

Angular Momentum

We will now look at angular momentum in quantum mechanics. We'll start with a quick reminder about the canonical commutation relation: $[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i\hbar$. It is also the case that momentum and position operators along orthogonal directions will in fact commute: $[\hat{x}, \hat{y}] = 0$, $[\hat{p}_x, \hat{p}_y] = 0$, $[\hat{x}, \hat{p}_y] = 0$, etc.

Angular momentum is defined as $\mathbf{L} \equiv \mathbf{r} \times \mathbf{p}$. Expanding this cross product we obtain $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$, $\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$, and $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$. We can use the canonical commutation relation on these:

$$\begin{aligned}
 [\hat{L}_x, \hat{L}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \\
 &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\
 &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{y}, \hat{x}]\hat{p}_z - \hat{z}[\hat{p}_y, \hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\
 &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\
 &= (\hat{y}\hat{p}_z\hat{z}\hat{p}_x - \hat{z}\hat{p}_x\hat{y}\hat{p}_z) + (\hat{z}\hat{p}_y\hat{x}\hat{p}_z - \hat{x}\hat{p}_z\hat{z}\hat{p}_y)
 \end{aligned}$$

Because position and momentum components along orthogonal directions commute we are allowed to rearrange these terms so long as we never reverse the order of a position and momentum operator along the same direction: $\hat{y}\hat{p}_z\hat{z}\hat{p}_x = \hat{y}\hat{p}_x\hat{p}_z\hat{z}$ for example.

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

We therefore find that the various components of the angular momentum vector do not commute with each other: $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$, as well as the cyclic permutations $[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$ and $[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$.

This means that there will be an uncertainty relation between any two components of angular momentum: these are incompatible observables. Put another way, it is not possible to construct a set of functions that are simultaneous eigenfunctions of all angular momentum coordinates.

Now we will determine the commutator of $\hat{L}^2$ (the square of the angular momentum, which obviously tells us its magnitude) with $\hat{L}_z$.

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

where in the second line I've used the relation $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$. It can similarly be shown that $\hat{L}^2$ also commutes with both $\hat{L}_x$ and $\hat{L}_y$. Therefore it IS possible to construct a complete basis of functions that are simultaneous eigenfunctions of both $\hat{L}^2$ and $\hat{L}_z$. This is what we will do. Note: it is conventional to choose $\hat{L}_z$ here, but the z -axis is not unique and any other axis could have been chosen instead.

Let us say that function f is a simultaneous eigenfunction of these two operators: $\hat{L}^2 f = \lambda f$ and $\hat{L}_z f = \mu f$. Now let us define $\hat{L}_+ \equiv \hat{L}_x + i\hat{L}_y$ as the raising operator. You can prove that $[\hat{L}_z, \hat{L}_+] = \hat{L}_z\hat{L}_+ - \hat{L}_+\hat{L}_z = +\hbar\hat{L}_+$. Now we ask ourselves, what is $\hat{L}_z\hat{L}_+f$? Using the commutation relation, $\hat{L}_z\hat{L}_+f = (\hat{L}_+\hat{L}_z + \hbar\hat{L}_+)f$. We know that $\hat{L}_z f = \mu f$, so applying this we end up with $\hat{L}_z\hat{L}_+f = (\mu + \hbar)\hat{L}_+f$. This means that if f is an eigenfunction of $\hat{L}_z$ then $\hat{L}_+f$ is also an eigenfunction of $\hat{L}_z$ with an eigenvalue that is bigger than the eigenvalue of f by a difference of $+\hbar$. Or $\hat{L}_+$ is a raising operator that raises an eigenfunction to the next highest 'rung' on a ladder of eigenfunctions. By the same logic, $\hat{L}_- \equiv \hat{L}_x - i\hat{L}_y$ is the lowering operator because $[\hat{L}_z, \hat{L}_-] = -\hbar\hat{L}_-$.

$[\hat{L}^2, \hat{L}_+] = 0$. Therefore $\hat{L}^2 \hat{L}_+ f = \lambda \hat{L}_+ f$: after applying the raising operator the resulting function is still an eigenfunction of $\hat{L}^2$ with the same eigenvalue. The raising operator can not be applied forever: the z -component of the angular momentum can't be bigger than the magnitude of the angular momentum. Therefore there must be a 'top rung' to the ladder. We'll call this top rung f_t , and we know that $\hat{L}_+ f_t = 0$. (Why do we know this? Our logic that $\hat{L}_+ f_t$ must be an eigenfunction of $\hat{L}_z$ still stands. But we know that we can't raise this state any higher. The way to cut this Gordian knot is that the function 0 is an eigenfunction of any operator.) So this leaves us with:

$$\hat{L}_+ f_t = 0 \quad \hat{L}^2 f_t = \lambda f_t \quad \hat{L}_z f_t = \hbar l f_t$$

