Quantum Mechanics

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Contents

1 Review

Here we review the 4 postulates of quantum mechanics.

1.1 Postulate 1

Every dynamical system can be described by a wavefunction from which all possible predictions about the physical properties can be obtained:

$$\psi(x, y, z, t) \tag{1.1}$$

The wavefunction is normalised:

$$\int \psi^* \psi \, d\tau = 1 \tag{1.2}$$

From the wavefunction ψ, we are able to determine all dynamical variables; such as momentum, energy, angular momentum....

1.2 Postulate 2

Every dynamical variable may be represented by a Hermitian operator, whose eigenvalues represent the possible results of a measurement on the wavefunction ψ.
Immediately after the measurement, the wavefunction of the system will be identical to the eigenfunction corresponding to the eigenvalue obtained in the measurement.
Consider an operator $\hat{Q}$. There will be an eigenvalue equation:

$$\hat{Q}\phi_n = q_n\phi_n \tag{1.3}$$

Where q_n are eigenvalues: if q_n is measured, then the state is definitely in the state ϕ_n.
The definition of a Hermitian operator is: if the following integral holds:

$$\int f\hat{Q}g \, d\tau = \int g\hat{Q}^* f \, d\tau \tag{1.4}$$

Then $\hat{Q}$ is said to be Hermitian; if f, g are well behaved functions of position, which go to zero at infinity.
Here are the properties of Hermitian operators:

1.2.1 Hermitian Operators have Real Eigenvalues

Proof of Real Eigenvalues Now, starting with an eigenvalue equation

$$\hat{Q}\phi_n = q_n\phi_n, \tag{1.5}$$

we may take the complex conjugate of everything, to give:

$$\hat{Q}^*\phi_n^* = q_n^*\phi_n^*. \tag{1.6}$$

Now, if we multiply (1.5) by ϕ_n^*, we have:

$$\phi_n^* \hat{Q} \phi_n = \phi_n^* q_n \phi_n. \tag{1.7}$$

Taking the integral over all space gives:

$$\int \phi_n^* \hat{Q} \phi_n \, d\tau = q_n \int \phi_n^* \phi_n \, d\tau. \tag{1.8}$$

If we similarly multiply (1.6) by ϕ_n, we have; and writing down the corresponding integral:

$$\int \phi_n \hat{Q}^* \phi_n^* \, d\tau = q_n^* \int \phi_n \phi_n^* \, d\tau. \tag{1.9}$$

Now, due to the condition that $\hat{Q}$ is a Hermitian operator, we apply its condition:

$$\int \phi_n^* \hat{Q} \phi_n \, d\tau = \int \phi_n \hat{Q}^* \phi_n^* \, d\tau, \tag{1.10}$$

the RHS of which we notice is the integral in the LHS of (1.6). Hence, we have that:

$$q_n^* \int \phi_n \phi_n^* \, d\tau = q_n \int \phi_n^* \phi_n \, d\tau \tag{1.11}$$

$$\Rightarrow q_n^* = q_n. \tag{1.12}$$

Hence showing that q_n are real.

1.2.2 Eigenfunctions are Orthonormal

This says that:

$$\int \phi_m^* \phi_n \, d\tau = \delta_{nm} \tag{1.13}$$

Proof of Orthonomality Starting from the standard eigenvalue equation: $\hat{Q}\phi_n = q_n \phi_n$, where $\hat{Q}$ is some Hermitian operator. Now, we multiply both sides by some ϕ_m^*, and integrate:

$$\phi_m^* \hat{Q} \phi_n = \phi_m^* q_n \phi_n \tag{1.14}$$

$$\int \phi_m^* \hat{Q} \phi_n \, d\tau = \int \phi_m^* q_n \phi_n \, d\tau \tag{1.15}$$

Now, we use a property of the Hermiticity of the operator $\hat{Q}$: We write the LHS of (1.15) as:

$$\int \phi_m^* \hat{Q} \phi_n \, d\tau = \int \phi_n \hat{Q}^* \phi_m^* \, d\tau \tag{1.16}$$

Now, the RHS of (1.16) can be expressed using the standard eigenvalue equation:

$$\int \phi_n \hat{Q}^* \phi_m^* \, d\tau = \int \phi_n q_m^* \phi_m^* \, d\tau \tag{1.17}$$

Now, by working backwards, the RHS of (1.17) is equal to the RHS of (1.15):

$$\int \phi_n q_m^* \phi_m^* \, d\tau = \int \phi_m^* q_n \phi_n \, d\tau \tag{1.18}$$

Hence, we have that:

$$q_m^* \int \phi_n \phi_m^* \, d\tau = q_n \int \phi_m^* \phi_n \, d\tau \tag{1.19}$$

$$\Rightarrow (q_m^* - q_n) \int \phi_n \phi_m^* \, d\tau = 0 \tag{1.20}$$

Now, using another property of Hermiticity: eigenvalues of a Hermitian operator are real. Hence, we have that $q_m^* = q_m$. Hence, (1.5) is:

$$(q_m - q_n) \int \phi_n \phi_m^* \, d\tau \quad = \quad 0 \tag{1.21}$$

Hence, so long as $m \neq n$, we have that

$$\int \phi_n \phi_m^* \, d\tau = 0 \tag{1.22}$$

And the only thing that this proof shows about the $m = n$ case is that

$$\int \phi_n \phi_m^* \, d\tau \neq 0 \tag{1.23}$$

1.2.3 Eigenfunctions Form a Complete Set

Any arbitrary function can be described as a linear combination:

$$\psi = \sum_n a_n \phi_n \tag{1.24}$$

Where the expansion coefficients a_n are found from the overlap integral:

$$a_m = \int \phi_m^* \psi \, d\tau \tag{1.25}$$

Proof of Completeness

$$\begin{aligned} a_m &= \int \phi_m^* \psi \, d\tau && (1.26)\\ &= \int \phi_m^* \sum a_n \phi_n \, d\tau && (1.27)\\ &= \sum a_n \int \phi_m^* \phi_n \, d\tau && (1.28)\\ &= \sum a_n \delta_{mn} && (1.29)\\ &= a_m. && (1.30) \end{aligned}$$

1.3 Postulate 3

The operators are:

$$\hat{r} = r \tag{1.31}$$

$$\hat{P}_x = -i\hbar\frac{\partial}{\partial x} \tag{1.32}$$

$$\hat{P} = -i\hbar\nabla \tag{1.33}$$

All other operators can be deduced from these; and they bear the same functional relation as their classical counterparts:

$$E = \frac{P^2}{2m} + V \tag{1.34}$$

$$\Rightarrow \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V \tag{1.35}$$

$$\mathbf{L} = \mathbf{r} \times \mathbf{P} \tag{1.36}$$

$$\Rightarrow \hat{L} = -i\hbar(\mathbf{r} \times \nabla) \tag{1.37}$$

1.4 Postulate 4

When a measurement of the physical property, represented by $\hat{Q}$, is carried out on ψ, the probability that the result will be q_m will be:

$$|a_m|^2 \tag{1.38}$$

e.g Let $\psi = a_1\phi_1 + a_2\phi_2 + a_3\phi_3 + \ldots$, where ϕ_n are eigenfunctions of $\hat{Q}$. The measurement forces ψ to collapse into one of the eigenfunctions of $\hat{Q}$, ϕ_m, say, and will return the value q_m, with probability $|a_m|^2$.
Now, as $\int \psi^*\psi \, d\tau = 1$ (i.e. normalisation of the wavefunction), this implies that:

$$|a_1|^2 + |a_2|^2 + |a_3|^2 + \ldots = 1, \tag{1.39}$$

the sum of all probabilities of the different outcomes is equal to unity.
This allows us to define an expectation value $\langle\hat{Q}\rangle$, which is the average value of many measurements on ψ:

$$\begin{aligned}
\langle\hat{Q}\rangle &= \int \psi^*\hat{Q}\psi \, d\tau \\
&= \int \left(\sum_m a_m^*\phi_m^*\right)\hat{Q}\left(\sum_n a_n\phi_n\right) d\tau \\
&= \int a_m^*\phi_m^* q_n a_n \phi_n \, d\tau \\
&= a_m^* a_n q_n \int \phi_m^*\phi_n \, d\tau \\
&= a_m^* a_n q_n \delta_{mn} \\
&= a_n^* a_n q_n \\
&= \sum_n |a_n|^2 q_n
\end{aligned}$$

Which is back to the definition of an average, with $|a_n|^2$ being the probability of measuring the value q_n. We have made use of the eigenvalue equation: $\hat{Q}a_n\phi_n = a_n\hat{Q}q_n = a_nq_n\phi_n$.

2 1D QM for Finite Wells, Potential Barriers & Tunelling

We will find that quantum fluctuations in energy allow for violation of conservation of energy for a short time, according to the HUP: $\Delta E\Delta t \geq \frac{\hbar}{2}$.

2.1 Infinite Well

Review of the infinite square well.
We have a potential $V = 0$ inside a well which sits on $-a \leq x \leq a$, and $V = \infty$ outside the well. The Schrodinger equation inside the well has the form:

$$-\frac{\hbar^2}{2m}\frac{d^2u_2}{dx^2} = Eu_2 \tag{2.1}$$

Where the eigenfunction solution is of the form:

$$u_2(x) = A\cos kx + A\sin kx \tag{2.2}$$

$$k^2 \equiv \frac{2mE}{\hbar^2}, \tag{2.3}$$

due to the boundary condition that $u_2(\pm a) = 0$.
With wavefunction and probability distributions looking like:

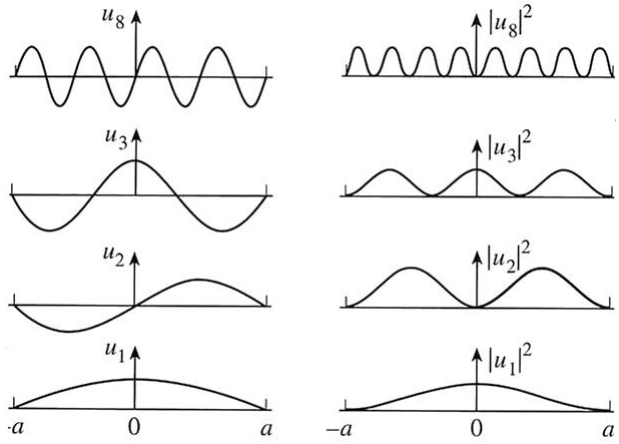

Figure 1: Wavefunctions and probability distributions for the infinite square well. Notice that the wavefunctions are all confined to the region within the box: $-a \leq x \leq a$.

2.2 Finite Square Well

Here, we have the situtation that we have 3 regions: u_1 for $x < -a$, where $V = V_0$; u_2 for $-a \leq x \leq a$, where $V = 0$; and u_3 for $x > a$ where $V = V_0$. So, we have a potential of $V = 0$ inside, and $V = V_0$ outside a box of size $2a$. The energy of the particle is E, where $E < V_0$ give rise to bound states.
Now, we expect that due to symmetry, u_1 and u_3 should have the same form.

The Schrodinger equation, in region 2 (inside the box) is:

$$-\frac{\hbar^2}{2m}\frac{d^2u_2}{dx^2} = Eu_2$$

Hence, we have the solution:

$$\begin{aligned} u_2 &= A\cos kx + B\sin kx \\ k^2 &= \frac{2mE}{\hbar^2} \end{aligned}$$

In region 1 (to the left of the box), we have a Schrodinger equation looking like:

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2u_1}{dx^2} + V_0u_1 &= Eu_1 \\ \Rightarrow \frac{\hbar^2}{2m}\frac{d^2u_1}{dx^2} &= (V_0 - E)u_1 \end{aligned}$$

So, we have solution:

$$\begin{aligned} u_1 &= Ce^{\mu x} + De^{-\mu x} \\ \mu^2 &= \frac{2m(V_0 - E)}{\hbar^2} \end{aligned}$$

Note that μ is real, if $V_0 > E$.
So, the task is to find relations between the coefficients A, B, C, D. To do this, we look at the boundary conditions of the problem: continuity.
At $x = -a$, the wavefunctions

$$u_1(-a) = u_2(-a)$$

And their derivatives

$$\left.\frac{du_1}{dx}\right|_{x=-a} = \left.\frac{du_2}{dx}\right|_{x=-a}$$

Match up so. Similarly, at $x = a$, the wavefunctions

$$u_2(a) = u_3(a)$$

And their derivatives

$$\left.\frac{du_2}{dx}\right|_{x=a} = \left.\frac{du_3}{dx}\right|_{x=a}$$

Notice, infact, we have that the wavefunction must decay for $x \to \pm\infty$, so we may write the seperate wavefunctions for all 3 regions:

$$\begin{aligned} u_1 &= Ce^{\mu x} \\ u_2 &= A\cos kx + A\sin kx \\ u_3 &= De^{-\mu x} \end{aligned}$$

Now, at $x = a$, we apply the continuity boundary conditions:

$$A\cos ka + B\sin ka = De^{-\mu a} \tag{2.4}$$
$$-Ak\sin ka + Bk\cos ka = -\mu De^{-\mu a} \tag{2.5}$$

And at $x = -a$:

$$A\cos ka - B\sin ka = Ce^{-\mu a} \tag{2.6}$$
$$Ak\sin ka + Bk\cos ka = C\mu e^{-\mu a} \tag{2.7}$$

Now, there is one solution with (2.4) - (2.5) / (2.6)+ (2.7), which gives us:

$$\begin{aligned} \frac{Ak\sin ka}{A\cos ka} &= \frac{(C+D)e^{-\mu a}}{(C+D)e^{-\mu a}} \\ \Rightarrow \tan ka &= \frac{\mu}{k} \quad or \quad D = -C, A = 0 \end{aligned}$$

And a second solution with (2.4) + (2.5) / (2.6) - (2.7), which gives us:

$$\cot ka = -\frac{\mu}{k} \quad or \quad D = C, B = 0$$

So, if we use the tan solution, we also have that $D = C$ and $B = 0$. If we go with the cot solution, we also have that $D = -C$ and $A = 0$.
So, taking the tan solution:

$$\tan ka = \frac{\mu}{k} \tag{2.8}$$

With $D = C, B = 0$, the wavefunctions look like:

$$\begin{aligned} u_1 &= Ce^{\mu x} \\ u_2 &= A\cos kx \\ u_3 &= Ce^{-\mu x} \end{aligned}$$

Now, to solve the tan solution (2.8), we do so graphically, by plotting $y = \tan ka$ and lines of $\frac{\mu}{k}$. To do this:

$$\begin{aligned} \mu^2 &= \frac{2m(V_0 - E)}{\hbar^2} \\ &= \frac{2mV_0}{\hbar^2} - k^2 \\ \Rightarrow \frac{\mu}{k} &= \frac{\sqrt{\lambda - k^2a^2}}{ka} \\ \lambda &\equiv \frac{2mV_0a^2}{\hbar^2} \end{aligned}$$

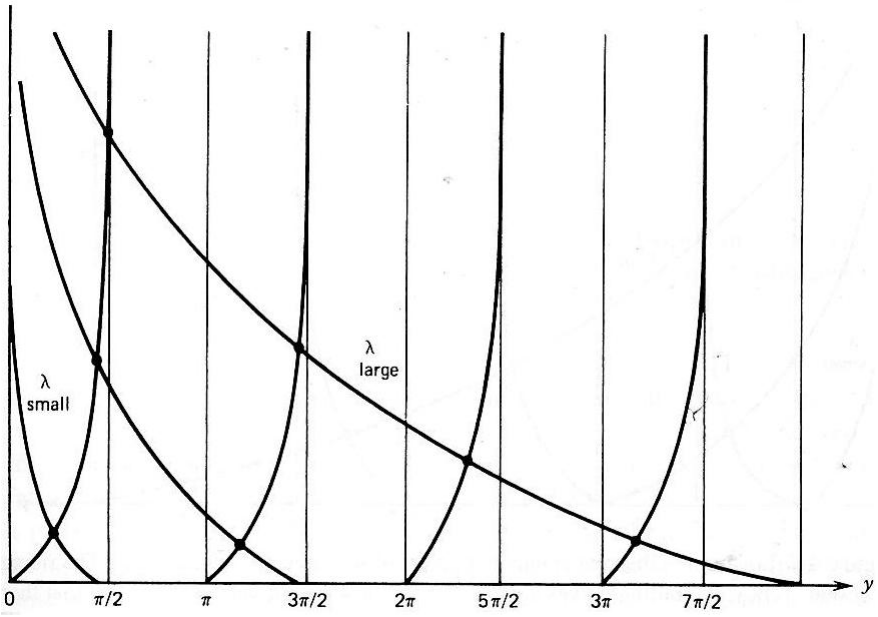

Figure 2: The graphical method for solving (2.8). Notice that the lines of $\tan ka$ only cross lines of particular λ at discrete points.

So, for a 'shallow well', we have V_0 is small, hence λ is small, hence a small number of solutions of bound states.
Note, if $V = \infty$, then λ is large, hence an infinite number of bound states. Which is what has been previously derived for the infinite square well.
No matter how shallow the well is, there will always be bound states.
The interesting thing is, that the wavefunction seeps into classically forbidden region! This is a very odd result: remembering that the probability to find a particle somewhere is the square of its wavefunction, means that there is a finite probability to find any particle anywhere at all!

