

Quantum Theory

D.D.Kodwani

Lectures by Dr Andrew Ho

ABSTRACT. Lecture notes and extensions for PH 3210 given in Autumn 2013. Course lecturer was Dr Andrew Ho, at Royal Holloway, University of London.

Last updated on May 25, 2014

Contents

Preface	v
Part 1. Wavefunction description	1
Chapter 1. Schrodinger's formulation of Quantum Mechanics	3
1. Matter waves	3
2. Interpretation of the wavefunction	5
3. Superposition & Stationary states	9
Chapter 2. Operators	13
1. Canonical quantisation	13
2. Hermitian operators	17
3. Examples of Hermitian operators	19
Part 2. Dirac representation	23
Chapter 3. Bra-Ket notation	25
1. Introduction	25
2. Schmidt procedure and completeness	26
3. Operators in Dirac notation	30
4. Eigenvalue equation	31
5. Time evolution	32
6. Recovering wavefunctions	34
7. Momentum representation	36
Chapter 4. Conserved quantities	39
1. Introduction	39
2. Probability current	40
3. Ehrenfests's theorem	41
4. Complete set of Quantum numbers	45
5. Uncertainty principle	45
Chapter 5. Simple Harmonic Oscillator	51
1. Introduction	51
2. Framework of Harmonic Oscillator	51
3. Operator Method	56
4. Ladder operators in Dirac notation	59
Chapter 6. Angular momentum	63
1. Quantising classical angular momentum	63
2. Eigenvalues and eigenvectors	65
3. Ladder operators	65
4. Spin	71
5. Addition of angular momentum	73
Chapter 7. Hydrogen Atom	79

1. Hydrogen-like atoms	79
2. Angular (θ, ϕ) equation	80
3. Radial equation	80
4. Dipole - matrix elements	81
Part 3. Approximate methods	85
Chapter 8. Time independent perturbation theory	87
1. Formalism	87
2. Particle in a box	90
3. Quadratic Stark effect	92
4. Degenerate perturbation theory and linear Stark effect	93
5. Effects of magnetic field on Hydrogen-like atoms	94
6. Variational method	99
Chapter 9. Time dependent perturbation theory	103
1. Formalism	103
2. Sinusoidal or constant in potential in time perturbation	107
3. Fermi's Golden Rule	108
Chapter 10. Identical Particles	111
1. Formalism	111
2. Dirac notation of identical particles	114
3. Identical fermions with spin	115
4. Helium atom	116

Preface

This course builds on the second year course in Quantum mechanics, still a course in non-relativistic Quantum mechanics. A brief overview of the wavefunction framework is provided. Swiftly moving on to the much more powerful and abstract Dirac notation. First part of the course focuses on the formalism of operators, commutation relations and matrix elements. This formalism is used to describe some of the previously solved problems like the harmonic oscillator. This problem specifically is solved using the ladder operators. Next the concepts of angular momentum are discussed, first in the wavefunction approach and then in the Dirac notation. The Dirac notation approach also sheds light on the fact that the angular momentum problem is in fact a more general problem involving rotation and the intrinsic property of spin can be motivated in this description.

The last part is based on approximate methods, which includes first and second order time independent perturbation theory and first order time dependent perturbation theory. These methods are applied to some real physical examples like the hydrogen atom and this shows how useful approximate methods can be for any experimental quantum physics.

Part 1

Wavefunction description

CHAPTER 1

Schrodinger's formulation of Quantum Mechanics

1. Matter waves

To explain wave like properties that particles exhibited under certain circumstances, De Broglie postulated that every particle can have a wave associated with it that has the wavelength, λ (known as *De Broglie* wavelength):

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

where h is Planck's constant and p is the momentum. Schrodinger introduced an object known as a wavefunction, $\psi(x, t)$, which is a complex valued function that satisfies the following partial differential equation:

$$\hat{\mathbb{H}}\psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad (1.2)$$

This is called *Schrodinger's equation*. $\hat{\mathbb{H}}$ is the *Hamiltonian operator*, which is a partial differential equation that has eigenvalues corresponding to the total energy of a system. In general, the Hamiltonian operator has the form:

$$\hat{\mathbb{H}} = \frac{\hat{p}^2}{2m} + V(r) \quad (1.3)$$

where \hat{p}^2 is the momentum operator:

$$\hat{p}^2 = -i\hbar \nabla^2 \quad (1.4)$$

and $V(r)$ is a potential energy operator, which is determined by the system in question. m is just the mass of the particle corresponding to the wavefunction $\psi(x, t)$. Therefore the Schrodinger equation (SE) in 3-D becomes:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}, t) + V(r)\psi(\vec{r}, t) = i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} \quad (1.5)$$

Or in one dimension:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x)\psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad (1.6)$$

This is a second order partial differential equation. Since there are no terms that depend on both the differential variables, this equation can be solved by *separation of variables*. The idea is to look for product solutions of the form:

$$\psi(x, t) = \phi(x)T(t) \quad (1.7)$$

Now substitute Eq 10.7 into Eq 8.6:

$$-\underbrace{\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} (\phi(x)T(t))}_1 + \underbrace{V(x)\phi(x)T(t)}_2 = i\hbar \underbrace{\frac{\partial}{\partial t} \phi(x)T(t)}_3 \quad (1.8)$$

Notice that in term 1, the $T(t)$ function can be taken outside the differential operator as it is not dependent on x and a similar thing can be done for term 3 (except with the other variable):

$$-\frac{\hbar^2}{2m}T(t)\frac{\partial^2\phi(x)}{\partial x^2} + V(x)\phi(x)T(t) = i\hbar\phi(x)\frac{\partial T(t)}{\partial t} \quad (1.9)$$

Now comes the trick of using separation of variables; divide both sides by $\phi(x)T(t)$:

$$\frac{1}{\psi(x)} \left[-\frac{\hbar^2}{2m} \frac{\partial^2\phi(x)}{\partial x^2} + V(x)\phi(x) \right] = \frac{i\hbar}{T(t)} \frac{\partial T(t)}{\partial t} \quad (1.10)$$

The L.H.S of Eq 1.10 is a function of only x and the R.H.S is only a function of t , therefore the only way this equation can be true is if both sides are equal to a constant (call it E). Hence we get two linear ordinary differential equations:

$$-\frac{\hbar^2}{2m} \frac{d^2\phi(x)}{dx^2} + V(x)\phi(x) = E\phi(x) \quad (1.11)$$

$$i\hbar \frac{dT(t)}{dt} = ET(t) \quad (1.12)$$

Eq 8.11 is called the *time independent Schrodinger equation (TISE)* and Eq 8.12 is called the *time dependent Schrodinger equation(TDSE)*. The TDSE is easy to solve:

$$\begin{aligned} \int \frac{i\hbar}{T(t)} dT(t) &= \int E dT \\ T(t) &= Ae^{-\frac{itE}{\hbar}} \end{aligned} \quad (1.13)$$

where A is a constant that is determined by the initial condition. The TISE depends on the potential, which can make it potentially (pardon the pun) more difficult to solve. The easiest TISE to solve is that for a free particle, i.e no potential energy:

$$-\frac{\hbar^2}{2m} \frac{d^2\phi(x)}{dx^2} = E\phi(x) \quad (1.14)$$

Look for a solution of the form:

$$\phi(x) = Ae^{\alpha x} \quad (1.15)$$

Substitute this into the TISE:

$$-\frac{\hbar^2}{2m} \alpha^2 = E \quad (1.16)$$

Therefore:

$$\alpha = i\sqrt{\frac{2mE}{\hbar^2}} \quad (1.17)$$

Which can be re-written as:

$$\alpha = \pm ik \quad (1.18)$$

where:

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad (1.19)$$

Hence the solution takes the form:

$$\phi(x) = Ae^{ikx} + B^{-ikx} \quad (1.20)$$

Eq 10.13 and 1.20 can be combined to give the overall solution to the TISE for a free particle:

$$\psi(x, t) = Ce^{i(kx - \frac{Et}{\hbar})} + De^{-i(kx + \frac{Et}{\hbar})} \quad (1.21)$$

The first term in this equation corresponds to a wave moving in the positive x direction and second term corresponds to a wave moving in the negative x direction. Considering an analogy with a phase term of the form $e^{i\omega t}$ means that:

$$\omega = \frac{E}{\hbar} \quad (1.22)$$

So we see that all solutions produce Einstein's relation between energy and frequency, that was first used to explain the photo-electric effect. By equating this energy to that of a classical particle, $E = \frac{p^2}{2m}$:

$$\frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} \quad (1.23)$$

Which gives back the De Broglie postulate of matter waves:

$$p = \hbar k \quad (1.24)$$

2. Interpretation of the wavefunction

$\psi(x, t)$ cannot be a physical wave like an oscillating string or an Electro-magnetic wave of Maxwell theory because it is inherently complex (the real and imaginary parts of ψ do not separately solve the Schrodinger equation). The problem is that anything that has imaginary parts cannot be directly measured. Max Born postulated that the wavefunctions, $\psi(x, t)$, can have no interpretation by itself. Instead he suggested that the probability of measuring a particle between x and $x + \delta x$ is:

$$\begin{aligned} Prob(x \in x, x + \delta x) &= P(x, t)\delta x \\ &= \psi(x, t) * \psi(x, t) \\ &= |\psi(x, t)|^2 \end{aligned} \quad (1.25)$$

This is not an obvious step, even though we know the wavefunction is imaginary, one might think that the modulus might correspond to a physical observable. However this is not true and the postulate above has always held up against experiment. The usual laws of statistics follow once this postulate is accepted, a few examples are:

$$\begin{aligned} \langle x \rangle &\equiv \int_{-\infty}^{\infty} xP(x, t)dx \\ &= \int_{-\infty}^{\infty} x|\psi(x, t)|^2 dx \end{aligned} \quad (1.26)$$

$$\begin{aligned} \langle x^2 \rangle &\equiv \int_{-\infty}^{\infty} x^2 P(x, t)dx \\ &= \int_{-\infty}^{\infty} x^2 |\psi(x, t)|^2 dx \end{aligned} \quad (1.27)$$

The total probability of finding the particle anywhere must be 1, therefore a condition is imposed on the wavefunction:

$$1 = \int_{-\infty}^{\infty} P(x, t)dx \quad (1.28)$$

$$= \int_{-\infty}^{\infty} |\psi(x, t)|^2 dx \quad (1.29)$$

In general there are 3-D, in which this condition can be written as:

$$\begin{aligned}
1 &= \int_{-\infty}^{\infty} P(\vec{r}, t) d\vec{r} \\
&= \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} \psi^*(\vec{r}, t) \psi(\vec{r}, t) d\vec{r}
\end{aligned} \tag{1.30}$$

This is called the normalisation condition on $\psi(x, t)$. This must be imposed on $\psi(x, t)$ as the Schrodinger equation is linear in $\psi(x, t)$. Note that if $\psi(x, t)$ is a solution then so is $A\psi(x, t)$, where A is a constant. The constant is fixed by the normalisation condition.

Now consider a wavefunction that is formed of a plane wave:

$$\psi(x, t) = G e^{\frac{i}{\hbar}(px - Et)} \tag{1.31}$$

Therefore the probability is:

$$\int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = \int_{-\infty}^{\infty} |G|^2 dx \rightarrow \infty \tag{1.32}$$

So plane waves are not normalizable, this is because plane waves are not physical solutions as they exist for all time and all space. A more physical situation is a plane wave confined to some finite region (e.g in some experimental apparatus), then the integral can be computed:

$$\int_{-L}^L |G|^2 dx = 1 \tag{1.33}$$

if:

$$G = \frac{1}{\sqrt{2L}} \tag{1.34}$$

where L is the size of the confining apparatus.

Now lets consider the infinite square well potential of the form:

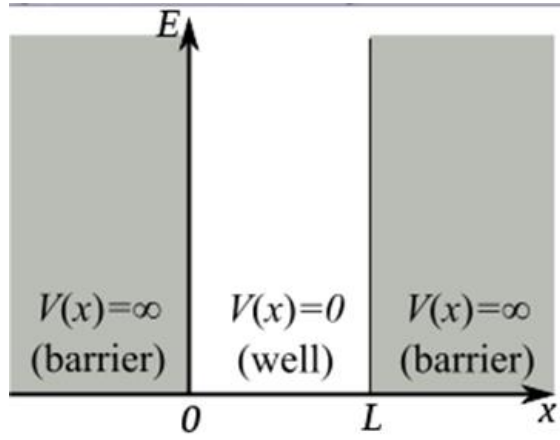


FIGURE 1. Infinite square well potential

Since the potential is independent of time, the Schrodinger equation can be separated into the TISE and TDSE as was done for the free particle solutions. Hence the solutions to this problem will be of the form:

$$\psi(x, t) = \phi(x)e^{-it\frac{E}{\hbar}} \quad (1.35)$$

The Schrodinger equation of this system is:

$$-\frac{\hbar^2}{2m} \frac{d^2\phi}{dx^2} + V(x)\phi = E\phi \quad (1.36)$$

In the region of the infinite potential, $V = \infty$, ϕ must be zero for a finite E solution. Therefore the only position where the Schrodinger equation holds and can be solved is inside the potential well, where the potential is 0:

$$-\frac{\hbar^2}{2m} \frac{d^2\phi}{dx^2} = E\phi \quad (1.37)$$

The solutions are of the same form as the free particle solutions:

$$\phi(x) = Ae^{ikx} + Be^{-ikx} \quad (1.38)$$

where:

$$E = \frac{\hbar^2 k^2}{2m} \quad (1.39)$$

The difference between these solutions and the free particle solution is that here we have boundary conditions that need to be satisfied. The condition is that $\phi(x)$ must be continuous; i.e:

$$\phi(0) = 0 \Rightarrow A + B = 0 \quad (1.40)$$

$$\phi(a) = 0 \Rightarrow Ae^{ika} + Be^{-ika} = 2iA \sin ka = 0 \quad (1.41)$$

So the solution to the TISE becomes:

$$\phi(x) = 2iA \sin kx = B \sin kx \quad (1.42)$$

The only non-trivial solution that satisfies Eq 1.41 is if:

$$k = \frac{n\pi}{a} \quad (1.43)$$

where n can take on any integer value. Substituting these values of k into the expression for the energy:

$$E = \frac{\hbar^2 \pi^2}{2ma^2} n^2 \quad (1.44)$$

So the possible energies of particles are quantised. This is in fact typical for particles in bound potentials, such as atoms. The final step is to normalise the solutions:

$$\begin{aligned} \int_0^a |\phi(x)|^2 dx &= A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx \\ &= A^2 \frac{a}{2} \\ &= 1 \end{aligned} \quad (1.45)$$

Therefore:

$$A = \sqrt{\frac{2}{a}} \quad (1.46)$$

A property of the ϕ_n 's is that they are *orthogonal*:

$$\begin{aligned} \int_{-\infty}^{\infty} \phi_n^*(x) \phi_m(x) dx &= \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx \\ &= \delta_{nm} \end{aligned} \quad (1.47)$$

This system behaves very differently to the classical systems, as long as the quantum number, n is 'relatively' low. We can consider a ball bouncing back and forth in a well of length a , the ball will have a uniform probability density of being in the well given by:

$$P(x) = \frac{1}{a} \quad (1.48)$$

Therefore:

$$\begin{aligned} \langle x \rangle &= \int_0^a x P(x) dx \\ &= \frac{1}{a} \int_0^a x dx \\ &= \frac{a}{2} \end{aligned} \quad (1.49)$$

$$\begin{aligned} \langle x^2 \rangle &= \int_0^a x^2 P(x) dx \\ &= \frac{a^2}{3} \end{aligned} \quad (1.50)$$

Consider the quantum analogue for $n = 1$ state:

$$\begin{aligned} \langle x \rangle &= \int_0^a x \sin^2\left(\frac{\pi x}{a}\right) dx \\ &= \frac{a}{2} \end{aligned} \quad (1.51)$$

$$\begin{aligned} \langle x^2 \rangle &= \int_0^a x^2 \sin^2\left(\frac{\pi x}{a}\right) dx \\ &= \frac{a^2}{3} - \frac{a^2}{2\pi} \end{aligned} \quad (1.52)$$

So we see that the expectation value for x is the same in both the classical and the quantum scenarios. However x^2 is different, as it has an extra $-\frac{\alpha^2}{2\pi^2}$ term. For large n , the behavior of quantum system tends towards classical systems. This is known as *Bohr's correspondence principle*.

3. Superposition & Stationary states

Suppose there is a system α , described by the following wavefunction:

$$\psi_\alpha(x, t) = \phi_\alpha(x)e^{iE_\alpha \frac{t}{\hbar}} \quad (1.53)$$

A wavefunction of this form is special, because whenever a measurement is made on its energy (i.e applying the Hamiltonian operator):

$$\hat{H}\psi_\alpha(x, t) = E_\alpha\psi_\alpha(x, t) \quad (1.54)$$

We are guaranteed a result of E_α . This means the system is in a state of definite energy (here E_α), this is known as an *energy eigenstate* or a *stationary state*. The TDSE is a linear equation therefore the general solutions are of the form:

$$\psi(x, t) = \sum_n a_n \phi_n(x) e^{-iE_n \frac{t}{\hbar}} \quad (1.55)$$

where a_n are arbitrary complex coefficients. Now lets consider a superposition of 2 energy eigenstates:

$$\psi(x, t) = a_1\phi_1(x)e^{-iE_1 \frac{t}{\hbar}} + a_2\phi_2(x)e^{-iE_2 \frac{t}{\hbar}} \quad (1.56)$$

If we want to find the energy of the system, apply the Hamiltonian operator:

$$\begin{aligned} \hat{H}\psi(x, t) &= a_1e^{-iE_1 \frac{t}{\hbar}}\hat{H}\phi_1(x) + a_2e^{-iE_2 \frac{t}{\hbar}}\hat{H}\phi_2(x) \\ &= a_1E_1\phi_1(x)e^{-iE_1 \frac{t}{\hbar}} + a_2E_2\phi_2(x)e^{-iE_2 \frac{t}{\hbar}} \\ &= E_1 + E_2 \left(a_1\phi_1(x)e^{-iE_1 \frac{t}{\hbar}} + a_2\phi_2(x)e^{-iE_2 \frac{t}{\hbar}} \right) \end{aligned} \quad (1.57)$$

Therefore it can be seen from Eq 9.46 that $\psi(x, t)$ is a solution of the TDSE, but it is not a stationary state as $E_1 \neq E_2$. This means that whenever a measurement is made, either E_1 or E_2 will be observed. Which of the two will be observed is not completely random, as we shall see. For $\psi(x, t)$ to be a valid wavefunction, it must be normalisable:

$$\begin{aligned} \int_0^a dx \left[a_1^*\phi_1^*e^{iE_1 \frac{t}{\hbar}} + a_2^*\phi_2^*e^{iE_2 \frac{t}{\hbar}} \right] \left[a_1\phi_1e^{-iE_1 \frac{t}{\hbar}} + a_2\phi_2e^{-iE_2 \frac{t}{\hbar}} \right] &= 1 \\ \int_0^a dx |a_1|^2\phi_1^2 + |a_2|^2\phi_2^2 + a_1a_2^*\phi_1\phi_2e^{i(E_2-E_1)\frac{t}{\hbar}} + a_1^*a_2\phi_1\phi_2e^{i(E_1-E_2)\frac{t}{\hbar}} &= 1 \end{aligned} \quad (1.58)$$

Using the orthogonality of the wavefunction, the final normalisation condition is:

$$|a_1|^2 + |a_2|^2 = 1 \quad (1.59)$$

This looks like a sum of probabilities, which is called the *interpretation* of superposition. This can be verified by computing the energy expectation value:

$$\begin{aligned}
\langle \hat{H} \rangle &= \int_0^a dx \left[a_1^* \phi_1 * e^{iE_1 \frac{t}{\hbar}} + a_2^* \phi_2 e^{iE_2 \frac{t}{\hbar}} \right] \left[a_1 E_1 \phi_1 e^{-iE_1 \frac{t}{\hbar}} + a_2 E_2 \phi_2 e^{-iE_2 \frac{t}{\hbar}} \right] \\
&= \int_0^a dx |a_1|^2 |\phi_1|^2 E_1 + |a_2|^2 |\phi_2|^2 E_2 \\
&= |a_1|^2 E_1 \int_0^a dx |\phi_1|^2 + |a_2|^2 E_2 \int_0^a dx |\phi_2|^2 \\
&= |a_1|^2 E_1 + |a_2|^2 E_2
\end{aligned} \tag{1.60}$$

In a measurement, E_1 will be measurement with probability $|a_1|^2$ and E_2 with probability $|a_2|^2$. Notice that the expectation value of the energy does not have any time dependence. This is not the case for all expectation values, for example; consider a wavefunction of energy superposition of the form:

$$\psi(x, t) = a_1 \sin\left(\frac{\pi x}{a}\right) e^{-iE_1 \frac{t}{\hbar}} + a_2 \sin\left(\frac{2\pi x}{a}\right) e^{-iE_2 \frac{t}{\hbar}} \tag{1.61}$$

These are the spatial wavefunctions for the infinite square well example for the lowest two energy levels ($n = 1, 2$). Now compute:

$$\begin{aligned}
\langle \hat{p} \rangle &= \int_0^a dx \psi^* \hat{p} \psi \\
&= \int_0^a dx \psi^* \left(-i\hbar \frac{\partial}{\partial x} \psi \right) \\
&= -\frac{2i\hbar}{a} \int_0^a dx \left[a_1^* \sin\left(\frac{\pi x}{a}\right) e^{iE_1 \frac{t}{\hbar}} + a_2^* \sin\left(\frac{2\pi x}{a}\right) e^{iE_2 \frac{t}{\hbar}} \right] \\
&\quad \left[a_1 \frac{\pi}{a} \cos\left(\frac{\pi x}{a}\right) e^{-iE_1 \frac{t}{\hbar}} + a_2 \frac{2\pi}{a} \cos\left(\frac{2\pi x}{a}\right) e^{-iE_2 \frac{t}{\hbar}} \right] \\
&= -\frac{2i\hbar}{a} \int_0^a dx |a_1|^2 \frac{\pi}{a} \sin\left(\frac{\pi x}{a}\right) \cos\left(\frac{\pi x}{a}\right) + a_1^* a_2 \frac{2\pi}{a} \sin\left(\frac{\pi x}{a}\right) \cos\left(\frac{2\pi x}{a}\right) e^{i(E_1 - E_2) \frac{t}{\hbar}} \\
&\quad + a_2^* a_1 \frac{\pi}{a} \sin\left(\frac{2\pi x}{a}\right) \cos\left(\frac{\pi x}{a}\right) e^{i(E_2 - E_1) \frac{t}{\hbar}} + |a_2|^2 \frac{2\pi}{a} \sin\left(\frac{2\pi x}{a}\right) \cos\left(\frac{2\pi x}{a}\right)
\end{aligned} \tag{1.62}$$

Using the following identities:

$$\int_0^a dx \sin\left(\frac{\pi x}{a}\right) \cos\left(\frac{\pi x}{a}\right) = 0 \tag{1.63}$$

$$\int_0^a dx \sin\left(\frac{2\pi x}{a}\right) \cos\left(\frac{2\pi x}{a}\right) = 0 \tag{1.64}$$

$$\int_0^a dx \sin\left(\frac{m\pi x}{a}\right) \cos\left(\frac{n\pi x}{a}\right) = \frac{2am}{\pi(m^2 - n^2)} \quad \text{when } m + n \neq \text{even}, m + n = \text{even} \rightarrow 0 \tag{1.65}$$

Therefore the final result is:

$$\langle \hat{p} \rangle = -\frac{8i\hbar}{3a} \left[a_1 a_2^* e^{i(E_2 - E_1) \frac{t}{\hbar}} - c.c \right] \tag{1.66}$$

where $c.c$ is a complex conjugate expression. Taking a simplified case where the coefficients are both real:

$$\langle \hat{p} \rangle = \frac{16\hbar}{3a} a_1 a_2 \sin\left(\frac{(E_2 - E_1)t}{\hbar}\right) \tag{1.67}$$

This means that the momentum fluctuates in time, as supposed to the constant energy.

CHAPTER 2

Operators

1. Canonical quantisation

Most courses on QM will define operators for various quantities and just state that they work. This is true, infact it is one of the 'postulates' of QM that all physical observables are represented by *Hermitian* operators.

It is therefore not possible to trace the steps of operators as they are completely abstract, mathematical entities in their own right. However, I believe that understanding the similarities between QM and classical mechanics (CM) in the Hamiltonian and Lagrangian framework, makes it much easier to digest this abstract context.

Quantum mechanics was first developed as a 'semi-quantum' theory of classical mechanics by Heisenberg and Schrodinger. In this framework, particles are treated as waves, discussed in the opening section and the state of a particle is described by a wavefunction. In classical mechanics the state of a particle is described by its momentum and position (In general there will be three of each coming from the 3 spatial dimensions). In this 'semi-classical' picture of QM, the particle was treated according to the laws of QM, however the overall system in which the particle sits is still treated in the classical framework (i.e E-M fields are still modeled by Maxwell's equations, Newtonian gravity is used etc.) This whole framework is known as *First quantisation*.

The operators appear as simply the postulated of the framework, however in 1926 Paul Dirac re-developed this framework. His description of QM makes it much easier to see how or why the operators are what they are and this is called *Second quantisation*. In CM, described in the Hamiltonian and Lagrangian framework, there exist dynamical variables that the equations are functions of. They are the position coordinates, x and the momenta, p . A Poisson bracket is defined as:

$$\{f(q, p, t), g(q, p, t)\} = \frac{\partial f(q, p, t)}{\partial q} \frac{\partial g(q, p, t)}{\partial p} - \frac{\partial f(q, p, t)}{\partial p} \frac{\partial g(q, p, t)}{\partial q} \quad (2.1)$$

The *canonical* structure of CM is defined as consisting of *Poisson brackets*, between these dynamical variables:

$$\{x, p\} = 1 \quad (2.2)$$

Any dynamical variables that satisfies this structure are called *canonical* transformations in classical mechanics. For example, if one defines a set, with elements that are all the variables of CM:

$$S_{CM} = \{A_1, A_2, A_3, A_4, \dots\} \quad (2.3)$$

Then any variables that satisfy the Poisson bracket:

$$\{A_i, A_j\} = 1 \quad \forall A_i, A_j \in S_{CM} \quad (2.4)$$

are called canonical transformations, infact any motion in 3-D is a canonical transformation. The idea of second quantisation is to take the dynamical variables of CM and promote them to

operator valued functions and to convert the Poisson bracket structure to commutation relations (this is also sometimes referred to as *canonical quantisation*):

$$[\hat{x}, \hat{p}] = i\hbar \quad (2.5)$$

Dirac proposed that the method to 'quantise' the Poisson brackets structure was the following:

$$\{A, B\} \rightarrow \frac{1}{i\hbar} \hat{A}, \hat{B}$$

where in general A and B are functions of dynamical variables and \hat{A} , \hat{B} are the operators corresponding to these dynamical variables (notice that there is no rule or set method to take $A \rightarrow \hat{A}$). However this rule is not correct as it does not hold for all commutation relations. For example, consider the Poisson bracket:

$$\{x^3, p^3\} + \frac{1}{12} \{p^2, x^3\} \{x^2, p^3\} \quad (2.7)$$

Following Dirac's method of quantisation, this Poisson bracket would become the following commutation relation:

$$\frac{1}{i\hbar} [\hat{x}^3, \hat{p}^3] + \frac{1}{12i\hbar} \left[\frac{1}{i\hbar} [\hat{p}^2, \hat{x}^3], \frac{1}{i\hbar} [\hat{x}^2, \hat{p}^3] \right] \quad (2.8)$$

Both the equations should yield the same answer if Dirac is right, so lets check it by explicitly computing the Poisson bracket and commutation relation. Start with the Poisson bracket:

$$\underbrace{\{x^3, p^3\}}_1 + \frac{1}{12} \underbrace{\{p^2, x^3\}}_2 \underbrace{\{x^2, p^3\}}_3 \quad (2.9)$$

Compute each term individually:

$$\begin{aligned} \{x^3, p^3\} &= \frac{\partial x^3}{\partial x} \frac{\partial p^3}{\partial p} - \frac{\partial x^3}{\partial p} \frac{\partial p^3}{\partial x} \\ &= (3x^2)(3p^2) \\ &= 9x^2p^2 \end{aligned} \quad (2.10)$$

$$\begin{aligned} \{p^2, x^3\} &= \frac{\partial p^2}{\partial x} \frac{\partial x^3}{\partial p} - \frac{\partial p^2}{\partial p} \frac{\partial x^3}{\partial x} \\ &= -(2p)(3x^2) \\ &= -6px^2 \end{aligned} \quad (2.11)$$

$$\begin{aligned} \{x^3, p^2\} &= \frac{\partial x^3}{\partial x} \frac{\partial p^2}{\partial p} - \frac{\partial x^3}{\partial p} \frac{\partial p^2}{\partial x} \\ &= 2x(3p^2) - 0 \\ &= 6xp^2 \end{aligned} \quad (2.12)$$

Taking the Poisson bracket between Eq 2.11 and 2.12:

$$\begin{aligned} \{-6px^2, 6xp^2\} &= \frac{\partial -6px^2}{\partial x} \frac{\partial 6xp^2}{\partial p} - \frac{\partial -6px^2}{\partial p} \frac{\partial 6xp^2}{\partial x} \\ &= (-12px)(12px) + (6x^2)(6p^2) \\ &= -144p^2x^2 + 36x^2p^2 \\ &= -108p^2x^2 \end{aligned} \quad (2.13)$$

Substitute Eq 2.13 and 2.10 into Eq 2.9:

$$\begin{aligned} \{x^3, p^3\} + \frac{1}{12} \{ \{p^2, x^3\} \{x^2, p^3\} \} &= 9x^2p^2 - \frac{108p^2x^2}{9} \\ &= 0 \end{aligned} \quad (2.14)$$

Now lets check the commutation relation in Eq 5.79:

$$\frac{1}{i\hbar} \underbrace{[\hat{x}^3, \hat{p}^3]}_1 + \frac{1}{12i\hbar} \left[\frac{1}{i\hbar} \underbrace{[\hat{p}^2, \hat{x}^3]}_2, \frac{1}{i\hbar} \underbrace{[\hat{x}^2, \hat{p}^3]}_3 \right] \quad (2.15)$$

where:

$$\hat{x} = x \quad (2.16)$$

$$\hat{p} = -i\hbar \frac{\partial}{\partial x} \quad (2.17)$$

$$[\hat{x}, \hat{p}] = i\hbar \quad (2.18)$$

First compute term 1:

$$\begin{aligned} [\hat{x}^3, \hat{p}^3] &= [\hat{x}\hat{x}^2, \hat{p}\hat{p}^2] \\ &= \underbrace{\hat{x} [\hat{x}^2, \hat{p}\hat{p}^2]}_{1a} + \underbrace{[\hat{x}, \hat{p}^2\hat{p}] \hat{x}^2}_{1b} \end{aligned} \quad (2.19)$$

Term 1a:

$$\begin{aligned} \hat{x} [\hat{x}^2, \hat{p}\hat{p}^2] &= \hat{x} [\hat{x}\hat{x}, \hat{p}\hat{p}^2] \\ &= \underbrace{\hat{x} [\hat{x}, \hat{p}\hat{p}^2]}_{1a_1} + \underbrace{[\hat{x}, \hat{p}^2\hat{p}] \hat{x}}_{1a_2} \end{aligned} \quad (2.20)$$

Term $1a_1$:

$$\begin{aligned} \hat{x} [\hat{x}, \hat{p}\hat{p}^2] &= \hat{x} ([\hat{x}, \hat{p}] \hat{p}^2 + \hat{p} [\hat{x}, \hat{p}^2]) \\ &= \hat{x} (i\hbar \hat{p}^2 + \hat{p} [\hat{x}, \hat{p}\hat{p}]) \\ &= \hat{x} (i\hbar \hat{p}^2 + \hat{p} ([\hat{x}, \hat{p}] \hat{p} + \hat{p} [\hat{x}, \hat{p}])) \\ &= \hat{x} (i\hbar \hat{p}^2 + \hat{p} (i\hbar \hat{p} + i\hbar \hat{p})) \\ &= 3i\hbar \hat{x} \hat{p}^2 \end{aligned} \quad (2.21)$$

Similarly term $1a_2$:

$$[\hat{x}, \hat{p}^2\hat{p}] \hat{x} = 3i\hbar \hat{p}^2 \hat{x} \quad (2.22)$$

Therefore:

$$\hat{x} [\hat{x}^2, \hat{p}\hat{p}^2] = 3i\hbar (\hat{x}^2 \hat{p}^2 + \hat{p}^2 \hat{x}^2) \quad (2.23)$$

Similarly computing term 1b:

$$\begin{aligned} [\hat{x}, \hat{p}^2\hat{p}] \hat{x}^2 &= ([\hat{x}, \hat{p}^2] \hat{p} + \hat{p}^2 [\hat{x}, \hat{p}]) \hat{x}^2 \\ &= 3i\hbar \hat{p}^2 \hat{x}^2 \end{aligned} \quad (2.24)$$

So term 1 is:

$$[\hat{x}^3, \hat{p}^3] = 3i\hbar \hat{x}^2 \hat{p}^2 + 6i\hbar \hat{p}^2 \hat{x}^2 \quad (2.25)$$

I invite the reader to compute terms 2 and 3 (note that term 2 is the same as the negative of term 3) and see that the final result is $-3\hbar^2$. So the commutation relation is not the same as the Poisson bracket and therefore Dirac's method of canonical quantisation does not hold here. I hope this brief discussion will give the reader more of a feel for the idea of quantisation and operators.

Numerical values of classical dynamical variables, like momentum and energy become differential operators in QM:

$$\text{Momentum, } \hat{p} = -i\hbar\nabla \quad (2.26)$$

The energy operator is the Hamiltonian:

$$\begin{aligned} \text{Energy, } \hat{H} &= \frac{\hat{p}^2}{2m} + V(\vec{r}) \\ &= -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \end{aligned} \quad (2.27)$$

As stated before, it is the general principle in QM that there is a Hermitian operator associated with all physics observables. Measured values in experiments are related to operators via eigenvalue equations of the form:

$$\hat{Q}\psi_n(x) = q_n\psi_n(x) \quad (2.28)$$

where $\psi_n(x)$ is the eigenfunction and q_n is the eigenvalue corresponding to the operator \hat{Q} . The set of all q_n is called a *spectrum*, for example the energy spectrum of a Harmonic oscillator is:

$$E_n = \hbar\omega \left(\frac{1}{2} + n \right) \quad (2.29)$$

In fact the energy eigenvalue equation for the Harmonic oscillator is of the form:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_n(x)}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \psi_n(x) = E_n \psi_n(x) \quad (2.30)$$

This means that when a measurement is made on a quantum system, the observed value is one of the eigenvalues of the operator (corresponding to this observable).