In the last equation we have not yet made any assumptions about l : this just states that there is some eigenvalue and we will define l such that the eigenvalue is $\hbar l$. With some algebra, it is possible to show that $\hat{L}^2 = \hat{L}_- \hat{L}_+ + \hat{L}_z^2 + \hbar \hat{L}_z$. Therefore

$$\hat{L}^2 f_t = \hat{L}_- \hat{L}_+ f_t + \hat{L}_z^2 f_t + \hbar \hat{L}_z f_t = 0 + (\hbar l)^2 f_t + \hbar(\hbar l) f_t = \hbar^2 l(l+1) f_t$$

Repeating this logic, there will be a 'bottom rung' f_b such that

$$\hat{L}_- f_b = 0 \quad \hat{L}^2 f_b = \lambda f_b \quad \hat{L}_z f_b = -\hbar l f_b$$

and because $\hat{L}^2 = \hat{L}_+ \hat{L}_- + \hat{L}_z^2 - \hbar \hat{L}_z$ we again have $\hat{L}^2 f_b = \hbar^2 l(l+1) f_b$.

There must be an integer number of steps between the top rung and the bottom rung, which implies that $2l$ is an integer. This is important to note: This operator based theory allows for l to be either an integer OR A HALF INTEGER. However, it turns out that normalizable eigenfunctions exist only for integer values of l (these eigenfunctions being the spherical harmonics). You might know by now that half-integer values ARE allowed for intrinsic (spin) angular momentum. Because spin is truly intrinsic spin states are not functions of θ and ϕ

- they aren't functions at all. For that reason the half-integer values allowed by this operator theory are fully valid. Putting it all together we have angular momentum eigenstates $|l\ m\rangle$:

$$\begin{aligned}\hat{L}^2|l\ m\rangle &= \hbar^2 l(l+1)|l\ m\rangle & \hat{L}_z|l\ m\rangle &= m\hbar|l\ m\rangle \\ \hat{L}_{\pm}|l\ m\rangle &= \hbar\sqrt{l(l+1) - m(m\pm 1)}|l\ (m\pm 1)\rangle \\ l &= 0, 1, 2, 3, \dots & m &= -l, -l+1, \dots, l-1, l\end{aligned}$$

At this point it is worth it to think a little about degeneracy. There are three distinct states that are eigenstates of the $\hat{L}^2$ operator with eigenvalue $2\hbar^2$: $|1\ -1\rangle$, $|1\ 0\rangle$, and $|1\ +1\rangle$. Now when I describe these states as distinct I mean that they are mutually orthogonal: $\langle l_1\ m_1|l_2\ m_2\rangle = \delta_{l_1,l_2}\delta_{m_1,m_2}$ where the Kronecker δ functions show us that this inner product is zero unless the two states are the same.

So there are three distinct states with the same eigenvalue. Therefore we would say that the $2\hbar^2$ eigenvalue of $\hat{L}^2$ has a three-fold degeneracy or a degeneracy of three. But are those three states the only three states with this eigenvalue? No, any linear combination of these three states, such as $\frac{1}{\sqrt{3}}[|1\ -1\rangle + |1\ 0\rangle + |1\ +1\rangle]$, will also be an eigenstate with this same eigenvalue. But that doesn't increase the degeneracy because this new state is obviously not orthogonal to the three states we had earlier.

So we say that the $L^2 = 2\hbar^2$ state is three-fold degenerate. So we can construct a basis with three distinct states that share this eigenvalue. But there are infinitely many different ways of choosing the three states and all are in some sense equally valid. We typically choose $|1\ -1\rangle$, $|1\ 0\rangle$, and $|1\ +1\rangle$ as the three states. But the z -axis is not unique or special. We could just as easily choose the x -axis or the y -axis (or any other direction) as our quantization axis. If we chose the x -axis as our quantization axis we might say that $|1\ -1\rangle^{(x)}$, $|1\ 0\rangle^{(x)}$, and $|1\ +1\rangle^{(x)}$

are the three states that are simultaneous eigenstates of both the $\hat{L}^2$ and $\hat{L}_x$ operators. Those three states are mutually orthogonal with each other, but each one can be written as a linear superposition of the states that are eigenfunctions of $\hat{L}_z$ that we normally use.

And there are other possible bases as well. Chemists refer to orbitals with $l = 1$ as p orbitals. Chemists describe the three states as the p_x , p_y , and p_z orbitals. The p_z orbital is just the $|1\ 0\rangle$ state that we typically use. But the other two orbitals are linear superpositions of the $|1\ -1\rangle$ and $|1\ +1\rangle$ states. The p_x orbital is $\frac{1}{\sqrt{2}}[-|1\ +1\rangle + |1\ -1\rangle]$ while the p_y orbital is $\frac{i}{\sqrt{2}}[|1\ +1\rangle + |1\ -1\rangle]$.