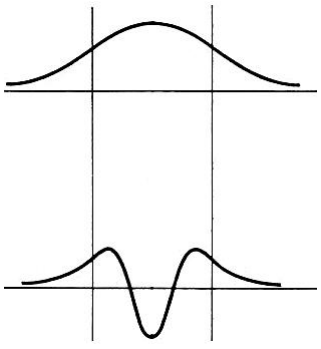

Figure 3: The first two wavefunctions for bound states of the finite well. Notice the seepage of the wavefunction into classically forbidden regions.

Things to note:

There is always bound states (i.e. at least one solution), no matter how small the value of $\lambda = \frac{2mV_0a^2}{\hbar^2}$.
As V_0 or a increases, there are more bound solutions (e.g. bound energy levels) and lowest solution tends towards infinite square well solution.
Energies are slightly lower than for the infinite well.

2.3 Finite Well in 3D

Here, we have a well of depth V_0, width a, starting from $r = 0$ to $r = a$. There are two wavefunctions: inside u_1 and outside u_2. Now, the Schrodinger equation has the form:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)u = Eu \tag{2.9}$$

We look for solutions with $E < V_0$: i.e. bound solutions.
We assume spherical symmetry, hence independant of θ, ϕ; and the Laplacian operator looks like:

$$\nabla^2 u = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right)$$

We try solutions of the form:

$$\begin{aligned} u(r) &= \frac{1}{r}\phi(r) \\ \Rightarrow \nabla^2 u &= \frac{1}{r}\frac{\partial^2\phi}{\partial r^2} \end{aligned}$$

Hence, the TISE (2.9) becomes:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\phi}{\partial r^2} + V\phi = E\phi$$

So, for the case $V = 0$, i.e. inside the well, we have wavefunction:

$$\begin{aligned} \phi_1 &= A\cos kr + B\sin kr \\ k^2 &= \frac{2mE}{\hbar^2} \end{aligned}$$

And for outside, $V = V_0$:

$$\begin{aligned} \phi_2 &= Ce^{-\mu r} + De^{\mu r} \\ \mu^2 &= \frac{(V_0 - E)2m}{\hbar^2} \end{aligned}$$

Now, $u_2 = \frac{\phi_2}{r}$ must remain finite as $r \to \infty$, so $D = 0$. Similarly, $u_1 = \frac{\phi_1}{r}$ must remain finite as $r \to 0$, so $A = 0$. Hence, we have:

$$\begin{aligned} u_1 &= \frac{B\sin kr}{r} \\ u_2 &= \frac{Ce^{-\mu r}}{r} \end{aligned}$$

We apply the countinuity boundary conditions:

$$\begin{aligned} u_1(r=a) &= u_2(r=a) \\ u_1'(r=a) &= u_2'(r=a) \end{aligned}$$

This easily gives:

$$\begin{aligned} \cot ka &= -\frac{\mu}{k} \\ &= -\sqrt{\frac{2mV_0}{\hbar^2 k^2} - 1} \end{aligned}$$

Which we solve graphically. In a similar way to the 1D solution, we find that there are no solutions for $ka < \frac{\pi}{2}$. Hence, as:

$$k^2 a^2 = \frac{2mV_0 a^2}{\hbar^2}$$

Then have that

$$V_0 > \frac{\pi^2 \hbar^2}{8ma^2}$$

For a (bound) solution. Basically, when we plot the wavefunctions, we find that the $\sin kr$ must have started to 'turn over' for it to match the gradient of $e^{-\mu r}$. Hence, k has a lower limit. If the sine just about peaks where it joins the exponential, there is a lot of wavefunction outside the well, and is hence very loosely bound.
An example of this is the Deuteron: ${}^2H$; (pn):
Experimentally, we find that $(V_0 - E) = 2.23$MeV i.e. the binding energy. And that $a = 2 \times 10^{-15}$m.
There are no (bound) excited states of the deuteron - and that the first excited state is unbound by 0.06MeV.

2.4 Quantum Mechanical Tunnelling

Consider a flux of particles of energy $E = \frac{\hbar^2 k^2}{2m}$ approaching a barrier of width a, height V_0 ($E > V_0$).
We assume that some flux of particles emerges on the other side.
Basically, we havea zero potential setup, with a barrier of height V_0 starting on $x = 0$ to a.
The momentum of incoming particles is $p = \hbar k$. What are the momentum eigenfunction?

$$\begin{aligned} \hat{P}_x &= -i\hbar \frac{\partial}{\partial x} \\ \Rightarrow \hat{P}_x \phi &= (\hbar k)\phi \\ \Rightarrow \phi &= e^{ikx} \end{aligned}$$

So, we have flux of particles incident, assume some to be reflected, and some that appear on the other side of the barrier. In the region $x < 0$, we have wavefunction u_1:

$$u_1 = Ae^{ikx} + Be^{-ikx}$$

Where $|A|^2$ denotes the number of incoming particles per unit length; and B being the eqivalent for reflected particles.
For the region $0 \leq x \leq a$, we solve:

$$\begin{aligned} \frac{d^2u_2}{dx^2} &= \frac{2m(V_0 - E)}{\hbar^2}u_2 \\ \Rightarrow u_2 &= Ce^{\mu x} + De^{-\mu x} \\ \mu^2 &\equiv \frac{2m(V_0 - E)}{\hbar^2} \end{aligned}$$

For $x > a$, we have that $u_3 = Fe^{ikx}$.
Now, to progress, we do the standard 'boundary conditon' match-up.
At $x = 0$ we have $u_1(0) = u_2(0)$ and their derivatives:

$$A + B = C + D \tag{2.10}$$

$$A - B = \frac{\mu}{ik}(C - D) \tag{2.11}$$

Similarly for at $x = a$, with u_2, u_3:

$$Ce^{\mu a} + De^{-\mu a} = Fe^{ika} \tag{2.12}$$

$$Ce^{\mu a} - De^{\mu a} = \frac{ik}{\mu}Fe^{ika} \tag{2.13}$$

Now, we want F in terms of A: i.e. we want to find out how many particles we expect to emerge from the barrier, if we know how many we are firing at it. To do so, we begin with doing the following operations, in order: (2.10) + (2.11), (2.12) + (2.13), (2.12) - (2.13):

$$2A = \left(1 + \frac{\mu}{ik}\right)C + \left(1 - \frac{\mu}{ik}\right)D \tag{2.14}$$

$$2Ce^{\mu a} = \left(1 + \frac{ik}{\mu}\right)Fe^{ika} \tag{2.15}$$

$$2De^{-\mu a} = \left(1 - \frac{ik}{\mu}\right)Fe^{ika} \tag{2.16}$$

And, substituting C, D from (2.15) and (2.16) into (2.14), gives (after a bit of algebra):

$$\frac{F}{A} = \frac{4i\mu k}{(2i\mu k + \mu^2 - k^2)e^{-\mu a} + (2i\mu k - \mu^2 + k^2)e^{\mu a}}e^{-ika} \tag{2.17}$$

Now, if the tunnelling probability is small (which is what we are assuming), we neglect the $e^{-\mu a}$ term in (2.17). We define $\left|\frac{F}{A}\right|^2$ as the tunnelling probability, and we find it to be:

$$\begin{aligned} \left|\frac{F}{A}\right|^2 &= \frac{16\mu^2k^2}{(\mu^2 + k^2)^2}e^{-2\mu a} \\ &= \frac{16(V_0 - E)E}{V_0^2}e^{-2\mu a} \end{aligned}$$

Hence, the tunnelling probabilty is largely determined by the exponential decay within the barrier:

$$exp(-const \times width \times \sqrt{height})$$

Where *height* is the difference between the energy of the particle, and the barrier height, so is $V_0 - E$.

2.4.1 Examples of QM Tunnelling

α-Decay: The potential well for a preformed α-particle in the nucleus is the sum of the strong (short range) nuclear attraction, and the weaker (long range) Coulomb repulsion.
We also have the exmples of the Scanning Tunnelling Microscope, and thermonuclear fusion in stars.

3 Orbital Angular Momentum

3.1 Comments & Introduction

3.1.1 Commutation Relations

The order of QM operators is important. Consider the difference in sequential operations on ψ:

$$\begin{aligned}(\hat{P}_x\hat{x} - \hat{x}\hat{P}_x)\psi &= -i\hbar\frac{\partial}{\partial x}(x\psi) - \left(-xi\hbar\frac{\partial\psi}{\partial x}\right) \\ &= -i\hbar\left(x\frac{\partial\psi}{\partial x} + \psi\right) - \left(-xi\hbar\frac{\partial\psi}{\partial x}\right) \\ &= -i\hbar\psi \\ \Rightarrow (\hat{P}_x\hat{x} - \hat{x}\hat{P}_x)\psi &\neq 0\end{aligned}$$

This result is independant of the form of ψ, so we can write:

$$\left[\hat{P}_x, \hat{x}\right] \equiv \hat{P}_x\hat{x} - \hat{x}\hat{P}_x = -i\hbar$$

Where we call $\left[\hat{P}_x, \hat{x}\right]$ the 'commutator'. Obviously, we could also write:

$$\begin{aligned}\left[\hat{P}_y, \hat{y}\right] &= \left[\hat{P}_z, \hat{z}\right] = -i\hbar \\ \left[\hat{x}, \hat{P}_x\right] &= -\left[\hat{P}_x, \hat{x}\right]\end{aligned}$$

It is evident that:

$$[\hat{x}, \hat{y}] = [\hat{y}, \hat{z}] = [\hat{z}, \hat{x}] = 0$$

And also, there are things like:

$$\left[\hat{P}_x, \hat{y}\right] = \left[\hat{P}_x, \hat{z}\right] = 0$$

If $\left[\hat{Q}, \hat{R}\right] = 0$, then we say that the operators 'commute'. It is more instructive to write:

$$\begin{aligned}\left[\hat{P_{x_i}}, \hat{x_j}\right] &= -\delta_{ij}i\hbar \\ [\hat{x_i}, \hat{x_j}] &= 0\end{aligned}$$

We also see that:

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

3.1.2 Compatibility of Physical Variables

If $\left[\hat{Q}, \hat{R}\right] = 0$, the physical observables they represent are said to be 'compatible': the operators $\hat{Q}, \hat{R}$ have a common set of eigenfunctions.
Thus, a measurement of $\hat{Q}$ on ψ will collapse the state into a common eigenfunction of $\hat{Q}$: ϕ_n.
A subsequent measurement of the other quantity (represented by $\hat{R}$) will have an exactly predictable result ($\hat{R}\phi_n = r_n\phi_n$) and will leave the wavefunction unchanged.
Operators of compatible observables commute:
If we have that $\psi = \sum a_n\phi_n$, and if we consider:

$$\begin{aligned}
\left[\hat{Q}, \hat{R}\right]\psi &= \sum a_n(\hat{Q}\hat{R}\phi_n - \hat{R}\hat{Q}\phi_n) \\
&= \sum a_n(\hat{Q}r_n\phi_n - \hat{R}q_n\phi_n) \\
&= \sum a_n(r_n\hat{Q}\phi_n - q_n\hat{R}\phi_n) \\
&= \sum a_n(r_nq_n\phi_n - q_nr_n\phi_n) \\
&= 0
\end{aligned}$$

Hence proved; as we have assumed that $\hat{R}$ and $\hat{Q}$ posses common sets of eigenfunctions, the ϕ_n.

3.1.3 Comments on the Uncertainty Principle

If two operators do not commute, there is a fundamental limit on the products of the root-mean-square deviations associated with measurements of their eigenvalues. Now, Rae 4.5 proves the following statement:

$$\Delta q\Delta r \geq \frac{1}{2}\left|\langle\left[\hat{Q}, \hat{R}\right]\rangle\right|$$

Where we have:

$$\begin{aligned}
\Delta q^2 &= \int \psi^*(\hat{Q} - \langle\hat{Q}\rangle)^2\psi\, d\tau \\
\langle\hat{Q}\rangle &= \int \psi^*\hat{Q}\psi\, d\tau
\end{aligned}$$

In later lectures, we used:

$$\Delta q^2 = \langle\hat{Q}^2\rangle - \langle\hat{Q}\rangle^2$$

For example, since $\left[\hat{x}, \hat{P_x}\right] = i\hbar$, then $\Delta x\Delta P_x \geq \frac{\hbar}{2}$.
The UP does not imply

- Measurement of P_x affect subsequent measurement of x.
- If two operators commute, then the product of their uncertainties must be zero.

However, if ψ is one of the common eigenfunctions ϕ_n, then both observables have exactly determined values and state stays in ϕ_n.
So, if $\left[\hat{Q}, \hat{R}\right] = 0$, then $\hat{Q}\phi_n = q_n\phi_n$ and $\hat{R}\phi_n = r_n\phi_n$, we have a common set of eigenfunctions.

3.1.4 Degeneracy

Here, if we have:

$$\begin{aligned}\hat{Q}\phi_n &= q\phi_n \\ \hat{Q}\phi_m &= q\phi_m\end{aligned}$$

Then ϕ_n is degenerate: we have the same eigenvalue for two or more eigenfunctions.
It was assumed in the proof of orthonormality, that if $\hat{Q}\phi_n = q_n\phi_n$, then $q_n \neq q_m$, for all n, m. So, we had that:

$$\begin{aligned}\int \phi_n^*\phi_m \, d\tau &= 0 \quad if \quad n \neq m \\ q_n &= q_m \quad if \quad n = m\end{aligned}$$

This is only the case if there is no degeneracy.
Hence, a set of non-degenerate eigenfunctions are orthonormal, but a set of degenerate eigenfunctions are not nessecarily orthonormal.

Orthonormality It is always possible to construct a set of orthonormal eigenfunctions, from a set of non-orthonormal eigenfunctions.
Consider:

$$\begin{aligned}\hat{Q}\phi_1 &= q\phi_1 \\ \hat{Q}\phi_2 &= q\phi_2\end{aligned}$$

Now, any linear combination of ϕ_1, ϕ_2 is also an eigenfunction of $\hat{Q}$:

$$\begin{aligned}\hat{Q}(\alpha\phi_1 + \beta\phi_2) &= \alpha q\phi_1 + \beta q\phi_2 \\ &= q(\alpha\phi_1 + \beta\phi_2)\end{aligned}$$

So, if we construct:

$$\begin{aligned}\phi_2' &= S_{12}\phi_1 - \phi_2 \\ S_{12} &\equiv \int \phi_1^*\phi_2 \, d\tau\end{aligned}$$

Thus, we show that ϕ_2' is orthonormal to ϕ_1:

$$\begin{aligned}\int \phi_1^*\phi_2' \, d\tau &= S_{12}\int \phi_1^*\phi_1 \, d\tau - \int \phi_1^*\phi_2 \, d\tau \\ &= S_{12} - S_{12} \\ &= 0\end{aligned}$$

Hence orthonormal.
For 3 or more degenerate states, see Rae for 'Schmidt Orthogonalisation Procedure'.

Compatibility If $\left[\hat{Q}, \hat{R}\right] = 0$, then there exists a common set of eigenfunctions. Again, before, $q_n \neq q_m$ was assumed before.
If $q_n = q_m$, a measurement result of q_n would not tell you which eigenfunction the state collapsed into.
Once again, let $\hat{Q}\phi_1 = q\phi_1, \hat{Q}\phi_2 = q\phi_2$. Then, any combination of $\phi' = (\alpha\phi_1 + \beta\phi_2)$ is an eigenfunction of $\hat{Q}$, but not necessarily $\hat{R}$:

$$\begin{aligned} \hat{R}\phi' &= (\alpha r_1\phi_1 + \beta r_2\phi_2) \\ &\neq const \times (\alpha\phi_1 + \beta\phi_2) \end{aligned}$$

Nevertheless, a set of eigenfunctions can be found, that are common to both operators.
Now, this happens:

- Measurement with $\hat{Q}$ on arbitrary ψ; gives a collapse into ϕ_n, with result q_n.
- ϕ_n may not be an eigenfunction of $\hat{R}$.
- Measurement with $\hat{R}$ on ϕ_n; giving further collapse, into common eigenfunctions.
- Leaving q_n unchanged, and results in value r_n.
- All subsequent measurements with $\hat{Q}$ or $\hat{R}$ will always give q_n, r_n.
- In this case, $\Delta q \Delta r = 0$.

An example of this is orbital angular momentum:
The $n = 2$ state is split into $L = 0$ and $L = 1$. So, a measurement using $\hat{L}^2$ gives an eigenvalue $L(L+1)\hbar^2$; so, either $0\hbar^2$ or $2\hbar^2$.
For the zero measurement, there is a unique, common eigenfunction of $\hat{L}^2$ and $\hat{L}_z$; and $m = 0$ being our eigenvalue.
However, for the $2\hbar^2$ case, we have 3 possible states when we measure with $\hat{L}_z$: ones where $m = -1, 0, 1$.
All further measurements will find the same eigenvalues.

