \\ \Rightarrow (\hat{A}\hat{B})^\dagger &= \hat{B}^\dagger \hat{A}^\dagger \end{aligned}$$

- The expectation values of hermitian operators are always real

$$\begin{aligned} \left(\int \Psi^* \hat{A} \Psi d\vec{r} \right)^* &= \int \Psi \hat{A}^* \Psi^* d\vec{r} \\ &= \int \Psi (\hat{A}\Psi)^* d\vec{r} \\ &= \int \Psi^* \hat{A}^\dagger \Psi d\vec{r} \\ &= \int \Psi^* \hat{A} \Psi d\vec{r} \end{aligned}$$

- If a number equals its complex conjugate, then it must be real.

Example

- Consider the position operator \hat{x} which satisfies $\hat{x}f(x) = xf(x)$:

$$\begin{aligned} \int \Psi^*(\vec{r}) \hat{x}^\dagger \Phi(\vec{r}) d\vec{r} &= \int (\hat{x}\Psi(\vec{r}))^* \Phi(\vec{r}) d\vec{r} \\ &= \int (x\Psi(\vec{r}))^* \Phi(\vec{r}) d\vec{r} \\ &= \int \Psi(\vec{r})^* x \Phi(\vec{r}) d\vec{r} \\ &= \int \Psi(\vec{r})^* \hat{x} \Phi(\vec{r}) d\vec{r} \end{aligned}$$

- Now consider the momentum operator $-i\hbar \frac{\partial}{\partial x}$. This also is hermitian:

$$\begin{aligned} \int \Psi(x)^* \left(-i\hbar \frac{\partial}{\partial x}\right) \Phi(x) dx &= -i\hbar \left[\Psi(x)^* \Phi(x) - \int \frac{\partial}{\partial x} \Psi(x)^* \Phi(x) dx \right] \\ &= \int \left(-i\hbar \frac{\partial}{\partial x} \Psi(x)\right)^* \Phi(x) dx \end{aligned}$$

- In the first line we have used integration by parts. In the second line we have assumed that at infinity the wave functions decay to zero.

1.6 Eigenstates

- We can ask the question: is there a state that produces one, and only one, value for measurements of a particular observable? Mathematically, we want a state that produces a particular expectation value for that observable, and for which the standard deviation of the measurements is zero. That is, $\langle A \rangle = \mu$ and $0 = \int \Psi^*(\hat{A} - \mu)^2 \Psi \, d\vec{r}$. For an hermitian operator this produces the following

$$\begin{aligned} 0 &= \int \Psi^*(\hat{A} - \mu)^2 \Psi \, d\vec{r} \\ &= \int \Psi^*(\hat{A} - \mu)(\hat{A} - \mu)\Psi \, d\vec{r} \\ &= \int [(\hat{A} - \mu)\Psi]^*(\hat{A} - \mu)\Psi \, d\vec{r} \\ &= \int |(\hat{A} - \mu)\Psi|^2 \, d\vec{r} \end{aligned}$$

- Because the integrand is positive definite, it must be the case that $\hat{A}\Psi = \mu\Psi$. This is an eigenequation.
- We can generalise the above and say that eigenstates correspond to the value measured in individual experiments (in contrast to expectation values which are averages over many experiments).
- Eigenstates are properties of operators and are defined by the equation

$$\hat{O}f_\lambda = \lambda f_\lambda$$

- where f_λ is an eigenfunction, and λ is a scalar, the eigenvalue.
- An operator will in general have many eigenfunctions with corresponding eigenvalues.

Example

- Considered the momentum operator

$$\begin{aligned} i\hbar \frac{\partial}{\partial x} f_\lambda(x) &= \lambda f_\lambda(x) \\ f_\lambda(x) &= A \exp(\lambda x / i\hbar) \end{aligned}$$

- Thus eigenfunctions of the momentum operator are complex exponentials (or plane waves).
- Note that in this example that there are no constraints on the value of λ .

- Hermitian operators have the very important property that all their eigenvalues are real. This is necessary if they are to correspond to physical observables.
- Let \hat{H} be an hermitian operator which satisfies the following eigenequation $\hat{H}f_\lambda = \lambda f_\lambda$. We shall now prove that its eigenvalues are real:

$$\begin{aligned}\int f_\lambda^* \hat{H} f_\lambda \, d\vec{r} &= \lambda \int f_\lambda^* f_\lambda \, d\vec{r} \\ \int f_\lambda \hat{H}^* f_\lambda^* \, d\vec{r} &= \lambda^* \int f_\lambda^* f_\lambda \, d\vec{r}\end{aligned}$$

- The second line is just the complex conjugate of the first line. Since \hat{H} is hermitian:

$$\int f_\lambda \hat{H}^* f_\lambda^* \, d\vec{r} = \int (\hat{H} f_\lambda)^* f_\lambda \, d\vec{r} = \int f_\lambda^* \hat{H}^\dagger f_\lambda \, d\vec{r} = \int f_\lambda^* \hat{H} f_\lambda \, d\vec{r}$$

- Therefore $\lambda^* = \lambda$, and therefore the eigenvalues is real.
- The eigenfunctions of hermitian operators have the property that two different eigenfunctions are orthogonal to one another: $\int f_1^* f_2 \, d\vec{r} = 0$. To prove this considered to different eigenstates of the same operator

$$\begin{aligned}\hat{H} f_1 &= \lambda_1 f_1 \\ \hat{H} f_2 &= \lambda_2 f_2\end{aligned}$$

- This allows us then to write the following integrals

$$\begin{aligned}\int f_2^* \hat{H} f_1 \, d\vec{r} &= \lambda_1 \int f_2^* f_1 \, d\vec{r} \\ \int f_1^* \hat{H} f_2 \, d\vec{r} &= \lambda_2 \int f_1^* f_2 \, d\vec{r}\end{aligned}$$

- We now take the complex conjugate of the second equation, while recalling that the eigenvalues are real

$$\int f_1 \hat{H}^* f_2^* \, d\vec{r} = \lambda_2 \int f_2^* f_1 \, d\vec{r}$$

- If we now make use of the fact that the operator is hermitian we get from above

$$\lambda_2 \int f_2^* f_1 \, d\vec{r} = \int (\hat{H} f_1) f_2^* \, d\vec{r} = \lambda_1 \int f_2^* f_1 \, d\vec{r}$$

- Hence we get $(\lambda_1 - \lambda_2) \int f_2^* f_1 \, d\vec{r} = 0$, which means either the eigenvalues are the same, which is not the case by construction, or that the eigenfunctions are orthogonal.
- If it turns out that two eigenvalues are in fact the same (the states are degenerate), we can form linear combinations of the corresponding eigenfunctions which will also satisfy the eigenequation. We can choose those linear combinations such that they are orthogonal to each other. Therefore, all eigenfunctions are orthogonal to one another.

Example

- Once again we will consider the Hamiltonian for a particle in a box with infinitely hard walls

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_{\text{box}}(x)$$

- Inside the box potential is 0, and so we have

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Phi_n(x)}{\partial x^2} = E_n \Phi_n(x)$$

- This has the eigenvalues and eigenfunctions

$$\Phi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) & 0 \leq x \leq L \\ 0 & \text{Otherwise} \end{cases}$$

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2$$

- We see that E_n is real for all n . The wave functions are also orthonormal:

$$\begin{aligned} O_{nm} &= \int \Phi_n^*(x) \Phi_m(x) dx \\ &= \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) dx \\ &= \frac{1}{L} \int_0^L \left[\cos\left(\frac{(n-m)\pi x}{L}\right) - \cos\left(\frac{(n+m)\pi x}{L}\right) \right] dx \\ &= \begin{cases} 0 & n \neq m \\ 1 & n = m \end{cases} \end{aligned}$$

1.7 Expansion Postulate and Complete Sets of Eigenfunctions

- Suppose we have two Hamiltonians that are different, but they operate in the same space. For example we could have a particle in a box, and another particle in a similar box but which has a sloping floor. That is, in both cases we need to find a wave function for one particle in one dimension over the same range of positions. What distinguishes the two cases is just the shape of the potential. We thus solve very similar equations for the two cases, but they have different eigenfunctions:

$$\begin{aligned} \hat{H}_1 \Phi_n^{(1)} &= E_n^{(1)} \Phi_n^{(1)} \\ \hat{H}_2 \Phi_n^{(2)} &= E_n^{(2)} \Phi_n^{(2)} \end{aligned}$$

- But because they operate in the same space we can expand one set of eigenfunctions in terms of the other. This is analogous to choosing a different set of axes to define coordinates. Thus we can write:

$$\Phi_n^{(2)}(x) = \sum_m c_{nm} \Phi_m^{(1)}(x)$$

- The coefficients C_{mn} can be determined by making use of the orthonormality of the eigenfunctions:

$$\int \Phi_p^{(1)*}(x) \Phi_q^{(1)}(x) dx = \delta_{pq}$$

- Thus we get:

$$\begin{aligned} \int \Phi_p^{(1)*}(x) \Phi_n^{(2)}(x) dx &= \sum_m c_{mn} \int \Phi_p^{(1)*}(x) \Phi_m^{(1)}(x) dx \\ &= \sum_m c_{nm} \delta_{pm} \\ &= c_{np} \end{aligned}$$

- The expansion is exact in this case if we include all the eigenfunctions.
- An alternative way of generating a set of eigenfunctions is to consider the same system twice, but consider two different operators. This reveals more about the nature of expectation values.
- Consider the following

$$\begin{aligned} \hat{O}f_n &= \lambda_n f_n \\ \Phi(x) &= \sum_m c_m f_m(x) \\ c_m &= \int f_m^* \Phi dx \end{aligned}$$

- Where Φ is the wave function that we are interested in. The expectation value of the operator is then given by

$$\begin{aligned} \langle O \rangle &= \int \Phi^* \hat{O} \Phi dx \\ &= \sum_{mn} \int c_m f_m^* \hat{O} c_n f_n dx \\ &= \sum_{mn} c_m c_n \int f_m^* \lambda_n f_n dx \\ &= \sum_{mn} c_m c_n \lambda_n \delta_{mn} \\ &= \sum_n |c_n|^2 \lambda_n \end{aligned}$$

- Thus we can interpret $|c_n|^2 = |\int \Phi^* f_n dx|^2$ as the probability of measuring the physical quantity associated with the operator \hat{O} and finding that it has a value λ_n .
- There is an important property of orthogonal functions that makes the use of expansions very robust for practical calculations. Suppose we were only allowed to use a fraction of the total number of functions to approximate

our wave function $\Psi \approx \sum_{n=1}^N \gamma_n \Phi_n$. We now try to find the best possible set of coefficients:

$$\begin{aligned} R &= \int |\Psi - \sum_n \gamma_n \Phi_n|^2 d\vec{r} \\ \frac{\partial R}{\partial \gamma_m^*} &= \int \Phi_m^* (\Psi - \sum_n \gamma_n \Phi_n) d\vec{r} = 0 \\ \int \Phi_m^* \Psi d\vec{r} &= \gamma_m = c_m \end{aligned}$$

- Thus the best possible coefficients for a finite sequence are identical to those for the full expansion.

1.8 Compatible Observables

- An observable corresponds to an eigenvalue of an hermitian operator ($\hat{O}\Psi_\lambda = \lambda\Psi_\lambda$).
- Compatible observables share eigenfunctions:

$$\begin{aligned} \hat{A}\Psi &= a\Psi \\ \hat{B}\Psi &= b\Psi \end{aligned}$$

1.9 Simultaneous Measurement

Once a wave function collapses due to a measurement, and so enters an eigenstate, you can extract all the eigenvalues of simultaneous observables without disturbing the wave function further.

1.10 Commuting Operators

- We define a commutator by the following equation

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

Example

- We will consider the commutator between the position and momentum operators.

$$\begin{aligned} \hat{A} &= \hat{x} \\ \hat{B} &= \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \\ [\hat{A}, \hat{B}]\Psi &= \hat{A}\hat{B}\Psi - \hat{B}\hat{A}\Psi \\ [\hat{x}, \hat{p}_x]\Psi &= \hat{x}\hat{p}_x\Psi - \hat{p}_x\hat{x}\Psi \\ &= \hat{x}(-i\hbar \frac{\partial}{\partial x})\Psi - (-i\hbar \frac{\partial}{\partial x})(x\Psi) \\ &= i\hbar(-x \frac{\partial \Psi}{\partial x} + \Psi + x \frac{\partial \Psi}{\partial x}) \end{aligned}$$

$$\begin{aligned}
&= i\hbar\Psi \\
[\hat{x}, \hat{p}_x] &= i\hbar
\end{aligned}$$

- We now make the connection between commuting operators and simultaneous observables.
- Suppose we have the following

$$\begin{aligned}
\hat{A}\Psi_n &= a_n\Psi_n \\
\hat{B}\Psi_n &= b_n\Psi_n \\
\Psi &= \sum_n c_n\Psi_n
\end{aligned}$$

- We then obtain the following result

$$\begin{aligned}
[\hat{A}, \hat{B}]\Psi &= (\hat{A}\hat{B} - \hat{B}\hat{A})\Psi \\
&= \sum_n c_n(\hat{A}\hat{B} - \hat{B}\hat{A})\Psi_n \\
&= \sum_n c_n(\hat{A}b_n - \hat{B}a_n)\Psi_n \\
&= \sum_n c_n(a_n b_n - b_n a_n)\Psi_n \\
&= 0
\end{aligned}$$

- If $[\hat{A}, \hat{B}] = 0$, the operators are said to commute.
- Thus we see that simultaneous observables will have quantum mechanical operators that commute.

Example

- Consider a free particle. The Hamiltonian operator in this case is $\hat{H} = -\hat{p}^2/2M$.
- Now consider the commutator between the Hamiltonian and the momentum operator

$$\begin{aligned}
[\hat{H}, \hat{p}] &= \hat{H}\hat{p} - \hat{p}\hat{H} \\
&= -\frac{1}{2M}(\hat{p}^3 - \hat{p}^3) \\
&= 0
\end{aligned}$$

- Thus the wave functions for this Hamiltonian are also eigenstates of the momentum operator. Thus a free particle has a well-defined momentum.

1.11 The Generalised Uncertainty Relations

- The uncertainty principle relates to two sets of repeated measurements on the same system. In one set we measure one quantity (for example position), while in the other set we measure another quantity (for example momentum).

- For each set we can calculate a mean value and a standard deviation. Let the mean values be $\langle A \rangle$ and $\langle B \rangle$ and let the standard deviations be σ_A and σ_B .
- In classical mechanics it is possible in theory to perform measurements for which σ_A and σ_B are both arbitrarily small. That is, the system can have unique values of both A and B .
- In quantum mechanics there are pairs of observables (for example position and momentum) for which this is not true.
- Variables for which this is not true, have corresponding quantum operators that fail to commute. We have already seen that $[\hat{x}, \hat{p}_x] = i\hbar$.
- We can now put this on a proper mathematical footing. Let the two operators corresponding to the two observables be \hat{A} and \hat{B} , and let them satisfy $[\hat{A}, \hat{B}] = i\hbar$. We then have the following definitions of the expectation values and variances

$$\begin{aligned}\langle A \rangle &= \int \Psi^* \hat{A} \Psi \, dx \\ \langle B \rangle &= \int \Psi^* \hat{B} \Psi \, dx \\ \sigma_A^2 &= \int \Psi^* (\hat{A} - \langle A \rangle)^2 \Psi \, dx = \int ((\hat{A} - \langle A \rangle) \Psi)^* (\hat{A} - \langle A \rangle) \Psi \, dx \\ \sigma_B^2 &= \int \Psi^* (\hat{B} - \langle B \rangle)^2 \Psi \, dx = \int ((\hat{B} - \langle B \rangle) \Psi)^* (\hat{B} - \langle B \rangle) \Psi \, dx\end{aligned}$$

- Let us now define

$$\begin{aligned}a(x) &= (\hat{A} - \langle A \rangle) \Psi(x) \\ b(x) &= (\hat{B} - \langle B \rangle) \Psi(x)\end{aligned}$$

- We then get

$$\begin{aligned}\sigma_A^2 &= \int |a(x)|^2 \, dx \\ \sigma_B^2 &= \int |b(x)|^2 \, dx\end{aligned}$$

- Let us now define a new function $\chi(x) = a(x)/\sigma_A - e^{i\alpha} b(x)/\sigma_B$.
- Clearly this function satisfies the following inequality $\int |\chi(x)|^2 \, dx \geq 0$. We therefore obtain the following

$$\begin{aligned}0 &\leq \int (a^*(x)/\sigma_A - e^{-i\alpha} b^*(x)/\sigma_B)(a(x)/\sigma_A - e^{i\alpha} b(x)/\sigma_B) \, dx \\ &\leq \frac{1}{\sigma_A^2} \int |a(x)|^2 \, dx + \frac{1}{\sigma_B^2} \int |b(x)|^2 \, dx - \frac{1}{\sigma_A \sigma_B} \int [a^*(x) b(x) e^{i\alpha} + b^*(x) a(x) e^{-i\alpha}] \, dx \\ &\leq 1 + 1 - \frac{1}{\sigma_A \sigma_B} \int [a^*(x) b(x) e^{i\alpha} + b^*(x) a(x) e^{-i\alpha}] \, dx\end{aligned}$$

$$\begin{aligned}
\sigma_A \sigma_B &\geq \frac{1}{2} \int [a^*(x)b(x)e^{i\alpha} + b^*(x)a(x)e^{-i\alpha}] dx \\
&\geq \frac{1}{2} [e^{i\alpha} \int \Psi^*(x)(\hat{A} - \langle A \rangle)(\hat{B} - \langle B \rangle)\Psi(x) dx + \\
&\quad e^{-i\alpha} \int \Psi^*(x)(\hat{B} - \langle B \rangle)(\hat{A} - \langle A \rangle)\Psi(x) dx]
\end{aligned}$$

- If we let $e^{i\alpha} = -i$, then we obtain

$$\begin{aligned}
\sigma_A \sigma_B &\geq \frac{-i}{2} \int \Psi^*(x)[(\hat{A} - \langle A \rangle), (\hat{B} - \langle B \rangle)]\Psi(x) dx \\
&\geq \frac{-i}{2} \int \Psi^*(x)[\hat{A}\hat{B} - \hat{A}\langle B \rangle - \langle A \rangle\hat{B} + \langle A \rangle\langle B \rangle - \hat{B}\hat{A} + \langle B \rangle\hat{A} + \hat{B}\langle A \rangle - \langle B \rangle\langle A \rangle]\Psi(x) dx \\
&\geq \frac{-i}{2} \int \Psi^*(x)[\hat{A}, \hat{B}]\Psi(x) dx \\
&\geq \frac{\hbar}{2}
\end{aligned}$$

- The wave function with the smallest combined uncertainty ($\sigma_A \sigma_B = \hbar/2$) satisfies the equation $\chi(x) = 0$. Therefore it satisfies $a(x)/\sigma_A + ib(x)/\sigma_B = 0$.

Example

- If we choose our operators to be the position and momentum operators then the equation we have to solve is

$$\left[\left(\frac{x - \langle x \rangle}{\sigma_x} \right) + \left(\frac{\hbar \frac{\partial}{\partial x} - i\langle p \rangle}{\sigma_p} \right) \right] \Psi(x) = 0$$

- The solution to this equation is the following

$$\Psi(x) = N \exp \left[\frac{ix\langle p \rangle}{\hbar} - \left(\frac{x - \langle x \rangle}{2\sigma_x} \right)^2 \right]$$

- This is a Gaussian wave packet. It forms one possible link with classical mechanics.

1.12 Dirac Notation

- This is a very convenient notation that achieves two things
 1. It allows us to represent integrals in a compact fashion
 2. It allows us to write quantum mechanics in a more abstract, and hence general, fashion.
- This is achieved by thinking of functions as vectors in an abstract space, and integrals as dot products.