2. Hermitian operators

It goes without saying, that any experiment will always yield a real value (i.e not a complex number). This is one of the key problems in QM, that the first people developing it (Heisenberg, Pauli, Schrodinger, Bohr...etc.) had to think about, since the state of a quantum system, is described by a wavefunction, that is complex.

The 'correct' interpretation of the wavefunction, sometimes also known as the 'Born' interpretation (first put forward by Max Born) is that the magnitude square of the wavefunction, represents the *probability density* of a system being in that state. As stated above, the values observed in experiment are real numbers, which leads to a constraint on the operators corresponding to physical observables. They must have real eigenvalues. This class of operators are called *Hermitian* operators. A Hermitian operator, \hat{Q} must satisfy:

$$\int_{-\infty}^{\infty} \phi^* \hat{Q}\psi dx = \int_{-\infty}^{\infty} (\hat{Q}\phi)^* \psi dx \quad (2.31)$$

Which is equivalent to saying:

$$Q = Q^\dagger \quad (2.32)$$

$\forall \phi(x), \psi(x)$ which are normalised and are not plane waves, i.e:

$$\phi(x), \psi(x) = 0 \quad x \rightarrow \pm\infty \quad (2.33)$$

Lets check that they have real eigenvalues, consider the eigenvalue equation:

$$\hat{Q}\psi_n = q_n\psi_n \quad (2.34)$$

Multiplying both sides by ψ_m^* and integrate between $\pm\infty$:

$$\int_{-\infty}^{\infty} \psi_m^* \hat{Q}\psi_n dx = \int_{-\infty}^{\infty} \psi_m^* q_n \psi_n dx \quad (2.35)$$

If \hat{Q} is Hermitian the L.H.S is:

$$\begin{aligned} \int_{-\infty}^{\infty} (\hat{Q}\psi_m)^* \psi_n dx &= \int_{-\infty}^{\infty} (q_m\psi_m)^* \psi_n dx \\ &= q_m^* \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \end{aligned} \quad (2.36)$$

Equating this to the R.H.S:

$$q_m^* \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = q_n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \quad (2.37)$$

Now, if we choose $m = n$, and the equation has to hold $\forall m, n$, then:

$$(q_n - q_n^*) \int_{-\infty}^{\infty} |\psi_n|^2 dx = 0 \quad (2.38)$$

Assuming ψ_n are normalised:

$$q_n = q_n^* \quad (2.39)$$

Therefore q_n must be real in general. Notice that we assumed that the wavefunction were ortho-normal, however this is also provable very easily. Lets go back to:

$$q_m^* \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = q_n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \quad (2.40)$$

which can be re-written as:

$$(q_n - q_m^*) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad (2.41)$$

Again, this equation has to hold $\forall n, m$ therefore in general $q_n \neq q_m^*$, so:

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad (2.42)$$

There ψ_m^* and ψ_n must be orthogonal. Infact this was already observed in the infinite square well example.

Another, final property of Hermitian operators that is very useful is the fact that the eigenvectors of the Hermitian operators form a complete set of basis vectors in a *Hilbert* space. This means that any function $f(x)$ can be expressed as a linear combination of these basis vectors:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) \quad (2.43)$$

Proof of this is actually very difficult and so it is not shown. We can say something about what it means for the sum on the R.H.S to converge to the function $f(x)$. If we carry out the some not obey all of the infinite number of eigenfunctions, but only the first N , we can obtain an approximation for $f(x)$:

$$f_N(x) = \sum_{n=1}^N c_n \psi_n(x) \quad (2.44)$$

The amount by which the approximation this approximation is wrong is:

$$f(x) - f_N(x) \quad (2.45)$$

this approximation will be sufficient if the difference is small, i.e:

$$\|f(x) - f_N(x)\|^2 \quad (2.46)$$

Mean square convergence of $f_N(x)$ to $f(x)$ means:

$$\lim_{N \rightarrow \infty} \|f(x) - f_N(x)\|^2 = 0 \quad (2.47)$$

and it is in this sense that the basis states are said to be *complete*. However since the Hermitian operators are a postulate themselves, we can simply consider the fact that the eigenvectors form a complete basis in the Hilbert space can also be considered a postulate.

The completeness of states leads to a connection between the operators and probabilities. Suppose a state is prepared at $t = 0$, the wavefunction is $\phi(x, 0)$. Consider an experiment that makes the measurement, Q . Firstly, lets expand the wavefunction in the basis vectors, $\psi_n(x)$:

$$\phi(x, 0) = \sum_n a_n \psi_n(x) \quad (2.48)$$

Finding the coefficients is easy, multiply both sides by $\psi_m^*(x)$ and integrate. Suppose we want to find the value of the physical observable Q in this state:

$$\langle \hat{Q} \rangle_\phi = \int (\psi(x, 0))^* \hat{Q} \psi(x, 0) \quad (2.49)$$

Substitute the expansion of the states $\psi(x, 0)$:

$$\begin{aligned} \langle \hat{Q} \rangle_\phi &= \int \left(\sum_n a_n \psi_n(x) \right)^* \hat{Q} \left(\sum_m a_m \psi_m(x) \right) \\ &= \int \left(\sum_n a_n \psi_n(x) \right)^* \sum_m a_m q_m \psi_m(x) \\ &= \sum_{n,m} a_n^* a_m q_m \int \psi_n^*(x) \psi_m(x) dx \\ &= \sum_{n,m} a_n^* a_m q_m \delta_{nm} \\ &= \sum_n |a_n|^2 q_n \end{aligned} \quad (2.50)$$

Recall the under the Born interpretation the probability is the amplitude square of the wavefunction, which in this case is $|a_n|^2$. This is also similar to classical probabilities for a quantity. For example, the expectation value of a quantity (also known as the average or mean) is just the probability times the value itself, which is exactly what we have here.

3. Examples of Hermitian operators

- Position operator:

$$\hat{x} = x \quad (2.51)$$

Check that this is Hermitian:

$$\begin{aligned} \langle x \rangle &= \int \phi^* x \psi dx \\ &= \int (x^* \phi)^* \psi dx \end{aligned} \quad (2.52)$$

but x is a real number, therefore:

$$\begin{aligned} \langle x \rangle &= \int (x\phi)^* \psi dx \\ &= \int \phi^* x \psi dx \end{aligned} \quad (2.53)$$

This is the condition for an operator to be Hermitian. The easy to see this, is to check that the operator is its own Hermitian conjugate. Since x is just a real number, it is always its own Hermitian conjugate. Another result follows immediately from this:

$$(xQ)^* = x^*Q^* = xQ^* = Q^*x \quad (2.54)$$

- Potential energy operator $V(x)$:

$$\begin{aligned} \langle V(x) \rangle &= \int_{-\infty}^{\infty} \phi^* V(x) \psi dx \\ &= \int_{-\infty}^{\infty} (V(x)^* \phi)^* \psi dx \end{aligned} \quad (2.55)$$

as long as the coefficients in $V(x)$ are real we have:

$$V(x)^\dagger = V(x) \quad (2.56)$$

Of course the potential cannot be complex.

- Momentum operator (1 -D):

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad (2.57)$$

Therefore:

$$\int_{-\infty}^{\infty} \phi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi dx = -i\hbar \int_{-\infty}^{\infty} \phi^* \frac{\partial \psi}{\partial x} dx \quad (2.58)$$

We want to check what happens when the operator acts on ϕ^* , so the R.H.S needs to be integrated by parts:

$$-i\hbar \int_{-\infty}^{\infty} \phi^* \frac{\partial \psi}{\partial x} dx = -i\hbar [\phi^* \psi]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial \phi^*}{\partial x} \psi dx \quad (2.59)$$

The wavefunctions are demanded to be normalisable, therefore the boundary term is 0:

$$\int_{-\infty}^{\infty} \phi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi dx = i\hbar \int_{-\infty}^{\infty} \frac{\partial \phi^*}{\partial x} \psi dx \quad (2.60)$$

$$-i\hbar \int_{-\infty}^{\infty} \phi^* \frac{\partial \psi}{\partial x} dx = i\hbar \int_{-\infty}^{\infty} \frac{\partial \phi^*}{\partial x} \psi dx \quad (2.61)$$

$$\int_{-\infty}^{\infty} \phi^* \hat{p} \psi dx = \int_{-\infty}^{\infty} (\hat{p} \phi)^* \psi dx \quad (2.62)$$

So the condition of Hermitian operators is met.

- Kinetic energy operator (1-D):

$$\hat{K} = -\frac{\hat{p}}{2m} \frac{\partial^2}{\partial x^2} \quad (2.63)$$

Therefore:

$$\int_{-\infty}^{\infty} \phi^* \left(-\frac{\hbar^2}{2m} \right) \frac{\partial^2 \psi}{\partial x^2} dx = -\hbar^2 2m \int_{-\infty}^{\infty} \phi^* \frac{\partial^2 \psi}{\partial x^2} dx \quad (2.64)$$

Once again integrate the R.H.S by parts:

$$\begin{aligned} -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \phi^* \frac{\partial^2 \psi}{\partial x^2} dx &= \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{\partial \phi^*}{\partial x} \frac{\partial \psi}{\partial x} dx \\ &= -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{\partial^2 \phi^*}{\partial x^2} \psi dx \\ &= \int_{-\infty}^{\infty} (\hat{K} \phi)^* \psi dx \end{aligned} \quad (2.65)$$

which satisfies the property of the Hermitian operator.

- Hamiltonian operator:

$$\hat{\mathbb{H}} = \hat{T} + \hat{V} \quad (2.66)$$

Since \hat{T} and \hat{V} are both Hermitian, $\hat{\mathbb{H}}$ is also Hermitian. It is an easy check as \hat{T} and \hat{V} are both real valued functions, therefore:

$$\hat{\mathbb{H}} = \hat{\mathbb{H}}^\dagger \quad (2.67)$$

So $\hat{\mathbb{H}}$ is Hermitian.

- Finally lets consider a full example and return to the infinite square well, the eigenvalue equation is:

$$\hat{\mathbb{H}} \phi_n = E_n \phi_n \quad (2.68)$$

where:

$$\phi_n = \sqrt{\frac{2}{q}} \sin\left(\frac{\pi n x}{a}\right) \quad (2.69)$$

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2ma^2} \quad (2.70)$$

The solution can also be written in terms of the momenta of the particles:

$$\tilde{\phi}_{p_n} = \frac{1}{\sqrt{a}} e^{ip_n \frac{x}{\hbar}} \quad (2.71)$$

Lets write out the energy eigenfunctions in terms of $\tilde{\phi}_{p_n}$:

$$\phi_n = \sqrt{\frac{2}{a}} \frac{1}{2i} \left(e^{\frac{i\pi n x}{a}} - e^{-\frac{i\pi n x}{a}} \right) \quad (2.72)$$

Multiply the top and bottom in the exponent by \hbar :

$$\phi_n = \sqrt{\frac{2}{a}} \frac{1}{2i} \left(e^{\frac{in\pi x \hbar}{a\hbar}} - e^{-\frac{in\pi x \hbar}{\hbar a}} \right) \quad (2.73)$$

Substitute the momenta, $p_n = \frac{n\pi\hbar}{a}$ into the exponent:

$$\phi_n = -i \left(\frac{1}{\sqrt{2}} \tilde{\phi}_{p_n} - \frac{1}{\sqrt{2}} \tilde{\phi}_{-p_n} \right) \quad (2.74)$$

Physically, this means that if a particle is in energy eigenstate ϕ_n and we measure its momentum we find:

$$\begin{aligned} \frac{n\pi\hbar}{a} & \quad \text{with probability } \left| \frac{1}{\sqrt{2}} \right|^2 = \frac{1}{2} \\ -\frac{n\pi\hbar}{a} & \quad \text{with probability } \left| -\frac{1}{\sqrt{2}} \right|^2 = \frac{1}{2} \end{aligned} \quad (2.75)$$

This is intuitively pleasing as a wave should have an equal probability to travel in either direction (in 1D), and that is what the momentum values show. The positive momentum value represents the wave moving in the positive x direction and the negative momentum value represents the wave moving in the negative x direction.

Part 2

Dirac representation

CHAPTER 3

Bra-Ket notation

1. Introduction

Dirac introduced an object, $|\psi\rangle$ called 'ket psi', which represents the state of a system. This notation is completely abstract, the ket donates a complete set of amplitudes for the system. If the system consists of a particle in a potential well, $|\psi\rangle$ could consist of amplitudes a_n that the energy is E_n , where E_n is the spectrum of all possible energies, or it might consist of the amplitude $a(p)$ that the momentum is measured to be p .

Using the abstract symbol $|\psi\rangle$ enables us to think about the system without committing ourselves to what complete set of amplitudes we are going to use (i.e the state is in the basis of position or energy or momentum). As an analogy, a position vector \vec{x} , enables us to think about a geometrical point independently of the coordinates, i.e in Cartesian, Spherical polar, Cylindrical... etc.

Complex conjugates of wavefunction are called 'Bras' and are represented by $\langle\psi|$. The overlap of wavefunction, which in wavefunction representation is given by:

$$\int dx \phi^*(x)\psi(x) \quad (3.1)$$

is written as:

$$\langle\phi|\psi\rangle \quad (3.2)$$

in the Dirac notation (sometimes also called the inner product of the two vectors). This is infact the most general, mathematical description for states in an arbitrary vector space. We can also obtain a relation relating the complex conjugate:

$$\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^* \quad (3.3)$$

A ket is normalised if:

$$\langle\psi|\psi\rangle = 1 \quad (3.4)$$

The orthogonality condition is:

$$\langle\psi_n|\psi_m\rangle = 0 \quad n \neq m \quad (3.5)$$

So the ortho-normality condition is written as:

$$\langle\psi_n|\psi_m\rangle = \delta_{nm} \quad (3.6)$$

The complex vector space possessing the function of the inner product, which describes the possible states of the system us called the *Hilbert* space, \mathcal{H} . In other words, the eigenstates of a system will span the Hilbert space. All linear spaces have a limited number of basis vectors. For example, our 3-D space has 3 basis vectors, $\underline{\hat{x}}, \underline{\hat{y}}, \underline{\hat{z}}$, infact this is why it is called a 3 dimensional space. However, the dimension of a space can also be infinite and typically a Hilbert space is infinitely dimensional (for example it is known that a particle in a box has an infinite energy spectrum and hence an infinite number of energy eigenstates that are linearly independent).

Existence of the inner product in the vector space means it is possible to form complete sets of ortho-normal kets via the Schmidt procedure.

2. Schmidt procedure and completeness

Given a set of α linearly independent, normalisable functions, ψ_α , one can always construct a new set of *mutually orthogonal* functions, ϕ_α , via the Schmidt procedure. Start with the function, ψ , construct the following series:

$$\begin{aligned}\phi_1 &= \psi_1 \\ \phi_2 &= a_{21}\phi_1 + \psi_2 \\ \phi_3 &= a_{31}\phi_1 + a_{32}\phi_2 + \psi_3 \\ &\vdots \\ \phi_\alpha &= a_{\alpha 1}\phi_1 + a_{\alpha 2}\phi_2 + \dots + a_{\alpha, \alpha-1}\phi_{\alpha-1} + \psi_\alpha\end{aligned}\tag{3.7}$$

Lets find the form of the a coefficients. To do this, we follow the usual procedure of exploiting the ortho-normality of the function. Starting with a_{21} , multiply both sides of the ϕ_2 equation by ϕ_1^* and integrate over the vector space:

$$\int \phi_1^* \phi_2 dV = \int a_{21} \phi_1^* \phi_1 + \int \phi_1^* \psi_2 dV\tag{3.8}$$

by definition the ϕ states are orthogonal and as $\phi_1 = \psi_1$ and the ψ 's are normalised, the result is:

$$a_{21} = - \int \phi_1^* \psi_2 dV\tag{3.9}$$

Substitute this back into the equation for ϕ_2 :

$$\phi_2 = - \left(\int \phi_1^* \psi_2 dV \right) \phi_1 + \psi_2\tag{3.10}$$

It can be shown that this is orthogonal to ϕ_1 . Next we can find the form of ϕ_3 . To do so, first multiply the ϕ_3 equation by ϕ_1^* and integrate over the vector space:

$$0 = a_{31} \int \phi_1^* \phi_1 dV + a_{32} \int \phi_1^* \phi_2 dV + \int \phi_1^* \psi_3 dV\tag{3.11}$$

therefore:

$$a_{31} = - \int \phi_1^* \psi_3 dV\tag{3.12}$$

To find the a_{32} multiplying the ϕ_3 equation by ϕ_2^* and integrate to get:

$$a_{32} = \frac{\int \phi_2^* \psi_3 dV}{\int \phi_2^* \phi_2 dV}\tag{3.13}$$

So the full form of ϕ_3 is:

$$\phi_3 = - \left[\int \phi_1^* \psi_3 dV \right] \phi_1 - \frac{\int \phi_2^* \psi_3 dV}{\int \phi_2^* \phi_2 dV} \phi_2 + \psi_3\tag{3.14}$$

This procedure is repeated until we get to the state α :

$$\phi_\alpha = - \sum_{i=1}^{\alpha-1} \frac{\int \phi_i^* \psi_\alpha dV}{\int \phi_i^* \phi_i dV} \phi_i + \psi_\alpha\tag{3.15}$$

The entire derivation can be followed step by step in the Dirac notation and I will just quote the final result of it, as we shall only work in the Dirac notation from now on:

$$|\phi_\alpha\rangle = - \sum_{i=1}^{\alpha-1} |\phi_i\rangle \frac{\langle \phi_i | \psi_\alpha \rangle}{\langle \phi_i | \phi_i \rangle} + |\psi_\alpha\rangle \quad (3.16)$$

To have an ortho-normal set, these states have to be normalised:

$$\langle \phi_\alpha | \phi_\alpha \rangle = 1 \quad (3.17)$$

The result for the normalised states $|U_m\rangle$ is:

$$|U_m\rangle = \frac{|\phi_m\rangle}{\sqrt{\langle \phi_m | \psi_m \rangle}} \quad (3.18)$$

Even though we did not fully derive this, something can be said to motivate this result. In general, if one wants a normalised basis vector, the vector being normalised would be divided by the modulus (length) of itself. A similar procedure is happening here, the projection of ϕ_m on ψ_m is being taken as the modulus or length of the vector $|\phi_m\rangle$. This is analogous to the dot product in a R^3 vector space.

Now a complete set of orthonormal kets (a basis set for the Hilbert space) is available:

$$|U_m\rangle \text{ with } \langle U_n | U_m \rangle = \delta_{nm} \quad (3.19)$$

This means any key vector representing a state for a quantum system, who's space of states corresponds to this particular Hilbert space can be expressed as:

$$|\psi\rangle = \sum_{n=1}^{\dim \mathcal{H}} c_n |U_n\rangle \quad (3.20)$$

Once again, to obtain the coefficients, c_n , the ortho-normality conditions for the states are exploited:

$$\begin{aligned} \langle U_m | \psi \rangle &= \sum_{n=1}^{\dim \mathcal{H}} c_n \langle U_m | U_n \rangle \\ &= \sum_{n=1}^{\dim \mathcal{H}} c_n \delta_{nm} \end{aligned} \quad (3.21)$$

By definition, since U_m is a state represented by a vector in the \mathcal{H} , then the value of U_m must be in the vector space and therefore available in the sum. Hence the sum will just pick out that value due to the Kronecker delta function being there:

$$c_m = \langle U_m | \psi \rangle \quad (3.22)$$

Substituting back in for c_n in Eq 3.20:

$$|\psi\rangle = \sum_{n=1}^{\dim \mathcal{H}} |U_n\rangle \langle U_n | \psi \rangle \quad (3.23)$$

the bra vectors are the Hermitian adjoint of the ket vectors:

$$(|\psi\rangle)^\dagger = \left(\sum_{n=1}^{\dim \mathcal{H}} c_n^* \langle U_n | \right)^\dagger \quad (3.24)$$

$$\langle \psi | = \sum_{n=1}^{\dim \mathcal{H}} c_n^* \langle U_n | \quad (3.25)$$

The normalisation condition gives:

$$\begin{aligned}
1 &= \langle \psi | \psi \rangle \\
&= \sum_n^{\dim \mathcal{H}} c_n^* \langle U_n | c_n | U_n \rangle \\
&= \sum_n^{\dim \mathcal{H}} |c_n|^2
\end{aligned} \tag{3.26}$$

This is basically stating that the probabilities must add up to 1. A key principle in QM is that all operators are linear, therefore the eigenfunctions corresponding to them can form superposition states, i.e if:

$$|\psi\rangle = c_1|U_1\rangle + c_2|U_2\rangle \tag{3.27}$$

Then:

$$\hat{O}|\psi\rangle = c_1(\hat{O}|U_1\rangle) + c_2(\hat{O}|U_2\rangle) \tag{3.28}$$

Operators also act on vector spaces of bra's linearly:

$$\langle \psi | = c_1^* \langle U_1 | + c_2^* \langle U_2 | \tag{3.29}$$

Then:

$$\begin{aligned}
\langle \psi | \hat{O} &= (c_1^* \langle U_1 | + c_2^* \langle U_2 |) \hat{O} \\
&= c_1^* (\langle U_1 | \hat{O}) + c_2^* (\langle U_2 | \hat{O})
\end{aligned} \tag{3.30}$$

Since the bra's and ket's are exchanged by taking their adjoint, it is useful to define the action of adjoint operators:

$$\langle \psi | \hat{O}^\dagger | \phi \rangle \equiv \langle \phi | \hat{O} | \psi \rangle^* \tag{3.31}$$

or in words, the bra and kets are swapped and the entire expression is complex conjugated. It will become clear when looking at the matrix representation of the bras and kets that turning a bra into a ket is equivalent to transposing it. Hermitian operators satisfy:

$$\hat{O}^\dagger = \hat{O} \tag{3.32}$$

therefore they are also called 'self-adjoint' operators. Therefore we arrive at a crucial result for Hermitian operators:

$$\langle \psi | \hat{O} | \phi \rangle \equiv \langle \phi | \hat{O} | \psi \rangle^* \tag{3.33}$$

In general the quantity $\langle \psi | \hat{O} | \phi \rangle$ is called a 'matrix element' of \hat{O} between states $\langle \phi |$ and $|\psi\rangle$. If U_n is an orthonormal basis, then $\langle U_m | \hat{O} | U_n \rangle$ is a matrix element in the conventional sense (and can be represented by O_{mn}). Recall that the expansion of general ket state takes the form:

$$|\psi\rangle = \sum_{n=1}^{\dim \mathcal{H}} |U_n\rangle \langle U_n | \psi \rangle \tag{3.34}$$

Since this holds for any $|\psi\rangle$, an identity operator can be extracted:

$$\hat{I} = \sum_{n=1}^{\dim \mathcal{H}} |U_n\rangle \langle U_n | \tag{3.35}$$

So any state can be expanded as:

$$\hat{\mathcal{I}}|\phi\rangle = \sum_{n=1}^{\dim\mathcal{H}} |U_n\rangle\langle U_n|\phi\rangle = |\phi\rangle \quad (3.36)$$

The matrix element of $\hat{\mathcal{I}}$ in any basis can be calculated:

$$\begin{aligned} \langle U_p|\hat{\mathcal{I}}|U_q\rangle &= \langle U_p|\sum_{n=1}^{\dim\mathcal{H}} |U_n\rangle\langle U_n|U_q\rangle \\ &= \sum_{n=1}^{\dim\mathcal{H}} \langle U_p|U_n\rangle\langle U_n|U_q\rangle \\ &= \sum_{n=1}^{\dim\mathcal{H}} \delta_{pn}\delta_{nq} \\ &= \sum_{n=1}^{\dim\mathcal{H}} \delta_{pq} \end{aligned} \quad (3.37)$$

Of-course the δ_{pq} represents a matrix element and any matrix formed by a delta function is just a diagonal unit matrix. The dimensions of the matrix are just the dimension of the Hilbert space. Another important example is the matrix element of a product of operators:

$$\langle U_p|\hat{A}\hat{B}|U_q\rangle = \langle U_p|\hat{A}\hat{\mathcal{I}}\hat{B}|U_p\rangle \quad (3.38)$$

One can always insert the identity matrix, since it will just leave the expression unchanged:

$$\langle U_p|\hat{A}\hat{\mathcal{I}}\hat{B}|U_p\rangle = \sum_n \langle U_p|\hat{A}|U_n\rangle\langle U_n|\hat{B}|U_p\rangle \quad (3.39)$$

Since U_p and U_n form an orthonormal bra-ket basis, the expression above can be written as a product of matrix elements:

$$\sum_n \langle U_p|\hat{A}|U_n\rangle\langle U_n|\hat{B}|U_p\rangle = \sum_n A_{pn}B_{nq} \quad (3.40)$$

Which is just the usual matrix multiplication of matrices representing \hat{A} and \hat{B} . This is where it becomes clear that the previous operation of the adjoint on the operator works because the operators are represented by matrices:

$$\begin{aligned} (\hat{O}^\dagger)_{mn} &\equiv \langle U_m|\hat{O}^\dagger|U_n\rangle \\ &= \langle U_n|\hat{O}|U_m\rangle \\ &= (\hat{O}^*)_{nm} \end{aligned} \quad (3.41)$$

which is just the complex conjugate of the operator, transposed (as expected).

3. Operators in Dirac notation

A very useful form of an operator is:

$$\hat{O} = \sum_i O_i |i\rangle\langle i| \quad (3.42)$$

where $|i\rangle$ and $\langle i|$ are eigenfunctions of the operator \hat{O} and O_i are the respective eigenvalues. This follows immediately by inserting the identity:

$$\hat{O} = \hat{O}\hat{\mathcal{I}} = \hat{O} \sum_{n=1}^{\dim\mathcal{H}} |i\rangle\langle i| \quad (3.43)$$

Now if $|i\rangle$ forms a complete set of basis kets and is an eigenvector of \hat{O} we get:

$$\hat{O} = \sum_{n=1}^{dim\mathcal{H}} O_n |i\rangle \langle i| \quad (3.44)$$

As an example, consider the expectation value of the Hamiltonian operator:

$$\begin{aligned} \langle \hat{H} \rangle &= \langle \psi | \hat{H} | \psi \rangle \\ &= \sum_i E_i \langle \psi | i \rangle \langle i | \psi \rangle \end{aligned} \quad (3.45)$$

where $|i\rangle$ are the eigenvectors of the Hamiltonian. Recall that the Hamiltonian operator is a Hermitian operator and eigenvectors of Hermitian operators form a complete set of orthonormal basis vectors. This means that the $|\psi\rangle$ can be expanded in this basis:

$$|\psi\rangle = \sum_i^{dim\mathcal{H}} c_i |i\rangle \quad (3.46)$$

$$\langle \psi | = \sum_j^{dim\mathcal{H}} \langle j | c_j^* \quad (3.47)$$

Substituting these into the expectation value of the energy:

$$\begin{aligned} \langle \hat{H} \rangle &= \sum_i E_i \left(\sum_{i,j} c_j^* \langle j | i \rangle c_i \langle i | j \rangle \right) \\ &= \sum_i E_i \sum_{i,j} c_j^* c_i \delta_{ji} \delta_{ij} \\ &= \sum_n E_n |c_n|^2 \end{aligned} \quad (3.48)$$

This is exactly the expected spectrum of energy values. To be more precise each state of the system corresponding to this particular Hamiltonian will have the energy E_i in the state $|i\rangle$ which occurs with probability $|c_i|^2$ where:

$$c_i = \langle i | \psi \rangle \quad (3.49)$$

4. Eigenvalue equation

The eigenvalue equation that has been used in the wavefunction representation (evaluated in the coordinates \vec{r} and t) is written as:

$$\hat{Q}\psi_n(x) = q_n\psi_n(x) \quad (3.50)$$

In the previous section, this equation was written in the matrix representation of the operator and states. In the more general Dirac notation it is:

$$\hat{Q}|n\rangle = q_n|n\rangle \quad (3.51)$$

where n labels the state of the system and the eigenvector and q_n is the eigenvalue corresponding to the state $|n\rangle$. It was seen that a state $|\psi\rangle$ can be expanded in terms of a set of normalised eigenvectors $|n\rangle$ as:

$$|\psi\rangle = \sum_n a_n |n\rangle \quad (3.52)$$

As usual the coefficients are given by $\langle n | \psi \rangle$, which, as has been shown, leads to the expansion of a complete set of states:

$$|\psi\rangle = \sum_n |n\rangle \langle n|\psi\rangle \quad (3.53)$$

Suppose a system is prepared such that:

$$a_1 = \langle 1|\psi\rangle = 2 \quad (3.54)$$

$$a_4 = \langle 4|\psi\rangle = 2i \quad (3.55)$$

$$a_8 = \langle 8|\psi\rangle = 5 \quad (3.56)$$

and all the other coefficients are zero. This means the system is currently in a superposition state of the form:

$$|\psi\rangle = 2|1\rangle + 2i|4\rangle + 5|8\rangle \quad (3.57)$$

But notice that this state is not normalised, therefore the first thing to do is to normalise it. The normalisation condition is:

$$\langle \psi|\psi\rangle = 1 \quad (3.58)$$

Therefore:

$$\begin{aligned} (\langle 1|2 - \langle 4|2i + \langle 8|5)(2|1\rangle + 2i|4\rangle + 5|8\rangle) &= 4\langle 1|1\rangle + 4i\langle 1|4\rangle + 10\langle 1|8\rangle - 4i\langle 4|1\rangle + 4\langle 4|4\rangle \\ &\quad - 10i\langle 4|8\rangle + 10\langle 8|1\rangle + 10i\langle 8|4\rangle + 25\langle 8|8\rangle \end{aligned} \quad (3.59)$$

By definition the states are orthonormal therefore the only nonzero terms are:

$$4\langle 1|1\rangle + 4\langle 4|4\rangle + 25\langle 8|8\rangle = 33 \quad (3.60)$$

Therefore $\langle \psi|\psi\rangle = 33$, to make this state normalised, divide each state by a factor of $\frac{1}{\sqrt{33}}$:

$$|\psi\rangle = \frac{1}{\sqrt{33}} (2|1\rangle + 2i|4\rangle + 5|8\rangle) \quad (3.61)$$

Suppose now, one wants to know the outcome of a measurement of the physical quantity corresponding to the operator \hat{Q} . We know that \hat{Q} forms eigenvalue equations with states $|n\rangle$. Since there are three possible states, there will be three possible outcomes of the measurement. The probability of measuring the system in state $|1\rangle$ (corresponding to an eigenvalue of q_i) is:

$$\begin{aligned} |\langle 1|\psi\rangle|^2 &= \left| \langle 1| \left(\frac{1}{\sqrt{33}} (2|1\rangle + 2i|4\rangle + 5|8\rangle) \right) \right|^2 \\ &= \left| \langle 1| \frac{2}{\sqrt{33}} |1\rangle \right|^2 \\ &= \frac{4}{33} \end{aligned} \quad (3.62)$$

Similarly for state $|4\rangle$ and $|8\rangle$:

$$Prob(|4\rangle) = \langle 4|\psi\rangle = \frac{4}{33} \quad (3.63)$$

$$Prob(|8\rangle) = \langle 8|\psi\rangle = \frac{25}{33} \quad (3.64)$$

Note that the probability of the system being found in some state must be 1, therefore the probabilities corresponding to the individual states must add up to 1 (which they do!).

Another thing one may want to know is the expectation value of the observable Q . To do this one needs to find the following matrix element:

$$\begin{aligned}
\langle \psi | \hat{Q} | \psi \rangle &= \left(\frac{1}{\sqrt{33}} (\langle 1|2 + \langle 4|2i + \langle 8|5) \hat{Q} (2|1 + 2i|4 + 5|8) \right) \\
&= \frac{1}{33} (\langle 1|2 + \langle 4|2i + \langle 8|5) (2\hat{Q}|1 + 2i\hat{Q}|4 + 5\hat{Q}|8) \\
&= \frac{1}{33} (4\langle 1|\hat{Q}|1 + 4\langle 4|\hat{Q}|4 + 25\langle 8|\hat{Q}|8) \\
&= \frac{4}{33}q_1 + \frac{4}{33}q_4 + \frac{25}{33}q_8 \tag{3.65}
\end{aligned}$$

Which is the same as what one would expect from classical statistics. After a measurement is made on the state $|\psi\rangle$, the system will be in a state, that is not a superposition, but in the state that has just been measured. For example, if the state $|\psi\rangle$ is made measured with operator \hat{Q} , and the result is eigenvalue q_4 , it means that immediately after the measurement the state of the system is $|\psi\rangle = |4\rangle$.

This is known as the *collapse of the state* postulate. This concept cannot be derived or motivated by anything, it is simply true as it agrees with experiment. Note that if the operator \hat{Q} has some degenerate eigenvectors (i.e the vector corresponding to the same eigenvalue), then this approach is not quite right. As the system might still be in a superposition state after the measurement. In this case, the procedure of reduction is slightly more involved and is not discussed here.

5. Time evolution

In the absence of a measurement, the system evolves in time, as described by the TDSE:

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \hat{H} |\psi(t)\rangle \tag{3.66}$$

The TDSE is a linear equation, which is also deterministic, i.e given the initial state $|\psi(t=0)\rangle$, one can work out (not always practically possible for a sufficiently complex system, but in principle) the state of the system at a later time t' ($t' > 0$), as long as no measurements are performed in the time $t = t' > t > 0$.

The probabilistic (non-deterministic) aspects of QM are purely due to the collapse of the state when a measurement is made. This may be confusing, as some may think; how can a system that can be in a superposition state, like Schrodinger's cat being dead and alive at the same time, be deterministic. The answer comes in two parts; firstly superposition states do not just exist in the state of quantum system, but they also exist in other physical phenomena, especially ones involving waves, like E-M waves. Therefore as counter-intuitive as it may seem, superposition systems can be deterministic.

