# 5 Angular Momentum

In the previous chapter we obtained the fundamental commutation relations among the position, momentum and angular momentum operators, together with an understanding of how a dynamical relation $H = H(\mathbf{X}, \mathbf{P})$ allows us to understand how such quantities evolve in time. However, with the exception of the parity operator, we've not yet said anything about the spectrum — the set of possible eigenvalues — of these operators, nor have we been specific about the precise Hilbert space on which they act. Answering such questions is an important part of the subject of *representation theory* in mathematics; the study of how group actions can be realised on a given vector space. In physics, understanding this will provide essential information about the nature of our quantum system.

To a large extent, both questions are determined by the operator algebra itself. For example, taking the trace of the commutation relations $[X_i, P_j] = \mathrm{i}\hbar\,\delta_{ij}\,I_{\mathcal{H}}$ in any finite-dimensional Hilbert space $\mathcal{H}$ gives

$$\dim(\mathcal{H})\,\delta_{ij} = -\frac{\mathrm{i}}{\hbar}\,\mathrm{tr}_{\mathcal{H}}(X_iP_j - P_jX_i) = 0 \tag{5.1}$$

for all $i, j$ by the cyclic property of the trace. So there is no realisation of the position and translation operators on any non-trivial finite dimensional Hilbert space (and if $\dim(\mathcal{H}) = 0$ then $\mathbf{X}$ and $\mathbf{P}$ necessarily act trivially). The above argument fails in an infinite dimensional Hilbert space, where neither $\mathrm{tr}_{\mathcal{H}}(I_{\mathcal{H}})$ nor $\mathrm{tr}_{\mathcal{H}}(X_iP_j)$ is defined. Thus, if we wish to discuss the position and momentum of a quantum system, we're necessarily in the world of function spaces[46].

On the other hand, taking the trace of the commutation relations

$$[J_i, J_j] = \mathrm{i}\hbar\sum_k \epsilon_{ijk}J_k \tag{5.2}$$

for the rotation generators just gives $\mathrm{i}\hbar\,\epsilon_{ijk}\,\mathrm{tr}_{\mathcal{H}}(J_k) = \mathrm{tr}_{\mathcal{H}}(J_iJ_j - J_jJ_i) = 0$, so it is possible to represent each component of $\mathbf{J}$ on a finite dimensional Hilbert space in terms of a traceless matrix[47]. This is often a useful thing to do, particularly when discussing the internal structure of a system.

In this chapter, we'll consider finite–dimensional Hilbert spaces $\mathcal{H}_j$ whose elements transform among themselves under rotations. In mathematics, the $\mathcal{H}_j$ are known as *irreducible representations* of the rotation group, whilst in physics they're called *multiplets* of definite total angular momentum. This chapter will also substantiate the link between the rotation generators $\mathbf{J}$ and the physics of angular momentum, by examining a simple Hamiltonian for rotating diatomic molecule. We'll also flesh out the details of exactly how the orientation of a system is encoded in the amplitudes for it to be found in different eigenstates of appropriate angular momentum operators.

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[46] Even here we should really be more careful. As mentioned in a previous footnote, $\mathbf{X}$ and $\mathbf{P}$ are not defined as linear operators on the whole of a Hilbert space such as $L^2(\mathbb{R}^3, d^3x)$, because a state that is initially square-integrable may not remain so after the application of the unbounded operator $\mathbf{X}$ or $\mathbf{P}$.

[47] This traceless condition in $\mathcal{H}$ is closely related to – but distinct from – the fact that the generators of $SO(3)$ can also be represented by antisymmetric (hence traceless) matrices acting on $\mathbb{R}^3$.

## 5.1 Angular Momentum Eigenstates *(A Little Representation Theory)*

Let's begin by seeing how the algebra $[J_i, J_j] = \mathrm{i}\hbar \sum_k \epsilon_{ijk} J_k$ determines the spectrum of the angular momentum operators. Since no two components of $\mathbf{J}$ commute, we cannot find a complete set of simultaneous eigenstates of two components of $\mathbf{J}$. However, since $[\mathbf{J}, \mathbf{J}^2] = 0$ we can find a complete set of simultaneous eigenstates of (any) one component of $\mathbf{J}$ and $\mathbf{J}^2$. Without loss of generality, we orient our coordinate system so that the chosen component of $\mathbf{J}$ is $J_z$. We let $|\beta, m\rangle$ denote a simultaneous eigenstate of $J_z$ and $\mathbf{J}^2$, where

$$\mathbf{J}^2|\beta, m\rangle = \beta\hbar^2|\beta, m\rangle \qquad \text{and} \qquad J_z|\beta, m\rangle = m\hbar\,|\beta, m\rangle \tag{5.3}$$

and the factors of $\hbar$ are for later convenience. We also choose all the states $\{|\beta, m\rangle\}$ to be properly normalised. Since they are eigenstates of Hermitian operators, they must then be orthonormal:

$$\langle\beta', m'|\beta, m\rangle = \delta_{\beta\beta'}\,\delta_{mm'}\,. \tag{5.4}$$

Finally, since we're looking for the simplest possible way to realize our commutation relations, we'll assume that the states $\{|\beta, m\rangle\}$ are non-degenerate; that is, we want a Hilbert space where $|\beta, m\rangle$ is the *unique* eigenstate of $\mathbf{J}^2$ and $J_z$ with the given eigenvalues. I'll comment more on this assumption in the next chapter.

We now define

$$J_\pm = J_x \pm \mathrm{i}J_y \tag{5.5}$$

which obey $J_\pm^\dagger = J_\mp$ and so are eachother's adjoint. As they are built from linear combinations of the components of $\mathbf{J}$, clearly $J_\pm$ each commute with $\mathbf{J}^2$, while their commutation relations with $J_z$ are

$$[J_z, J_\pm] = [J_z, J_x] \pm \mathrm{i}[J_z, J_y] = \mathrm{i}\hbar\,(J_y \mp \mathrm{i}J_x) = \pm\hbar\,J_\pm\,. \tag{5.6}$$

We learn that

$$\mathbf{J}^2(J_\pm|\beta, m\rangle) = J_\pm\mathbf{J}^2|\beta, m\rangle = \hbar^2\beta\,J_\pm|\beta, m\rangle \tag{5.7}$$

and

$$J_z(J_\pm|\beta, m\rangle) = ([J_z, J_\pm] + J_\pm J_z)\,|\beta, m\rangle = (m \pm 1)\hbar\,(J_\pm|\beta, m\rangle)\,. \tag{5.8}$$

This shows that the new states $J_\pm|\beta, m\rangle$, if not zero, are still eigenstates of both $\mathbf{J}^2$ and $J_z$, with the same eigenvalue $\beta\hbar^2$ for $\mathbf{J}^2$. However, their $J_z$ eigenvalue is shifted up or down (respectively for $J_+|\beta, m\rangle$ and $J_-|\beta, m\rangle$) by one unit of $\hbar$. We see that the role of $J_\pm$ in angular momentum is similar to the role of $A$ and $A^\dagger$ for energy of the harmonic oscillator. Again, $J_+$ and $J_-$ are often called *raising* and *lowering* operators. Their role is to rotate our system, aligning more or less of its total angular momentum along the $z$-axis without changing the total angular momentum available. (See figure 7.)

Just as for the harmonic oscillator, examining the algebra of our raising and lowering operators has told us the separation between angular momentum eigenstates, given a starting point $|\beta, m\rangle$. To fix our initial states, we must examine the norm. By assumption, $|\beta, m\rangle$ itself is correctly normalized and we compute

$$\begin{aligned} \|J_+|\beta, m\rangle\|^2 &= \langle\beta, m|J_-J_+|\beta, m\rangle = \langle\beta, m|(J_x - \mathrm{i}J_y)(J_x + \mathrm{i}J_y)|\beta, m\rangle \\ &= \langle\beta, m|(\mathbf{J}^2 - J_z^2 - \hbar J_z)|\beta, m\rangle = \hbar^2(\beta - m(m+1)) \end{aligned} \tag{5.9}$$

**Figure 7**: *The angular momentum raising and lowering operators $J_\pm$ realign the system's angular momentum to place more or less of it along the $z$-axis.*

where we've used the fact that $J_+^\dagger = J_-$. Similarly, we find $\|J_-|\beta, m\rangle\|^2 = \hbar^2(\beta - m(m-1))$. But since this is a norm, whatever state $|beta, m\rangle$ we started with we must have

$$\|J_+|\beta, m\rangle\|^2 = \beta - m(m+1) \geq 0 \tag{5.10}$$

with equality iff $J_+|\beta, m\rangle = 0$ is the trivial state. This shows that it cannot be possible to always keep applying $J_+$, repeatedly raising the $J_z$ eigenvalue $m$ whilst leaving $\beta$ unchanged. There must be some maximum value of $m$ – let's call it $j$ – for which $J_+|\beta, j\rangle = 0$. By (5.10) this can only be the case if $\beta$ obeys

$$\beta = j(j+1) \tag{5.11}$$

and so is fixed in terms of the maximum allowed value of $m$.