3.2 Commutation Relations for Orbital Angular Momentum

Now, from postulate 3, we can go from the classical $\mathbf{l} = \mathbf{r} \times \mathbf{p}$, to the quantum mechanical:

$$\hat{L} = \hat{R} \times \hat{P}$$

Hence, we can write that the components of $\hat{L}$ are:

$$\begin{aligned} \hat{L}_x &= \hat{y}\hat{P}_z - \hat{z}\hat{P}_y \\ \hat{L}_y &= \hat{z}\hat{P}_x - \hat{x}\hat{P}_z \\ \hat{L}_z &= \hat{x}\hat{P}_y - \hat{y}\hat{P}_x \end{aligned}$$

Where we have used standard Cartesian coordinates. Notice the cyclic nature of the coordinates.
We can write that:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Now, to find out if there exists a common set of eigenfunctions of $\hat{L}^2, \hat{L}_x^2, \hat{L}_y^2, \hat{L}_z^2$, we consider the commutation relations (where we now omit the hat):

$$\begin{aligned}\left[\hat{L_x}, \hat{L_y}\right] = & \quad (yP_z - zP_y)(zP_x - P_z) - (zP_x - xP_z)(yP_z - zP_y) \\ = & \quad yP_zzP_x - yP_zxP_z - zP_yzP_x + zP_yxP_z \\ & -zP_xyP_z + zP_xzP_y + xP_zyP_z - xP_zzP_y\end{aligned}$$

Watch out for the order of operators!
Now, remember that $[\hat{x}, \hat{y}] = 0$, and $\left[\hat{P_x}, \hat{P_y}\right] = 0$ etc; but $\left[\hat{P_x}, \hat{x}\right] = -i\hbar = \left[\hat{P_y}, \hat{y}\right] = \left[\hat{P_z}, \hat{z}\right]$.
Hence, we have that:

$$\begin{aligned}zP_yxP_z &= P_yzxP_z \\ &= P_yxzP_z \\ &= xP_yzP_z\end{aligned}$$

Hence, we have that:

$$\begin{aligned}\left[\hat{L_x}, \hat{L_y}\right] &= yP_x(P_zz - zP_z) + xP_y(zP_z - P_zz) \\ &= yP_x\left[\hat{P_z}, \hat{z}\right] + xP_y\left[\hat{z}, \hat{P_z}\right] \\ &= (yP_x - xP_y)\left[\hat{P_z}, \hat{z}\right] \\ &= (-\hat{L}_z)(-i\hbar) \\ &= i\hbar\hat{L}_z \\ \Rightarrow \left[\hat{L_x}, \hat{L_y}\right] &= i\hbar\hat{L}_z\end{aligned}$$

Similarly, by cycling over indices, we have all together:

$$\begin{aligned}\left[\hat{L_x}, \hat{L_y}\right] &= i\hbar\hat{L}_z \\ \left[\hat{L_y}, \hat{L_z}\right] &= i\hbar\hat{L}_x \\ \left[\hat{L_z}, \hat{L_x}\right] &= i\hbar\hat{L}_y\end{aligned}$$

Hence, no set of common eigenfunctions exist for any of the pairs of operators.
A system in a state of definite L_z (say) cannot have a definite value of L_x or L_y. Thus, we cannot determine the direction of $\mathbf{L}$.
Now, let us consider:

$$\left[\hat{L^2}, \hat{L_x}\right] = \left[\hat{L_x^2}, \hat{L_x}\right] + \left[\hat{L_y^2}, \hat{L_x}\right] + \left[\hat{L_z^2}, \hat{L_x}\right]$$

We can immediately see that $\left[\hat{L_x^2}, \hat{L_x}\right] = \hat{L}_x^2\hat{L}_x - \hat{L}_x\hat{L}_x^2 = 0$, as being almost trivial. We look at:

$$\begin{aligned}\left[\hat{L_y^2}, \hat{L_x}\right] &= L_y^2L_x - L_xL_y^2 \\ &= L_y(L_xL_y - i\hbar L_z) - (i\hbar L_z + L_yL_x)L_y \\ &= -i\hbar(L_yL_z + L_zL_y)\end{aligned}$$

Similarly:

$$\left[\hat{L_z^2}, \hat{L_x}\right] = i\hbar(L_y L_z + L_z L_y)$$

Hence, we have that $\left[\hat{L^2}, \hat{L_x}\right] = 0$. Similarly then for the other indices.

Thus, there exists a common set of eigenfunctions of $\hat{L}^2$ and $\hat{L}_x$.
There exists a different set of common eigenfunction of $\hat{L}^2$ and $\hat{L}_y$; as well as for $\hat{L}^2$ and $\hat{L}_y$. Hence, three different sets of common eigenfunctions.
By convention, we work with the last set, in $\hat{L}^2$ and $\hat{L}_z$. We can always describe a state which is an eigenfunction of $\hat{L}_y$ (say) by a linear combination of the $\hat{L}_z$ eigenfunctions; as we shall see later in the course.

3.3 $\hat{L}^2, \hat{L}_z$ Operators in Spherical Polars

Once again, we start with $\hat{L} = \hat{R} \times P = -i\hbar(\mathbf{r} \times \nabla)$. Now, we write del in spherical polars thus:

$$\nabla = \hat{\mathbf{r}}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}$$

Hence, if we do the cross-product, with $\mathbf{r} = r$ in spherical polars, we get that:

$$\hat{L} = (-i\hbar)\left(\hat{\phi}\frac{\partial}{\partial \theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right)$$

Now, we have the transformation of the unit vector in the $z-$direction is $\mathbf{z} = \mathbf{r}\cos\theta - \hat{\theta}\sin\theta$. Hence:

$$\begin{aligned} \hat{L}_z &= \mathbf{z} \cdot \hat{L} \\ &= -i\hbar\frac{\partial}{\partial \phi} \end{aligned}$$

And, with much more effort, we find that:

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

3.3.1 Spherical Harmonics

The eigenfunctions of $\hat{L}^2$ are called spherical harmonics $Y(\theta, \phi)$. To find them, we use separation of variables:

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

From this procedure (found in Rae pp46-49), we find that:

$$\Theta = \sum_{\ell} a_\ell \cos^\ell\theta \qquad \ell = 0, 1, 2, \ldots$$

With conditions on a_ℓ (such as avoiding infinities, so the series must terminate). And we also find that:

$$\Phi(\phi) = \frac{1}{\sqrt{2}} e^{im\phi}$$

(note the normalisation: $\int_0^{2\pi} |\Phi|^2 d\phi = 1$). With $|m| \leq \ell$. So, we have that m is constrained:

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

So that we have $2\ell + 1$ values of m for each ℓ. Hence, we find that solutions have the form:

$$\begin{aligned} Y_{\ell,m}(\theta,\phi) &= norm \times associated\, Legendre\, Polynomial \times e^{im\phi} \\ &= (-1)^m \left[\frac{(2\ell+1)(\ell-|m|)!}{4\pi(\ell+|m|)!} \right]^{\frac{1}{2}} P_\ell^{|m|}(\cos\theta) e^{im\phi} \end{aligned}$$

Then these eigenvalues are found:

$$\begin{aligned} \hat{L}^2 Y_{\ell,m} &= \ell(\ell+1)\hbar^2 Y_{\ell,m} \quad \ell = 0, 1, 2, \ldots \\ \hat{L}_z Y_{\ell,m} &= m\hbar Y_{\ell,m} \quad m = \ell, \ldots, 0, \ldots, -\ell \end{aligned}$$

3.4 Ladder Operators

We can find the eigenvalues and develop a complete set of eigenfunctions of the $\hat{L}^2, \hat{L}_z$ (i.e. commuting) operators; by using 'ladder operators':

$$\hat{L}_+ \equiv \hat{L}_x + i\hat{L}_y \tag{3.1}$$
$$\hat{L}_- \equiv \hat{L}_x - i\hat{L}_y \tag{3.2}$$

Thus, these operators are non-Hermitian, and do not represent physical observables; But they change the eigenfunctions $Y_{\ell,m}$ to $const \times Y_{\ell,m\pm1}$, and are so sometimes called 'raising and lowering operators'.
So, the first thing to do is to establish commutation relations. We initally mulitply the two operators together:

$$\begin{aligned} \hat{L}_+\hat{L}_- &= (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) \\ &= \hat{L}_x^2 + \hat{L}_y^2 - i\hat{L}_x\hat{L}_y + i\hat{L}_y\hat{L}_x \\ &= \hat{L}_x^2 + \hat{L}_y^2 - i\left[\hat{L_x}, \hat{L_y}\right] \end{aligned}$$

Now, we know that $\left[\hat{L_x}, \hat{L_y}\right] = i\hbar\hat{L}_z$, and $\hat{L}_x^2 + \hat{L}_y^2 = \hat{L}^2 - \hat{L}_z^2$. Hence:

$$\hat{L}_+\hat{L}_- = \hat{L}^2 - \hat{L}_z^2 + \hbar\hat{L}_z$$

We see similarly, that:

$$\hat{L}_-\hat{L}_+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z \tag{3.3}$$

Hence, we have the commutation relation:

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

Similarly, we have:

$$\begin{aligned}\left[\hat{L_z}, \hat{L_+}\right] &= \left[\hat{L_z}, \hat{L_x}\right] + i\left[\hat{L_z}, \hat{L_y}\right] && (3.4)\\ &= i\hbar(\hat{L}_y - i\hat{L}_x) && (3.5)\\ &= \hbar\hat{L}_+ && (3.6)\\ \Rightarrow \left[\hat{L_z}, \hat{L_+}\right] &= \hbar\hat{L}_+ && (3.7)\end{aligned}$$

Similarly, we find that $\left[\hat{L_z}, \hat{L_-}\right] = -\hbar\hat{L}_-$.
Now, consider the eigenvalue equation:

$$\hat{L}_z\phi = \beta\phi$$

So that we have that β is some eigenvalue ($= m\hbar$), for the eigenfunction ϕ.
Now, operate on this whole equation with $\hat{L}_+$:

$$\hat{L}_+\hat{L}_z\phi = \beta\hat{L}_+\phi \tag{3.8}$$

Now, from (3.7), we have that $\hat{L}_z\hat{L}_+ - \hat{L}_+\hat{L}_z = \hbar\hat{L}_+ \Rightarrow \hat{L}_+\hat{L}_z = \hat{L}_z\hat{L}_+ - \hbar\hat{L}_+$. Thus, we put this into (3.8):

$$\begin{aligned}(\hat{L}_z\hat{L}_+ - \hbar\hat{L}_+)\phi &= \beta\hat{L}_+\phi && (3.9)\\ \Rightarrow \hat{L}_z(\hat{L}_+\phi) &= (\beta+\hbar)(\hat{L}_+\phi) && (3.10)\end{aligned}$$

Similarly:

$$\hat{L}_z(\hat{L}_-\phi) = (\beta-\hbar)(\hat{L}_-\phi)$$

Hence, we see that $(\hat{L}_+\phi)$ and $(\hat{L}_-\phi)$ are (unnormalised) eigenfunctions of $\hat{L}_z$, with eigenvalues $(m+1)\hbar$ and $(m-1)\hbar$.
Now, consider

$$\hat{L}^2\phi = \alpha\phi$$

- we know that $\alpha = \ell(\ell+1)\hbar^2$. Now, if we operate on this, from the left, with both ladder operators:

$$\begin{aligned}\hat{L}_+\hat{L}^2\phi &= \alpha\hat{L}_+\phi \\ \hat{L}_-\hat{L}^2\phi &= \alpha\hat{L}_-\phi\end{aligned}$$

Now, we also know that $\hat{L}^2$ commutes with $\hat{L}_x, \hat{L}_y$, so therefore $\hat{L}^2$ commutes with $\hat{L}_+, \hat{L}_-$; hence, we can change the order to:

$$\begin{aligned}\hat{L}^2(\hat{L}_+\phi) &= \alpha(\hat{L}_+\phi) \\ \hat{L}^2(\hat{L}_-\phi) &= \alpha(\hat{L}_-\phi)\end{aligned}$$

Which are just eigenvalue equations. So therefore, both $\hat{L}_+$ and $\hat{L}_-$ are eigenfunctions of the $\hat{L}^2$ operator, with the same eigenvalue α.

Now, imagine we project the L^2 eigenfunction onto the $z-$axis; to give L_z. Now, the length of each L line is just $|L| = \sqrt{\alpha}$. We can use the ladder operators to move from one L_z eigenfunction to the next. If the maximum L_z eigenvalue/functions are β_1, ϕ_1, and the minimum β_2, ϕ_2; then operating on the maximum with the raising operator will produce zero; similarly for the lowering and minimum.
So, we have that $\beta_1^2, \beta_2^2 < \alpha$, and $\hat{L}_z\phi_1 = \beta_1\phi_1$. Now, we suppose that:

$$\hat{L}_+\phi_1 = 0 \tag{3.11}$$
$$\hat{L}_-\phi_2 = 0 \tag{3.12}$$

Now, operating on (3.11) with $\hat{L}_-$ and then use (3.3):

$$\hat{L}_-\hat{L}_+\phi_1 = (\hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z)\phi_1 = 0 \tag{3.13}$$
$$= (\alpha - \beta_1^2 - \hbar\beta_1)\phi_1 = 0 \tag{3.14}$$
$$\Rightarrow \alpha = \beta_1(\beta_1 + \hbar) \tag{3.15}$$

Hence, what we have shown is that α, which is the eigenvalue of $\hat{L}^2$ is the same as $\beta_1(\beta_1+\hbar)$, where β_1 is the maximum eigenvalue of $\hat{L}_z$.
We can do a similar operation on (3.12), to give:

$$\alpha = \beta_2(\beta_2 - \hbar)$$

Which is equivalent. Thus, these two equations give a symmetry property:

$$\beta_1 = -\beta_2$$

Now, as β changes by 1 unit of $\hbar$ in raising and lowering operations, it follows that:

$$\beta_1 - \beta_2 = n\hbar$$

Where n is an integer. If arrangement is symmetrical about $L_z = 0$ state, then n is even $= 2\ell$ (say). Thus it follows that:

$$\alpha = \ell(\ell+1)\hbar^2$$
$$\beta = m\hbar \qquad -\ell \leq m \leq +\ell$$

Notice:

$$\hat{L}_x = \frac{1}{2}(\hat{L}_+ + \hat{L}_-)$$
$$\hat{L}_y = \frac{1}{2i}(\hat{L}_+ - \hat{L}_-)$$

3.4.1 Axial Symmetry of L_z Eigenstates

Here, we show that $\left\langle \hat{L}_x \right\rangle = 0$ & $\left\langle \hat{L}_y \right\rangle = 0$.
Now, since we have the definitions:

$$\hat{L}_+ \equiv \hat{L}_x + i\hat{L}_y$$
$$\hat{L}_- \equiv \hat{L}_x - i\hat{L}_y$$

We can write:

$$\hat{L}_x = \frac{1}{2}\left(\hat{L}_+ + \hat{L}_-\right)$$

And similarly for $\hat{L}_-$.
Now, let ϕ_m be an eigenstate of $\hat{L}_z$. For this state, we write:

$$\begin{aligned}\left\langle \hat{L}_x \right\rangle &= \int \phi_m^* \hat{L}_x \phi_m \, d\tau \\ &= \frac{1}{2}\int \phi_m^* (\hat{L}_+ + \hat{L}_-)\phi_m \, d\tau \\ &= \frac{1}{2}\int c_1 \phi_m^* \phi_{m+1} + c_2 \phi_m^* \phi_{m-1} \, d\tau \\ &= 0\end{aligned}$$

Where the last two steps are done using $\hat{L}_+\phi_m = c_1\phi_{m+1}$ and using the fact that the eigenfunctions are orthonormal. We similarly show that $\left\langle \hat{L}_y \right\rangle = 0$.
Therefore, a state ϕ_m has axial symmetry about $z-$axis, since no preferred $x-$ or $y-$projection.