The underlying reason for this is the fact that the state that the QM systems (or other physical systems that give rise to superposition states) are infact solutions of the Schrodinger equation which is a *linear* differential equation. So the mathematical foundation is that any system, which has an equation of motion (like the Schrodinger equation) that is linear will have solutions that can be superpositions and at the same time be deterministic, as described by the equation.

Secondly, and this is fundamental to QM, the state of a system is not a physical observable. So even though the state of a system can be deterministically predicted, the only observable quantities can come from measurements on the system, which will cause a collapse in the system and destroy the deterministic nature of the state.

Going back to time evolution, the TDSE can be integrated from time t_0 to t_f to give the evolution in time of the state. This is trivially easy:

$$|\psi(t)\rangle = e^{-i\hat{\mathbb{H}}\frac{(t_f-t_0)}{\hbar}}|\psi(t_0)\rangle \quad (3.67)$$

I have left the Hamiltonian operator in the exponent, this can equally be replaced by a scalar value E_n which just represent the energy spectrum of the given Hamiltonian. The reason the operator is left in the exponent is if the exponential is expanded in a power series:

$$e^{\hat{\mathbb{H}}} = 1 + \hat{H} + \frac{\hat{H}^2}{2} + \dots \quad (3.68)$$

it is easy to see that this term is *unitary* as the Hamiltonian operator is Hermitian:

$$U^\dagger U = e^{i\hat{\mathbb{H}}^\dagger\frac{(t_f-t_0)}{\hbar}} e^{-i\hat{\mathbb{H}}\frac{(t_f-t_0)}{\hbar}} = 1 \quad (3.69)$$

which is the condition for a unitary operator. This means time evolution is *unitary evolution*. Suppose $\forall\{|E_n\rangle\}\exists$:

$$\hat{\mathbb{H}}|E_n\rangle = E_n|E_n\rangle \quad (3.70)$$

Using the states $|E_n\rangle$ for the TDSE, one can obtain the time evolution of these states:

$$|E_n(t)\rangle = e^{-iE_n\frac{t}{\hbar}}|E_n(0)\rangle \quad (3.71)$$

Now lets go back to a general state $|\psi\rangle$. We can find the time evolution of any $|\psi\rangle$ in terms of the $|E_n\rangle$ basis:

$$|\psi\rangle = \sum_n a_n(t)|E_n(t)\rangle \quad (3.72)$$

Apply the time evolution operator $i\hbar\frac{\partial}{\partial t}$:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\psi\rangle &= i\hbar\frac{\partial}{\partial t}\sum_n a_n(t)|E_n(t)\rangle \\ &= i\hbar\left(\dot{a}_n|E_n(t)\rangle + a_n(t)\frac{\partial|E_n(t)\rangle}{\partial t}\right) \end{aligned} \quad (3.73)$$

the R.H.S of the TDSE:

$$\begin{aligned} \hat{\mathbb{H}}|\psi(t)\rangle &= \hat{\mathbb{H}}\sum_n a_n(t)|E_n(t)\rangle \\ &= \sum_n a_n\hat{\mathbb{H}}|E_n(t)\rangle \end{aligned} \quad (3.74)$$

Equate the L.H.S to the R.H.S of TDSE:

$$i\hbar\sum_n\left(\dot{a}_n|E_n(t)\rangle + a_n(t)\frac{\partial|E_n(t)\rangle}{\partial t}\right) = \sum_n a_n(t)\hat{\mathbb{H}}|E_n(t)\rangle \quad (3.75)$$

But we know:

$$i\hbar\frac{\partial|E_n(t)\rangle}{\partial t} = \hat{\mathbb{H}}|E_n(t)\rangle \quad (3.76)$$

Therefore the second term on in Eq 3.75 on the L.H.S is equal to the R.H.S, therefore:

$$i\hbar\sum_n\dot{a}_n|E_n(t)\rangle = 0 \quad (3.77)$$

To obtain the coefficients \dot{a}_n , go through the usual procedure of exploiting ortho-normality of the states; multiply both sides by $\langle E_n(t)|$:

$$\dot{a}_n = 0 \quad (3.78)$$

$\forall n$. Remembering that $|E_n(t)\rangle = e^{-iE_n \frac{t}{\hbar}} |E_n(0)\rangle$, the expansion for the time evolution for any state $|\psi\rangle$ of a system can be written as:

$$|\psi(t)\rangle = \sum_n a_n e^{-iE_n \frac{t}{\hbar}} |E_n(0)\rangle \quad (3.79)$$

where a_n 's are constants. This equation will be very useful when we come to discuss time dependent perturbation theory.

6. Recovering wavefunctions

So far the switch between wavefunctions and the bra-ket notation has been a rather informal one, in the sense that the ket vectors are said to represent the state of a system and so are the wavefunction. However, they do not mean the same thing:

$$|\psi\rangle \neq \psi(x, t) \quad (3.80)$$

To see how the wavefunctions are related to the ket (or bra) vectors, consider the position operator \hat{x} acting on its eigenstate $|x\rangle$:

$$\hat{x}|x\rangle = x|x\rangle \quad (3.81)$$

This has a complete spectrum of eigenvalues. The eigenkets are normalised as:

$$\langle x|x'\rangle = \delta(x - x') \quad (3.82)$$

This is the analogue of the:

$$\langle x|x'\rangle = \delta_{xx'} \quad (3.83)$$

in the discrete case. Some useful identities of the Dirac delta function are:

$$\int_{-\infty}^{\infty} e^{ik(x-x')} dk = 2\pi\delta(x - x') \quad (3.84)$$

$$\int_{-\infty}^{\infty} f(x)\delta(x - a)dx = f(a) \quad (3.85)$$

here $f(x)$ has to be a 'well behaved' function of x (i.e no singularities).

$$\int_{-\infty}^{\infty} e^{i\vec{k}\cdot\vec{x}} d^3k = (2\pi)^3 \delta^3(x) \quad (3.86)$$

We have seen before that the general rules of the Dirac formalism lead to $\langle x|\psi\rangle^2$ giving the probability of the system in state $|\psi\rangle$ being in $|x\rangle$, at a given time. In other words $\langle x|\psi\rangle$ is the probability amplitude that a particle in state $|\psi\rangle$ is located at x . This is precisely what was previously called the wavefunction.

The description of states by wavefunction is called the 'x-representation' (or coordinate representation). The expansion of a normalised state $|\psi\rangle$ in the position representation is given by:

$$|\psi\rangle = \int |x\rangle \langle x|\psi\rangle dx \quad (3.87)$$

which is the continuous analogue of of the discrete representation:

$$|\psi\rangle = \sum_{n=1}^{dim\mathcal{H}} |n\rangle \langle n|\psi\rangle \quad (3.88)$$

We know that $\psi(x) = \langle x|\psi\rangle$:

$$|\psi\rangle = \int |x\rangle \psi(x) dx \quad (3.89)$$

Multiplying both sides by $\langle x'|$:

$$\langle x'|\psi\rangle = \int \langle x'|x\rangle\psi(x)dx \quad (3.90)$$

$$\langle x'|\psi\rangle = \int_{-\infty}^{\infty} \psi(x)\delta(x'-x)dx \quad (3.91)$$

$$\langle x'|\psi\rangle = \psi(x') \quad (3.92)$$

which is what was expected Schrodinger's wave mechanics is the form QM takes if the coordinates of a particle are all one cares about (e.g no spin, no anti-particle creation). Since the Dirac formalism is the more general theory of QM, then it is expected that all representations, including wavefunctions, should be derivable from the Dirac formalism and indeed this is true:

$$\begin{aligned} \langle\psi|\phi\rangle &= \int dx\langle\psi|x\rangle\langle x|\phi\rangle \\ &= \int dx\langle\psi|x\rangle\langle x|\phi\rangle \\ &= \int dx\langle x|\psi\rangle^*\langle x|\phi\rangle \\ &= \int dx\psi^*\phi \end{aligned} \quad (3.93)$$

Which is also expected from wave-mechanics and similarly all properties of wave mechanics can be derived by the Dirac framework.

7. Momentum representation

The entire works of Schrodinger formulation of QM, concentrate on the position representation. Now let's look at the momentum eigenstates:

$$\hat{p}|p\rangle = p|p\rangle \quad (3.94)$$

First, consider the state $\langle r|p\rangle$ (3-D equivalent to $\langle x|p\rangle$). This is equivalent to the momentum eigenfunction in terms of the wavefunction approach, i.e:

$$\langle r|p\rangle = \psi_p(x, t) \quad (3.95)$$

such that:

$$\hat{p}\psi_p(x, t) = p\psi_p(x, t) \quad (3.96)$$

where the momentum operator \hat{p} is:

$$\hat{p} = -i\hbar\nabla \quad (3.97)$$

It is easy to check that the solution to this differential equation is:

$$\psi_p(x, t) = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{ipx}{\hbar}} \equiv \langle r|p\rangle \quad (3.98)$$

lets check the normalisation of the momentum eigenkets $|p\rangle$:

$$\langle p|p'\rangle = \delta(p-p') \quad (3.99)$$

Insert the identity operator into the inner product:

$$\begin{aligned}
\langle p|p' \rangle &= \int_{-\infty}^{\infty} \langle p|r \rangle \langle r|p' \rangle dr \\
&= \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi\hbar}} e^{-\frac{ipr}{\hbar}} \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{ip'r}{\hbar}} dr \\
&= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i(p'-p)\frac{r}{\hbar}} dr \\
&= \frac{1}{2\pi\hbar} \hbar 2\pi \delta(p' - p) \\
&= \delta(p' - p)
\end{aligned} \tag{3.100}$$

which is the condition for normalisation. We can also rewrite the following:

$$\begin{aligned}
\langle r|\hat{p}|\psi \rangle &= \int dp \langle r|p \rangle \langle r|p' \rangle \frac{1}{\sqrt{2\pi\hbar}} e^{ip\frac{r}{\hbar}} \\
&= \int dp \frac{1}{2\pi\hbar} \langle p|\hat{p}|\psi \rangle e^{ip\frac{r}{\hbar}}
\end{aligned} \tag{3.101}$$

But $\langle p|\hat{p} = \langle p|p$, therefore:

$$\langle r|\hat{p}|\psi \rangle = \frac{1}{\sqrt{2\pi\hbar}} \int dp p \langle p|\psi \rangle e^{ip\frac{r}{\hbar}} \tag{3.102}$$

Now substitute the following:

$$\begin{aligned}
\hat{p}\langle r|p \rangle &= p\langle r|p \rangle \\
&= p \frac{e^{ip\frac{r}{\hbar}}}{\sqrt{2\pi\hbar}}
\end{aligned} \tag{3.103}$$

into Eq 3.102:

$$\begin{aligned}
\langle r|\hat{p}|\psi \rangle &= \int dp \hat{p}\langle r|p \rangle \langle p|\psi \rangle \\
&= -i\hbar \frac{\partial}{\partial r} \int dp \langle r|p \rangle \langle p|\psi \rangle
\end{aligned} \tag{3.104}$$

Substitute back for the identity:

$$\int dp \langle p|p \rangle \langle p| = \mathcal{I} \tag{3.105}$$

Therefore:

$$\begin{aligned}
\langle r|\hat{p}|\psi \rangle &= -\hbar \frac{\partial}{\partial r} \langle r|\psi \rangle \\
&= -i\hbar \frac{\partial}{\partial r} \psi(r)
\end{aligned} \tag{3.106}$$

Similar the kinetic energy operator is:

$$\begin{aligned}\langle r | \frac{\hat{p}}{2m} | \psi' \rangle &= \frac{1}{2m} \langle r | \hat{p}^2 | \psi \rangle \\ &= \frac{1}{2m} \int \langle r | p^2 | p \rangle \langle p | \psi \rangle dp \\ &= \frac{1}{2m} p^2 \int \langle r | p \rangle \langle p | \psi \rangle dp \\ &= \frac{1}{2m} p^2 \langle r | \psi \rangle \\ &= \frac{p^2}{2m} \psi(r) \\ &= -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(r)}{\partial r^2}\end{aligned}\tag{3.107}$$

Conserved quantities

1. Introduction

Conserved quantities like energy, momentum, angular momentum are crucial in all of physics and it would be almost impossible to solve any problems without these. There is a fundamental theorem in physics that states an important property of conserved quantities. It was first discovered in the Lagrangian and Hamiltonian formulation of classical mechanics.

This theorem is known as *Noether's* theorem derived by Emmy Noether and it states that all conserved quantities arise due to symmetries in the equations. However in QM we will not derive conserved quantities from Noether's theorem and we will not discuss this any further.

Consider the expectation value of some operator \hat{Q} which does not have any explicit time dependence (i.e x or $-i\hbar\frac{\partial}{\partial x}$):

$$\langle Q \rangle_\psi = \int_{-\infty}^{\infty} \psi^*(x, t) \hat{Q} \psi(x, t) dx \quad (4.1)$$

Since ψ is a function of t , in general $\langle Q \rangle$ will also be a function of t . So lets examine this time dependence:

$$\frac{d\langle \hat{Q} \rangle_\psi}{dt} = \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial t} \hat{Q} \psi + \psi^* \hat{Q} \frac{\partial \psi}{\partial t} dx \quad (4.2)$$

From the TDSE:

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (4.3)$$

Substitute this into Eq 4.2:

$$\begin{aligned} \frac{d\langle \hat{Q} \rangle_\psi}{dt} &= \int_{-\infty}^{\infty} \left(\frac{\hat{H}\psi}{i\hbar} \right)^* \hat{Q} \psi + \psi^* \hat{Q} \left(\frac{\hat{H}\psi}{i\hbar} \right) dx \\ &= \int_{-\infty}^{\infty} -\frac{\psi^* \hat{H} \hat{Q} \psi}{i\hbar} + \frac{\psi^* \hat{Q} \hat{H} \psi}{i\hbar} dx \\ &= \frac{i}{\hbar} \int_{-\infty}^{\infty} \psi^* \left(\hat{H} \hat{Q} - \hat{Q} \hat{H} \right) \psi dx \\ &= \frac{1}{\hbar} \int_{-\infty}^{\infty} \psi^* \left[\hat{H}, \hat{Q} \right] \psi dx \end{aligned} \quad (4.4)$$

For a conserved quantity:

$$\frac{d\langle Q \rangle_\psi}{dt} = 0 \quad (4.5)$$

$\forall \psi$, the only way this can be true is if:

$$\left[\hat{H}, \hat{Q} \right] = 0 \quad (4.6)$$

In other words if an observable has an operator that commutes with the Hamiltonian operator, then the observable will be a conserved quantity. For example if $\hat{Q} = 1$, then its expectation value is:

$$\langle |\hat{Q}| \rangle = \langle \psi | \psi \rangle \quad (4.7)$$

and the time derivative is:

$$\begin{aligned} \frac{d\langle \hat{Q} \rangle}{dt} &= \frac{d}{dt} \langle \psi | \psi \rangle \\ &= \frac{i}{\hbar} \int_{-\infty}^{\infty} \psi^* [\hat{H}, 1] \psi dx \end{aligned} \quad (4.8)$$

However, 1 is just a constant, therefore obviously commutes with the Hamiltonian, meaning:

$$\frac{d}{dt} \langle Q \rangle = 0 \quad (4.9)$$

What this mean is that the probability is conserved independent of time, i.e $\langle \psi | \psi \rangle = 1$.

2. Probability current

We know that $\psi^* \psi =$ Probability density, ρ . Lets see how the probability density changes over time:

$$\frac{\partial \rho}{\partial t} = \frac{\partial \psi^*}{\partial t} \psi + \frac{\partial \psi}{\partial t} \psi^* \quad (4.10)$$

From the TDSE:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi \quad (4.11)$$

Therefore:

$$\frac{\partial \psi}{\partial t} = \frac{i}{\hbar} \left(\frac{\hbar^2}{2m} \nabla^2 \psi - V \psi \right) \quad (4.12)$$

$$\frac{\partial \psi^*}{\partial t} = -\frac{i}{\hbar} \left(\frac{\hbar^2}{2m} \nabla^2 \psi^* - V \psi^* \right) \quad (4.13)$$

Now substitute Eq 4.11, 9.39, 4.13 into Eq 4.10:

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \frac{i}{\hbar} \left(\frac{\hbar^2}{2m} \nabla^2 \psi^* - V \psi^* \right) \psi - \frac{i}{\hbar} \left(\frac{\hbar^2}{2m} \nabla^2 \psi - V \psi \right) \psi^* \\ &= \frac{i\hbar}{2m} \nabla^2 \psi^* \psi - \frac{i}{\hbar^2} V \psi^* \psi - \frac{i\hbar}{2m} \nabla^2 \psi \psi^* + \frac{iV}{\hbar} \psi \psi^* \\ &= \frac{i\hbar}{2m} (\nabla^2 \psi^* \psi - \nabla^2 \psi \psi^*) \\ &= -\frac{i\hbar}{2m} \nabla (\psi \nabla \psi^* - \psi^* \nabla \psi) \end{aligned} \quad (4.14)$$

The probability current, j is defined as:

$$\vec{j} = \frac{i\hbar}{2m} (\psi \nabla \psi^* - \psi^* \nabla \psi) \quad (4.15)$$

finally we have the conservation law:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0 \quad (4.16)$$

3. Ehrenfests's theorem

Coming back to the condition for a conserved quantity:

$$\frac{d\langle\psi|Q|\psi\rangle}{dt} = \frac{i}{\hbar}\langle\psi|[\hat{\mathbb{H}}, \hat{Q}]|\psi\rangle \quad (4.17)$$

Now we can consider operators that are known to correspond to a given physical observable and check weather it commutes with the Hamiltonian operator to see weather that that quantity is conserved or not.

Note that this commutation relation has to be calculated for each different system. A conserved quantity in one system may not be conserved in another system. For example, the system of a free particle will conserve momenta as there are no external fields, however if an E-M field is applied, momentum may no longer be conserved. But the crucial difference (and specially) about the Hamiltonian is that it corresponds to the energy of the system and obviously the Hamiltonian will commute with itself. So energy is always conserved in any system.

Lets consider the momentum with a general Hamiltonian:

$$\begin{aligned} [\hat{\mathbb{H}}, \hat{p}] \psi &= \left[\frac{\hat{p}^2}{2m} + \hat{V}, \hat{p} \right] \psi \\ &= \left[\frac{\hat{p}^2}{2m}, \hat{p} \right] \psi + [\hat{V}, \hat{p}] \psi \end{aligned} \quad (4.18)$$

\hat{p}^2 will always commute with p (infact p^n will always commute with p), therefore the only non-zero term is:

$$[\hat{\mathbb{H}}, \hat{p}] \psi = [\hat{V}, \hat{p}] \psi \quad (4.19)$$

The L.H.S is:

$$\begin{aligned} \left[\hat{V}, -i\hbar \frac{\partial}{\partial x} \right] \psi &= \left[-i\hbar \hat{V} \frac{\partial}{\partial x} - i\hbar \frac{\partial V(x)}{\partial x} \right] \psi \\ &= -i\hat{V}\hbar \frac{\partial \psi}{\partial x} + i\hbar \frac{\partial V(x)}{\partial x} \psi + i\hbar V \frac{\partial \psi}{\partial x} \\ &= i\hbar \frac{\partial V(x)}{\partial x} \end{aligned} \quad (4.20)$$

Therefore:

$$[\hat{\mathbb{H}}, \hat{p}] = i\hbar \frac{\partial V(x)}{\partial x} \quad (4.21)$$

which is not zero in general and perfectly illustrates the point that was made before that the momentum may not be conserved for all systems. Here one learns a little bit more about it. A system which has a potential which is not explicitly a function of position, will conserve momentum, i.e constant electromagnetic fields will conserve momentum, but a changing field will not.

Conceptually this agrees with Newtonian physics. Newton's second law may be written as:

$$-\nabla V(x) = m\ddot{x} = \dot{p} \quad (4.22)$$

So a potential that is changing from place to place will change the momentum, say of a particle traveling in its vicinity by inducing a force. However, if there is no change in the potential, then there will be no force and the momentum will be the same at all times. This is a conserved quantity.

In fact Newton's second law comes out explicitly:

$$\begin{aligned}
\frac{d}{dt}\langle p \rangle &= \frac{d}{dt}\langle \psi | p | \psi \rangle \\
&= \frac{i}{\hbar} \langle \psi | [\hat{H}, \hat{p}] | \psi \rangle \\
&= \frac{i}{\hbar} (i\hbar) \langle \psi | \frac{\partial V(x)}{\partial x} | \psi \rangle \\
&= -\langle \frac{\partial V(x)}{\partial x} \rangle
\end{aligned} \tag{4.23}$$

So on *average* QM is the same as CM. No lets check weather the position is conserved. Intuitively one can easily think of a (sufficient) condition for the conservation of position (not talking relativistically, hence ignoring the effect of moving reference frames); the particle must have any velocity. Lets see if the equations predict this result aswell:

$$\frac{d}{dt}\langle \psi | x | \psi \rangle = \frac{i}{\hbar} \langle \psi | [\hat{H}, \hat{x}] | \psi \rangle \tag{4.24}$$

Compute the commutator:

$$\begin{aligned}
[\hat{H}, \hat{x}] | \psi \rangle &= \left[\frac{\hat{p}^2}{2m} + \hat{V}, \hat{x} \right] | \psi \rangle \\
&= \left[\frac{\hat{p}^2}{2m}, \hat{x} \right] \psi + [\hat{V}(x), \hat{x}] \psi \\
&= \left[\frac{\hat{p}^2}{2m}, \hat{x} \right] \psi \\
&= \frac{\hat{p}^2}{2m} \hat{x} \psi - \frac{\hat{x} \hat{p}^2}{2m} \psi \\
&= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} (\hat{x} \psi) + \frac{x \hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi \\
&= -\frac{\hbar^2}{2m} \frac{\partial}{\partial x} (\psi + x \psi') + \frac{\hat{x} \hbar^2}{2m} \psi'' \\
&= -\frac{\hbar^2}{2m} (\psi' + x \psi'' + \psi') + \frac{x \hbar^2}{2m} \psi'' \\
&= -\frac{\hbar^2}{m} \frac{\partial \psi}{\partial x} \\
&= -i\hbar \frac{\hat{p}}{m}
\end{aligned} \tag{4.25}$$

Therefore:

$$[\hat{H}, \hat{x}] = -i\hbar \frac{p}{m} \tag{4.26}$$

Therefore:

$$\begin{aligned}
\frac{d\langle x \rangle}{dt} &= \frac{i}{\hbar} \frac{d}{dt} \langle \psi | i\hbar \frac{\hat{p}}{m} | \psi \rangle \\
&= \frac{\langle p \rangle}{m}
\end{aligned} \tag{4.27}$$

Which is exactly what was expected.

Note that we have just shown that the classical equations of motion are obeyed on average in QM. So far, only the expectation values of quantities have been taken into consideration, regarding the commutation relation in Ehrenfests theorem. However now one would like to know whether the commutation relation:

$$\left[\hat{H}, \hat{Q} \right] = 0 \quad (4.28)$$

has any consequences for individual measurements. Consider again the Hamiltonian operator and its eigenvalue equation:

$$\hat{H}\phi_n = E_n\phi_n \quad (4.29)$$

This means that if:

$$\psi(x, t) = e^{-iE_n \frac{t}{\hbar}} \phi_n(x) \quad (4.30)$$

(where $\phi_n(x)$ is not a superposition state) then anytime a measurement is made on the system, the observed value will be E_n . Now suppose the same functions are also eigenfunctions of another operator \hat{Q} :

$$\hat{Q}\phi_n = q_n\phi_n \quad (4.31)$$

This just means that as long as ϕ_n is not a superposition state, every time a measurement is made via the \hat{Q} operator, the result will always be q_n . To see the condition this imposes on both the operators, consider the eigenvalue equation of \hat{H} again:

$$\hat{H}\phi_n = E_n\phi_n \quad (4.32)$$

act on both sides with \hat{Q} :

$$\begin{aligned} \hat{Q}\hat{H}\phi_n &= E_n\hat{Q}\phi_n \\ &= E_nq_n\phi_n \\ &= q_nE_n\phi_n \end{aligned} \quad (4.33)$$

Now start with the eigenvalue equation for \hat{Q} and act on it with \hat{H} :

$$\hat{H}\hat{Q}\phi_n = q_nE_n\phi_n \quad (4.34)$$

which are the same therefore:

$$\hat{H}\hat{Q}\phi_n = \hat{Q}\hat{H}\phi_n \quad (4.35)$$

This just tells us that the operator \hat{Q} must commute with the Hamiltonian for them to have the same eigenvectors. This means that it is possible for a particle to be in a state of definite energy (stationary state) in which the value of the observable \hat{Q} is also definite. This whole derivation was done in terms of the Hamiltonian operator and the energy eigenvalues, however notice that there is nothing specific used that is characteristic of the Hamiltonian. In fact this condition of $\left[\hat{H}, \hat{Q} \right] = 0$ holds for any two operators that have the same eigenfunctions.

The obvious question to ask next is what if $\psi(x, t)$ is not an eigenstate. Suppose it is a superposition state of the form:

$$\psi(x, t) = a_1\phi_1(x)e^{-iE_1 \frac{t}{\hbar}} + a_2\phi_2(x)e^{-iE_2 \frac{t}{\hbar}} \quad (4.36)$$

where ϕ_1 and ϕ_2 are both individually eigenstates, and the requirement for the probabilities to add up means:

$$|a_1|^2 + |a_2|^2 = 1 \quad (4.37)$$

therefore:

$$Prob(E = E_1) = |a_1|^2 \quad (4.38)$$

$$Prob(E = E_2) = |a_2|^2 \quad (4.39)$$

Now lets compute the expectation value of \hat{Q} :

$$\begin{aligned}
\langle Q \rangle &= \int \psi^* \hat{Q} \psi dx \\
&= \int \left(a_1^* \phi_1^*(x) e^{iE_1 \frac{t}{\hbar}} + a_2^* \phi_2^*(x) e^{iE_2 \frac{t}{\hbar}} \right) \hat{Q} \left(a_1 \phi_1(x) e^{-iE_1 \frac{t}{\hbar}} + a_2 \phi_2(x) e^{-iE_2 \frac{t}{\hbar}} \right) dx \\
&= \int \left(a_1^* \phi_1^*(x) e^{iE_1 \frac{t}{\hbar}} + a_2^* \phi_2^*(x) e^{iE_2 \frac{t}{\hbar}} \right) \left(a_2 a_1 \phi_1(x) e^{-iE_1 \frac{t}{\hbar}} + a_2 q_2 \phi_2(x) e^{-iE_2 \frac{t}{\hbar}} \right) dx \\
&= \int |a_1|^2 |\phi_1(x)|^2 q_1 + a_1^* a_2 \phi_1^*(x) \phi_2(x) e^{i(E_1 - E_2) \frac{t}{\hbar}} q_2 \\
&\quad + q_1 a_2^* a_1 \phi_2^*(x) \phi_1(x) e^{i(E_2 - E_1) \frac{t}{\hbar}} + q_2 |a_2|^2 |\phi_2(x)|^2 dx
\end{aligned} \tag{4.40}$$

Using the ortho-normality of the wavefunctions, the final result:

$$\langle Q \rangle = q_1 |a_1|^2 + q_2 |a_2|^2 \tag{4.41}$$

This just means that when a measurement is made on the state for the observable \hat{Q} , the outcome will be q_1 with probability $|a_1|^2$ and q_2 with probability $|a_2|^2$. Thus if a measurement of both \hat{H} and \hat{Q} , the result is:

$$E_1, q_1 \text{ with probability } = |a_1|^2 \tag{4.42}$$

$$E_2, q_2 \text{ with probability } = |a_2|^2 \tag{4.43}$$

The fundamental point is that if two operators commute, then the physical observables they correspond to will have precise values and will be measurable simultaneously. Next, lets examine what happens when two operators do not commute. Start with the example that was seen previously, of the infinite square well. Consider the Hamiltonian and the momentum to be the two operators in question. It was shown in the previous section that:

$$[\hat{H}, \hat{p}] = i\hbar \frac{\partial V}{\partial x} \tag{4.44}$$

the potential has the form given in Fig 1. This means that in general $\frac{\partial V}{\partial x}$ is not zero and hence the two operators do not commute. When discussing the infinite square well problem, it was seen that if the particle had a definite energy:

$$\psi(x, t) = e^{-iE_n \frac{t}{\hbar}} \phi_n(x) \tag{4.45}$$

then ψ is a superposition of states with different momenta. This proves the previous premise that once cannot know both the energy and momentum at the same time as the operators do not commute. This is a general statement in QM; if A and B are physical observables with Hermitian operators \hat{A} and \hat{B} with:

$$[\hat{A}, \hat{B}] \neq 0 \tag{4.46}$$

then it is not possible to simultaneously know the values of A and B .

4. Complete set of Quantum numbers

Suppose there are two operators \hat{Q} and R , that satisfy:

$$[\hat{H}, \hat{Q}] = [\hat{H}, \hat{R}] = 0 \tag{4.47}$$

then:

$$\frac{d}{dt} \langle Q \rangle = \frac{d}{dt} \langle R \rangle = 0 \tag{4.48}$$

\hat{Q} and \hat{R} are both conserved. However if:

$$[\hat{Q}, \hat{R}] \neq 0 \quad (4.49)$$

then it is not possible to make a definite measurement of both the quantities simultaneously. But if they do commute, then it is always possible to find simultaneous eigenfunctions of \hat{Q} and \hat{R} and \hat{H} and they all can be measured precisely and simultaneously.

In this case the wavefunction is:

$$\psi(x, t) = e^{-iE_n \frac{t}{\hbar}} \phi_n(x) \quad (4.50)$$

which has definite energy, E_n , definite Q , q_n , definite R , r_n . E_n, q_n, r_n are all quantum numbers of the state ψ . The operators \hat{Q} and \hat{P} are called compatible as they commute with each other and the Hamiltonian. In the case that $[\hat{Q}, \hat{R}] \neq 0$, \hat{Q} and \hat{R} are called incompatible and it is not possible to find a state, in which all 3 of the physical quantities are simultaneously measurable. Instead one can find a state in which either E and q_n are measured or E and r_n are measured.

As an example, consider the momentum and position operators in general:

$$[\hat{p}, \hat{x}] = i\hbar \quad (4.51)$$

therefore it is not possible to find a state in which both p and x have definite values. It is said that E forms a complete set of Quantum numbers if the maximal number of simultaneous eigenvalues are specified.

5. Uncertainty principle

Now we want to know what happens in general when a measurement is made on a general state that is a superposition itself. First consider the energy superposition:

$$\psi(x, t) = a_1 \phi_1 e^{-iE_1 \frac{t}{\hbar}} + a_2 \phi_2 e^{-iE_2 \frac{t}{\hbar}} \quad (4.52)$$

Consider a measurement being made on the energy at time t_0 . The possible measured values are E_1 or E_2 with probabilities $|a_1|^2$ and $|a_2|^2$ respectively. Suppose the result is E_1 , from the postulate of the collapse of the wavefunction, we know that the system will be in the state:

$$\psi(x, t) = \phi_1(x) e^{-iE_1 \frac{t}{\hbar}} \quad (4.53)$$

at time $t = t_0 + \delta t$. Every experiment ever performed leads to results that are consistent with the 'collapse' postulate, however the true interpretation of what exactly happens at this point is still any body's guess. Suppose a series of measurements is to be made in an experiment. Consider the experimental set-up to be one that reproduces the infinite square well system (of course it is not possible to have a truly 'infinite' potential, however very large potentials can be sufficient as an approximation to the infinite square well). The system will have the states of the form:

$$\psi(x, t) = \sum_n a_n \phi_n(x) e^{-iE_n \frac{t}{\hbar}} \quad (4.54)$$

$$\phi_n = \frac{\sqrt{2}}{a} \sin\left(\frac{n\pi x}{a}\right) \quad (4.55)$$

the energy spectrum of the system has the form:

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2} \quad (4.56)$$

Now measure the energy of the system. Suppose the measured value is E_1 ; the wavefunction immediately after is:

$$\psi(x, t) = \phi_1(x) e^{-iE_1 \frac{t}{\hbar}} \quad (4.57)$$

Now measure the momentum. Since the momentum eigenstates are not the same as the energy eigenstates, one must rewrite the energy eigenstates given in Eq 4.57 as:

$$\begin{aligned}\psi(x, t) &= e^{-iE_1 \frac{t}{\hbar}} \sqrt{\frac{2}{a}} \frac{1}{2i} \left(e^{\frac{i\pi\hbar x}{\hbar a}} + e^{-\frac{i\pi\hbar x}{\hbar a}} \right) \\ &= e^{-iE_1 \frac{t}{\hbar}} \sqrt{\frac{2}{a}} \frac{1}{2i} \left(e^{ip_+ \frac{x}{\hbar}} + e^{-ip_- \frac{x}{\hbar}} \right)\end{aligned}\quad (4.58)$$

This is now a superposition of two momentum states. After the measurement, the system will collapse into either the state with p_+ or p_- . Consider it collapsing to the p_+ state:

$$\psi(x, t) = e^{-iE_1 \frac{t}{\hbar}} \frac{1}{\sqrt{a}} e^{ip_+ \frac{x}{\hbar}} \quad (4.59)$$

Finally, consider making a measurement on the energy again. Once more the state needs to be written in terms of energy eigenstates, i.e get the exponential s into the sine function. The exponential can be expanded using Euler's identity:

$$\psi(x, t) = \frac{e^{-iE_1 \frac{t}{\hbar}}}{\sqrt{a}} \left(\cos\left(\frac{\pi x}{a}\right) + i \sin\left(\frac{\pi x}{a}\right) \right) \quad (4.60)$$

The sine term is already an energy eigenstate, but the cosine term must be turned into a sine function and this can be done using Fourier series, expand the cosine term as:

$$\frac{1}{\sqrt{a}} \cos\left(\frac{\pi x}{a}\right) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} a_n \sin\left(\frac{n\pi x}{a}\right) \quad (4.61)$$

Note that the expansion basis is the earlier eigenfunctions. The coefficients are given by:

$$a_n = \frac{1}{\sqrt{a}} \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \cos\left(\frac{\pi x}{a}\right) dx \quad (4.62)$$

These coefficients are 0 if n is odd and $\frac{2\sqrt{2}n}{\pi(n^2-1)}$ if n is even. Intuitively, this makes sense as the cosine function is an even function, therefore the expansion should only have even terms in it. Therefore the exponential term becomes:

$$\frac{e^{i\pi \frac{x}{a}}}{\sqrt{a}} = \frac{i}{\sqrt{2}} \phi_1(x) + \sum_{n=even} \frac{2\sqrt{2}n}{\pi(n^2-1)} \phi_n(x) \quad (4.63)$$

Therefore the overall wavefunction is:

$$\psi(x, t) = e^{-iE_1 \frac{t}{\hbar}} \left(\frac{i}{\sqrt{2}} \phi_1(x) + \sum_{n=even} \frac{2\sqrt{2}n}{\pi(n^2-1)} \phi_n(x) \right) \quad (4.64)$$

So the observed value for the energy are:

$$\begin{array}{lll} E_1 & \text{with probability} & \frac{1}{2} \\ E_2 & \text{with probability} & \frac{32}{9\pi^2} \\ E_4 & \text{with probability} & \frac{128}{225\pi^2} \\ \vdots & \vdots & \vdots \\ E_n & \text{with probability} & \frac{8n^2}{(n^2-1)^2\pi^2} \end{array} \quad (4.65)$$

Thus even though the system started off in an energy eigenstate, by a making a measurement of momentum (and from the fact that the momentum operator does not commute with the Hamiltonian) the particle is now in a state of indefinite energy, i.e all information about the energy is lost.