Similarly, for a generic $m$ value we find

$$\|J_-|\beta, m\rangle\|^2 = \beta - m(m-1) \tag{5.12}$$

so it also cannot be possible to keep lowering the $J_z$ eigenvalue whilst remaining in the Hilbert space. There must be some minimum value of $m$, say $j'$, for which $J_-|\beta, j'\rangle = 0$ and by (5.12) this can only be the case if

$$\beta = j'(j'-1)\,. \tag{5.13}$$

Applying $J_+$ or $J_-$ doesn't change the $\mathbf{J}^2$ eigenvalue $\beta$, so these two values of $\beta$ must agree. Comparing them, we obtain a quadratic equation for $j'$ that we solve in terms of $j$, finding $j' = j+1$ or $j' = j$. Since the minimum value of $m$ can't be greater than the maximum value, we must choose the root $j' = -j$. The $\mathbf{J}^2$ eigenvalue $\beta\hbar^2 = j(j+1)\hbar^2$ is determined by $j$, so we henceforth label our states as $|j, m\rangle$; this labelling is simply less cluttered than $|j(j+1), m\rangle$ would be.

Finally, we note that since applying $J_-$ repeatedly will take us from the highest state $|\beta, j\rangle$ through $|\beta, j-1\rangle, \ldots$ down to $|\beta, -j\rangle$, it must be that $2j$ is a non-negative integer. In other words, the possible values for $j$ are

$$j \in \{0, 1/2, 1, 3/2, \ldots\}\,. \tag{5.14}$$

Once the total angular momentum quantum number $j$ is fixed, we have

$$m \in \{-j, -j+1, \ldots, j-1, j\} . \tag{5.15}$$

Thus there's a total of $2j+1$ states in any given $j$ multiplet, and $\mathcal{H}_j$ is the Hilbert space of dimension $2j+1$ spanned by the $\{|j,m\rangle\}$ of fixed $j$. We can move between states in $\mathcal{H}_j$ using the raising and lowering operators $J_+$ and $J_-$ which obey

$$\begin{aligned} J_+|j,m\rangle &= \hbar\sqrt{j(j+1)-m(m+1)}\,|j,m+1\rangle \\ J_-|j,m\rangle &= \hbar\sqrt{j(j+1)-m(m-1)}\,|j,m-1\rangle \end{aligned} \tag{5.16}$$

These operators only change the $J_z$ eigenvalue, not the $\mathbf{J}^2$ one. They just realign a given system, placing more ($J_+$) or less ($J_-$) of its angular momentum along the $z$-axis. Although we know we can choose multiplets with different values of $j$, we've not yet discovered a mathematical operator that alters this $\mathbf{J}^2$ eigenvalue; this will be done in section 6.2.1.

## 5.2 Rotations and Orientation

This section should talk about how eigenfunctions of angular momentum are related to an object's *orientation*. In particular, a classical object has a well-defined orientation because it is in a superposition of very many nearby angular momentum eigenstates. I think this is likely to mean lots of values of $j$ as well as $m$, but not sure of the best example to use to illustrate this.

Note that, since $J_x$ and $J_y$ can be written in terms of the raising and lowering operators $J_\pm$, rotations around an arbitrary axis transform states in a given $\mathcal{H}_j$ into other states in the same $\mathcal{H}_j$. Since $J_x = (J_+ + J_-)/2$, we see that when $j > 0$, the state $|j,m\rangle$ is never an eigenstate of $J_x$. Hence, for $j > 0$, we can never be certain of the outcome of measurements of both $J_x$ and $J_z$. This argument applies equally to $J_y$, so it's impossible to be certain of the outcome of measurements of more than one component of $\mathbf{J}$. If $j = 0$, every component of $\mathbf{J}$ yields zero, but a null vector in $\mathbb{R}^3$ has no direction. Consequently, there are no states in which the vector $\mathbf{J}$ has a well-defined direction. This situation contrasts with the momentum vector $\mathbf{P}$ which can have a well–defined direction since all its components commute with one another.

In the mathematical literature, states with $m = j$ are known as *highest weight* states. They play a key role in the representation theory of any group $G$, because once we know the highest weight state the rest of the multiplet can be constructed by applying lowering operators such as $J_-$. Physically, a highest weight state is one in which the body's angular momentum is most nearly aligned along the $z$-axis. In this state, the ratio of the squared angular momentum that lies in the $xy$-plane to that parallel to the $z$-axis is

$$\frac{\langle j,j|J_x^2 + J_y^2|j,j\rangle}{\langle j,j|J_z^2|j,j\rangle} = \frac{\langle j,j|\mathbf{J}^2 - J_z^2|j,j\rangle}{\hbar^2 j^2} = \frac{1}{j} . \tag{5.17}$$

As $J_x = (J_+ + J_-)/2$ we have $\langle j,j|J_x|j,j\rangle = 0$ and similarly $\langle j,j|J_y|j,j\rangle = 0$. Thus we have no information about the direction in the $xy$-plane any angular momentum points.

Macroscopic bodies, for which $j \gg 1$, have only a tiny fraction of their total angular momentum in the $xy$-plane when they're in state $|j,j\rangle$, so the uncertain direction of this component of angular momentum does not lead to significant uncertainty in the total direction of the angular momentum vector. By contrast, when $j = 1/2$, even in state $|1/2,1/2\rangle$ there's twice as much angular momentum associated with the $xy$-plane as with the $z$-axis and the uncertain direction of this planar component makes it impossible to say anything more specific than that the angular momentum vector lies somewhere in the northern, rather than southern, hemisphere. Even when $j = 1$ and $m = 1$, the state $|1,1\rangle$ has as much angular momentum along the $xy$-plane as it has parallel to the $z$-axis, so the direction of the angular momentum vector is still very uncertain. This is no surprise: since $\dim(\mathcal{H}_j) = 2j + 1$, when $j = \frac{1}{2}$ there are only two independent states the orientation of our body can take. With such a limited Hilbert space it's no wonder we only have a fuzzy notion of where the body's angular momentum lies.

### 5.2.1 Rotation of Diatomic Molecules

Our deduction of the possible eigenvalues and eigenstates of $\mathbf{J}^2$ and $\mathbf{J}_z$ came from considering rotations: the states $|j,m\rangle$ simply enable us to describe what happens when an object is rotated around some axis, as we'll understand in more detail and with many examples later in the chapter. In particular, it's important to understand that *a priori* these states have nothing to do with the energy levels of any given particle. As always, there's no way to tell how rotating an object may or may not change its energy until we specify a form for the Hamiltonian. In this section, we'll choose a simple form of dynamical relation $H = H(\mathbf{J})$ that will enable us to understand an important part of the dynamics of a diatomic molecule.

For some purposes, a diatomic molecule such as CO molecule can be considered to consist of two point masses, the nuclei of the oxygen and carbon atoms, joined by a 'light rod' provided by the electrons. Following the analogous formula in classical mechanics, we model the dynamics of this molecule by the Hamiltonian

$$H = \frac{1}{2}\left(\frac{J_x^2}{I_x} + \frac{J_y^2}{I_y} + \frac{J_z^2}{I_z}\right) . \tag{5.18}$$

where $I_x$ is the moment of inertia along the $x$-axis, and similarly for $I_y$ and $I_z$. Though motivated by classical mechanics, the best justification for this form of Hamiltonian is ultimately that it agrees with detailed experiments.

In our axisymmetric case, we choose coordinates whose origin is at the centre of mass of the molecule (somewhere between the C and O atoms) and orient our coordinates so that the $z$-axis lies along the molecule's axis of symmetry. Then $I_x = I_y = I$, say, whilst $I_z$ is different. In fact, since the centre of mass of the C and O atoms lie along the $z$-axis, the molecule's moment of inertia around this axis is negligible, $I_z \ll I$ (see figure 8). We can thus rewrite our Hamiltonian as

$$H = \frac{1}{2}\left[\frac{\mathbf{J}^2}{I} + J_z^2\left(\frac{1}{I_z} - \frac{1}{I}\right)\right] . \tag{5.19}$$

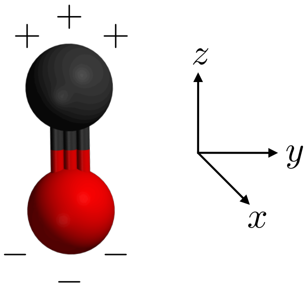

**Figure 8**: *A simple model of carbon monoxide. By symmetry,* $I_x = I_y$ *whilst* $I_z$ *is much smaller.*

The virtue of expressing $H$ in terms of $\mathbf{J}^2$ and $J_z$ is that our knowledge of the spectrum of these operators immediately allows us to write down the spectrum of this Hamiltonian: the state $|j, m\rangle$ is an energy eigenstate with

$$E_{jm} = \frac{\hbar^2}{2}\left[\frac{j(j+1)}{I} + m^2\left(\frac{1}{I_z} - \frac{1}{I}\right)\right], \tag{5.20}$$

with $|m| \leq j$. Since $I_z \ll I$ for our diatomic molecule, the coefficient of $m^2$ is very much greater than that of $j(j+1)$, so states with $m \neq 0$ will only occur very far above the ground state. Consequently, the low lying states have energies of the form

$$E_j = j(j+1)\frac{\hbar^2}{2I} \tag{5.21}$$

for some $j$. As we saw in the previous section, only discrete values of $j$ are allowed, so the energy levels are quantized. One can excite a CO molecule, causing it to rotate faster, only by supplying a definite amount of energy. Similarly, for the molecule to relax down to a state of lower angular momentum, it must emit a quantized lump of energy.