- Consider the following integral $\int \Psi^* \Phi \, d\vec{r}$. In Dirac notation we would write this as $\langle \Psi | \Phi \rangle$.
- The quantity $\langle \Psi |$ is called a bra, and $|\Phi \rangle$ is called a ket. Think bra-c-ket. Note that these exist in different spaces (they are complex conjugates of one another), so cannot be added to each other.
- The absence of explicit coordinates is what allows us to be more abstract.
- We immediately have the following result $\langle \Psi | \Phi \rangle = \langle \Phi | \Psi \rangle^*$.
- If $\langle \Psi | \Phi \rangle = 0$ then $|\Phi \rangle$ and $|\Psi \rangle$ are orthogonal.
- We have the following relations between bras and kets:

$$\begin{aligned}
 |\Phi \rangle = |a \rangle + |b \rangle &\Rightarrow \langle \Phi | = \langle a | + \langle b | \\
 c|a \rangle = |a \rangle c &\Rightarrow c^* \langle a | = \langle a | c^* \\
 |\Phi \rangle = c_1|a \rangle + c_2|b \rangle &\Rightarrow \langle \Phi | = c_1^* \langle a | + c_2^* \langle b | \\
 \hat{A}|\Phi \rangle &\Rightarrow \langle \Phi | \hat{A}^\dagger \\
 |a \rangle + |b \rangle = |b \rangle + |a \rangle &\Rightarrow \langle a | + \langle b | = \langle b | + \langle a | \\
 |a \rangle + (|b \rangle + |c \rangle) = (|a \rangle + |b \rangle) + |c \rangle &\Rightarrow \langle a | + (\langle b | + \langle c |) = (\langle a | + \langle b |) + \langle c | \\
 c(|a \rangle + |b \rangle) = c|a \rangle + c|b \rangle &\Rightarrow c^* (\langle a | + \langle b |) = c^* \langle a | + c^* \langle b | \\
 \langle c | (|a \rangle + |b \rangle) = \langle c | a \rangle + \langle c | b \rangle &\Rightarrow (\langle a | + \langle b |) |c \rangle = \langle a | c \rangle + \langle b | c \rangle
 \end{aligned}$$

- What is the meaning of $|a \rangle \langle b |$? Now $|a \rangle \langle b | p \rangle$ is a ket ($|a \rangle$) multiplied by a number ($\langle b | p \rangle$), which is another ket. Thus the action of $|a \rangle \langle b |$ on a ket is to generate another ket. Thus $|a \rangle \langle b |$ is a linear operator.
- $|a \rangle \langle b |$ also operates on bras: $\langle p' | = \langle p | a \rangle \langle b |$.
- The expectation value of an operator \hat{A} is written:

$$\begin{aligned}
 \int \Psi^* \hat{A} \Psi \, d\vec{r} &= \langle \Psi | \hat{A} | \Psi \rangle \\
 \int (\hat{A} \Psi)^* \Psi \, d\vec{r} &= \langle \Psi | \hat{A}^\dagger | \Psi \rangle
 \end{aligned}$$

- We can extend our use of the notation to eigenequations $\hat{A}|\Phi_n \rangle = a_n|\Phi_n \rangle$. Here $|\Phi_n \rangle$ is an abstract representation of an eigenfunction.
- We can write expansions for functions in the following way: $|\Psi \rangle = \sum_n c_n |\Phi_n \rangle$.
- This can be very convenient. For example

$$\begin{aligned}
 \langle \Psi | \hat{A} | \Psi \rangle &= \sum_{nm} (c_n^* \langle \Phi_n |) \hat{A} (c_m |\Phi_m \rangle) \\
 &= \sum_{nm} c_n^* c_m \langle \Phi_n | \hat{A} | \Phi_m \rangle \\
 &= \sum_{nm} c_n^* c_m \langle \Phi_n | a_m | \Phi_m \rangle
 \end{aligned}$$

$$\begin{aligned}
&= \sum_{nm} c_n^* c_m a_m \langle \Phi_n | \Phi_m \rangle \\
&= \sum_{nm} c_n^* c_m a_m \delta_{nm} \\
&= \sum_n |c_n|^2 a_n
\end{aligned}$$

- We can use this result to produce a very convenient way to represent operators. First we notice the following: $\langle \Phi_n | \Psi \rangle = \sum_m c_m \langle \Phi_n | \Phi_m \rangle = c_n$. This allows us to write our expectation value as $\langle \Psi | \hat{A} | \Psi \rangle = \sum_n \langle \Psi | \Phi_n \rangle a_n \langle \Phi_n | \Psi \rangle$. This suggests that we can represent our operator by

$$\hat{A} = \sum_n |\Phi_n\rangle a_n \langle \Phi_n|$$

- There is an important special case of this, which is the unit operator. For this operator all the eigenvalues are equal to 1. This use of the unit operator is called inserting a complete set of states. To see this consider the following two states:

$$\begin{aligned}
|\Psi\rangle &= \sum_n c_n |\Phi_n\rangle \\
|\chi\rangle &= \sum_n d_n |\Phi_n\rangle \\
\langle \Psi | \chi \rangle &= \sum_{mn} c_n^* d_m \langle \Phi_n | \Phi_m \rangle \\
&= \sum_n c_n^* d_n
\end{aligned}$$

- But $c_n = \langle \Phi_n | \Psi \rangle$ and $d_n = \langle \Phi_n | \chi \rangle$. Hence we can write

$$\langle \Psi | \chi \rangle = \langle \Psi | \left(\sum_n |\Phi_n\rangle \langle \Phi_n| \right) | \chi \rangle$$

- This is an example of the insertion of a complete set of states.

1.13 Matrix Representation of States and Operators

- As we have seen, we are able to represent wave functions as sums over complete sets of states. The matrix notation allows us to exploit this fact more easily.
- Consider a wave function Ψ and an operator \hat{A} . We can define the function χ by $\chi = \hat{A}\Psi$.
- We can now introduce the complete set of states $\{\Phi_n\}$. We can expand our previous two functions in this set of states giving

$$\Psi = \sum_n \Phi_n c_n$$

$$\chi = \sum_n \Phi_n d_n$$

- We can then combine these equations to produce $\sum_n \Phi_n d_n = \sum_n \hat{A} \Phi_n c_n$.
- We can now perform some integrals on this equation to produce the following expression: $\sum_n \int \Phi_m^* \Phi_n d_n = \sum_n \int \Phi_m^* \hat{A} \Phi_n d_n$.
- We can of course write this using Dirac notation $\sum_n \langle \Phi_m | \Phi_n \rangle d_n = \sum_n \langle \Phi_m | \hat{A} | \Phi_n \rangle c_n$.
- If the set of states is orthonormal then we obtain the following result $d_m = \sum_n \langle \Phi_m | \hat{A} | \Phi_n \rangle c_n$.
- We can think of $\langle \Phi_m | \hat{A} | \Phi_n \rangle$ as a matrix element, which we can represent as A_{mn} . Thus we have $d_m = \sum_n A_{mn} c_n$, which in matrix notation we can write as $\vec{d} = \mathbf{A} \vec{c}$.
- In this notation eigenequations become $\mathbf{A} \vec{c}_n = \lambda_n \vec{c}_n$. This is the approach normally used to perform quantum mechanics on a computer.
- The time dependent Schrodinger equation can also be written in this form:

$$\begin{aligned} \hat{H} \Psi(\vec{r}t) &= i\hbar \frac{\partial \Psi(\vec{r}t)}{\partial t} \\ \Psi(\vec{r}t) &= \sum_n c_n(t) \Phi_n(\vec{r}) \\ \hat{H} \sum_n c_n(t) \Phi_n(\vec{r}) &= i\hbar \frac{\partial}{\partial t} \sum_n c_n(t) \Phi_n(\vec{r}) \\ \sum_n c_n(t) \int \Phi_m^*(\vec{r}) \hat{H} \Phi_n(\vec{r}) d\vec{r} &= \sum_n i\hbar \frac{\partial c_n(t)}{\partial t} \int \Phi_m^*(\vec{r}) \Phi_n(\vec{r}) d\vec{r} \\ \sum_n H_{mn} c_n(t) &= i\hbar \frac{\partial c_m(t)}{\partial t} \\ H_{mn} &= \int \Phi_m^*(\vec{r}) \hat{H} \Phi_n(\vec{r}) d\vec{r} \\ \mathbf{H} \vec{c} &= i\hbar \frac{\partial \vec{c}}{\partial t} \end{aligned}$$

- Matrix elements of the hermitian conjugate of an operator has the following property

$$\begin{aligned} \int \Phi_n^* \hat{A}^\dagger \Phi_m d\vec{r} &= \int (\hat{A} \Phi_n)^* \Phi_m d\vec{r} \\ &= \left(\int \Phi_m^* \hat{A} \Phi_n d\vec{r} \right)^* \\ A_{nm}^\dagger &= A_{mn}^* \end{aligned}$$

- Therefore matrix elements of hermitian operators obey the condition $A_{nm}^\dagger = A_{mn}^*$.

- Inner products and overlaps of wave functions are easy to evaluate

$$\begin{aligned}
 \Psi &= \sum_n \Phi_n c_n \\
 \chi &= \sum_n \Phi_n d_n \\
 \int \Psi^* \chi \, d\vec{r} &= \sum_{nm} c_n^* d_m \int \Phi_n^* \Phi_m \, d\vec{r} \\
 &= \sum_n c_n^* d_n \\
 &= \vec{c}^* \cdot \vec{d}
 \end{aligned}$$

1.14 Time Evolution of Operators

- Schrodinger's equation gives us the time evolution of the wave function. Operators (such as those for position and momentum) have no time dependence. However, their expectation values do

$$\begin{aligned}
 \langle A(t) \rangle &= \langle \Psi(t) | \hat{A} | \Psi(t) \rangle \\
 \hat{H} | \Psi(t) \rangle &= i\hbar \frac{\partial}{\partial t} | \Psi(t) \rangle
 \end{aligned}$$

- In the Heisenberg picture we turn this round, and let the operators vary in time, keeping the wavefunction constant.
- The two approaches must yield the same expectation values. Let us look at the rate of change of this expectation value

$$\begin{aligned}
 \frac{d}{dt} \langle A(t) \rangle &= \left\langle \frac{\partial}{\partial t} \Psi(t) | \hat{A} | \Psi(t) \right\rangle + \langle \Psi(t) | \frac{\partial \hat{A}}{\partial t} | \Psi(t) \rangle + \langle \Psi(t) | \hat{A} | \frac{\partial}{\partial t} \Psi(t) \rangle \\
 &= \int \frac{\partial \Psi^*(t)}{\partial t} \hat{A} \Psi \, d\vec{r} + \int \Psi^*(t) \frac{\partial \hat{A}}{\partial t} \Psi(t) \, d\vec{r} + \int \Psi^* \hat{A} \frac{\partial \Psi(t)}{\partial t} \, d\vec{r} \\
 &= \int \left(\frac{1}{i\hbar} \hat{H} \Psi(t) \right)^* \hat{A} \Psi(t) \, d\vec{r} + \int \Psi^*(t) \frac{\partial \hat{A}}{\partial t} \Psi(t) \, d\vec{r} + \int \Psi^*(t) \hat{A} \left(\frac{1}{i\hbar} \hat{H} \Psi(t) \right) \, d\vec{r} \\
 &= \frac{1}{i\hbar} \int [-(\hat{H} \Psi(t))^* \hat{A} \Psi(t) + \Psi^*(t) \frac{\partial \hat{A}}{\partial t} \Psi(t) + \Psi^*(t) \hat{A} \hat{H} \Psi(t)] \, d\vec{r} \\
 &= \frac{1}{i\hbar} \int [-\Psi^*(t) \hat{H} \hat{A} \Psi(t) + \Psi^*(t) \frac{\partial \hat{A}}{\partial t} \Psi(t) + \Psi^*(t) \hat{A} \hat{H} \Psi(t)] \, d\vec{r} \\
 &= \frac{1}{i\hbar} \int \Psi^*(t) [\hat{A}, \hat{H}] \Psi(t) \, d\vec{r} + \int \Psi^*(t) \frac{\partial \hat{A}}{\partial t} \Psi(t) \, d\vec{r}
 \end{aligned}$$

- Heisenberg suggested that we treat the wave function as constant in time, and allow the operators to be time varying:

$$\langle A(t) \rangle = \langle \Psi(0) | \hat{A}(t) | \Psi(0) \rangle$$

- Let us write $|\Psi(t)\rangle = \hat{U}(t)|\Psi(0)\rangle$. Then $\langle A(t)\rangle = \langle\Psi(0)|\hat{U}^\dagger(t)\hat{A}\hat{U}(t)|\Psi(0)\rangle = \langle\Psi(0)|\hat{A}(t)|\Psi(0)\rangle$, and hence

$$\hat{A}(t) = \hat{U}^\dagger(t)\hat{A}\hat{U}(t)$$

- The equation of motion is thus

$$\begin{aligned}\frac{d\hat{A}(t)}{dt} &= \hat{U}^\dagger(t) \left(\frac{1}{i\hbar} [\hat{A}, \hat{H}] + \frac{\partial\hat{A}}{\partial t} \right) \hat{U}(t) \\ &= \frac{1}{i\hbar} [\hat{A}(t), \hat{H}(t)] + \hat{U}^\dagger(t) \frac{\partial\hat{A}}{\partial t} \hat{U}(t)\end{aligned}$$

Examples

1. The Hamiltonian is time invariant

$$\begin{aligned}\hat{A} &= \hat{H} \\ \frac{d\hat{H}(t)}{dt} &= \frac{1}{i\hbar} [\hat{H}(t), \hat{H}(t)] = 0 \\ \Rightarrow \hat{H}(t) &= \hat{H}(0)\end{aligned}$$

Thus the Schroedinger and Heisenberg Hamiltonians are the same.

2. The time rate of change of position is velocity

$$\begin{aligned}\hat{A} &= \hat{x} \\ \hat{H} &= \frac{\hat{p}^2}{2m} + \hat{V} \\ \frac{d\hat{x}}{dt} &= \frac{1}{i\hbar} [\hat{x}, \frac{\hat{p}^2}{2m} + \hat{V}] \\ &= \frac{1}{i\hbar} [\hat{x}, \frac{\hat{p}^2}{2m}] + \frac{1}{i\hbar} [\hat{x}, \hat{V}] \\ [\hat{x}, f(\hat{x})] &= 0 \\ \frac{d\hat{x}}{dt} &= \frac{1}{i\hbar} [\hat{x}, \frac{\hat{p}^2}{2m}] \\ &= \frac{1}{i\hbar} \frac{1}{2m} (\hat{x}\hat{p}^2 - \hat{p}^2\hat{x}) \\ &= \frac{1}{i\hbar} \frac{1}{2m} ([\hat{x}, \hat{p}]\hat{p} + \hat{p}[\hat{x}, \hat{p}]) \\ [\hat{x}, \hat{p}] &= i\hbar \\ \frac{d\hat{x}}{dt} &= \frac{\hat{p}}{m}\end{aligned}$$

- Compare this last result with the classical expression $p = m dx/dt$.

3. The rate of change of momentum equals the force:

$$\begin{aligned}\hat{A} &= \hat{p} \\ \frac{d\hat{p}}{dt} &= \frac{1}{i\hbar} [\hat{p}, \frac{\hat{p}^2}{2m} + \hat{V}] \\ &= \frac{1}{i\hbar} [\hat{p}, \frac{\hat{p}^2}{2m}] + \frac{1}{i\hbar} [\hat{p}, \hat{V}] \\ &= \frac{1}{i\hbar} [\hat{p}, \hat{V}]\end{aligned}$$

- If we work in a position representation then we have $\hat{p} = -i\hbar \frac{\partial}{\partial x}$. And hence we get

$$\begin{aligned} \frac{d\hat{p}}{dt} &= -\left[\frac{\partial}{\partial x}, V(x)\right] \\ &= -\left(\frac{\partial V}{\partial x} + V \frac{\partial}{\partial x} - V \frac{\partial}{\partial x}\right) \\ &= -\frac{\partial V}{\partial x} \end{aligned}$$

- Compare this with the classical expression $dp/dt = F = -dV/dx$.

1.15 Step-Operator Approach to Harmonic Oscillator

- Let us begin by recalling the standard way of finding the eigenstates for an harmonic oscillator.

$$\begin{aligned} \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right]\Psi_n(x) &= E_n\Psi_n(x) \\ E_n &= \lambda_n\hbar\omega \\ \omega^2 &= k/m \\ \xi &= \alpha x \\ \alpha^2 &= m\omega/\hbar \\ \frac{d^2\Psi_n}{d\xi^2} + (\lambda_n - \xi^2)\Psi_n &= 0 \end{aligned}$$

- We now consider the limit of very large displacements

$$\begin{aligned} \lim_{\xi \rightarrow \infty} \Psi_n = 0 &\Rightarrow \lim_{\xi \rightarrow \infty} \left(\frac{d^2\Psi_n}{d\xi^2} - \xi^2\Psi_n\right) = 0 \\ \Psi_n(\xi \rightarrow \infty) &\propto \xi^p \exp(-\xi^2/2) \end{aligned}$$

- This suggests that we try the following form for the wave functions

$$\begin{aligned} \Psi_n(\xi) &= N_n H_n(\xi) \exp(-\xi^2/2) \\ 0 &= \frac{d^2 H_n}{d\xi^2} - 2\xi \frac{dH_n}{d\xi} + (\lambda_n - 1)H_n \end{aligned}$$

- The function $H_n(\xi)$ is a polynomial. The full solution is

$$\begin{aligned} E_n &= \left(n + \frac{1}{2}\right)\hbar\omega \\ H_n(\xi) &= \exp(\xi^2/2) \left[\xi - \frac{d}{d\xi}\right]^n \exp(-\xi^2/2) \end{aligned}$$

- We can now turn to the step operator method of Dirac. We begin by defining three new operators in terms of which we can write Hamiltonian

operator:

$$\begin{aligned}\hat{a} &= \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\sqrt{\frac{1}{2m\hbar\omega}}\hat{p} \\ \hat{a}^\dagger &= \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\sqrt{\frac{1}{2m\hbar\omega}}\hat{p} \\ \hat{N} &= \hat{a}^\dagger\hat{a} \\ \hat{H} &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \\ &= \hbar\omega\left(\hat{N} + \frac{1}{2}\right)\end{aligned}$$

- The proof that we can rewrite the Hamiltonian in this form proceeds as follows

$$\begin{aligned}\hat{N} &= \hat{a}^\dagger\hat{a} \\ &= \left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\sqrt{\frac{1}{2m\hbar\omega}}\hat{p}\right)\left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\sqrt{\frac{1}{2m\hbar\omega}}\hat{p}\right) \\ &= \frac{m\omega}{2\hbar}\hat{x}^2 + \frac{1}{2m\hbar\omega}\hat{p}^2 + \frac{i}{2\hbar}[\hat{x}, \hat{p}] \\ &= \frac{1}{\hbar\omega}\hat{H} - \frac{1}{2}\end{aligned}$$

- We are now in a position to go through a series of steps to find the eigenstates of the harmonic oscillator using these operators.