This, I believe, is one of the most mysterious aspects of quantum mechanics. With the collapse of the state postulate interpreting this phenomena is not easy. What is being observed is that a state with definite energy, is disturbed to such an extent by the measurement of the momentum, that the energy spectrum becomes infinite!(even though the individual values of the energy are finite). This is suggesting that the role of an observation is absolutely key and of fundamental importance in QM, and this same suggestion also support for the collapse of the state interpretation.

It is these considerations that lead Heisenberg to his famous uncertainty principle. In fact the uncertainty principle is not 'put in by hand' into the theory of QM, i.e it is not an axiom of the theory. It can be derived by the already stated axioms. In general, the uncertainty in a measured quantity q , is defined as:

$$\langle \Delta q \rangle^2 \equiv \langle q^2 \rangle - \langle q \rangle^2 \quad (4.66)$$

Notice again that these quantities are all expectation values. This means, for this equation to be useful, 'sufficient' amount of data has to be accumulated. Δq is just zero for a single measurement. Heisenberg's uncertainty principle considers x and p and states:

$$\Delta x \Delta p \geq \frac{\hbar}{a} \quad (4.67)$$

There is an analogous relation for energy and time aswell. The important thing to realise is that this principle is intrinsic to theory of Quantum mechanics and is not an artifact of imprecise measurement. It says that if the position of a particle is known to a precision of Δx , then the *maximum* precision one could know its momentum is:

$$\Delta p = \frac{\hbar}{2\Delta x} \quad (4.68)$$

Suppose one has Gaussian wavefunction:

$$\phi(x) = \frac{1}{\sqrt{a\pi}^{\frac{1}{4}}} e^{-\frac{x^2}{2a^2}} \quad (4.69)$$

The expectation value of x in this state is:

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} x |\phi(x)|^2 dx \\ &= \frac{1}{\sqrt{\pi}a} \int_{-\infty}^{\infty} x e^{-\frac{x^2}{a^2}} dx \end{aligned} \quad (4.70)$$

Notice that the function being integrated is an odd function, therefore integrating it over an even limit, like ∞ to $-\infty$ will give 0:

$$\langle x \rangle = 0 \quad (4.71)$$

Now compute:

$$\langle x^2 \rangle = \frac{1}{a\sqrt{\pi}} \int_{-\infty}^{\infty} x^2 e^{-\frac{x^2}{a^2}} dx = \frac{a^2}{2} \quad (4.72)$$

Substitute the results for the uncertainty in x :

$$\Delta x = [\langle x^2 \rangle - \langle x \rangle^2]^{\frac{1}{2}} = \frac{a}{\sqrt{2}} \quad (4.73)$$

Do the same for momentum:

$$\langle p \rangle = -\frac{i\hbar}{a\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{2a^2}} \frac{\partial}{\partial x} e^{-\frac{x^2}{2a^2}} dx = 0 \quad (4.74)$$

$$\begin{aligned} \langle p^2 \rangle &= -\frac{\hbar^2}{a\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{2a^2}} \frac{\partial^2}{\partial x^2} e^{-\frac{x^2}{2a^2}} dx \\ &= -\frac{\hbar^2}{a\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{2a^2}} \left(\frac{x^2}{a^4} - \frac{1}{a^2} \right) dx \\ &= \frac{\hbar^2}{2a^2} \end{aligned} \quad (4.75)$$

Therefore:

$$\begin{aligned} \Delta p &= [\langle p^2 \rangle - \langle p \rangle^2]^{\frac{1}{2}} \\ &= \frac{\hbar}{\sqrt{2}a} \end{aligned} \quad (4.76)$$

Multiply Δp with Δx :

$$\Delta p \Delta x = \frac{\hbar}{a\sqrt{2}} \frac{a}{\sqrt{2}} = \frac{\hbar}{2} \quad (4.77)$$

This is exactly at the boundary of the Heisenberg uncertainty principle, this means Gaussian wavefunctions give the possible overall uncertainty (i.e least possible $\Delta x \Delta p$). Since $\Delta p \neq 0$, the momentum of the particle will have some distribution of values. We know the distribution of the position values, they are simply represented by the wavefunctions of the system:

$$\phi(x) = \frac{1}{\sqrt{a\pi^{\frac{1}{4}}}} e^{-\frac{x^2}{2a^2}} \quad (4.78)$$

In Dirac notation this is $\langle x|\phi \rangle$, the amplitude for particles in state ϕ to be in position x . The question being asked now is; what about the amplitude for the particle in state ϕ to have momentum p :

$$\langle p|\phi \rangle \quad (4.79)$$

To convert from x basis to a p basis, one simply has to take the Fourier transform of the x wavefunction:

$$\tilde{\phi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx e^{\frac{ipx}{\hbar}} \phi(x) \quad (4.80)$$

Recall in Dirac notation, we could use the identity matrix in the x basis to find $\langle p|\phi \rangle$:

$$\langle p|\phi \rangle = \int_{-\infty}^{\infty} \langle p|x \rangle \langle x|\phi \rangle \quad (4.81)$$

where $\langle p|x \rangle = \langle x|p \rangle^* = \frac{e^{\frac{ipx}{\hbar}}}{\sqrt{2\pi\hbar}}$. Now the integral from the Dirac relation becomes:

$$\langle p|\phi \rangle = \int_{-\infty}^{\infty} dx \frac{e^{\frac{ipx}{\hbar}}}{\sqrt{2\pi\hbar}} \phi(x) \quad (4.82)$$

Which is the same as Eq 4.80 as expected, so lets do the integral:

$$\begin{aligned} \langle p|\phi \rangle &= \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{2\pi\hbar}} \frac{1}{\sqrt{a\pi^{\frac{1}{4}}}} e^{\frac{ipx}{\hbar}} e^{-\frac{x^2}{2a^2}} \\ &= \frac{1}{\sqrt{2\pi\hbar}} \sqrt{a\pi^{\frac{1}{4}}} \int_{-\infty}^{\infty} dx e^{\frac{ipx}{\hbar} - \frac{x^2}{2a^2}} \end{aligned} \quad (4.83)$$

Now one has to complete the square in the exponent:

$$\begin{aligned}\langle p|\phi\rangle &= \frac{1}{\sqrt{2\pi\hbar}}\sqrt{a\pi^{\frac{1}{4}}}\int_{-\infty}^{\infty} dx e^{-\frac{1}{2a^2}\left(\left(x-\frac{ip_0}{\hbar}\right)^2+\frac{p^2 a^4}{\hbar^2}\right)} \\ &= \sqrt{\frac{a}{\hbar\pi^{\frac{1}{2}}}}e^{-\frac{p^2 a^2}{2\hbar^2}}\end{aligned}\tag{4.84}$$

Which is just another Gaussian.

Simple Harmonic Oscillator

1. Introduction

When I was in high school, I used to wonder why we study the framework of a Simple Harmonic Oscillator. All the teachers would say that it is very important and comes up everywhere in physics. In fact, Sidney Coleman (an American theoretical physicist) once said:

The career of a young theoretical physicist consists of treating the harmonic oscillator in ever-increasing levels of abstraction.

But why is this? Consider any system in nature, the fact that a system is observed, means it will exist and this will be, I believe a crucial point in explaining the importance of the Harmonic oscillator. Most systems (that are interesting!) will involve at least two particles and particles can interact with each other via four forces; Gravity, Strong nuclear force, Weak nuclear force, Electro-magnetism.

Which of these forces is used will depend on the two particles themselves, however that is not important in this discussion. Suppose, one of the particles carries a charge $+q$ and the other carries a charge $-q$. This means that there will be a Coulomb force between the two particles of the form:

$$F \propto \frac{q^2}{r^2} \quad (5.1)$$

This form of force will obviously start increasing very rapidly as $r < 1$. Of course in reality, we know that there are other forces in nature that will stop the particles coming too close, however there is always a regime in which the becomes very large, without intervention from another force. If there really were no forces to stop this electro-magnetic attraction then the particles would end up coming closer and closer and one would get a singularity from the equation. To stop this happening, there always has to be a *restoring* force.

The mathematical nature of this force only really has one key property that it must satisfy; the force must oppose the attractive force. This has the effect of restoring the system back into a previous configuration and this is a key requirement for systems that are stable for long periods of time. This is of utmost importance for systems in nature, as a system that will be unstable i.e has runaway effects as described above, will not exist for long and therefore is less likely to be observed.

So now I have the answer of why Harmonic oscillators appear everywhere in nature. Now let's move on to the technical aspects of the Harmonic Oscillator in QM.

2. Framework of Harmonic Oscillator

The harmonic oscillator usually has a restoring force of the form:

$$F = -kx \quad (5.2)$$

the sign is a matter of notation, the important thing is that the sign must be opposite to the other force of the system. The force is give by:

$$F = -V \quad (5.3)$$

which in 1-D reduces to:

$$F = -\frac{\partial V}{\partial x} \quad (5.4)$$

Therefore equating the two forces gives:

$$\begin{aligned} -kx &= -\frac{\partial V}{\partial x} \\ V &= \frac{kx^2}{2} \end{aligned} \quad (5.5)$$

Using this potential one can construct the TISE for a SHO:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} + \frac{kx^2}{2} \phi = E\phi \quad (5.6)$$

it turns out that it is convenient to rewrite this equation in terms of a variable transformation defined by:

$$y = \alpha x \quad (5.7)$$

Computing the transformations from $x \rightarrow y$:

$$\begin{aligned} \frac{\partial}{\partial x} &= \frac{\partial}{\partial y} \frac{\partial y}{\partial x} = \alpha \frac{\partial}{\partial y} \\ \frac{\partial^2}{\partial x^2} &= \alpha^2 \frac{\partial^2}{\partial y^2} \\ x^2 &= \frac{y^2}{\alpha} \end{aligned} \quad (5.8)$$

So the TISE becomes:

$$-\frac{\hbar^2 \alpha^2}{2m} \frac{\partial^2 \phi}{\partial y^2} + \frac{1}{2} \frac{k}{\alpha^2} y^2 \phi = E\phi \quad (5.9)$$

The idea now is that since this is an energy eigenvalue equation, the terms on both sides must be energies. This gives a motivation for equating the coefficients of the K.E and P.E to sure the dimensions are correct. This gives a condition for α :

$$\begin{aligned} \frac{\hbar^2 \alpha^2}{2m} &= \frac{1}{2} \frac{k}{\alpha^2} \\ \alpha^2 &= \frac{\sqrt{mk}}{\hbar} \end{aligned} \quad (5.10)$$

Now we define $\omega = \sqrt{\frac{k}{m}}$, which is the same as the classical angular frequency, this means α can be rewritten as:

$$\alpha = \sqrt{\frac{m\omega}{\hbar}} \quad (5.11)$$

Substituting into the TISE gives:

$$\frac{\hbar\omega}{2} \left(-\frac{d^2 \phi}{dy^2} + y^2 \phi \right) = E\phi \quad (5.12)$$

Finally to make this differential equation a dimensionless equation, one further substitution is required:

$$\epsilon \equiv \frac{E}{\frac{\hbar\omega}{2}} \quad (5.13)$$

Substituting this into Eq 5.12:

$$-\frac{d^2\phi}{dy^2} + y^2\phi = \epsilon\phi \quad (5.14)$$

Just looking at this equation, it is obvious that the solution will be in the form of a Gaussian, so try the solution:

$$\phi_0 = e^{-\frac{y^2}{2}} \quad (5.15)$$

Substitute into Eq 5.14:

$$\begin{aligned} -\frac{d}{dy} \left(-ye^{-\frac{y^2}{2}} \right) + y^2\phi &= \epsilon\phi \\ -\left(-e^{-\frac{y^2}{2}} + y^2e^{-\frac{y^2}{2}} \right) + y^2\phi &= \epsilon\phi \\ e^{-\frac{y^2}{2}} - y^2e^{-\frac{y^2}{2}} + y^2e^{-\frac{y^2}{2}} &= \epsilon e^{-\frac{y^2}{2}} \end{aligned} \quad (5.16)$$

This is a solution if $\epsilon = 1$ and from Eq 5.13:

$$E = \frac{\hbar\omega}{2} \quad (5.17)$$

Which is the ground state energy of the harmonic oscillator (Note that this is not zero). The obvious next question is, what are the other eigenstates. It turns out that there are two ways of finding them. One way is to try a solution of the form:

$$\phi = H(y)e^{-\frac{y^2}{2}} \quad (5.18)$$

where $H(y)$ is a polynomial in y . Substituting this into the TISE:

$$\begin{aligned} -\frac{d}{dy} \left(H'(y)e^{-\frac{y^2}{2}} - yH(y)e^{-\frac{y^2}{2}} \right) + y^2H(y)e^{-\frac{y^2}{2}} &= \epsilon H(y)e^{-\frac{y^2}{2}} \\ -\left(H''(y)e^{-\frac{y^2}{2}} - H'(y)ye^{-\frac{y^2}{2}} - \left(H(y)e^{-\frac{y^2}{2}} + yH'(y)e^{-\frac{y^2}{2}} + y^2H(y)e^{-\frac{y^2}{2}} \right) \right) + y^2H(y)e^{-\frac{y^2}{2}} &= \epsilon H(y)e^{-\frac{y^2}{2}} \\ -H''(y)e^{-\frac{y^2}{2}} + H'(y)ye^{-\frac{y^2}{2}} + H(y)e^{-\frac{y^2}{2}} + yH'(y)e^{-\frac{y^2}{2}} - y^2H(y)e^{-\frac{y^2}{2}} + y^2H(y)e^{-\frac{y^2}{2}} &= \epsilon H(y)e^{-\frac{y^2}{2}} \\ -H''(y)e^{-\frac{y^2}{2}} + 2yH'(y)e^{-\frac{y^2}{2}} + H(y)e^{-\frac{y^2}{2}} &= \epsilon H(y)e^{-\frac{y^2}{2}} \\ -H''(y) + 2yH'(y) + H(y) - \epsilon H(y) &= 0 \\ H''(y) - 2yH'(y) + H(y)(\epsilon - 1) &= 0 \end{aligned} \quad (5.19)$$

This is called *Hermite's* equation and can be solved by using the Frobenius method:

$$\begin{aligned} H(y) &= \sum_n a_n y^n \\ H'(y) &= \sum_n a_n n y^{n-1} \\ H''(y) &= \sum_n n(n-1) y^{n-2} \end{aligned} \quad (5.20)$$

Substitute these into Eq 5.19:

$$\sum_n a_n n(n-1)y^{n-2} - 2 \sum_n a_n n y^n + (\epsilon - 1) \sum_n a_n y^n = 0 \quad (5.21)$$

Equating the coefficients of the same powers of y :

$$\sum_n a_n n(n-1) = 0 \quad (5.22)$$

Since this must hold for all n :

$$n = 1 \text{ or } 0 \quad (5.23)$$

$n = 0$ is just the trivial solution. The coefficients for the power of n :

$$\begin{aligned} -2 \sum_n a_n n + (\epsilon - 1) \sum_n a_n &= 0 \\ -2a_n n + (\epsilon - 1)a_n &= 0 \end{aligned} \quad (5.24)$$

Therefore:

$$\epsilon = 2n + 1 \quad (5.25)$$

Even though this solution gives the correct eigenvalues of energy ϵ , it does not provide the full spectrum of solutions to the Hermite equation. Instead we have to try the more general solution:

$$H(y) = \sum_{n=0}^{\infty} a_n y^{n+\alpha} \quad (5.26)$$

The difference between this and the previous guess is that now the powers of y can be non-integers or even negative numbers. Once again, let's compute the ingredients for Hermite's equation:

$$\begin{aligned} H'(y) &= \sum_{n=0}^{\infty} a_n (n+\alpha) y^{n+\alpha-1} \\ H''(y) &= \sum_{n=0}^{\infty} a_n (n+\alpha)(n+\alpha-1) y^{n+\alpha-2} \end{aligned} \quad (5.27)$$

Change the variables in $H''(y)$ by defining:

$$m = n - 2 \quad (5.28)$$

$$\begin{aligned} H''(y) &= \sum_{m=0}^{\infty} a_{m+2} (m+2\alpha) (m+\alpha+1) y^m \\ &= \sum_{n=0}^{\infty} a_{n+2} (n+\alpha+2)(n+\alpha+1) y^n \end{aligned} \quad (5.29)$$

Substituting these into Hermite's equation:

$$a_0 \alpha(\alpha-1) y^{\alpha-2} - 2a_1 \alpha(\alpha+1) y^{\alpha-1} + \sum_{n=0}^{\infty} [a_{n+2} (n+\alpha+2)(n+\alpha+1) - 2a_n (n+\alpha) + (\epsilon-1)a_n] y^{n+\alpha} = 0 \quad (5.30)$$

The term that corresponds to the lowest power of y (in this case $n = -2$) is called the *indicial* equation. Equating all the powers of y to zero:

$$\begin{aligned}
a_0\alpha(\alpha - 1) &= 0 \\
2a_1\alpha(\alpha + 1) &= 0 \\
a_{n+2}(n + \alpha + 2)(n + \alpha + 1) - 2a_n(n + \alpha) + (\epsilon - 1)a_n &= 0
\end{aligned} \tag{5.31}$$

The indicial equation gives two possible solutions for α , either 0 or 1. Now one has to choose a value to proceed with the calculation. If $\alpha = 0$, then a_1 can be non-zero in general, if $\alpha = 1$, then a_1 must be zero. Either way a_0 is not zero in general, so let's proceed with $\alpha = 0$. This now gives the recurrence relation from Eq 5.31:

$$\begin{aligned}
a_{n+2}(n + 2)(n + 1) - 2a_0n + (\epsilon - 1)a_n &= 0 \\
a_{n+2} &= \frac{2a_0n - (\epsilon - 1)a_n}{(n + 2)(n + 1)} \\
&= a_n \frac{(2n - (\epsilon - 1))}{(n + 2)(n + 1)}
\end{aligned} \tag{5.32}$$

Because the recurrence relation connects the coefficients a_{n+2} and a_n , one obtains two independent series, one with even numbered and one with odd numbered coefficients, and the full series is the sum of the two. Since these series are to be part of quantum wavefunctions, they have to be normalisable, therefore the next step is to investigate under what circumstances the series converges. To do this the odd numbered and even numbered series can be considered separately.

The ratio of neighboring coefficients for the even numbered series is:

$$\frac{a_{n+2}}{a_n} = \frac{2n + 1 - \epsilon}{(n + 1)(n + 2)} \tag{5.33}$$

For large n :

$$\frac{a_{n+2}}{a_n} \approx \frac{2}{n} \approx 0 \tag{5.34}$$

And of course it is the same for the odd-numbered series, so the coefficients converge which is a good thing. Now the y component of the series has to be checked; first expand e^{y^2} using the Taylor series:

$$e^{y^2} = 1 + y^2 + \frac{y^4}{2!} + \frac{y^6}{3!} + \dots = \sum_{n=0,2,4,\dots}^{\infty} \frac{y^n}{\left(\frac{n}{2}\right)!} \tag{5.35}$$

which is equivalently written as:

$$e^{y^2} = \sum_{n=0,2,4,\dots}^{\infty} c_n y^n \tag{5.36}$$

with $c_n = \left(\frac{n}{2}\right)!$, once again for large n , the coefficient ratio goes as:

$$\frac{c_{n+2}}{c_n} \approx \frac{2}{n} \tag{5.37}$$

This tells us that for large y the behavior of the series solution is like e^{y^2} , i.e.:

$$\phi(y) = H(y)e^{-\frac{y^2}{2}} \approx e^{\frac{y^2}{2}} \quad \text{for large } y \tag{5.38}$$

This means that the wavefunction $\phi(y)$ will diverge for large y and hence it will not be normalisable. The only way to make the wavefunction go to zero is if the series does not get summed over to infinity. This is where the clever part comes in, look again at Eq 5.32, it is easy to see that the coefficients will terminate if:

$$\epsilon = 2n + 1 \quad (5.39)$$

If this holds, then all terms higher than n are zero and this makes $H(y)$ a polynomial of order n . Since the overall wavefunction is a product of the polynomial and the exponential term, the wavefunction goes to zero for $y \rightarrow \pm\infty$ and this is a normalisable wavefunction. Using the relation between ϵ and energy, E :

$$E = \left(n + \frac{1}{2}\right)\hbar\omega \quad (5.40)$$

where n can take on any integer values. These set of polynomials are called the *Hermite* polynomials of order n , written as $H(y)$. They are defined by choosing the constants a_0 and a_1 so that:

$$H_0(y) = 1 \quad (5.41)$$

$$H_1(y) = 2y \quad (5.42)$$

One can show that application of the recurrence relation is equivalent to:

$$H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n} e^{-y^2} \quad (5.43)$$

The overall normalised wavefunction of the Harmonic oscillator takes the form:

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!} (\pi a^2)^{\frac{1}{4}}} H_n\left(\frac{x}{a}\right) e^{-\frac{x^2}{2a^2}} \quad (5.44)$$

3. Operator Method

A much more instructive method that makes calculations much easier is the operator method. In fact this method extends into Quantum Field Theory aswell. In the previous section, it was shown that the Hamiltonian operator, in the y coordinates can be written as:

$$H = \frac{\hbar\omega}{2} \left(-\frac{d^2}{dy^2} + y^2 \right) \quad (5.45)$$

The idea is to now define operators of the form:

$$a_+ = \frac{1}{\sqrt{2}} \left(-\frac{d}{dy} + y \right) \quad (5.46)$$

$$a_- = \frac{1}{\sqrt{2}} \left(\frac{d}{dy} + y \right) \quad (5.47)$$

These are called the *raising* and *lowering* operators respectively (sometimes also called *ladder operators*). Lets check the commutation relation between these operators:

$$[a_-, a_+] = \underbrace{a_- a_+}_{1} f(y) - \underbrace{a_+ a_-}_{2} f(y) \quad (5.48)$$

First deal with term 1:

$$a_+ f(y) = \frac{1}{2} \left(-\frac{d^2 f}{dy^2} + y^2 f - f \right) \quad (5.49)$$

Term 2:

$$a_+ a_- f(y) = \frac{1}{2} \left(-\frac{d^2 f}{dy^2} + y^2 f + f \right) \quad (5.50)$$

Therefore:

$$\begin{aligned}
[a_-, a_+]f(y) &= \frac{1}{2} \left(-\frac{d^2 f}{dy^2} + y^2 f + f + \frac{d^2 f}{dy^2} - y^2 f + f \right) \\
&= \frac{1}{2} (2f(y))
\end{aligned} \tag{5.51}$$

deleting the function $f(y)$ from both sides:

$$[a_-, a_+] = 1 \tag{5.52}$$

Now the Hamiltonian can be written in terms of these operators:

$$H = \hbar\omega \left(a_+ a_- + \frac{1}{2} \right) \tag{5.53}$$

Therefore the TISE is:

$$\hbar\omega \left(a_+ a_- + \frac{1}{2} \right) \phi = E\phi \tag{5.54}$$

Substitute $\epsilon = \frac{E}{\hbar\omega}$:

$$(2a_+ a_- + 1)\phi = \epsilon\phi \tag{5.55}$$

Lets see how the ladder operators act on the eigenstates:

$$\begin{aligned}
a_- \phi_0 &= \frac{1}{\sqrt{2}} \left(\frac{d}{dy} + y \right) e^{-\frac{y^2}{2}} \\
&= \frac{1}{\sqrt{2}} \left(-ye^{-\frac{y^2}{2}} + ye^{-\frac{y^2}{2}} \right) \\
&= 0
\end{aligned} \tag{5.56}$$

Since ϕ_0 is taken to be the ground state wavefunction, we see that the a_- operator reduced the ground state wavefunction to 0, hence its name *annihilation* operator. Using this result one can check that the expansion for the Hamiltonian in terms of the ladder operators is correct:

$$\begin{aligned}
(2a_+ a_- + 1)\phi_0 &= 2a_+ a_- \phi_0 + \phi_0 \\
&= \phi_0
\end{aligned} \tag{5.57}$$

This means that $\epsilon_0 = 1$, which is the same as before and therefore it is confirmation that the Hamiltonian is accurate. In fact the relation of the ladder operators on the eigenstates can be generalised even further. Act on the TISE with the raising operator:

$$a_+(2a_+ a_- + 1)\phi = \epsilon a_+ \phi \tag{5.58}$$

Use the commutation relation:

$$a_- a_+ - a_+ a_- = 1 \tag{5.59}$$

Therefore:

$$\begin{aligned}
a_+(2a_- a_+ - 1)\phi &= \epsilon a_+ \phi \\
(2a_+ a_- a_+ - 1a_+)\phi &= \epsilon a_+ \phi \\
(2a_- a_+ + 1)a_+ \phi &= (\epsilon + 2)a_+ \phi \\
Ha_+ \phi &= (\epsilon + 2)a_+ \phi
\end{aligned} \tag{5.60}$$

This means that if ϕ has an eigenvalue ϵ , then $a_+ \phi$ has an eigenvalue $\epsilon + 2$. Following the same method one can apply the a_- operator to the TISE:

$$\begin{aligned}
a_-(2a_+a_- + 1)\phi &= \epsilon a_- \phi \\
(2a_-a_+ + 1)a_- \phi &= \epsilon a_- \phi \\
(2a_+a_- + 3)a_- \phi &= \epsilon a_- \phi \\
(2a_+a_+1)a_- \phi &= (\epsilon - 2)a_- \phi
\end{aligned} \tag{5.61}$$

This shows that if ϕ has an eigenvalue ϵ , then $a_- \phi$ has eigenvalue $\epsilon - 2$. There is no state with lower energy than ϕ_0 , therefore ϕ_0 is indeed the ground state with $\epsilon = 1$.

These results show the power of these operators. We can generate the entire energy spectrum by repeated application of a_+ and a_- operators, the spectrum has the following form:

$$\begin{aligned}
\epsilon_n &= 2n + 1\omega \\
E_n &= (n + \frac{1}{2})\hbar\omega \\
\phi_n &= \left(\frac{1}{\sqrt{2}} \left(-\frac{\partial}{\partial y} + y \right) \right)^n \phi_0
\end{aligned} \tag{5.62}$$

This is a complete solution for the Quantum Harmonic Oscillator, apart from the final normalisation of the eigenfunctions. The normalisation can be computed by the integral corresponding to $\langle \phi_0 | \phi_0 \rangle$:

$$\int_{-\infty}^{\infty} dx |\phi_0|^2 = \int_{-\infty}^{\infty} dx e^{-x^2 \alpha^2} = \frac{\pi^{\frac{1}{2}}}{\alpha} \tag{5.63}$$

Therefore the normalised wavefunction is:

$$\phi_0 = \sqrt{\frac{\alpha}{\pi^{\frac{1}{2}}}} e^{-x^2 \alpha^2} \tag{5.64}$$

Recall $\alpha^2 = \frac{\sqrt{mk}}{\hbar}$. Similarly one can normalise higher order wavefunctions (they will all come down to computing some form of Gaussian integrals). The other key property of wavefunctions is orthogonality. This comes naturally from the fact that they are eigenfunctions of Hermitian operators. Therefore the overall condition on wavefunctions is:

$$\langle \phi_n | \phi_m \rangle = \delta_{nm} \tag{5.65}$$

There are similarities between the SHO and the infinite square well. As was seen in the solutions formed by solving via the Frobenius method, the wavefunctions $\phi_n(x)$ are in an even-odd sequence like the infinite square well. Also the n^{th} excited state has n nodes.

Finally lets discuss some properties of the ground states. Consider a classical particle with the ground state energy $\frac{\hbar\omega}{2}$, this particle will be confined to a region where:

$$E \geq V(x) \quad \frac{1}{2}\hbar\omega \geq \frac{1}{2}kx^2 \tag{5.66}$$

This means $x^2 = \frac{1}{\alpha^2}$ at the limiting case, therefore the particle is confined in the region:

$$x = \pm \frac{1}{\alpha} \rightarrow -\frac{1}{\alpha} \leq x \leq \frac{1}{\alpha} \tag{5.67}$$

Suppose the particle now decides (as if it has a choice!) to show its quantum nature, still in the ground state of the Harmonic Oscillator. In the classical case the limiting factor was $E = V(x)$, in this case lets substitute this into the TISE:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} + V(x)\phi = E\phi \tag{5.68}$$

Since $E = V$:

$$\frac{\partial^2 \phi}{\partial x^2} = 0 \quad (5.69)$$

Substitute in the ground state wavefunction:

$$\begin{aligned} \frac{\partial^2 \phi}{\partial x^2} &= \frac{\partial}{\partial x} \left(\frac{\alpha^{\frac{1}{2}}}{\pi^{\frac{1}{4}}} - x\alpha^2 e^{-\frac{(x\alpha)^2}{2}} \right) = 0 \\ &= -\frac{\alpha^{\frac{1}{2}} \alpha^2}{\pi^{\frac{1}{4}}} \left(e^{-\frac{(x\alpha)^2}{2}} - x \left(\frac{x\alpha^2}{2} \right) e^{-\frac{(x\alpha)^2}{2}} \right) = 0 \\ &= \frac{x^2 \alpha^2}{2} \frac{\alpha^{\frac{1}{2}} \alpha^2}{\pi^{\frac{1}{4}}} - \frac{\alpha^{\frac{1}{2}} \alpha^2}{\pi^{\frac{1}{4}}} = 0 \end{aligned} \quad (5.70)$$

Therefore:

$$x^2 = \frac{2}{\alpha^2} \rightarrow x = \pm \frac{\sqrt{2}}{\alpha} \quad (5.71)$$

Which is of course different to the classical case!

4. Ladder operators in Dirac notation

Now lets formulate the Harmonic oscillator in Dirac notation. First define the normalised eigenkets $|n\rangle$, where:

$$H|n\rangle = E_n|n\rangle \quad (5.72)$$

Another operator, called the 'number operator' can be defined as:

$$N = a_+ a_- \quad (5.73)$$

This operator commutes with the Hamiltonian:

$$\begin{aligned} [H, N] &= [\hbar\omega(a_+ a_- + \frac{1}{2}), a_+ a_-] \\ &= \hbar\omega[(N + \frac{1}{2}), N] \\ &= \hbar\omega \left([N, N] + [\frac{1}{2}, N] \right) \\ &= 0 \end{aligned} \quad (5.74)$$

The eigenkets $|n\rangle$ are labeled by the eigenvalues of this operator, which are just the number of particles in the system:

$$N|n\rangle = n|n\rangle \quad (5.75)$$

Previously we saw that a_- annihilates the vacuum (ground) state, so in Dirac notation we have:

$$a_-|0\rangle = 0 \quad (5.76)$$

The effect of the raising operator is:

$$a_+|n\rangle = A|n+1\rangle \quad (5.77)$$

where A is a normalising factor, to find it we take the length squared of both sides:

$$\begin{aligned} \langle n|(a_+)^\dagger a_+|n\rangle &= \langle n+1|A^* A|n+1\rangle \\ &= |A|^2 \end{aligned} \quad (5.78)$$

it is also known that $(a_+)^\dagger = a_-$ therefore:

$$|A|^2 = \langle n | a_- a_+ | n \rangle \quad (5.79)$$

use the commutation relation:

$$[a_-, a_+] = 1 \quad (5.80)$$

Substitute this into:

$$\begin{aligned} |A|^2 &= \langle n | a_+ a_- + 1 | n \rangle \\ &= \langle n | N + 1 | n \rangle \\ &= n + 1 \\ A &= \sqrt{n + 1} \end{aligned} \quad (5.81)$$

Similarly the lowering operator has the relation:

$$a_- | n \rangle = B | n - 1 \rangle \quad (5.82)$$

B is worked out in a similar way to A :

$$\begin{aligned} |B|^2 &= \langle n | a_+ a_- | n \rangle \\ &= \langle n | N | n \rangle \\ &= n \\ B &= \sqrt{n} \end{aligned} \quad (5.83)$$

Since $|A|^2$ and $|B|^2$ are the only physical observables there can, in principle be a phase term in front of A and B . So in summary we have:

$$\begin{aligned} a_+ | n \rangle &= \sqrt{n + 1} | n + 1 \rangle \\ a_- | n \rangle &= \sqrt{n} | n - 1 \rangle \end{aligned} \quad (5.84)$$

Note that a_- acting on $|0\rangle$ does indeed annihilate this state. There is no lower energy state than the ground state (hence called the ground state).