Carbon monoxide is a significantly dipolar molecule. The carbon atom has a smaller share of the binding electrons that does the oxygen, with the result that it is positively charged while the oxygen atom gains negative charge. In Maxwell's theory of electrodynamics, a rotating electric dipole is expected to emit electromagnetic radiation. Because we're in the quantum regime, this radiation emerges as photons which, as we'll see later in the chapter, can add or carry away only one unit $\hbar$ of angular momentum. Thus the energies of the photons that can be emitted or absorbed by a rotating dipolar molecule are

$$E_\gamma = \pm(E_j - E_{j-1}) = \pm\frac{j\hbar^2}{I}\,. \tag{5.22}$$

Using the relation $E = \hbar\omega$, the angular frequencies in the rotation spectrum of the molecule are

$$\omega_j = \frac{j\hbar}{I} \tag{5.23}$$

In the case of $^{12}$CO, $2\pi\hbar/I$ evaluates to a frequency $\nu \sim 113.1724$ GHz and spectral lines occur at multiples of this frequency. In the classical limit of large $j$, the molecule's total angular momentum $|\mathbf{J}| \approx j\hbar$. This is related to the angular frequency $\Omega$ at which the molecule rotates by $|\mathbf{J}| = I\Omega$. Comparing to (5.23) we see that in the classical limit $\omega_{j\gg 1} = \Omega$, so the frequency of the emitted radiation is just the frequency at which the molecule rotates.

Measurements of the radiation at 113.1724 GHz provide one of the two most important probes of interstellar gas[48]. In denser, cooler regions, hydrogen atoms combine to form $H_2$ molecules which are bisymmetric and do not have an electric dipole moment when they rotate. Consequently, these molecules, which together with similarly uncommunicative Helium make up the vast majority of cold interstellar gas, lack readily observable spectral lines. Astronomers are thus obliged to study the interstellar medium through the rotation spectrum of the few parts in $10^6$ of CO it contains.

### 5.3 Spin

In section 5.3 we saw that the orbital angular momentum operator $\mathbf{L}$ and spin operator $\mathbf{S}$ each obeyed an identical algebra to that of the rotation generators,

$$\begin{aligned} [L_i, L_j] &= \mathrm{i}\hbar \sum_k \epsilon_{ijk} L_k \qquad & [L_i, \mathbf{L}^2] &= 0 \\ [S_i, S_j] &= \mathrm{i}\hbar \sum_k \epsilon_{ijk} S_k \qquad & [S_i, \mathbf{S}^2] &= 0 \end{aligned} \tag{5.24}$$

as well as $[S_i, L_j] = 0$. Since the algebra of the $\mathbf{J}$s was all we used to deduce their spectra, it follows immediately that $(\mathbf{L}^2, L_z)$ and $(\mathbf{S}^2, S_z)$ have the same possible spectra as we found for $(\mathbf{J}^2, J_z)$. It's traditional to label eigenstates of $(\mathbf{L}^2, L_z)$ as $|\ell, m\rangle$ and those of $(\mathbf{S}^2, S_z)$ as $|s, \sigma\rangle$, where $\ell$ and $s$ correspond to the eigenvalues of $\mathbf{L}^2$ and $\mathbf{S}^2$, respectively, and $m$ and $\sigma$ label the eigenvalues of $L_z$ and $S_z$. (Unfortunately, it's traditional to label the eigenvalue of both $J_z$ and $L_z$ by the same letter $m$, even though they mean different things and may take different values in any given state. Which is meant is usually clear from the context.)

#### 5.3.1 Large Rotations

Our claim that the possible values of $(j, m)$ are

$$j \in \{0, 1/2, 1, 3/2, \ldots\} \qquad \text{and then} \qquad m \in \{-j, -j+1, \ldots, j-1, j\} \tag{5.25}$$

was based on examining the algebra $[J_i, J_j] = \mathrm{i}\hbar \sum_k \epsilon_{ijk} J_k$, and likewise for $(\ell, m_\ell)$ or $(s, \sigma)$. In turn, this algebra originally came from considering the behaviour of objects under very small rotations. We now check whether these spectra are also compatible with large rotations.

Suppose we rotate the state $|j, m\rangle$ through an amount $\alpha$ around the $z$-axis. Then

$$|j, m\rangle \ \rightarrow \ U(\alpha\hat{\mathbf{z}})|j, m\rangle = \mathrm{e}^{-\mathrm{i}\alpha J_z/\hbar}|j, m\rangle = \mathrm{e}^{-\mathrm{i}m\alpha}|j, m\rangle \,. \tag{5.26}$$

since it is an eigenstate of $J_z$. Rotations through $2\pi$ around any axis return us to our starting point, so are equivalent to no rotation. Thus, for $U(\boldsymbol{\alpha})$ to be a homomorphism

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[48] The other key probe is the hyperfine line of atomic hydrogen that will be discussed in chapter 8.

from $SO(3)$ to the group of unitary operators on $\mathcal{H}$, we must have $U(2\pi\hat{\boldsymbol{\alpha}}) = 1_{\mathcal{H}}$. In particular, when $\hat{\boldsymbol{\alpha}} = \hat{\mathbf{k}}$, from above we must have $\mathrm{e}^{-2\pi\mathrm{i}m} = 1$. This is true if $m$ is an integer, but not if it is an odd-half-integer. Since $m$ is an integer or (odd) half-integer iff $j$ is, we conclude that odd half-integer values of $j$ are in fact not compatible with the behaviour of objects under large rotations: they're ruled out by our basic requirement that $U(\boldsymbol{\alpha})$ represents the action of $SO(3)$ on $\mathcal{H}$.

The fact that global properties of rotations rule out some of the eigenvalues allowed by the rotation algebra is an example of a phenomenon familiar from IB Methods. The behaviour of function in the neighbourhood of a point may be governed by some differential equation. The associated differential operator (if it's linear) typically has a large spectrum, which is cut down by boundary conditions or periodicity conditions. For example, on any open set $U \subset \mathbb{R}$ the linear operator $-\mathrm{i}d/dx$ has eigenfunctions $\mathrm{e}^{\mathrm{i}kx}$ for any $k \in \mathbb{C}$. However, if we know that globally $\psi : S^1 \to \mathbb{C}$ so is periodic, then $k$ must be quantized in units of the circle's radius. The only difference in our case is that the non-trivial algebra of the rotation generators already restricted the possible eigenvalues of $\mathbf{J}^2$ and $J_z$ to be quantized in units of $\hbar$. Global properties of the rotation group still remove some of the eigenvalues that were allowed locally. More succinctly, states where $j \in \mathbb{N}_0 + \frac{1}{2}$ do form representations of the rotation algebra $\mathfrak{so}(3)$, but not of the rotation group $SO(3)$.

In fact, we'll see that our arguments above have been rather too hasty.

### 5.3.2 The Stern–Gerlach Experiment

Quantization of angular momentum in units of $\hbar$ was originally proposed by Bohr & Sommerfeld as a means by which the stability of atomic orbits could be understood; we've now seen how this quantization arises automatically in the full mathematical framework of quantum mechanics. However, back in 1922 it still seemed very mysterious, so Stern and Gerlach designed and conducted experiments to check whether angular momentum is really quantized in Nature.

In the Stern–Gerlach experiments, a beam of uncharged atoms of the same type is passed through a region of slowly varying magnetic field. If the atoms have mass $M$, the Hamiltonian for this process is[49]

$$H = \frac{\mathbf{P}^2}{2M} - \boldsymbol{\mu} \cdot \mathbf{B} \tag{5.27}$$

where $\mathbf{B}$ is the applied magnetic field, and $\boldsymbol{\mu}$ is known as the *magnetic dipole moment* of the atom. Ultimately, the reason the atom can be treated as a magnetic dipole is because of detailed properties of the distribution of its electrons. It would take us too far afield to explain this precisely, but the dipole moment arises because the atom has an orientation: a perfectly spherically symmetric atom cannot have any dipole moment as there is no preferred direction for the 'north' or 'south' poles. Thus the dipole moment is

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[49] The potential energy resulting from coupling a magnetic dipole to an applied magnetic field is similar to the (perhaps more familiar) energy $-\mathbf{p} \cdot \mathbf{E}$ of an electric dipole $\mathbf{p}$ in an applied electric field $\mathbf{E}$. Note that the atoms carry no net electric charge, so there's no Lorentz force.

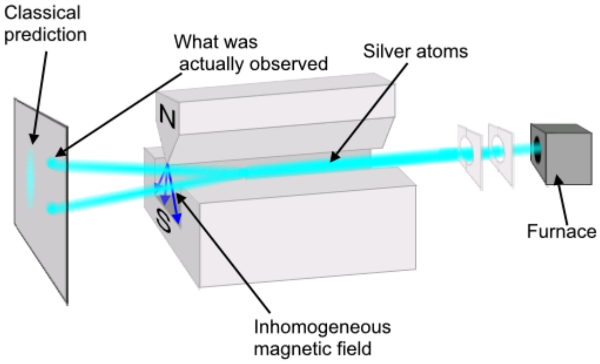

**Figure 9**: *A schematic picture of the Stern–Gerlach experiment, borrowed from the Astronomy Cast site.*

only non-zero for atoms that transform non-trivially under $\mathbf{S}$. If the atom is in the spin $s$ representation, we can write $\boldsymbol{\mu} = (\mu/\hbar s)\,\mathbf{S}$.