1. The eigenstates of \hat{N} are also eigenstates of the Hamiltonian.

$$\begin{aligned}\hat{N}|n\rangle &= n|n\rangle \\ \hat{H}|n\rangle &= \left(n + \frac{1}{2}\right)\hbar\omega|n\rangle\end{aligned}$$

2. Note that the number operator \hat{N} is hermitian: $\hat{N}^\dagger = (\hat{a}^\dagger\hat{a})^\dagger = \hat{a}^\dagger(\hat{a}^\dagger)^\dagger = \hat{a}^\dagger\hat{a} = \hat{N}$.
3. The eigenvalues of the number operator are non-negative: $n = \langle n|\hat{N}|n\rangle = \langle n|\hat{a}^\dagger\hat{a}|n\rangle = \langle \Phi|\Phi\rangle \geq 0$, where $|\Phi\rangle = \hat{a}|n\rangle$.
4. The operators \hat{a} and \hat{a}^\dagger do not commute:

$$\begin{aligned}[\hat{a}, \hat{a}^\dagger] &= \left[\sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\sqrt{\frac{1}{2m\hbar\omega}}\hat{p}, \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\sqrt{\frac{1}{2m\hbar\omega}}\hat{p}\right] \\ &= \frac{[\hat{x}, \hat{p}]}{i\hbar} \\ &= 1\end{aligned}$$

5. These operators do not commute with the number operator either:

$$[\hat{N}, \hat{a}] = \hat{a}^\dagger\hat{a}\hat{a} - \hat{a}\hat{a}^\dagger\hat{a}$$

$$\begin{aligned}
&= (\hat{a}\hat{a}^\dagger - 1 - \hat{a}\hat{a}^\dagger)\hat{a} \\
&= -\hat{a} \\
[\hat{N}, \hat{a}^\dagger] &= \hat{a}^\dagger\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}^\dagger\hat{a} \\
&= \hat{a}^\dagger(1 + \hat{a}^\dagger\hat{a}^\dagger - \hat{a}^\dagger\hat{a}^\dagger) \\
&= \hat{a}^\dagger
\end{aligned}$$

6. We can use our operators to generate new eigenstates of the number operator: $\hat{N}\hat{a}|n\rangle = \hat{a}(\hat{N} - 1)|n\rangle = (n - 1)\hat{a}|n\rangle$. Therefore if $|n\rangle$ is an eigenstate of the number operator with eigenvalue n , then $\hat{a}|n\rangle$ is also an eigenstate of the number operator but with the new eigenvalue $n - 1$. By considering normalisation we obtain the following:

$$\begin{aligned}
\hat{a}|n\rangle &= \alpha|n - 1\rangle \\
\langle n - 1|n - 1\rangle = \langle n|n\rangle &= 1 \\
\alpha^2 &= \langle n|\hat{a}^\dagger\hat{a}|n\rangle \\
&= \langle n|\hat{N}|n\rangle \\
&= n \\
\hat{a}|n\rangle &= \sqrt{n}|n - 1\rangle
\end{aligned}$$

7. Thus if n is an eigenvalue of \hat{N} then so is $n - 1$, and therefore so are $n - 2, n - 3, \dots$. But we have the condition $n \geq 0$. Therefore the eigenvalues must be integers so that this sequence terminates: $\hat{a}|0\rangle = 0$.
8. We are also able to generate eigenstates using the conjugate operator: $\hat{N}\hat{a}^\dagger|n\rangle = \hat{a}^\dagger(\hat{N} + 1)|n\rangle = (n + 1)\hat{a}^\dagger|n\rangle$. Thus if n is an eigenvalue of \hat{N} , so is $n + 1$. Thus the eigenvalues of the number operator are elements of the set of non-negative integers. Once again by considering normalisation we obtain

$$\begin{aligned}
\hat{a}^\dagger|n\rangle &= \alpha|n + 1\rangle \\
\langle n + 1|n + 1\rangle = \langle n|n\rangle &= 1 \\
\alpha^2 &= \langle n|\hat{a}\hat{a}^\dagger|n\rangle \\
&= \langle n|1 + \hat{N}|n\rangle \\
&= n + 1 \\
\hat{a}^\dagger|n\rangle &= \sqrt{n + 1}|n + 1\rangle
\end{aligned}$$

9. Thus if we know $|0\rangle$ then we can generate all other eigenstates

$$\begin{aligned}
|1\rangle &= \hat{a}^\dagger|0\rangle \\
|2\rangle &= \sqrt{\frac{1}{2}}\hat{a}^\dagger|1\rangle = \sqrt{\frac{1}{2}}(\hat{a}^\dagger)^2|0\rangle \\
|n\rangle &= \sqrt{\frac{1}{n!}}(\hat{a}^\dagger)^n|0\rangle
\end{aligned}$$

10. We have thus found all the eigenvalues of the Hamiltonian ($E_n = (n + \frac{1}{2})\hbar\omega$), and know how to generate all the eigenvectors once we have at

least one of them. What we now need is a procedure to generate one eigenvector. We do this as follows:

$$\begin{aligned}
 \hat{a}|0\rangle &= 0 \\
 \left(\sqrt{\frac{m\omega}{2\hbar}}x + i\sqrt{\frac{1}{2m\hbar\omega}} \left(-i\hbar\frac{\partial}{\partial x} \right) \right) \Psi_0(x) &= 0 \\
 \frac{\partial\Psi_0}{\partial x} &= -\frac{m\omega x}{\hbar}\Psi_0 \\
 \Psi_0(x) &= A \exp\left(-\frac{m\omega x^2}{2\hbar}\right) \\
 \int \Psi_0^* \Psi_0 dx &= 1 \\
 \Rightarrow A &= \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}
 \end{aligned}$$

Chapter 2

Angular Momentum [8]

2.1 A Refresher on Commutation Relations

1. The classical expression for orbital angular momentum is $\vec{L} = \vec{r} \times \vec{p}$. In quantum mechanics it is defined by

$$\hat{L} = \begin{pmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{pmatrix} \times \begin{pmatrix} \hat{p}_x \\ \hat{p}_y \\ \hat{p}_z \end{pmatrix}$$
$$\begin{pmatrix} \hat{L}_x \\ \hat{L}_y \\ \hat{L}_z \end{pmatrix} = \begin{pmatrix} \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \end{pmatrix}$$

2. We have the commutation relations for position and momentum:

$$\begin{aligned} [\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] &= [\hat{z}, \hat{p}_z] = i\hbar \\ [\hat{x}, \hat{p}_y] = [\hat{x}, \hat{p}_z] &= [\hat{y}, \hat{p}_x] = [\hat{y}, \hat{p}_z] = [\hat{z}, \hat{p}_x] = [\hat{z}, \hat{p}_y] = 0 \end{aligned}$$

3. The angular momentum operator is hermitian:

$$\begin{aligned} \hat{L}_x^\dagger &= (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)^\dagger \\ &= (\hat{y}\hat{p}_z)^\dagger - (\hat{z}\hat{p}_y)^\dagger \\ &= \hat{p}_z^\dagger \hat{y}^\dagger - \hat{p}_y^\dagger \hat{z}^\dagger \\ &= \hat{p}_z \hat{y} - \hat{p}_y \hat{z} \\ &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ &= \hat{L}_x \text{ etc.} \end{aligned}$$

4. The commutators between angular momentum and position are

$$\begin{aligned} [\hat{L}_x, \hat{x}] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{x}] = 0 \\ [\hat{L}_x, \hat{y}] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{y}] = -\hat{z}[\hat{p}_y, \hat{y}] = i\hbar\hat{z} \\ [\hat{L}_x, \hat{z}] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}] = \hat{y}[\hat{p}_z, \hat{z}] = -i\hbar\hat{y} \\ [\hat{L}_y, \hat{x}] &= -i\hbar\hat{z} \end{aligned}$$

$$\begin{aligned}
[\hat{L}_y, \hat{y}] &= 0 \\
[\hat{L}_y, \hat{z}] &= i\hbar\hat{x} \\
[\hat{L}_z, \hat{x}] &= i\hbar\hat{y} \\
[\hat{L}_z, \hat{y}] &= -i\hbar\hat{x} \\
[\hat{L}_z, \hat{z}] &= 0
\end{aligned}$$

- This can be written compactly as $[\vec{n} \cdot \hat{L}, \hat{r}] = i\hbar\hat{r} \times \vec{n}$ where \vec{n} is a unit vector, and \hat{r} is the position operator.

5. The commutators between angular momentum and momentum operators are:

$$\begin{aligned}
[\hat{L}_x, \hat{p}_x] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{p}_x] = 0 \\
[\hat{L}_x, \hat{p}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{p}_y] = \hat{p}_z[\hat{y}, \hat{p}_y] = i\hbar\hat{p}_z \text{ etc.}
\end{aligned}$$

- This can be written compactly as $[\vec{n} \cdot \hat{L}, \hat{p}] = i\hbar\hat{p} \times \vec{n}$

6. The commutators between angular momentum operators are:

$$\begin{aligned}
[\hat{L}_x, \hat{L}_x] &= 0 \\
[\hat{L}_x, \hat{L}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] = i\hbar\hat{L}_z \text{ etc.}
\end{aligned}$$

- This can be written compactly as $\hat{L} \times \hat{L} = i\hbar\hat{L}$.

7. The commutators between the squares of the angular momentum operators and the angular momentum operators is given by the following:

$$\begin{aligned}
[\hat{L}_x^2, \hat{L}_x] &= 0 \\
[\hat{L}_y^2, \hat{L}_x] &= -i\hbar(\hat{L}_z\hat{L}_y + \hat{L}_y\hat{L}_z) \\
[\hat{L}_z^2, \hat{L}_x] &= i\hbar(\hat{L}_z\hat{L}_y + \hat{L}_y\hat{L}_z) \\
\Rightarrow [\hat{L}^2, \hat{L}_x] &= [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x] = 0
\end{aligned}$$

- More generally we have $[\hat{L}^2, \hat{L}] = 0$.

2.2 Eigenvalues and Eigenfunctions of Orbital Angular Momentum Operators

1. Consider $[\hat{L}^2, \hat{L}_z] = 0$. This implies that the eigenstates of \hat{L}_z are also eigenstates of \hat{L}^2 . Let us define one of these eigenstates by $|\Lambda\lambda\rangle$ where $\hat{L}^2|\Lambda\lambda\rangle = \Lambda|\Lambda\lambda\rangle$ and $\hat{L}_z|\Lambda\lambda\rangle = \lambda|\Lambda\lambda\rangle$.
2. We now show that the eigenvalues Λ are not negative.

$$\begin{aligned}
\langle\Lambda\lambda|\hat{L}^2|\Lambda\lambda\rangle &= \sum_i \langle\Lambda\lambda|\hat{L}_i^\dagger\hat{L}_i|\Lambda\lambda\rangle = \Lambda \\
\hat{L}_i|\Lambda\lambda\rangle &= |\Lambda\lambda i\rangle \\
\Rightarrow \Lambda &= \sum_i \langle\Lambda\lambda i|\Lambda\lambda i\rangle \geq 0
\end{aligned}$$

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- In the light of this, we shall write $\Lambda = \hbar^2 l(l+1)$, $\lambda = \hbar m$, and the eigenstates as $|lm\rangle$.
3. Note that $[\hat{L}_x, \hat{L}_z] \neq 0$ and $[\hat{L}_y, \hat{L}_z] \neq 0$. Therefore the eigenstates of \hat{L}_x and \hat{L}_y are not $|lm\rangle$. However these operators commute with \hat{L}^2 . These apparently contradictory statements can be satisfied if the eigenstates of these operators are linear combinations of $|lm\rangle$, where all eigenstates in the sum have the same value of l .
 4. We shall now write the operators and eigenfunctions for orbital angular momentum in terms of specific coordinates. This will allow us to produce functions that we can visualise. It is conventional to use spherical coordinates, and this is what we shall use here. The formulae that connect rectangular coordinates to spherical coordinates are the following

$$\begin{aligned} \begin{pmatrix} x \\ y \\ z \end{pmatrix} &= \begin{pmatrix} r \sin \theta \cos \phi \\ r \sin \theta \sin \phi \\ r \cos \theta \end{pmatrix} \\ \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} &= \begin{pmatrix} \frac{\partial r}{\partial x} & \frac{\partial \theta}{\partial x} & \frac{\partial \phi}{\partial x} \\ \frac{\partial r}{\partial y} & \frac{\partial \theta}{\partial y} & \frac{\partial \phi}{\partial y} \\ \frac{\partial r}{\partial z} & \frac{\partial \theta}{\partial z} & \frac{\partial \phi}{\partial z} \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \phi} \end{pmatrix} \\ \begin{pmatrix} \frac{\partial r}{\partial x} & \frac{\partial \theta}{\partial x} & \frac{\partial \phi}{\partial x} \\ \frac{\partial r}{\partial y} & \frac{\partial \theta}{\partial y} & \frac{\partial \phi}{\partial y} \\ \frac{\partial r}{\partial z} & \frac{\partial \theta}{\partial z} & \frac{\partial \phi}{\partial z} \end{pmatrix} &= \begin{pmatrix} \sin \theta \cos \phi & \frac{\cos \theta \cos \phi}{r} & -\frac{\sin \phi}{r} \\ \sin \theta \sin \phi & \frac{\cos \theta \sin \phi}{r} & \frac{\cos \phi}{r} \\ \cos \theta & -\frac{\sin \theta}{r} & 0 \end{pmatrix} \\ \hat{L} = \begin{pmatrix} \hat{L}_x \\ \hat{L}_y \\ \hat{L}_z \end{pmatrix} &= \begin{pmatrix} y\hat{p}_z - z\hat{p}_y \\ z\hat{p}_x - x\hat{p}_z \\ x\hat{p}_y - y\hat{p}_x \end{pmatrix} \\ &= -i\hbar \begin{pmatrix} y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \\ z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \\ x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \end{pmatrix} \\ &= -i\hbar \begin{pmatrix} -\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \\ \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \\ \frac{\partial}{\partial \phi} \end{pmatrix} \end{aligned}$$

5. We get immediately

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

6. We want states that are simultaneous eigenstates of \hat{L}_z and \hat{L}^2 . We give the symbol $Y_{lm}(\theta, \phi)$ to the eigenstates. Thus we have:

$$\begin{aligned} \hat{L}_z Y_{lm}(\theta, \phi) &= \hbar m Y_{lm}(\theta, \phi) \\ \Rightarrow -i\hbar \frac{\partial}{\partial \phi} Y_{lm}(\theta, \phi) &= \hbar m Y_{lm}(\theta, \phi) \\ \Rightarrow \frac{\partial}{\partial \phi} Y_{lm}(\theta, \phi) &= im Y_{lm}(\theta, \phi) \\ \Rightarrow Y_{lm}(\theta, \phi) &= e^{im\phi} f_{lm}(\theta) \end{aligned}$$

7. For a single valued wave function we must have $Y_{lm}(\theta, \phi + 2\pi) = Y_{lm}(\theta, \phi)$. Therefore m must be an integer.
8. To determine the function $f_{lm}(\theta)$ we make use of the fact that our state is also an eigenstate of \hat{L}^2 .

$$\begin{aligned} \hat{L}^2 e^{im\phi} f_{lm}(\theta) &= \hbar^2 l(l+1) e^{im\phi} f_{lm}(\theta) \\ \Rightarrow -\hbar^2 \left[\cot \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] e^{im\phi} f_{lm}(\theta) &= \hbar^2 l(l+1) e^{im\phi} f_{lm}(\theta) \\ \Rightarrow - \left[\cot \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} - \frac{m^2}{\sin^2 \theta} \right] f_{lm}(\theta) &= l(l+1) f_{lm}(\theta) \end{aligned}$$

9. We can eliminate all the trigonometric functions by making the following substitution $\mu = \cos \theta$. If we define $F_{lm}(\mu) = f_{lm}(\theta)$ we get

$$\begin{aligned} \frac{df_{lm}(\theta)}{d\theta} &= \frac{d\mu}{d\theta} \frac{dF_{lm}(\mu)}{d\mu} \\ &= -\sin \theta \frac{dF_{lm}(\mu)}{d\mu} \\ \Rightarrow \frac{d^2 f_{lm}(\theta)}{d\theta^2} &= \left(-\sin \theta \frac{d}{d\mu} \right)^2 F_{lm}(\mu) \\ &= \left(-\cos \theta \frac{d}{d\mu} + \sin \theta^2 \frac{d^2}{d\mu^2} \right) F_{lm}(\mu) \\ \Rightarrow l(l+1) F_{lm}(\mu) &= \left[2\mu \frac{d}{d\mu} - (1-\mu^2) \frac{d^2}{d\mu^2} + \frac{m^2}{1-\mu^2} \right] F_{lm}(\mu) \end{aligned}$$

10. The factor of $1/(1-\mu^2)$ makes finding a solution problematic. So we introduce another substitution to remove it $F_{lm}(\mu) = [1-\mu^2]^{|m|/2} G_{lm}(\mu)$. Hence

$$\begin{aligned} \frac{dF_{lm}(\mu)}{d\mu} &= -|m|\mu[1-\mu^2]^{|m|/2-1} G_{lm}(\mu) + [1-\mu^2]^{|m|/2} \frac{dG_{lm}(\mu)}{d\mu} \\ \frac{d^2 F_{lm}(\mu)}{d\mu^2} &= [1-\mu^2]^{|m|/2} \left\{ -\frac{|m|}{1-\mu^2} + \frac{2\mu^2|m|(|m|/2-1)}{(1-\mu^2)^2} - \frac{2|m|}{1-\mu^2} \frac{d}{d\mu} + \frac{d^2}{d\mu^2} \right\} G_{lm}(\mu) \\ \Rightarrow 0 &= [1-\mu^2]^{|m|/2} \left\{ l(l+1) - |m|(|m|+1) - 2\mu(|m|+1) \frac{d}{d\mu} + (1-\mu^2) \frac{d^2}{d\mu^2} \right\} G_{lm}(\mu) \end{aligned}$$

11. We now make a polynomial expansion for $G_{lm}(\mu) = \sum_{n=0}^{\infty} C_{lm}^{(n)} \mu^n$. This gives:

$$C_{lm}^{(n+2)} = \left[\frac{n(n-1) + 2n(|m|+1) + |m|(|m|+1) - l(l+1)}{(n+1)(n+2)} \right] C_{lm}^{(n)}$$

12. To obtain a convergent series, there must be an N such that $C_{lm}^{(N+2)} = 0$. Hence

$$\begin{aligned} 0 &= N(N-1) + 2N(|m|+1) + |m|(|m|+1) - l(l+1) \\ \Rightarrow N &= -(|m| + \frac{1}{2}) \pm (l + \frac{1}{2}) \\ \Rightarrow N &= l - |m| \quad \text{as } N \geq 0 \\ \Rightarrow l &= \text{integer} \end{aligned}$$

2.3. GENERALIZED ANGULAR MOMENTUM AND STEP OPERATOR TECHNIQUES IN ANGULAR MOMENTUM

13. Thus, putting all this together we have

$$\begin{aligned} Y_{lm}(\theta, \phi) &= N_{lm} e^{im\phi} (\sin \theta)^{|m|} \sum_{n=0}^{l-|m|} C_{lm}^{(n)} (\cos \theta)^n \\ &= (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\cos \theta) e^{im\phi} \end{aligned}$$

14. $P_l^m(\mu)$ is an associated Legendre polynomial given by $P_l^m(\mu) = (1 - \mu^2)^{|m|/2} \frac{d^m}{d\mu^m} P_l(\mu)$, and $P_l(\mu)$ is a Legendre polynomial, where

$$\begin{aligned} P_0(\mu) &= 1 \\ P_1(\mu) &= \mu \\ 0 &= (l+1)P_{l+1}(\mu) - (2l+1)\mu P_l(\mu) + lP_{l-1}(\mu) \end{aligned}$$

15. The eigenstates are orthonormal

$$\int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) = \delta_{ll'} \delta_{mm'}$$

16. Some of the functions are

Table 2.1: Spherical harmonics

$$\begin{aligned} Y_{00}(\theta, \phi) &= \frac{1}{\sqrt{4\pi}} \\ Y_{10}(\theta, \phi) &= \sqrt{\frac{3}{4\pi}} \cos \theta \quad Y_{1\pm 1}(\theta, \phi) = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi} \end{aligned}$$

2.3 Generalized Angular Momentum and Step Operator Techniques in Angular Momentum Theory

- We now write down formal expressions for angular momenta that apply to orbital angular momentum, but also more generally to things like spin.
 - Generalised angular momenta are defined by the commutation relations between the operators.
1. We define the raising and lowering operators $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$. Note that $\hat{L}_-^\dagger = \hat{L}_+$.
 2. We now consider the commutation relations for the raising and lowering operators

$$\begin{aligned} \hat{L}_+ \hat{L}_- &= (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) \\ &= \hat{L}_x^2 + \hat{L}_y^2 + i(\hat{L}_y \hat{L}_x - \hat{L}_x \hat{L}_y) \\ &= \hat{L}^2 - \hat{L}_z^2 + \hbar \hat{L}_z \end{aligned}$$

$$\begin{aligned}
\hat{L}_- \hat{L}_+ &= \hat{L}^2 - \hat{L}_z^2 - \hbar \hat{L}_z \\
[\hat{L}_+, \hat{L}_-] &= 2\hbar \hat{L}_z \\
[\hat{L}_z, \hat{L}_\pm] &= \pm \hbar \hat{L}_\pm
\end{aligned}$$

3. Equipped with these commutation relations we are now in a position to determine the eigenvalues and eigenvectors of the angular momenta operators. First we determine the range for the magnetic quantum number. If we define $\hat{L}_- |lm\rangle = |\chi\rangle$, then we have $\langle lm | \hat{L}_+ \hat{L}_- |lm\rangle = \langle \chi | \chi \rangle \geq 0$. Similarly we have $\langle lm | \hat{L}_- \hat{L}_+ |lm\rangle \geq 0$. Therefore we can write

$$\begin{aligned}
\langle lm | \hat{L}_- \hat{L}_+ |lm\rangle &= \langle lm | \hat{L}^2 - \hat{L}_z^2 + \hbar \hat{L}_z |lm\rangle \\
&= \hbar^2 [l(l+1) - m^2 + m] \\
&\geq 0 \\
\Rightarrow (l + \frac{1}{2})^2 &\geq (m - \frac{1}{2})^2 \\
\Rightarrow l &\geq -m \\
\langle lm | \hat{L}_+ \hat{L}_- |lm\rangle &= \langle lm | \hat{L}^2 - \hat{L}_z^2 - \hbar \hat{L}_z |lm\rangle \\
&= \hbar^2 [l(l+1) - m^2 - m] \\
&\geq 0 \\
\Rightarrow (l + \frac{1}{2})^2 &\geq (m + \frac{1}{2})^2 \\
\Rightarrow l &\geq m \\
\Rightarrow -l &\leq m \leq l
\end{aligned}$$

4. Now we build the eigenstates using the step operators

$$\begin{aligned}
\hat{L}_z \hat{L}_- |lm\rangle &= \hat{L}_- (\hat{L}_z - \hbar) |lm\rangle \\
&= \hat{L}_- (m\hbar - \hbar) |lm\rangle \\
&= \hbar(m-1) \hat{L}_- |lm\rangle \\
\Rightarrow \hat{L}_- |lm\rangle &= \alpha |lm-1\rangle \\
\Rightarrow \langle lm | \hat{L}_+ \hat{L}_- |lm\rangle &= \alpha^2 \langle lm-1 | lm-1\rangle \\
\text{But } \langle lm | \hat{L}_+ \hat{L}_- |lm\rangle &= \hbar^2 [l(l+1) - m^2 - m] \\
\Rightarrow \alpha^2 &= \hbar^2 [l(l+1) - m^2 - m] \\
\Rightarrow \hat{L}_- |lm\rangle &= \hbar \sqrt{[l(l+1) - m(m-1)]} |lm-1\rangle
\end{aligned}$$

5. By a similar argument we can show that

$$\hat{L}_+ |lm\rangle = \hbar \sqrt{[l(l+1) - m(m+1)]} |lm+1\rangle$$

6. From the above we see that if $\hbar m$ is an eigenstate of \hat{L}_z , then so are $\hbar(m+1)$, $\hbar(m+2)$, etc. But we have the condition that $m \leq l$, therefore for some $m \leq l$ the coefficient $\sqrt{[l(l+1) - m(m+1)]}$ must vanish in order for the series of eigenstates to terminate. Clearly this occurs for $m = l$. Thus $m \in \{l, l-1, l-2, \dots\}$.