3.4.2 What is Constant c_1 in $\hat{L}_+\phi_m = c_1\phi_{m+1}$?

We want to find the constant c_1 in the eigenequation:

$$\hat{L}_+\phi_m = c_1\phi_{m+1}$$

We need this relationship:

$$\begin{aligned}\int f\hat{L}_- g \, d\tau &= \int f(\hat{L}_x - i\hat{L}_y)g \, d\tau \\ &= \int g(\hat{L}_x^* - i\hat{L}_y^*)f \, d\tau\end{aligned}$$

Which we are able to do via the definition of Hermitian operators.
Now, using the normalised wavefunction ϕ_m, we have:

$$\begin{aligned}|c_1|^2 \int \phi_{m+1}^*\phi_{m+1} \, d\tau &= \int (\hat{L}_+\phi_m)(\hat{L}_+\phi_m)^* \, d\tau \\ &= \int \phi_m^* \hat{L}_-\hat{L}_+\phi_m \, d\tau \\ &= \int \phi_m^*(\hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z)\phi_m \, d\tau \\ &= \ell(\ell+1)\hbar^2 - m^2\hbar^2 - m\hbar^2 \\ \Rightarrow |c_1|^2 &= \ell(\ell+1)\hbar^2 - m^2\hbar^2 - m\hbar^2\end{aligned}$$

From (3.3). Thus, as $\int \phi_{m+1}^*\phi_{m+1} \, d\tau = 1$, as ϕ_m normalised:

$$\hat{L}_+\phi_m = \hbar\sqrt{\ell(\ell+1) - m(m+1)}\,\phi_{m+1}$$

Similarly:

$$\hat{L}_{-}\phi_m = \hbar\sqrt{\ell(\ell+1) - m(m-1)}\,\phi_{m-1}$$

Notice, from these, we immediately see that:

$$\begin{aligned}\hat{L}_{+}\phi_{m=+\ell} &= 0\\ \hat{L}_{-}\phi_{m=-\ell} &= 0\end{aligned}$$

Therefore, to combine the knowledge we just gained:

$$\hat{L}_{\pm}\phi_m = \hbar\sqrt{\ell(\ell+1) - m(m\pm1)}\,\phi_{m\pm1}$$

4 Spin

This appears naturally, from the Dirac formalism of relativistic quantum mechanics, but has no classical analogue. There is no differential operator for spin, but we can use the same algebra as for orbital angular momentum.
An electron is a spin $\frac{1}{2}$ particle, so $s = \frac{1}{2}\hbar$, and the possible values of the projection of spin onto the 'z-axis' are $m_s = \pm\frac{1}{2}\hbar$.
We have spin angular momentum operators:

$$\begin{aligned} \hat{S} &= (\hat{S}_x, \hat{S}_y, \hat{S}_z) \\ \hat{S}^2 &= \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \end{aligned}$$

4.1 Commutation Relations

We use the orbital angular momentum analogues, to write:

$$\begin{aligned} \left[\hat{S}_x, \hat{S}_y\right] &= i\hbar\hat{S}_z \\ \left[\hat{S}^2, \hat{S}_z\right] &= 0 \end{aligned}$$

With another two of each, which are similar.
By convention, we work with common set of eigenfunctions for $\hat{S}^2, \hat{S}_z$. We call the eigenvalues α, β:

$$\begin{aligned} \hat{S}_z\alpha &= +\frac{1}{2}\hbar\alpha \\ \hat{S}_z\beta &= -\frac{1}{2}\hbar\beta \end{aligned}$$

So that α corresponds to a spin-up state, and β to spin-down. We also have:

$$\begin{aligned} \hat{S}^2\alpha &= \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\alpha = \frac{3}{4}\hbar^2\alpha \\ \hat{S}^2\beta &= \frac{3}{4}\hbar^2\beta \end{aligned}$$

So, we have that $|S| = \sqrt{\frac{3}{4}}\hbar$, and the projection onto the $z-$axis is $\pm\frac{1}{2}\hbar$.
Now, a general spin $\frac{1}{2}$ wavefunction χ (e.g. spin polarised along the $x-$axis), may be expressed as a linear combination of the $\hat{S}^2, \hat{S}_z$ eigenfunctions:

$$\chi = a\alpha + b\beta$$

Where a, b are coefficients which determine relative populations and relative phases of α, β space. We also have that $a^2 + b^2 = 1$; i.e. normalisation.
A bit of notation: When we refer to either α or β, we'll use χ_{m_s}. Thus:

$$\begin{aligned} \chi_{+\frac{1}{2}} &\equiv \alpha \\ \chi_{-\frac{1}{2}} &\equiv \beta \end{aligned}$$

4.1.1 Ladder Operators

Here, we define thus:

$$\hat{S}_+ \equiv \hat{S}_x + i\hat{S}_y \tag{4.1}$$
$$\hat{S}_- \equiv \hat{S}_x - i\hat{S}_y \tag{4.2}$$

Hence, we have similar results as for orbital angular momentum ladder operators:

$$\begin{aligned}
\hat{S}_x &= \frac{1}{2}(\hat{S}_+ + \hat{S}_-) \\
\hat{S}_y &= \frac{1}{2i}(\hat{S}_+ - \hat{S}_-) \\
\hat{S}_+\chi_{m_s} &= \sqrt{s(s+1) - m_s(m_s+1)}\hbar\chi_{m_s+1} \\
\hat{S}_-\chi_{m_s} &= \sqrt{s(s+1) - m_s(m_s-1)}\hbar\chi_{m_s-1}
\end{aligned}$$

Now, as for the α state we have $m_s = +\frac{1}{2}$, and for the β state $m_s = -\frac{1}{2}$; and that $s = \frac{1}{2}$; hence, we see that:

$$\begin{aligned}
\hat{S}_+\alpha &= 0 \\
\hat{S}_-\alpha &= \hbar\beta \\
\hat{S}_+\beta &= \hbar\alpha \\
\hat{S}_-\beta &= 0
\end{aligned}$$

So then, what are the eigenfunctions of $\hat{S}_x$?
Consider:

$$\begin{aligned}
\hat{S}_x\alpha &= \frac{1}{2}(\hat{S}_+ + \hat{S}_-)\alpha \\
&= \frac{1}{2}\hbar\beta \\
\hat{S}_x\beta &= \frac{1}{2}(\hat{S}_+ + \hat{S}_-)\beta \\
&= \frac{1}{2}\hbar\alpha
\end{aligned}$$

So, we see that α, β are not individually eigenfunctions of $\hat{S}_x$, but, adding the two results:

$$\hat{S}_x(\alpha + \beta) = \frac{1}{2}\hbar(\alpha + \beta)$$

Therefore, we find that $(\alpha + \beta)$ is an eigenfunction: the combination is, but seperately neither are. Hence, the normalised eigenfunction of $\hat{S}_x$ is $\frac{1}{\sqrt{2}}(\alpha + \beta)$, with eigenvalue $\frac{1}{2}\hbar$. Notice, subtracting the results gives a different eigenfunction:

$$\begin{aligned}
\hat{S}_x(\alpha - \beta) &= \frac{1}{2}\beta(\beta - \alpha) \\
&= -\frac{1}{2}(\alpha - \beta)
\end{aligned}$$

Hence, the only other eigenfunction is $\frac{1}{\sqrt{2}}(\alpha - \beta)$, with eigenvalue $-\frac{1}{2}\hbar$.
Similarly, for $\hat{S}_y$, the eigenfunctions and eigenvalues are:

$$\begin{aligned} \frac{1}{\sqrt{2}}(\alpha + i\beta) \qquad & +\frac{1}{2}\hbar \\ \frac{1}{\sqrt{2}}(\alpha - i\beta) \qquad & -\frac{1}{2}\hbar \end{aligned}$$

4.2 Dirac Notation

Simple shorthand that can be used for all aspects of quantum mechanics, but particularly for spin-space, where we need a scheme to handle objects equivalent to $\int \chi^* \chi \, d\tau$, where we dont know the space we are integrating over. So, we write:

- Wavefunction ϕ as $|\phi\rangle$, a state vector 'ket';
- Complex conjugate ϕ^* as $\langle\phi|$ a 'bra';
- Normalisation $\int \phi^* \phi \, d\tau = 1$ as $\langle\phi|\phi\rangle = 1$;
- Hydrogen wavefunction $\phi_{n\ell m}(r, \theta, \phi)$ as $|n, \ell, m\rangle$;
- Spherical harmonics $Y_{\ell m}(\theta, \phi)$ as $|\ell, m\rangle$;
- Expectation value $\langle\hat{Q}\rangle = \int \phi^* \hat{Q} \phi \, d\tau$ as $\langle\phi|\hat{Q}|\phi\rangle$;
- Orthonormality $\int \phi_n^* \phi_m \, d\tau = \delta_{nm}$ as $\langle\phi_n|\phi_m\rangle = \delta_{nm}$ or $\langle n|m\rangle = \delta_{nm}$;
- Expansion coefficients $\psi = \sum a_n \phi_n$, where $a_m = \int \phi_m^* \psi \, d\tau$ as $|\psi\rangle = \sum a_n |\phi_n\rangle$ where $a_m = \langle\phi_m|\psi\rangle$.

We shall see that a ket $|\phi\rangle$ is a column vector, and that the bra $\langle\phi|$ is related to the ket by being a row vector, whose elements are the complex-conjugates of the ket:

$$|\phi\rangle = \begin{pmatrix} a \\ b \\ c \end{pmatrix} \qquad \langle\phi| = (a^*, b^*, c^*)$$

In the same way that a vector must be expressed in terms of some basis (for example, the $\boldsymbol{e}_i, \boldsymbol{e}_j, \boldsymbol{e}_k$ unit vectors in Cartesian coordinates), a ket $|\phi\rangle$ must be expressed in terms of some basis functions.
We can also see that if $|\phi\rangle$ is some orthonormal vector, then $\langle\phi|\phi\rangle = 1$, as $aa^* + bb^* + cc^* = 1$.
We shall thus see (this is all used later on) that the expectation value of some operator $\hat{A}$, represented by some matrix A can be written $\langle\phi|A|\phi\rangle$; thus:

$$\langle\phi|A|\phi\rangle = (a^*, b^*, c^*) \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

Which can obviously be expanded out to a scalar quantity.

4.3 Matrix Representations in QM

4.3.1 Introduction

Let us work with a complete set of eigenfunctions ϕ_n. We call this a basis: a coordinate system for wavefunctions.
Consider the eigenvalue equation of an operator $\hat{Q}$:

$$\hat{Q}\psi = q\psi$$

Where ψ is an eigenfunction of $\hat{Q}$. We can express ψ in our chosen basis:

$$\psi = \sum_n a_n \phi_n$$

Hence, the eigenvalue equation becomes:

$$\sum_n a_n \hat{Q}\phi_n = q \sum_n a_n \phi_n$$

Now, if we multiply from the left by ϕ_m^*, and integrate:

$$\begin{aligned} \sum_n a_n \int \phi_m^* \hat{Q} \phi_n \, d\tau &= q \sum_n a_n \int \phi_m^* \phi_n \, d\tau \\ &= q \sum_n a_n \delta_{mn} \\ &= q a_m \end{aligned}$$

Now, let us define:

$$\int \phi_m^* \hat{Q} \phi_n \, d\tau \equiv Q_{mn}$$

Hence, we have that:

$$\sum_n Q_{mn} a_n = q a_m$$

Which is just standard matrix multiplication! The dimension of the matrix $[Q]$ (which has elements Q_{mn}), is the number of eigenfunctions in the basis.
This is known as a matrix eigenvalue equation. Expanded out, this is:

$$\begin{pmatrix} Q_{11} & Q_{12} & \cdots \\ Q_{21} & Q_{22} & \cdots \\ \vdots & & \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix} = q \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix}$$

The eigenvalue solutions q_n are identical in the matrix representation, and in $\hat{Q}\psi_n = q_n \psi_n$.
For matrix equations, we have that eigenvalues are the roots of the determinant:

$$\begin{vmatrix} Q_{11} - q & Q_{22} & \cdots \\ Q_{21} & Q_{22} - q & \cdots \\ \vdots & & \end{vmatrix} = 0$$

Where we will get the same number of eigenvalues as the dimension of the matrix.
Each solution (each eigenvalue) has an associated eigenvector:

$$\begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix}$$

Equivalent to the eigenfunction:

$$\psi_n = a_1\phi_1 + a_2\phi_2 + a_3\phi_3 + \ldots$$

Where we will obviously have n running up to the dimension of the matrix.
The matrix $[Q]$ is known as an Hermitian Matrix. That is, $[Q]$ is the Hermitian conjugate of $[Q^\dagger]$:

$$[Q^\dagger] \equiv [\tilde{Q}^*]$$

The transpose of the complex conjugate. With $\tilde{Q}_{mn} = Q_{nm}$. We can also see how this works from the integral defintions:

$$\begin{aligned} Q_{mn} &= \int \phi_m^* \hat{Q} \phi_n \, d\tau \\ \Rightarrow \tilde{Q}_{mn} &= \int \phi_n^* \hat{Q} \phi_m \, d\tau \\ \Rightarrow \tilde{Q}_{mn}^* &= \int \phi_n \hat{Q}^* \phi_m^* \, d\tau \end{aligned}$$

Which is the same as the definition of an Hermitian operator:

$$\int \phi_n \hat{Q} \phi_m \, d\tau = \int \phi_m \hat{Q}^* \phi_n \, d\tau$$

Hence, as we have that $[Q]$ is an Hermitian matrix, we can therefore say that it has real eigenvalues.
Now, if we had chosen to work in terms of the basis of eigenfunctions of $\hat{Q}$, so that we have $\hat{Q}\phi_n = q_n\phi_n$:

$$Q_{mn} = \int \phi_m^* \hat{Q} \phi_n \, d\tau = q_n \delta_{mn}$$

That is, the matrix $[Q]$ will be diagonal, with entries q_i:

$$\begin{pmatrix} q_1 & 0 & \ldots \\ 0 & q_2 & \ldots \\ \vdots & & \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix} = q \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix}$$

Thus, $q_1 a_1 = q_2 a_2 = \ldots \Rightarrow q = q_i$. Therefore, eigenvectors will be:

$$\begin{pmatrix} 1 \\ 0 \\ \vdots \end{pmatrix} \quad \begin{pmatrix} 0 \\ 1 \\ \vdots \end{pmatrix} \quad \ldots$$

With eigenvalues $q_1, q_2, \ldots$
The elements of $[Q]$ therefore depend on our choice of basis (our eigenfunction set). The elements

of $[Q]$ contain all the relations we need in order to know everything about $\hat{Q}$.
In many cases, we will have an infinite set of eigenfunctions, and matrices of infinite order are generally very hard to handle!
They are however, very useful in angular momentum problems, as we have a limited set of eigenfunctions: $Y_{\ell m}(\theta, \phi)$ has $2\ell + 1$ eigenfunctions. In the case of intrinsic spin, we have no possibility to represent spin operators by differential operators, so we can use matrix operators instead.

4.3.2 Matrix Representations of $\hat{S}_x, \hat{S}_y$ and $\hat{S}_z$

Matrix Representation of $\hat{S}_z$

We choose a basis formed from the eigenfunctions of $\hat{S}_z$: α, β. Now, continuing with the notation of $[S_z]$ for a matrix, we can write:

$$\begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}$$

Now, we recall that the element Q_{ij} is generated via:

$$Q_{ij} = \int \phi_j^* \hat{Q} \phi_i \, d\tau = \langle \phi_j | \hat{Q} | \phi_i \rangle$$

Thus, we have:

$$S_{11} = \langle \alpha | \hat{S}_z | \alpha \rangle$$

Now, we also know:

$$\hat{S}_z \alpha = \frac{1}{2} \hbar \alpha \qquad \hat{S}_z \beta = -\frac{1}{2} \hbar \beta$$

Thus:

$$\begin{aligned} S_{11} &= \frac{1}{2} \hbar \langle \alpha | \alpha \rangle \\ &= \frac{1}{2} \hbar \end{aligned}$$

Via orthogonality. Similarly, we see:

$$\begin{aligned} S_{22} &= \langle \beta | \hat{S}_z | \beta \rangle \\ &= -\frac{1}{2} \hbar \langle \beta | \beta \rangle \\ &= -\frac{1}{2} \hbar \end{aligned}$$

For the non-diagonal entries:

$$\begin{aligned} S_{12} &= \langle \alpha | \hat{S}_z | \beta \rangle \\ &= \frac{1}{2} \hbar \langle \alpha | \beta \rangle \\ &= 0 \\ &= S_{21} \end{aligned}$$

Where we have used the fact that two eigenfunctions are orthogonal.
Hence, we can write:

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

This is usually written as:

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

Where σ_z is known as a Pauli spin matrix. You need to be careful about the factor of $\frac{1}{2}\hbar$ in front of the matrix: it is technically inside the operator matrix, but its written outside; it does not cancel off in operations.
If we can to find the eigenvalues, we need to solve:

$$\frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = q \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \tag{4.3}$$

Which we do by bringing the column on the RHS over:

$$\begin{pmatrix} \frac{1}{2}\hbar - q & 0 \\ 0 & -\frac{1}{2}\hbar - q \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$$

Which is solved by setting the determinant of the matrix to zero, and solving the characteristic equation for the eigenvalue q:

$$\left(\frac{1}{2}\hbar - q\right)\left(-\frac{1}{2}\hbar - q\right) = 0$$

Therefore, the eigenvalues are $q = \pm\frac{1}{2}\hbar$, which we already knew, but were able to recover from the matrix representation.
To find the eigenvectors, we stick each eigenvalue in turn, into (4.3), and solve for a_1, a_2. So, for $q = +\frac{1}{2}\hbar$, and multiply the matrix out:

$$\begin{aligned} \frac{1}{2}\hbar a_1 + 0a_2 &= \frac{1}{2}\hbar a_1 \\ 0a_1 - \frac{1}{2}\hbar a_2 &= \frac{1}{2}\hbar a_2 \\ \Rightarrow a_1 = 1 \qquad & a_2 = 0 \end{aligned}$$

Thus, the eigenvector is:

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

Notice, we could have made a_1 anything, but we chose 1 as we want orthonormal normalised eigenvectors.
If we do the same for $q = -\frac{1}{2}\hbar$, we find:

$$\beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Matrix Representation of $\hat{S}_x$

We have previously shown that:

$$\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-)$$

So therefore, we can write that

$$\begin{aligned} \hat{S}_x\alpha &= \frac{1}{2}\hbar|\beta\rangle \\ \hat{S}_x\beta &= \frac{1}{2}\hbar|\alpha\rangle \end{aligned}$$

Hence, we write the matrix, and compute its elements:

$$\begin{aligned} [S_x] &= \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \\ &= \begin{pmatrix} \langle\alpha|\hat{S}_x|\alpha\rangle & \langle\alpha|\hat{S}_x|\beta\rangle \\ \langle\beta|\hat{S}_x|\alpha\rangle & \langle\beta|\hat{S}_x|\beta\rangle \end{pmatrix} \\ &= \begin{pmatrix} 0 & \frac{1}{2}\hbar \\ \frac{1}{2}\hbar & 0 \end{pmatrix} \\ &= \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ &= \frac{1}{2}\hbar\sigma_x \end{aligned}$$

Where we have notices things like:

$$\begin{aligned} \langle\alpha|\hat{S}_x|\alpha\rangle &= \frac{1}{2}\hbar\langle\alpha|\beta\rangle = 0 \\ \langle\beta|\hat{S}_x|\alpha\rangle &= \frac{1}{2}\hbar\langle\beta|\beta\rangle = \frac{1}{2}\hbar \end{aligned}$$

To find the eigenvectors, we must solve

$$\begin{pmatrix} 0 & \frac{1}{2}\hbar \\ \frac{1}{2}\hbar & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = q \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

For each eigenvalue $q = \pm\frac{1}{2}\hbar$.
Thus, we have:

$$\begin{aligned} \alpha_x &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ \beta_x &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \end{aligned}$$

The factor of $\frac{1}{\sqrt{2}}$ outfront is to keep the vectors having length one.