Angular Momentum Eigenfunctions

So far we have used the algebraic operator theory to determine the angular momentum eigenvalues. But what are the eigenfunctions? In spherical coordinates the angular momentum operator can be written as $\hat{\mathbf{L}} = \frac{\hbar}{i}(\hat{\phi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi})$. If we write the eigenfunctions as f_l^m that gives us the differential equations

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

$$\hat{L}_z f_l^m = \frac{\hbar}{i} \frac{\partial}{\partial\phi} f_l^m = m\hbar f_l^m$$

These are identical to the angular equations that were already solved, so we know the eigenfunctions are just the spherical harmonics! Therefore $Y_l^m(\theta, \phi)$ is the eigenfunction for a state with angular momentum quantum number l and m . This explains why l needs to be an integer: normalizable solutions only exist to these equations for integer l .

A Complete Set of Commuting Observables

It is now worthwhile to spend a bit more time exploring what it means when we do quantum mechanics in three dimensions. First we can look back on the simpler one dimensional case. The key insight here is that in one dimensional problems there is never any degeneracy. This means that, for a one dimensional problem, there will never be two distinct wavefunctions that have the same energy. The obvious (simplest) example is the infinite square well: the stationary state wave function are $\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ with energies $E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$. Each energy eigenvalue corresponds to an E_n with some value of n , and each value of n has only one associated stationary state ψ_n .

- This is a one dimensional problem, so we need one quantum number to list out the allowed stationary states. This quantum number is just n .
- Because there is no degeneracy, the list of stationary states is unique. The stationary states list that we wrote above is the only valid way of writing the stationary states (up to a complex phase for any state, which is arbitrary).

We will see that neither of these remain true for problems in more than one dimension. We will consider a 3D simple harmonic oscillator: $V = \frac{1}{2}m\omega^2 r^2 = \frac{1}{2}m\omega^2(x^2 + y^2 + z^2)$. In the broadest sense we start with the question: do we solve this problem in Cartesian coordinates or in spherical coordinates? If we choose Cartesian coordinates we would proceed using separation of variables, and we find that the portion of the stationary states along each direction can be reduced to a one dimensional simple harmonic oscillator. This leaves us with

$$\psi_{n_x, n_y, n_z}(x, y, z) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z) \text{ and } E_{n_x, n_y, n_z} = \hbar\omega \left(n_x + n_y + n_z + \frac{3}{2} \right).$$

We see two facts right away:

- This is a three dimensional problem, so we need three quantum numbers to list out the possible stationary states. In this case the three quantum numbers were n_x , n_y , and n_z .
- There will be degeneracies for most energies. There will be more than one combination of these three numbers that add up to the same energy.

But what if we instead wanted to solve this problem in spherical coordinates? This is a central potential: $V(r) = \frac{1}{2}m\omega^2 r^2$ depends only upon r (not θ or ϕ). Therefore the stationary states can be written as products of a radial part with a spherical harmonic: $R_{nl}(r)Y_l^m(\theta, \phi)$. I am simply going to write down the solutions:

$$\psi_{n_r, l, m} = R_{n_r, l}(r)Y_l^m(\theta, \phi) \quad \text{and} \quad E_{n_r, l, m} = \hbar\omega \left(2n_r + l + \frac{3}{2} \right).$$

In either case the ground state (with $E = \frac{3}{2}\hbar\omega$) is non-degenerate ($n_x = n_y = n_z = 0$ or $n_r = l = m = 0$). The first excited state (with $E = \frac{5}{2}\hbar\omega$) will be 3-fold degenerate. How would we write these three states? In Cartesian coordinates they are

$$\begin{aligned} \psi_{n_x=1, n_y=0, n_z=0} &= \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} x e^{-\frac{m\omega}{2\hbar} x^2} \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} y^2} \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} z^2} \\ \psi_{n_x=0, n_y=1, n_z=0} &= \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} x^2} \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} y e^{-\frac{m\omega}{2\hbar} y^2} \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} z^2} \\ \psi_{n_x=0, n_y=0, n_z=1} &= \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} x^2} \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} y^2} \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} z e^{-\frac{m\omega}{2\hbar} z^2} \end{aligned}$$

while in spherical coordinates the three stationary states are

$$\begin{aligned}\psi_{n_r=0, l=1, m=-1}(r, \theta, \phi) &= \sqrt{\frac{8}{3\sqrt{\pi}}} \left(\frac{m\omega}{\hbar}\right)^{5/4} r e^{-\frac{m\omega}{2\hbar} r^2} \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi} \\ \psi_{n_r=0, l=1, m=0}(r, \theta, \phi) &= \sqrt{\frac{8}{3\sqrt{\pi}}} \left(\frac{m\omega}{\hbar}\right)^{5/4} r e^{-\frac{m\omega}{2\hbar} r^2} \sqrt{\frac{3}{4\pi}} \cos \theta \\ \psi_{n_r=0, l=1, m=+1}(r, \theta, \phi) &= -\sqrt{\frac{8}{3\sqrt{\pi}}} \left(\frac{m\omega}{\hbar}\right)^{5/4} r e^{-\frac{m\omega}{2\hbar} r^2} \sqrt{\frac{3}{8\pi}} \sin \theta e^{+i\phi}.\end{aligned}$$

