

Chapter 7

Intrinsic Spin and Addition of Angular Momentum

When we model a quantum mechanical particle or system that has some internal structure, the action of the rotation group can be more complicated than what we have in the case of wave functions. We could describe such a system in terms of its center of mass, which will be labelled by a point in \mathbb{R}^3 , as well as some internal structure whose quantum mechanical configurations are encoded in a Hilbert space $\mathcal{H}_{\text{internal}}$. The full Hilbert space for such a structured particle will then given by

$$\mathcal{H} = L^2(\mathbb{R}^3) \otimes \mathcal{H}_{\text{internal}} . \quad (7.1)$$

We will then have a (projective) unitary representation of $\text{SO}(3)$ on this Hilbert space generated by some *total angular momentum operators* \mathbf{J} . At the infinitesimal level, we know that \mathbf{J} will act on the center of mass wave function as the orbital angular momentum operator \mathbf{L} , while we can introduce operators \mathbf{S} that describe the action on $\mathcal{H}_{\text{internal}}$,

$$\mathbf{J} = \mathbf{L} \otimes 1_{\mathcal{H}_{\text{internal}}} + 1_{L^2(\mathbb{R}^3)} \otimes \mathbf{S} , \quad (7.2)$$

where the \mathbf{L} and \mathbf{S} operators commute and each satisfy the angular momentum commutation relations,

$$[L_i, L_j] = i\hbar \sum_k \varepsilon_{ijk} L_k , \quad [S_i, S_j] = i\hbar \sum_k \varepsilon_{ijk} S_k . \quad (7.3)$$

If we are describing *elementary* particles, we expect $\mathcal{H}_{\text{internal}}$ to support an irreducible angular momentum representation; otherwise we would think of the different subrepresentations as corresponding to (detectably!) different versions of the elementary particle, and therefore we would call them different types of elementary particles. If a particle has $\mathcal{H}_{\text{spin } j}$ as its internal Hilbert space with the attendant operators \mathbf{S} describing rotations, then we say the particle itself has *intrinsic spin* j (though often we simply shorten this to say the particle has spin j). This intrinsic spin is the quantity that appears in the spin statistics theorem of [Chapter 4](#).

7.1 Addition of angular momentum

To understand the full action of rotations on a system with both orbital angular momentum and intrinsic spin, we will have to understand the action of the total angular momentum operators in a system where we initially understand the action of the components \mathbf{L} and \mathbf{S} separately. Similarly, if we have a system of n particles each of which has some angular momentum operator \mathbf{J}_i acting on its single-particle Hilbert space, then we will want to understand the total angular momentum⁴¹ $\mathbf{J} = \mathbf{J}_{(1)} + \dots + \mathbf{J}_{(n)}$ acting on the composite Hilbert space starting with an understanding of the individual angular momentum representations. This procedure is, in the physics literature, usually referred to as the *addition of angular momentum*. We first pose the problem in the context of there being two constituent representations of angular momentum.

Problem 7.1.1. Consider the Hilbert space $\mathcal{H} \cong \mathcal{H}_1 \otimes \mathcal{H}_2$ where \mathcal{H}_i supports an irreducible representation of the angular momentum operators $\mathbf{J}^{(i)}$ with spin j_i . We have $\dim \mathcal{H} = (2j_1 + 1)(2j_2 + 1)$. How does this composite system decompose into irreducible representations of the total angular momentum operator $\mathbf{J} = \mathbf{J}^{(1)} + \mathbf{J}^{(2)}$?

The answer is given in the following Proposition.

Proposition 7.1.2. Under the action of the total angular momentum, the tensor product $\mathcal{H} \cong \mathcal{H}_1 \otimes \mathcal{H}_2$ of irreducible representations with spins j_1 and j_2 , respectively, decomposes into irreducible representations according to

$$\mathcal{H}_1 \otimes \mathcal{H}_2 = \bigoplus_{J=|j_1-j_2|}^{j_1+j_2} \mathcal{H}_{\text{spin } J} . \quad (7.4)$$

⁴¹Here and in what follows we drop the explicit tensor notation for these sums of operators acting on different tensor factors of a composite Hilbert space.