Angular momentum

1. Quantising classical angular momentum

In classical physics the angular momentum, \vec{L} , is the amount of rotation of an object has, taking into account its mass and shape:

$$\vec{L} = I\omega \quad (6.1)$$

I is the moment of inertia (the inertia related to rotation), ω is the angular velocity:

$$\begin{aligned} I &= \sum_i m_i \bar{r}_i^2 \\ \omega &= \frac{\vec{r} \times \vec{v}}{|\vec{r}|^2} \end{aligned} \quad (6.2)$$

Therefore:

$$\begin{aligned} \vec{L} &= \vec{r} \times m\vec{V} \\ &= \vec{r} \times \vec{p} \end{aligned} \quad (6.3)$$

where \vec{p} is the momentum. Of course in QM the angular momentum must be an operator associated with it. So we use the usual canonical quantisation method (i.e take classical dynamical variables and equate them to operators):

$$\vec{L} = -i\hbar\vec{r} \times \nabla \quad (6.4)$$

where:

$$\nabla = \left(\frac{\partial}{\partial x} \underline{\vec{i}} + \frac{\partial}{\partial y} \underline{\vec{j}} + \frac{\partial}{\partial z} \underline{\vec{k}} \right) \quad (6.5)$$

The underlined vectors represent the unit vectors in the x, y, z directions respectively. The \vec{r} is the radial vector:

$$\vec{r} = x\underline{\vec{i}} + y\underline{\vec{j}} + z\underline{\vec{k}} \quad (6.6)$$

Computing the cross product in Eq 6.4:

$$\begin{aligned} \vec{r} \times \nabla &= \epsilon_{ijk} \underline{\vec{i}}_i \underline{\vec{j}}_j \nabla_k \\ &= \epsilon_{ijk} \underline{\vec{i}}_1 \underline{\vec{j}}_j \nabla_k + \epsilon_{2jk} \underline{\vec{i}}_j \nabla_k + \epsilon_{3jk} \underline{\vec{i}}_3 \underline{\vec{j}}_j \nabla_k \\ &= (\underline{\vec{r}}_2 \nabla_3 - \underline{\vec{r}}_3 \nabla_2) \underline{\vec{i}}_1 + (-\underline{\vec{r}}_1 \nabla_3 + \underline{\vec{r}}_3 \nabla_1) \underline{\vec{i}}_2 + (\underline{\vec{r}}_1 \nabla_2 - \underline{\vec{r}}_2 \nabla_1) \underline{\vec{i}}_3 \end{aligned} \quad (6.7)$$

here the subscripts represent the coordinates as follows:

$$1 \rightarrow x, 2 \rightarrow y, 3 \rightarrow z \quad (6.8)$$

Therefore the cross product is:

$$\vec{L} = \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \underline{\vec{x}} + \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \underline{\vec{y}} + \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \underline{\vec{z}} \quad (6.9)$$

Thus the angular momentum operators in Eq 6.4 become:

$$\begin{aligned} L_x &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ L_y &= -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ L_z &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \end{aligned} \quad (6.10)$$

The total angular momentum operator is given by:

$$L^2 = L_x^2 + L_y^2 + L_z^2 \quad (6.11)$$

In classical physics all the components and the total angular momentum are physical observables and can be measured *simultaneously*. The simultaneous measurement of all the components and the total angular momentum is not possible in QM. Recall that for two observables to be simultaneously measurable, the operators they correspond to must commute, so let's test this for each of the components:

$$\begin{aligned} [L_x, L_y] &= [(yp_z - zp_y), (zp_x - xp_z)] \\ &= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \\ &= [yp_z, zp_x] - 0 - 0 + [zp_y, xp_z] \\ &= yp_x[p_z, z] + p_yx[z, p_z] \\ &= yp_x[p_z, z] - p_yx[p_z, z] \\ &= (yp_x - p_yx)[p_z, z] \end{aligned} \quad (6.12)$$

Recall that:

$$[p_z, z] = -i\hbar \quad (6.13)$$

Therefore Eq 8.12 becomes:

$$\begin{aligned} [L_x, L_y] &= -i\hbar(yp_x - p_yx) \\ &= i\hbar L_z \end{aligned} \quad (6.14)$$

Similarly we have the following commutation relations:

$$\begin{aligned} [L_y, L_z] &= i\hbar L_x \\ [L_z, L_x] &= i\hbar L_y \end{aligned} \quad (6.15)$$

These relations can be written out compactly as:

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k \quad (6.16)$$

where the subscript's take on the usual values of x, y, z . This means out of three components of angular momentum only one quantum number (measurable quantity) can be obtained. In addition we have the commutation relation:

$$\begin{aligned} [L_x, L^2] &= [L_x, L_x^2 + L_y^2 + L_z^2] \\ &= [L_x, L_x^2] + [L_x, L_y^2] + [L_x, L_z^2] \\ &= [L_x, L_y]L_y + L_y[L_x, L_y] + [L_x, L_z]L_z + L_z[L_x, L_z] \\ &= i\hbar L_z L_y + i\hbar L_y L_z - i\hbar L_y L_z - i\hbar L_z L_y \\ &= 0 \end{aligned} \quad (6.17)$$

2. Eigenvalues and eigenvectors

We will not derive the eigenfunctions and eigenvalues of the angular momentum here are:

$$L^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm} \quad (6.18)$$

$$L_z Y_{lm} = \hbar m Y_{lm} \quad (6.19)$$

where $l = 0, 1, 2, 3$ and for a fixed l , the possible values for m are:

$$m = -l, -l+1, \dots, l-1, l \quad (6.20)$$

The eigenfunctions Y_{lm} are called spherical harmonics and are functions of (θ, ϕ) and normalised as follows:

$$\int Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) d\Omega = \delta_{ll'} \delta_{mm'} \quad (6.21)$$

$d\Omega$ is the solid angle θ & ϕ are coordinates in the spherical polar coordinates:

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned} \quad (6.22)$$

3. Ladder operators

For the SHO we had two frameworks to work in; differential equations and the other one is the operator method using the raising and lowering operators. A similar method will be used now to formalise the concept of angular momentum. The creation and annihilation operators will be defined abstractly, this will show that there are more possible eigenvalues of L^2 and L_z than found using differential equations. To see how this happens, start from the beginning and propose eigenvalue equations of the form:

$$\begin{aligned} L^2 \psi &= \hbar^2 K^2 \psi \\ L_z \psi &= \hbar k \psi \end{aligned} \quad (6.23)$$

To find K^2 and k , introduce the operators:

$$\begin{aligned} L_+ &= L_x + iL_y \\ L_- &= L_x - iL_y \end{aligned} \quad (6.24)$$

these are sometimes called the angular momentum 'step' operators and they follow the following commutation relations:

$$\begin{aligned} [L_+, L_z] &= -\hbar L_+ \\ [L_-, L_z] &= \hbar L_- \end{aligned} \quad (6.25)$$

Now consider a wavefunction that satisfies:

$$L_z \psi_k = \hbar k \psi_k \quad (6.26)$$

Define a new function:

$$\psi' = L_+ \psi_k \quad (6.27)$$

in general this wavefunction will not always be non-zero. Lets try to find out what happens when ψ' is acted upon by L_z :

$$L_z \psi'_k = L_z L_+ \psi_k \quad (6.28)$$

But we know the commutation relation:

$$L_+ L_z - L_z L_+ = -\hbar L_+ \quad (6.29)$$

Therefore:

$$L_z L_+ = L_+ L_z + \hbar L_+ \quad (6.30)$$

Substitute Eq 6.30 into Eq 6.28:

$$\begin{aligned} L_z \psi' &= (\hbar L_+ + L_+ L_z) \psi_k \\ &= \hbar L_+ \psi_k + L_+ L_z \psi_k \\ &= \hbar \psi' + \hbar k L_+ \psi_k \\ &= \hbar \psi' + \hbar k \psi' \\ &= \hbar(1+k) \psi' \end{aligned} \quad (6.31)$$

Thus the state ψ must be at least proportion to (if not equal to) a state with L_z eigenvalue $\hbar(k+1)$:

$$L_+ \psi_k = \psi' = c_+(k) \psi_{k+1} \quad (6.32)$$

where $c_+(k)$ is just the normalisation constant. So it is seen that L_+ acting on ψ_k 'raises' the states eigenvalues by 1 to $k+1$. Similarly define:

$$\psi'_- + L_- \psi_k \quad (6.33)$$

Act on it with L_z :

$$\begin{aligned} L_z \psi'_- &= L_z L_- \psi_k \\ &= (L_- L_z - \hbar L_-) \psi_k \\ &= L_- L_z \psi_k - \hbar L_- \psi_k \\ &= L_- \hbar k \psi_k - \hbar \psi'_- \\ &= \hbar \psi'_- (k-1) \\ &= \hbar(k-1) \psi'_- \end{aligned} \quad (6.34)$$

L_- is sometimes called the step down operator, together this step operators move the eigenvalues of L_z up or down in units of \hbar . The obvious next question to ask is, what is the effect of L_+, L_- on the L^2 eigenvalues. Firstly, notice that since the step operators are just a linear combination of these two:

$$L_{\pm} = L_x \pm iL_y \quad (6.35)$$

It is obvious that L^2 will commute with them:

$$[L^2, L_{\pm}] = 0 \quad (6.36)$$

Of course this means that L^2 and L_{\pm} will share the same eigenfunctions, i.e if $\psi_{k,k}$ satisfies:

$$L^2 \psi_{k,k^2} = \hbar^2 K^2 \psi_{k,k^2} \quad (6.37)$$

then:

$$\begin{aligned}
L^2(L_+\psi_{k,K^2}) &= L_+L^2\psi_{k,K^2} \\
&= L_+\hbar^2K^2\psi_{k,K^2} \\
&= \hbar^2K^2(L_+\psi_{k,K^2})
\end{aligned} \tag{6.38}$$

And similarly, the $L_-\psi_{k,K^2}$ yields the same result, thus L_+ , L_- do not change the L^2 eigenvalue (i.e they do not change the total angular momentum). To summarise what has been shown so far; the L_x operator generates a tower of L_z eigenstates with eigenvalues:

$$-\hbar(k-2), \hbar(k-1), \hbar k, \hbar(k+1) \tag{6.39}$$

by repeatedly acting of ψ_k . However L_\pm do alter the total angular momentum eigenvalues, K^2 , this means the, k , values must be bounded such that the total angular momentum does not change. To see how they are bounded, note that:

$$L^2 - L_z^2 = L_x^2 + L_y^2 \tag{6.40}$$

Now consider an arbitrary member of the tower, say $\psi_{k'_1K^2}$ ($|k'_1K^2\rangle$) and take the expectation values of both the operators above in this state:

$$\begin{aligned}
\langle k'_1K^2|L^2 - L_z^2|k'_1K^2\rangle &= \langle k'_1K^2|(L^2|k'_1K^2\rangle - L_z^2|k'_1K^2\rangle) \\
&= \langle k'_1K^2|\hbar^2K^2|k'_1K^2\rangle - \langle k'_1K^2|L_z^2|k'_1K^2\rangle \\
&= \hbar^2K^2 - \hbar^2k_1'^2
\end{aligned} \tag{6.41}$$

The $L_x^2 + L_y^2$ operator gives:

$$\langle k'_1K^2|L_x^2 + L_y^2|k'_1K^2\rangle \geq 0 \tag{6.42}$$

as the sum of the expectation values of Hermitian operators is always positive. To see this, consider the expectation value of an arbitrary operator O squared, where O is Hermitian, i.e it obeys:

$$O = O^\dagger \tag{6.43}$$

$$\begin{aligned}
\langle O^2\rangle &= \int \psi^* O^2 \psi dx \\
&= \int (O\psi)^* O\psi dx \\
&= \int |O\psi|^2 dx
\end{aligned} \tag{6.44}$$

and the integral of a positive quantity is a positive quantity!, therefore we have shown that the sum of expectation values of two Hermitian operators will also be positive. Returning to Eq 6.41, we now get:

$$K^2 \geq k_1'^2 \tag{6.45}$$

This is the bounding condition on the L_z operator eigenvalue. Since k'^2 is bounded by K^2 there must be a state with the highest L_z , lets call it ψ_{k_{max},K^2} , or in Dirac notation $|k_{max},K^2\rangle$ and a state with lowest L_z ; ψ_{k_{min},K^2} , $|k_{min},K^2\rangle$. These states, by definition must follow the following conditions

$$L_+|k_{max},K^2\rangle = 0 \quad C_+(k_{max}) = 0 \tag{6.46}$$

$$L_-|k_{min},K^2\rangle = 0 \quad C_-(k_{min}) = 0 \tag{6.47}$$

There is a connection between the values k_{max} and K^2 or k_{min} and K^2 . To see this, L_-L_+ and L_+,L_- need to be manipulated:

$$\begin{aligned}
L_-L_+ &= (L_x - iL_y)(L_x + iL_y) \\
&= L_x^2 - iL_xL_y + iL_yL_x + L_y^2 \\
&= L_x^2 + L_y^2 + i[L_x, L_y] \\
&= L_x^2 + L_y^2 + i(i\hbar L_z) \\
&= L_x^2 + L_y^2 - \hbar L_z \\
&= L^2 - L_z^2 - \hbar L_z
\end{aligned} \tag{6.48}$$

Similarly:

$$L_+L_- = L^2 - L_z^2 + \hbar L_z \tag{6.49}$$

Now act on $L + 1|k_{max}, K^2\rangle = 0$ with L_- :

$$L_-L_+|k_{max}, K^2\rangle \tag{6.50}$$

but $L_-L_+ = L^2 - L_z^2 - \hbar L_z$:

$$\begin{aligned}
L^2 - L_z^2 - \hbar L_z|k_{max}, K^2\rangle &= L^2|k_{max}, K^2\rangle - L_z^2|k_{max}, K^2\rangle - \hbar L_z|k_{max}, K^2\rangle \\
&= \hbar^2 K^2|k_{max}, K^2\rangle - \hbar^2 k_{max}^2|k_{max}, K^2\rangle - \hbar^2 k_{max}|k_{max}, K^2\rangle \\
&= \hbar^2(K^2 - k_{max}^2 - k_{max})|k_{max}, K^2\rangle = 0
\end{aligned} \tag{6.51}$$

Therefore we have:

$$K^2 = k_{max}^2 + k_{max} = k_{max}(k_{max} + 1) \tag{6.52}$$

Now image starting at the top of the tower of $|k_{max}, K^2\rangle$ and acting q times on it with L_- until we reach $|k_{min}, K^2\rangle$, in this state, by definition:

$$L_-|k_{min}, K^2\rangle = 0 \tag{6.53}$$

Lets act on this with L_+ :

$$L_+L_-|k_{min}, K^2\rangle = 0 \tag{6.54}$$

use:

$$L_+L_- = L^2 - L_z^2 + \hbar L_z \tag{6.55}$$

therefore:

$$\begin{aligned}
L^2 - L_z^2 + \hbar L_z|k_{min}, K^2\rangle &= L^2|k_{min}, K^2\rangle - L_z^2|k_{min}, K^2\rangle + \hbar L_z|k_{min}, K^2\rangle \\
&= \hbar^2 K^2|k_{min}, K^2\rangle - \hbar^2 k_{min}^2|k_{min}, K^2\rangle + \hbar^2 k_{min}|k_{min}, K^2\rangle \\
&= \hbar^2(K^2 - k_{min}^2 + k_{min})|k_{min}, K^2\rangle \\
&= \hbar^2(K^2 - k_{min}(k_{min} - 1))|k_{min}, K^2\rangle = 0
\end{aligned} \tag{6.56}$$

Therefore:

$$K^2 = k_{min}(k_{min} - 1) \tag{6.57}$$

Comparing with:

$$K^2 = k_{max}(k_{max} + 1) \tag{6.58}$$

Therefore we get the final relation:

$$k_{max} = -k_{min} \quad (6.59)$$

As one goes from k_{min} to k_{max} , in say q steps, we have:

$$k_{max} - k_{min} = 2k_{max} = q \Rightarrow k_{max} = \frac{q}{2} \quad (6.60)$$

where q can take any positive integer value (and zero). It is conventional to refer to the maximum value of k as j , i.e $j = \frac{q}{2}$, therefore:

$$K^2 = j(j+1) \quad (6.61)$$

In this convention, the eigenvalues equations are:

$$\begin{aligned} J^2|j, m\rangle &= \hbar^2 j(j+1)|j, m\rangle \\ J_z|j, m\rangle &= \hbar m|j, m\rangle \end{aligned} \quad (6.62)$$

where the quantum numbers are:

$$\begin{aligned} j &= 0, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots \\ m &= -j, -j+1, \dots, j-1, j \end{aligned} \quad (6.63)$$

This means that there are $2j+1$ possible states of the same j but with different values of m . Interpreting the results so far; we have seen that angular momentum, j , can take on both integer and half integer values. However, when the eigenvalues were calculated by solving the associated Legendre equation, j was only allowed to be a integer for normalisable solutions.

The reason this has happened, is that in the operator method of solving for eigenvalues, we just use the commutation relations:

$$[L_i, L_j] = i\hbar\epsilon_{ijk}L_k \quad (6.64)$$

Nowhere was the differential representation of L_z, L^2 , used. What has actually happened is that a more general problem has been solved, the commutation relation reflects the law of the combination of relations in 3-dimensions and is satisfies whatever the nature of the wavefunctions they rotate. This means that the there must be another source that follows the commutation relations for a rotation in $3-D$, indeed we have discovered a property of *spin*, however this property does not have anything to do with spinning, i.e an electron with a nonzero spin values, does not actually have anything to do with the fact that the electron is spinning. Spin wavefunctions are not functions of angular coordinates θ, ϕ .

The representation of spin wavefunction is completely abstract, and only comes from experimental observation (Stern-Gerlachs's famous experiment was the first evidence for spin), particle with $j = \frac{1}{2}$ are represented by a state vector of the form:

$$\begin{pmatrix} \cdot \\ \cdot \end{pmatrix}$$

Similarly for a particle with $j = 1$:

$$\begin{pmatrix} \cdot \\ \cdot \\ \cdot \end{pmatrix}$$

For $j = \frac{3}{2}$:

$$\begin{pmatrix} \cdot \\ \cdot \\ \cdot \\ \cdot \end{pmatrix}$$

When these spin states are present, L_x, L_y, L_z, L^2 are also represented by matrices and these matrices act on the spin state vectors to 're-shuffle' their component. In fact, this intrinsic property of spin means if one would like to make further progress in QM, then the Heisenberg formulation of matrix mechanics has to be used. This means the manipulations are simply done via algebra computation, which is more general and abstract than the wave mechanics formulation of Schrodinger.

It is useful to make a distinction between the matrix/operator method and the differential equation method here, since the both gave different results for the angular momentum. The solution to the differential equations are called the *orbital* part of the angular momentum. The orbital angular momentum has the quantum number l and it can only take on integer values. The wavefunctions for this are the usual spherical harmonics, Y_{lm} , that carry a ϕ and θ dependence. The eigenvalue equations are:

$$\begin{aligned} L^2 Y_{lm}(\theta, \phi) &= \hbar^2 l(l+1) Y_{lm}(\theta, \phi) \\ L_z Y_{lm}(\theta, \phi) &= \hbar m Y_{lm}(\theta, \phi) \end{aligned} \quad (6.65)$$

were:

$$\begin{aligned} l &= 0, 1, 2, 3, \dots \\ m &= -l, -l+1, \dots, l-1, l \end{aligned} \quad (6.66)$$

The *spin* angular momentum will have quantum number s and s_z . The wavefunctions are column vectors of dimension depending on the spin itself. If the wavefunctions are labeled $|s, s_z\rangle$, then the eigenvalue equations are:

$$\begin{aligned} S^2 |s, s_z\rangle &= \hbar^2 s(s+1) |s, s_z\rangle \\ S_z |s, s_z\rangle &= \hbar s_z |s, s_z\rangle \end{aligned} \quad (6.67)$$

where:

$$\begin{aligned} s &= 0, \frac{1}{2}, 1, \frac{3}{2}, \dots \\ s_z &= -s, -s+1, \dots, s-1, s \end{aligned} \quad (6.68)$$

Since the spin follows the same commutation relations as the orbital part:

$$[S_x, S_y] = i\hbar S_z \quad (6.69)$$

We define the *total* angular momentum as:

$$J_i = L_i + S_i \quad (6.70)$$

where $i = x, y, z$ and J_i carries the quantum number that was found in solving for the angular momentum in the operator framework:

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots \quad (6.71)$$

The similarity between the commutation relations of the spin angular momentum and the orbital angular momentum, means the linear combination of the two, which is the total angular momentum, also carry the same commutation relations and the total angular momentum quantum number is just the sum of the individual angular momenta:

$$j_z = l_z + s_z \quad (6.72)$$

we also define:

$$l_z = m_l \quad s_z = m_s \quad (6.73)$$

4. Spin

To understand the formulation of the spin property, let's look at a spin $\frac{1}{2}$ example (that has 0 orbital angular momentum). If a general state is labeled as $|j, j_z\rangle$, for spin $\frac{1}{2}$ particles it will become $|\frac{1}{2}, \pm\frac{1}{2}\rangle$. The action of the J^2 and J_z is already known from the previous section:

$$\begin{aligned} J^2|j, j_z\rangle &= \hbar^2 j(j+1) |\frac{1}{2}, \pm\frac{1}{2}\rangle \\ &= \hbar^2 \frac{3}{4} |\frac{1}{2}, \pm\frac{1}{2}\rangle \end{aligned} \quad (6.74)$$

$$\begin{aligned} J_z|j, j_z\rangle &= J_z |\frac{1}{2}, \pm\frac{1}{2}\rangle \\ &= \pm \frac{\hbar}{2} |\frac{1}{2}, \pm\frac{1}{2}\rangle \end{aligned} \quad (6.75)$$

The spin $\frac{1}{2}$ case is particularly important as electrons, protons, neutrons, quarks... all have spin $\frac{1}{2}$. Since $j = \frac{1}{2}$ in this case, it is not possible to represent angular momentum operators as differential operators. So what are the operators corresponding to angular momentum for $j = \frac{1}{2}$? Once again the fundamental reason for them being what they are, is experimental observation, however one can put some constraints on it before 'guessing' at their form.

Firstly, we know that the wavefunctions for spin $\frac{1}{2}$ particles is a 2 dimensional state, column vector, therefore the operator must be a 2×2 matrix. In addition it must have the usual properties of other properties in quantum mechanics, i.e they must be *Hermitian*. So consider the matrices:

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (6.76)$$

$$S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (6.77)$$

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (6.78)$$

Check the condition for them being Hermitian, i.e $S_x = S_x^\dagger$. It is obvious for S_x as the matrix elements are all real. For S_y :

$$S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \xrightarrow{\text{Complex conjugate}} \frac{\hbar}{2} \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \xrightarrow{\text{Transpose}} \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = S_y \quad (6.79)$$

and S_z is also real therefore $S_z = S_z^\dagger$. Therefore the matrices are indeed Hermitian, and could be operators for spin $\frac{1}{2}$ particles. The next thing to check is whether they follow the commutation relation that is already known:

$$\begin{aligned}
[S_x, S_y] &= \frac{\hbar^2}{4} \left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right] \\
&= \frac{\hbar^2}{4} \left[\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} \right] \\
&= \frac{\hbar^2}{4} \begin{pmatrix} 2i & 0 \\ 0 & -2i \end{pmatrix} \\
&= \frac{\hbar^2}{2} \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} \\
&= i\hbar S_z
\end{aligned} \tag{6.80}$$

as expected and the commutation relation follows:

$$[S_i, S_j] = i\hbar\epsilon_{ijk}S_k \tag{6.81}$$

Using these matrices, one can also calculate S^2 :

$$\begin{aligned}
S^2 &= S_x^2 + S_y^2 + S_z^2 \\
&= \frac{\hbar^2}{4} \left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right] \\
&= \frac{\hbar^2}{4} \left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right] \\
&= \frac{3\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
&= \frac{3\hbar^2}{4} \mathbb{I}
\end{aligned} \tag{6.82}$$

Which is exactly what is expected for S^2 , this means any two dimensional state vectors will have eigenvalue $\frac{3\hbar^2}{4}$, when acted upon by this operator. It is also useful to check the eigenvalue for S_z :

$$\begin{aligned}
S_z - \lambda \mathbb{I} &= 0 \\
\begin{vmatrix} \frac{\hbar}{2} - \lambda & 0 \\ 0 & -\frac{\hbar}{2} - \lambda \end{vmatrix} &= 0 \\
\left(\frac{\hbar}{2} - \lambda\right)\left(\frac{\hbar}{2} + \lambda\right) &= 0
\end{aligned} \tag{6.83}$$

Therefore:

$$\frac{\hbar}{2} - \lambda^2 = 0 \rightarrow \lambda = \pm \frac{\hbar}{2} \tag{6.84}$$

So the eigenvectors are:

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \pm \begin{pmatrix} a \\ b \end{pmatrix} \tag{6.85}$$

Therefore $a = \pm a$, $-b = \pm b$, this means for eigenvalue $+1$ the relation of a and b are $a = a$ and $-b = b$, therefore the eigenvectors must be:

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{6.86}$$

for eigenvalue -1 , the relations between a and b are $a = -a$ and $-b = -b$, therefore the eigenvectors must be:

$$\begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (6.87)$$

Hence the conclusion is that $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ is the state of spin $\frac{1}{2}$ with $S_z = \frac{1}{2}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ is the state with $S_z = -\frac{1}{2}$. Similarly eigenvalues and eigenvectors for S_x can be found:

$$\begin{vmatrix} -\lambda & \frac{\hbar}{2} \\ \frac{\hbar}{2} & -\lambda \end{vmatrix} = 0 \quad (6.88)$$

Similarly the eigenvalues and eigenvectors can be calculated for S_z , the results are shown in the table below:

Operator	Eigenvalues	Eigenvectors
S_x	$\frac{\hbar}{2}, -\frac{\hbar}{2}$	$\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$
S_y	$\frac{\hbar}{2}, -\frac{\hbar}{2}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$
S_z	$\frac{\hbar}{2}, -\frac{\hbar}{2}$	$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}, \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$

5. Addition of angular momentum

So far only isolated single particle systems have been considered in analysing their angular momentum. In most situations of physical interest, one has to deal with systems of more than one particle.

In this case, one needs to know how to deal with these composite systems in terms of their sub-systems (i.e individual particles). To begin with, lets look at the simplest case of two commuting angular momenta:

$$J_z = J_1 + J_2 \quad (6.89)$$

The fact that they are commuting is crucial here as it means that the two subsystems are independent of each other. Thus J_1 and J_2 are any two angular momenta corresponding to independent sub-systems (i.e two particle) 1 and 2. Similarly:

$$J_z = J_{1z} + J_{2z} \quad (6.90)$$

Define the eigenvectors for each subsystem as:

$$\begin{aligned} |j_1, m_1\rangle &= \text{for sub-system 1} \\ |j_2, m_2\rangle &= \text{for sub-system 2} \end{aligned} \quad (6.91)$$

It is possible to construct a normalised simultaneous eigenvector of $J_1^2, J_2^2, J_{1z}, J_{2z}$ operators, that carry the eigenvalues $\hbar^2 j(j+1), \hbar^2 j_2(j_2+1), \hbar m_1, \hbar m_2$ respectively. The eigenvector is given by the *direct product*:

$$|j_1, j_2, m_1, m_2\rangle = |j_1, m_1\rangle |j_2, m_2\rangle \quad (6.92)$$

For a fixed value of j_1, m_1 can take on any of $2j_1 + 1$ values, similarly for a fixed value of j_2, m_2 can take on one of $2j_2 + 1$ values. Hence for given values of j_1, j_2 there are $(2j_1 + 1)(2j_2 + 1)$ *direct products* which form a complete set of ortho-normal states.

Apply J_z to the overall solution:

$$J_z |j_1, j_2, m_1, m_2\rangle = (J_{1z} + J_{2z}) |j_1, m_1\rangle |j_2, m_2\rangle \quad (6.93)$$

The operators act separately on each state, as the states are independent of each other:

$$\begin{aligned} J_{1z}|j_1, m_1\rangle + J_{2z}|j_2, m_2\rangle &= (m_1 + m_2)\hbar|j_1, m_1\rangle|j_2, m_2\rangle \\ &= (m_1 + m_2)\hbar|j_1, j_2, m_1, m_2\rangle \end{aligned} \quad (6.94)$$

This means $|j_1, j_2, m_1, m_2\rangle$ is an eigenstate of the operator corresponding to the total angular momentum J_z , with eigenvalues $(m_1 + m_2)\hbar$. Compare this to single particle eigenvalues, $m\hbar$, it is obvious that when a large system of many particles is considered as a whole and the particles are independent of each other, the z components of the angular momentum is the sum of the individual z components. This happens because of the assumption that $J_1^2, J_2^2, j_{1z}, j_{2z}$ commutes with J_z .

Now lets consider the total angular momentum, J^2 , of the whole system. J is defined as:

$$J^2 = (J_1 + J_2)^2 = J_1^2 + J_2^2 + 2J_1J_2 \quad (6.95)$$

Because all components of $J_1(J_{1x}, J_{1y}, J_{1z})$ commute with all of these of $J_z(J_{2x}, J_{2y}, J_{2z})$ and since:

$$[J_1^2, J_1] = 0 = [J_2^2, J_2] \quad (6.96)$$

it follows that:

$$[J^2, J_1^2] = 0 = [J^2, J_2^2] \quad (6.97)$$

However as:

$$J_1 \cdot J_2 = J_{1x}J_{2x} + J_{1y}J_{2y} + J_{1z}J_{2z} \quad (6.98)$$

and J_{1z} does not commute with J_{1x}, J_{1y} , this implies:

$$[J^2, J_{1z}] = 0 \quad (6.99)$$

similarly:

$$[J^2, J_{2z}] = 0 \quad (6.100)$$

This leads to a bizarre consequence, that simultaneous eigenfunctions of J^2 and J_z are eigenfunctions of J_1^2 and J_2^2 but not in general of J_{1z} and J_{2z} . This means that the system can be in a state of fixed total angular momentum and the z component of the whole system is also fixed. At the same time one can know the total angular momentum of the individual sub-systems (particles) and yet the individual z components of the sub-systems cannot be known simultaneously (so in a way, you know the whole system but not the things its made from!).

This is typical of emergent phenomena, when the information regarding individual constituents of a system are unknown, however the 'bulk' behavior of a system can still be modeled. Anyway for this system, the bottom line is that the system can be formed in terms of distinct descriptions:

(1) In terms of eigenfunctions of $J_1^2, J_2^2, J_{1z}, J_{2z}$

or

(2) In terms of eigenfunctions of J_1^2, J_2^2, J^2, J_z

Note here that in each description there are four operators with the same eigenfunction. Of course, operators in QM correspond to physical observables, therefore each eigenstates carries four bits of information. It is interesting that the bits of information in either description is conserved.

Description 1) has already been labeled with eigenkets:

$$|j_1, j_2, m_1, m_2\rangle \quad (6.101)$$

Similarly description two can be labeled by:

$$|j_1, j_2, j, m\rangle \quad (6.102)$$

Both of these eigenkets form a complete orthonormal basis. Therefore these two sets can be related via a unitary transformation by inserting the identity:

$$\mathbb{I} = \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2| \quad (6.103)$$

Therefore:

$$\begin{aligned} |j_1, j_2, j, m\rangle &= \mathbb{I}|j_1, j_2, j, m\rangle \\ &= \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2|j_1, j_2, j, m\rangle \end{aligned} \quad (6.104)$$

$\langle j_1, j_2, m_1, m_2|j_1, j_2, j, m\rangle$ are called the *Clebsch-Gordon* coefficients sometimes written as:

$$\langle m_1, m_2|j, m\rangle \quad (6.105)$$

In order to find at what values of j are allowed for j_1 and j_2 , apply the J_z operator to both sides of Eq 6.104:

$$\begin{aligned} J_z|j_1, j_2, j, m\rangle &= J_z \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2|j_1, j_2, j, m\rangle \\ m\hbar|j_1, j_2, j, m\rangle &= (J_{1z} + J_{2z}) \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2|j_1, j_2, j, m\rangle \\ &= \hbar(m_1 + m_2) \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2|j_1, j_2, j, m\rangle \end{aligned} \quad (6.106)$$

Therefore $m = m_1 + m_2$ for the Clebsch-Gordon(CG) coefficients to be non-zero. The maximum values for m_1 & m_2 are j_1 and j_2 respectively, so the maximum value for m is $j_1 + j_2$. This also means that the maximum value of j is $j_1 + j_2$. Clearly if j is larger than this, then we must have states with m_j larger as well, and this is not possible. Therefore:

$$|j_1, j_2, j = j_1 + j_2, m = j_1 + j_2\rangle = |j_1, j_2, m_1 = j_1, m_2 = j_2\rangle \quad (6.107)$$

In this case the CG coefficient is:

$$\langle j_1, j_2, m_1 = j_1, m_2 = j_2|j_1, j_2, j = j_1 + j_2, m = j_1 + j_2\rangle = 1 \quad (6.108)$$

Consider next the states with $m = j_1 + j_2 - 1$. There are two such states; $|m_1 = j_1, m_2 = j_2 - 1\rangle$ and $|m_1 = j_1 - 1, m_2 = j_2\rangle$. Either of them must give $j = j_1 + j_2, m = j_1 + j_2 - 1$, which can be obtained by applying to $j = j_1 + j_2, m = j_1 + j_2$:

$$\begin{aligned} J_-|j, j_2\rangle &\approx |j_1 + j_2, j_1 + j_2 - 1\rangle \\ &= \sqrt{\frac{j_2}{j_1 + j_2}}|j_1, j_2 - 1\rangle + \sqrt{\frac{j_1}{j_1 + j_2}}|j_1 - 1, j_2\rangle \end{aligned} \quad (6.109)$$

From these, we have the following CG coefficients:

$$\begin{aligned} \langle j_1 + j_2, j_1 + j_2 - 1|j_1, j_2 - 1\rangle &= \sqrt{\frac{j_2}{j_1 + j_2}} \\ \langle j_1 + j_2, j_1 + j_2 - 1|j_1 - 1, j_2\rangle &= \sqrt{\frac{j_1}{j_1 + j_2}} \end{aligned} \quad (6.110)$$

There is another orthogonal combination of the two:

$$\sqrt{\frac{j_1}{j_1 + j_2}} |j_1, j_2 - 1\rangle - \sqrt{\frac{j_2}{j_1 + j_2}} |j_1 - 1, j_2\rangle \quad (6.111)$$

these states must have $j = j_1 + j_2 - 1$. Therefore another set of CG is obtained:

$$\begin{aligned} \langle j_1 + j_2 - 1, j_1 + j_2 - 1 | j_1, j_2 - 1 \rangle &= \sqrt{\frac{j_1}{j_1 + j_2}} \\ \langle j_1 + j_2 - 1, j_1 + j_2 - 1 | j_1 - 1, j_2 \rangle &= -\sqrt{\frac{j_2}{j_1 + j_2}} \end{aligned} \quad (6.112)$$

This can be generalised even more for states where $m = j_1 + j_2 - 2$ which will have three linearly independent states: $j = j_1 + j_2, j = j_1 + j_2 - 1, j = j_1 + j_2 - 2$. If one keeps repeating this, a minimum value of j will be found for $|j_1 - j_2|$, as all combinations will have been extracted.