These appear to be wildly different answers, so who's right? BOTH ARE EQUALLY RIGHT! It turns out the state with $n_x = 0$, $n_y = 0$, and $n_z = 1$ is the same as the state with $n_r = 0$, $l = 0$, and $m = 0$. The other states are not the same but are linear combinations of each other.

This is broadly true: whenever there is a degeneracy, any linear combination of the degenerate states will also be an eigenstate with the same eigenvalue. In the above example this state was 3-fold degenerate: we can write three distinct (orthonormal) stationary states that have this energy. But there are an infinite number of ways of writing this set of three, and in a sense any of these infinite combinations is just as valid as the others.

Usually, we want to express our stationary states with a complete set of commuting observables. For a three dimensional problem we will need three quantum numbers. For that reason we will choose three commuting hermitian operators: for example $\hat{H}$, $\hat{L}^2$, and $\hat{L}_z$. These three operators all commute with each other, so they will share a set of common eigenstates. But each state will have a unique set of eigenvalues (and the associated quantum numbers) over the three. In the spherical case the eigenvalues of $\hat{H}$ are $\hbar\omega(2n_r + l + 3/2)$, the eigenvalues of $\hat{L}^2$ are $\hbar^2 l(l+1)$, and the eigenvalues of $\hat{L}_z$ are $m\hbar$.

Spin

In classical mechanics a solid object can have two types of angular momentum: an orbital angular momentum $\vec{L}_{\text{orb}} = \vec{r} \times \vec{p}$ due to the motion of the object's center of mass and a spin angular momentum $\vec{S} = I\vec{\omega}$ due to the motion of the object about its own center of mass. The earth has orbital angular momentum due to its revolution around the sun and spin angular momentum due to its rotation about its own axis. But breaking classical angular momentum up into two parts like this is a choice we make: it really is just one type of angular momentum due to moving mass.

It turns out that electrons (and other fundamental particles) have an intrinsic angular momentum: an electron at rest will still carry an angular momentum. This is proved in experiments such as the Stern-Gerlach experiment or the anomalous Zeeman effect. We call this intrinsic angular momentum spin, so it seems like we should carry this analogy further and associate this with an electron spinning about its own axis. But this analogy can't be right. First, the electron is assumed to be a true point particle. It has no size and so can't spin. But let's assume that the electron is a solid, uniform ball of mass whose size is given by r_c , the *classical electron radius*. This is given by

$$\frac{e^2}{4\pi\epsilon_0 r_c} = mc^2$$

i.e. it is the radius such that the electrostatic potential energy will equal the rest mass energy. $r_c \approx 2.8$ fm and is a measure of the largest an electron could ever be (experiments constrain any size to be much, much smaller). A uniform sphere has a moment of inertia of $I = \frac{2}{5}mr^2$ so we assume that an electron is spinning with angular frequency ω and set its angular momentum to the magnitude of any electron's angular

momentum:

$$\frac{2}{5}mr_c^2\omega = \frac{\sqrt{3}}{2}\hbar$$

and we find an angular frequency of $\omega \approx 3.1 \times 10^{25}$ rad/s. With this angular frequency the speed of a point on the electron's "equator" would be $v = \omega r_c \approx 8.9 \times 10^{10}$ m/s which is about 300 times the speed of light! Further, our previously derived algebraic theory of angular momentum allowed for l quantum numbers that could be an integer or a half-integer. Yet for orbital angular momentum we find that only integer values of l exist because normalizable eigenfunctions (the spherical harmonics) only exist for integer values. For intrinsic spin angular momentum on the other hand, half-integer quantum numbers do in fact exist. There are no eigenfunctions because there are no functions. Spin is the first quantum state we will approach that can not be written as a wave function. This angular momentum is not caused by the wave function of mass; it just exists. But other than the half-integer quantum numbers being allowed spin angular momentum behaves just like orbital angular momentum. Though we use the operator $\hat{S}$ instead of $\hat{L}$ and the quantum number s instead of l .

$$\begin{aligned}\hat{S}^2|s\ m\rangle &= \hbar^2 s(s+1)|s\ m\rangle & \hat{S}_z|s\ m\rangle &= m\hbar|s\ m\rangle \\ \hat{S}_{\pm}|s\ m\rangle &= \hbar\sqrt{s(s+1) - m(m \pm 1)}|s\ (m \pm 1)\rangle \\ s &= 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots & m &= -s, -s+1, \dots, s-1, s\end{aligned}$$

The quantum number m is used for both orbital and spin angular momentum; if there is any risk of confusion we can call them m_l and m_s to differentiate.