Choosing our coordinates so that the $z$-axis points along the direction of the magnetic field, the Hamiltonian becomes

$$H = \frac{\mathbf{P}^2}{2M} - \frac{\mu}{\hbar s} B S_z\,, \tag{5.28}$$

where $B = |\mathbf{B}|$. The equations of motion (obtained, say, using the Heisenberg picture) tell us that the expectation values of position and momentum in any state $|\psi\rangle$ obey

$$\frac{d}{dt}\langle\mathbf{X}\rangle = \frac{\langle\mathbf{P}\rangle}{M} \qquad \text{and} \qquad \frac{d}{dt}\langle\mathbf{P}\rangle = \frac{\mu}{\hbar s}\langle(\boldsymbol{\nabla} B)\, S_z\rangle\,. \tag{5.29}$$

The second of these equations is analogous to the classical $\mathbf{F} = -\boldsymbol{\nabla} V$.

We see that the force experienced by any given atom depends on its value of $S_z$. For a spin $s$ particle, these are $\hbar\{-s, -s+1, \ldots, s-1, s\}$ and in particular can be of either sign. If an atom is in the state $|s, s\rangle$ with all its spin aligned along the direction of $\mathbf{B}$, then it will experience a force pushing it in the direction of increasing magnetic field. On the other hand, those atoms in the state $|s, -s\rangle$ will be pushed in the direction of decreasing $B$, while atoms with $\sigma = 0$ (when $s$ is an integer) are unaffected. In total, when an initial beam of atoms in which the spins are randomly aligned passes through the region of magnetic field, it will be split into $2s+1$ different trajectories. Thus, if the atoms are perfectly spherical, they will pass through unaffected, whereas if they have $s = 1$ the beam will be split into three, corresponding to the three possible eigenvalues $\{\hbar, 0, \hbar\}$, if they have $s = 2$ the beam will split into five, and so on. Finally, if the atoms have very large spin (and so a very definite orientation in space) the beam will be split into so many paths that we can no longer distinguish the individual paths, seeing instead a broad smear. This is the same result we'd expect to find if angular momentum is not quantised, where the amount by which an atom is deflected would depend smoothly on its orientation with respect to $\mathbf{B}$.

Stern and Gerlach's original experiment in fact used silver atoms. Their magnetic was controlled by a dial. Initially, as $\mathbf{B} = 0$ the atoms all passed straight through. As they turned up the magnetic field, the beam split – into *two* separate paths. As $B$ was further increased, the separation between these two beams increased, but no further splitting was observed. Thus, not only is angular momentum quantized as Bohr & Sommerfeld had predicted, but silver atoms have spin $s = \frac{1}{2}$!

### 5.3.3 Spinors and Projective Representations

*This section lies beyond the Schedules and is non-examinable.*

The Stern–Gerlach experiment shows that, despite our arguments, half–integer values of $s$ actually arise in Nature. In fact, the chemical properties of the elements and the structure of the periodic table, together with properties of materials such as metals, conductors and insulators depends crucially on particles having half-integer values of spin. These values are in conflict with our current mathematical formalism, so we must have made a mistake, imposing too strong a condition that ruled out the possibility of half-integer spins.

The error lay in our claim that we needed to represent the action a transformation group $G$ on Hilbert space $\mathcal{H}$, rather than just on projective Hilbert space $\mathbb{P}\mathcal{H}$. (Recall that states which differ only by an overall constant – which does not need to have modulus 1 provided we use the general form (2.69) of the Born rule – yield the same results in all experiments. Thus physical systems are represented by states in *projective* Hilbert space.) Projectively, it's enough to require

$$U(g_2) \circ U(g_1) = \mathrm{e}^{\mathrm{i}\phi(g_2,g_1)}\, U(g_2 \cdot g_1) \tag{5.30}$$

rather than (4.7), where $\phi(g_1, g_2)$ is a real phase. This phase does not affect which *ray* in $\mathcal{H}$ the state lies in, so leaves the physics unchanged. The operator algebra is associative, so we must have

$$U(g_3) \circ (U(g_2) \circ U(g_1)) = (U(g_3) \circ U(g_2)) \circ U(g_1) \tag{5.31}$$

which implies the phases obey

$$\phi(g_2, g_1) + \phi(g_3, g_2 \cdot g_1) = \phi(g_3, g_2) + \phi(g_3 \cdot g_2, g_1)\,. \tag{5.32}$$

Phase factors $\mathrm{e}^{\mathrm{i}\phi(g_2,g_1)}$ obeying this condition are known as *cocycles* on the group $G$. One possible solution of (5.32) is to take

$$\phi(g_2, g_1) = \beta(g_2 \cdot g_1) - \beta(g_2) - \beta(g_1)\,. \tag{5.33}$$

for some arbitrary (smooth) function $\beta : G \to \mathbb{R}$. This solution is 'trivial', because if $\phi(g_2, g_1)$ takes this form, then can define a new unitary transformation operator $U'(g) = \mathrm{e}^{\mathrm{i}\beta(g)}U(g)$ which obeys our original condition (4.7). By agreeing to work with the new operator, the phases never arise. The interesting question is whether there are other, non-trivial solutions to (5.32).

A theorem in group cohomology[50] states that it's possible for non-trivial projective representations to arise for groups that are not simply connected[51]. In fact, this is the case for SO(3). The topology of the rotation group can be seen by viewing each rotation as parametrised by a vector $\boldsymbol{\alpha}$. If we allow the axis of rotation $\hat{\boldsymbol{\alpha}}$ to point in any direction, then rotations with $|\alpha| \in (0, \pi)$ are uniquely specified. However, when rotating through $\pi$ we get the same rotation whether rotating around $\hat{\boldsymbol{\alpha}}$ or $-\hat{\boldsymbol{\alpha}}$. Thus, we can picture the space of all rotations as a solid, three dimensional ball $|\boldsymbol{\alpha}| \leq \pi$, but with antipodal points on the surface $|\boldsymbol{\alpha}| = \pi$ identified.

This description show that SO(3) contains smooth, closed paths, beginning and ending at the identity rotation (the origin of the 3-ball) that cannot be continuously shrunk to a point. For example, consider paths which start and end at the identity rotation, *i.e.* the centre of the sphere. Figure **??** shows a loop which is contractible; it can obviously be shrunk to a point. On the other hand, figure **??** shows a loop for which the angle of rotation starts at zero, smoothly increasing to $\pi$ at the point $A$. At this point it reaches the boundary and reappears at the antipodal point $A'$, before continuing to increase to $2\pi$ back at the identity. It should be intuitively clear that this loop cannot be shrunk to a point whilst keeping both its ends fixed at the identity.

Next, consider the loop in figure **??**, along which the angle of rotation increases from 0 to $4\pi$, reaching the boundary of the ball twice, once at $A$, reappearing at $A'$ and then again at $B$ reappearing at $B'$. By moving the second antipodal pair $B$ and $B'$ (as shown in figure **??**) the section of the path between $A'$ and $B$ can be pulled across the boundary, smoothly deforming the loop back to the situation in figure **??**. Thus, after *two* complete rotations the situation becomes simple once more. In general, the angle along any closed path must increase by an integer multiple of $2\pi$. The resulting loop will be contractible if this integer is even, but non-contractible if it is odd.

The topological properties of paths in $G$ become important when we consider the behaviour of $U(g)$ as the group element $g$ varies around a loop $L$, beginning and ending at some fixed $g_0$. It is quite possible for $U(g)$ to change smoothly with $g$ along $L$ in such a way that the operators at each end of the loop do not coincide: they may differ by a phase

$$U(g_0) \xrightarrow{L} \alpha_L U(g_0)$$

where the phase $\alpha_L$ depends on the loop. This is consistent with the projective homomorphism (5.30).

To investigate the possibilities for $\alpha_L$, let's specialize to the case in which the operators act on a Hilbert space of finite dimension $N$, so that each $U(g)$ can be regarded as an $N \times N$ unitary matrix. We can use up some of the freedom in (5.30) by requiring that each such matrix has unit determinant. This does not fix things completely, but the residual freedom

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[50] Unfortunately, I won't prove this here. If you're interested, you can find a proof (given in the context of quantum mechanics) in either Weinberg's *The Quantum Theory of Fields*, vol. 1 (chapter 2, appendix B), or else in Hall's *Quantum Theory for Mathematicians.*

[51] There's one other possibility: that the Lie algebra $\mathfrak{g}$ contains *central elements* (vectors $e \in \mathfrak{g}$ s.t. $[e, \mathfrak{g}] = 0$) that cannot be removed by a redefinition of the generators. This case is not relevant for us.

is discrete:

$$\det U(g) = +1 \ \text{ for all } g \in G \qquad \Rightarrow \qquad \mathrm{e}^{\mathrm{i}N\phi(g_1,g_2)} = 1$$

If $G$ is simply connected, meaning that any closed loop is contractible, then the determinant condition implies $\alpha_L = 1$ for all loops $L$. This follows straightforwardly using continuity: $\alpha_L$ must be an $N^{\text{th}}$ root of unity, but if it varies continuously as we vary our loop $L$ and if all such loops are contractible to the single point $g_0$, then we must have the same matrix at the beginning and ending of each loop, so $\alpha_L = 1$.

If $G$ is not simply connected, the same argument still shows that $\alpha_L = 1$ for any contractible $L$, but there may also be non-contractible loops with $\alpha_L \neq 1$. In this case, we can at least deduce that $\alpha_L = \alpha_{L'}$ whenever the loops $L$ and $L'$ are in the same homology class, meaning that they can be smoothly deformed into one another. Furthermore, if loops $L$ and $L'$ are traversed successively, then $U(g_0) \xrightarrow{L} \alpha_L U(g_0) \xrightarrow{L'} \alpha_L \alpha_{L'} U(g_0)$, so there are self-consistency constraints.