7. We also have $m \geq -l$. The smallest value of m satisfies $\sqrt{[l(l+1) - m(m-1)]} = 0$. This occurs for $m = -l$. Thus $m \in \{l, l-1, l-2, \dots, -l+1, -l\}$. Therefore $l = -l + N$ where N is a non-negative integer. Thus

$$l = \frac{N}{2} = \begin{cases} \text{integer} & N \text{ even} \\ \text{integer} + \frac{1}{2} & N \text{ odd} \end{cases}$$

2.4 Spin-1/2 Angular Momentum and Pauli Matrices

- Electrons have an internal degree of freedom (spin), as seen in the Stern-Gerlach experiment.
- It is a form of angular momentum with magnitude $\frac{1}{2}\hbar$.
- The operator for spin is \hat{s} . It obeys the rules of angular momentum operators:

$$\begin{aligned} \hat{s} \times \hat{s} &= i\hbar\hat{s} \\ [\hat{s}^2, \hat{s}] &= 0 \\ \hat{s}^2 \left| \frac{1}{2} m_s \right\rangle &= \frac{1}{2} \left(\frac{1}{2} + 1 \right) \hbar^2 \left| \frac{1}{2} m_s \right\rangle \\ &= \frac{3}{4} \hbar^2 \left| \frac{1}{2} m_s \right\rangle \\ \hat{s}_z \left| \frac{1}{2} m_s \right\rangle &= m_s \hbar \left| \frac{1}{2} m_s \right\rangle \\ m_s &\in \left\{ \frac{1}{2}, -\frac{1}{2} \right\} \end{aligned}$$

- The convention for the state vectors (Dirac notation) is

Table 2.2: Spin states

$$\begin{array}{ll} |\alpha\rangle = \left| \frac{1}{2} \frac{1}{2} \right\rangle & |\beta\rangle = \left| \frac{1}{2} -\frac{1}{2} \right\rangle \\ \hat{s}^2 |\alpha\rangle = \frac{3}{4} \hbar^2 |\alpha\rangle & \hat{s}^2 |\beta\rangle = \frac{3}{4} \hbar^2 |\beta\rangle \\ \hat{s}_z |\alpha\rangle = \frac{1}{2} \hbar |\alpha\rangle & \hat{s}_z |\beta\rangle = -\frac{1}{2} \hbar |\beta\rangle \\ \langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 & \langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0 \end{array}$$

- Now consider \hat{s}_x and \hat{s}_y :

Table 2.3: \hat{s}_x and \hat{s}_y

$$\begin{array}{ll}
\hat{s}_+ = \hat{s}_x + i\hat{s}_y & \hat{s}_- = \hat{s}_x - i\hat{s}_y \\
\hat{s}_+|\alpha\rangle = 0 & \hat{s}_-|\alpha\rangle = \hbar|\beta\rangle \\
\hat{s}_+|\beta\rangle = \hbar|\alpha\rangle & \hat{s}_-|\beta\rangle = 0 \\
\hat{s}_x = \frac{1}{2}(\hat{s}_+ + \hat{s}_-) & \hat{s}_y = \frac{1}{2i}(\hat{s}_+ - \hat{s}_-) \\
\hat{s}_x|\alpha\rangle = \frac{1}{2}\hbar|\beta\rangle & \hat{s}_x|\beta\rangle = \frac{1}{2}\hbar|\alpha\rangle \\
\hat{s}_y|\alpha\rangle = i\frac{1}{2}\hbar|\beta\rangle & \hat{s}_y|\beta\rangle = -i\frac{1}{2}\hbar|\alpha\rangle \\
\hat{s}_z|\alpha\rangle = \frac{1}{2}\hbar|\alpha\rangle & \hat{s}_z|\beta\rangle = -\frac{1}{2}\hbar|\beta\rangle
\end{array}$$

- We now derive the Pauli spin matrices. A general spin state can be written as $|\chi\rangle = a|\alpha\rangle + b|\beta\rangle$. A general spin operator \hat{o} acting on $|\chi\rangle$ produces a new vector $|\Phi\rangle = \hat{o}|\chi\rangle$. But we can expand this state vector in our original basis set: $|\Phi\rangle = c|\alpha\rangle + d|\beta\rangle$. Combining these equations we obtain $(c|\alpha\rangle + d|\beta\rangle) = \hat{o}(a|\alpha\rangle + b|\beta\rangle)$. Evaluating overlap integrals gives us

$$\begin{aligned}
c &= \langle\alpha|\hat{o}|\alpha\rangle a + \langle\alpha|\hat{o}|\beta\rangle b \\
d &= \langle\beta|\hat{o}|\alpha\rangle a + \langle\beta|\hat{o}|\beta\rangle b
\end{aligned}$$

- In matrix notation we can write this as

$$\begin{pmatrix} c \\ d \end{pmatrix} = \begin{pmatrix} \langle\alpha|\hat{o}|\alpha\rangle & \langle\alpha|\hat{o}|\beta\rangle \\ \langle\beta|\hat{o}|\alpha\rangle & \langle\beta|\hat{o}|\beta\rangle \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}$$

- Therefore we can represent the operator \hat{o} by the matrix

$$\mathbf{o} = \begin{pmatrix} \langle\alpha|\hat{o}|\alpha\rangle & \langle\alpha|\hat{o}|\beta\rangle \\ \langle\beta|\hat{o}|\alpha\rangle & \langle\beta|\hat{o}|\beta\rangle \end{pmatrix}$$

- The spin matrices are thus given by

Table 2.4: Spin matrices

$$\begin{aligned}
\mathbf{s}^2 &= \begin{pmatrix} \frac{3}{4}\hbar^2 & 0 \\ 0 & \frac{3}{4}\hbar^2 \end{pmatrix} & \mathbf{s}_x &= \begin{pmatrix} 0 & \frac{1}{2}\hbar \\ \frac{1}{2}\hbar & 0 \end{pmatrix} \\
\mathbf{s}_y &= \begin{pmatrix} 0 & -i\frac{1}{2}\hbar \\ i\frac{1}{2}\hbar & 0 \end{pmatrix} & \mathbf{s}_z &= \begin{pmatrix} \frac{1}{2}\hbar & 0 \\ 0 & -\frac{1}{2}\hbar \end{pmatrix}
\end{aligned}$$

- Pauli introduced the matrices $\sigma_i = \frac{2}{\hbar}\mathbf{s}_i$

Table 2.5: Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \mathbf{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

- The Pauli spin matrices obey the following relations

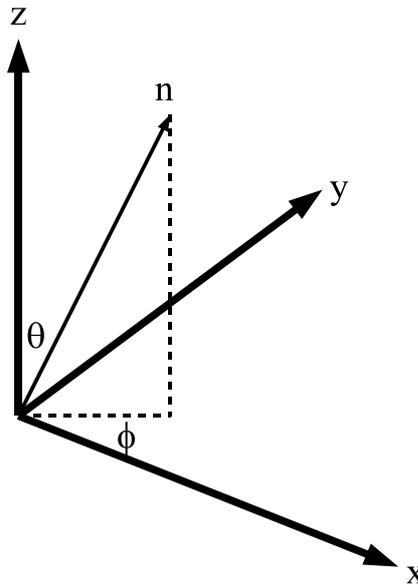
$$\begin{aligned}
 [\sigma_x, \sigma_y] &= 2i\sigma_z \\
 [\sigma_y, \sigma_z] &= 2i\sigma_x \\
 [\sigma_z, \sigma_x] &= 2i\sigma_y \\
 \sigma_x^2 = \sigma_y^2 = \sigma_z^2 &= 1 \\
 \text{Tr}\sigma_x = \text{Tr}\sigma_y = \text{Tr}\sigma_z &= 0 \\
 \det\sigma_x = \det\sigma_y = \det\sigma_z &= -1 \\
 [\sigma_i, \sigma_j]_+ &= 2\mathbf{I}\delta_{ij} \\
 \text{where } [A, B]_+ &= AB + BA \\
 \sigma_z\alpha &= \alpha \\
 \sigma_z\beta &= -\beta \\
 \sigma^2\alpha &= 3\alpha \\
 \sigma^2\beta &= 3\beta
 \end{aligned}$$

Example - spin about an arbitrary axis

- Consider the operator for a spin aligned along an arbitrary direction \hat{n} ($\hat{s} \cdot \hat{n}$) where

$$\hat{n} = \begin{pmatrix} \sin\theta \cos\phi \\ \sin\theta \sin\phi \\ \cos\theta \end{pmatrix}$$

Figure 2.1: Axes



- The matrix representing the operator equals

$$\begin{aligned}
 s_n &= s \cdot \hat{n} = \frac{\hbar}{2} \sigma \cdot \hat{n} \\
 &= \frac{\hbar}{2} \begin{pmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{pmatrix} \cdot \begin{pmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{pmatrix} \\
 &= \frac{\hbar}{2} \begin{pmatrix} \cos \theta & \sin \theta e^{-i\phi} \\ \sin \theta e^{i\phi} & -\cos \theta \end{pmatrix}
 \end{aligned}$$

- The eigenvalues of this operator are found from

$$\begin{aligned}
 \det |s_n - \lambda I| &= 0 \\
 \Rightarrow \frac{\hbar}{2} \begin{pmatrix} \cos \theta - \frac{2\lambda}{\hbar} & \sin \theta e^{-i\phi} \\ \sin \theta e^{i\phi} & -\cos \theta - \frac{2\lambda}{\hbar} \end{pmatrix} &= 0 \\
 \Rightarrow \lambda^2 &= \frac{\hbar^2}{4} \\
 \Rightarrow \lambda &= \pm \frac{\hbar}{2}
 \end{aligned}$$

- The eigenvalues are independent of direction. The eigenvectors ($X_\lambda(\hat{n})$) satisfy

$$\begin{aligned}
 s_n X_\lambda(\hat{n}) &= \lambda X_\lambda(\hat{n}) \\
 \frac{\hbar}{2} \begin{pmatrix} \cos \theta & \sin \theta e^{-i\phi} \\ \sin \theta e^{i\phi} & -\cos \theta \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} &= \lambda \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \\
 \Rightarrow X_+(\hat{n}) &= \begin{pmatrix} \cos(\theta/2) \\ \sin(\theta/2) e^{i\phi} \end{pmatrix} \\
 X_-(\hat{n}) &= \begin{pmatrix} -\sin(\theta/2) \\ \cos(\theta/2) e^{i\phi} \end{pmatrix}
 \end{aligned}$$

- We have normalised the vectors to 1. In Dirac notation

$$\begin{aligned}
 |X_+(\hat{n})\rangle &= \cos(\theta/2)|\alpha\rangle + \sin(\theta/2) e^{i\phi} |\beta\rangle \\
 |X_-(\hat{n})\rangle &= -\sin(\theta/2)|\alpha\rangle + \cos(\theta/2) e^{i\phi} |\beta\rangle
 \end{aligned}$$

- Consider the special cases of the axes

$$\begin{aligned}
 |X_+(\hat{x})\rangle &= \frac{1}{\sqrt{2}}[|\alpha\rangle + |\beta\rangle] \\
 |X_-(\hat{x})\rangle &= \frac{1}{\sqrt{2}}[-|\alpha\rangle + |\beta\rangle] \\
 |X_+(\hat{y})\rangle &= \frac{1}{\sqrt{2}}[|\alpha\rangle + i|\beta\rangle] \\
 |X_-(\hat{y})\rangle &= \frac{1}{\sqrt{2}}[-|\alpha\rangle + i|\beta\rangle] \\
 |X_+(\hat{z})\rangle &= |\alpha\rangle \\
 |X_-(\hat{z})\rangle &= |\beta\rangle
 \end{aligned}$$

- If the system starts in the up eigenstate of $\hat{s} \cdot \hat{n}$, then the probability of a measurement of \hat{s}_z giving up or down are $\cos^2(\theta/2)$ and $\sin^2(\theta/2)$ respectively. If the system started in the down eigenstate they are $\sin^2(\theta/2)$ and $\cos^2(\theta/2)$ respectively.

2.5 Magnetic Moments

- The electron has an intrinsic magnetic moment associated with its spin $\vec{m}_s = -g_s \mu_B \vec{s} / \hbar = -g_s \mu_B \vec{\sigma} / 2$, where g_s is the gyromagnetic ratio. $g_s \approx 2$. μ_B is the Bohr magneton.
- Protons also have a spin of $\frac{1}{2}\hbar$, and a magnetic moment. However the constants differ from those for the electron: $\vec{m}_s = +g_P \mu_N \vec{\sigma} / 2$, $\mu_N = e\hbar/2M_P$ and $g_P \approx 5.5883$.
- The magnetic moment couples to a magnetic field. The contribution to the Hamiltonian from this coupling is $\Delta\hat{H} = -\hat{m}_s \cdot \vec{B}$

2.6 Combination of Angular Momenta

- We will deal with this as an abstract problem first of all, and then apply it to specific cases.
- Consider the two general angular momenta which belong to two independent subsystems \hat{J}_1 and \hat{J}_2 . For example they might be orbital angular momentum and spin. Because they belong to independent subsystems they must commute $[\hat{J}_1, \hat{J}_2] = 0$.
- These operators obey the usual angular momentum eigenequations

$$\begin{aligned}\hat{J}_1^2 |j_1 m_1\rangle &= j_1(j_1 + 1)\hbar^2 |j_1 m_1\rangle \\ \hat{J}_2^2 |j_2 m_2\rangle &= j_2(j_2 + 1)\hbar^2 |j_2 m_2\rangle \\ \hat{J}_{1,z} |j_1 m_1\rangle &= m_1 \hbar |j_1 m_1\rangle \\ \hat{J}_{2,z} |j_2 m_2\rangle &= m_2 \hbar |j_2 m_2\rangle\end{aligned}$$

- If we work with wave functions, then the combined wave function for two angular momenta is just the product of the individual wave functions: $\Psi(j_1 m_1 j_2 m_2) = \Psi_1(j_1 m_1) \Psi_2(j_2 m_2)$. We represent this by the following state vector $|j_1 j_2 m_1 m_2\rangle$.
- This joined vector satisfies the following relations

$$\begin{aligned}\hat{J}_1^2 |j_1 j_2 m_1 m_2\rangle &= j_1(j_1 + 1)\hbar^2 |j_1 j_2 m_1 m_2\rangle \\ \hat{J}_2^2 |j_1 j_2 m_1 m_2\rangle &= j_2(j_2 + 1)\hbar^2 |j_1 j_2 m_1 m_2\rangle \\ \hat{J}_{1,z} |j_1 j_2 m_1 m_2\rangle &= m_1 \hbar |j_1 j_2 m_1 m_2\rangle \\ \hat{J}_{2,z} |j_1 j_2 m_1 m_2\rangle &= m_2 \hbar |j_1 j_2 m_1 m_2\rangle \\ \hat{J}_z &= \hat{J}_{1,z} + \hat{J}_{2,z} \\ \hat{J}_z |j_1 j_2 m_1 m_2\rangle &= (m_1 + m_2)\hbar |j_1 j_2 m_1 m_2\rangle\end{aligned}$$

- We also have the following commutation relations

$$\begin{aligned}\hat{J}^2 &= (\hat{J}_1 + \hat{J}_2)^2 = \hat{J}_1^2 + \hat{J}_2^2 + 2\hat{J}_1 \cdot \hat{J}_2 \\ [\hat{J}^2, \hat{J}_1^2] &= [\hat{J}^2, \hat{J}_2^2] = 0 \\ [\hat{J}^2, \hat{J}_{1,z}] &\neq 0 \\ [\hat{J}^2, \hat{J}_{2,z}] &\neq 0\end{aligned}$$

- Therefore the eigenfunctions of \hat{J}^2 and \hat{J}_z are also eigenfunctions of \hat{J}_1^2 and \hat{J}_2^2 , but not of $\hat{J}_{1,z}$ and $\hat{J}_{2,z}$.
- We therefore have two complete, but distinct, descriptions of our system:
 1. Eigenfunctions of \hat{J}_1^2 , \hat{J}_2^2 , $\hat{J}_{1,z}$ and $\hat{J}_{2,z}$ ($|j_1 j_2 m_1 m_2\rangle$).
 2. Eigenfunctions of \hat{J}_1^2 , \hat{J}_2^2 , \hat{J}^2 and \hat{J}_z ($|j_1 j_2 j m\rangle$).
- The two sets of eigenstates are related by $|j_1 j_2 j m\rangle = \sum_{m_1 m_2} |j_1 j_2 m_1 m_2\rangle \langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle$.
- $\langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle$ is a Clebsch-Gordan coefficient.
- We can immediately define one condition for the Clebsch-Gordan coefficients

$$\begin{aligned}\hat{J}_z |j_1 j_2 j m\rangle &= m\hbar |j_1 j_2 j m\rangle \\ &= \sum_{m_1 m_2} (m_1 + m_2)\hbar |j_1 j_2 m_1 m_2\rangle \langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle \\ \Rightarrow \langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle &= 0 \text{ if } m_1 + m_2 \neq m\end{aligned}$$

- We can impose upper limits on the values of the eigenvalues of the total angular momentum operators as follows

$$\begin{aligned}\max m_1 &= j_1 \\ \max m_2 &= j_2 \\ \Rightarrow \max m &= j_1 + j_2 \\ m &\in \{-j, -j + 1, \dots, j - 1, j\} \\ \Rightarrow \max j &= j_1 + j_2\end{aligned}$$

- We can impose a lower bound on the eigenvalues of the total angular momentum as follows
 - There are $(2j_1 + 1)(2j_2 + 1)$ possible states which we break up into multiplets corresponding to different values of the total angular momentum.
 - For $j = j_1 + j_2$, we have a multiplet of $2(j_1 + j_2) + 1$ states.
 - For $j = j_1 + j_2 - 1$, we have a multiplet of $2(j_1 + j_2 - 1) + 1$ states.
 - We run out of states when $j = |j_1 - j_2|$. Therefore $|j_1 - j_2| \leq j \leq j_1 + j_2$. This is the relation obeyed by the third side of a triangle given the first two.