For each value of j there are $2j + 1$ values of m so that the total number of eigenfunctions $|j_1, j_2, j, m\rangle$ is given by:

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1) = (2j_1+1)(2j_2+1) \quad (6.113)$$

In general, for given values of j_1 and j_2 , the allowed values of j are:

$$|j_1 - j_2| \leq j \leq j_1 + j_2 \quad (6.114)$$

Hydrogen Atom

1. Hydrogen-like atoms

Consider a single electron in a central Coulomb potential of a charge, Ze , nucleus. A central potential is a potential that only depends on radial distance r between the electron and nucleus. Coulomb means the potential has $\frac{1}{r}$ dependence:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad (7.1)$$

the Hamiltonian is:

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \quad (7.2)$$

The Hamiltonian is:

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon r} \quad (7.3)$$

The Hamiltonian is used in the TISE:

$$H\psi(\vec{r}) = E\psi(\vec{r}) \quad (7.4)$$

It is natural to work in spherical polar coordinates for this system as it has spherical symmetry. The solution to the TISE is obtained using separation of variables:

$$\psi(\vec{r}) \rightarrow \psi(\vec{r})_{nlm} = \underbrace{R_{nl}(r)}_{\text{Radial part}} \underbrace{Y_{lm}(\theta, \phi)}_{\text{Angular part}} \quad (7.5)$$

In spherical polar coordinates, the transformations to Cartesian coordinates are:

$$\begin{aligned} x &= r \cos \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned} \quad (7.6)$$

The Laplace operator is:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\vec{L}^2}{\hbar^2 r^2} \quad (7.7)$$

where \vec{L}^2 is the angular momentum operator:

$$L^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad (7.8)$$

Hence the product solution separates the TISE into a radial and angular part.

2. Angular (θ, ϕ) equation

Since the potential has no angular dependence:

$$[L^2, V(r)] = 0 \quad (7.9)$$

$$[L^2, -\frac{\hbar^2}{2m}\nabla^2] = 0 \quad (7.10)$$

$$[L^2, H] = 0 = [L, H] \quad (7.11)$$

This implies that the wavefunction of H is also the eigenfunction of L , in fact the wavefunctions are the spherical harmonics that satisfy the following equations:

$$L^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi) \quad (7.12)$$

where:

$$Y_{lm}(\theta, \phi) = A_{lm} P_l^m[\cos\theta] e^{im\phi} \quad (7.13)$$

where the orbital angular momentum quantum number, l and the azimuthal quantum number satisfies:

$$\begin{aligned} l &= \text{integer } (\geq 0) \\ -l &\leq m \leq l \end{aligned} \quad (7.14)$$

and $P_l^m[\cos\theta]$ are the associated *Laguerre* polynomials. A_{lm} is just a normalisation factor. The spherical harmonics satisfy the following orthogonality:

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta Y_{l'm'}^*(\theta, \phi) Y_{lm}(\theta, \phi) = \delta_{ll'} \delta_{mm'} \quad (7.15)$$

this orthogonality condition is only satisfied when the normalisation factor is:

$$A_{lm} = (-1)^m \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!} \right]^{\frac{1}{2}} \quad (7.16)$$

In bra-ket notation the ortho-normality is written as:

$$\langle l', m' | l, m \rangle = \delta_{ll'} \delta_{mm'} \quad (7.17)$$

3. Radial equation

The radial equation takes the form:

$$\left(-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{L^2}{\hbar^2 r^2} \right) + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \right) R_{nl}(r) = E_n R_{nl}(r) \quad (7.18)$$

Of course the radius can never be negative here. The energies only depend on the principle quantum number here. This means that there is a $2l+1$ fold degeneracy for each l ($-l \leq m \leq l$). This comes from the central potential which is spherically symmetric (recall that $[L^2, H] = [L, H] = 0$, showing rotational invariance w.r.t H and therefore no dependence of l and m on energy).

Define a new variable:

$$u_n(r) = r R_{nl}(r) \quad (7.19)$$

This makes the radial equation:

$$-\frac{\hbar^2}{2m} \frac{d^2 u_{nl}(r)}{dr^2} + V_{eff}(r) u_{nl}(r) = E_n u_{nl}(r) \quad (7.20)$$

where $V_{eff}(r)$ is called the effective potential defined as:

$$V_{eff}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2mr^2} \quad (7.21)$$

the first term in the effective potential is just the Coulombic potential acting between the electron and the nucleus. The second term comes from the angular momentum term in the Hamiltonian and represents the centrifugal potential. The full general solution of this equation involves the Laguerre polynomials with a new quantum number, n , in addition to the angular momentum quantum number l . These follows the conditions:

$$n = 1, 2, 3 \quad l = 0, 1, 2, 3 \dots n - 1 \quad (7.22)$$

The energies are of the form:

$$E_n = -\frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon} \right)^2 \frac{1}{n^2} \quad (7.23)$$

Note that these are bound state energies, i.e it takes energy to take an electron away from the nucleus. There is an exponential in the solution of the radial equation of the form $e^{-\frac{Zr}{a}}$, which ensures the electron remains close to the nucleus (the higher the nucleus charge, the closer the electron is).

Infact, these are not the only solutions, the radial TISE also has energies that are positive. These correspond to scattering states where a far away energetic electron can just 'bounce off' the nucleus and go back. A note on spectroscopic notation. In atomic physics different l wavefunctions (orbitals) are given in the following notation:

1	0	1	2	3
label	s	p	d	f

4. Dipole - matrix elements

Often one has to calculate dipole matrix elements of the form:

$$\langle n', l', m' | z | n, l, m \rangle \quad (7.24)$$

in spherical polar coordinates $z = r \cos \theta$; so the matrix element corresponds to a triple integral:

$$\begin{aligned} \langle n', l', m' | z | n, l, m \rangle &= A_{l', m'} A_{lm} \int_0^\infty dr r^2 R_{n'l'}(r) r R_{nl}(r) \\ &\times \int_0^\pi d\theta \sin \theta P_{l'}^{m'}[\cos \theta] \cos \theta P_l^m[\cos \theta] \\ &\times \int_0^{2\pi} d\phi e^{i(m-m')\phi} \end{aligned} \quad (7.25)$$

First lets deal with the azimuthal quantum number. The only dependence of m , is in the third integral:

$$\begin{aligned} \int_0^{2\pi} \pi_0 d\phi e^{i(m-m')\phi} &= \frac{1}{i(m-m')} \left[e^{i(m-m')\phi} \right]_0^{2\pi} \\ &= \frac{1}{i(m-m')} e^{i(m-m')(2\pi)} = 0 \end{aligned} \quad (7.26)$$

Except if $m = m'$ the integral becomes:

$$\int_0^{2\pi} d\phi = 2\pi \quad (7.27)$$

therefore the selection rule for m is:

$$\langle n', l', m' | z | n, l, m \rangle = \delta_{mm'} \quad (7.28)$$

Now consider the orbital angular momentum quantum number. For this the $d\theta$ integral has to be considered:

$$\int_0^\pi d\theta \sin \theta P_l^{m'}[\cos \theta] \cos \theta P_l^m[\cos \theta] \quad (7.29)$$

Instead of evaluating an integral like this, which can get messy, one can obtain useful results by considering parity transformations. Let's use the Parity operator \mathbb{P} to determine the symmetry of the integrand. The parity operator is defined as:

$$\mathbb{P}\vec{r} = -\vec{r}, \quad r \xrightarrow{\mathbb{P}} -r \quad (7.30)$$

in polar coordinates, this will be:

$$r \xrightarrow{\mathbb{P}} r, \quad \theta \xrightarrow{\mathbb{P}} \pi - \theta, \quad \phi \xrightarrow{\mathbb{P}} \phi + \pi \quad (7.31)$$

Therefore under \mathbb{P} , the spherical harmonics transform as:

$$Y_{lm}(\theta, \phi) \xrightarrow{\mathbb{P}} Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi) \quad (7.32)$$

After this transformation, let's look at the θ integral again. First do a change of variables:

$$\hat{\theta} = \pi - \theta \quad (7.33)$$

and then put back the Y_{lm} instead of P_l^m :

$$\begin{aligned} d\theta &= -d\hat{\theta} \\ \sin \hat{\theta} &= \sin(\pi - \theta) = -\sin \theta \\ \cos \hat{\theta} &= \cos \pi - \theta = \cos \theta \end{aligned} \quad (7.34)$$

Therefore:

$$\int_0^\pi d\theta \sin \theta Y_{l'm'}^*(\theta, \phi) \cos \theta Y_{lm}(\theta, \phi) \xrightarrow{\mathbb{P}} (-1)^{l+l'+1} \int_0^\pi d\hat{\theta} \sin \hat{\theta} Y_{l'm'}^*(\hat{\theta}, \hat{\phi}) \cos \hat{\theta} Y_{lm}(\hat{\theta}, \hat{\phi}) \quad (7.35)$$

The physics should remain the same under a parity transformation, therefore both sides of the equation must be equivalent, the only way this can be true is; either the integrals are both zero (in which case the entire wavefunction will become zero, this is just a trivial solution) or the power $l + l' + 1$ must be an even number, which is equivalent to saying that $l + l'$ must be an off number, or put another way:

$$l' = l \pm 1 \quad (7.36)$$

To summarise, the selection rule obtained is:

$$\langle n', l', m' | z | n, l, m \rangle = \delta_{l', l \pm 1} \quad (7.37)$$

Similar reasoning can be used to work out the selection rules for x :

$$x = r \sin \theta \cos \phi \quad (7.38)$$

or y which has the same dipole properties. The selection rules are:

$$\langle n', l', m' | x | n, l, m \rangle = \delta_{m, m' \pm 1} \Rightarrow m = m' \pm 1 \quad (7.39)$$

$$\langle n', l', m' | y | n, l, m \rangle = \delta_{l, l' \pm 1} \Rightarrow l = l' \pm 1 \quad (7.40)$$

Part 3

Approximate methods

Time independent perturbation theory

It is very rare in physics or any other real world problems that exact solutions can be found or are even available. Time independent perturbation theory (TIPT) is an approximation scheme that applies to problems in which a solutions needs to be found which is close to a known exact solution.

For instance, H^0 can be the Coulomb Hamiltonian for an electron bound to a proton, and H^1 is an addition due to the Hamiltonian, H^0 through an external weak $E - M$ field.

1. Formalism

Often the Hamiltonian system that one is interested in, is close to one that is already known and has exact solutions. Lets call this new Hamiltonian, H_λ , the known Hamiltonian, H_0 and the perturbation term is given by λV :

$$H_\lambda = H_0 + \lambda V \quad (8.1)$$

the new Hamiltonian is given a label λ , since it only depends on this parameter. Once can imagine λ to be a dial that can continuously turn up or down the perturbation. In the case where $\lambda = 0$, the system is in an exact eigenstate of H_0 ($H_\lambda = H_0$):

$$H_0|\phi_a^{(0)}\rangle = E_a^{(0)}|\phi_a^{(0)}\rangle \quad (8.2)$$

the notation used for the kets is that the '0' in the superscript represents the order of perturbation, i.e in this case it is 0 as there is no perturbation, for the next order the superscript will be '1' and the perturbation to the Hamiltonian will be λV , for the next order the superscript will be '2' and the perturbation will be $\lambda^2 V$ and so on. The eigenstates $|\phi_k^{(0)}\rangle$ form a complete basis set for the unperturbed problem:

$$H_0|\phi_k^{(0)}\rangle = E_k^{(0)}|\phi_k^{(0)}\rangle \quad (8.3)$$

The state $|\phi_a^{(0)}\rangle$ belongs to this set. The set follows the ortho-normality condition as:

$$\langle\phi_j^{(0)}|\phi_k^{(0)}\rangle = \delta_{jk} \quad (8.4)$$

The fact that this state is a complete set of basis vectors is crucial here, as this means any wavefunctions $|\psi\rangle$ can be expressed in terms of these states with some coefficients a_j :

$$|\psi\rangle = \sum_j a_j |\psi_j^{(0)}\rangle \quad (8.5)$$

The idea is that we want to find for the perturbed system, H_λ , the eigenstate $|\psi_a\rangle$:

$$H_\lambda|\psi_a\rangle = (H_0 + \lambda V)|\psi_a\rangle = E_a^\psi|\psi_a\rangle \quad (8.6)$$

The way this problem is constructed, the perturbed eigenstate $|\psi\rangle$ must look a lot like the unperturbed one $|\phi_a^{(0)}\rangle$, when λ is 'small' (the exact scale of 'small' will depend on a given problem). Therefore the natural thing to do, is to try a power series in λ :

$$E_a^\psi = E_a^{(0)} + \lambda E_a^{(1)} + \lambda^2 E_a^{(2)} + \dots \quad (8.7)$$

$$|\psi_a\rangle = |\phi_a^{(0)}\rangle + \lambda|\phi_a^{(1)}\rangle + \lambda^2|\phi_a^{(2)}\rangle \quad (8.8)$$

It is important to remember which things are already known and which things need to be worked out (in terms of the things that are known). In this case $|\phi_a^{(0)}\rangle$ and $E_a^{(0)}$ are the known eigenstates and energy, respectively, of the unperturbed system. $|\phi_a^{(1)}\rangle$, $|\phi_a^{(2)}\rangle$, $E_a^{(1)}$, $E_a^{(2)}$ are the eigenstates and energies of the first and second order perturbations respectively, these are all unknown and need to be worked out in terms of $|\phi_a^{(0)}\rangle$ and $E_a^{(0)}$.

Only the terms upto λ^2 are considered here. Now lets substitute Eq 8.8 into Eq 8.6:

$$\begin{aligned} (H_0 + \lambda V) \left(|\phi_a^{(0)}\rangle + \lambda|\phi_a^{(1)}\rangle + \lambda^2|\phi_a^{(2)}\rangle \right) &= \left(E^{(0)} + \lambda E_a^{(1)} + \lambda^2 E_a^{(2)} \right) \left(|\phi_a^{(0)}\rangle + \lambda|\phi_a^{(1)}\rangle + \lambda^2|\phi_a^{(2)}\rangle \right) \\ &= H_0|\phi_a^{(0)}\rangle + \lambda H_0|\phi_a^{(1)}\rangle + \lambda^2 H_0|\phi_a^{(2)}\rangle \\ &\quad + \lambda V|\phi_a^{(0)}\rangle + \lambda^2 V|\phi_a^{(1)}\rangle + \lambda^3 V|\phi_a^{(2)}\rangle \\ &= E_a^{(0)}|\phi_a^{(0)}\rangle + E_a^{(0)}\lambda|\phi_a^{(1)}\rangle + E_a^{(0)}\lambda^2|\phi_a^{(2)}\rangle \\ &\quad + \lambda E_a^{(1)}|\phi_a^{(0)}\rangle + \lambda^2 E_a^{(1)}|\phi_a^{(1)}\rangle + \lambda^3 E_a^{(1)}|\phi_a^{(2)}\rangle \\ &\quad + \lambda^2 E_a^{(2)}|\phi_a^{(0)}\rangle + \lambda^3 E_a^{(2)}|\phi_a^{(1)}\rangle + \lambda^4 E_a^{(2)}|\phi_a^{(2)}\rangle \end{aligned} \quad (8.9)$$

Equate the coefficients of λ on both sides and ignore terms with coefficients of λ^3 or greater powers:

$$\lambda^0 \Rightarrow H_0|\phi_a^{(0)}\rangle = E_a^{(0)}|\phi_a^{(0)}\rangle \quad (8.10)$$

This is just the unperturbed system as expected.

$$\lambda^1 \Rightarrow H_0|\phi_a^{(1)}\rangle + V|\phi_a^{(0)}\rangle = E_a^{(0)}|\phi_a^{(1)}\rangle + E_a^{(1)}|\phi_a^{(0)}\rangle \quad (8.11)$$

$$\lambda^2 \Rightarrow H_0|\phi_a^{(2)}\rangle + V|\phi_a^{(1)}\rangle = E_a^{(0)}|\phi_a^{(2)}\rangle + E_a^{(1)}|\phi_a^{(1)}\rangle + E_a^{(2)}|\phi_a^{(0)}\rangle \quad (8.12)$$

To begin with, lets find the change in energy due to a first order perturbation; multiply both sides of Eq 8.11 by $\langle\phi_a^{(0)}|$:

$$\langle\phi_a^{(0)}|H_0|\phi_a^{(1)}\rangle + \langle\phi_a^{(0)}|V|\phi_a^{(0)}\rangle = \langle\phi_a^{(0)}|E_a^{(0)}|\phi_a^{(1)}\rangle + \langle\phi_a^{(0)}|E_a^{(1)}|\phi_a^{(0)}\rangle \quad (8.13)$$

In the first term, we can act with H_0 on the bra $\langle\phi_a^{(0)}|$:

$$E_a^{(0)}\langle\phi_a^{(0)}|\phi_a^{(1)}\rangle + \langle\phi_a^{(0)}|V|\phi_a^{(0)}\rangle = E_a^{(0)}\langle\phi_a^{(0)}|\phi_a^{(1)}\rangle + E_a^{(1)} \quad (8.14)$$

Using the ortho-normality of the bra-kets:

$$E_a^{(1)} = \langle\phi_a^{(0)}|V|\phi_a^{(0)}\rangle \quad (8.15)$$

This is the *first order* change in energy due to the perturbation. It is the expectation value of the perturbation potential, which is intuitively pleasing. Now lets compute the second order change in energy by multiplying Eq 8.12 by $\langle\phi_a^{(0)}|$:

$$\langle\phi_a^{(0)}|H_0|\phi_a^{(2)}\rangle + \langle\phi_a^{(0)}|V|\phi_a^{(1)}\rangle = \langle\phi_a^{(0)}|E_a^{(0)}|\phi_a^{(2)}\rangle + \langle\phi_a^{(0)}|E_a^{(1)}|\phi_a^{(1)}\rangle + \langle\phi_a^{(0)}|E_a^{(2)}|\phi_a^{(0)}\rangle \quad (8.16)$$

$$E_a^{(0)}\langle\phi_a^{(0)}|\phi_a^{(2)}\rangle + \langle\phi_a^{(0)}|V|\phi_a^{(1)}\rangle = E_a^{(0)}\langle\phi_a^{(0)}|\phi_a^{(2)}\rangle + E_a^{(1)}\langle\phi_a^{(0)}|\phi_a^{(1)}\rangle + E_a^{(2)} \quad (8.17)$$

Once again using the ortho-normality properties:

$$E_a^{(2)} = \langle\phi_a^{(0)}|V|\phi_a^{(1)}\rangle - E_a^{(1)}\langle\phi_a^{(0)}|\phi_a^{(1)}\rangle \quad (8.18)$$

This is the second order change in energy, however it is in terms of $|\phi_a^{(0)}\rangle$ and $|\phi_a^{(1)}\rangle$ and $|\phi_a^{(1)}\rangle$ is unknown. Now we use the fact that the eigenkets $|\phi_k^{(0)}\rangle$ form a complete basis set, therefore it is possible to expand $|\phi_a^{(1)}\rangle$ in terms of $|\phi_k^{(0)}\rangle$:

$$|\phi_a^{(1)}\rangle = \sum_k a_k |\phi_k^{(0)}\rangle \quad (8.19)$$

Substitute this into Eq 8.11:

$$H_0 \sum_k a_k |\phi_k^{(0)}\rangle + V |\phi_a^{(0)}\rangle = E_a^{(0)} \sum_k a_k |\phi_k^{(0)}\rangle + E_a^{(1)} |\phi_a^{(0)}\rangle \quad (8.20)$$

Now multiply both sides by $\langle \phi_j^{(0)} |$ as we have already multiplied by $\langle \phi_a^{(0)} |$, hence $\langle \phi_j^{(0)} | \neq \langle \phi_a^{(0)} |$:

$$\langle \phi_j^{(0)} | H_0 | \sum_k |\phi_k^{(0)}\rangle + \langle \phi_j^{(0)} | V | \phi_a^{(0)}\rangle = \langle \phi_j^{(0)} | E_a^{(0)} | \sum_k a_k |\phi_k^{(0)}\rangle + \langle \phi_j^{(0)} | E_a^{(1)} | \phi_a^{(0)}\rangle \quad (8.21)$$

$$\sum_k E_k^{(0)} a_k \langle \phi_j^{(0)} | \phi_k^{(0)}\rangle + \langle \phi_j^{(0)} | V | \phi_a^{(0)}\rangle = \sum_k a_k E_a^{(0)} \langle \phi_j^{(0)} | \phi_k^{(0)}\rangle + E_a^{(1)} \langle \phi_j^{(0)} | \phi_a^{(0)}\rangle \quad (8.22)$$

$$a_j E_j^{(0)} + \langle \phi_j^{(0)} | V | \phi_a^{(0)}\rangle = a_j E_a^{(0)} \quad (8.23)$$

Therefore:

$$a_{j(\neq a)} = \frac{\langle \phi_j^{(0)} | V | \phi_a^{(0)}\rangle}{E_a^{(0)} - E_j^{(0)}} \quad (8.24)$$

Substitute this back into the expansion of $|\phi_a^{(1)}\rangle$:

$$|\phi_a^{(1)}\rangle = \sum_{j(\neq a)} \frac{\langle \phi_j^{(0)} | V | \phi_a^{(0)}\rangle}{E_a^{(0)} - E_j^{(0)}} |\phi_j^{(0)}\rangle \quad (8.25)$$

This is the first order perturbation in state. In the derivation above we have found $a_{j(\neq a)}$, but what about a_a ? Well if the expansion term for a_a is written out:

$$|\phi_a^{(1)}\rangle = a_a |\phi_a^{(0)}\rangle \quad (8.26)$$

However the way $|\phi_a^{(0)}\rangle$ has been defined in the unperturbed system means for the overall wavefunction $|\psi\rangle$ to be normalised a_a must be zero. Now the first order perturbation in state can be substituted into Eq 8.18:

$$\begin{aligned} E_a^{(2)} &= \langle \phi_a^{(0)} | V | \sum_{j \neq a} \frac{\langle \phi_j^{(0)} | V | \phi_a^{(0)}\rangle}{E_a^{(0)} - E_j^{(0)}} |\phi_j^{(0)}\rangle - E_a^{(1)} \langle \phi_j^{(0)} | \sum_{j \neq a} \frac{\langle \phi_j^{(0)} | V | \phi_a^{(0)}\rangle}{E_a^{(0)} - E_j^{(0)}} |\phi_j^{(0)}\rangle \\ &= \sum_{j \neq a} \frac{\langle \phi_a^{(0)} | V | \phi_j^{(0)}\rangle \langle \phi_j^{(0)} | V | \phi_a^{(0)}\rangle}{E_a^{(0)} - E_j^{(0)}} \\ &= \sum_{j \neq a} \frac{|\langle \phi_j^{(0)} | V | \phi_a^{(0)}\rangle|^2}{E_a^{(0)} - E_j^{(0)}} \end{aligned} \quad (8.27)$$

This is the second order change in energy. Lets summarise the results so far:

$$\begin{aligned} E_a^\psi &= E_a^{(0)} + \lambda E_a^{(1)} + \lambda^2 E_a^{(2)} + \dots \\ &= E_a^{(0)} + \langle \phi_a^{(0)} | \lambda V | \phi_a^{(0)}\rangle + \sum_{j \neq a} \frac{|\langle \phi_j^{(0)} | \lambda V | \phi_a^{(0)}\rangle|^2}{E_a^{(0)} - E_j^{(0)}} \end{aligned} \quad (8.28)$$

$$\begin{aligned}
|\psi_a\rangle &= |\phi_a^{(0)}\rangle + \lambda|\phi_a^{(1)}\rangle + \dots \\
&= |\phi_a^{(0)}\rangle + \sum_{j \neq a} \frac{\langle \phi_a^{(0)} | \lambda V | \phi_j^{(0)} \rangle}{E_a^{(0)} - E_j^{(0)}} |\phi_j^{(0)}\rangle
\end{aligned} \tag{8.29}$$

2. Particle in a box

Consider a particle trapped in a one dimensional box of length d , that is perturbed by a small potential of the form:

$$\begin{aligned}
V_{\text{box}}(x) &= 0 : 0 < x < d \\
&= \infty : \text{Otherwise} \\
\lambda V(x) &= \epsilon : 0 < x < b < d \\
&= 0 : \text{Otherwise}
\end{aligned} \tag{8.30}$$

The Hamiltonian for this system is:

$$H = H_0 + \lambda V(x) \tag{8.31}$$

where:

$$H_0 = \frac{p_x^2}{2m} + V_{\text{box}}(x) \tag{8.32}$$

For the unperturbed Hamiltonian the solutions are:

$$\phi_n^{(0)}(x) = \langle x | \phi_n^{(0)} \rangle = \sqrt{\frac{2}{d}} \sin \frac{n\pi x}{d} \tag{8.33}$$

$$E_n^{(0)} = \frac{1}{2m} \left(\frac{\hbar n\pi}{d} \right)^2 \tag{8.34}$$

$\phi_n^{(0)}(x)$ are the complete set of energy eigenstates. The first order change in energy is given by:

$$\begin{aligned}
E_n^{(1)} &= \langle \phi_n^{(0)} | \lambda V | \phi_n^{(0)} \rangle \\
&= \epsilon \int_0^b dx \left(\sqrt{\frac{2}{d}} \sin \frac{n\pi x}{d} \right)^\dagger \left(\sqrt{\frac{2}{d}} \sin \frac{n\pi x}{d} \right) \\
&= \frac{2\epsilon}{d} \int_0^b \sin^2 \frac{n\pi x}{d} dx \\
&= \epsilon \left(\frac{b}{d} - \frac{\sin \frac{2n\pi b}{d}}{2n\pi} \right)
\end{aligned} \tag{8.35}$$

Now lets calculate the first order change in the state. Using the equation calculated previously for the coefficients:

$$a_{j(\neq a)} = \frac{\langle \phi_j^{(0)} | V | \phi_a^{(0)} \rangle}{E_a^{(0)} - E_j^{(0)}} \tag{8.36}$$

First lets calculate the matrix element:

$$\begin{aligned}
\langle \phi_j^{(0)} | \lambda V | \phi_a^{(0)} \rangle &= \frac{2\epsilon}{d} \int_0^b \sin \frac{m\pi x}{d} \sin \frac{n\pi x}{d} dx \\
&= \frac{2\epsilon}{d} \int_0^b \frac{1}{2} \left(\cos \frac{\pi x}{d} (m-n) - \cos \frac{\pi x}{d} (m+n) \right) dx \\
&= \frac{\epsilon}{d} \int_0^b \cos \frac{\pi x}{d} (m-n) - \cos \frac{\pi x}{d} (m+n) dx \\
&= \frac{\epsilon}{d} \left[\frac{1}{\frac{\pi}{d}(m-n)} \sin \frac{\pi x}{d} (m-n) - \frac{1}{\frac{\pi}{d}(m+n)} \sin \frac{\pi x}{d} (m+n) \right]_0^b \\
&= \frac{\epsilon}{d} \left(\frac{1}{\frac{\pi}{d}(m-n)} \sin \frac{\pi b}{d} (m-n) - \frac{1}{\frac{\pi}{d}(m+n)} \sin \frac{\pi b}{d} (m+n) \right)
\end{aligned} \tag{8.37}$$

Now all that needs to be done is substituting in for $E_a^{(0)}, E_j^{(0)}$:

$$E_a^{(0)} = \frac{1}{2m} \left(\frac{\hbar a \pi}{d} \right)^2 \quad E_j^{(0)} = \frac{1}{2m} \left(\frac{\hbar j \pi}{d} \right)^2 \tag{8.38}$$

Substitute these ingredients into Eq 8.36:

$$a_{j(\neq a)} = \frac{\frac{\epsilon}{d} \left(\frac{1}{\frac{\pi}{d}(m-n)} \sin \frac{\pi b}{d} (m-n) - \frac{1}{\frac{\pi}{d}(m+n)} \sin \frac{\pi b}{d} (m+n) \right)}{\frac{1}{2m} \left(\frac{\hbar a \pi}{d} \right)^2 - \frac{1}{2m} \left(\frac{\hbar j \pi}{d} \right)^2} \tag{8.39}$$

So the first order change in state is:

$$|\phi_n^{(1)}\rangle = \sum_{j(\neq a)} \frac{\frac{\epsilon}{d} \left(\frac{1}{\frac{\pi}{d}(m-n)} \sin \frac{\pi b}{d} (m-n) - \frac{1}{\frac{\pi}{d}(m+n)} \sin \frac{\pi b}{d} (m+n) \right)}{\frac{1}{2m} \left(\frac{\hbar a \pi}{d} \right)^2 - \frac{1}{2m} \left(\frac{\hbar j \pi}{d} \right)^2} |\phi_a^{(0)}\rangle \tag{8.40}$$

3. Quadratic Stark effect

Lets apply the framework of time independent perturbation theory for a hydrogen atom that has been placed in a *weak* electric field:

$$E = -\nabla \phi \tag{8.41}$$

Electric fields can be considered *weak* inside an atom for strengths up to $5.11 \times 10^{11} \text{Vm}^{-1}$. It is very rare that one comes across fields with such high values in everyday life, therefore perturbation theory should give a good estimate of the shifts in energy levels that ordinary fields effect.

By definition of the electrostatic potential ϕ , the applied field changes the energy of the atom by:

$$\delta E = e (\phi(\vec{x}_e) - \phi(\vec{x}_p)) \tag{8.42}$$

where \vec{x}_p and \vec{x}_e are the position vectors of the proton and electron, respectively. We assume that the field changes very little on the scale of the atom, and lets define:

$$e \equiv \vec{x}_e - \vec{x}_p \tag{8.43}$$

Then we may write:

$$\delta E \approx -e\vec{r} \cdot \nabla \phi = e\vec{r} \cdot E \tag{8.44}$$

Note that this change in energy has the form of an electric dipole ($e\vec{r}$ has units of the electric dipole moment) and indeed this is what the electric field is inducing. Suppose the system is set

up such that \vec{E} is parallel to the z-axis and use notation $\epsilon = |\vec{E}|$; the change in energy can now be written as:

$$\nabla E = e\epsilon_z \quad (8.45)$$

Suppose the atom is in its ground state $|100\rangle$, where the ket vector is using the notation $|nlm\rangle$ (i.e the quantum numbers that the state is in). The 1st order change in energy to this ground state is given by the matrix element:

$$E_b = e\epsilon\langle 100|z|100\rangle \quad (8.46)$$

As shown in the section of the dipole matrix elements in the hydrogen atom chapter, the ground state is symmetric and therefore the matrix element integrates to zero (proved using parity transformations). In general, if a perturbation takes state $|a\rangle$ into a state that is orthogonal to $|a\rangle$, the first order correction to energy in this state $|a\rangle$ is zero. Therefore lets calculate the second order change in energy:

$$E_c = e^2\epsilon^2 \sum_{n=2}^{\infty} \sum_{l < n, |m| \leq l} \frac{\langle 100|z|nlm\rangle\langle nlm|z|100\rangle}{E_1 - E_n} \quad (8.47)$$

Symmetry considerations make it possible to simplify this sum dramatically. Since $[L_z, L] = 0$, $z|nlm\rangle$ is an eigenfunction of L_z with eigenvalue m , and therefore is orthogonal to the ground state unless $m = 0$ (i.e the matrix element will be zero). Now we can delete all the even values of l from the sum over l because the matrix elements of an odd-parity operator between states of the same parity vanish (i.e under parity $|100\rangle \rightarrow +|100\rangle$ which means $|nlm\rangle \rightarrow -|nlm\rangle$). In fact doing the integrals for the matrix elements shows that $l = 1$ is the only allowed value. So the final answer is:

$$E_{100}^{(2)} = (e\epsilon)^2 \sum_{n \geq 2} \frac{|\langle n10|z|100\rangle|^2}{E^2(0)_{100} - E_{n10}^{(0)}} \quad (8.48)$$

4. Degenerate perturbation theory and linear stark affect

In second order perturbation theory, the denominator contains the energy terms $E_k^{(0)} = E_a^{(0)}$. If there are two states that carry k and a quantum numbers (or sets of quantum numbers), but have the same energy, $E_k^{(0)} = E_a^{(0)}$, then the denominator goes to zero and the equation becomes singular. Of course in reality this does not happen, therefore one needs a different framework to describe situations like this, and this is called *Degenerate* time independent perturbation theory.

In the previous section, the ground state of the hydrogen atom $|100\rangle$ was considered. Now consider the shift in energy of the $|200\rangle$ state of hydrogen under the influence of a weak magnetic field. The energies of the states in the hydrogen atom only depend on the n quantum number. This means the state $|200\rangle$ has the unperturbed energy $E_{210}^{(0)} = E_{200}^{(0)}$. Furthermore the matrix element is:

$$A \equiv \langle 210|z|200\rangle \neq 0 \quad (8.49)$$

thus the perturbation mixes up states of the same energy. As stated before, this would lead to a singularity in the non-degenerate framework. The error that has led to this singularity, is to assume at the outset that a small disturbance produces a small response in the equations. The singularities first arise in the equation for coefficients, a_k . Recall that this was part of calculating the change in the state due to the perturbation. The idea behind this assumption is that a small perturbation in energy will induce a small change in the wavefunction of the state. This singularity is showing that no change in energy is changing the state by an arbitrarily large magnitude. This is understandable as the states are degenerate in this case, i.e they have the same energy. In other words no change in energy is required to change the state.