Spin-1/2

Electrons (and many other fundamental particles) are spin-1/2, so they are described by the quantum number $s = 1/2$. There will therefore be two states, corresponding to $m = -1/2$ and $m = +1/2$. These two states are often referred to as spin-up and spin-down:

$$\begin{array}{ll} \text{Spin-up} & |s\ m\rangle = \left| \frac{1}{2} \quad \frac{+1}{2} \right\rangle \quad |\uparrow\rangle \\ \text{Spin-down} & |s\ m\rangle = \left| \frac{1}{2} \quad \frac{-1}{2} \right\rangle \quad |\downarrow\rangle \end{array}$$

It is also conventional to describe spin-1/2 particles with a two-dimensional vector known as a spinor. In this case the general spin state can be described as

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_- \quad \text{with } \chi_+ = |\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \chi_- = |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

In this notation a and b are complex numbers that normalize as $|a|^2 + |b|^2 = 1$. A measurement of S_z (the z -component of the intrinsic angular momentum) would have a $|a|^2$ probability of returning $+\hbar/2$ and a $|b|^2$ probability of returning $-\hbar/2$.

In this notation operators will be 2×2 matrices. We can write $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$ where the Pauli spin matrices are

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

Example: Larmor Precession

An interesting problem is that of an electron in a magnetic field. A spinning charged particle will have a magnetic dipole moment. So we can define the magnetic dipole moment of our particle as $\vec{\mu} = \gamma\vec{S}$ where γ is known as the gyromagnetic ratio for the particle. The Hamiltonian

is therefore $\hat{H} = -\vec{\mu} \cdot \vec{B}$. We'll assume that $\vec{B} = B_0 \hat{k}$ (the magnetic field is along the z -axis) so

$$\hat{H} = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Since the Hamiltonian is a multiple of the $\hat{S}_z$ operator, the energy eigenstates will be the same as the eigenstates of $\hat{S}_z$: χ_+ with energy $-\frac{\gamma B_0 \hbar}{2}$ and χ_- with energy $+\frac{\gamma B_0 \hbar}{2}$. This gives a time-dependent spinor state of

$$\chi(t) = \begin{pmatrix} a e^{i\gamma B_0 t/2} \\ b e^{-i\gamma B_0 t/2} \end{pmatrix}$$

I'm going to assume that a and b are both real and write them as $a \equiv \cos(\alpha/2)$ and $b \equiv \sin(\alpha/2)$ (note: if a and b are both real then this must be true for some angle α). We'll now calculate the expectation value $\langle S_x \rangle$ as a function of time:

$$\begin{aligned} & \begin{pmatrix} \cos(\alpha/2) e^{-i\gamma B_0 t/2} & \sin(\alpha/2) e^{+i\gamma B_0 t/2} \end{pmatrix} \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos(\alpha/2) e^{+i\gamma B_0 t/2} \\ \sin(\alpha/2) e^{-i\gamma B_0 t/2} \end{pmatrix} \\ &= \frac{\hbar}{2} \begin{pmatrix} \cos(\alpha/2) e^{-i\gamma B_0 t/2} & \sin(\alpha/2) e^{+i\gamma B_0 t/2} \end{pmatrix} \begin{pmatrix} \sin(\alpha/2) e^{-i\gamma B_0 t/2} \\ \cos(\alpha/2) e^{+i\gamma B_0 t/2} \end{pmatrix} \\ &= \frac{\hbar}{2} \cos(\alpha/2) \sin(\alpha/2) (e^{-i\gamma B_0 t} + e^{+2i\gamma B_0 t}) \end{aligned}$$

and with some trig identities we have $\langle S_x \rangle = \frac{\hbar}{2} \sin(\alpha) \cos(\gamma B_0 t)$

Similar math tells us that $\langle S_y \rangle = -\frac{\hbar}{2} \sin(\alpha) \sin(\gamma B_0 t)$ and $\langle S_z \rangle = \frac{\hbar}{2} \cos(\alpha)$

Basically, the expectation value makes a constant angle α with the z -axis, and sweeps around a cone precessing in the xy -plane with an angular frequency of $\omega = \gamma B_0$ which is called the Larmor frequency.