Matrix Representation of $\hat{S}_y$

Again, we have shown that:

$$\hat{S}_y = \frac{1}{2i}(\hat{S}_+ - \hat{S}_-)$$

So, we have that:

$$\begin{aligned}
\hat{S}_y\alpha &= -\frac{1}{2i}|\beta\rangle = \frac{1}{2}i|\beta\rangle \\
\hat{S}_y\beta &= -\frac{1}{2}i|\alpha\rangle
\end{aligned}$$

And we notice that:

$$\langle\alpha|\hat{S}_x|\beta\rangle = -\frac{1}{2}\hbar i\langle\alpha|\alpha\rangle = -i\frac{1}{2}\hbar$$

And similar, untill we get to being able to write all the elements of the matrix:

$$\begin{aligned}
[S_y] &= \frac{1}{2}\hbar\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\
&= \frac{1}{2}\hbar\sigma_y
\end{aligned}$$

And, upon solving for the eigenvectors:

$$\begin{aligned}
\alpha_y &= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} \\
\beta_y &= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}
\end{aligned}$$

Other Uses

We can also demonstrate the commutation relations by matrix multiplication. For example:

$$\left[\hat{S}_x, \hat{S}_y\right] = [S_x][S_y] - [S_y][S_x]$$

Being careful of the rubbish notation! So, we multiply the spin matrices together:

$$\begin{aligned}
\left[\hat{S}_x, \hat{S}_y\right] &= \frac{1}{4}\hbar^2(\sigma_x\sigma_y - \sigma_y\sigma_x) \\
&= \frac{1}{4}\hbar^2\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right] \\
&= \frac{1}{4}\hbar^2\left[\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}\right] \\
&= \frac{1}{4}\hbar^2\begin{pmatrix} 2i & 0 \\ 0 & -2i \end{pmatrix} \\
&= \frac{i}{2}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
&= \frac{i}{2}\hbar^2\sigma_z
\end{aligned}$$

Similarly, we can also find $\hat{S}^2$ in matrix representation:

$$\begin{aligned}\hat{S}^2 &= \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \\ &= \frac{1}{4}\hbar^2 \left(\sigma_x\sigma_x + \sigma_y\sigma_y + \sigma_z\sigma_z\right) \\ &= \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\end{aligned}$$

Which is the unity matrix.
Any spin $\frac{1}{2}$ vector $\begin{pmatrix} a \\ b \end{pmatrix}$ is an eigenfunction of $\hat{S}^2$:

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

Notice, if $s = \frac{1}{2}$, then $\frac{3}{4}\hbar^2 = s(s+1)\hbar^2$.

4.3.3 Matrix Representation for Spin-1

We can find the matrices for spin-1 operators $(L_x, L_y, L_z, L_+, L_-, L^2)$, in, for example, a basis spanned by the eigenfunctions of L^2 and L_z. I have left off hats! This basis is denoted by $|m\rangle$, where $m \equiv m_z = \pm 1, 0$.
So, if we define $|m_z = 1\rangle = |1\rangle, |m_z = 0\rangle = |0\rangle$ and $|m_z = -1\rangle = |-1\rangle$ as our basis, we can compute the elements of $[L_x]$:

$$[L_x] = \begin{pmatrix} L_{11} & L_{12} & L_{13} \\ L_{21} & L_{22} & L_{23} \\ L_{31} & L_{32} & L_{33} \end{pmatrix}$$

Where the elements can be computed;

$$\begin{aligned}L_{ij} &= \langle m_i|\hat{L}_x|m_j\rangle \\ &= \frac{1}{2}\langle m_i|\hat{L}_+|m_j\rangle + \frac{1}{2}\langle m_i|\hat{L}_-|m_j\rangle \\ \Rightarrow [L_x] &= \begin{pmatrix} \langle 1|\hat{L}_x|1\rangle & \langle 1|\hat{L}_x|0\rangle & \langle 1|\hat{L}_x|-1\rangle \\ \langle 0|\hat{L}_x|1\rangle & \langle 0|\hat{L}_x|0\rangle & \langle 0|\hat{L}_x|-1\rangle \\ \langle -1|\hat{L}_x|1\rangle & \langle -1|\hat{L}_x|0\rangle & \langle -1|\hat{L}_x|-1\rangle \end{pmatrix}\end{aligned}$$

Be careful, as we have defined $|m_1\rangle = |m_z = 1\rangle, |m_3\rangle = |m_z = -1\rangle$ etc. We have used the ladder operator representation for $\hat{L}_x = \frac{1}{2}(\hat{L}_+ + \frac{1}{2}L_-)$. We also need the previous relations:

$$\begin{aligned}\hat{L}_+|m\rangle &= \hbar\sqrt{\ell(\ell+1) - m(m+1)}|m+1\rangle \\ \hat{L}_-|m\rangle &= \hbar\sqrt{\ell(\ell+1) - m(m-1)}|m-1\rangle\end{aligned}$$

We also have that $\ell = 1$. So, to compute a few elements:

$$\begin{aligned} L_{11} &= \langle 1|\hat{L}_x|1\rangle \\ &= \frac{1}{2}\langle 1|\hat{L}_+|1\rangle + \frac{1}{2}\langle 1|\hat{L}_-|1\rangle \\ &= 0 + \frac{1}{2}\hbar\sqrt{2}\langle 1|0\rangle \\ &= 0 \\ L_{21} &= \langle 0|\hat{L}_x|1\rangle \\ &= \frac{1}{2}\langle 0|\hat{L}_+|1\rangle + \frac{1}{2}\langle 0|\hat{L}_-|1\rangle \\ &= 0 + \frac{1}{2}\hbar\sqrt{2}\langle 0|0\rangle \\ &= \frac{1}{2}\hbar\sqrt{2} \end{aligned}$$

Continuing for all other elements, we find:

$$[L_x] = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

And, if we want eigenvalues, we must find the roots of:

$$\begin{vmatrix} -q & 1 & 0 \\ 1 & -q & 1 \\ 0 & 1 & -q \end{vmatrix} = 0$$
$$\Rightarrow -q(q^2 - 1) - 1(-q) = 0$$

Hence, the roots are either $q = 0, \pm\sqrt{2}$. However, q is already in units of $\hbar/\sqrt{2}$. Thus, we have that $q = 0, \pm\hbar$; which is again a result we already had!
The eigenvectors for $q_1 = +\hbar$ are found by solving the system

$$\frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = +1\hbar \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$
$$\Rightarrow \frac{b}{\sqrt{2}} = a$$
$$\frac{1}{\sqrt{2}}(a + c) = b$$
$$\frac{b}{\sqrt{2}} = c$$

Thus, the (normalised) eigenvector is:

$$\frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}$$

So, this is the eigenvector of the $+\hbar$ eigenvalue, of the x-component of angular momentum, with respect to the z-basis. Hence, in Dirac notation, this is:

$$|m_x = +1\rangle = \frac{1}{2}|m_z = +1\rangle + \frac{1}{\sqrt{2}}|m_z = 0\rangle + \frac{1}{2}|m_z = -1\rangle$$

Now, in Dirac notation, we have the interpretation that

$$|m\rangle = \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

We can thus write the interpretation of $\langle m|$:

$$\langle m| = (a^* \, b^* \, c^*)$$

Thus, when we write an object like $\langle m|m\rangle$, we actually have;

$$\begin{aligned} \langle m|m\rangle &= (a^* \, b^* \, c^*) \begin{pmatrix} a \\ b \\ c \end{pmatrix} \\ &= aa^* + bb^* + cc^* \\ &= 1 \end{aligned}$$

Which is done via standard matrix multiplication. We hence can say that $\langle m|m\rangle$ is like the dot product.

Example Suppose we have a state initially in the $m_z = 0$ eigenstate. Compute $\langle \hat{L}_x \rangle$ and $\langle \hat{L}_x^2 \rangle$.

So, we start on $\langle L_x \rangle$. We know that $|m_z = 0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$:

$$\begin{aligned} \langle L_x \rangle &= \langle m_z = 0|\hat{L}_x|m_z = 0\rangle \\ &= \frac{\hbar}{\sqrt{2}}(0\,1\,0) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \\ &= \frac{\hbar}{\sqrt{2}}(0\,1\,0) \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \\ &= 0 \\ \Rightarrow \langle L_x \rangle &= 0 \end{aligned}$$

Now for $\langle \hat{L}_x^2 \rangle$:

$$\begin{aligned}
\langle \hat{L}_x^2 \rangle &= \langle m_z = 0 | \hat{L}_x \hat{L}_x | m_z = 0 \rangle \\
&= \frac{\hbar^2}{2} (0\,1\,0) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \\
&= \frac{\hbar^2}{2} (0\,1\,0) \begin{pmatrix} 0 \\ 2 \\ 0 \end{pmatrix} \\
&= \hbar^2
\end{aligned}$$

Hence, we can write down the overall uncertainty in $\hat{L}_x$:

$$\begin{aligned}
\Delta \hat{L}_x &= \sqrt{\langle \hat{L}_x^2 \rangle - \langle \hat{L}_x \rangle^2} \\
&= \hbar
\end{aligned}$$

Example Find the eigenvectors of $\hat{S}_x$.

We know:

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

Thus, we must solve the equation:

$$\begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = q \begin{pmatrix} a \\ b \end{pmatrix}$$

Eigenvalues are the roots of the determinant, and can easily be shown to be $q_1 = +\frac{1}{2}\hbar$, $q_2 = -\frac{1}{2}\hbar$. Now, for the q_1 eigenvalue, to find the corresponding eigenvector, we must solve:

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

Easily resulting in $a = b$. Thus, the eigenvector $\mathbf{v}_1$ is:

$$\mathbf{v}_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Which, in Dirac notation, is the same as:

$$|m_x = +\frac{1}{2}\rangle = \frac{1}{\sqrt{2}} |m_z = +\frac{1}{2}\rangle + \frac{1}{\sqrt{2}} |m_z = -\frac{1}{2}\rangle$$

Similarly, for $q_2 = -\frac{1}{2}\hbar$, we end up with

$$\mathbf{v}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Or:

$$|m_x = -\frac{1}{2}\rangle = \frac{1}{\sqrt{2}} |m_z = +\frac{1}{2}\rangle - \frac{1}{\sqrt{2}} |m_z = -\frac{1}{2}\rangle$$

And, to show that these two eigenvectors are orthogonal (which they should be), we write:

$$\begin{aligned}\langle v_1|v_2\rangle &= \left(\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\right)\begin{pmatrix}\frac{1}{\sqrt{2}}\\ -\frac{1}{\sqrt{2}}\end{pmatrix}\\ &= 0\end{aligned}$$

Thus the eigenvectors are orthogonal.

4.3.4 Raising Operators

If we want the matrix representation of the raising operator $\hat{S}_+$, we write:

$$\begin{aligned}\hat{S}_+ &= \hat{S}_x + i\hat{S}_y\\ &= \frac{1}{2}\hbar(\sigma_x + i\sigma_y)\\ &= \frac{1}{2}\hbar\left[\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} + i\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\right]\\ &= \hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}\end{aligned}$$

We can use this on (say) β:

$$\begin{aligned}\hat{S}_+\beta &=\\ \hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}\begin{pmatrix}0\\ 1\end{pmatrix} &= \hbar\begin{pmatrix}1\\ 0\end{pmatrix}\\ &= \hbar\alpha\end{aligned}$$

Which again, is a result we already knew.

4.4 Measuring a Spin Component

Charged particles with intrinsic spin, or orbital angular momentum have a magnetic moment $\boldsymbol{\mu}$. For some classical current loop, where a current I is going round an area A, we have $\boldsymbol{\mu} = I\boldsymbol{A}$; where the area vector points according to the right-hand-rule.
For some classical electron orbit, we have that the charge flowing per unit time is $I = \frac{e}{T} = \frac{e\omega}{2\pi}$, where the period $T \equiv \frac{2\pi}{\omega}$. If the area of the orbit is $A = \pi r^2$, then we easily have that:

$$\mu = \frac{e\omega r^2}{\pi}$$

Now, we also have that $\ell\hbar = rp = m_e\omega r^2$. Hence:

$$\begin{aligned}\mu &= \frac{\ell\hbar}{m_e\omega}\frac{e\omega}{2}\\ &= \frac{\ell\hbar e}{2m_e}\\ &= g_\ell \ell \mu_B\end{aligned}$$

It is actually more correct to write this as:

$$\mu_z = g_\ell \ell_z \mu_B$$

Just in terms of notation, $\ell_z = m_z$. Where we have defined the Bohr Magneton μ_B, and the gyromagnetic ratio $g_\ell = -1$ for electrons.

$$\mu_B \equiv \frac{e\hbar}{2m_e}$$

So, in vector form, we have:

$$\boldsymbol{\mu} = g_\ell \boldsymbol{\ell} \mu_B$$

Where μ_z is the projection of $\boldsymbol{\mu}$ along the z-axis, and is always in the same direction as $\boldsymbol{\ell}$.

Now, the electron also has an intrinsic magnetic moment - like a bar magnet - along the direction of $\boldsymbol{s}$:

$$\boldsymbol{\mu}_s \quad = \quad g_s \boldsymbol{s} \mu_B$$

Simple Dirac theory (apparentyl) yields $g_s = -2$, and we use the approximation $\mu_s \approx -\mu_B$.

The nuclear magneton is pretty much identical, except it uses the mass of the proton. Hence, spin effects due to the nucleus are tiny, as $m_p >> m_e$:

$$\mu_N = \frac{e\hbar}{2m_p}$$

If we remember the classical gyroscope, if it has angular momentum, it does not fall over, but precesses about the vertical axis (direction of gravity).
Thus, a magnetic moment $\boldsymbol{\mu}$ would align itself with an applies magnetic field $\boldsymbol{B}$ (like a compass needle), except if the particle also has spin, when the particle will then precess about $\boldsymbol{B}$.

4.4.1 The Stern-Gerlach Experiment

The experiment has the following setup:
An oven evaporates silver atoms which are emitted in all direction, but are collimated by some aperture. This beam of silver atoms then passes through an inhomogeneous magnetic field. The valence electrons spin will interact with the field, and will produce a discrete pattern on the screen: atoms with different spins leave the field in different directions.
Now, as force = -grad PE, we hence have:

$$\begin{aligned} F &= +\boldsymbol{\mu} \cdot \frac{\partial \boldsymbol{B}}{\partial z} \\ &= \mu_z \frac{\partial B_z}{\partial z} \end{aligned}$$

Hence, a beam of atoms is deflected either up or down, depending on the sign component of $\boldsymbol{\mu}$ along the z-axis: $m_z = +\frac{1}{2}$ or $m_z = -\frac{1}{2}$.
So, an unpolarised beam will be in the state:

$$50\%|\alpha\rangle + 50\%|\beta\rangle$$

Where $|\alpha\rangle = |m_z = +\frac{1}{2}\rangle$, and $|\beta\rangle = |m_z = -\frac{1}{2}\rangle$.
Now, suppose we have selected the $|\alpha\rangle$ component, via a Stern-Gerlach type-experiment, we now have the state:

$$100\%|\alpha\rangle$$

Which is actually half of the initial state.
Now, if we want to then measure S_x, we need to know how to describe the $|\alpha\rangle$ eigenstate in terms of eigenstates of S_x. We have previously done this:

$$\begin{aligned} |m_x = +\frac{1}{2}\rangle &= \frac{1}{\sqrt{2}}(|\alpha\rangle + |\beta\rangle) \\ |m_x = -\frac{1}{2}\rangle &= \frac{1}{\sqrt{2}}(|\alpha\rangle - |\beta\rangle) \end{aligned}$$

Hence:

$$|\alpha\rangle = \frac{1}{\sqrt{2}}\left(|m_x = +\frac{1}{2}\rangle + |m_x = -\frac{1}{2}\rangle\right)$$

Now, suppose we further select the $|m_x = +\frac{1}{2}\rangle$ state using another magnet, we then get half of what enters the second magent, which was half of what entered the first magnet.