Since it takes no energy to connect between these states, simply by just keeping these states in computing the perturbed energy. In matrix notation:

$$\begin{aligned}
H_\lambda &= H_0 + e\epsilon z \\
&= \begin{pmatrix} \langle 200|H_0|200\rangle & \langle 200|H_0|210\rangle \\ \langle 210|H_0|200\rangle & \langle 210|H_0|210\rangle \end{pmatrix} + \begin{pmatrix} \langle 200|e\epsilon z|200\rangle & \langle 200|e\epsilon z|210\rangle \\ \langle 210|e\epsilon z|200\rangle & \langle 210|e\epsilon z|210\rangle \end{pmatrix} \\
&= \begin{pmatrix} E_2 & 0 \\ 0 & E_2 \end{pmatrix} + e\epsilon \begin{pmatrix} 0 & A^* \\ A & 0 \end{pmatrix} \\
&= \begin{pmatrix} E_2^{(0)} & e\epsilon A^* \\ e\epsilon A & E_2^{(0)} \end{pmatrix} \tag{8.50}
\end{aligned}$$

Finding the perturbed energies means solving the TISE in matrix form:

$$\sum_b H_{ab}\nu_b = \lambda\nu_b = E\nu_b \tag{8.51}$$

Note that the eigenvalues λ are the energy values, E . For a 2 component eigenvector ν with components ν_b . This involves solving:

$$\det(H - E\mathbb{I}) = 0 = \begin{vmatrix} E_{200}^{(0)} - E & e\epsilon A^* \\ e\epsilon A & E_{200}^{(0)} - E \end{vmatrix} \tag{8.52}$$

So we get:

$$(E_{200}^{(0)} - E)^2 - e^2\epsilon^2 A^* A = 0 \tag{8.53}$$

So the energy eigenvalues are:

$$E_\pm = E_{200}^{(0)} \pm \sqrt{A^* A} e\epsilon \tag{8.54}$$

the eigenfunctions are:

$$\nu_\pm = \frac{1}{\sqrt{2}} (|200\rangle + |210\rangle) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \tag{8.55}$$

From electromagnetism it is known that the total dipole moment consists of a permanent dipole + induced dipole:

$$\vec{p} = \vec{p}_0 + \alpha\vec{E} \tag{8.56}$$

α represents the polarizability of the atom in consideration. The energy change is the usual:

$$\nabla E = -\vec{p} \cdot \vec{E} \tag{8.57}$$

In the quadratic Stark effect there is no linear part in \vec{E} as the ground state is symmetric and hence has no permanent dipole, \vec{p}_0 . This explains why the change in energy only comes from the quadratic term, E^2 :

$$\delta E = -\alpha|E|^2 \tag{8.58}$$

We have just seen that in the linear stark effect there is no linear \vec{E} part which means the eigenstates $|\nu_\pm\rangle$ must have a permanent dipole moment such that:

$$\delta E = -\vec{p}_0 \cdot \vec{E} \tag{8.59}$$

5. Effects of magnetic field on Hydrogen-like atoms

When the hydrogen like atom is placed in a magnetic field, there are three perturbations to consider:

- (1) Effect of B field on orbital angular momentum.
- (2) Effect of B field on intrinsic spin angular momentum.
- (3) Relativistic spin-orbit coupling.

5.1. Orbital angular momentum. For a particle of charge Q , moving in external magnetic field \vec{B} , the momentum becomes:

$$\vec{p} \rightarrow \vec{p} - Q\vec{A} \quad (8.60)$$

where:

$$\vec{B} = \nabla \times \vec{A} \quad (8.61)$$

Thus the kinetic energy of the atom takes the form:

$$\begin{aligned} H_{KE} &= \frac{1}{2m} (\vec{p} + e\vec{A})^2 \\ &= \frac{1}{2m} (|\vec{p}|^2 + 2e\vec{A} \cdot \vec{p} + e^2|\vec{A}|^2) \end{aligned} \quad (8.62)$$

the first implication of this equation is that one can drop the \vec{A}^2 term as its energy will be small compared to the potential energy term, for experimentally relevant \vec{B} strength. In experiment, $\vec{B}(x)$ is essentially constant over the size of the atom. This reduces \vec{A} to the form:

$$\vec{A} = \frac{1}{2} \vec{B} \times \vec{r} \quad (8.63)$$

To check this is true, it can be substituted back into Eq . The kinetic energy transforms under the \vec{B} as:

$$\begin{aligned} H_{KE} &= -\frac{\hbar^2}{2m} \nabla^2 + \frac{e}{2m} (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) + \frac{e^2 \vec{A}^2}{2m} \\ &= -\frac{\hbar^2}{2m} \nabla^2 + \frac{e}{2m} (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) \end{aligned} \quad (8.64)$$

Substitute:

$$\vec{A} = \frac{1}{2} \vec{B} \times \vec{r} \quad (8.65)$$

This gives:

$$\begin{aligned} H_{KE} &\approx -\frac{\hbar^2}{2m} \nabla^2 + \frac{e}{4m} (\vec{p} \cdot \vec{B} \times \vec{r} + \vec{B} \times \vec{r} \cdot \vec{p}) \\ &\approx -\frac{\hbar^2}{2m} \nabla^2 + \frac{e}{2m} (\vec{B} \cdot (\vec{r} \times \vec{p})) \\ &\approx -\frac{\hbar^2}{2m} \nabla^2 + \frac{e}{2m} \vec{B} \cdot \vec{L} \end{aligned} \quad (8.66)$$

Note that we can move the p as the operator around as \vec{p} and \vec{r} commute and we use the vector triple product identity. Thus the addition to the Hamiltonian due to the orbital angular momentum's interaction with the \vec{B} field is given by:

$$\begin{aligned} \delta H_L &= \frac{e}{2m} \vec{B} \cdot \vec{L} \\ &= \frac{\mu_B}{\hbar} \vec{B} \cdot \vec{L} \end{aligned} \quad (8.67)$$

where μ_B is the *Bohr magneton*:

$$\mu_B = \frac{e\hbar}{2m} \quad (8.68)$$

Classically, the circulating electron has a magnetic momentum of $\frac{eL}{2m}$.

5.2. Spin angular momentum. Electron also has an intrinsic angular momentum, \vec{S} which makes a separate contribution to the Hamiltonian (note there is no derivation for this, as spin is just an intrinsic property of the electron):

$$s(\vec{B}) = \frac{e}{m} \vec{B} \cdot \vec{S} = \frac{\mu_B}{\hbar} \vec{B} \cdot \vec{S} \quad (8.69)$$

5.3. Relativistic effects: spin-orbit coupling. The Schrodinger equation is a non-relativistic equation of motion. The relativistic equation of motion is the *Dirac equation*, from which there is an extra term that couples the orbital and spin angular momentum:

$$\begin{aligned} \delta H_{LS} &= \xi(r) \vec{L} \cdot \vec{S} \\ &= \frac{1}{2m^2 c^2} \frac{Ze^2}{4\pi\epsilon r^3} \vec{L} \cdot \vec{S} \end{aligned} \quad (8.70)$$

By combining all three effects and taking the magnetic field to be along the z direction, we can obtain the final Hamiltonian:

$$H = H_0 + \frac{\mu_B}{\hbar} (L_z + 2S_z) \vec{B} + \frac{1}{2m^2 c^2} \frac{Ze^2}{4\pi\epsilon} \frac{1}{r^3} \vec{L} \cdot \vec{S} \quad (8.71)$$

where H_0 :

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon r} \quad (8.72)$$

The idea now is to study the solutions of this Hamiltonian for different regimes (limiting cases) as it is very difficult to find general solutions.

5.3.1. *Strong field: Zeeman effect.* When \vec{B} is very large, one can ignore the spin-orbit coupling term, making the Hamiltonian:

$$H \approx H_0 + \frac{\mu_B}{\hbar} (L_z + 2S_z) \vec{B} \quad (8.73)$$

the complete set of quantum numbers for this state of a single electron atom are n, l, m_s :

$$H_0 |n, l, m_l\rangle = E_0 |n, l, m_l\rangle \quad (8.74)$$

Since the electron is a fermion it carries spin $\frac{1}{2}$, and therefore carries spin quantum numbers. In general these spin quantum numbers will not play a part in the interaction, however in the presence of a \vec{B} field they become important. Thus the state can be labeled as $|n, l, m_l, s, m_s\rangle$, with the following relations:

$$\begin{aligned} H_0 |n, l, m_l, s, m_s\rangle &= E_0 |n, l, m_l, s, m_s\rangle \\ L^2 |n, l, m_l, s, m_s\rangle &= l(l+1)\hbar^2 |n, l, m_l, s, m_s\rangle \\ S^2 |n, l, m_l, s, m_s\rangle &= s(s+1)\hbar^2 |n, l, m_l, s, m_s\rangle \\ L_z |n, l, m_l, s, m_s\rangle &= m_l \hbar |n, l, m_l, s, m_s\rangle \\ S_z |n, l, m_l, s, m_s\rangle &= m_s \hbar |n, l, m_l, s, m_s\rangle \end{aligned} \quad (8.75)$$

Now the perturbation $\delta H(\vec{B}) = \frac{\mu_B}{\hbar} (L_z + 2S_z) \vec{B}$ commutes with H_0 :

$$[H_0, \delta H(\vec{B})] = 0 \quad (8.76)$$

The change in energy due to the $\delta H(\vec{B})$ perturbation:

$$\begin{aligned}
\frac{\mu_B}{\hbar} \langle n, l, m_l, s, m_s | L_z + 2S_z | n, l, m_l, s, m_s \rangle \vec{B} &= E_{n, m_l, m_s} \\
&= (\hbar m_l + 2m_s \hbar) \frac{\mu_B}{\hbar} \\
&= \mu_B (m_l + 2m_s) \vec{B}
\end{aligned} \tag{8.77}$$

So we see that the \vec{B} field splits the degeneracies of the spin eigenvalues and for different l quantum numbers. Now we add back the spin orbit term using first order perturbation theory. The change in the Hamiltonian due to the spin orbit coupling is:

$$\delta H_{SL} = \xi(r) \vec{L} \cdot \vec{S} \tag{8.78}$$

the change in energy due to this perturbation is given by:

$$\delta E_{SL} = \langle n, l, m_l, s, m_s | \xi(r) \vec{L} \cdot \vec{S} | n, l, m_l, s, m_s \rangle \tag{8.79}$$

Recall that the eigenstates of H_0 , $|n, l, m_l, s, m_s\rangle$ factor out into a radial part, $R_{n,l}(r)$ and an angular part Y_{lm_l} and spin parts. This means the matrix element can be separated and treated individually; first the angular part:

$$\begin{aligned}
\langle l, m_l, s, m_s | \vec{L} \cdot \vec{S} | l, m_l, s, m_s \rangle &= \langle l, m_l, s, m_s | L_z, S_z | l, m_l, s, m_s \rangle \\
&= m_l m_s \hbar^2
\end{aligned} \tag{8.80}$$

this is because:

$$\langle l, m_l, s, m_s | L_x | l, m_l, s, m_s \rangle = \langle l, m_l, s, m_s | L_y | l, m_l, s, m_s \rangle = 0 \tag{8.81}$$

Now the radial part (for $l > 0$, otherwise, this term is zero):

$$\lambda_{nl} = \hbar^2 \langle n, l | \xi(r) | n, l \rangle = \hbar^2 \int_0^\infty dr r^2 R_{nl}(r) \xi(r) R_{nl}(r) = - \left(\frac{e^2}{4\pi\epsilon\hbar c} \right)^2 \frac{Z^2}{r} \left(\frac{E_n^{(0)}}{l(l + \frac{1}{2})(l + 1)} \right)$$

Collecting all the energy terms:

$$E_{n, l, m_l, s, m_s} = \underbrace{E_n^{(0)}}_{\text{Unperturbed}} + \underbrace{\mu_B B_z (m_l + 2m_s)}_{\text{Spin and orbital angular momentum}} + \underbrace{\lambda_{nl} m_l m_s}_{\text{Paschen-Beck effect}} \tag{8.82}$$

5.4. Weak field Zeeman effect. In this case the angular and spin momentum parts are treated as perturbations and group the spin-orbit term with the unperturbed H_0 :

$$\begin{aligned}
\vec{L} \cdot \vec{S} &= \frac{1}{2} \left((\vec{L} + \vec{S})^2 - L^2 - S^2 \right) \\
&= \frac{1}{2} (J^2 - L^2 - S^2)
\end{aligned} \tag{8.83}$$

where:

$$J = L + S \tag{8.84}$$

With the total angular momentum being introduced, it is better to work in an alternate description of states:

$$|n, j, m_j, l, s\rangle \tag{8.85}$$

This works as the following operators commute:

$$\begin{aligned}
[J^2, \vec{L} \cdot \vec{S}] &= 0 \\
[J_z, \vec{L} \cdot \vec{S}] &= 0 \\
[L^2, \vec{L} \cdot \vec{S}] &= 0 \\
[S^2, \vec{L} \cdot \vec{S}] &= 0
\end{aligned} \tag{8.86}$$

Sp these are all 'good' quantum numbers, (of course they all also commute with the Hamiltonian). These states satisfy:

$$J^2 |n, l, m_j, l, s\rangle = j(j+1)\hbar^2 |n, j, m_j, j, s = \frac{1}{2}\rangle \tag{8.87}$$

$$J_z |n, j, m_j, l, s = \frac{1}{2}\rangle = m_j \hbar |n, j, m_j, l, s = \frac{1}{2}\rangle \tag{8.88}$$

Now lets compute the energy from the spin orbit term (of course we already know the unperturbed energies!):

$$\langle n, j, m_j, l, s | \xi(r) \vec{L} \cdot \vec{S} | n, j, m_j, l, s \rangle = \delta E_{njl} \tag{8.89}$$

Once again separate out the angular and radial part. For the angular part it is useful to write:

$$\vec{L} \cdot \vec{S} = \frac{1}{2} (J^2 - L^2 - S^2) \tag{8.90}$$

Substitute this into Eq 8.89:

$$\langle n, j, m_j, l, s | \frac{1}{2} (J^2 - L^2 - S^2) | n, j, m_j, l, s \rangle = \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1)) \tag{8.91}$$

with $s = \frac{1}{2}$. The radial part is the same as the previous part:

$$\begin{aligned}
\delta E_{njl} &= \langle n, l, j, m_j | \xi(r) \vec{L} \cdot \vec{S} | n, l, j, m_j \rangle \\
&= \frac{1}{2} \hbar^2 \left(j(j+1) - l(l+1) - \frac{3}{4} \right) \frac{1}{2m^2 c^2} \frac{Ze^2}{4\pi\epsilon} \frac{Z^3}{a_0^3 n^3 l(l + \frac{1}{2})(l+1)}
\end{aligned} \tag{8.92}$$

The perturbation due to a weak magnetic field is given by the matrix element:

$$\begin{aligned}
\delta E_{m_j} &= \langle n, l, j, m_j | \frac{\mu_B}{\hbar} (L_z + 2S_z) B | n, l, j, m_j \rangle \\
&= g_L \mu_B m_j B
\end{aligned} \tag{8.93}$$

where:

$$g_L = \frac{1 + j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \tag{8.94}$$

Collecting all the energies for the weak \vec{B} field gives:

$$\begin{aligned}
E_{n,j,m_j,l} &= E_n^{(0)} + \delta E_{njl} + \delta E_{m_j} \\
&= E_n^{(0)} + \frac{1}{2} \hbar^2 \left(j(j+1) - l(l+1) - \frac{3}{4} \right) \frac{1}{2m^2 c^2} \frac{Ze^2}{4\pi\epsilon} \frac{Z^3}{a_0^3 n^3 l(l + \frac{1}{2})(l+1)} \\
&+ \left(1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right) \mu_B m_j B
\end{aligned} \tag{8.95}$$

6. Variational method

This method does not require a small perturbation to a known problem, unlike the perturbation theory. The ket ingredient for this method is a 'good' guess for a trial wavefunction. The problem that needs to be solved is:

$$H|\psi_i\rangle = E_i|\psi_i\rangle \quad (8.96)$$

This defines the energy eigenstates and eigenvalues for the Hamiltonian H . Since H is Hermitian the eigenvectors must form a complete orthonormal basis:

$$\langle\psi_i|\psi_j\rangle = \delta_{ij} \quad (8.97)$$

These states or energies are unknown, Lets guess a state ϕ_{var} which can be expanded in the basis of the eigenstates of H :

$$\psi_{var} = \sum_i c_i |\psi_i\rangle \quad (8.98)$$

The expectation value of the energy in state ϕ_{var} is:

$$\langle E_{var} \rangle = \frac{\langle\phi_{var}|H|\phi_{var}\rangle}{\langle\phi_{var}|\phi_{var}\rangle} = \frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} \quad (8.99)$$

Now subtract the ground state energy from both sides:

$$\begin{aligned} E_{var} - E_0 &= \frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} - E_0 \\ &= \frac{\sum_i |c_i|^2 E_i - |c_i|^2 E_0}{\sum_i |c_i|^2} \\ &= \frac{\sum_i |c_i|^2 (E_i - E_0)}{\sum_i |c_i|^2} \end{aligned} \quad (8.100)$$

By definition $E_i \geq E_0$ (as E_0 is the ground state), it is equal if $E_i = E_0$, i.e the guess was perfect. This means every term on the R.H.S is positive, and thus the L.H.S is positive. The implication of this is that any approximate trial wavefunction gives an energy that is always above (or at best equal to) the true ground state energy.

The strategy now is to consider the trial wavefunction being dependent on a parameter a . The E_{var} can be minimised w.r.t a to get the *best approximation* to the ground state energy:

$$\frac{dE_{var}(a)}{da} = 0 \quad (8.101)$$

As an example, consider the trial wavefunction is infact the ground state $|\psi_0\rangle$ with energy E_0 , plus a little bit of some excited state $|\psi_e\rangle$ at energy $E_e(> E_0)$:

$$|\phi_{var}\rangle = \frac{1}{\sqrt{1 + |c_e|^2}} (|\psi_0\rangle + c_e |\psi_e\rangle) \quad (8.102)$$

The variational energy in this state is:

$$\begin{aligned} E_n &= \frac{\langle\phi_{var}|H|\phi_{var}\rangle}{\langle\phi_{var}|\phi_{var}\rangle} \\ &= \frac{(\langle\phi_0| + \langle\psi_e|c_e^*) H (|\psi_0\rangle + c_e |\psi_e\rangle)}{(\langle\phi_0| + \langle\psi_e|c_e^*) (|\psi_0\rangle + c_e |\psi_e\rangle)} \\ &= \frac{E_0 + E_e |c_e|^2}{1 + |c_e|^2} \\ &\approx E_0 + |c_e|^2 (E_e - E_0) (> E_0) \end{aligned} \quad (8.103)$$

An important property is that the error in the wavefunction is $\approx |c_e|$ and the error in the energy is $\approx |c_e|^2$.

6.1. Variational method for the simple harmonic oscillator. The Hamiltonian of the usual Harmonic oscillator is:

$$H = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad (8.104)$$

And the eigenvalue equation it obeys is:

$$H|n\rangle = E_n|n\rangle \quad (8.105)$$

Of course in this example, the exact eigenstates and energies are known:

$$E_n = (n + \frac{1}{2})\hbar\omega \quad (8.106)$$

$$\phi_0(x) \approx e^{-\frac{x^2}{a^2}} \quad (8.107)$$

Lets just check that this method works by pretending the eigenfunctions are not known. Suppose that the only information one has is that the ground state is even in x , so lets try a normalised wavefunction that is also even in x :

$$\phi_{var}(x, a) = \sqrt{\frac{2a^3}{\pi}} \frac{1}{x^2 + a^2} \quad (8.108)$$

The the variational energy is given by:

$$E_{var}(\phi_{var}(a)) = \langle \phi_{var} | H | \phi_{var} \rangle = \frac{\hbar^2}{2ma^2} + \frac{1}{2}m\omega^2 a^2 \quad (8.109)$$

By the variational principle, the best approximate energy is found by minimising E_{var} w.r.t a :

$$\frac{dE_{var}}{da} = 0 \rightarrow a_{min}^2 = \frac{\hbar}{\sqrt{2}m\omega} \quad (8.110)$$

Substitute this back into the expression of energy yields:

$$E_{var} = \frac{1}{\sqrt{2}}\hbar\omega \quad (8.111)$$

The true ground state energy is $\frac{1}{2}\hbar\omega$, therefore it is seen that indeed $E_{var} > E_0$.

6.2. Ground state of Helium. The Helium atom contains two protons (and 2 neutrons) and two electrons ($Z=2e$). The total Hamiltonian of the Helium atom is of the form:

$$H_{He} = -\frac{\hbar^2}{2m} (\nabla_{r_1}^2 + \nabla_{r_2}^2) - \frac{e^2}{2\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0(r_1 - r_2)} \quad (8.112)$$

the labels 1 and 2 correspond to the two electrons. The last term in the Hamiltonian described the Coulomb interaction between the two electrons. The first two terms are just like two copies of the Hydrogen atom, with the kinetic and Coulomb energies between the nucleus (charge $+2e$) and electrons 1 and 2:

$$H_{He} = H_1 + H_2 + V_{12} \quad (8.113)$$

First consider the simplest case by ignoring the interaction between electrons; the two electron wavefunction will depend on \vec{r}_1 and \vec{r}_2 :

$$\psi(\vec{r}_1, \vec{r}_2) = \phi_a(\vec{r}_1)\phi_b(\vec{r}_2) \quad (8.114)$$

a and b represent the complete set of quantum numbers in each state (n,l,m) . This can be rewritten as:

$$\phi_{var}(\vec{r}_1, \vec{r}_2) = \phi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) = \frac{8}{\pi a_0^3} e^{-\frac{2(\vec{r}_1 + \vec{r}_2)}{a_0}} \quad (8.115)$$

Therefore the variational energy is:

$$E_{var}(\phi_0) = 2E_0^{H(Z=Z)} \quad (8.116)$$

where $E_0^{H(Z=Z)}$ is just the ground state energy for one electron in a hydrogen-like atom of nuclear charge $Z = 2$. Thus the variation energy is just twice the hydrogen-like atom energy. Note that the electrons wavefunctions are products of individual electrons and the energies are summed. This is because without interaction between the electrons and the Helium Hamiltonian just factors out precisely into two copies of the Hamiltonian of the Hydrogen like atom.

However we can do better than this in determining the wavefunctions and energies of the Helium atom with explicitly solving the total Helium Hamiltonian with the Coulomb interaction between the two electrons. The key idea is that each electron will 'see' the total nuclear charge $2e$ partially screened by the other electron. So we can try an effective nuclear charge $Z < 2$:

$$\phi_{var}^0(\vec{r}_1, \vec{r}_2, Z) = \frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 e^{-\frac{(\vec{r}_1 + \vec{r}_2)Z}{a_0}} \quad (8.117)$$

in this case Z becomes the variational parameter and $\phi_{var}^0(\vec{r}_1, \vec{r}_2, Z)$ is the guess solution. Therefore the variational energy is:

$$E_{var} = \langle \phi_{var}(z) | H_{He} | \phi_{var}(z) \rangle \quad (8.118)$$

where:

$$H_{He} = -\frac{\hbar^2}{2m} (\nabla_{\vec{r}_1}^2 + \nabla_{\vec{r}_2}^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (8.119)$$

$$\phi_{var} = \frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 e^{-\frac{(\vec{r}_1 + \vec{r}_2)Z}{a_0}} \quad (8.120)$$

First compute:

$$H_{He}|\phi_{var}(2)\rangle = \left(-\frac{\hbar^2}{2m} (\nabla_{\vec{r}_1}^2 + \nabla_{\vec{r}_2}^2) - \frac{e^2}{2\pi\epsilon} \left(\frac{1}{\vec{r}_1} + \frac{1}{\vec{r}_2} \right) \right) \frac{1}{\pi} \left(\frac{Z}{a_0} \right)^4 e^{-\frac{(\vec{r}_1 + \vec{r}_2)Z}{a_0}} \quad (8.121)$$

Compute each of the components:

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla_{\vec{r}_1}^2 \frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 e^{-\frac{(\vec{r}_1 + \vec{r}_2)Z}{a_0}} &= -\frac{\hbar^2}{2m} \frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 e^{-\frac{(\vec{r}_1 + \vec{r}_2)Z}{a_0}} \\ &= -\frac{\hbar^2}{2m} \frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 \left(-\frac{Z}{a_0} \right)^2 e^{-\frac{(\vec{r}_1 + \vec{r}_2)Z}{a_0}} \\ &= -\frac{\hbar^2 Z^5}{2m\pi a_0^5} e^{-\frac{(\vec{r}_1 + \vec{r}_2)Z}{a_0}} \end{aligned} \quad (8.122)$$

Similarly:

$$-\frac{\hbar^2}{2m} \nabla_{\vec{r}_2}^2 \left(\frac{1}{\pi} \left(\frac{Z}{a_0} \right)^3 e^{-\frac{(\vec{r}_1 + \vec{r}_2)Z}{a_0}} \right) = -\frac{\hbar^2 Z^5}{2m\pi a_0^5} e^{-\frac{(\vec{r}_1 + \vec{r}_2)Z}{a_0}} \quad (8.123)$$

Combining these with the Coulomb terms, we get:

$$H_{He}|\phi_{var}(2)\rangle = \left(-\frac{\hbar^2 Z^5}{m\pi a_0^5} - \frac{e^2 Z^3}{2\pi^2 \epsilon_0 a_0^3} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right) e^{-\frac{(\vec{r}_1 + \vec{r}_2)Z}{a_0}} \quad (8.124)$$

Now the matrix element becomes:

$$\langle \phi_{var} | H_{He} | \phi_{var} \rangle = \int dr_1 \int dr_2 \left(-\frac{\hbar^2 Z^8}{m\pi^2 a_0^8} - \frac{2e^2 Z^6}{4\pi^3 \epsilon_0^6} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right) e^{-\frac{(r_1+r_2)Z}{a_0}} \quad (8.125)$$

The integral is very long and I will just quote the result now:

$$E_{var} = \left(-2Z^2 + \frac{27}{4}Z \right) E_1 \quad (8.126)$$

E_1 is the *Rydberg* energy:

$$E_1 = \frac{m_e e^4}{(4\pi)^3 \epsilon_0^2 \hbar^2} \quad (8.127)$$

To find the best approximation, the energy is minimised w.r.t Z :

$$Z_{min} = \frac{27}{16} \approx 1.688 \quad (8.128)$$

therefore $Z_{min} < Z$ shows that indeed there exists some screening effect.

Time dependent perturbation theory

All the approximate methods of finding wavefunctions and energies that have been used so far, do not have any time dependence in them. This limits the number of solvable problems to a considerable extent, as in real experiments one would generally consider a system in a known state and then at some particular time, a perturbation is applied (like the application of an external \vec{E} field). In fact, perturbations themselves have inherent time-dependence in them, like a sinusoidally varying electric field.

A description of obtaining solutions to time- dependent problems, i.e solutions to the TDSE is now provided. Using these methods, phenomena like scattering, absorption and radiation of photons by atoms and molecules can be explained.

1. Formalism

Start with the unperturbed Hamiltonian with its associated unperturbed energies and eigenstates:

$$H_0|\phi_n^{(0)}\rangle = E_n^{(0)}|\phi_n^{(0)}\rangle \quad (9.1)$$

At time $t = 0$, a perturbation, $\lambda V(t)$, is switches on:

$$H(t < 0) = H_0 \quad \text{Hamiltonian before perturbation} \quad (9.2)$$

$$H(t \geq 0) = H_0 + \lambda V(t) \quad \text{Hamiltonian after perturbation} \quad (9.3)$$

After the perturbation has been applied the TDSE becomes:

$$i\hbar \frac{d}{dt}|\psi(t)\rangle - [H_0 + \lambda V(t)]|\psi(t)\rangle \quad (9.4)$$

which described the time evolution of the states $|\psi(t)\rangle$. Lets assume that the system is prepared initially at $t \leq 0$ to be in the unperturbed eigenstate $|\phi_i^{(0)}\rangle$:

$$H_0|\phi_i^{(0)}\rangle = E_i^{(0)}|\phi_i^{(0)}\rangle \quad (9.5)$$

$$|\psi(t = 0)\rangle \equiv |\phi_i^{(0)}\rangle \quad (9.6)$$

This is an initial condition for the time evolution wavefunction, $\psi(t)$. The objective is to find the probability that due to the perturbation, there is a transition from the initial state $|\phi_i^{(0)}\rangle$ to some other final state $|\phi_f^{(0)}\rangle$. This new state must also be an unperturbed eigenstate of the system with H_0 :

$$H_0|\phi_f^{(0)}\rangle = E_f^{(0)}|\phi_f^{(0)}\rangle \quad (9.7)$$

The probability of this transition is written as:

$$P_{fi}(t) = |\langle \phi_i^{(0)}|\psi(t)\rangle|^2 \quad (9.8)$$

In other words, the expression $\langle \phi_i^{(0)}|\psi(t)\rangle$ is showing that the probability is for the time evolving state $|\psi(t)\rangle$ to be in state $|\phi_i^{(0)}\rangle$ (the projection of $\langle \phi_i^{(0)}|$ on $|\psi(t)\rangle$).

Now we have to use the usual trick that is used wherever there is a complete basis set available. Expand the unknown state $|\psi(t)\rangle$ in this basis:

$$|\psi(t)\rangle = \sum_n c_n(t) |\phi_n^{(0)}\rangle \quad (9.9)$$

Substitute this into the TDSE:

$$i\hbar \frac{d}{dt} \sum_n c_n(t) |\phi_n^{(0)}\rangle = (H_0 + \lambda V(t)) \sum_n c_n(t) |\phi_n^{(0)}\rangle \quad (9.10)$$

Since the $|\phi_n^{(0)}\rangle$'s have no time dependence, they can be brought outside the derivative on the R.H.S:

$$i\hbar \sum_n |\phi_n^{(0)}\rangle \frac{d}{dt} c_n(t) = \sum_n c_n(t) E_n^{(0)} |\phi_n^{(0)}\rangle + \sum_n V(t) c_n(t) |\phi_n^{(0)}\rangle \quad (9.11)$$

Multiply both sides by $\langle \phi_k^{(0)} |$:

$$i\hbar \sum_n \langle \phi_k^{(0)} | \phi_n^{(0)} \rangle \frac{d}{dt} c_n(t) = \sum_n c_n(t) E_n^{(0)} \langle \phi_k^{(0)} | \phi_n^{(0)} \rangle + \sum_n \lambda c_n(t) \langle \phi_k^{(0)} | V(t) | \phi_n^{(0)} \rangle \quad (9.12)$$

$$i\hbar \sum_n \delta_{kn} \frac{d}{dt} c_n(t) = \sum_n c_n(t) E_n^{(0)} \delta_{kn} + \sum_n \lambda c_n(t) \langle \phi_k^{(0)} | V(t) | \phi_n^{(0)} \rangle \quad (9.13)$$

$$i\hbar \frac{d}{dt} c_k(t) = c_k(t) E_k^{(0)} + \sum_n \lambda V_{kn}(t) c_n(t) \quad (9.14)$$

where:

$$V_{kn}(t) \equiv \langle \phi_k^{(0)} | V(t) | \phi_n^{(0)} \rangle \quad (9.15)$$

Lets look at this equation closely, for no perturbation ($\lambda = 0$), the equation becomes:

$$i\hbar \frac{d}{dt} c_k(t) = c_k(t) E_k^{(0)} \quad (9.16)$$

Which is trivially solved with a solution:

$$c_k(t) = b_k e^{-\frac{iE_k^{(0)} t}{\hbar}} \quad (9.17)$$

b_k is a constant that can be determined from the initial condition that:

$$|\psi(t=0)\rangle = |\phi_i^{(0)}\rangle \quad (9.18)$$

thus the expansion:

$$|\psi(t)\rangle = \sum_n c_n(t) |\phi_n^{(0)}\rangle = \sum_n c_n(0) |\phi_n^{(0)}\rangle = |\phi_i^{(0)}\rangle = c_i(0) = 1 \quad (9.19)$$

Therefore:

$$c_k(0) = c_i(0) = b_k = 1 \quad (9.20)$$

which gives the specific solution for this problem:

$$c_k(t) = e^{-\frac{i\hbar E_k^{(0)}}{\hbar} t} \quad (9.21)$$

Returning to the perturbation part, lets guess that when $\lambda \neq 0$ (but still small), $c_k(t)$ sill looks quite like b_k , at least shortly after the perturbation is switched on. This means an appropriate guess may be:

$$c_k(t) = b_k(t)e^{-\frac{iE_k^{(0)}t}{\hbar}} \quad (9.22)$$

The idea used to guess this is that the exponential term carries the time evolution of the unperturbed system (i.e H_0) and the new coefficient $b_k(t)$ deals with any left over time dependence coming from the perturbation. This coefficient does not restrict the possibilities for $|\psi(t)\rangle$ as the $|\phi_n^{(0)}\rangle$'s are a complete basis anyway and the functions $a_n(t)$ are completely arbitrary. Substitute Eq 9.22 into Eq 9.16:

$$\begin{aligned} i\hbar \frac{d}{dt} \left(b_k(t)e^{-\frac{iE_k^{(0)}t}{\hbar}} \right) &= b_k(t)e^{-\frac{iE_k^{(0)}t}{\hbar}} E_k^{(0)} + \sum_n \lambda V_{kn}(t)b_n(t)e^{-\frac{iE_n^{(0)}t}{\hbar}} \\ i\hbar \left(\frac{db_k(t)}{dt} e^{-\frac{iE_k^{(0)}t}{\hbar}} - i \frac{b_k(t)E_k^{(0)}}{\hbar} e^{-\frac{iE_k^{(0)}t}{\hbar}} \right) &= b_k(t)e^{-\frac{iE_k^{(0)}t}{\hbar}} E_k^{(0)} + \sum_n \lambda V_{kn}(t)b_n(t)e^{-\frac{iE_n^{(0)}t}{\hbar}} \\ i\hbar \left(\frac{db_k(t)}{dt} - i \frac{b_k(t)E_k^{(0)}}{\hbar} \right) &= b_k(t)E_k^{(0)} + \sum_n \lambda V_{kn}(t)b_n(t) \frac{e^{-i\frac{E_n^{(0)}t}{\hbar}}}{e^{-\frac{iE_k^{(0)}t}{\hbar}}} \\ i\hbar \frac{db_k(t)}{dt} &= \sum_n \lambda V_{kn}(t)b_n(t)e^{-i\frac{t}{\hbar}(E_n^{(0)}-E_k^{(0)})} \\ &= \lambda \sum_n e^{i\omega_{kn}t} V_{kn}(t)b_n(t) \end{aligned} \quad (9.23)$$

where:

$$\omega_{kn} = \frac{E_k^{(0)} - E_n^{(0)}}{\hbar} \quad (9.24)$$

So far this is still an exact solution that is derived from the TDSE. To look for perturbation solutions, the coefficients $b_k(t)$ are expanded in a series for a small parameter λ :

$$b_k(t) = b_k^{(0)}(t) + \lambda b_k^{(1)}(t) + \lambda^2 b_k^{(2)}(t) + \dots \quad (9.25)$$

the notation used here is that the subscripts, k , represent the state of the system (i.e it stands for the complete set of quantum numbers for a given system) and the superscript identify the order of the coefficients. This will be useful to keep track as later on the parameters will not be written out. Just as was done for the time-dependent perturbation theory, substitute Eq 10.25 into Eq 10.23:

$$i\hbar \frac{d}{dt} \left(b_k^{(0)}(t) + \lambda b_k^{(1)}(t) + \lambda^2 b_k^{(2)}(t) + \dots \right) = \lambda \sum_n e^{i\omega_{kn}t} V_{kn}(t) \left(b_k^{(0)}(t) + \lambda b_k^{(1)}(t) + \lambda^2 b_k^{(2)}(t) \right) \quad (9.26)$$

Once again, equate the coefficients of equal powers on both sides:

$$\lambda^0 \Rightarrow i\hbar \frac{d}{dt} b_k^{(0)}(t) = 0 \quad (9.27)$$

$$\lambda^1 \Rightarrow i\hbar \frac{d}{dt} b_k^{(1)}(t) = \sum_n e^{i\omega_{kn}t} V_{kn}(t)b_n^{(0)}(t) \quad (9.28)$$

$$\lambda^2 \Rightarrow i\hbar \frac{d}{dt} b_k^{(2)}(t) = \sum_n e^{i\omega_{kn}t} V_{kn}(t)b_n^{(1)}(t) \quad (9.29)$$

and so on... One can see that generally, the L.H.S is proportional to the $b_n^{(q-1)}(t)$ term on the R.H.S of the equation. The λ^0 equation can be solved trivially; since the R.H.S is zero, $b_k^{(0)}(t)$ has to be constant and moreover using the initial condition that $|\psi(t=0)\rangle = |\phi_i^{(0)}\rangle$, tells us the $b_i^{(0)}$ must be 1, thus:

$$b_k^{(0)} = \delta_{ki} \quad (9.30)$$

The λ^1 equation gives:

$$\frac{d}{dt} b_k^{(1)}(t) = \frac{1}{i\hbar} \sum_n e^{i\omega_{kn}t} V_{kn}(t) b_n^{(0)}(t) \quad (9.31)$$

$$b_k^{(1)}(t) = \frac{1}{i\hbar} \int_0^{t'} \sum_n e^{i\omega_{kn}t} V_{kn}(t) b_n^{(0)}(t) dt \quad (9.32)$$

But we know that $b_n^{(0)}(t) = \delta_{ni}$, therefore the sum in the integral goes and one is left with:

$$b_k^{(1)}(t') = \frac{1}{i\hbar} \int_0^{t'} dt e^{i\omega_{ki}t} V_{ki}(t') \quad (9.33)$$

This is the key result for calculating transition probabilities. The transition probability for an initial state $|\phi_i^{(0)}\rangle$ to some other state $|\phi_f^{(0)}\rangle$ at time t is:

$$\begin{aligned} P_{fi}(t) &= \left| \langle \phi_f^{(0)} | \psi(t) \rangle \right|^2 \\ &= \left| \sum_n b_n(t) \langle \phi_f^{(0)} | \phi_i^{(0)} \rangle \right|^2 \\ &= |b_f(t)|^2 \quad \text{assuming the state is normalised} \\ &\approx \left| b_f^{(0)}(0) + \lambda b_f^{(1)}(t) \right|^2 \end{aligned} \quad (9.34)$$

If the final state $|\phi_f^{(0)}\rangle$ is not the same as the initial state $|\phi_i^{(0)}\rangle$, the coefficients $b_f^{(0)}$ will be zero (using again the initial condition), therefore:

$$P_{fi} \approx \left| \lambda b_f^{(1)}(t) \right|^2 \quad (9.35)$$

Which is just the integral calculated in Eq 9.33:

$$P_{fi} = \left(\frac{\lambda}{\hbar} \right)^2 \left| \int_0^{t'} dt e^{i\omega_{fi}t} V_{fi}(t) \right|^2 \quad (9.36)$$

This is the probability of the transition being made from state $|\phi_i^{(0)}\rangle$ to $|\phi_f^{(0)}\rangle$. Although one can keep going to any desired order using this method, we will stop here though.