Addition of Angular Momentum

Suppose that you have two particles, particle #1 and particle #2, each of which has intrinsic (spin) angular momentum. Let's say that particle #1 has spin s_1 and that particle #2 has spin s_2 . I like to start by considering the commutation relations of the relevant operators: when two operators commute they will share a complete set of eigenstates, but if the operators don't commute they won't. We already know that the $\hat{S}^2$ and $\hat{S}_z$ operators will commute for either particle. Further, operators relating to particle #1 will commute with operators relating to particle #2. This means that, for example, that $[(\hat{S}^{(1)})^2, \hat{S}_z^{(2)}] = 0$ where $(\hat{S}^{(1)})^2$ is the $\hat{S}^2$ operator for particle #1 and $\hat{S}_z^{(2)}$ is the $\hat{S}_z$ operator for particle #2. The fact that the operators for the two different particles commute means that we can write our quantum ket states in terms of $|s_1 m_1\rangle|s_2 m_2\rangle$ states.

Now consider the TOTAL spin angular momentum: the combined spin of the two particles. The total spin angular momentum operator is the sum of the spin operators for each particle individually: $\mathbf{S} \equiv \mathbf{S}^{(1)} + \mathbf{S}^{(2)}$. The z -component of the total spin is $\hat{S}_z = \hat{S}_z^{(1)} + \hat{S}_z^{(2)}$ while the total spin squared operator is $\hat{S}^2 = (\hat{S}^{(1)})^2 + (\hat{S}^{(2)})^2 + 2\hat{S}_x^{(1)}\hat{S}_x^{(2)} + 2\hat{S}_y^{(1)}\hat{S}_y^{(2)} + 2\hat{S}_z^{(1)}\hat{S}_z^{(2)}$.

It turns out that $\hat{S}^2$ does NOT commute with either $\hat{S}_z^{(1)}$ or $\hat{S}_z^{(2)}$ but it DOES commute with $\hat{S}_z = \hat{S}_z^{(1)} + \hat{S}_z^{(2)}$. You will prove this for the homework. On the other hand, $\hat{S}_z$ does commute with all of $(\hat{S}^{(1)})^2$, $(\hat{S}^{(2)})^2$, $\hat{S}_z^{(1)}$, and $\hat{S}_z^{(2)}$. In the end this means that the product state $|s_1 m_1\rangle|s_2 m_2\rangle$ is in fact an eigenstate of $\hat{S}_z$ (the z -component of the total spin) with eigenvalue $(m_1 + m_2)\hbar$ but it is NOT necessarily an eigenstate of $\hat{S}^2$.

Therefore, we have two different bases that could be used to expand our quantum ket states. We could use $|s m\rangle$ states which are eigenstates of $\hat{S}^2$ and $\hat{S}_z$: $\hat{S}^2|s m\rangle = \hbar^2 s(s+1)|s m\rangle$ and $\hat{S}_z|s m\rangle = m\hbar|s m\rangle$.

Alternatively we could use $|s_1 m_1\rangle|s_2 m_2\rangle$ states which are eigenstates of $\hat{S}_z^{(1)}$ and $\hat{S}_z^{(2)}$: $\hat{S}_z^{(1)}|s_1 m_1\rangle|s_2 m_2\rangle = m_1\hbar|s_1 m_1\rangle|s_2 m_2\rangle$ and $\hat{S}_z^{(2)}|s_1 m_1\rangle|s_2 m_2\rangle = m_2\hbar|s_1 m_1\rangle|s_2 m_2\rangle$. Each basis is complete, so it is of course possible to write the eigenstates of one basis as a superposition of the eigenstates of the other basis.

Two Spin- $\frac{1}{2}$ Particles.

The simplest case will be two spin-1/2 particles. In the $|s_1 m_1\rangle|s_2 m_2\rangle$ basis these four states will be $\uparrow\uparrow$, $\uparrow\downarrow$, $\downarrow\uparrow$, and $\downarrow\downarrow$. You will note that , for the sake of brevity, we will write the state

$|s_1 = 1/2 m_1 = +1/2\rangle|s_2 = 1/2 m_2 = -1/2\rangle$ as $\uparrow\downarrow$, etc.

$\uparrow\downarrow$ is an eigenstate of $\hat{S}_z$ with eigenvalue $0\hbar$. But is it also an eigenstate of $\hat{S}^2$? It turns out that it is not. $\hat{S}^2 \uparrow\downarrow = [(\hat{S}^{(1)})^2 + (\hat{S}^{(2)})^2 + 2\hat{S}_x^{(1)}\hat{S}_x^{(2)} + 2\hat{S}_y^{(1)}\hat{S}_y^{(2)} + 2\hat{S}_z^{(1)}\hat{S}_z^{(2)}] \uparrow\downarrow$. Using the facts that $\hat{S}_x \uparrow = \frac{\hbar}{2} \downarrow$, $\hat{S}_x \downarrow = \frac{\hbar}{2} \uparrow$, $\hat{S}_y \uparrow = \frac{i\hbar}{2} \downarrow$, and $\hat{S}_y \downarrow = \frac{-i\hbar}{2} \uparrow$ (use the Pauli spin matrices to prove this to yourself if need be) we wind up with