Thus we can find an orthonormal basis for this tensor product that we denote by $|J, M\rangle$ with $J = |j_1 - j_2|, |j_1 - j_2| + 1, \dots, j_1 + j_2 - 1, j_1 + j_2$ and $M = -J, -J + 1, \dots, J - 1, J$ which obey⁴²

$$(\mathbf{J}^{(1)})^2 |J, M\rangle = \hbar^2 j_1(j_1 + 1) |J, M\rangle, \quad J^2 |J, M\rangle = \hbar^2 J(J + 1) |J, M\rangle, \quad (7.5)$$

$$(\mathbf{J}^{(2)})^2 |J, M\rangle = \hbar^2 j_2(j_2 + 1) |J, M\rangle, \quad J_3 |J, M\rangle = \hbar M |J, M\rangle. \quad (7.6)$$

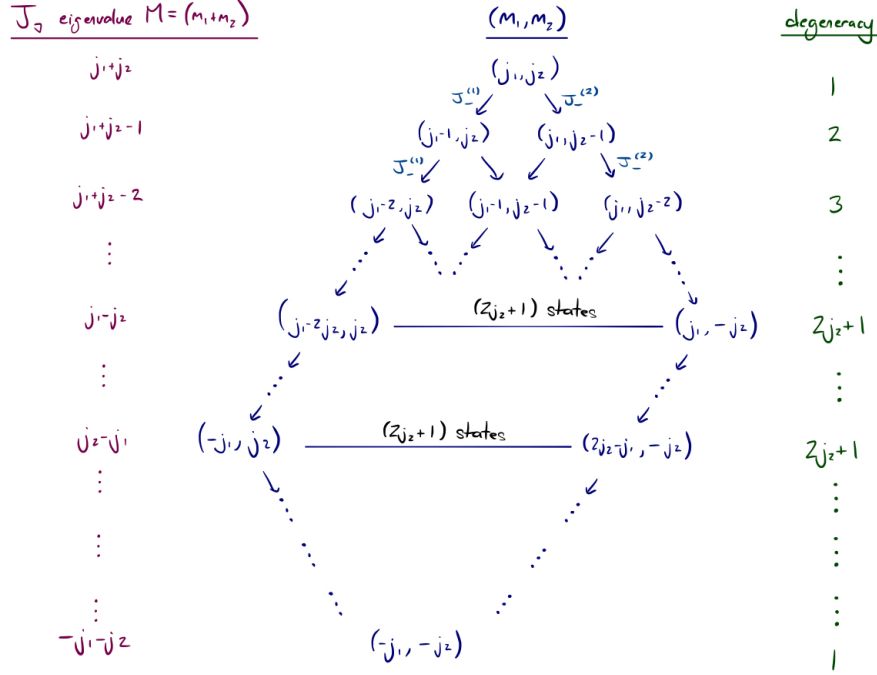


Figure 3. Depiction of states in the tensor product of irreducible representations of angular momentum with spins j_1 and j_2 , where we assume $j_1 \geq j_2$.

Proof. The situation described in the following proof is illustrated in Figure 3, which hopefully makes the combinatorics of the proof easier to follow.

We assume, without loss of generality, that $j_1 \geq j_2$. We then proceed inductively, first finding the representation of highest total spin $\mathcal{H}_{\text{spin}(j_1+j_2)}$ inside \mathcal{H} , then in the complement $\mathcal{H}_{\text{spin}(j_1+j_2)}^\perp \subset \mathcal{H}$ finding the representation of next highest total spin, and so on.

We will write our pure-tensor basis vectors as $|j_1, m_1\rangle \otimes |j_2, m_2\rangle = |m_1; m_2\rangle$,⁴³ which as a reminder, obey

$$\begin{aligned} (\mathbf{J}^{(1)})^2 |m_1; m_2\rangle &= \hbar^2 j_1(j_1 + 1) |m_1; m_2\rangle, & J_3^{(1)} |m_1; m_2\rangle &= \hbar m_1 |m_1; m_2\rangle, \\ (\mathbf{J}^{(2)})^2 |m_1; m_2\rangle &= \hbar^2 j_2(j_2 + 1) |m_1; m_2\rangle, & J_3^{(2)} |m_1; m_2\rangle &= \hbar m_2 |m_1; m_2\rangle. \end{aligned} \quad (7.7)$$

These are evidently already eigenvectors of $J_3 = (J^{(1)})_3 + (J^{(2)})_3$, with eigenvalues $M = m_1 + m_2$. There is a unique state with maximum $M = j_1 + j_2$, which we must be able to identify with the “top” state in a spin $j_1 + j_2$ representation; we can therefore identify

$$|J = j_1 + j_2, M = j_1 + j_2\rangle = |j_1; j_2\rangle. \quad (7.8)$$

⁴²These states are often written as $|j_1, j_2; J, M\rangle$ to make manifest the constituent spins that are being combined. We will leave these implicit to avoid overly burdensome notation whenever possible.