4.5 Precession in Magnetic Fields

4.5.1 Solutions to TDSE

These give the time-evolutioon of the wavefunction for a particle in a potential $V(\mathbf{r})$:

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

If $V(\mathbf{r})$ is not a function of time, we can apply the standard separation of variables technique. Let $\psi(\mathbf{r},t) = \phi(\mathbf{r})T(t)$, and substitute into the above TDSE, and divide by ψ:

$$-\frac{\hbar^2}{2m}\frac{1}{\phi}\nabla^2\phi + V(\mathbf{r}) = i\hbar\frac{1}{T}\frac{\partial T}{\partial t} = const = E$$

Where we have called the constant E, say. So, we can separate the two halfs of the equation, so looking at the time equation:

$$i\hbar\frac{\partial T}{\partial t} = ET$$

Which has solutions of the form:

$$T(t) = const \cdot e^{-iEt/\hbar}$$

Sometimes, using $E = \hbar\omega$, this is written:

$$T(t) = const \cdot e^{-i\omega t}$$

And the spatial part of the TDSE looks like:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\phi = E\phi$$

Which has eigenvalues E_n for eigenfunctions ϕ_n.
Any arbitrary state $|\psi\rangle$ at $t = 0$ could be described by:

$$|\psi\rangle = \sum_n a_n |\phi_n\rangle$$

Then we now know how the state evolves in time:

$$|\psi(t)\rangle = \sum_n a_n e^{-i\omega_n t} |\phi_n\rangle$$

4.5.2 Quantum Beats

Consider an initial state which is a linear combination of energy states, for example:

$$\psi = \phi_1 + \phi_2$$

Where, for this example, ϕ_1, ϕ_2 are real functions. So we can write the time evolution version of the wavefunction:

$$\begin{aligned} \psi(t) &= \phi_1 e^{-i\omega_1 t} + \phi_2 e^{-i\omega_2 t} \\ &= e^{-i\omega_2 t}(\phi_1 e^{i\omega t} + \phi_2) \end{aligned}$$

Where we have defined $\omega \equiv \omega_2 - \omega_1$. We can compute the probability distribution function via:

$$\begin{aligned} \psi^*\psi &= (\phi_1 e^{-i\omega t} + \phi_2)(\phi_1 e^{i\omega t} + \phi_2) \\ &= |\phi_1|^2 + |\phi_2|^2 + \phi_1\phi_2(e^{i\omega t} + e^{-i\omega t}) \\ &= |\phi_1|^2 + |\phi_2|^2 + 2\phi_1\phi_2 \cos\omega t \end{aligned}$$

The interference between the two phase factors creates a time-dependance of the probability distribution that has the appearance of motion.

4.5.3 Classical Precession of Spin

Consider a magnetic dipole moment $\boldsymbol{\mu}$ in a uniform magnetic field $\boldsymbol{B}$ along the z-axis. The torque on such a dipole is given by:

$$\boldsymbol{\Gamma} = \boldsymbol{\mu} \times \boldsymbol{B}$$

$\boldsymbol{\Gamma}$ acts to align the dipole with the magnetic field, and acts perpendicular to the plane containing both. If the dipole also has orbital angular momentum $\boldsymbol{L}$, we also have:

$$\frac{d\boldsymbol{L}}{dt} = \boldsymbol{\Gamma}$$

We find that (a) solution is given by:

$$\begin{aligned} L_x &= L\sin\theta\cos\omega t \\ L_y &= L\sin\theta\sin\omega t \\ L_z &= L\cos\theta \end{aligned}$$

Where we have that θ is a constant, measured from the z-axis, and ωt the precession 'speed'. Hence, we have described a precession, where:

$$\omega = \frac{\mu B}{L}$$

Is called the Larmor precession frequency. Note, this is the case for 'simple precession' only!
Notice, if

$$\boldsymbol{\mu} = g_\ell \frac{\boldsymbol{L}}{\hbar} \mu_B$$

Then the Larmor frequency is:

$$\omega = \frac{g_\ell \mu_B B}{\hbar}$$

4.5.4 QM Description of Precession

If we have the Hamiltonian due to magnetic field:

$$\begin{aligned} \hat{H}_{mag} &= -\boldsymbol{\mu} \cdot \boldsymbol{B} \\ &= -\hat{\mu}_z B \\ &= -g_\ell \frac{\hat{L}_z}{\hbar} \mu_B B \end{aligned}$$

Eigenfunctions of which are $|\ell, m_\ell\rangle$, and $\hat{L}_z|\ell, m_\ell\rangle = m_\ell \hbar |\ell, m_\ell\rangle$; we hence see that energy eigenvalues are:

$$E_m = -g_\ell m_\ell \mu_B B = +\hbar \omega m_\ell$$

Where:

$$\omega = \left| \frac{g_\ell \mu_B B}{\hbar} \right|$$

So, to summarise, we have a Hamiltonian due to the applied magnetic field $\hat{H}_{mag} = -\boldsymbol{\mu} \cdot \boldsymbol{B}$, with eigenstates $|\ell, m_\ell\rangle$, and eigenvalues $-g_\ell m_\ell \mu_B B$.

Now, as $\hat{H}_{mag}$ is not a function of time, energy is conserved in the system. Hence, m_ℓ is a constant of motion. Thus, the state $|m_\ell = +1\rangle$ (say) is a stationary state.
$\boldsymbol{L}$ points with equal probability everywhere on the surface of the cone that the spin 'marks out'.

The time evolution of the stationary state $|\ell, m_\ell\rangle$ is given by:

$$\begin{aligned} |\psi(t)\rangle &= e^{-iE_m t/\hbar} |\ell, m_\ell\rangle \\ &= e^{-i\omega m_\ell t} |\ell, m_\ell\rangle \end{aligned}$$

Where ω is the previous Larmor frequency.
The phase factor ($e^{-i\omega m_\ell t}$) cannot be directly measured by any experiment: we cannot observe any precession if the system is in an eigenstate $|\ell, m_\ell\rangle$.

However, consider a spin $L = i\hbar$, polarised along the x-axis at time $t = 0$ in a field B along z. Now, for reference:

$$[L_x] = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

And, we have already seen that:

$$\begin{aligned} |\psi(t=0)\rangle &= |m_x = +1\rangle \\ &= \frac{1}{2}|m_z = +1\rangle + \frac{1}{\sqrt{2}}|m_z = 0\rangle + \frac{1}{2}|m_z = -1\rangle \end{aligned}$$

Which is found from finding the normalised eigenvectors of $[L_x]$, where the fraction out-front is from the normalisation.
The time evolution of the state is found by multiplying each term by the phase factor $e^{-i\omega m_\ell t}$:

$$|\psi(t)\rangle = \frac{1}{2}e^{-i\omega t}|m_z = +1\rangle + \frac{1}{\sqrt{2}}|m_z = 0\rangle + \frac{1}{2}e^{i\omega t}|m_z = -1\rangle$$

Where:

$$\omega = \left|\frac{g_\ell \mu_B B}{\hbar}\right|$$

We are now able to observe interference between the different phase factors, which will give us quantum beats.
So, let us compute $\langle \hat{L}_x \rangle = \langle \psi(t)|\hat{L}_x|\psi(t)\rangle$:

$$\begin{aligned} \langle \hat{L}_x \rangle &= \frac{1}{2}\frac{\hbar}{\sqrt{2}}\frac{1}{2}\left(e^{i\omega t}, \sqrt{2}, e^{-i\omega t}\right)\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} e^{-i\omega t} \\ \sqrt{2} \\ e^{i\omega t} \end{pmatrix} \\ &= \frac{\hbar}{4\sqrt{2}}\left(e^{i\omega t}, \sqrt{2}, e^{-i\omega t}\right)\begin{pmatrix} \sqrt{2} \\ e^{-i\omega t} + e^{i\omega t} \\ \sqrt{2} \end{pmatrix} \\ &= \frac{\hbar}{4}\left(e^{i\omega t} + e^{-i\omega t} + e^{i\omega t} + e^{-i\omega t}\right) \\ &= \hbar \cos \omega t \end{aligned}$$

Thus, we have that $\hat{L}_x$ will sometimes be found along the $+1\hbar$ axis, and other times along the $-1\hbar$ axis.
Similarly, we can find $\langle \hat{L}_y \rangle = \hbar \sin \omega t$, and $\langle \hat{L}_z \rangle = 0$ =constant. Which is what we would expect for Larmor precession.

Hence, we see that putting an atom in a magnetic field has the effect of splitting the energy levels evenly, by $\hbar\omega$. If the magnetic field is non-homogeneous, then non-even splitting.

Note: The classical analogy does not generally work; if states $|m\rangle$ are not equally spaced in energy, then each spin appears to precess with a mixture of frequencies simultaneously.

5 Addition of Angular Momenta

We consider the vector addition of 2 angular mometa. In this example, they will be spin and orbital angular momentum, but the algebra below applies equally well to other types of angular momenta (e.g. spin-spin).
The vector equation is:

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} \tag{5.1}$$

Or, with a particular component:

$$J_z = L_z + S_z$$

J_z is now a constant of motion, whereas L_z, S_z are fuzzy; and only have the restriction of adding to $\boldsymbol{J}$. Squaring $\boldsymbol{J}$:

$$\begin{aligned} \boldsymbol{J}\cdot\boldsymbol{J} &= J^2 \\ &= L^2 + S^2 + 2\boldsymbol{L}\cdot\boldsymbol{S} \end{aligned}$$

Or, where everything is an operator:

$$\begin{aligned} \hat{J}^2 &= \hat{L}^2 + \hat{S}^2 + 2\hat{L}\cdot\hat{S} \\ \hat{J}_z &= \hat{L}_z + \hat{S}_z \end{aligned}$$

It can be easily shown that $\left[\hat{J}^2, \hat{L}^2\right] = \left[\hat{J}^2, \hat{S}^2\right] = 0$, thus there exists a common set of eigenfunctions.
But, $\hat{J}^2$ does not commute with either $\hat{L}_z$ or $\hat{S}_z$ due to the $\hat{L}\cdot\hat{S}$ term in $\hat{J}^2$. By writing:

$$\hat{L}\cdot\hat{S} = \hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z$$

We can show:

$$\begin{aligned} \left[(\hat{L}\cdot\hat{S}), \hat{L}_z\right] &= i\hbar\left(\hat{L}_x\hat{S}_y - \hat{S}_x\hat{L}_y\right) \\ \left[(\hat{L}\cdot\hat{S}), \hat{S}_z\right] &= -i\hbar\left(\hat{L}_x\hat{S}_y - \hat{S}_x\hat{L}_y\right) \end{aligned}$$

Which, upon adding, results in :

$$\left[(\hat{L}\cdot\hat{S}), \hat{J}_z\right] = 0$$

Therefore, we have been able to show that $\left[\hat{J}^2, \hat{J}_z\right] = 0$.

The operators $\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2$ have common sets of eigenstates, but are not eigenstates of $\hat{L}_z, \hat{S}_z$.

We write states as:

$$|j, j_z, \ell, s\rangle$$

So, in an isolated system, the total angular momentum $\boldsymbol{J}$ is a constant of motion, as is $j_z = m_\ell + m_s$. We will sometimes use $m_j = j_z$.

All the usual angular momentum relations apply to $\hat{J}^2$ and $\hat{J}_z$, as they did to $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_z$, $\hat{S}_z$:

$$\begin{aligned} \left[\hat{J}_x, \hat{J}_y\right] &= i\hbar\hat{J}_z \\ \hat{J}^2 &= \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 \\ \left[\hat{J}^2, \hat{J}_x\right] &= 0 \\ \hat{J}_\pm &= \hat{J}_x \pm i\hat{J}_y \\ &= \hat{L}_\pm + \hat{S}_\pm \\ \hat{J}^2|j, m_j\rangle &= j(j+1)\hbar^2|j, m_j\rangle \\ \hat{J}_z|j, m_j\rangle &= m_j\hbar|j, m_j\rangle \\ \hat{J}_\pm|j, m_j\rangle &= \hbar\sqrt{j(j+1) - m_j(m_j \pm 1)}|j, m_j \pm 1\rangle \\ \hat{J}_\pm|j, m_j = \pm j\rangle &= 0 \end{aligned}$$

Note: there also exists a common set of eigenfunctions of $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_z$, $\hat{S}_z$, which are more useful for an atom in a strong magnetic field, as $\boldsymbol{L}$ and $\boldsymbol{S}$ independently precess about the z-axis. So we use:

$$|\ell, m_\ell, s, m_s\rangle$$

Thus, for an atom in a strong magnetic field, j is not a good quantum number to use (but m_j still is).

We can always describe a state $|j, m_j, \ell, s\rangle$ as a linear combination of $|\ell, m_\ell, s, m_s\rangle$ basis states:

$$|j, m_j, \ell, s\rangle = \sum_{m_\ell} C(m_\ell, m_s)|\ell, m_\ell, s, m_s\rangle$$

Note, only a sum over m_ℓ, as the m_s are already determined by the condition that $m_j = m_\ell + m_s$ is a constant of motion.
The coefficients $C(m_\ell, m_s)$ are called *Clebsch-Gardon coefficients*, and are generally tabulated for low-spin combinations of j, ℓ, s. From the table, we see that:

Table 6.2. Clebsch–Gordan coefficients for the case $l = 1$ and $s = \frac{1}{2}$. Eigenfunctions of the total angular momentum with given values of (j, m_j) are constructed as linear combinations of products of the angular momentum eigenfunctions denoted by the values of (m_l, m_s).

	(m_l, m_s)					
(j, m_j)	$(1, \frac{1}{2})$	$(1, -\frac{1}{2})$	$(0, \frac{1}{2})$	$(0, -\frac{1}{2})$	$(-1, \frac{1}{2})$	$(-1, -\frac{1}{2})$
$(\frac{3}{2}, \frac{3}{2})$	1	0	0	0	0	0
$(\frac{3}{2}, \frac{1}{2})$	0	$\frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$	0	0	0
$(\frac{3}{2}, -\frac{1}{2})$	0	0	0	$\frac{2}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	0
$(\frac{3}{2}, -\frac{3}{2})$	0	0	0	0	0	1
$(\frac{1}{2}, \frac{1}{2})$	0	$\sqrt{\frac{2}{3}}$	$-\frac{1}{\sqrt{3}}$	0	0	0
$(\frac{1}{2}, -\frac{1}{2})$	0	0	0	$-\frac{1}{\sqrt{3}}$	$\sqrt{\frac{2}{3}}$	0

Figure 4: Table taken from Rae, showing Clebsch-Gordan coefficients. Note, there is an error on both lines 2 and 3. They should have $\sqrt{\frac{2}{3}}$ rather than $\frac{2}{\sqrt{3}}$, to make the wavefunctions normalised.

$$|j = \frac{3}{2}, m_j = \frac{3}{2}\rangle = 1.|\ell = 1, m_\ell = 1, s = \frac{1}{2}, m_s = \frac{1}{2}\rangle \tag{5.2}$$

$$|j = \frac{3}{2}, m_j = \frac{1}{2}\rangle = \frac{1}{\sqrt{3}}.|m_\ell = 1, m_s = -\frac{1}{2}\rangle + \sqrt{\frac{2}{3}}|m_\ell = 0, m_s = +\frac{1}{2}\rangle \tag{5.3}$$

We can work out the coefficients, for example, we can work out (5.3) via (5.2). First, we apply $\hat{J}_- = \hat{L}_- + \hat{S}_-$ to the LHS of (5.2):

$$\begin{aligned}\hat{J}_-|j=\frac{3}{2},m_j=\frac{3}{2}\rangle &= \hbar\sqrt{j(j+1)-m_j(m_j-1)}|j=\frac{3}{2},m_j=\frac{1}{2}\rangle \\ &= \sqrt{3}\hbar|j=\frac{3}{2},m_j=\frac{1}{2}\rangle\end{aligned}$$

And, applying to the RHS of (5.2):

$$\begin{aligned}(\hat{L}_-+\hat{S}_-)|m_\ell=1,m_s=\frac{1}{2}\rangle &= \hat{L}_-|m_\ell=1,m_s=\frac{1}{2}\rangle + \hat{S}_-|m_\ell=1,m_s=\frac{1}{2}\rangle \\ &= \sqrt{2}\hbar|m_\ell=0,m_s=\frac{1}{2}\rangle + \hbar|m_\ell=1,m_s=-\frac{1}{2}\rangle\end{aligned}$$

Thus, equating these two:

$$\begin{aligned}\hat{J}_- &= \hat{L}_- + \hat{S}_- \\ \Rightarrow \sqrt{3}|j=\frac{3}{2},m_j=\frac{1}{2}\rangle &= \sqrt{2}\hbar|m_\ell=0,m_s=\frac{1}{2}\rangle + \hbar|m_\ell=1,m_s=-\frac{1}{2}\rangle \\ \Rightarrow |j=\frac{3}{2},m_j=\frac{1}{2}\rangle &= \sqrt{\frac{2}{3}}|m_\ell=0,m_s=\frac{1}{2}\rangle + \frac{1}{\sqrt{3}}|m_\ell=1,m_s=-\frac{1}{2}\rangle\end{aligned}$$

Which is what we had from looking up the coefficients.