$$\hat{S}^2 \uparrow\downarrow = \frac{3\hbar^2}{4} \uparrow\downarrow + \frac{3\hbar^2}{4} \uparrow\downarrow + 2\left(\frac{\hbar}{2} \downarrow\right)\left(\frac{\hbar}{2} \uparrow\right) + 2\left(\frac{i\hbar}{2} \downarrow\right)\left(\frac{-i\hbar}{2} \uparrow\right) + 2\left(\frac{\hbar}{2} \uparrow\right)\left(\frac{-\hbar}{2} \downarrow\right)$$

$$\hat{S}^2 \uparrow\downarrow = \hbar^2 \uparrow\downarrow + \hbar^2 \downarrow\uparrow$$

demonstrating that $\uparrow\downarrow$ is NOT an eigenstate of $\hat{S}^2$. In the end it is of course possible to construct linear combinations of $\uparrow\downarrow$ and $\downarrow\uparrow$ that are eigenstates of $\hat{S}^2$. We end up with one state with $s = 0$ and therefore $m = 0$; this is referred to as the singlet state. There will be three states with $s = 1$; with $m = -1$, 0 , or $+1$. These are referred to as the triplet states.

$$\begin{aligned}
 s = 0 \text{ (singlet)} \quad |0\ 0\rangle &= \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \\
 s = 1 \text{ (triplet)} \quad &\begin{cases} |1\ 1\rangle = \uparrow\uparrow \\ |1\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1\ -1\rangle = \downarrow\downarrow \end{cases}
 \end{aligned}$$

Let us consider the state $|1\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$. We will apply the relevant operators to it. First we will do the $\hat{S}_z$ operator: $\hat{S}_z|1\ 0\rangle = (\hat{S}_z^{(1)} + \hat{S}_z^{(2)})(\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow))$. Operators with the superscript (1) affect only the first spin and do nothing to the second spin, and vice versa. So therefore

$$\hat{S}_z|1\ 0\rangle = \frac{1}{\sqrt{2}} \left[(\hat{S}_z^{(1)} \uparrow) \downarrow + \uparrow (\hat{S}_z^{(2)} \downarrow) + (\hat{S}_z^{(1)} \downarrow) \uparrow + \downarrow (\hat{S}_z^{(2)} \uparrow) \right]$$

which gives

$$\hat{S}_z|1\ 0\rangle = \frac{1}{\sqrt{2}} \left[\left(\frac{+\hbar}{2} \uparrow\right) \downarrow + \uparrow \left(\frac{-\hbar}{2} \downarrow\right) + \left(\frac{-\hbar}{2} \downarrow\right) \uparrow + \downarrow \left(\frac{+\hbar}{2} \uparrow\right) \right] = 0$$

which confirms that $\hat{S}_z|1\ 0\rangle = 0|1\ 0\rangle$, meaning that $|1\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$ is an eigenstate of the $\hat{S}_z$ operator with eigenvalue $m\hbar$ where $m = 0$.

Now we'll consider the operator $\hat{S}^2$. We previously showed that $\hat{S}^2 \uparrow\downarrow = \hbar^2 \uparrow\downarrow + \hbar^2 \downarrow\uparrow$. By the same logic $\hat{S}^2 \downarrow\uparrow = \hbar^2 \uparrow\downarrow + \hbar^2 \downarrow\uparrow$. Putting this together

$$\hat{S}^2|1\ 0\rangle = \hat{S}^2 \left[\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \right] = \frac{1}{\sqrt{2}} (\hbar^2 \uparrow\downarrow + \hbar^2 \downarrow\uparrow + \hbar^2 \uparrow\downarrow + \hbar^2 \downarrow\uparrow)$$

which simplifies to

$$\hat{S}^2|1\ 0\rangle = \frac{2\hbar^2}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) = 2\hbar^2|1\ 0\rangle$$

confirming that $|1\ 0\rangle$ is an eigenstate of $\hat{S}^2$ with eigenvalue $\hbar^2 s(s+1)$ where $s = 1$.