We can now give a unique definition of $U(g)$ for all $g$ in a *simply connected* Lie group $G$. Recalling that $U(e) = \mathrm{id}_{\mathcal{H}}$, we define $U(g_0)$ by choosing any path from the identity $e$ to $g_0$ and demanding that $U(g)$ changes smoothly along this path. The values along the path are unique by the determinant and continuity conditions, but the end result $U(g_0)$ is also unique, because by traversing them in opposite directions, any two paths $e \to g_0$ can be combined to form a closed loop at $g_0$. This loop is contractible since our group is simply connected. With this definition, continuity also ensures that all cocylces are equal to one, so we have a genuine representation (not just a projective representation) of $G$.

Carrying out the same construction when $G$ is not simply connected, we'll encounter paths from $e$ to $g_0$ which cannot be smoothly deformed into one another. Thus, starting from $U(e) = \mathrm{id}_{\mathcal{H}}$, in general we obtain different values for $U(g_0)$ depending on the path we take. In this way we're forced to consider multi-valued functions on $G$ (just as when defining a continuous square root in the complex plane). The ambiguity, or multi-valuedness, in $U(g_0)$ can be resolved only by keeping track of the path we used to reach $g_0$, just as for the complex square root we must keep track of how many times we've encircled the origin to be sure which branch we're on. Such a multi-valued definition inevitably means that non-trivial cocyles appear.

As we saw above, the rotation group $G = \mathrm{SO}(3)$ is not simply connected, but there rae just two topological classes of loops, depending on whether the net angle of rotation is an even or odd multiple of $2\pi$. Any loop $l$ in the first class is contractible and so has $\alpha_L = 1$. Any loop $L'$ in the second class is non-contractible, but if we traverse $L'$ twice it becomes contractible again. Thus $\alpha_{L'}^2 = 1$ and $\alpha_{L'} = \pm 1$. The finite-dimensional spaces $\mathcal{H}_j$ on which the rotation operators act are nothing but the multiplets of total angular momentum $j(j+1)\hbar^2$, with a basis $\{|j,m\rangle\}$ where

$$m \in \{-j, -j+1, \ldots, j-1, j\}$$

Thus $\dim \mathcal{H}_j = 2j+1$. From the determinant condition $(\alpha_L)^{2j+1} = 1$ for any loop, but from our topological considerations $\alpha_L = \pm 1$. If $j$ is an integer then $2j+1$ is odd and it follows that $\alpha_L = 1$ for all loops, contractible or not. However, if $j$ is an odd half-integer then $2j+1$ is even and $\alpha_L = -1$ is possible for non-contractible loops. This is exactly the behaviour we found above: under the rotation operator $U(\alpha\hat{\mathbf{z}}) = \mathrm{e}^{-\mathrm{i}\alpha J_z/\hbar}$, a generic state in the $j$ multiplet transforms as

$$|\psi\rangle = \sum_{m=-j}^{j} c_m|j,m\rangle \qquad \mapsto \qquad U(\boldsymbol{\alpha})|\psi\rangle = \sum_{m=-j}^{j} c_m\,\mathrm{e}^{-\mathrm{i}\alpha m}|j,m\rangle\,. \tag{5.34}$$

Any state with $j$ (and hence all $m$) odd-half-integral changes sign under a rotation through an odd multiple of $2\pi$. The discussion of this section shows that the origin of this unexpected sign is the non-trivial topology of the rotation group – in our new terminology, we have a projective representation of SO(3). These projective representations play an important role in physics, and are often called *spinors*.

We have, finally, obtained the correct mathematical framework in which to describe rotations and angular momentum in quantum mechanics. The history of the subject developed rather differently to the exposition we've given here. By the 1920s, careful studies of atomic spectroscopy had revealed that many spectral lines were in fact doubled, composed of two lines, very close in frequency. In 1924 (even before Schrödinger published his famous equation) Pauli proposed that this doubling indicated that, in addition to the quantum numbers $n, \ell, m$ labelling their energy levels, electrons possessed a further quantum number that took just two values. A year later, Uhlenbeck & Goudsmit suggested that this could be associated to some form of internal angular momentum. Their idea was initially treated with suspicion. If one wished to suppose the electron was a small, rotating sphere, then for it to have the needed angular momentum $\hbar/2$ and yet keep its radius small enough so that its finite size would not have been detected by experiment[52], the surface of the sphere would need to be travelling faster than light.

Nevertheless, the Stern–Gerlach experiment showed that particles could indeed have spin, contributing to the Hamiltonian in the presence of a magnetic field in just the same way as would a classical spinning magnetic dipole. Heisenberg, Jordan and C. G. Darwin[53] then showed that the internal spin of the electron exactly accounted for the fine splitting of spectral lines that had puzzled Pauli, as we'll see in chapter 8.1.1.

We now understand that spin is an *intrinsic* property of fundamental particles: the Hilbert space of a fundamental particle is not simply $\mathcal{H}_{\mathrm{spat}} \cong L^2(\mathbb{R}^3, d^3x)$ describing its spatial wavefunction, but rather a tensor product $\mathcal{H}_{\mathrm{spat}} \otimes \mathcal{H}_s$. However we may excite, crash into, or generally interfere with the motion of an electron or W boson, for as long as they remain electrons and W bosons, their spin will always be $s = \frac{1}{2}$ and $s = 1$, respectively.

### 5.3.4 Spin Matrices

Since $\sigma \in \{-s, -s+1, \ldots, s-1, s\}$, states of definite total spin $s$ can be described by a finite dimensional Hilbert space $\mathcal{H}_s \cong \mathbb{C}^{2s+1}$. As always, once we pick a basis on $\mathcal{H}$ we can

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[52] To date, no experiment has ever detected a finite size, or any other non-trivial internal *spatial* structure in the electron.

[53] Charles Galton Darwin, grandson of Charles Robert Darwin.

describe the action of linear operators such as $\mathbf{S}$ explicitly in terms of matrices. Let's now carry this out the first few spin representations, working in the basis $\{|s,\sigma\rangle\}$ of eigenstates of $S_z$.

The simplest case is $s=0$, for which the only possible value of $\sigma$ is also zero. This state obeys $\mathrm{e}^{-\mathrm{i}\boldsymbol{\alpha}\cdot\mathbf{S}/\hbar}|0,0\rangle = |0,0\rangle$ for any $\boldsymbol{\alpha}$. Hence a spin-zero object, like a perfect sphere, is completely unchanged under any rotation. In view of this, spin-zero particles are known as *scalar* particles. The discovery of the Higgs boson, announced on 4th July 2012 at CERN in Geneva, was the first time a fundamental scalar particle had been observed in Nature.

The next case is $s=\frac{1}{2}$. Electrons, neutrinos and quarks are fundamental particles of spin $\frac{1}{2}$, whilst protons, neutrons and the silver atoms used by Stern & Gerlach are examples of composite spin-half particles. When $s=\frac{1}{2}$, $\sigma$ can only take one of the two values $\pm\frac{1}{2}$. For shorthand, we let $|\uparrow\rangle$ denote the state $|s,\sigma\rangle = |\frac{1}{2},\frac{1}{2}\rangle$ and $|\downarrow\rangle$ denote $|\frac{1}{2},-\frac{1}{2}\rangle$. A generic state of a spin-half system can thus be expanded as

$$|\psi\rangle = a|\uparrow\rangle + b|\downarrow\rangle \tag{5.35}$$

in this basis, where $a,b\in\mathbb{C}$ and $|a|^2+|b|^2=1$ so that $|\psi\rangle$ is correctly normalised.

In this basis, we can write the spin operators themselves as the $2\times 2$ matrices

$$\begin{gathered} S_x = \begin{pmatrix} \langle\uparrow|S_x|\uparrow\rangle & \langle\uparrow|S_x|\downarrow\rangle \\ \langle\downarrow|S_x|\uparrow\rangle & \langle\downarrow|S_x|\downarrow\rangle \end{pmatrix}, \qquad S_y = \begin{pmatrix} \langle\uparrow|S_y|\uparrow\rangle & \langle\uparrow|S_y|\downarrow\rangle \\ \langle\downarrow|S_y|\uparrow\rangle & \langle\downarrow|S_y|\downarrow\rangle \end{pmatrix}, \\ S_z = \begin{pmatrix} \langle\uparrow|S_z|\uparrow\rangle & \langle\uparrow|S_z|\downarrow\rangle \\ \langle\downarrow|S_z|\uparrow\rangle & \langle\downarrow|S_z|\downarrow\rangle \end{pmatrix}. \end{gathered} \tag{5.36}$$

Because $|\uparrow\rangle$ and $|\downarrow\rangle$ are eigenstates of $S_z$, evaluating $S_z$ in this basis is immediate. To also evaluate $S_x$ and $S_y$, we note that $S_x=(S_++S_-)/2$ and $S_y=(S_+-S_-)/2\mathrm{i}$ where $S_\pm$ are the spin raising and lowering operators defined just as for $J_\pm$. Using (5.16) with $j=s=\frac{1}{2}$ gives $S_+|\downarrow\rangle=\hbar|\uparrow\rangle$ and $S_-|\uparrow\rangle=\hbar|\downarrow\rangle$. In this way, we obtain

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \qquad S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{5.37}$$

The coefficients of $\hbar/2$ here are known as *Pauli matrices* and usually written[54] as $(\sigma_x,\sigma_y,\sigma_z)$. Thus, for $s=1/2$, we can write $\mathbf{S}=\hbar/2\,\boldsymbol{\sigma}$.