6 The Hydrogen Atom

6.1 Review

The TISE for an electron in potential:

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

Is given by:

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

Where the wavefunction $\psi(\boldsymbol{r}) = \psi(r,\theta,\phi)$. Now, we can show easily that the Laplacian in spherical polars has the form:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2\hbar^2}\hat{L}^2$$

Hence, we want to look for eigenfunctions of the form $\psi(\boldsymbol{r}) = R(r)Y_{\ell,m_\ell}(\theta,\phi)$.
We have that:

$$\hat{L}^2 Y_{\ell,m_\ell} = \ell(\ell+1)\hbar^2 Y_{\ell,m_\ell}$$

Then, we have that $R(r)$ satisfies:

$$\left[-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right]R(r) = ER(r)$$

This has all been done in previous QM courses, and we find energy eigenvalues:

$$E_n = \frac{E_1}{n^2}$$

Where $E_1 = -13.6\text{eV}$. n is the principal quantum number, and takes on integer values from 1 to infinity. We have that the allowed values of ℓ are from 0 to $(n-1)$, and the projection of orbital angular momentum onto the z-axis $m_\ell = -\ell, \ldots, 0, \ldots, +\ell$.

Hence, if we try to draw an energy level diagram for Hydrogen, we start with the ground state: $n = 1$. For this state, $\ell = 0$ only. Hence, as we can have $m_s = \pm\frac{1}{2}$, we can have 2 electrons in the $n = 1$ state, up and down.
For $n = 2$ we have that $\ell = 0, 1$ and hence $m_\ell = -1, 0, 1$ for the $\ell = 1$ state only. Hence, we can put 2 electrons into the $\ell = 0$ state and 6 into $\ell = 1$. Generally, for a given ℓ, we have $2(2\ell + 1)$ electrons in that state.

6.2 Spin-Orbit Coupling and Fine Structure

Classically, an electron orbiting a nucleus of charge $+Ze$ 'sees' the nucleus in orbit around it: a current loop.
This produces a magnetic field at the electron, which can be found via the Biot-Savart law to be:

$$B = \frac{\mu_0 I}{2r}$$

The current is found to be:

$$I = \frac{Ze\omega}{2\pi}$$

And we get ω from classical angular momentum of electron: $\boldsymbol{L} = m_e \boldsymbol{\omega} r^2$. Hence, putting this all together:

$$\boldsymbol{B} = \frac{\mu_0 Ze}{4\pi m_e r^3}\boldsymbol{L}$$

The nteraction energy with electrons magnetic moment is given by:

$$E = -\frac{1}{2}\boldsymbol{\mu}_s \cdot \boldsymbol{B}$$

Where the $\frac{1}{2}$ comes from a relativistic effect known as 'Thomas Precession', and will just have to be accepted. Now, using $\boldsymbol{\mu} = \frac{e}{m_e}\boldsymbol{S}$, we therefore have:

$$E = A\boldsymbol{L} \cdot \boldsymbol{S} \qquad A \equiv \frac{\mu_0 Ze^2}{8\pi m_e^2 r^3}$$

A is known as the fine structure coefficient. The Hamiltonian must now include a correction:

$$\hat{H}_{SO} = A\hat{L} \cdot \hat{S}$$

The spin-orbit correction.

We have already seen that $\hat{L}\cdot\hat{S}$ commutes with $\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{L}_z$, so the states $|j, m_j, \ell, s\rangle$ are eigenstates of $\hat{H}_{SO}$. The spin-orbit coupling results in all states with $\ell \neq 0$ being split into 2 components. One with $\boldsymbol{s}$ aligned parallel, and one anti-parallel to $\boldsymbol{L}$; where anti-parallel is the lowest energy state.

We can calculate the energy shifts due to the interaction $\hat{H}_{SO} = A\hat{L}\cdot\hat{S}$. Now, from $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$, we can right down $J^2 = \boldsymbol{J}\cdot\boldsymbol{J}$, and rearrange for the $\boldsymbol{L}\cdot\boldsymbol{S}$ term. This is then done with the operators, to give:

$$\hat{L}\cdot\hat{S} = \frac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)$$

Thus:

$$\hat{H}_{SO} = \frac{A}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)$$

Hence, we have that the eigenstate $|j, m_j, \ell, s\rangle$ have eigenvalues according to:

$$\begin{aligned}\hat{H}_{SO}|j, m_j, \ell, s\rangle &= \frac{A}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)|j, m_j, \ell, s\rangle \\ &= \frac{A\hbar^2}{2}\left(j(j+1) - \ell(\ell+1) - s(s+1)\right)|j, m_j, \ell, s\rangle\end{aligned}$$

Since $|j, m_j, \ell, s\rangle$ are eigenstates of $\hat{H}_{SO}$, then the expectation value $\langle j, m_j, \ell, s|\hat{H}_{SO}|j, m_j, \ell, s\rangle$ is just:

$$\frac{A\hbar^2}{2}\left(j(j+1) - \ell(\ell+1) - s(s+1)\right) \tag{6.1}$$

Example Suppose we have a system with $\ell = 1$, $s = \frac{1}{2}$. This is the $2p$ state in hydrogen.
Now, we have that there are two possible values of j which can be made: $j = \ell + s = \frac{3}{2}, \frac{1}{2}$.

Thus, pictorially, we see that from some unperturbed state, we have two states, splitting. for $j = \frac{3}{2}$ and $j = \frac{1}{2}$. We define the energy splitting ΔE_i as being measured from the unperturbed state (*centroid*).
So, if we have ΔE_1 for the $j = \frac{3}{2}$ state, we can stick our numbers into (6.1) to get:

$$\Delta E_1 = \frac{A\hbar^2}{2}\left[\frac{15}{4} - 2 - \frac{3}{4}\right] = \frac{A\hbar^2}{2}$$

Similarly, for ΔE_2 for $j = \frac{1}{2}$:

$$\Delta E_2 = -A\hbar^2$$

So, we see that the $j = \frac{3}{2}$ has more energy than the $j = \frac{1}{2}$ state.

Infact, we see that the spin-orbit splitting is asymmetric. However, it is such that the energy centroid of the $2p$ is 'unchanged'. This is actually a useful check to do on such calculations:
For the $j = \frac{3}{2}$ state, there are 4 possible m_j values. Thus 4 states shifted by $\frac{A\hbar^2}{2}$. For the $j = \frac{1}{2}$ state, there are 2 possible m_j values. Thus, the total energy shifting of all states combined should equal zero:

$$\frac{A\hbar^2}{2} \times 4 - A\hbar^2 \times 2 = 0$$

6.2.1 Magnitude of Spin-Orbit Splitting

Now, the total energy splitting has been written in terms of $A\hbar^2$, where A has previously been derived:

$$A \equiv \frac{\mu_0 e^2}{8\pi m_e^2 r^3}$$

Now, if we assume that $r = a_0$, the Bohr radius, and the Rydberg energy:

$$R_\infty = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 a_0} = 13.6eV$$

And writing $\mu_0 = \frac{1}{\varepsilon_0 c^2}$. Thus, a substitution and rearrangement:

$$A\hbar^2 = R_\infty \frac{\hbar^2}{c^2 a_0^2 m_e^2} = R_\infty \alpha^2$$

Where we have defined the 'fine structure constant':

$$\alpha \equiv \frac{\hbar}{c a_0 m_e} = \frac{1}{137}$$

Now, the total splitting between the very top $j = \frac{3}{2}$ and $j = \frac{1}{2}$ states is:

$$\frac{3}{2}A\hbar^2 = \frac{3}{2}R_\infty\alpha^2 = \frac{3}{2}13.6eV\frac{1}{137^2} = 1.1 \times 10^{-3}eV$$

Thus, the fine structure splitting is very small, compared with an optical transition of typlical energy level differences $\approx$ 2eV.

6.3 Zeeman Effect

If a magnetic field B is applied to an atom along the z-axis, then an extra term must be included in the Hamiltonian, of the form $-\boldsymbol{\mu} \cdot \boldsymbol{B}$. Thus, for a single electron-atom:

$$\hat{H} = \hat{H}_0 + \hat{H}_{SO} + \hat{H}_{mag}$$

Where:

$$\begin{aligned}
\hat{H}_0 &= \frac{\hat{p}^2}{2m} + \hat{V} \approx R_\infty = 13.6eV \\
\hat{H}_{SO} &= A\hat{L}\cdot\hat{S} \approx R_\infty\alpha^2 = 10^{-3}eV \\
\hat{H}_{mag} &= -\frac{\mu_B}{\hbar}(g_\ell \hat{L}_z + g_s \hat{S}_z)B \approx \mu_B B = 10^{-4}eVT^{-1}
\end{aligned}$$

So, we can see that if $B << 1$T, then the external interaction is negligible, compared with the internal spin-orbit coupling.

Now, we see that $\hat{H}_{mag}$ does not commute with $\hat{J}^2$, if $g_\ell \neq g_s$, which is generally true.
On the other hand, $\hat{H}_{SO} = \hat{L}\cdot\hat{S}$ does not commute with $\hat{L}_z$ or $\hat{S}_z$.

Therefore, eigenfunctions of $\hat{H}$ are a mixture of either sets of eigenfunctions. So, we can consider the following cases:

Suppose that $B = 0$, then we can just use the eigenstates $|j, m_j, \ell, s\rangle$.

For weak applied fields, we can use $|j, m_j, \ell, s\rangle$ as approximate eigenfunctions. J^2, J_z are still constants of motion, with $\boldsymbol{L}$ and $\boldsymbol{S}$ remaining coupled together.

For strong magnetic fields, $\hat{H}_{mag}$ dominates, and interaction with external field is much stronger than the internal spin-orbit interaction, and $\boldsymbol{L}$ and $\boldsymbol{S}$ precess independently about the applied field.

6.3.1 Weak Applied Field

The atomic state $\boldsymbol{J}$ ha s a composite magnetic moment made up of orbital and intrinsic spin components. We now derive the 'Lande g-factor'.

We may write:

$$\mu_J = \mu_\ell \cos\theta_\ell + \mu_s \cos\theta_s$$

Where μ_J is found from the projections onto the axis, from orbital and intrinsic spin. Now, if we think about the definition of the dot-product, of, say, the vector $\boldsymbol{L}$ along $\boldsymbol{J}$:

$$\boldsymbol{L} \cdot \boldsymbol{J} = |\boldsymbol{L}||\boldsymbol{J}| \cos\theta_\ell \quad \Rightarrow \quad \cos\theta_\ell = \frac{\boldsymbol{L} \cdot \boldsymbol{J}}{|\boldsymbol{L}||\boldsymbol{J}|}$$

And similar for $\cos\theta_s$.
Now, previously, we wrote that $\boldsymbol{\mu}_\ell = g_\ell |\boldsymbol{L}| \mu_B$, so we can write something like $g_J = \mu_J / |\boldsymbol{J}|$, in units of the Bohr-magneton. Now, we then find:

$$g_J = \frac{g_\ell (\boldsymbol{L} \cdot \boldsymbol{J} + g_s \boldsymbol{S} \cdot \boldsymbol{J})}{|\boldsymbol{J}|^2}$$

Using an approximation $g_s = 2g_\ell$, we can derive:

$$g_J = g_\ell \left(1 + \frac{j(j+1) - \ell(\ell+1) + s(s+1)}{2j(j+1)} \right)$$

Thus:

$$\mu_J = g_J j \mu_B$$

Thus, in a weak magnetic field, is the energy shift:

$$\begin{aligned} &= -\boldsymbol{\mu}_J \cdot \boldsymbol{B} \\ &= -g_J \mu_B \boldsymbol{j} \cdot \boldsymbol{B} \\ &= -g_J \mu_B m_j B \end{aligned}$$

Which is generally very small for small B.

6.3.2 Strong Applied Field

Here, we have that $\hat{H}_{mag} >> \hat{H}_{SO}$, so we ignore the spin-orbit coupling contribution. Hence, the Hamiltonian is:

$$\hat{H} = \hat{H}_0 - \frac{\mu_B}{\hbar}(g_\ell \hat{L}_z + g_s \hat{S}_z)B$$

All terms commute with $\hat{L}_z, \hat{S}_z, \hat{L}^2, \hat{S}^2$. Thus, we can find the energy shift of each state:

$$\hat{H}_{mag}|\ell, m_\ell, s, m_s\rangle = -\mu_B(g_\ell m_\ell + g_s m_s)B|\ell, m_\ell, s, m_s\rangle$$

We shall define this energy shift as ΔE in units of $\mu_B B$.

We use $g_\ell = -1, g_s = -2$; so, for each m_ℓ, m_s of the $\ell = 1$ state, the energy shifts are $(m_\ell, m_s) = \Delta E$:

$$(+1, +\frac{1}{2}) = +2 \quad (0, +\frac{1}{2}) = +1 \quad (-1, +\frac{1}{2}) = 0 \quad (+1, -\frac{1}{2}) = 0 \quad (0, -\frac{1}{2}) = -1 \quad (-1, -\frac{1}{2}) = -2$$

Notice, the two middle states are degenerate.

Also, via Clebsch-Gordan coefficients, we can find that $|j = \frac{3}{2}, m_j = \frac{3}{2}\rangle$ is a pure state, however, the others wont be.

For intermediate fields, states may be expressed as a linear combination of either the $|j, m_j\rangle$ or $|m_\ell, m_s\rangle$ set.

7 Time Independant Perturbation Theory

Suppose we have a system whose eigenstates and energies are given by:

$$\hat{H}_0 u_n = E_n^0 u_n$$

This we shall call our 'unperturbed system'. We now want to consider the effect of a weak perturbation of the field. For example, we could apply an external magnetic field to an atom. Now, let our perturbation have Hamiltonian $\hat{H}'$. Thus, let the new total Hamiltonian of the system be:

$$\hat{H} = \hat{H}_0 + \beta \hat{H}' \tag{7.1}$$

We introduce $\beta = 1$, to keep track of first and second order terms in β. So, the eigenvalue equation of our new system is just:

$$\hat{H}\psi_n = E_n \psi_n \tag{7.2}$$

Now, let us suppose that we have some higher order corrections to the unperturbed system E_n^0, u_n for our perturbed system, so that we now have:

$$E_n = E_n^0 + \beta E_n' + \beta^2 E_n'' + \ldots \tag{7.3}$$
$$\psi_n = u_n + \beta u_n' + \beta^2 u_n'' + \ldots \tag{7.4}$$

That we have specified the perturbation is weak allows us to expand like this. Let us now compute the shift in energy E' due to first order purturbations. Now, inserting all expressions (7.1), (7.3), (7.4) into (7.2) to give:

$$(\hat{H}_0 + \beta\hat{H}')(u_n + \beta u'_n) = (E^0_n + \beta E'_n)(u_n + \beta u'_n)$$

Where we have neglected higher order terms in β. Expanding this out results in:

$$\hat{H}_0 u_n + \hat{H}_0\beta u'_n + \beta\hat{H}' u_n + \beta\hat{H}'\beta u'_n = E^0_n u_n + E^0_n\beta u'_n + \beta E'_n u_n + \beta E'_n\beta u'_n$$

Notice, some of these terms involve β^2, so we neglect them:

$$\hat{H}_0 u_n + \hat{H}_0\beta u'_n + \beta\hat{H}' u_n = E^0_n u_n + E^0_n\beta u'_n + \beta E'_n u_n \tag{7.5}$$

Now, to zeroth-order, that is, terms that do not involve any powers of β this reads:

$$\hat{H}_0 u_n = E^0_n u_n$$

Which is what we stated as being our unperturbed system. If we write the first order terms of (7.5), that is, all coefficients of β:

$$\hat{H}' u_n + \hat{H}_0 u'_n = E^0_n u'_n + E'_n u_n \tag{7.6}$$

We know that we have write u'_n as a linear combination of other eigenfunctions:

$$u'_n = \sum_m a_m u_m$$

Where we have chosen to expand in terms of the basis states of the unperturbed system. Hence (7.6) becomes:

$$\hat{H}' u_n + \hat{H}_0 \sum_m a_m u_m = E^0_n \sum_m a_m u_m + E'_n u_n$$

We now multiply this expression from the left by u^*_n, and integrate over all space:

$$\int u^*_n \hat{H}' u_n \, d\tau + \int u^*_n \hat{H}_0 \sum a_m u_m \, d\tau = \int u^*_n E^0_n \sum a_m u_m \, d\tau + \int u^*_n E'_n u_n \, d\tau \tag{7.7}$$

We now look at each term. The second term can be writtem:

$$\begin{aligned}
\int u^*_n \hat{H}_0 \sum a_m u_m \, d\tau &= \int u^*_n \sum a_m E^0_m u_m \, d\tau \\
&= \sum a_m E^0_m \int u^*_n u_m \, d\tau \\
&= \sum a_m E^0_m \delta_{nm} \\
&= a_n E^0_n
\end{aligned}$$

The third term can be written similarly:

$$\int u^*_n E^0_n \sum a_m u_m \, d\tau = a_n E^0_n$$

And the fourth term:

$$\int u_n^* E_n' u_n \, d\tau = E_n' \int u_n^* u_n \, d\tau = E_n'$$

Hence, inserting these expressions into (7.7):

$$\begin{aligned} \int u_n^* \hat{H}' u_n \, d\tau + a_n E_n^0 &= a_n E_n^0 + E_n' \\ \Rightarrow E_n' &= \int u_n^* \hat{H}' u_n \, d\tau \end{aligned}$$

Where E_n' is the shift in energy due to a small perturbation with Hamiltonian $\hat{H}'$. And we see that u_n are eigenstates of the unperturbed system.