⁴³As with the previous basis states, these will sometimes be labelled $|j_1, m_1; j_2, m_2\rangle$ to indicate the constituent spins. We will avoid this when possible to minimise notational clutter.

The rest of the spin $J = j_1 + j_2$ representation can be recovered by acting with the total lowering operator $J_- = J_-^{(1)} + J_-^{(2)}$. Normalising these using (6.31), we obtain the states $|J = j_1 + j_2, M\rangle$ for $M < J$. These necessarily constitute a complete spin $J = j_1 + j_2$ subrepresentation in \mathcal{H} .

Next we consider the states with $M = j_1 + j_2 - 1$. There are two linearly independent such states, $|j_1 - 1; j_2\rangle$ and $|j_1; j_2 - 1\rangle$. One combination of these occurs in the spin $j_1 + j_2$ representation defined above as $|J = j_1 + j_2, M = j_1 + j_2 - 1\rangle$. Taking a vector in the orthogonal complement, we get a state vector that is necessarily the top state in a spin $j_1 + j_2 - 1$ representation, since acting with a raising operator must give zero, else this would be part of the previous spin $j_1 + j_2$ representation. We therefore denote a normalised element of this orthogonal complement by $|J = j_1 + j_2 - 1, M = j_1 + j_2 - 1\rangle$. Again acting with $J_-^{(1)} + J_-^{(2)}$ on this state generates a full irreducible subrepresentation, this time of spin $j_1 + j_2 - 1$.

If $j_2 = \frac{1}{2}$, then the degeneracy for M eigenvalues with $j_1 + j_2 - 1 \geq M \geq -(j_1 + j_2 - 1)$ is just two, corresponding to the $m_2 = \pm \frac{1}{2}$ states, and so must be spanned by the corresponding M -eigenstates of the two multiplets we have just found. In this case we would be done.

If $j_2 > \frac{1}{2}$, then the degeneracy for the $M = j_1 + j_2 - 2$ eigenvalue is three with $(m_1, m_2) = (j_1, j_2 - 2), (j_1 - 1, j_2 - 1)$ or $(j_1 - 2, j_2)$. Thus, as before, there is a nontrivial orthogonal normalised vector $|j_1 + j_2 - 2, j_1 + j_2 - 2\rangle$ orthogonal to those $M = j_1 + j_2 - 2$ eigenvalues of total spin $j_1 + j_2$ and $j_1 + j_2 - 1$, unique up to a phase. This gives rise to a spin $J = j_1 + j_2 - 2$ representation by lowering.

In general, the degeneracy states with J_3 eigenvalue M is given by $1 + j_1 + j_2 - |M|$ for $|M| \geq j_1 - j_2$, but is $2j_2 + 1$ otherwise as it cannot exceed the number of choices $2j_2 + 1$ for m_2 (see Figure 3). So we can carry on by induction, generating a new multiplet at each stage, until we eventually produce all the angular momentum multiplets with spins from $J = j_1 - j_2$ to $J = j_1 + j_2$, as required. This gives a total of $2j_2 + 1$ irreducible representations ($2j_2 + 1$ being the maximal degeneracy of the M eigenvalue, realised for $|M| \leq j_1 - j_2$). ■

Before moving on, we will look at the simplest case of addition of angular momentum: the tensor product of two spin $1/2$ systems.

Example 7.1.3 (Two qubits). We can be very explicit in examining the two-qubit system,

$$\mathcal{H} = \mathcal{H}_{\text{spin } \frac{1}{2}}^{\otimes 2}. \quad (7.9)$$

If we adopt the basis for the spin- $\frac{1}{2}$ qubit from the last chapter, we have as our basis for the tensor product Hilbert space $|\pm \frac{1}{2}; \pm \frac{1}{2}\rangle$, with the signs chosen independently. To make things easier on the eyes, we will adopt the notation $|\pm \pm\rangle$. If we organise these by J_3 eigenvalue $M = m_1 + m_2$, we have

$$\begin{aligned} M = +1 &: && |++\rangle \\ M = 0 &: && |+-\rangle \quad |-+\rangle \\ M = -1 &: && |--\rangle \end{aligned} \quad (7.10)$$

Starting with the top state, we produce the following states in the spin-one subrepresentation of this system,

$$|1, 1\rangle = |++\rangle, \quad |1, 0\rangle = \frac{|+-\rangle + |-+\rangle}{\sqrt{2}}, \quad |1, -1\rangle = |--\rangle. \quad (7.11)$$