Proceeding to spin-one, we find three possible values $\sigma\in\{-1,0,1\}$. Thus the spin-one Hilbert space is three (complex) dimensional, and when $s=1$ we can represent each component of $\mathbf{S}$ by a $3\times 3$ matrix. In this case, the spin raising and lowering operators $S_\pm$ act as

$$\begin{aligned} S_+|-1\rangle &= \sqrt{2}\hbar\,|0\rangle, \qquad & S_+|0\rangle &= \sqrt{2}\hbar\,|+1\rangle, \\ S_-|+1\rangle &= \sqrt{2}\hbar\,|0\rangle, \qquad & S_-|0\rangle &= \sqrt{2}\hbar\,|-1\rangle, \end{aligned} \tag{5.38}$$

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[54] Do note confuse this vector of Pauli matrices with the eigenvalue label of $S_z$.

as follows from (5.16) with $j = s = 1$. Using these results, one can check that

$$S_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad S_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{pmatrix}, \qquad S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{5.39}$$

Sadly, these matrices don't have any special name. Just as for spin-half, we can use this representation to express the state $|1, \theta\rangle$ in which a measurement of $\mathbf{n} \cdot \mathbf{S}$ along some axis $\mathbf{n}$ is certain to yield $+\hbar$. Examples of fundamental particles with spin-one are the somewhat unimaginatively named W and Z bosons[55]. These are responsible for the weak interactions that, among other things, allows two Hydrogen nuclei to fuse into Deuterium, powering nuclear fusion in the core of stars.

In just the same way, we can represent each component of the spin operator by a $(2s+1) \times (2s+1)$ matrix for any finite $s$. Since our basis is adapted to $S_z$, the matrix representation of $S_z$ will be

$$S_z = \hbar\,\mathrm{diag}(s, s-1, \ldots, -s+1, -s)\,. \tag{5.40}$$

Matrices for $S_x$ and $S_y$ may be constructed using the spin raising and lowering operators as above. Since $S_\pm$ only change the $z$-component of the spin by 1 unit, these matrices are very sparse. One finds that they have non-zero entries only along the subleading diagonals, given by

$$\begin{aligned} (S_x)_{\sigma'\sigma} &= \frac{\hbar}{2}\left[\alpha(\sigma)\,\delta_{\sigma'-1,\sigma} + \alpha(\sigma-1)\,\delta_{\sigma'+1,\sigma}\right] \\ (S_y)_{\sigma'\sigma} &= \frac{\hbar}{2\mathrm{i}}\left[-\alpha(\sigma)\,\delta_{\sigma'-1,\sigma} + \alpha(\sigma-1)\,\delta_{\sigma'+1,\sigma}\right]\,, \end{aligned} \tag{5.41}$$

where $\alpha(\sigma) = \sqrt{(s-\sigma)(s+\sigma+1)}$. Note that, whatever the value of $s$, we always have three matrices $(S_x, S_y, S_z)$ describing reorientations around the three independent axes in $\mathbb{R}^3$. Note also that each of these matrices is indeed traceless, as required by $\mathrm{i}\hbar\,\epsilon_{ijk}\mathrm{tr}_{\mathcal{H}}(S_k) = \mathrm{tr}_{\mathcal{H}}([S_i, S_j]) = 0$ as we said at the beginning of the chapter.

In elementary particle physics (and also in Tripos questions), one rarely encounters spins higher than 1. Nonetheless, it's interesting to consider the limit $s \gg 1$ of very high spins to see how our classical intuition emerges. For example, and electric motor that is roughly 1 cm in diameter and weighs about 10 gm might spin at $\sim 100$ revolutions per second. Its intrinsic angular momentum is then $\sim 10^3\,\mathrm{kg\,m^2\,s^{-1}} \approx 10^{31}\hbar$. The classical world thus involves *huge* values of $s$!

Let's now show that, when $s \gg 1$, there is very little uncertainty in the direction of a systems spin. Suppose our system is in the state $|s, s\rangle$ so that its spin is maximally aligned with the $z$-axis. Let's compute $\langle s, s|\mathbf{n} \cdot \mathbf{S}|s, s\rangle$ where $\mathbf{n} = (\sin\theta, 0, \cos\theta)$. That is, we want to know how much spin we expect to measure along the direction in the $xz$-plane, inclined

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[55] Although the photon carries one unit of $\hbar$ in intrinsic angular momentum, it has only two possible states corresponding to left- or right-circular polarized light. Because the photon is massless, one needs to consider representations of the Lorentz group, rather than the spatial rotation group, in order to describe it accurately. We won't do this in this course.

at angle $\theta$ to the $z$-axis. Classically, this would be just $\hbar s\,\cos\theta$, the projection of $s$ onto this axis. Quantum mechanically, we have

$$\langle s,s|\mathbf{n}\cdot\mathbf{S}|s,s\rangle = \sin\theta\,\langle s,s|S_x|s,s\rangle + \cos\theta\,\langle s,s|S_z|s,s\rangle = \hbar s\,\cos\theta\,, \tag{5.42}$$

using the fact that $S_x = (S_+ + S_-)/2$. Thus, on average the quantum result agrees with the classical intuition. This holds for any value of $s$, but now let's ask what the uncertainty in this result is. We compute

$$\begin{aligned}\langle s,s|(\mathbf{n}\cdot\mathbf{S})^2|s,s\rangle &= \sin^2\theta\,\langle s,s|S_x^2|s,s\rangle + \sin\theta\,\cos\theta\,\langle s,s|S_xS_z + S_zS_x|s,s\rangle + \cos^2\theta\,\langle s,s|S_z^2|s,s\rangle\\ &= \frac{1}{4}\sin^2\theta\langle s,s|S_+S_-|s,s\rangle + \hbar^2 s^2\cos^2\theta\\ &= \hbar^2\left(\frac{s}{2}\sin^2\theta + s^2\cos\theta\right)\,,\end{aligned} \tag{5.43}$$

with all other terms vanishing. Consequently

$$\sqrt{\langle(\mathbf{n}\cdot\mathbf{S})^2\rangle - \langle\mathbf{n}\cdot\mathbf{S}\rangle^2} = \sqrt{\frac{s}{2}}\,\hbar\,|\sin\theta| \tag{5.44}$$

and so, in the classical limit of large $s$, the uncertainty is small ($\sim\sqrt{1/s}$) compared to $\langle\mathbf{n}\cdot\mathbf{S}\rangle$.

### 5.3.5 Paramagnetic Resonance and MRI Scanners

In the presence of an external magnetic field, a classical magnetic dipole $\boldsymbol{\mu}$ experiences a torque

$$\frac{\partial\mathbf{L}}{\partial t} = \boldsymbol{\mu}\times\mathbf{B}\,. \tag{5.45}$$

The dipole will thus turn until it aligns itself along the direction of the field, minimizing its energy. This is familiar from a compass. However, suppose the dipole is already spinning around its centre of mass, such that $\boldsymbol{\mu} = \gamma\mathbf{L}$ where the constant $\gamma$ is known as the gyromagnetic ratio. Then instead one finds that the torque causes the dipole to precess around $\mathbf{B}$.

As in our discussion of the Stern-Gerlach experiment, particles such as a proton or electon do have magnetic dipole moments $\boldsymbol{\mu} = (2\mu/\hbar)\,\mathbf{S}$ proportional to their spin. We'll see that in quantum mechanics, this spin does indeed precess around the direction of an applied magnetic field. This is the basis of MRI scanners, which have become an enormously important diagnostic tool for both chemistry and medicine.

We can understand the basic principles of an MRI machine by using our spin matrices. Unlike the beam of silver atoms in the Stern-Gerlach experiment, here the protons are not free to move, because they're held in place by the electromagnetic binding forces of a complex molecule, and this molecule is also held in a (roughly) fixed place in our cells. Thus we take the Hamiltonian to be

$$H = -\boldsymbol{\mu}\cdot\mathbf{B} = -\frac{2\mu B}{\hbar}S_z\,, \tag{5.46}$$

with no kinetic term. Again, we've chosen the direction of the magnetic field to define the $\hat{\mathbf{z}}$ axis. In particular, for a spin-$\frac{1}{2}$ particle such as a proton, the eigenvalues of this Hamiltonian are $E_\pm = \mp\mu\mathrm{B}$, where $B = |\mathbf{B}$.