- We now begin the process of building the set of Clebsch-Gordan coefficients.

- For $m = j = j_1 + j_2$ there is only one term in the expansion $|j_1 j_2 j_1 + j_2 j_1 + j_2\rangle = |j_1 j_2 j_1 j_2\rangle \langle j_1 j_2 j_1 j_2 | j_1 j_2 j_1 + j_2 j_1 + j_2\rangle$. Normalisation then gives $|\langle j_1 j_2 j_1 j_2 | j_1 j_2 j_1 + j_2 j_1 + j_2\rangle| = 1$.
- We now introduce the raising and lowering operators $\hat{J}_\pm = \hat{J}_{1\pm} + \hat{J}_{2\pm}$. Matrix elements of these operators give

$$\begin{aligned} \langle j_1 j_2 m_1 m_2 | \hat{J}_\pm | j_1 j_2 j m \rangle &= \sqrt{j(j+1) - m(m \pm 1)} \hbar \langle j_1 j_2 m_1 m_2 | j_1 j_2 j m \pm 1 \rangle \\ &= \langle j_1 j_2 m_1 m_2 | \hat{J}_{1\pm} + \hat{J}_{2\pm} | j_1 j_2 j m \rangle \\ &= \sqrt{j_1(j_1+1) - m_1(m_1 \mp 1)} \langle j_1 j_2 m_1 \mp 1 m_2 | j_1 j_2 j m \rangle + \\ &\quad \sqrt{j_2(j_2+1) - m_2(m_2 \mp 1)} \langle j_1 j_2 m_1 m_2 \mp 1 | j_1 j_2 j m \rangle \end{aligned}$$

- These expressions allow us to build all the Clebsch-Gordan coefficients for a given multiplet starting from the one at the extreme value of the total angular momentum.
- To fix the absolute values of the Clebsch-Gordan coefficients within a given multiplet we need the following normalisation condition

$$\begin{aligned} 1 &= \langle j_1 j_2 j m | j_1 j_2 j m \rangle \\ &= \sum_{m_1 m_2} \langle j_1 j_2 j m | j_1 j_2 m_1 m_2 \rangle \langle j_1 j_2 m_1 m_2 | j_1 j_2 j m \rangle \\ &= \sum_{m_1 m_2} |\langle j_1 j_2 j m | j_1 j_2 m_1 m_2 \rangle|^2 \end{aligned}$$

Example - the addition of two spins

- The total spin operator is given by $\hat{s} = \hat{s}_1 + \hat{s}_2$. The maximum and minimum values of the total spin eigenvalues are 1 and 0 respectively. For the multiplet of maximum total spin (the triplet state) the largest magnetic quantum number that can be obtained is also 1. The state is given by $|sm\rangle = |11\rangle = |\alpha\alpha\rangle$.
- If we apply the lowering operator to the state we obtain the following

$$\begin{aligned} \hat{s}_- |11\rangle &= \hbar\sqrt{2} |10\rangle \\ &= (\hat{s}_{1-} + \hat{s}_{2-}) |\alpha\alpha\rangle \\ &= \hbar(|\beta\alpha\rangle + |\alpha\beta\rangle) \\ \Rightarrow |10\rangle &= \frac{1}{\sqrt{2}} (|\beta\alpha\rangle + |\alpha\beta\rangle) \\ \hat{s}_- |10\rangle &= \hbar\sqrt{2} |1-1\rangle \\ &= (\hat{s}_{1-} + \hat{s}_{2-}) \frac{1}{\sqrt{2}} (|\beta\alpha\rangle + |\alpha\beta\rangle) \\ &= \hbar\sqrt{2} |\beta\beta\rangle \\ \Rightarrow |1-1\rangle &= |\beta\beta\rangle \end{aligned}$$

- The other multiplet with $s = 0$ contains only one state (the singlet state). This must be normalised to 1 and be orthogonal to all the states in the above multiplet. Since its magnetic quantum number is 0 it must be formed from a linear combination of $|\beta\alpha\rangle$ and $|\alpha\beta\rangle$. If we solve the two equations $\langle 00|00\rangle = 1$ and $\langle 00|10\rangle = 0$ we obtain the result $|00\rangle = \frac{1}{\sqrt{2}}(|\beta\alpha\rangle - |\alpha\beta\rangle)$.

Chapter 3

Approximate Methods [6]

3.1 Time-Independent Perturbation Theory

- Suppose we have solved the time independent Schrodinger equation for some problem (for example the particle in a box). Now we want the solution for a problem in which a very small additional potential is applied to our original system.
- We wish to do this in a way that allows us to use all the work we have already done for the original problem.
- For the original problem we might have $\hat{H}|\Phi_n\rangle = \epsilon_n|\Phi_n\rangle$. For our new problem we would have $(\hat{H} + \lambda\hat{V})|\Psi_n\rangle = E_n|\Psi_n\rangle$, where \hat{V} is the additional potential, and λ is a scalar that we associate with the perturbing potential which allows us to perform systematic expansions as we shall now see.
- We make the following expansions in the parameter λ

$$E_n(\lambda) = \sum_{r=0}^{\infty} E_{n,r} \lambda^r$$
$$|\Psi_n(\lambda)\rangle = \sum_{r=0}^{\infty} |\Psi_{n,r}\rangle \lambda^r$$

- If we substitute our expansions into the original eigenequation we obtain the following $(\hat{H} + \lambda\hat{V}) \sum_{r=0}^{\infty} |\Psi_{n,r}\rangle \lambda^r = \sum_{s=0}^{\infty} E_{n,s} \lambda^s \sum_{r=0}^{\infty} |\Psi_{n,r}\rangle \lambda^r$.
- Since our parameter can have any value, for the above equation to always be true the coefficients preceding each power of the parameter must be the same on the left and on the right of the equation.

$$\begin{aligned} \lambda^0 & : \hat{H}|\Psi_{n,0}\rangle = E_{n,0}|\Psi_{n,0}\rangle \\ \lambda^1 & : \hat{H}|\Psi_{n,1}\rangle + \hat{V}|\Psi_{n,0}\rangle = E_{n,0}|\Psi_{n,1}\rangle + E_{n,1}|\Psi_{n,0}\rangle \\ \lambda^2 & : \hat{H}|\Psi_{n,2}\rangle + \hat{V}|\Psi_{n,1}\rangle = E_{n,0}|\Psi_{n,2}\rangle + E_{n,1}|\Psi_{n,1}\rangle + E_{n,2}|\Psi_{n,0}\rangle \end{aligned}$$

- From these equations we can obtain the following results. From the 0th power of the parameter (λ^0) we just obtain the eigenequation for the unperturbed system. Therefore we can write

$$\begin{aligned} |\Psi_{n,0}\rangle &= |\Phi_n\rangle \\ E_{n,0} &= \epsilon_n \end{aligned}$$

- From the first power of the parameter (λ^1)

$$\begin{aligned} (\hat{H} - \epsilon_n)|\Psi_{n,1}\rangle &= (E_{n,1} - \hat{V})|\Phi_n\rangle \\ |\Psi_{n,1}\rangle &= \sum_p C_p^{(n,1)}|\Phi_p\rangle \\ \Rightarrow (\hat{H} - \epsilon_n) \sum_p C_p^{(n,1)}|\Phi_p\rangle &= (E_{n,1} - \hat{V})|\Phi_n\rangle \\ \Rightarrow \sum_p C_p^{(n,1)}(\epsilon_p - \epsilon_n)|\Phi_p\rangle &= (E_{n,1} - \hat{V})|\Phi_n\rangle \\ \Rightarrow C_p^{(n,1)}(\epsilon_p - \epsilon_n) &= E_{n,1}\delta_{pn} - \langle\Phi_p|\hat{V}|\Phi_n\rangle \\ p = n : E_{n,1} &= \langle\Phi_n|\hat{V}|\Phi_n\rangle \\ p \neq n : C_p^{(n,1)} &= \frac{\langle\Phi_p|\hat{V}|\Phi_n\rangle}{\epsilon_n - \epsilon_p} \\ \Rightarrow |\Psi_{n,1}\rangle &= \sum_{p(\neq n)} |\Phi_p\rangle \frac{\langle\Phi_p|\hat{V}|\Phi_n\rangle}{\epsilon_n - \epsilon_p} + C_n^{(n,1)}|\Phi_n\rangle \end{aligned}$$

$C_n^{(n,1)}$ is found by normalizing the wavefunction $|\Psi_n\rangle$.

- From the square of the parameter (λ^2) we get the following results

$$\begin{aligned} E_{n,2}|\Phi_n\rangle &= (\hat{H} - \epsilon_n)|\Psi_{n,2}\rangle + (\hat{V} - E_{n,1})|\Psi_{n,1}\rangle \\ \Rightarrow E_{n,2} &= \langle\Phi_n|(\hat{H} - \epsilon_n)|\Psi_{n,2}\rangle + \langle\Phi_n|(\hat{V} - E_{n,1})|\Psi_{n,1}\rangle \\ &= \langle\Phi_n|(\epsilon_n - \epsilon_n)|\Psi_{n,2}\rangle + \langle\Phi_n|\hat{V}|\Psi_{n,1}\rangle - E_{n,1}\langle\Phi_n|\Psi_{n,1}\rangle \\ &= \langle\Phi_n|\hat{V}|\Psi_{n,1}\rangle - \langle\Phi_n|\hat{V}|\Phi_n\rangle\langle\Phi_n|\Psi_{n,1}\rangle \\ &= \sum_{p(\neq n)} \langle\Phi_n|\hat{V}|\Phi_p\rangle \frac{\langle\Phi_p|\hat{V}|\Phi_n\rangle}{\epsilon_n - \epsilon_p} \\ &= \sum_{p(\neq n)} \frac{|\langle\Phi_p|\hat{V}|\Phi_n\rangle|^2}{\epsilon_n - \epsilon_p} \end{aligned}$$

- Therefore to second order the perturbed energy is

$$E_n \approx \epsilon_n + \langle\Phi_n|\hat{V}|\Phi_n\rangle + \sum_{p(\neq n)} \frac{|\langle\Phi_p|\hat{V}|\Phi_n\rangle|^2}{\epsilon_n - \epsilon_p}$$

- The above theory breaks down when we have degenerate states ($\epsilon_n - \epsilon_p = 0$). This is because the terms in the perturbation expansion involve ratios of matrix elements divided by $\epsilon_n - \epsilon_p$. These terms are infinite unless

the matrix elements are zero. Degenerate states have the property that any normalised linear combination of them produces another state of the same energy. Therefore the procedure for handling degenerate states in perturbation theory is to take linear combinations that produce matrix elements of the perturbing potential that are zero. That is

$$\begin{aligned} |\chi_\alpha\rangle &= \sum_{p \in \{\text{degenerate states}\}} C_{\alpha,p} |\Phi_p\rangle \\ \langle \chi_\alpha | \hat{V} | \chi_\beta \rangle &= \langle \chi_\alpha | \hat{V} | \chi_\alpha \rangle \delta_{\alpha\beta} \end{aligned}$$

- The first order term in the perturbation expansion then obeys

$$\begin{aligned} C_\beta^{(\alpha,1)}(\epsilon_\beta - \epsilon_\alpha) &= E_{\alpha,1} \delta_{\alpha\beta} - \langle \chi_\beta | \hat{V} | \chi_\alpha \rangle \\ \Rightarrow 0 &= E_{\alpha,1} \delta_{\alpha\beta} - \langle \chi_\alpha | \hat{V} | \chi_\alpha \rangle \delta_{\alpha\beta} \\ \Rightarrow E_{\alpha,1} &= \langle \chi_\alpha | \hat{V} | \chi_\alpha \rangle \\ C_p^{(\alpha,1)}(\epsilon_p - \epsilon_\alpha) &= E_{\alpha,1} \delta_{\alpha p} - \langle \Phi_p | \hat{V} | \chi_\alpha \rangle \\ \Rightarrow C_p^{(\alpha,1)} &= \frac{\langle \Phi_p | \hat{V} | \chi_\alpha \rangle}{\epsilon_\alpha - \epsilon_p} \\ \Rightarrow |\Psi_{\alpha,1}\rangle &= \sum_{p \notin \{\text{degenerate states}\}} |\Phi_p\rangle \frac{\langle \Phi_p | \hat{V} | \chi_\alpha \rangle}{\epsilon_\alpha - \epsilon_p} \end{aligned}$$

- We find the orthogonal states by diagonalising the matrix $V_{pq} = \langle \Phi_p | \hat{V} | \Phi_q \rangle$:

$$\begin{aligned} \sum_q V_{pq} C_{\alpha,q} &= \eta_\alpha C_{\alpha,p} \\ \Rightarrow \sum_{pq} C_{\beta,p}^* V_{pq} C_{\alpha,q} &= \eta_\alpha \delta_{\alpha\beta} \\ \Rightarrow \langle \chi_\beta | \hat{V} | \chi_\alpha \rangle &= \eta_\alpha \delta_{\alpha\beta} \end{aligned}$$

Example - charged harmonic oscillator

- Consider a charged harmonic oscillator in an electric field. The electric field results in an additional force on the harmonic oscillator which can be represented by the additional potential $\hat{V} = QE\hat{x}$ where Q is the charge on the oscillator, E is the strength of the electric field and \hat{x} is the operator representing the displacement of the oscillator.
- The eigenstates of the harmonic oscillator are not degenerate in one dimension. Therefore we can use ordinary perturbation theory. For this we need the following matrix elements $\langle p | \hat{V} | n \rangle = QE \langle p | \hat{x} | n \rangle$, where $|p\rangle$ is an eigenstate of the unperturbed harmonic oscillator.
- We can use the Dirac raising and lowering operators to represent the displacement since $\hat{x} = \sqrt{\frac{\hbar}{2M\omega}}(\hat{a} + \hat{a}^\dagger)$. The matrix elements are thus

$$\begin{aligned} \langle p | \hat{V} | n \rangle &= QE \sqrt{\frac{\hbar}{2M\omega}} \langle p | (\hat{a} + \hat{a}^\dagger) | n \rangle \\ &= QE \sqrt{\frac{\hbar}{2M\omega}} (\sqrt{n} \delta_{p,n-1} + \sqrt{n+1} \delta_{p,n+1}) \end{aligned}$$

- The perturbed energy to second order is thus

$$\begin{aligned}
 E_n &= \epsilon_n + \langle \Phi_n | \hat{V} | \Phi_n \rangle + \sum_{p(\neq n)} \frac{|\langle \Phi_p | \hat{V} | \Phi_n \rangle|^2}{\epsilon_n - \epsilon_p} \\
 &= \left(n + \frac{1}{2}\right) \hbar\omega + 0 + \frac{Q^2 E^2 \hbar}{2M\omega} \left(\frac{n}{\hbar\omega} - \frac{n+1}{\hbar\omega} \right) \\
 &= \left(n + \frac{1}{2}\right) \hbar\omega - \frac{Q^2 E^2}{2M\omega^2}
 \end{aligned}$$

- Thus each level receives the same constant shift downwards.

Example - Stark effect

- The Stark effect in atomic spectra is observed when an electric field is applied to an atom. It can be understood from perturbation theory in which the perturbing potential is once again an electric field interacting with a charged particle (this time an electron).
- We will study this effect using the $n = 2$ levels of the hydrogen atom in a uniform electric field pointing in the z direction.
- There are four degenerate states in the $n = 2$ shell of hydrogen, namely $|S_0\rangle$, $|P_{-1}\rangle$, $|P_0\rangle$ and $|P_1\rangle$. The states are labelled by the orbital angular momentum. They satisfy the following equations

$$\begin{aligned}
 \hat{L}_z |S_0\rangle &= 0 \\
 \hat{L}_z |P_{-1}\rangle &= -\hbar |P_{-1}\rangle \\
 \hat{L}_z |P_0\rangle &= 0 \\
 \hat{L}_z |P_1\rangle &= \hbar |P_1\rangle
 \end{aligned}$$

- The perturbing potential we can write as $\hat{V} = -eE\hat{z}$. Therefore we need to consider matrix elements of the form $-eE\langle lm|\hat{z}|l'm'\rangle$.
- We now recall that $[\hat{z}, \hat{L}_z] = 0$. If we take matrix elements of this expression we obtain

$$\begin{aligned}
 0 &= \langle lm|[\hat{z}, \hat{L}_z]|l'm'\rangle \\
 &= \langle lm|\hat{z}\hat{L}_z - \hat{L}_z\hat{z}|l'm'\rangle \\
 &= \hbar(m' - m)\langle lm|\hat{z}|l'm'\rangle \\
 \Rightarrow \text{if } m' \neq m \text{ then } 0 &= \langle lm|\hat{z}|l'm'\rangle
 \end{aligned}$$

- Now consider $\langle lm|\hat{z}|lm\rangle$. These are all zero because the hydrogen wave functions have the following property $|\langle \vec{r} | nlm \rangle|^2 = |\langle -\vec{r} | nlm \rangle|^2$ (they are in variant under the parity operation).
- The full matrix of matrix elements of the perturbation potential is therefore

$$\mathbf{V} = \begin{pmatrix} 0 & v & 0 & 0 \\ v^* & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

- Where $v = \langle S_0 | -eE\hat{z} | P_0 \rangle = 3eEa_0$. Thus the electric field only causes two of the states to mix, namely $|S_0\rangle$ and $|P_0\rangle$. Therefore we only need to diagonalize a 2×2 matrix.

$$\begin{aligned} \begin{pmatrix} 0 & v \\ v & 0 \end{pmatrix} \begin{pmatrix} C_s \\ C_p \end{pmatrix} &= \eta \begin{pmatrix} C_s \\ C_p \end{pmatrix} \\ \Rightarrow vC_p &= \eta C_s \\ vC_s &= \eta C_p \\ \Rightarrow v^2 C_s C_p &= \eta^2 C_s C_p \\ \Rightarrow \eta &= \pm 3eEa_0 \\ \Rightarrow \begin{pmatrix} C_s \\ C_p \end{pmatrix} &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \end{aligned}$$

Example - spin-orbit coupling

- Our next example is the spin-orbit correction in hydrogen. The perturbing potential has the form

$$\begin{aligned} \hat{V} &= \frac{1}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_3} \hat{L} \cdot \hat{S} \\ &= \zeta(r) \hat{L} \cdot \hat{S} \end{aligned}$$

- As previously we will try to make use of as much symmetry as possible. We note the following commutation relation $[\hat{L}^2, \hat{L} \cdot \hat{S}] = [\hat{L}^2, \hat{L}] \cdot \hat{S} = 0$. Therefore $[\hat{L}^2, \hat{V}] = 0$, and so the total angular momentum remains a good quantum number, and the perturbation can only mix states which have the same value of l .
- For a given principal quantum number all the states are degenerate. Therefore we must use degenerate perturbation theory. The basis states for hydrogen we can represent by $|nlmm_s\rangle$, where m_s is the magnetic quantum number associated with spin.
- If we define $\hat{J} = \hat{L} + \hat{S}$, then we can obtain the following

$$\begin{aligned} \hat{J}^2 &= \hat{L}^2 + \hat{S}^2 + 2\hat{L} \cdot \hat{S} \\ \hat{V} &= \zeta(r) \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2) \\ \Rightarrow 0 &= [\hat{L}^2, \hat{V}] \\ &= [S^2, \hat{V}] \\ &= [\hat{J}^2, \hat{V}] \\ &= [\hat{J}_Z, \hat{V}] \end{aligned}$$

- Thus the eigenstates of the perturbing Hamiltonian will also be eigenstates of the total angular momentum, the spin, and the orbital angular momentum. To obtain eigenstates of the total angular momentum starting from our basis states we need to use the normal rules for coupling angular momentum. That is $|nljm_j\rangle = \sum_{mm_s} |nlmm_s\rangle \langle l\frac{1}{2}mm_s | l\frac{1}{2}jm_j\rangle$, where $\langle l\frac{1}{2}mm_s | l\frac{1}{2}jm_j\rangle$ is a Clebsch-Gordan coefficient.