There is an additional spin-zero state (so a rotationally-invariant state),⁴⁴

$$|0, 0\rangle = \frac{|+-\rangle - |-+\rangle}{\sqrt{2}}. \quad (7.12)$$

It may be worth remarking that the spin-one representation consists of bosonic (symmetric) states, while the spin-zero representation is the one fermionic (anti-symmetric) state in this tensor product. Indeed, the total angular momentum operators can be seen (by inspection) to commute with the action of permutations on the n -fold tensor product of identical representations of angular momentum, which means that the bosonic and fermionic subspaces will always transform among themselves under rotations.

⁴⁴You might recognise this as the EPR state from our brief discussion of entanglement.

Example 7.1.4 (Everything from spin one half). The previous example suggests a general construction of the spins j representation for any j using spin- $\frac{1}{2}$ representations as building blocks. Consider the n -fold symmetric tensor product of the qubit Hilbert space $\odot^n \mathcal{H}_{\text{spin } \frac{1}{2}}$. By our results in [Chapter 4](#), this has dimension

$$\dim \left(\odot^n \mathcal{H}_{\text{spin } \frac{1}{2}} \right) = n + 1 . \quad (7.13)$$

If we consider the state $|++ \cdots +\rangle$, this has

$$J_3^{(\text{tot})} |++ \cdots +\rangle = \frac{\hbar n}{2} |++ \cdots +\rangle , \quad (7.14)$$

so this must be an element of a representation with spin greater than or equal to $n/2$. But on dimensionality grounds, this can only be a representation of spin $n/2$ exactly, and indeed it is clear that this state is the top state of its angular momentum representation. Thus, if you like, you can think of any irreducible representation of angular momentum in terms of an appropriate number of identical (bosonic) qubits. This can prove a useful mental heuristic for these representations.

7.2 Clebsch–Gordan coefficients

Equation (7.4) tells us—in general terms—how the tensor product of irreducible angular momentum representations will transform under the total angular momentum. However, to work with these composite systems and do calculations in practice, one needs to be able to concretely construct and manipulate the elements of the different irreducible representations appearing in the direct sum on the right hand side of that equation. In practice, this usually means having expressions for the precise linear combinations of the states $|m_1; m_2\rangle$ that constitute the states $|J, M\rangle$ and *vice versa*. To this end we make the following definition.

Definition 7.2.1. The *Clebsch–Gordan coefficients* $C_{j_1 j_2}(J, M; m_1, m_2)$ are defined by

$$|J, M\rangle = \sum_{\substack{m_1, m_2 \\ m_1 + m_2 = M}} C_{j_1 j_2}(J, M; m_1, m_2) |m_1; m_2\rangle , \quad (7.15)$$

so these are the coefficients of the expansion of our orthonormal basis of states in the (J, M) basis in terms of those in the separable, (m_1, m_2) basis.

The coefficients defined as such are not uniquely specified defined, because there is some choice of overall phases in the states for each irreducible representation involved. However, this freedom can be fixed by requiring that the Clebsch–Gordan coefficients be real along with an additional convention that we will describe momentarily.

Because both bases are orthonormal, we can deduce a number of useful expressions involving the Clebsch–Gordan coefficients. For example, we can realise them explicitly in terms of inner products of the form

$$C_{j_1 j_2}(J, M; m_1, m_2) = \langle m_1; m_2 | J, M \rangle . \quad (7.16)$$

If we adopt the conventions mentioned above to ensure reality of the Clebsch–Gordan coefficients, then we will also have

$$C_{j_1 j_2}(J, M; m_1, m_2) = \langle J, M | m_1; m_2 \rangle . \quad (7.17)$$

The completeness relation for our Hilbert space leads to the following identity,

$$\begin{aligned} 1 &= \langle J, M | J, M \rangle , \\ &= \sum_{m_1, m_2} \langle J, M | m_1; m_2 \rangle \langle m_1; m_2 | J, M \rangle , \\ &= \sum_{m_1, m_2} |C_{j_1 j_2}(J, M; m_1, m_2)|^2 . \end{aligned} \quad (7.18)$$

Analogously, the completeness relation for the $|J, M\rangle$ states gives

$$\begin{aligned} 1 &= \langle m_1; m_2 | m_1; m_2 \rangle , \\ &= \sum_{J, M} \langle m_1, m_2 | J, M \rangle \langle J, M | m_1; m_2 \rangle , \\ &= \sum_{J, M} |C_{j_1 j_2}(J, M; m_1, m_2)|^2 . \end{aligned} \quad (7.19)$$