Initially, we cannot expect the protons in our body to have their spins already aligned along $\hat{\mathbf{B}}$. Suppose instead that some proton has its spin aligned along some axis $\mathbf{n} = (0, \sin\theta, \cos\theta)$ inclined at angle $\theta$ to $\hat{\mathbf{B}}$. That is, we consider a proton in the state $|\theta_\uparrow\rangle$ defined by

$$\mathbf{n}\cdot\mathbf{S}\,|\theta_\uparrow\rangle = \frac{\hbar}{2}\,|\theta_\uparrow\rangle\,. \tag{5.47}$$

We can always choose to expand this state in terms of our basis $\{|\uparrow\rangle, |\downarrow\rangle\}$, representing states of definite spin along $\hat{z}$, as

$$|\theta_\uparrow\rangle = a|\uparrow\rangle + b|\downarrow\rangle \tag{5.48}$$

where $|a|^2 + |b|^2 = 1$. In terms of our matrices (5.37) for spin-$\frac{1}{2}$, the eigenvalue equation (5.47) becomes

$$\frac{\hbar}{2}\sin\theta\begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} + \frac{\hbar}{2}\cos\theta\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}\cos\theta & -\mathrm{i}\sin\theta\\ \mathrm{i}\sin\theta & -\cos\theta\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix}a\\ b\end{pmatrix} \tag{5.49}$$

Solving this eigenvalue problem and the normalisation condition yields $a = \cos\frac{\theta}{2}$ and $b = \mathrm{i}\sin\frac{\theta}{2}$ (up to a possible phase), so a proton whose spin is aligned along the $\mathbf{n}$ axis is in state

$$|\theta_\uparrow\rangle = \cos\frac{\theta}{2}\,|\uparrow\rangle + \mathrm{i}\sin\frac{\theta}{2}\,|\downarrow\rangle \tag{5.50}$$

Note that $|\theta_\uparrow\rangle$ has the expected behaviour at $\theta = 0$ and $\theta = \pi$, and that it yields $-|\uparrow\rangle$ as $\theta$ is continuously increased to $2\pi$. (It's straightforward to generalise this example to the case of a state with spin aligned along an arbitrary axis $\mathbf{n}$.)

Applying the time evolution operator $U(t) = \mathrm{e}^{-\mathrm{i}Ht/\hbar}$ with the Hamiltonian (5.46), we find that at time $t$ the proton's state has evolved to

$$\begin{aligned}|\psi(t)\rangle = U(t)|\theta_\uparrow\rangle &= \cos\frac{\theta}{2}\,\mathrm{e}^{-\mathrm{i}Ht/\hbar}\,|\uparrow\rangle + \mathrm{i}\sin\frac{\theta}{2}\,\mathrm{e}^{-\mathrm{i}Ht/\hbar}\,|\downarrow\rangle\\ &= \cos\frac{\theta}{2}\,\mathrm{e}^{-\mathrm{i}\omega t/2}\,|\uparrow\rangle + \mathrm{i}\sin\frac{\theta}{2}\,\mathrm{e}^{+\mathrm{i}\omega t/2}\,|\downarrow\rangle\end{aligned} \tag{5.51}$$

where $\omega = 2\mu\mathrm{B}$ is the Larmor frequency. One can check that this state is an eigenstate of the spin operator aligned along the axis $\mathbf{n}(t) = (\sin\theta\sin\omega t, \sin\theta\cos\omega t, \cos\theta)$, so that at time $t$, the proton's spin is definitely aligned along $\mathbf{n}(t)$. Consequently, as time passes, the spin of any proton will precess around the direction of $\mathbf{B}$ with frequency $\omega$ that is independent of the angle of inclination $\theta$ – *i.e.* independent of the proton's initial orientation (provided it was not pointing *exactly* along $\hat{\mathbf{B}}$ in the first place). This is exactly the same behaviour as we found classically.

When a material that contains chemically bound hydrogen atoms is immersed in a strong magnetic field, over time the protons will emit radiation (not accounted for by our

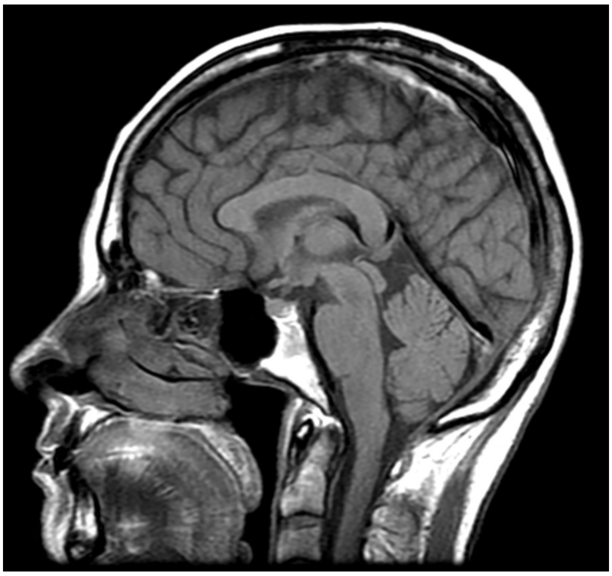

**Figure 10**: *An image of a cross-section of the head, produced by an MRI scan. Different regions contain different concentration of organic molecules, so react more or less strongly to the resonant magnetic field. MRI scanners are one of the most important diagnostic tools in modern medicine.*

above Hamiltonian) so as to sit in the ground state. Thus, eventually the precession will cease and most of the protons' spins will be aligned along the direction of **B**.

Now suppose that, in addition to the static external **B** field, we apply a small additional magnetic field $\mathbf{b}\cos(\omega t)$ that varies at the same Larmor frequency $\omega = 2\mu\mathrm{B}$. The Hamiltonian felt by the protons will then be

$$H = -\boldsymbol{\mu}\cdot(\mathbf{B} + \mathbf{b}\cos(\omega t)\,) = -\frac{2\mu}{\hbar}\begin{pmatrix} \mathrm{B} & \mathrm{b}\cos(\omega t) \\ \mathrm{b}\cos(\omega t) & -\mathrm{B} \end{pmatrix} \tag{5.52}$$

if the new field is in the $\hat{\mathbf{x}}$-direction. The TDSE for this system is thus

$$\begin{pmatrix} \dot{a} \\ \dot{b} \end{pmatrix} = -\mathrm{i}\begin{pmatrix} \mathrm{B} & \mathrm{b}\cos(\omega t) \\ \mathrm{b}\cos(\omega t) & -\mathrm{B} \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} \tag{5.53}$$

varies with frequency $\omega = 2\mu B/\hbar$ (which corresponds to radio frequencies for $\mu$ the dipole moment of the proton and B the strength of a typical magnetic field available in hospitals). This radiation has just the right energy to excite these protons into the state where their spin is aligned against **B**. Consequently, such radiation is readily absorbed by the sample, whereas radiation at nearby frequencies is not. As we have seen, interference between the two states causes the spin to precess around the direction of **B**, and this precessing magnetic moment couples resonantly to the applied radiation field.

MRI scanners are typically tuned to determine the concentration of a single type of atom, usually Hydrogen. However, in a complex molecule, not every Hydrogen nucleus (proton) feels the same magnetic field, because of additional contributions from the electrons that bind the atoms together in the molecule. For example, in methanol ($CH_3OH$) the magnetic field experienced by the proton that is attached to the oxygen atom differs from those experienced by the protons attached to the carbon atom. Also, of the 3 protons bound to the carbon atom, one is on the opposite side of carbon from oxygen, while the other two lie between the carbon and oxygen atoms. The first thus feels a different magnetic field to the other two. Now, the frequency $\omega$ of precession is proportional to the strength of the magnetic field at the location of the proton, so for any fixed strength of applied magnetic field, methanol has three different resonant frequencies. Clues to the chemical structure of a substance can thus be obtained by determining the frequencies at which magnetic resonance occurs in a given imposed field. If we choose $\mathbf{B}$ to have a spatial gradient, then only a thin slice of our sample material will have $\omega$ tuned to its resonant frequency, so we excite transitions to higher energy levels only in this thin slice. Varying this field in an orthogonal direction as the nuclear spins decay back down to the ground state allows us to recover three dimensional images.

### 5.4 Orbital Angular Momentum

The topological considerations that allowed us to admit half-integer values of $s$ do not apply to $\ell$. To understand this, recall from section 4.3.1 that $\mathbf{L}$ could be interpreted as the generator of circular translations — transformations that translate a state around a circle in space, without adjusting its orientation. Unlike the space $S^3/\mathbb{Z}_2$ of rotations, in $\mathbb{R}^3$ the space of such circular paths is contractible (see figure **??**). Consequently, translation around a circular path always leaves our state unchanged. In particular, we must have

$$\mathrm{e}^{-2\pi\mathrm{i}\hat{\mathbf{z}}\cdot\mathbf{L}/\hbar}|\ell,m\rangle = \mathrm{e}^{-2\pi\mathrm{i}m}|\ell,m\rangle = |\ell,m\rangle\,, \tag{5.54}$$

so that $m \in \mathbb{Z}$ and hence $\ell \in \mathbb{N}_0$.

#### 5.4.1 Spherical Harmonics

The commutation relations of the $\mathbf{L}$s are exactly the same as those of the $\mathbf{S}$s, so for any finite $\ell$ we could choose to represent the orbital angular momentum operators by the same $(2\ell+1)\times(2\ell+1)$ matrices as we obtained above. However, in practical applications we're usually interested in states whose orbital angular momentum quantum number $\ell$ may change, perhaps as a result of the particle being excited from one energy level to another. Thus it's more convenient to use a formalism that allows us to treat all values of $\ell$ simultaneously. Furthermore, we often want to know about $\mathbf{L}$ at the same time as knowing about linear momentum $\mathbf{P}$ or position $\mathbf{X}$, and we have seen that the $[X_i, P_j]$ commutation relations do not have any finite dimensional representation and we can only represent them as operators acting on (wave)functions. Let's now see how to reconstruct eigenfunctions of orbital angular momentum – the Legendre polynomials and spherical harmonics you met in IB – from the operator formalism.