- Using these new basis states we obtain the first order energy shifts as

$$\begin{aligned}
\Delta E_{nljm_j} &= \langle nljm_j | \hat{V} | nljm_j \rangle \\
&= \langle nljm_j | \zeta(r) \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2) | nljm_j \rangle \\
&= \frac{\hbar^2}{2} [j(j+1) - l(l+1) - \frac{3}{4}] \langle nljm_j | \zeta(r) | nljm_j \rangle \\
&= \frac{\hbar^2}{2} [j(j+1) - l(l+1) - \frac{3}{4}] \zeta_{nl} \\
\zeta_{nl} &= \langle nljm_j | \zeta(r) | nljm_j \rangle \\
&= \frac{1}{2m^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{Z^3}{a_0^3 n^3 l(l+1)(l+\frac{1}{2})}
\end{aligned}$$

- If $l = 0$ then the energy shift is 0. Otherwise we have $j = l \pm \frac{1}{2}$, and the energy shifts are

$$\Delta E_{nljm_j} = \begin{cases} \zeta_{nl} \frac{\hbar^2}{2} l & j = l + \frac{1}{2} \\ -\zeta_{nl} \frac{\hbar^2}{2} (l+1) & j = l - \frac{1}{2} \end{cases}$$

Example - positronium

- Positron (positive electron) and electron orbit about each other.
- The energy levels are the same as for hydrogen, except that they are multiplied by a factor of one half because the reduced mass in positronium is one half of that for hydrogen.
- The magnetic moments on the electron and positron interact to give a spin-spin interaction.

$$\hat{H} = \hat{H}_0 + A \hat{s}_e \cdot \hat{s}_p$$

- Both the spin operators commute with the Hamiltonian \hat{H}_0 , thus there are four degenerate eigenstates corresponding to the four possible spin states (one singlet state and three triplets states), provided we ignore the spin-spin interaction.
- The perturbation is already diagonal in the total spin states

$$\begin{aligned}
\langle SM_s | \hat{s}_e \cdot \hat{s}_p | S' M'_s \rangle &= \frac{1}{2} \langle SM_s | \hat{S}^2 - \hat{s}_e^2 - \hat{s}_p^2 | S' M'_s \rangle \\
&= \frac{\hbar^2}{2} (S(S+1) - \frac{3}{2}) \delta_{SS'} \delta_{M_s M'_s} \\
&= \begin{cases} -\frac{3\hbar^2}{4} & S = 0 \\ \frac{\hbar^2}{4} & S = 1 \end{cases}
\end{aligned}$$

- Thus the first order degenerate perturbation shift in energy is given by

$$\Delta E = \begin{cases} -\frac{3\hbar^2}{4} A & S = 0 \text{ (singlet)} \\ \frac{\hbar^2}{4} A & S = 1 \text{ (triplet)} \end{cases}$$

- Positronium decays when the positron and electron annihilate each other. To conserve energy, linear momentum, and angular momentum, the singlet state must decay into two photons, and the triplet state must decay into three photons. The photon carries a spin angular momentum of one.

3.2 Variational Principle

- Consider a system described by a Hamiltonian \hat{H} . Consider also a guess for the wave function for the system $|\Psi\rangle$. We define the energy of the system by $E_\Psi = \langle\Psi|\hat{H}|\Psi\rangle/\langle\Psi|\Psi\rangle$. We now expand this wave function in terms of the eigenstates of the Hamiltonian $|\Psi\rangle = \sum_n C_n|\Phi_n\rangle$ where $\hat{H}|\Phi_n\rangle = E_n|\Phi_n\rangle$. Therefore we get

$$\begin{aligned}
 E_\Psi &= \frac{\sum_{nm} C_n^* C_m \langle\Phi_n|\hat{H}|\Phi_m\rangle}{\sum_{nm} C_n^* C_m \langle\Phi_n|\Phi_m\rangle} \\
 &= \frac{\sum_n |C_n|^2 E_n}{\sum_n |C_n|^2} \\
 &= \frac{\sum_n |C_n|^2 (E_n - E_0 + E_0)}{\sum_n |C_n|^2} \\
 &= E_0 + \frac{\sum_n |C_n|^2 (E_n - E_0)}{\sum_n |C_n|^2} \\
 &\geq E_0
 \end{aligned}$$

- This tells us that for any guess for the wave function, our estimate for the energy will be no less than the ground state energy. This means that we can optimise our guess by varying it in such a way as to minimise the estimated energy E_Ψ .
- We can extend this idea to excited states as well. Here we consider just the first excited state. This will be orthogonal to the ground state, so we need to consider a trial wave function that obeys $\langle\Phi_0|\Psi\rangle = 0$. We can always achieve this by writing the trial wave function in the following way $|\Psi\rangle = \alpha|\tilde{\Psi}\rangle + \beta|\Phi_0\rangle$. Imposing the orthogonality condition gives $0 = \langle\Phi_0|\Psi\rangle = \alpha\langle\Phi_0|\tilde{\Psi}\rangle + \beta$. From this we get $|\Psi\rangle = \alpha(1 - |\Phi_0\rangle\langle\Phi_0|)|\tilde{\Psi}\rangle$. If we expand the function $|\tilde{\Psi}\rangle$ in terms of the eigenstates we have $|\tilde{\Psi}\rangle = \sum_{n=0}^{\infty} C_n|\Phi_n\rangle$, and hence

$$\begin{aligned}
 |\Psi\rangle &= \sum_{n=0}^{\infty} \alpha C_n (1 - |\Phi_0\rangle\langle\Phi_0|)|\Phi_n\rangle \\
 &= \sum_{n=0}^{\infty} \alpha C_n (1 - |\Phi_0\rangle\langle\Phi_0|)|\Phi_n\rangle \\
 &= \sum_{n=1}^{\infty} \alpha C_n |\Phi_n\rangle
 \end{aligned}$$

where in the last line we make use of the fact that the term $(1 - |\Phi_0\rangle\langle\Phi_0|)$ is 1 unless $n = 0$, in which case it is 0. This allows us to change the range

of the sum from $0 \rightarrow \infty$ to $1 \rightarrow \infty$. If we now use this to evaluate E_Ψ , we obtain the result $E_\Psi \geq E_1$. Therefore, provided our trial wave function is orthogonal to the ground state we can use exactly the same procedure for the first excited state as we use for the ground state.

Example - helium atom

- We now perform a variational calculation for the helium atom. The Hamiltonian is given by

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

- We now assume that the wave function has the form $\Psi(\vec{r}_1, \vec{r}_2) = \psi_{1s}(\vec{r}_1)\psi_{1s}(\vec{r}_2)$, where $\psi_{1s}(\vec{r}) = \frac{1}{\sqrt{\pi}} \left(\frac{Q}{a_0}\right)^{3/2} \exp(-Qr/a_0)$. Note that $\int d\vec{r}_1 d\vec{r}_2 |\Psi(\vec{r}_1, \vec{r}_2)|^2 = 1$.
- The estimate for the energy is then given by

$$\begin{aligned} E_\Psi &= \int d\vec{r}_1 d\vec{r}_2 \psi_{1s}(\vec{r}_1)\psi_{1s}(\vec{r}_2) \left[\frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right] \psi_{1s}(\vec{r}_1)\psi_{1s}(\vec{r}_2) \\ &= \int d\vec{r}_1 \psi_{1s}(\vec{r}_1) \left[\frac{\hat{p}_1^2}{2m} - \frac{Ze^2}{r_1} \right] \psi_{1s}(\vec{r}_1) + \int d\vec{r}_2 \psi_{1s}(\vec{r}_2) \left[\frac{\hat{p}_2^2}{2m} - \frac{Ze^2}{r_2} \right] \psi_{1s}(\vec{r}_2) \\ &\quad + \int d\vec{r}_1 d\vec{r}_2 \psi_{1s}(\vec{r}_1)\psi_{1s}(\vec{r}_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_{1s}(\vec{r}_1)\psi_{1s}(\vec{r}_2) \\ &= 2 \underbrace{\left(\frac{Q^2 e^2}{2a_0} - \frac{ZQe^2}{a_0} \right)}_{\text{Hydrogen-like}} + \underbrace{\frac{5Qe^2}{8a_0}}_{\text{e-e}} \end{aligned}$$

- To optimise our wave function we now minimise the energy with respect to our parameter Q . This gives

$$\begin{aligned} 0 &= \frac{\partial E_\Psi}{\partial Q} \\ &= \frac{e^2}{a_0} \left(\frac{5}{8} + 2Q - 2Z \right) \\ \Rightarrow Q &= Z - \frac{5}{16} \end{aligned}$$

- Thus we see that the effective charge appearing in the exponent of the wave function is reduced relative to the true nuclear charge by the amount $5/16$. This is a result of the repulsion between the electrons which screens the nucleus. The minimum energy is $E = -(Z - \frac{5}{16})^2 \frac{e^2}{a_0} = 7620 \text{ kJ/mol}$. The experimental value is 7477 kJ/mol . So we see that our calculated value is indeed larger than the true value. The error is a result of our very simple form for the wave function.

Chapter 4

Simple Time-dependent systems [3]

4.1 Superposition of States of Different Energies

- As we saw earlier the solution of the time-dependent Schroedinger equation for a system of fixed energy E_n is $\Psi_n(xt) = e^{E_n t/i\hbar} \Phi_n(x)$.
- A general wave function can be constructed as a linear combination of these functions $\Psi(xt) = \sum_n C_n e^{E_n t/i\hbar} \Phi_n(x)$, where $C_n = \int \Phi_n^*(x) \Psi(x0) dx$.
- Consider the expectation value of an operator \hat{O} with respect to this wave function

$$\begin{aligned}\langle O \rangle &= \langle \Psi | \hat{O} | \Psi \rangle \\ &= \sum_{nm} C_n^* C_m e^{(E_m - E_n)t/i\hbar} \langle \Phi_n | \hat{O} | \Phi_m \rangle\end{aligned}$$

- Suppose the operator is the Hamiltonian ($\hat{O} = \hat{H}$). Then we have $\hat{H} | \Phi_n \rangle = E_n | \Phi_n \rangle$, and hence

$$\begin{aligned}\langle H \rangle &= \sum_{nm} C_n^* C_m e^{(E_m - E_n)t/i\hbar} \langle \Phi_n | \hat{H} | \Phi_m \rangle \\ &= \sum_{nm} C_n^* C_m e^{(E_m - E_n)t/i\hbar} \langle \Phi_n | E_m | \Phi_m \rangle \\ &= \sum_{nm} |C_n|^2 E_n\end{aligned}$$

- This is independent of time. In fact in general it is straightforward to show that any operator that commutes with the Hamiltonian will have an expectation value that is independent of time

$$\begin{aligned}\frac{d\langle O \rangle}{dt} &= \frac{1}{i\hbar} \langle \Psi | [\hat{O}, \hat{H}] | \Psi \rangle \\ &= 0 \text{ since } [\hat{O}, \hat{H}] = 0\end{aligned}$$

- The expectation value of all other operators varies with time. Consider a wave function that is a linear superposition of just two states:

$$\begin{aligned}
|\Psi\rangle &= C_1 e^{E_1 t / i\hbar} |\Phi_1\rangle + C_2 e^{E_2 t / i\hbar} |\Phi_2\rangle \\
\langle O \rangle &= (C_1^* e^{-E_1 t / i\hbar} \langle \Phi_1| + C_2^* e^{-E_2 t / i\hbar} \langle \Phi_2|) \hat{O} (C_1 e^{E_1 t / i\hbar} |\Phi_1\rangle + C_2 e^{E_2 t / i\hbar} |\Phi_2\rangle) \\
&= |C_1|^2 O_{11} + |C_2|^2 O_{22} + C_1^* C_2 e^{(E_2 - E_1)t / i\hbar} O_{12} + C_2^* C_1 e^{(E_1 - E_2)t / i\hbar} O_{21} \\
O_{nm} &= \langle \Phi_n | \hat{O} | \Phi_m \rangle
\end{aligned}$$

- If the operator \hat{O} is hermitian then we have $O_{12} = O_{21}^*$. In this case we obtain

$$\langle O \rangle = |C_1|^2 O_{11} + |C_2|^2 O_{22} + \left[C_1^* C_2 e^{(E_2 - E_1)t / i\hbar} O_{12} \right] + \left[C_1^* C_2 e^{(E_2 - E_1)t / i\hbar} O_{12} \right]^*$$

- If we define $\hbar\omega = E_2 - E_1$, and further we assume that C_1 , C_2 and O_{12} are all real, then we obtain

$$\begin{aligned}
\langle O \rangle &= |C_1|^2 O_{11} + |C_2|^2 O_{22} + 2C_1 C_2 \cos(\omega t) O_{12} \\
&= \bar{O} + \Delta \cos(\omega t) \\
\bar{O} &= |C_1|^2 O_{11} + |C_2|^2 O_{22} \\
\Delta &= 2C_1 C_2 O_{12}
\end{aligned}$$

- If either C_1 or C_2 is zero then the expectation value is time independent because we are now in an eigenstate.

4.2 Electron in Magnetic Field

- We now consider a system that contains one electron. We now place this system in a magnetic field, and allow the electronic spin to couple to the magnetic field. We will neglect the interaction between the orbital motion of the electron and field (which is a much smaller effect). The Hamiltonian that describes this system is

$$\hat{H} = \hat{H}_0 - \frac{g_s \mu_B}{\hbar} \hat{S} \cdot \vec{B}$$

- We now assume that the magnetic field points in the z direction and is everywhere uniform $\vec{B} = B\vec{e}_z$. For this case the Hamiltonian simplifies to $\hat{H} = \hat{H}_0 - \frac{g_s \mu_B B}{\hbar} \hat{S}_z = \hat{H}_0 - \omega \hat{S}_z$.
- Provided the unperturbed Hamiltonian does not depend on spin then we have $[\hat{H}_0, \hat{H}] = 0$, and thus the eigenstates of the unperturbed Hamiltonian are also eigenstates of the perturbed Hamiltonian. Let the eigenstates be represented by $|nm_s\rangle$, where m_s is the spin magnetic quantum number.
- The eigenvalues of our Hamiltonian are then

$$\begin{aligned}
E_{nm_s} &= \langle nm_s | \hat{H} | nm_s \rangle \\
&= \langle nm_s | \hat{H}_0 | nm_s \rangle + \langle nm_s | -\omega \hat{S}_z | nm_s \rangle \\
&= E_n^{(0)} - \hbar\omega m_s
\end{aligned}$$

- Suppose we can ignore all eigenstates of the unperturbed Hamiltonian except the ground state. Then the general time-dependent wave function for our system in a magnetic field becomes

$$|\Psi(t)\rangle = C_1 e^{(E_0 + \frac{1}{2}\hbar\omega)t/i\hbar} |0 - \frac{1}{2}\rangle + C_2 e^{(E_0 - \frac{1}{2}\hbar\omega)t/i\hbar} |0 \frac{1}{2}\rangle$$

- If the system starts in an eigenstate of the operator \hat{S}_z , then one or other of the constant coefficients must be 0. Either way the system remains in that eigenstate for all time.
- Consider the expectation value of the z component of the spin operator

$$\begin{aligned} \langle S_z \rangle &= |C_1|^2 \left(-\frac{1}{2}\hbar\right) + |C_2|^2 \left(\frac{1}{2}\hbar\right) \\ &= \frac{1}{2}\hbar(|C_2|^2 - |C_1|^2) \\ &= \text{constant} \end{aligned}$$

- Now consider the expectation value of the x component of the spin operator

$$\begin{aligned} \hat{S}_x &= \frac{1}{2}(\hat{S}_+ + \hat{S}_-) \\ \hat{S}_+ | \frac{1}{2} \rangle &= 0 \\ \hat{S}_+ | -\frac{1}{2} \rangle &= \hbar | \frac{1}{2} \rangle \\ \hat{S}_- | \frac{1}{2} \rangle &= \hbar | -\frac{1}{2} \rangle \\ \hat{S}_- | -\frac{1}{2} \rangle &= 0 \\ \langle S_x \rangle &= 0 + 0 + 2\text{Re} \left\{ C_1^* C_2 e^{-\hbar\omega t/i\hbar} \langle 0 - \frac{1}{2} | \frac{1}{2} (\hat{S}_+ + \hat{S}_-) | 0 \frac{1}{2} \rangle \right\} \\ &= \text{Re} \{ C_1^* C_2 e^{i\omega t} \hbar \} \end{aligned}$$

- Similarly the expectation value of the y component of the spin operator is

$$\langle S_y \rangle = -\text{Im} \{ C_1^* C_2 e^{i\omega t} \hbar \}$$

- Now consider the special case $C_1 = C_2 = \frac{1}{\sqrt{2}}$

$$\begin{aligned} \langle S_z \rangle &= 0 \\ \langle S_y \rangle &= -\frac{\hbar}{2} \sin \omega t \\ \langle S_x \rangle &= \frac{\hbar}{2} \cos \omega t \end{aligned}$$

- For this special case the spin precesses perpendicular to the magnetic field.

4.3 Time Evolution of Entangled States of Two Spin-1/2 Particles with Total Spin Zero.

- If two particles are in an entangled state then any measurement made on one of the particles will influence the state of the other particle. Mathematically this means that the wave function for the combined system cannot be expressed as a single product of the wave functions for the two individual particles.
- If we have two electrons in a state of zero spin then we know that the wave function for the spins can be written as $|S = 0, m_s = 0\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle)$. This is clearly an entangled state.
- [THIS HAS YET TO BE FINISHED]

Chapter 5

Identical Particles [2]

- If you have many particles, you have a set of operators for each particle ($\hat{p}_i, \hat{r}_i, \hat{S}_i, \hat{L}_i \dots$).
- The Hamiltonian for a system of many particles is characterised by the following equations

$$\begin{aligned}\hat{H}(\{\hat{p}_i\}, \{\hat{q}_i\}) &= \sum_i \frac{\hat{p}_i^2}{2M_i} + \hat{V}(\{\hat{q}_i\}) \\ \hat{H}(\{\hat{p}_i\}, \{\hat{q}_i\})\Psi(\{q_i\}, t) &= i\hbar \frac{\partial}{\partial t} \Psi(\{q_i\}, t)\end{aligned}$$

- Other system wide operators include

$$\begin{aligned}\hat{L} &= \sum_i \hat{L}_i \\ \hat{P} &= \sum_i \hat{P}_i \\ \hat{S} &= \sum_i \hat{S}_i\end{aligned}$$

- All operators for particle i commute with those for particle j: $[\hat{P}_i, \hat{P}_j] = [\hat{P}_i, \hat{r}_j] = \dots = 0$.
- Identical particles cannot be distinguished by any intrinsic property (for example all electrons are equivalent to one another). Further, they cannot be distinguished by their trajectories in quantum mechanics. This opens the way for a new system wide operator which interchanges identical particles

$$\hat{P}_{ij}f(q_1 \dots q_i \dots q_j \dots q_N) = f(q_1 \dots q_j \dots q_i \dots q_N)$$

- Clearly $\hat{P}_{ij}^2 f = f$. Therefore the eigenvalues of \hat{P}_{ij} must be ± 1 . If $\hat{P}_{ij}f = +f$, then the function f is a symmetric eigenfunction of \hat{P}_{ij} , while if $\hat{P}_{ij}f = -f$, then the function f is an anti symmetric eigenfunction.

- For identical particles $\hat{P}_{ij}\hat{H}f = \hat{H}\hat{P}_{ij}f$ for all pairs of particles. Therefore the eigenfunctions of the Hamiltonian must also be eigenfunctions of all permutation operators \hat{P}_{ij} .
- However $[\hat{P}_{ij}, \hat{P}_{rs}] \neq 0$. To accommodate this fact the wave function must either be completely symmetric under interchange of particles, or completely anti symmetric. Under this condition we find that $\hat{P}_{ij}\hat{P}_{rs}f = \hat{P}_{rs}\hat{P}_{ij}f$.
- Therefore wave functions for identical particles must be fully symmetric or fully anti symmetric under exchange of particles
 - Bosons (particles with integer spin such as photons) have fully symmetric wave functions
 - Fermions (particles with half integer spin, such as electrons) have fully anti symmetric wave functions.