In the weak field Zeeman effect, we calculated:

$$\langle u_n | \hat{H}' | u_n \rangle$$

And made the assumption that wavefunctions we unchanged. We had that $\hat{H}' = -\boldsymbol{\mu}_J \cdot \boldsymbol{B}$ and $u_n = |j, m_j, \ell, s\rangle$.

Example The proton has a finite size, and is not a point charge, as has previously been assumed. Lets find the energy shift of a 1s electron orbital, taking the finite size of the proton into account.

We assume that the proton charge lies on the surface of a sphere radius $R = 10^{-15}$m.
We have that the potential $V(r)$ due to a point charge is:

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

And that for charge on a sphere radius R is constant:

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

And for outside the sphere:

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

Thus, the perturbation is the difference in the two potentials. We have that, due to a point charge, the unperturbed Hamiltonian is:

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$$

And the perturbation Hamiltonians are:

$$\begin{aligned} \hat{H}' &= 0 & r > R \\ \hat{H}' &= \tfrac{e^2}{4\pi\varepsilon_0 r} - \tfrac{e^2}{4\pi\varepsilon_0 R} & r \leq R \end{aligned}$$

Therefore, we have that the energy shift ΔE, E_0', of the 1s state is:

$$\Delta E = \int \psi^* \hat{H}' \psi d\tau$$

The non-zero contribution is hence:

$$\Delta E = \int_0^R |\psi|^2 \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r} - \frac{1}{R}\right) 4\pi r^2\, dr$$

Now, the wavefunction for the 1s state is:

$$|\psi|^2 = \frac{1}{\pi a_0^3} e^{-r/a_0}$$

Now, here, we note that $R << a_0$, hence:

$$|\psi|^2 \approx \frac{1}{\pi a_0^3}$$

Therefore:

$$\begin{aligned}
\Delta E &= \frac{4\pi e^2}{4\pi\varepsilon_0 \pi a_0^3} \int_0^R r - \frac{r^2}{R} dr \\
&= \frac{4\pi e^2}{4\pi\varepsilon_0 \pi a_0^3} \frac{R^2}{6} \\
&= \frac{R^2 e^2}{6\pi\varepsilon_0 a_0^3}
\end{aligned}$$

We look at this in terms of the unperturbed energy:

$$E_0 = R_\infty = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 a_0}$$

Hence:

$$\frac{\Delta E}{E_0} = \frac{4}{3}\frac{R^2}{a_0^2}$$

If $a_0 = 0.5 \times 10^{-10}$m and $R = 10^{-15}$m, then:

$$\frac{\Delta E}{E_0} = 5 \times 10^{-10}$$

Which is very small! Thus, we have calculated what the energy shift due to the correction of the proton being a sphere, as opposed to a point-like particle is, in the Hydrogen atom. For higher mass atoms, the nuclear radius gets bigger as $R \approx 1.3A^{1/3}$.
Some lasers have a precision $\frac{\Delta\nu}{\nu}$ of about 10^{-10}. Therefore, this shift can actually be measured using laser spectroscopy.

A Dirac Notation and Vectors

There is a very strong analogy between expressing an eigenfunction in terms of basis functions with expressing a vector in terms of basis vectors. Lets discuss vectors first:

A.1 Basis Vectors

Suppose we have the column vector:

$$\boldsymbol{v} = \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

Then this only has meaning if we express it in terms of some basis; it is a along a particular direction, b, c along others. In Cartesian coordinates, we use the unit vectors $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$. Better notation for a general unit vector is $\boldsymbol{e}_i$, where in the Cartesian system, $i = x, y, z$. Now, a unit vector, as implied by the name, has length one (that is $\boldsymbol{e}_i \cdot \boldsymbol{e}_i = 1$). We thus write a vector as being composed in various amounts of different basis vectors.

Infact, its fair to say that we must define all of our basis vectors in some way:

$$\boldsymbol{e}_x \equiv \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad \boldsymbol{e}_y \equiv \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \boldsymbol{e}_z \equiv \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

We see that the above unit vectors have the property of being orthonormal: $\boldsymbol{e}_i \cdot \boldsymbol{e}_j = \delta_{ij}$; all have length one, and are at 'right angles' to each other. Note, when multiplying vectors in this way, we actually take the complex conjugate transpose of the '$\boldsymbol{e}_i$' vector, before multiplication. That we take the complex conjugate is important in the subsequent discussion in eigenfunctions.
Thus, when we write a vector in the form $\boldsymbol{v} = a\boldsymbol{i} + b\boldsymbol{j} + c\boldsymbol{k}$, this is (in the previous notation) just:

$$\boldsymbol{v} = a\boldsymbol{e}_x + b\boldsymbol{e}_y + c\boldsymbol{e}_z$$

Then is it equivalent to writing it as:

$$\begin{aligned} \boldsymbol{v} &= a\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + b\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + c\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \\ &= \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ b \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix} \\ &= \begin{pmatrix} a \\ b \\ c \end{pmatrix} \end{aligned}$$

Which is back to our original vector. Thus, in a very non-rigourous fashion, we have introduced that a vector can be written in terms of some fundamental basis vector. We say that the basis vectors have unit length. This discussion does not (and was not intended to) form a complete definition of basis vectors, more to give an insight into the analogy with the next section:

A.2 Basis Eigenvectors

Now, the wavefunction ψ can be written in terms of a linear superposition of other wavefunctions (eigenfunctions) ϕ_i:

$$\psi = a_1\phi_1 + a_2\phi_2 + a_3\phi_3 + \dots$$

Now, we shall consider the case where we have a finite number of eigenfunctions to expand into. There can be an infinite amount, but then things become very complicated!

Now, we make the connection with the previous section: We are expanding a wavefunction in terms of basis eigenfunctions. In the previous section, where we had $\boldsymbol{e}_i$, we now have $|\phi_i\rangle$. Just as $\boldsymbol{e}_i$ had unit length and defined a particular direction, so $|\phi_i\rangle$ defines a 'particular direction', and has unit length.

A.2.1 Spin Angular Momentum

Making the connection with the 'intrinsic spin' parts of the QM course, we have that the state α represents a spin 'up' $+\frac{1}{2}\hbar$, and β spin 'down' $-\frac{1}{2}\hbar$ along the z-axis. That we use the z-axis is very important. We are basically using m_s to label basis states. We use these as basis functions for spin systems:

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Now, these can be derived from finding the matrix representation for such a spin system, but they require other definitions which kind of make the argument self-sufficient, so I may as well just state the above basis functions as being definitions, to aid the connection with basis vectors.

Just as we can make a vector have stretch different amounts along different basis vectors, a spin can have components in different directions:

$$\chi = A\alpha + B\beta$$

Now, Dirac notation lets us represent α, β as kets:

$$\begin{aligned} \alpha &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |\alpha\rangle = |m_s = +\frac{1}{2}\hbar\rangle \\ \beta &= \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |\beta\rangle = |m_s = -\frac{1}{2}\hbar\rangle \end{aligned}$$

Where I have now made the transition into specifying the value of the quantum number m_s. Note, $m_s \equiv m_z \equiv s_z$; where care must be taken in ensuring that the difference between spin and orbital angular momentum quantum numbers is noted when relevant.
Now, our spin 'vector' χ can then be represented as:

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

Now, this is fine for the above states, as they are just looking at spins along the z-direction. Suppose we have a spin $+\frac{1}{2}\hbar$ along the x-direction. How do we write this in terms of eigenfunctions (basis

vectors) of the above basis? The question we are asking is 'what is the projection of my spin onto the basis vectors?'.

I have not gone into formulating the matrix representation of spins here, but in the formulation of the matrix representation of the $\hat{S}_x$ operator, $[S_x]$, we use eigenfunctions of $\hat{S}_z$: the α, β states; and ladder operators. We find the following matrxix:

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

We find eigenvectors of this matrix to be:

$$\begin{aligned} \alpha_x &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ \beta_x = &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \end{aligned}$$

Note, there are eigenvalues $\pm\frac{1}{2}\hbar$ for this operator, where α_x refers to $+\frac{1}{2}\hbar$, and equivalent for β_x. Now, let us expand α_x in terms of its basis vectors:

$$\begin{aligned} \alpha_x &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= \frac{1}{\sqrt{2}}|\alpha\rangle + \frac{1}{\sqrt{2}}|\beta\rangle \\ &= \frac{1}{\sqrt{2}}|m_z = +\frac{1}{2}\hbar\rangle + \frac{1}{\sqrt{2}}|m_z = -\frac{1}{2}\hbar\rangle \end{aligned}$$

Thus, what we see is that a spin $+\frac{1}{2}\hbar$ along the x-direction can be decomposed into an amount $\frac{1}{\sqrt{2}}$ along both the $m_z = \pm\frac{1}{2}\hbar$ directions: spins in the z-direction.
Note, we can write $\alpha_x = |m_x = +\frac{1}{2}\hbar\rangle$; so that:

$$|m_x = +\frac{1}{2}\hbar\rangle = \frac{1}{\sqrt{2}}|m_z = +\frac{1}{2}\hbar\rangle + \frac{1}{\sqrt{2}}|m_z = -\frac{1}{2}\hbar\rangle$$

We can start to see how the eigenfunctions of spin in the z-direction are being used in the exact same way as basis vectors along the x, y, z-directions are used in a Cartesian coordinate system.

We do this similarly for β_x:

$$\begin{aligned} \beta_x &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} - \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= \frac{1}{\sqrt{2}}|m_z = +\frac{1}{2}\hbar\rangle - \frac{1}{\sqrt{2}}|m_z = -\frac{1}{2}\hbar\rangle \\ \Rightarrow |m_x = -\frac{1}{2}\hbar\rangle &= \frac{1}{\sqrt{2}}|m_z = +\frac{1}{2}\hbar\rangle - \frac{1}{\sqrt{2}}|m_z = -\frac{1}{2}\hbar\rangle \end{aligned}$$

Suppose we know that the eigenvector of the matrix $[S_y]$, corresponding to an eigenvalue $m_y = -\frac{1}{2}\hbar$ is:

$$\beta_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$$

Then we can immediately decompose it into 'amounts of spin' in terms of the eigenfunctions in the z-direction:

$$\begin{aligned} \beta_y &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} - i\frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} |m_z = +\frac{1}{2}\hbar\rangle - i\frac{1}{\sqrt{2}} |m_z = -\frac{1}{2}\hbar\rangle \end{aligned}$$

This is now basically impossible to visualise in our classical picture of spin creeping onto other directions by a certain amount: there is a complex component to the projection.

A.2.2 Orbital Angular Momentum

This works in the exact same way as for intrinsic spin angular momentum; except that we work in terms of the basis of eigenfunctions of the $\hat{L}_z$ operator: m_z.

We shall work in terms of spin-1 systems, so that there are 3 basis eigenfunctions:

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

Now, suppose we know that an eigenfunction of the $[L_x]$ operator, corresponding to an eigenvalue $m_x = +1$ is:

$$|m_x = +1\rangle = \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}$$

Then we can immediately decompose this:

$$\begin{aligned} |m_x = +1\rangle &= \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} \\ &= \frac{1}{2}. \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \frac{\sqrt{2}}{2} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + \frac{1}{2}. \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \\ &= \frac{1}{2}|m_z = +1\rangle + \frac{\sqrt{2}}{2}|m_z = 0\rangle + \frac{1}{2}|m_z = -1\rangle \end{aligned}$$

Note, I have not said anywhere how to find the eigenvectors of a matrix, that is for the next section! I have also been pretty lax in terms of $\hbar$'s; but hopefully the main ideas of what a basis vector is, or analogous to, has come across.

The final thing, is that a bra $\langle\phi|$ has the analogy of being the complex conjugate transpose of the ket $|\phi\rangle$. So, we can write both:

$$|\phi\rangle = \begin{pmatrix} a \\ b \\ c \end{pmatrix} \qquad \langle\phi| = (a^*, b^*, c^*)$$

In this way, if the above ket is normalised, then we should have that $\langle\phi|\phi\rangle = 1$, which we see is the case if we multiply the above two matrices together.

B Finding Eigenvalues/Vectors For $[L_x]$, Spin 1

Now, we have the matrix representation of $\hat{L}_x$, for spin-1 particles, in the basis of eigenfunctions of $\hat{L}_z$. This is:

$$[L_x] = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

We find eigenvalues λ by solving the determinant:

$$\begin{vmatrix} 0-\lambda & \hbar/\sqrt{2} & 0 \\ \hbar/\sqrt{2} & 0-\lambda & \hbar/\sqrt{2} \\ 0 & \hbar/\sqrt{2} & 0-\lambda \end{vmatrix} = 0$$

That is, solving the cubic:

$$\begin{aligned} (-\lambda)\left[\lambda^2 - \frac{\hbar^2}{2}\right] - \frac{\hbar}{\sqrt{2}}\left[-\frac{\lambda\hbar}{\sqrt{2}}\right] &= 0 \\ \Rightarrow -\lambda^3 + \frac{\hbar^3}{2}\lambda + \frac{\hbar^2}{2}\lambda &= 0 \\ \Rightarrow \lambda(-\lambda^2 + \hbar^2) &= 0 \end{aligned}$$

Hence, we see 3 solutions of the cubic: 3 eigenvalues of $[L_x]$:

$$\begin{aligned} \lambda_1 &= -\hbar \\ \lambda_2 &= 0 \\ \lambda_3 &= +\hbar \end{aligned}$$

Now, to find the eigenvectors of $[L_x]$, we must solve:

$$\begin{pmatrix} 0 & \hbar/\sqrt{2} & 0 \\ \hbar/\sqrt{2} & 0 & \hbar/\sqrt{2} \\ 0 & \hbar/\sqrt{2} & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \lambda \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

For each eigenvalue. Expanding this out, and collecting terms, results in:

$$\begin{aligned} -\lambda a + b\hbar/\sqrt{2} &= 0 \\ a\hbar/\sqrt{2} + c\hbar/\sqrt{2} &= 0 \\ b\hbar/\sqrt{2} - \lambda c &= 0 \end{aligned}$$

So, for $\lambda_2 = 0$, we have:

$$\begin{aligned} b\hbar/\sqrt{2} &= 0 \Rightarrow b = 0 \\ a\hbar/\sqrt{2} + c\hbar/\sqrt{2} &= 0 \Rightarrow a = -c \\ b\hbar/\sqrt{2} &= 0 \Rightarrow b = 0 \end{aligned}$$

Therefore, the (un-normalised) eigenvector corresponding to the eigenvalue $\lambda_2 = 0$ is:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \equiv \boldsymbol{v}_2'$$

To normalise this, we require that $\boldsymbol{v}_2^2 = 1$. We can do this by saying that there is some constant x infront of $\boldsymbol{v}_2$ that makes it normalised. So:

$$\begin{aligned} x(1,0,-1)x \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} &= x^2(1+1) \\ &= 2x^2 \\ &= 1 \\ \Rightarrow x &= \frac{1}{\sqrt{2}} \end{aligned}$$

Therefore, the normalised eigenvector corresponding to eigenvalue $\lambda_2 = 0$ is:

$$\boldsymbol{v}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

For the eigenvalue $\lambda_3 = +\hbar$, we have the system:

$$\begin{aligned} -a\hbar + b\hbar/\sqrt{2} &= 0 \Rightarrow a = b/\sqrt{2} \\ a\hbar/\sqrt{2} + c\hbar/\sqrt{2} &= 0 \Rightarrow a = c \\ b\hbar/\sqrt{2} - c\hbar &= 0 \Rightarrow b = c\sqrt{2} \end{aligned}$$

Hence, we see that the un-normalised eigenvector is:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} \equiv \boldsymbol{v}_3'$$

Again, to normalise this:

$$\begin{aligned} x^2(1,\sqrt{2},1) \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} &= x^2(1+2+1) \\ &= 4x^2 \\ &= 1 \\ \Rightarrow x &= \frac{1}{2} \end{aligned}$$

Thus, the normalised eigenvector, corresponding to the eigenvalue $\boldsymbol{v}_3$ is:

$$\boldsymbol{v}_3 = \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}$$

If we do the same thing for the $\lambda_1 = -\hbar$, then we get a normalised eigenvector:

$$\boldsymbol{v}_1 = \frac{1}{2} \begin{pmatrix} -1 \\ \sqrt{2} \\ -1 \end{pmatrix}$$

So, we have the states, in terms of eigenfunctions of $\hat{L}_z$ for a spin-1 particle:

$$|m_x = -1\hbar\rangle = \frac{1}{2}\begin{pmatrix} -1 \\ \sqrt{2} \\ -1 \end{pmatrix} \quad |m_x = 0\hbar\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \quad |m_x = +1\hbar\rangle = \frac{1}{2}\begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}$$

So, if we want to expand one of these in terms of $|m_z\rangle$:

$$\begin{aligned} |m_x = -1\hbar\rangle &= \frac{1}{2}\begin{pmatrix} -1 \\ \sqrt{2} \\ -1 \end{pmatrix} \\ &= -\frac{1}{2}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \frac{\sqrt{2}}{2}\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} - \frac{1}{2}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \\ &= -\frac{1}{2}|m_z = 1\rangle + \frac{\sqrt{2}}{2}|m_z = 0\rangle - \frac{1}{2}|m_z = -1\rangle \end{aligned}$$