Finally, we'll consider the raising operator where you should recall $\hat{S}_+|s\ m\rangle = \hbar\sqrt{s(s+1) - m(m+1)}|s\ (m+1)\rangle$.

$$\begin{aligned} \hat{S}_+|1\ 0\rangle &= (\hat{S}_+^{(1)} + \hat{S}_+^{(2)})\left(\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)\right) = \\ &= \frac{1}{\sqrt{2}} \left[(\hat{S}_+^{(1)} \uparrow) \downarrow + \uparrow (\hat{S}_+^{(2)} \downarrow) + (\hat{S}_+^{(1)} \downarrow) \uparrow + \downarrow (\hat{S}_+^{(2)} \uparrow) \right] \end{aligned}$$

Using our definition above we see that, for a single spin $\hat{S}_+ \uparrow = \hat{S}_+|\frac{1}{2}\ \frac{1}{2}\rangle = 0$ and $\hat{S}_+ \downarrow = \hat{S}_+|\frac{1}{2}\ -\frac{1}{2}\rangle = \hbar|\frac{1}{2}\ \frac{1}{2}\rangle = \hbar \uparrow$. This gives

$$\hat{S}_+|1\ 0\rangle = \frac{1}{\sqrt{2}} [(0) \downarrow + \uparrow (\hbar \uparrow) + (\hbar \uparrow) \uparrow + \downarrow (0)] = \sqrt{2}\hbar \uparrow\uparrow = \sqrt{2}\hbar|1\ 1\rangle$$

which perfectly matches our definition.

Clebsh-Gordan Tables

The previous example, with two spin-1/2 particles, was fairly difficult and larger spins only make addition of angular momentum more difficult. Luckily, there are some general rules that we can use and then we can apply available tables.

Let us assume we have two particles: particle #1 has spin s_1 and a magnetic quantum number of m_1 while particle #2 has spin s_2 and a magnetic quantum number of m_2 . We combine these two particles together, and the total spin angular momentum is described by quantum numbers s and m . How does these relate?

First, $m = m_1 + m_2$. The z -component of the total spin is just the sum of the z -components of the two individual particles. s has a maximum value of $s_1 + s_2$ and a minimum value of $|s_1 - s_2|$, with allowed values of s being integer steps between those limits. Finally, we always have $-s \leq m \leq s$ with m moving in integer steps. That also means that $s \geq |m|$.

$$m = m_1 + m_2$$

$$s = (s_1 + s_2), (s_1 + s_2 - 1), \dots, |s_1 - s_2|$$

$$s \geq |m|$$

Let's do an example. Say that you have a $s_1 = 2$ particle and a $s_2 = 1$ particle. $m_1 = m_2 = -1$, meaning that a measurement of the z -component of the spin angular momentum of either particle will yield a value of $-\hbar$. $m = m_1 + m_2 = -2$, so that a measurement of the z -component of the total spin angular momentum will yield a value of $-2\hbar$. What about s ? $|s_1 - s_2| \leq s \leq s_1 + s_2$, so $1 \leq s \leq 3$ and because this moves in steps of 1 s can take the values 1, 2, or 3. This is the general result for any addition of a spin-2 particle with a spin-1

fore we find the row that begins with $-1 \quad -1$, It is boxed in red in the table above. This row has two numbers: $2/3$ and $1/3$. These numbers (after taking their square root) are the coefficients of the $|s \ m\rangle$ states that are listed above these coefficients. Above the $2/3$ the column reads $s = 3, m = -2$ while above the $1/3$ the column reads $s = 2, m = -2$.

This tells us that: $|2 \ -1\rangle|1 \ -1\rangle = \sqrt{\frac{2}{3}}|3 \ -2\rangle + \sqrt{\frac{1}{3}}|2 \ -2\rangle$. This

means that if we were to measure S^2 , the square of the total spin angular momentum, there is a $|\sqrt{\frac{2}{3}}|^2 = \frac{2}{3}$ chance of measuring $\hbar^2 3(3+1) = 12\hbar^2$ and a $|\sqrt{\frac{1}{3}}|^2 = \frac{1}{3}$ chance of measuring $\hbar^2 2(2+1) = 6\hbar^2$.

Now let's do another example. Still assume that $s_1 = 2$ and $s_2 = 1$. But now assume that they are in the state $|s = 2, m = +1\rangle$. We know that $m_1 + m_2 = m = +1$. There are three possibilities: $(m_1 = 2, m_2 = -1)$, $(m_1 = 1, m_2 = 0)$, and $(m_1 = 0, m_2 = 1)$.

This time we find the column that corresponds to $s = 2$, $m = +1$; this column is shown in blue in the table above. Each coefficient corre-

sponds to the $m_1 m_2$ values at the left of the row. Again, taking square roots of each term and moving minus signs outside the square root, we

have: $|2 \ 1\rangle = \sqrt{\frac{1}{3}}|2 \ 2\rangle|2 \ -1\rangle + \sqrt{\frac{1}{6}}|2 \ 1\rangle|1 \ 0\rangle - \sqrt{\frac{1}{2}}|2 \ 0\rangle|1 \ 1\rangle$. This

means that if we were to measure $S_z^{(1)}$, the z -component of the spin of particle #1 (which has $s_1 = 2$), there is a $\frac{1}{3}$ probability of measuring $2\hbar$, a $\frac{1}{6}$ probability of measuring $\hbar$, and a $\frac{1}{2}$ probability of measuring 0.