5.1 Systems of Two Identical Particles

5.1.1 Two fermions

- We now consider two electrons. The wave function for one electron can be written as $\psi_{n\sigma} = \phi_n(\vec{r})\chi_\sigma$, where $\phi_n(\vec{r})$ is the spatial part of the wave function and χ_σ is the spin part.
- If we combine these for two electrons the natural starting point is to form a product $\Psi(1, 2) = \psi_{n\sigma}(1)\psi_{n'\sigma'}(2)$. But this has the wrong symmetry properties under exchange of particles 1 and 2. So consider

$$\Psi_A(1, 2) = \frac{1}{\sqrt{2}}(\psi_{n\sigma}(1)\psi_{n'\sigma'}(2) - \psi_{n\sigma}(2)\psi_{n'\sigma'}(1)) = -\Psi_A(2, 1)$$

- This wave function now has the correct symmetry. This is the simplest case of a Slater determinant.
- Consider the special case $n = n'$. We can now rewrite the wave function as

$$\Psi_A(1, 2) = \phi_n(1)\phi_n(2)\frac{1}{\sqrt{2}}(\chi_\sigma(1)\chi_{\sigma'}(2) - \chi_\sigma(2)\chi_{\sigma'}(1))$$

- If we now also set $\sigma = \sigma'$ then we find that the wave function vanishes. Thus we cannot have both electrons in the same single particle state. This is the Pauli exclusion principle for fermions.
- If we now set $\chi_\sigma = \alpha$ and $\chi_\sigma = \beta$, then we get

$$\Psi_A(1, 2) = \phi_n(1)\phi_n(2)\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

- But this new spin state is just the $S = 0, m_s = 0$ state.

- Now consider the alternative case in which $n \neq n'$. We are able in this case to obey the Pauli exclusion principle while having $\sigma = \sigma'$. There are two possible solutions

$$\begin{aligned}\Psi_A(1, 2) &= \frac{1}{\sqrt{2}}(\phi_n(1)\phi_{n'}(2) - \phi_n(2)\phi_{n'}(1))\alpha(1)\alpha(2) \\ \Psi_A(1, 2) &= \frac{1}{\sqrt{2}}(\phi_n(1)\phi_{n'}(2) - \phi_n(2)\phi_{n'}(1))\beta(1)\beta(2)\end{aligned}$$

- The spin parts of the wave function correspond to the states $S = 1$, $m_s = \pm 1$. This suggests that there should be a third possibility with $S = 1$, $m_s = 0$. This wave function would have the form

$$\Psi_A(1, 2) = \frac{1}{\sqrt{2}}(\phi_n(1)\phi_{n'}(2) - \phi_n(2)\phi_{n'}(1))\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(1))$$

- This wave function has the necessary property that $\Psi_A(1, 2) = -\Psi_A(2, 1)$. Thus we see that we have two sets of solutions
 - The singlet set with symmetric spatial part of the wave function but anti symmetric spin part ($S = 0$).
 - The triplet set with anti symmetric spatial part of the wave function but symmetric spin part ($S = 1$).
- That are also mixed solutions for which $n \neq n'$ and $\sigma \neq \sigma'$. But these are not good wave functions because they are not eigenstates of the spin operator. Provided $[\hat{H}, \hat{S}] = 0$, then the eigenstates of the Hamiltonian should also be eigenstates of the spin operator.

5.1.2 Two bosons

- Consider two photons. We can go through the same procedure as above, except that now we must produce a symmetric wave function.

$$\Psi_S(1, 2) = \frac{1}{\sqrt{2}}(\psi_{n\sigma}(1)\psi_{n'\sigma'}(2) + \psi_{n\sigma}(2)\psi_{n'\sigma'}(1)) = \Psi_S(2, 1)$$

- We can see the most important difference between bosons and fermions by considering the special case of $n = n'$ and $\sigma = \sigma'$. In the case of the fermions this caused the wave function to vanish. But in this case we get

$$\Psi_S(1, 2) = \psi_{n\sigma}(1)\psi_{n\sigma}(2)$$

- Notice that we have dropped a factor of $\sqrt{2}$ to obtain the correct normalisation. From this we see that more than one boson is able to occupy a particular single particle state. One consequence of this is that you can have many photons in one place with the same energy and travelling in the same direction.

5.2 Independent Particle Model of He Atom

- As we saw earlier when looking at the variational principle, the Hamiltonian for the helium atom is

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

- Note that $[\hat{L}^2, \hat{H}] = [\hat{L}_z, \hat{H}] = 0$. Therefore the eigenstates of the Hamiltonian will also be angular momentum eigenstates.
- If we have normalised wave functions then the energy of the atom is given by $E_\Psi = \langle \Psi | \hat{H} | \Psi \rangle$.
- For the singlet states we have

$$\begin{aligned} E_S &= \int d\vec{r}_1 d\vec{r}_2 \phi(\vec{r}_1) \phi(\vec{r}_2) \hat{H} \phi(\vec{r}_1) \phi(\vec{r}_2) \langle s = 0 m_s = 0 | s = 0 m_s = 0 \rangle \\ &= \int d\vec{r}_1 d\vec{r}_2 \phi(\vec{r}_1) \phi(\vec{r}_2) \hat{H} \phi(\vec{r}_1) \phi(\vec{r}_2) \\ &= \int d\vec{r}_1 \phi(\vec{r}_1) \left[\frac{\hat{p}_1^2}{2m} - \frac{Ze^2}{r_1} \right] \phi(\vec{r}_1) \int d\vec{r}_2 |\phi(\vec{r}_2)|^2 \\ &+ \int d\vec{r}_2 \phi(\vec{r}_2) \left[\frac{\hat{p}_2^2}{2m} - \frac{Ze^2}{r_2} \right] \phi(\vec{r}_2) \int d\vec{r}_1 |\phi(\vec{r}_1)|^2 \\ &+ \int d\vec{r}_1 d\vec{r}_2 \frac{e^2 |\phi(\vec{r}_1)|^2 |\phi(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} \\ &= 2 \int d\vec{r} \phi(\vec{r}) \left[\frac{\hat{p}^2}{2m} - \frac{Ze^2}{r} + \frac{1}{2} \int d\vec{x} \frac{e^2 |\phi(\vec{x})|^2}{|\vec{r} - \vec{x}|} \right] \phi(\vec{r}) \end{aligned}$$

- Thus the energy looks like that from two independent electrons each of which is moving in an effective potential

$$V(r) = -\frac{Ze^2}{r} + \frac{1}{2} \int d\vec{x} \frac{e^2 |\phi(\vec{x})|^2}{|\vec{r} - \vec{x}|}$$

- This potential is that generated by the nucleus plus a term produced by the average interaction between the electrons which partially screens the nuclear potential. This result is the single particle picture result.
- To determine the wave function we use the variational principle. We vary the wave function until we have minimised the energy E_s .
- We now consider the triplet state

$$\begin{aligned} E_T &= \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 (\phi_1(\vec{r}_1) \phi_2(\vec{r}_2) - \phi_1(\vec{r}_2) \phi_2(\vec{r}_1)) \hat{H} (\phi_1(\vec{r}_1) \phi_2(\vec{r}_2) - \phi_1(\vec{r}_2) \phi_2(\vec{r}_1)) \langle 1m_s | 1m_s \rangle \\ &= \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 (\phi_1(\vec{r}_1) \phi_2(\vec{r}_2) - \phi_1(\vec{r}_2) \phi_2(\vec{r}_1)) \hat{H} (\phi_1(\vec{r}_1) \phi_2(\vec{r}_2) - \phi_1(\vec{r}_2) \phi_2(\vec{r}_1)) \end{aligned}$$

- Consider the one body operators. We will use the operator $\frac{\hat{p}_1^2}{2m}$ as an example:

$$\begin{aligned}
\left\langle \frac{p_1^2}{2m} \right\rangle &= \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 (\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)) \frac{\hat{p}_1^2}{2m} (\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)) \\
&= \frac{1}{2} \int d\vec{r}_1 \phi_1(\vec{r}_1) \frac{\hat{p}_1^2}{2m} \phi_1(\vec{r}_1) \int d\vec{r}_2 \phi_2(\vec{r}_2)\phi_2(\vec{r}_2) \\
&+ \frac{1}{2} \int d\vec{r}_1 \phi_2(\vec{r}_1) \frac{\hat{p}_1^2}{2m} \phi_2(\vec{r}_1) \int d\vec{r}_2 \phi_1(\vec{r}_2)\phi_1(\vec{r}_2) \\
&- \frac{1}{2} \int d\vec{r}_1 \phi_1(\vec{r}_1) \frac{\hat{p}_1^2}{2m} \phi_2(\vec{r}_1) \int d\vec{r}_2 \phi_2(\vec{r}_2)\phi_1(\vec{r}_2) \\
&- \frac{1}{2} \int d\vec{r}_1 \phi_2(\vec{r}_1) \frac{\hat{p}_1^2}{2m} \phi_1(\vec{r}_1) \int d\vec{r}_2 \phi_1(\vec{r}_2)\phi_2(\vec{r}_2) \\
&= \frac{1}{2} \int d\vec{r}_1 \phi_1(\vec{r}_1) \frac{\hat{p}_1^2}{2m} \phi_1(\vec{r}_1) + \frac{1}{2} \int d\vec{r}_1 \phi_2(\vec{r}_1) \frac{\hat{p}_1^2}{2m} \phi_2(\vec{r}_1)
\end{aligned}$$

- Now consider the two body operator $\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$

$$\begin{aligned}
\left\langle \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right\rangle &= \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 (\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} (\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)) \\
&= \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{e^2 |\phi_1(\vec{r}_1)|^2 |\phi_2(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} \\
&+ \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{e^2 |\phi_1(\vec{r}_2)|^2 |\phi_2(\vec{r}_1)|^2}{|\vec{r}_1 - \vec{r}_2|} \\
&- \int d\vec{r}_1 d\vec{r}_2 \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \phi_1(\vec{r}_2)\phi_2(\vec{r}_1)
\end{aligned}$$

- Combining all the terms we obtain

$$\begin{aligned}
E_T &= \int d\vec{r} \phi_1(\vec{r}) \left[\frac{\hat{p}^2}{2m} - \frac{Ze^2}{r} + \frac{1}{2} \int d\vec{x} \frac{e^2 |\phi_2(\vec{x})|^2}{|\vec{r} - \vec{x}|} \right] \phi_1(\vec{r}) \\
&+ \int d\vec{r} \phi_2(\vec{r}) \left[\frac{\hat{p}^2}{2m} - \frac{Ze^2}{r} + \frac{1}{2} \int d\vec{x} \frac{e^2 |\phi_1(\vec{x})|^2}{|\vec{r} - \vec{x}|} \right] \phi_2(\vec{r}) \\
&- \int d\vec{r} d\vec{x} \phi_1(\vec{r})\phi_2(\vec{x}) \frac{e^2}{|\vec{r} - \vec{x}|} \phi_1(\vec{x})\phi_2(\vec{r})
\end{aligned}$$

- The first two terms are clearly completely analogous to the single term in the singlet state.
- However the third term is new. It is called the exchange energy, and is a direct consequence of the anti symmetric form of the spatial part of the wave function.
- The exchange energy lowers the energy of states with parallel spins. This is because the symmetry of the wave function keeps these electrons spatially separated from each other. That is, it is a result of correlation in the motion of the electrons.

Chapter 6

Interpretations of quantum mechanics [4]

6.1 Wave-Particle Duality and Indeterminacy

We wish to clarify the key concepts of quantum mechanics, which involves some strange concepts. We will illustrate these concepts by reference to experiments. The concepts are

- *Waveparticle duality*: consider one component of the material world (for example, electrons). Some experiments are best understood by thinking of it as a wave (for example, diffraction effects), while others are best understood by thinking of it as a particle (for example, momentum transfer).
- *Indeterminacy*: a wave function does not tell you what you will measure. Instead it gives you probabilities. But you in fact measure definite values. Heisenberg's uncertainty principle quantifies this: if you make many measurements of non simultaneous observables, then the product of the standard deviations of their measured values has a lower bound ($\Delta A \Delta B \geq \hbar/2$).

6.2 Double slit experiment

- If light from a point source passes through a pair of slits, then you get a diffraction pattern (Young's slits experiment). This is easily explained in terms of waves. It is possible to perform the experiment one photon at a time, producing one dot at a time on the recording screen. This is also particle like.
- If one slit is closed, a single slit diffraction pattern is produced
- If a slit changes from open to closed once the photon is in-flight, the pattern is still correct for the single slit.
- If we monitor the slits we can observe whether the photon goes to one or the other.

- We can make this quantitative

$$|\Psi\rangle = \alpha|A\rangle + \beta|B\rangle$$

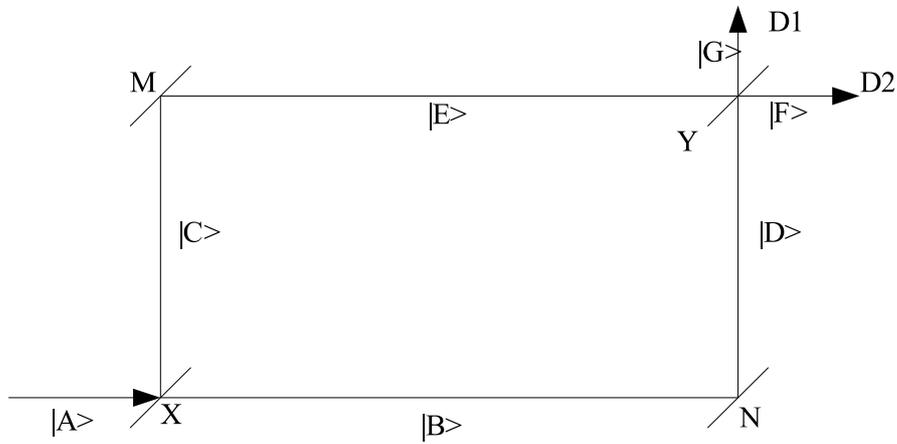
- where $|A\rangle$ is the wave from slit A, and $|B\rangle$ is the wave from slit B. Thus $|\langle\vec{r}|\Psi\rangle|^2 = |\alpha|^2|\langle\vec{r}|A\rangle|^2 + |\beta|^2|\langle\vec{r}|B\rangle|^2 + \alpha\beta^*\langle B|\vec{r}\rangle\langle\vec{r}|A\rangle + \alpha^*\beta\langle A|\vec{r}\rangle\langle\vec{r}|B\rangle$, which gives interference.
- We introduce a two state monitor with state vectors $|M\rangle$ (registered that a particle is present) and $|\bar{M}\rangle$ (did not register that a particle is present). The motion of a particle after passing through a slit is defined by its momentum vector \vec{k} . Therefore the amplitudes that tell us what the probabilities are that the particle is travelling with a particular momentum after passing through a particular slit are

$$\begin{aligned}\langle\vec{k}M|\Psi\rangle &= \alpha\langle\vec{k}M|A\rangle + \beta\langle\vec{k}M|B\rangle \\ \langle\vec{k}\bar{M}|\Psi\rangle &= \alpha\langle\vec{k}\bar{M}|A\rangle + \beta\langle\vec{k}\bar{M}|B\rangle\end{aligned}$$

- If $\langle\vec{k}M|B\rangle = \langle\vec{k}\bar{M}|A\rangle = 0$ then we know which slit the particle went through.

6.3 Beam splitter experiment

Figure 6.1: Beam splitter experiment



$$\begin{aligned}|A\rangle &\rightarrow \frac{1}{\sqrt{2}}(|B\rangle + i|C\rangle) \\ &\rightarrow \frac{1}{\sqrt{2}}(i|D\rangle - |E\rangle) \\ &\rightarrow \frac{1}{\sqrt{2}}\left(i\left[\frac{1}{\sqrt{2}}(|G\rangle + i|F\rangle)\right] - \left[\frac{1}{\sqrt{2}}(|F\rangle + i|G\rangle)\right]\right) = -|F\rangle\end{aligned}$$

- A measurement at M or N gives a 50% chance of detection.
- If an obstruction is placed at N then

$$\begin{aligned}
 |A\rangle &\rightarrow \frac{1}{\sqrt{2}}(|B\rangle + i|C\rangle) \\
 &\rightarrow \frac{1}{\sqrt{2}}(|B\rangle - |E\rangle) \\
 &\rightarrow \frac{1}{\sqrt{2}}(|B\rangle - \frac{1}{\sqrt{2}}(|F\rangle + i|G\rangle))
 \end{aligned}$$

- Thus the photon strikes D1 and D2 with equal probability.
- If we remove Y, then the final state is $\frac{1}{\sqrt{2}}(i|D\rangle - |E\rangle)$. Therefore D1 and D2 respond with equal probability.
- Note that we can insert or remove Y after the photon has left X and we get the same results.

6.4 Copenhagen Interpretation

- This is a scheme for providing outcomes of measurements, and not for explaining mechanisms.
- Collapse of the wave function: the system enters an eigenstate during a measurement.
- Principle of complementarity: mutually exclusive descriptions can be applied to a quantum system, but not simultaneously (for example, waves and particles).
- This interpretation has several problems, despite being the most commonly used one:
 - Measurements are macroscopic and deterministic. This interpretation says the microscopic world is probabilistic. Where is the boundary?
 - A measurement involves interactions between the quantum system and measuring device. If this obeyed Schroedinger's equation it would not lead to the collapse of the wave function. Thus we have an inconsistency.
 - Complementarity is vague and may not even be true.
 - It appears to reject objective reality.

6.5 Hidden Variables

- Statistics is about averaging over many measurements. This averaging could be hiding the effects of variables we are not treating explicitly. For example, the kinetic theory of gases allows us to talk about pressure, temperature etc by averaging over the atomic positions and momenta.

- The main contenders for hidden variable theory are
 - de Broglie pilot wave theory
 - David Bohm's (from Birkbeck College) quantum force theory

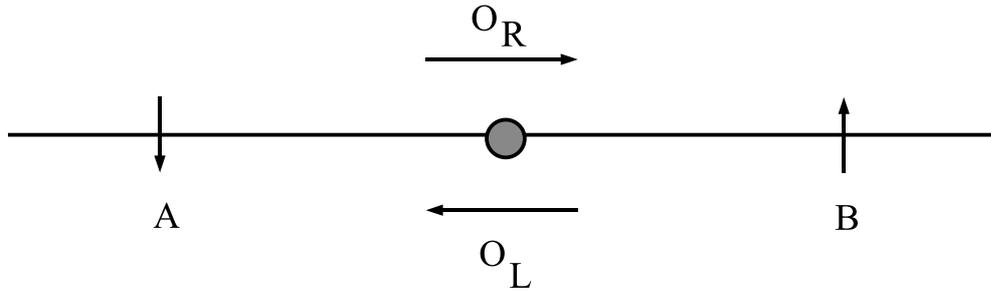
6.6 Non-Locality and the Einstein, Podolsky, Rosen (EPR) Paradox

- The EPR thought experiment proceeds as follows
 - A single stationary particle explodes into two identical fragments
 - Momentum conservation requires that the measured momentum of the two particles be equal and opposite
 - Symmetry requires that each particle has travelled the same distance
 - Does measurement of position (momentum) of A reveals the position (momentum) of B.
 - This measurement gives B a fixed position (momentum) instantaneously.

- David Bohm modified the experiment to use spin.
 - Two spin $\frac{1}{2}$ particles, with zero total spin, move apart. The spin part of the wave function is $1/\sqrt{2}(\alpha_1\beta_2 - \beta_1\alpha_2)$.
 - Measurement of one spin causes collapse of the wave function to $\alpha_1\beta_2$ or $\beta_1\alpha_2$, so if particle 1 is spin up, then particle 2 is spin down, and vice versa.
 - Thus if the z component of the spin of particles 1 and 2 are measured then they will have opposite values. But if the z component of the spin of particle 1 is measured, and then the x component of the spin of particle 2, there will be a 50% chance of getting either of the two possible values.
 - If the x component of the spin had been measured for particles 1 and 2, then particle 2 would have the opposite value to particle 1.