In the position representation, the orbital angular momentum operators become

$$\mathbf{L} = \mathbf{X}\times\mathbf{P} = -\mathrm{i}\hbar\,\mathbf{x}\times\boldsymbol{\nabla} \tag{5.55}$$

so that in particular

$$L_z = -\mathrm{i}\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) . \tag{5.56}$$

In terms of spherical polar coordinates we have $(x, y, z) = (r\sin\theta\cos\phi, r\sin\theta\sin\phi, r\cos\theta)$, so

$$\frac{\partial}{\partial\phi} = \frac{\partial x}{\partial\phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\phi}\frac{\partial}{\partial y} + \frac{\partial z}{\partial\phi}\frac{\partial}{\partial z} \quad = -y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y} \tag{5.57}$$

so that $L_z = -\mathrm{i}\hbar\,\partial/\partial\phi$. Thus, using these coordinates, the eigenvalue equation for $L_z$ becomes

$$\langle\mathbf{x}|L_z|\ell, m\rangle = -\mathrm{i}\hbar\frac{\partial}{\partial\phi}\langle\mathbf{x}|\ell, m\rangle = m\hbar\,\langle\mathbf{x}|\ell, m\rangle \tag{5.58}$$

or $-\mathrm{i}\partial\psi_{\ell,m}(\mathbf{x})/\partial\phi = m\psi_{\ell,m}(\mathbf{x})$, where $\psi_{\ell,m}(\mathbf{x}) = \langle\mathbf{x}|\ell, m\rangle$ is the position space wavefunction. This is solved by

$$\psi_{\ell,m}(\mathbf{x}) = K(r,\theta)\,\mathrm{e}^{\mathrm{i}m\phi} \tag{5.59}$$

for some function $K(r,\theta)$. Since $m \in \mathbb{Z}$, $\psi_{\ell,m}$ is a single–valued function of the azimuthal angle $\phi$. This is often given as a further reason why only integer values of $m$ (and hence $\ell$) should be allowed.

A straightforward, though somewhat tedious calculation shows that the raising and lowering operators

$$L_\pm = L_x \pm \mathrm{i}L_y = \pm\hbar\,\mathrm{e}^{\pm\mathrm{i}\phi}\left(\frac{\partial}{\partial\theta} \pm \mathrm{i}\cot\theta\frac{\partial}{\partial\phi}\right) \tag{5.60}$$

in the position representation. The condition $L_+\psi_{\ell,\ell} = 0$ then fixes

$$\psi_{\ell,\ell}(\mathbf{x}) = R(r)\,\sin^\ell\theta\,\mathrm{e}^{\mathrm{i}\ell\phi} . \tag{5.61}$$

Applying the lowering operators one finds that all the other $\psi_{\ell,m}(\mathbf{x})$s are of the form

$$\psi_{\ell,m}(\mathbf{x}) = R(r)\,\mathrm{Y}_\ell^m(\theta,\phi) \tag{5.62}$$

where the *spherical harmonic*

$$\mathrm{Y}_\ell^m(\theta,\phi) = (-1)^m\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\,\mathrm{P}_\ell^m(\cos\theta)\,\mathrm{e}^{\mathrm{i}m\phi} \tag{5.63}$$

is given in terms of the *associated Legendre polynomial*

$$\mathrm{P}_\ell^m(x) = \frac{1}{2^\ell\ell!}(1-x^2)^{m/2}\frac{d^{\ell+m}}{dx^{\ell+m}}(x^2-1)^\ell . \tag{5.64}$$

In particular, the spherical harmonics with $m = 0$ are proportional to the ordinary Legendre polynomial

$$\mathrm{Y}_\ell^0(\theta) = \sqrt{\frac{2\ell+1}{4\pi}}\,\mathrm{P}_\ell(\cos\theta) . \tag{5.65}$$

which is a odd or even polynomial in $\cos\theta$, according to whether $\ell$ is odd or even. In particular, the $\mathrm{P}_\ell^m$s are only single–valued as functions on $S^2$ when $\ell$ is an integer, providing

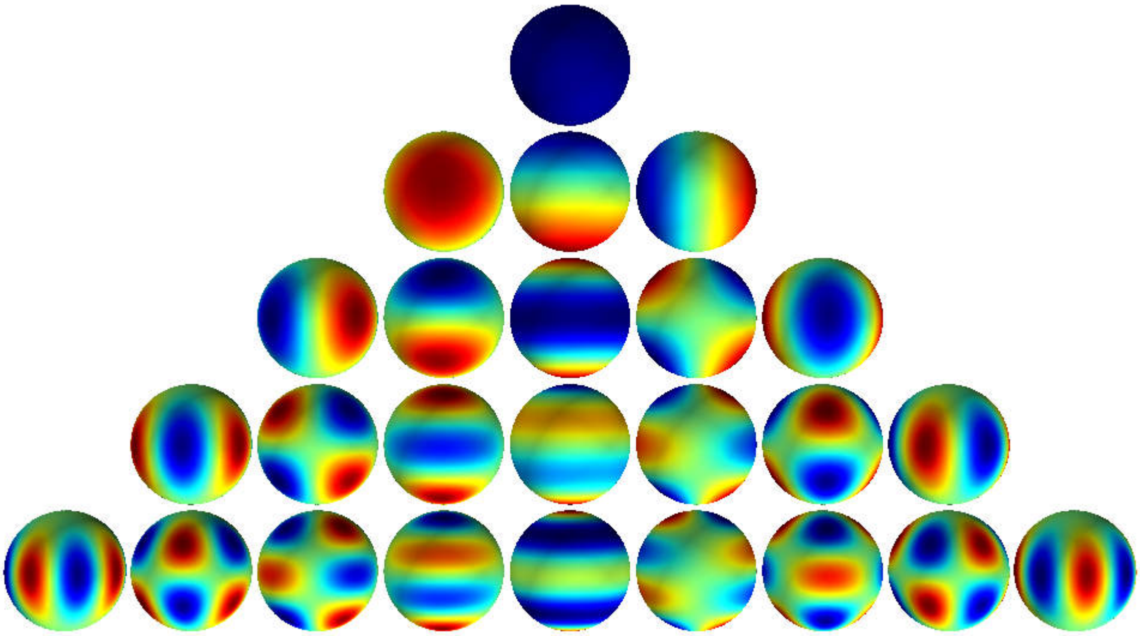

**Figure 11**: *The first few spherical harmonics* $\mathrm{Y}_\ell^m(\theta,\phi)$*. Each row contains pictures of the* $2\ell+1$ *spherical harmonics at fixed* $\ell$*, with* $m$ *increasing from* $-\ell$ *to* $\ell$ *along each row.*

another reason why the half–integer values allowed by general considerations of the algebra must in fact be discarded for **L**.

We won't be concerned with the detailed form of these spherical harmonics, though you may wish to note the orthogonality condition

$$\int_{S^2} \overline{\mathrm{Y}_{\ell'}^{m'}}(\theta,\phi)\,\mathrm{Y}_\ell^m(\theta,\phi)\,\sin\theta\,d\theta\,d\phi = \delta_{\ell\ell'}\,\delta_{mm'} \tag{5.66}$$

and the fact that

$$r^2\nabla^2\mathrm{Y}_\ell^m(\theta,\phi) = -\ell(\ell+1)\,\mathrm{Y}_\ell^m(\theta,\phi) \tag{5.67}$$

where $\nabla^2$ is the Laplacian. Furthermore, since $\mathbf{L}$ is invariant under parity, $\Pi^{-1}\mathbf{L}\Pi = +\mathbf{L}$, it follows that so too are the raising and lowering operators $L_\pm$. Therefore, all states in a given $\ell$ multiplet have the same parity. To determine what that parity is, note that in spherical polar coordinates the transformation $\mathbf{x}\mapsto -\mathbf{x}$ becomes

$$(r,\theta,\phi)\mapsto(r,\theta-\pi,\phi+\pi) \tag{5.68}$$

so in particular $\cos\theta\mapsto-\cos\theta$. Since $\mathrm{P}_\ell(-\cos\theta) = (-1)^\ell\mathrm{P}_\ell(\cos\theta)$, we see that the parity of $\mathrm{Y}_\ell^0$ is odd or even, according to whether $\ell$ is odd or even, and hence

$$\mathrm{Y}_\ell^m(\theta-\pi,\phi+\pi) = (-1)^\ell\,\mathrm{Y}_\ell^m(\theta,\phi) \tag{5.69}$$

for all spherical harmonics with a given value of $\ell$.

It's occasionally useful to have an alternative form of the spherical harmonics. Consider the polynomial in $\mathbb{R}^3$

$$\psi(x) = \sum_{i_1, i_2, \ldots, i_\ell = 1}^{3} \psi_{i_1 i_2 \ldots i_\ell} x^{i_1} x^{i_2} \cdots x^{i_\ell} \tag{5.70}$$

that is homogeneous of degree $\ell$. The coefficients $\psi_{i_1 i_2 \ldots i_\ell} \in \mathbb{C}$ are necessarily totally symmetric in their indices, and the polynomial is harmonic, *i.e.* $\nabla^2 \psi(x) = 0$ if $\psi_{i_1 i_2 \ldots i_\ell}$ are traceless on any pair of indices.

Finally, notice that so far we've said nothing about the radial profile of the wavefunction, $R(r)$. Since this function is certainly spherically symmetric, the rotation generators cannot tell us anything about it and to determine $R(r)$ we'd need further information, such as the Hamiltonian.