2. Sinusoidal or constant in potential in time perturbation

Lets define:

$$V(t) = \hat{V}_0 \cos \Omega t \quad (9.37)$$

with \hat{V}_0 being some time independent perturbing operator, and Ω being the frequency of the perturbation. Then the matrix element $V_{fi}(t)$ becomes:

$$V_{fi}(t) = V_{fi} \cos \Omega t = \langle \phi_f^{(0)} | \hat{V}_0 | \phi_i^{(0)} \rangle \cos \Omega t \quad (9.38)$$

Therefore the probability of transition is:

$$\begin{aligned} P_{fi} &= \left(\frac{\lambda |V_{fi}|}{2\hbar} \right)^2 \left| \int_0^{t'} dt e^{i\omega_{fi}t} \cos \Omega t \right|^2 \\ &= \left(\frac{\lambda |V_{fi}|}{2\hbar} \right)^2 \left| \frac{e^{it(\omega_{fi}+\Omega)} - 1}{\omega_{fi} + \Omega} + \frac{e^{it(\omega_{fi}-\Omega)} - 1}{\omega_{fi} - \Omega} \right|^2 \end{aligned} \quad (9.39)$$

A special case of this probability is when the frequency of a perturbation $\Omega = 0$, i.e the perturbation is constant (except when it is switched on):

$$\begin{aligned}
P_{fi}(t, \Omega = 0) &= \left(\frac{\lambda |V_{fi}|}{2\hbar} \right)^2 \left| \frac{e^{it\omega_{fi}} - 1}{\omega_{fi}} + \frac{e^{it\omega_{fi}} - 1}{\omega_{fi}} \right|^2 \\
&= \left(\frac{\lambda |V_{fi}|}{\hbar} \right)^2 \left| \frac{e^{it\omega_{fi}} - 1}{\omega_{fi}} \right|^2 \\
&= \left(\frac{\lambda |V_{fi}|}{\hbar} \right)^2 \left[\frac{\sin \frac{t\omega_{fi}}{2}}{\frac{\omega_{fi}}{2}} \right]^2
\end{aligned} \tag{9.40}$$

For either $\Omega = 0$ or $\Omega \neq 0$ cases, if the perturbation matrix element $V_{fi} = \langle \phi_f^{(0)} | \hat{V}_0 | \phi_i^{(0)} \rangle = 0$, there can be no transition at all from $|\phi_i^{(0)}\rangle$ to this state $|\phi_f^{(0)}\rangle$ at anytime. This, in fact, forms the foundation of selection rules in atomic and nuclear physics.

From Eq 9.39, if $\Omega \approx \omega_{fi}$, (i.e the input frequency of the perturbation, matches the frequency corresponding to the change in energy of the initial and final states), the probability very quickly grows to one and perturbation theory breaks down. This means the system very quickly makes the transition into the final state from its initial state, when $\Omega = \pm\omega_{fi}$. If $\Omega > 0$ then if $E_f^{(0)} > E_i^{(0)}$, the system *absorbs* a quanta of energy $\hbar\omega_{fi} (\equiv \hbar\Omega)$ from the perturbation source to go from $|\phi_i^{(0)}\rangle$ to state $|\phi_f^{(0)}\rangle$. Conversely, if $E_f^{(0)} < E_i^{(0)}$, the system has an *induced emission*, caused by the perturbation, emitting a quanta of $\hbar\omega_{fi} + \Omega$ in the denominator can be ignored as the other term will become very large:

$$\begin{aligned}
P_{fi}(t, -\Omega > 0) &\approx \left(\frac{\lambda |V_{fi}|}{2\hbar} \right)^2 \left| \frac{e^{it(\omega_{fi} - \Omega)} - 1}{(\omega_{fi} - \Omega)} \right|^2 \\
&= \left(\frac{\lambda |V_{fi}|}{2\hbar} \right)^2 \left[\frac{\sin \left(\frac{t(\omega_{fi} - \Omega)}{2} \right)}{\frac{\omega_{fi} - \Omega}{2}} \right]^2
\end{aligned} \tag{9.41}$$

This is a *sinc*² function with a maximum at $\omega_{fi} = \Omega$ and height $\left(\frac{\lambda |V_{fi}|}{2\hbar} \right)^2 t^2$, there it grows quickly with time. The peak at the position has width $\frac{4\pi}{t}$ which gets sharper in time.

3. Fermi's Golden Rule

Take $\Omega = 0$ case, but now consider that instead of just a single discrete energy level at $E_f^{(0)}$, we allow the initial state $|\phi_i^{(0)}\rangle$ to go to a continuum of energy around $E_f^{(0)}$. Thus we have:

$$P_{fi}(t) \approx \left(\frac{\lambda |V_{fi}|}{\hbar} \right)^2 F \left(t, \frac{(E_f^{(0)} - E_i^{(0)})}{\hbar} \right) \tag{9.42}$$

$$F \left(t, \frac{E}{\hbar} \right) = \left(\frac{\sin \left(\frac{Et}{2\hbar} \right)}{\left(\frac{E}{2\hbar} \right)} \right)^2 \tag{9.43}$$

Now, the function $F \left(t, \frac{E}{\hbar} \right)$ is very rapidly oscillating when $Et \gg 2\hbar$ and in fact:

$$\lim_{Et \gg 2\hbar} F \left(t, \frac{E}{\hbar} \right) = \lim_{Et \gg 2\hbar} \left(\frac{\sin \left(\frac{Et}{2\hbar} \right)}{\left(\frac{E}{2\hbar} \right)} \right)^2 \rightarrow 2\pi\hbar\delta(E)t \tag{9.44}$$

Since the final state belongs to a continuum of energies, we can only measure the probability of transition to the final state within a resolution of energy width Δ . Thus we need to sum up all the probabilities for energies E such that:

$$E_f^{(0)} - \frac{\Delta}{2} < E < E_f^{(0)} + \frac{\Delta}{2} \quad (9.45)$$

So the integral becomes:

$$\bar{P}_i(t, E_f^{(0)}) = \int_{E_f^{(0)} - \frac{\Delta}{2}}^{E_f^{(0)} + \frac{\Delta}{2}} dE \rho(E) P_{E_i}(t) \quad (9.46)$$

where $\rho(E)$ is the density of states at energy E , or in other words, $\rho(E)dE$ gives the number of states within the energy window, E to $E+dE$. Note that the final state index has been changed from f to E as now the final state is just a state within the energy range E .

Substitute Eq 9.43 and Eq 9.44 into Eq 9.46:

$$\begin{aligned} \bar{P}_i(t, E_f^{(0)}) &= \int_{E_f^{(0)} - \frac{\Delta}{2}}^{E_f^{(0)} + \frac{\Delta}{2}} dE \rho(E) \left(\frac{\lambda |V_{E_i}|}{\hbar} \right)^2 2\pi \hbar \delta(E - E_i^{(0)}) t \\ &= \frac{2\pi t}{\hbar} \left| \langle \phi_{E_f^{(0)}=E_i^{(0)}}^{(0)} | \lambda \hat{V} | \phi_i^{(0)} \rangle \right|^2 \rho(E_f^{(0)} = E_i^{(0)}) \end{aligned} \quad (9.47)$$

Therefore the differential transition transition rate is written as:

$$\frac{d\bar{P}_i(t, E_f^{(0)})}{dt} = \frac{2\pi}{\hbar} \left| \langle \phi_{E_f^{(0)}=E_i^{(0)}}^{(0)} | \lambda \hat{V} | \phi_i^{(0)} \rangle \right|^2 \rho(E_f^{(0)} = E_i^{(0)}) \quad (9.48)$$

This is the celebrated *Fermi's Golden Rule* which is used in every corner of quantum physics. If we allow for a perturbation of frequency $\Omega \neq 0$, this generalised to:

$$\frac{d\bar{P}_i(t, E_f^{(0)}, \Omega)}{dt} = \frac{2\pi}{\hbar} \left| \langle \phi_{E_f^{(0)}=E_i^{(0)}+\hbar\Omega}^{(0)} | \lambda \hat{V} | \phi_i^{(0)} \rangle \right|^2 \rho(E_f^{(0)} = E_i^{(0)} + \hbar\Omega) \quad (9.49)$$

Identical Particles

1. Formalism

For a system of two particles of mass m in a potential $V(\vec{r})$, the Hamiltonian in co-ordinate, \vec{r} , representation is written as:

$$H = H_1 + H_2 + H_{12} \quad (10.1)$$

where \vec{r}_1 is the coordinate of particle 1, \vec{r}_2 , is the coordinate of particle 2, so the Hamiltonian components become:

$$H_1 = -\frac{\hbar^2}{2m}\nabla_{\vec{r}_1}^2 + V(\vec{r}_1) \quad (10.2)$$

$$H_2 = -\frac{\hbar^2}{2m}\nabla_{\vec{r}_2}^2 + V(\vec{r}_2) \quad (10.3)$$

Therefore H_1 only acts on particle 1 and H_2 only acts on particle 2. H_{12} is part of the Hamiltonian that involves both particle 1 and 2 coordinates, for example it could be a Coulombic potential between the two electrons:

$$H_{12} = \frac{e^2}{4\pi\epsilon|\vec{r}_1 - \vec{r}_2|} \quad (10.4)$$

Since H_1 is the Hamiltonian for particle 1, we have the energies and eigenfunctions for particle 1 and 2:

$$H_1\phi_n(\vec{r}_1) = E_n^{single}\phi_n(\vec{r}_1) \quad (10.5)$$

$$H_2\phi_n(\vec{r}_2) = E_n^{single}\phi_n(\vec{r}_2) \quad (10.6)$$

The objective now is to solve for the two-particle Schrodinger equation:

$$H\psi(\vec{r}_1, \vec{r}_2) = E^{total}\psi(\vec{r}_1, \vec{r}_2) \quad (10.7)$$

The two particle wavefunction $\psi(\vec{r}_1, \vec{r}_2)$ is the amplitude (not probability) for finding particle 1 at \vec{r}_1 and particle 2 at \vec{r}_2 . The convention used here is that the left slot inside the bracket carrying the argument of the wavefunction is used for particle 1 and the right side is for particle 2.

Consider the simplest case when there is no interaction between the two particles, i.e $H_{12} = 0$. The solution to Eq 10.7 is:

$$\psi(\vec{r}_1, \vec{r}_2) = \phi_n(\vec{r}_1)\phi_m(\vec{r}_2) \quad (10.8)$$

Check this by substituting this into Eq 10.7:

$$\begin{aligned}
H\psi(\vec{r}_1, \vec{r}_2) &= \left(-\frac{\hbar^2}{2m}\nabla_{\vec{r}_1}^2 + V(\vec{r}_1) - \frac{\hbar^2}{2m}\nabla_{\vec{r}_2}^2 + V(\vec{r}_2) \right) \psi(\vec{r}_1, \vec{r}_2) \\
&= \left(-\frac{\hbar^2}{2m}\nabla_{\vec{r}_1}^2 + V(\vec{r}_1) - \frac{\hbar^2}{2m}\nabla_{\vec{r}_2}^2 + V(\vec{r}_2) \right) \phi_n(\vec{r}_1)\phi_m(\vec{r}_2) \\
&= -\frac{\hbar^2}{2m}\nabla_{\vec{r}_1}^2\phi_n(\vec{r}_1) + V(\vec{r}_1)\phi_n(\vec{r}_1) - \frac{\hbar^2}{2m}\nabla_{\vec{r}_2}^2\phi_m(\vec{r}_2) + V(\vec{r}_2)\phi_m(\vec{r}_2) \\
&= \left(-\frac{\hbar^2}{2m}\nabla_{\vec{r}_1}^2 + V(\vec{r}_1) \right) \phi_n(\vec{r}_1) + \left(-\frac{\hbar^2}{2m}\nabla_{\vec{r}_2}^2 + V(\vec{r}_2) \right) \phi_m(\vec{r}_2) \\
&= H_1\phi_n(\vec{r}_1) + H_2\phi_m(\vec{r}_2)
\end{aligned} \tag{10.9}$$

Therefore the R.H.S of Eq 10.7 must be:

$$E_1\phi_n(\vec{r}_1) + E_2\phi_m(\vec{r}_2) \tag{10.10}$$

Thus:

$$E^{Total} = E_n^{single} + E_m^{single} \tag{10.11}$$

So the wavefunctions multiply and the energies add. In quantum mechanics, if the two particles are indistinguishable, there are important consequences to what are the allowed two-particle wavefunctions that represent physical solutions.

If particle 1 is a neutron and particle 2 is a proton, then the amplitude for finding the neutron at \vec{r}_1 and the proton at \vec{r}_2 is not generally the same as finding the neutron at \vec{r}_2 and the proton at \vec{r}_1 :

$$\psi(\vec{r}_1, \vec{r}_2) \neq \psi(\vec{r}_2, \vec{r}_1) \tag{10.12}$$

Both these particles can be distinguished from each other (e.g by measuring charge or the small discrepancy in their mass). Suppose now that both particles 1 and 2 are indistinguishable, for the sake of argument, say they are electrons. Finding electron 1 at \vec{r}_1 and 2 at \vec{r}_2 is the same as finding electron 1 at \vec{r}_2 and 2 at \vec{r}_1 . This is because electron 1 and 2 are identical particles; unlike in classical physics, in quantum physics one can, at most, specify a complete set of commuting variables. We know that the position does not commute with the momentum (as shown by Heisenberg's uncertainty principle). This means the trajectories taken by particles cannot be exactly mapped (in phase space or in real space). Therefore one cannot know which particle is which if the trajectories approach each other. In particular, when two identical particles approach each other, the two possibilities are:

- (1) The two particles cross each other
- (2) The two particles scatter each other backwards

In the quantum world (specifically due to Heisenberg's uncertainty principle), both these cases are identical. Recall that for distinguishable particles, we could say that $\psi(\vec{r}_1, \vec{r}_2) \neq \psi(\vec{r}_2, \vec{r}_1)$, this is simply because the equation was not the same. However for indistinguishable particles one cannot say:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1) \tag{10.13}$$

This might be confusing at first sight, as this was done for the distinguishable particles. The reason this equation does not necessarily have to be true, is that the wavefunctions are not by themselves observable quantities. Therefore, even though the equations of the wavefunctions in Eq 10.13 are satisfied by identical particles, one cannot test them *directly*. The only observable is the probability density:

$$|\psi(\vec{r}_1, \vec{r}_2)|^2 = |\psi(\vec{r}_2, \vec{r}_1)|^2 \tag{10.14}$$

This means one can choose a gauge containing a phase factor for the wavefunction and the physics will still be the same:

$$\psi(\vec{r}_1, \vec{r}_2) = e^{i\theta} \psi(\vec{r}_2, \vec{r}_1) \quad (10.15)$$

Note that Eq 10.15 can take the form of Eq 10.13, however this would not be the most general solution. The wavefunction obeys:

$$\begin{aligned} \psi(\vec{r}_1, \vec{r}_2) &= e^{i\theta} (\psi(\vec{r}_2, \vec{r}_1)) \\ &= e^{i\theta} e^{i\theta} \psi(\vec{r}_1, \vec{r}_2) \Rightarrow \theta = 0, \pi \end{aligned} \quad (10.16)$$

This implies the key result:

$$\psi(\vec{r}_1, \vec{r}_2) = \pm \psi(\vec{r}_2, \vec{r}_1) \quad (10.17)$$

Using the unsymmetrized two particle wavefunction:

$$\psi(\vec{r}_1, \vec{r}_2) = \phi_n(\vec{r}_1) \phi_m(\vec{r}_2) \quad (10.18)$$

we can form the symmetrized (+sign) and anti-symmetrized (-sign) physical wavefunctions as:

$$\psi_{\pm}(\vec{r}_1, \vec{r}_2) = \phi_n(\vec{r}_1) \phi_m(\vec{r}_2) \pm \phi_m(\vec{r}_1) \phi_n(\vec{r}_2) \quad (10.19)$$

To make sure these work, check that they satisfy Eq 10.17:

$$\psi_{\pm}(\vec{r}_2, \vec{r}_1) = \phi_n(\vec{r}_2) \phi_m(\vec{r}_1) \pm \phi_m(\vec{r}_2) \phi_n(\vec{r}_1) \quad (10.20)$$

Thus:

$$\psi_{\pm}(\vec{r}_1, \vec{r}_2) = \psi_{\pm}(\vec{r}_2, \vec{r}_1) \quad (10.21)$$

In general some particles have spin aswell. As we saw in the angular momentum chapter, spin is an intrinsic property of a particle and therefore cannot be part of the spatial wavefunction. In fact, any spatially independent quantum number cannot be represented as a part of the spatial wavefunction. Thus a new notation is introduced:

$$\psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2) \quad (10.22)$$

where σ 's represent the spin part of the total wavefunctions. $\psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2)$ is the amplitude for finding particle 1 with spin σ_1 and at position \vec{r}_1 and likewise for particle 2. Condition in Eq 10.17 applies to the overall wavefunction:

$$\psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2) = \pm \psi(\vec{r}_2, \sigma_2; \vec{r}_1, \sigma_1) \quad (10.23)$$

In nature, particles with integer spin obey:

$$\psi_{boson}(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2) = \pm \psi_{boson}(\vec{r}_2, \sigma_2; \vec{r}_1, \sigma_1) \quad (10.24)$$

these particles are called *bosons*. Particles with half-integer spin obey:

$$\psi_{fermion}(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) = -\psi_{fermion}(\vec{r}_2, \sigma_2; \vec{r}_1, \sigma_1) \quad (10.25)$$

these particles are called *fermions*. Eq 10.25 leads to a remarkable conclusion, that can be seen by substituting Eq 10.25 into Eq 10.23 and try to put two fermions with the same spin and position:

$$\sigma_1 = \sigma_2 = \sigma \quad (10.26)$$

$$\vec{r}_1 = \vec{r}_2 = \sigma \quad (10.27)$$

We get:

$$\psi_{fermion}(\vec{r}, \sigma; \vec{r}', \sigma) = -\psi_{fermion}(\vec{r}', \sigma; \vec{r}, \sigma) \quad (10.28)$$

Thus $\psi_{fermion}$ must equal zero. Physically this means that fermions can never exist in the same quantum state (i.e with the same quantum numbers). This is called *Pauli's exclusion principle*.

There is no such problem for bosons. In fact, at 'zero' temperature it turns out that any number of bosons tend to go to the lowest energy (ground state) of the system. This phenomena is called *Bose-Einstein condensation*.

2. Dirac notation of identical particles

Let $|k_1\rangle|k_2\rangle$ be the state for 2 particles (k_1, k_2 are some quantum number labels such as momentum, position, spin etc). Once again, the convection is used in which the first ket represents particle one and the second ket (to the right) represents particle 2.

The next thing to do is define a permutation operator, \mathbb{P}_{12} such that:

$$\mathbb{P}_{12}|k_1\rangle|k_2\rangle = |k_2\rangle|k_1\rangle \quad (10.29)$$

The subscript 1,2 shows that shows that particle one is being changed into particle 2. Obviously applying the operator twice on a given wavefunction will just take us back to the original wavefunction, i.e $P_{12}^2 = 1$, thus eigenkets for P_{12} can be found with eigenvalues ± 1 :

$$\begin{aligned} |k_1, k_2\rangle_+ &= \frac{1}{\sqrt{2}} (|k_1\rangle|k_2\rangle + |k_2\rangle|k_1\rangle) \\ |k_1, k_2\rangle_- &= \frac{1}{\sqrt{2}} (|k_1\rangle|k_2\rangle - |k_2\rangle|k_1\rangle) \end{aligned} \quad (10.30)$$

apply the permutation operator to each expression to find its eigenvalues:

$$\begin{aligned} \mathbb{P}_{12}|k_1, k_2\rangle_+ &= \frac{1}{\sqrt{2}} (|k_2\rangle|k_1\rangle + |k_1\rangle|k_2\rangle) \\ &= +1|k_1, k_2\rangle_+ \end{aligned} \quad (10.31)$$

thus the eigenvalue is +1 for this state.

$$\begin{aligned} P_{12}|k_1, k_2\rangle_- &= \frac{1}{\sqrt{2}} (|k_2\rangle|k_1\rangle - |k_1\rangle|k_2\rangle) \\ &= -1|k_1, k_2\rangle_- \end{aligned} \quad (10.32)$$

this state has eigenvalue of -1.

The symmetrization postulate is that for identical particles, physical kets are symmetric with respect to the permutation operator for two particles that are bosons and anti-symmetric for fermions.

3. Identical fermions with spin

Suppose a system contains two electrons (fermions with spin $\frac{1}{2}$). The overall wavefunction of the system will be a product of the spatial part of the wavefunction and the spin part. Therefore the permutation operator can separately interchange the spin part and the space part:

$$P_{12}^{tot} = P_{12}^{spin} P_{12}^{space} \quad (10.33)$$

such that:

$$\begin{aligned} P_{12}^{spin} |\sigma_1\rangle |\sigma_2\rangle &= |\sigma_2\rangle |\sigma_1\rangle \\ P_{12}^{space} |\vec{r}_1\rangle |\vec{r}_2\rangle &= |\vec{r}_2\rangle |\vec{r}_1\rangle \end{aligned} \quad (10.34)$$

hence:

$$P_{12}^{tot} |\vec{r}_1, \sigma_1\rangle |\vec{r}_2, \sigma_2\rangle = |\vec{r}_2, \sigma_2\rangle |\vec{r}_1, \sigma_1\rangle \quad (10.35)$$

Spin wavefunctions can also be formed as symmetric or anti-symmetric under the permutation operator, when the spin states are different:

$$\begin{aligned} |\sigma_1, \sigma_2\rangle_{\pm} &= \frac{1}{\sqrt{2}} (|\sigma_1\rangle |\sigma_2\rangle \pm |\sigma_2\rangle |\sigma_1\rangle) \\ P_{12}^{spin} |\sigma_1, \sigma_2\rangle_{\pm} &= \pm |\sigma_1, \sigma_2\rangle_{\pm} \end{aligned} \quad (10.36)$$

The spatially symmetric and anti-symmetric states are the same as before:

$$\begin{aligned} |\vec{r}_1, \vec{r}_2\rangle_{\pm} &= \frac{1}{\sqrt{2}} (|\vec{r}_1\rangle |\vec{r}_2\rangle \pm |\vec{r}_2\rangle |\vec{r}_1\rangle) \\ P_{12}^{space} |\vec{r}_1, \vec{r}_2\rangle_{\pm} &= \pm |\vec{r}_1, \vec{r}_2\rangle_{\pm} \end{aligned} \quad (10.37)$$

From the theory of addition of two spin angular momentum, for two $s = \frac{1}{2}$ spins, four possible states can be formed:

- (1) $|\uparrow\uparrow\rangle$ $s = 1, m_s = +1$, symmetric under particle exchange.
- (2) $\frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ $s = 1, m_s = +1$, symmetric under particle exchange.
- (3) $|\downarrow\downarrow\rangle$, $s = 1, m_s = -1$, symmetric under particle exchange.
- (4) $\frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$, $s = 0, m_s = 0$ anti-symmetric under particle exchange.

States with total spin, s_1 equal to 1 are called the triplet states (for obvious reasons), while for $s = 0$, the state is called a singlet. For Fermions the total wavefunction must be anti-symmetric under the permutation operator. Therefore there are two possibilities for the overall wavefunction:

$$\begin{aligned} |\psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2)\rangle^{tot} &= |\text{symmetric}\rangle_{space} |\text{anti-symmetric}\rangle_{spin} \quad \text{OR} \\ &= |\text{symmetric}\rangle_{spin} |\text{anti-symmetric}\rangle_{space} \end{aligned} \quad (10.38)$$

For example, if two fermions with $s = \frac{1}{2}$ are put into a harmonic potential and they have the same energy level, n , the spatial wavefunction must take the form:

$$\phi_n(\vec{r}_1) \phi_n(\vec{r}_2) \quad (10.39)$$

This wavefunction is symmetric under the permutation operator:

$$P_{12}^{space} \phi_n(\vec{r}_1) \phi_n(\vec{r}_2) = \phi_n(\vec{r}_2) \phi_n(\vec{r}_1) \quad (10.40)$$

Thus, to make the overall wavefunction anti-symmetric, the spin part of the wavefunction must be anti-symmetric. From the results about the spin states, the only anti-symmetric spin wavefunction is the singlet state $\chi_{singlet}$:

$$P_{12}^{spin} \chi_{singlet} = -\chi_{singlet} \quad (10.41)$$

Therefore the only allowed two particle wavefunction is:

$$|\psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2)\rangle^{tot} = \phi_n(\vec{r}_1) \phi_n(\vec{r}_2) \otimes \chi_{singlet} \quad (10.42)$$

The only other alternate is that spatial wavefunctions are anti-symmetric and then the spin can be symmetric:

$$\phi^{spatial} = \frac{1}{\sqrt{2}} (\phi_n(\vec{r}_1) \phi_m(\vec{r}_2) - \phi_m(\vec{r}_1) \phi_n(\vec{r}_2)) \quad (10.43)$$

note that the quantum numbers here have to be different in order to obey the Pauli Exclusion Principle. In general in the quantum numbers are different, i.e the possible wavefunctions are:

$$\begin{aligned} |\psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2)\rangle^{tot} &= \frac{1}{\sqrt{2}} (\phi_n(\vec{r}_1)\phi_m(\vec{r}_2) + \phi_m(\vec{r}_1)\phi_n(\vec{r}_2)) \otimes \chi_{singlet} \quad \text{OR} \\ &= \frac{1}{\sqrt{2}} (\phi_n(\vec{r}_1)\phi_m(\vec{r}_2) - \phi_m(\vec{r}_1)\phi_n(\vec{r}_2)) \otimes \chi_{triplet} \end{aligned} \quad (10.44)$$

4. Helium atom

The Helium atom is a system of two spin $\frac{1}{2}$ fermions, electrons in a Coulombic potential coming from the nucleus of charge $+2e$. The spatial part of the overall wavefunction is:

$$\phi_{\pm}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\phi_A(\vec{r}_1)\phi_B(\vec{r}_2) \pm \phi_B(\vec{r}_1)\phi_A(\vec{r}_2)) \quad (10.45)$$

where ϕ_A and ϕ_B are the hydrogen-like wavefunctions for a single electron with quantum numbers labels of A, B being short hand n, l, m . The two allowed wavefunctions are shown in Eq 10.44. The Hamiltonian for the Helium atom is:

$$H_{He} = -\frac{\hbar^2}{2m} (\nabla_{r_1}^2 + \nabla_{r_2}^2) - \frac{2e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon|\vec{r}_1 - \vec{r}_2|} \quad (10.46)$$

Notice there is no spin dependent interaction. This is induced if there is a magnetic field. Lets try using first-order, time independent perturbation theory by treating the final term in the Hamiltonian (the Coulomb interaction between the two e^-) as the perturbation. The energy change δE , due to this perturbation is then:

$$\begin{aligned} \delta E &= \langle \psi_{He} | \frac{e^2}{4\pi\epsilon|\vec{r}_1 - \vec{r}_2|} | \psi_{He} \rangle \\ &= \langle \phi_+ | \frac{e^2}{4\pi\epsilon|\vec{r}_1 - \vec{r}_2|} | \phi_+ \rangle \quad \text{OR} \\ &= \langle \phi_- | \frac{e^2}{4\pi\epsilon|\vec{r}_1 - \vec{r}_2|} | \phi_- \rangle \end{aligned} \quad (10.47)$$

In fact, lets define:

$$\begin{aligned} \delta E_+ &= \langle \phi_+ | V_{12} | \phi_+ \rangle = \langle \phi_+ | \frac{e^2}{4\pi\epsilon|\vec{r}_1 - \vec{r}_2|} | \phi_+ \rangle \\ \delta E_- &= \langle \phi_- | V_{12} | \phi_- \rangle = \langle \phi_- | \frac{e^2}{4\pi\epsilon|\vec{r}_1 - \vec{r}_2|} | \phi_- \rangle \end{aligned} \quad (10.48)$$

Start with δE_+ :

$$\begin{aligned} \delta E_+ &= \frac{1}{2} \int dr_1 dr_2 (\phi_A^*(\vec{r}_1)\phi_B^*(\vec{r}_2) + \phi_A^*(\vec{r}_2)\phi_B^*(\vec{r}_1)) \frac{e^2}{4\pi\epsilon|\vec{r}_1 - \vec{r}_2|} (\phi_A(\vec{r}_1)\phi_B(\vec{r}_2) + \phi_A(\vec{r}_2)\phi_B(\vec{r}_1)) \\ &= \frac{1}{2} \int dr_1 dr_2 (|\phi_A^*(\vec{r}_1)\phi_B(\vec{r}_2)|^2 + \phi_A^*(\vec{r}_1)\phi_B^*(\vec{r}_2)\phi_A(\vec{r}_1)\phi_B(\vec{r}_2)) \frac{e^2}{4\pi\epsilon|\vec{r}_1 - \vec{r}_2|} \end{aligned} \quad (10.49)$$

We have two types of terms here:

$$I = \int \int d\vec{r}_1 d\vec{r}_2 |\phi_A^*(\vec{r}_1)\phi_B(\vec{r}_2)|^2 \frac{e^2}{4\pi\epsilon|\vec{r}_1 - \vec{r}_2|} \quad (10.50)$$

This term is easy to interpret, the mod squared is simply the probability density of particle one being at position 1 with the quantum numbers, A , and particle 2 being at position \vec{r}_2 with quantum numbers, B . The other term is:

$$J = \int \int d\vec{r}_1 d\vec{r}_2 \phi_A^*(\vec{r}_1) \phi_B^*(\vec{r}_2) \phi_A(\vec{r}_1) \phi_B(\vec{r}_2) \frac{e^2}{4\pi\epsilon|\vec{r}_1 - \vec{r}_2|} \quad (10.51)$$

This term is not so easy to interpret as $\phi_A(\vec{r}_1)$ is mixed up with $\phi_B(\vec{r}_2)$ in an insuperable way. Thus we have:

$$\delta E_+ = I + J \quad (10.52)$$

I is sometimes called the *direct* term and J is called the *exchange* energy term. Similarly:

$$\delta E_- = I - J \quad (10.53)$$

It turns out that I is always positive and so is J , therefore $\delta E_+ > \delta E_-$. Since δE_+ corresponds to the total wavefunction being symmetric in space and anti-symmetric in spin (singlet) state with respect to the permutation operator. The δE_- corresponds to the total wavefunction being symmetric in spin and anti-symmetric in space, we see that the wavefunctions containing the singlet state actually have greater energy than wavefunctions with the triplet state.

The physical reason for this is that for the anti-symmetric space wavefunction, the two electrons cannot occupy the same state. i.e they can not be in the same position at the same time (as the wavefunction will just become zero!). This means in general there is a tendency to remain further apart and hence reducing the Coulombic energy between them and this is not what is observed in δE_- .

It is strange that even though there is no explicit spin dependence in the Hamiltonian, the exchange term prefers the triplet spin state as it has a lower energy and therefore the system is in the lowest energy state.