- Special relativity can introduce a further complication. Depending on your state of motion, the order of two measurements can change:

Figure 6.2: Relativistic measurement



- If A and B flashlight when they are making measurements, O_L and O_R might disagree about the order in which pulses reached them.

6.7 Bell's Inequalities

- These are a test of the constraints of hidden variable theories
- Bell provided inequalities that must hold between joint probabilities of spin measurements made on two particle systems and that are a necessary consequence of their being separate entities.
- Consider spins in a singlet state $|\chi\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle)$
- Consider the correlation between measurements $\hat{K} = (\hat{S}_1 \cdot \hat{a})(\hat{S}_2 \cdot \hat{b})$
- The expectation value of the correlation is $E(\hat{a}, \hat{b}) = \langle K \rangle = \langle \chi | (\hat{S}_1 \cdot \hat{a})(\hat{S}_2 \cdot \hat{b}) | \chi \rangle = -\hat{a} \cdot \hat{b} = \cos \gamma$
- Suppose that λ is a hidden variable that allows the system to be completely defined. Each spin 0 system has a value for this variable. Let the probability distribution of λ be $P(\lambda)$, with $\int d\lambda P(\lambda) = 1$.
- Let measurement of spin 1 be $\hbar/2A(\hat{a}, \lambda)$, and of spin 2 be $\hbar/2B(\hat{b}, \lambda)$. $A, B \in \{\pm 1\}$. Since $S = 0$, $A(\hat{a}, \lambda) = -B(\hat{a}, \lambda)$.
- Correlation coefficient

$$\begin{aligned} \epsilon(\hat{a}, \hat{b}) &= \int P(\lambda) A(\hat{a}, \lambda) B(\hat{b}, \lambda) d\lambda \\ \Rightarrow \epsilon(\hat{a}, \hat{b}) - \epsilon(\hat{a}, \hat{c}) &= \int P(\lambda) [A(\hat{a}, \lambda) B(\hat{b}, \lambda) - A(\hat{a}, \lambda) B(\hat{c}, \lambda)] d\lambda \end{aligned}$$

$$\begin{aligned}
&= - \int P(\lambda) A(\hat{a}, \lambda) A(\hat{b}, \lambda) [1 + A(\hat{b}, \lambda) B(\hat{c}, \lambda)] d\lambda \\
\Rightarrow |\epsilon(\hat{a}, \hat{b}) - \epsilon(\hat{a}, \hat{c})| &\leq \int |P(\lambda) A(\hat{a}, \lambda) A(\hat{b}, \lambda) [1 + A(\hat{b}, \lambda) B(\hat{c}, \lambda)]| d\lambda \\
P(\lambda) &\geq 0 \\
1 + A(\hat{b}, \lambda) B(\hat{c}, \lambda) &\geq 0 \\
|A(\hat{a}, \lambda) A(\hat{b}, \lambda)| &= 1 \\
\Rightarrow |\epsilon(\hat{a}, \hat{b}) - \epsilon(\hat{a}, \hat{c})| &\leq \int P(\lambda) [1 + A(\hat{b}, \lambda) B(\hat{c}, \lambda)] d\lambda \\
\Rightarrow |\epsilon(\hat{a}, \hat{b}) - \epsilon(\hat{a}, \hat{c})| &\leq 1 + \epsilon(\hat{b}, \hat{c}) \\
\Rightarrow |\epsilon(\hat{a}, \hat{b}) - \epsilon(\hat{a}, \hat{c}) - \epsilon(\hat{b}, \hat{c})| &\leq 1
\end{aligned}$$

- If \hat{a} , \hat{b} and \hat{c} lie in a plane with \hat{b} bisecting the angle between \hat{a} and \hat{c} , then

$$\begin{aligned}
E(\hat{a}, \hat{b}) &= -\cos \gamma \\
E(\hat{a}, \hat{c}) &= -\cos 2\gamma \\
E(\hat{b}, \hat{c}) &= -\cos \gamma \\
\Rightarrow |-\cos \gamma + \cos 2\gamma| + \cos \gamma &\leq 1
\end{aligned}$$

- The inequality is violated for $0 \leq \gamma \leq \pi/2$.

6.8 The Aspect Experiments

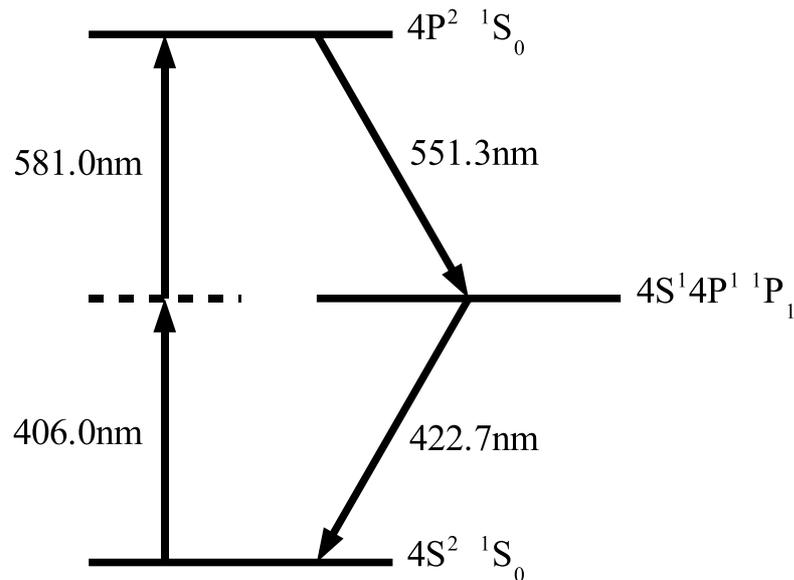
- Measurements were made on the polarisation of a pair of photons emitted by a calcium atom.
- The atom was put into an excited state by two lasers
- It then relaxes in two stages releasing two photons
- These photons then meet polarisers: they either pass through or are reflected. The detectors record +1 if the photon is found to be linearly polarised parallel to the polariser, or -1 if normal to it.
- For an emitted photon pair $|\chi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\uparrow\rangle + |\rightarrow\rightarrow\rangle)$
- We defined coincidence rates by $N_{++}(\hat{a}, \hat{b})$ = the rate for recording +1 in both detectors etc. The correlation function is then

$$E(\hat{a}, \hat{b}) = \left(\frac{N_{++} + N_{--} - N_{+-} - N_{-+}}{N_{++} + N_{--} + N_{+-} + N_{-+}} \right)$$

- We now define $X = \epsilon(\hat{a}, \hat{b}) + \epsilon(\hat{a}, \hat{b}') - \epsilon(\hat{a}', \hat{b}) + \epsilon(\hat{a}', \hat{b}')$
- For a local real theory we have the condition $-2 \leq X \leq 2$
- Aspect chose $\hat{a} \cdot \hat{b} = \hat{a}' \cdot \hat{b} = \hat{a}' \cdot \hat{b}' = \cos \phi$, and $\hat{a} \cdot \hat{b}' = \cos 3\phi$. The inequality was violated.

- This shows that the hidden variable theory must be nonlocal.

Figure 6.3: Calcium energy levels



6.9 The Problem of Measurement

- Copenhagen interpretation
 - During measurement the wave function collapses to an eigenstate
 - Only then do we have knowledge of the quantum system
- But
 - When does measurement take place?
 - How do we separate system, apparatus and observer?
 - When does the collapse of the wave function take place?
- The von Neuman chain
 - Supposed polarised light is incident at 45° to a polariser.
 - The photon is in a superposition of two states: one parallel and one perpendicular to the polariser.

- The measuring apparatus will thus have two states, and prior to measurement will be in a superposition.
 - The measurement apparatus only makes a measurement when a measurement is made on it.
 - Etc.
- Consider the following example
 - Suppose we have an electron that can be in one of two spin states $|\alpha\rangle$ and $|\beta\rangle$, and that we have a measuring device with two lights on it: one for up ($|u\rangle$) and one for down ($|d\rangle$).
 - Before any interaction the system is in the state $|B\rangle = (C_\alpha|\alpha\rangle + C_\beta|\beta\rangle) \otimes (a_u|u\rangle + a_d|d\rangle)$
 - After the interaction it becomes $|A\rangle = C_\alpha|\alpha\rangle \otimes |u\rangle + C_\beta|\beta\rangle \otimes |d\rangle$
 - Which light is shining? It is not defined.
 - To collapse the wave function we need a second measurement. Etc.

6.10 Schrodinger's Cat

- This famous thought experiment highlights the nature of the measurement problem.
- A cat in a sealed box with a Geiger counter, some radioactive material, a flask of hydrogen cyanide, and a mechanism for breaking the flask.
- After one hour this radioactive material will have undergone either zero or one decay events. If there was a decay the Geiger counter will register this, and cause the flask of hydrogen cyanide to break, killing the cat.
- From quantum mechanics, after one hour the state of the system will be $|\Psi\rangle = C_a|\text{No decay; Cat alive}\rangle + C_d|\text{Decay; Cat dead}\rangle$.
- Before opening the box the cat is in a superposition of states. After the box is opened, and a measurement is made, the cat's wave function collapses into one state or the other.
- At which point is the fate of the cat determined?

6.11 Mind and Matter

- It is possible that consciousness leads to collapse of the wave function
- But how complex a being is needed for this?
- What happened before life appeared in the universe?

6.12 Indelible Records

- An isolated quantum system evolves reversibly according to Schroedinger's equation.
- If a measurement is made then an irreversible process takes place that cannot be undone.
- If the system could be described by a single wave function before the measurement, this is no longer true afterwards. The system is in a mixed state.
- Bohr spoke of a process of irreversible amplification. Quantum effects are amplified to the classical level.

6.13 Path Integral Approach

- This was developed by Richard Feynman
- It calculates the probability that a particle starting at position a at time t_a arrives at b at time t_b .
- This approach does not work with wave functions, but instead takes the view that the particle travels every single trajectory between a and b .
- The probability is given by the square of the following term

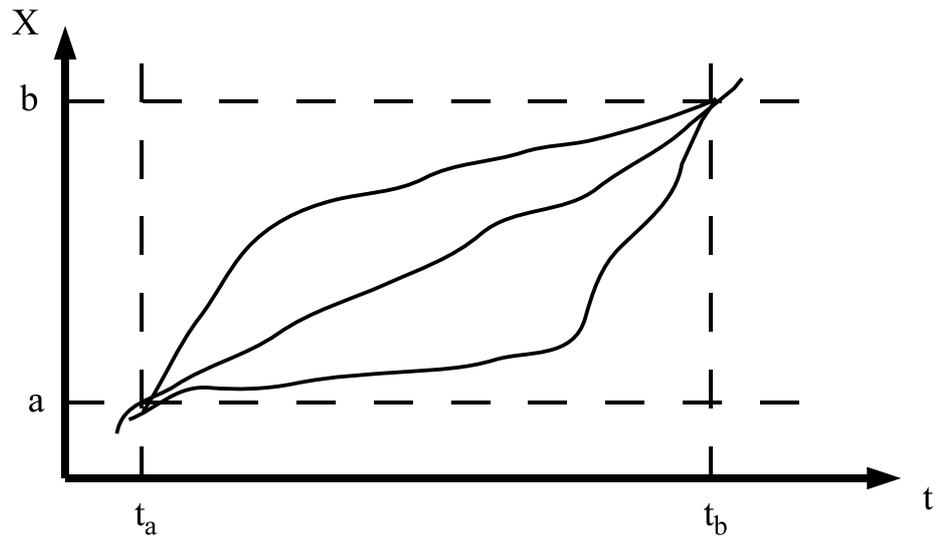
$$K(b, a) = \sum_{\text{all paths } a \rightarrow b} e^{-S(a,b)/i\hbar}$$

- $S(a, b)$ is the action associated with a path and is given by

$$S(a, b) = \int_{t_a}^{t_b} dt (K.E. - P.E.)$$

- The classical path is the one with the minimum value of the action.
- The final probability is a result of interference between neighbouring paths.

Figure 6.4: Path integral



6.14 The Many Universes Interpretation

- This was first proposed by Hugh Everett
- When a measurement is made the universe splits into a number of copies in each of which one of the outcomes is realised. There is no communication between the universes.
- For example, if we measure an electron spin, the universe branches into two copies, one in which the electron has spin up, and the other in which it has spin down.
- Proponents point out its simplicity: only one assumption is needed.
- Opponents protest that invoking infinitely many universes to solve the problem of wave function collapse is excessive.
- It also does not explain what a measurement is.
- David Deutsch has reformulated the theory to work with a pre-existing finite number of universes. When quantum alternatives are presented, the universes partitioned themselves into groups, in each of which a different outcome happens. The universes exist in parallel and change in content completely in accordance with the principle of increase of entropy.

6.15 Alternative Histories

- A history is a sequence in time of events.
- There is no distinction between microscopic and macroscopic, no split between system, apparatus and environment.
- Focuses on probabilities for different histories.

6.15.1 Fine-grained and coarse-grained histories

- This approach was proposed by Gell-Mann and Hartle.
- It does not assign probabilities to histories, but instead a decoherence functional $D(A, B)$ to a pair of histories A and B.
- If $(A \text{ or } B)$ is the combined history of A or B then

$$\begin{aligned} D(A \text{ or } B, A \text{ or } B) &= D(A, A) + D(B, B) + D_i(A, B) \\ D_i(A, B) &= D(A, B) + D(B, A) \end{aligned}$$

- Where D_i is the interference term. If $D_i(A, B) \neq 0$, then A and B cannot be assigned probabilities as they interfere with each other. If $D_i(A, B) = 0$ then $D(A, A)$ and $D(B, B)$ can be interpreted as the probabilities of histories A and B respectively.
- Fine-grained histories give as complete a description of the universe as is possible. Interference between two fine-grained histories does not generally vanish.
- In coarse-grained histories only certain things are followed, and with a limited amount of detail. The rest of the universe is not followed.

6.15.2 Decoherence

- Two histories decohere if their interference term is zero.
- Decoherence occurs because of the entanglement of what is followed with what is not. It gives rise to branching of histories into distinct alternatives with real probabilities, and thus can explain the transition to the classical domain.
- Consider Schroedinger's cat. $|cat\rangle = \sum_l a_l |l\rangle + \sum_d b_d |d\rangle$. There are many scenarios involving the living cat, and many involving the dead cat. These interfere, and after the decoherence time they cancel out. Thus there is no interference between live and dead.

6.16 The Ghiradi-Rimini-Weber scheme

- Schroedinger's equation is modified by the introduction of random hits.

- At random times the wave function is multiplied by a narrow Gaussian (about once every 10^8 years per particle). This causes collapse of the wave function and suppresses linear superpositions.
- However, it is ad hoc, not based on known physical laws, and involves small violations of energy conservation.

6.17 Gravitationally Induced Reduction

- Roger Penrose believes that incorporation of gravity into quantum mechanics could provide an explanation of wave function reduction as a real physical process.
- Suppose a system evolves by Schroedinger's equation into a linear superpositions of two states that occupy significantly different locations in space. The evolved state must then involve a superpositions of gravitational fields with different space-time geometries. Reduction of the wave function could occur if the geometries of the superposed states became so different that they could not coexist.

6.18 Quantum Information

- The unit of information is the bit (binary digit), equal to 0 or 1.
- A classical system can reside in one of the two states.
- A quantum system can exist in a superposition of both states at once: $|\Psi\rangle = C_0|0\rangle + C_1|1\rangle$.
- These qubits can be represented by electron spins, photon polarisations, atomic energy levels, states of trapped ions...

6.18.1 Quantum computers

- For a qubit, the probability of measuring 0 is $|C_0|^2$, and of measuring 1 is $|C_1|^2$.
- A classical register composed of L bits can store one of 2^L possible numbers.
- A quantum register can store all 2^L possible numbers simultaneously in superposition. But we can only see one of them after a measurement. Thus this is not useful for bulk storage.
- Operations can be performed simultaneously on all the numbers, so that 2^L parallel operations can be performed.
- This can produce important savings in time and memory for some algorithms
 - searches

- factorisation (the factorisation of a 100 bit number takes about 10^{44} s on a classical computer, but only a few seconds on a quantum computer. The age of the universe is 10^{17} s).
- Logical gates have already been demonstrated.
- A major obstacle is decoherence (the destruction of the coherent state).

6.18.2 Quantum cryptography

- Cryptography is the art of concealing the content of messages.
- We know how to generate an unbreakable cipher. You need a genuinely random string of bits with which to modify your message (for example, using exclusive or). The encoded message can now be sent by a public channel (for example electronic mail).
- The problem is to transmit this random series of bits (the key) between two people (Alice and Bob) without others being able to intercept it.
- Quantum mechanics can be used to solve the problem of communicating the key.
- One scheme is the following
 - Alice has a source of photons and two polarisers. One polariser linearly polarises the light vertically (0) and the other at 45° (1).
 - Bob has two analysers. One measures photons linearly polarised at -45° (0) and the other horizontally (1).
 - Alice chooses a polariser at random and sends a photon to Bob.
 - Bob chooses an analyser at random and records whether he detects a signal or not.
 - For example, if Alice sends a vertical photon and Bob uses a -45° analyser, then Bob has a 50% chance of detecting a photon. If he does detect a photon both Bob and Alice selected the same value for the bit. Bob tells Alice if he detected the photon or not.
 - Bob and Alice only retain bits for which a photon was detected and use this string as the key.
- A second scheme uses entangled photons
- a supply of pairs of entangled photons is available to Alice and Bob.
- From each pair, one goes to Alice and one to Bob.
- They each make a series of plane polarisation measurements, half the time distinguishing between perpendicular directions, and the other half between 45° rotated directions.
- When the measurements are finished they exchange information about what measurement was made on each photon so that they know on which occasions they made the same measurement. Then by the EPR effect they know that common measurements give the same result.

- This produces a string of random bits.
- If there is an eavesdropper (Eve), then Alice and Bob will not always get the same result, which can be detected by comparing a fraction of their results.

6.18.3 Quantum Teleportation

- We can make an exact replica of a photon at a remote location.
- Consider the following four Bell states

$$\begin{aligned} |\Psi^+\rangle &= \frac{1}{\sqrt{2}}(|10\rangle + |01\rangle) \\ |\Psi^-\rangle &= \frac{1}{\sqrt{2}}(|10\rangle - |01\rangle) \\ |\phi^+\rangle &= \frac{1}{\sqrt{2}}(|11\rangle + |00\rangle) \\ |\phi^-\rangle &= \frac{1}{\sqrt{2}}(|11\rangle - |00\rangle) \end{aligned}$$

- We can switch between these Bell states by means of the following operations
 - phase shift (change of sign)
 - bit flip ($|0\rangle \rightarrow |1\rangle$ or $|1\rangle \rightarrow |0\rangle$)
 - combined phase shift and bit flip
 - identity operation
- The states can all be generated and operated on using a combination of non linear crystals, polarisers and mirrors.
- Alice wishes to teleport a photon (A) in state $|T\rangle = u|1\rangle + v|0\rangle$ to Bob.
 - A pair of entangled photons are sent to Alice and Bob (B and C).
 - Alice performs a joint measurement on photons A and B, and obtains one of the Bell states with probability $\frac{1}{4}$. This collapses photon C into a well-defined state uniquely related to the state of A.
 - Alice then transmits the result of her measurement to Bob over a public channel.
 - Bob can then perform the required unitary transforms on C to produce a photon in state $|T\rangle$.
- Example
- the ancillary photons are prepared in state $|\Psi^-\rangle$. The three photon state of A, B and C is

$$|\Psi\rangle = \frac{1}{\sqrt{2}}[u|110\rangle + v|010\rangle - u|101\rangle - v|001\rangle]$$

- This can be regrouped in terms of Bell states

$$|\Psi\rangle = \frac{1}{2}[u|\phi^+0\rangle - v|\phi^+1\rangle + u|\phi^-0\rangle + v|\phi^-1\rangle - u|\Psi^+1\rangle + v|\Psi^+0\rangle - u|\Psi^-1\rangle - v|\Psi^-0\rangle]$$

- Suppose Alice, in her Bell states measurement, finds $|\Psi^-\rangle$. Then C is projected into the state $|c\rangle = u|1\rangle + v|0\rangle = |T\rangle$.
- Alice tells Bob the result of her measurement, and Bob knows he need do nothing.