More generally, we have

$$\begin{aligned} \delta_{J' J} \delta_{M M'} &= \sum_{m_1, m_2} \langle J, M | m_1; m_2 \rangle \langle m_1; m_2 | J', M' \rangle , \\ &= \sum_{m_1, m_2} \overline{C_{j_1 j_2}(J, M; m_1, m_2)} C_{j_1 j_2}(J', M'; m_1, m_2) , \\ \delta_{m_1 m'_1} \delta_{m_2 m'_2} &= \sum_{J, M} \langle m_1, m_2 | J, M \rangle \langle J, M | m'_1; m'_2 \rangle , \\ &= \sum_{J, M} C_{j_1 j_2}(J, M; m_1, m_2) \overline{C_{j_1 j_2}(J, M; m'_1, m'_2)} . \end{aligned} \quad (7.20)$$

We will now see take a look at how the computation of these coefficients works out in some simple examples.

Example 7.2.2. Let $j_2 = \frac{1}{2}$ with $j_1 \neq 0$ an arbitrary spin. Then the highest-spin state takes the usual form $|j_1 + \frac{1}{2}, j_1 + \frac{1}{2}\rangle = |j_1; \frac{1}{2}\rangle$. Acting with the total lowering operators, we get

$$\begin{aligned} |j_1 + \frac{1}{2}, j_1 - \frac{1}{2}\rangle &= \frac{1}{\hbar\sqrt{2j_1 + 1}} J_- |j_1 + \frac{1}{2}, j_1 + \frac{1}{2}\rangle , \\ &= \frac{1}{\hbar\sqrt{2j_1 + 1}} \left(J_-^{(1)} + J_-^{(2)} \right) |j_1; \frac{1}{2}\rangle , \\ &= \frac{1}{\sqrt{2j_1 + 1}} \left(\sqrt{2j_1} |j_1 - 1; \frac{1}{2}\rangle + |j_1; -\frac{1}{2}\rangle \right) . \end{aligned} \quad (7.21)$$

We can identify the most general (normalised) orthogonal complement in the $M = j_1 - \frac{1}{2}$ eigenspace as

$$|j_1 - \frac{1}{2}, j_1 - \frac{1}{2}\rangle \sim \frac{1}{\sqrt{2j_1 + 1}} \left(|j_1 - 1; \frac{1}{2}\rangle - \sqrt{2j_1} |j_1; -\frac{1}{2}\rangle \right) . \quad (7.22)$$

At this point we can use some of our freedom in introducing phases to fix the overall phase of this state. Demanding that the Clebsch–Gordan coefficients (so the coefficients of the expansion) be real gives us

$$|j_1 - \frac{1}{2}, j_1 - \frac{1}{2}\rangle = \pm \frac{1}{\sqrt{2j_1 + 1}} \left(\sqrt{2j_1} |j_1; -\frac{1}{2}\rangle - |j_1 - 1; \frac{1}{2}\rangle \right) . \quad (7.23)$$

To fix the final sign ambiguity, one may adopt a standard convention known as the *Condon–Shortley convention*. This amounts to declaring that

$$C_{j_1 j_2}(J, J; j_1, J - j_1) > 0 . \quad (7.24)$$

In the above, this selects the plus sign, and with that highest state fixed, we can produce the rest of the spin $j_1 - \frac{1}{2}$ multiplet by acting with J_- . (Note that this convention depends on the order of the two constituent spins j_1 and j_2 .)

One can read off the Clebsch–Gordan coefficients from the resulting expressions for our states, e.g., from (7.21) and

(7.23). We have:

$$\begin{aligned}
C_{j_1 \frac{1}{2}} \left(j_1 + \frac{1}{2}, j_1 + \frac{1}{2}; j_1, \frac{1}{2} \right) &= 1, \\
C_{j_1 \frac{1}{2}} \left(j_1 + \frac{1}{2}, j_1 - \frac{1}{2}; j_1, -\frac{1}{2} \right) &= \frac{1}{\sqrt{2j_1 + 1}}, \\
C_{j_1 \frac{1}{2}} \left(j_1 + \frac{1}{2}, j_1 - \frac{1}{2}; j_1 - 1, \frac{1}{2} \right) &= \sqrt{\frac{2j_1}{2j_1 + 1}}, \\
C_{j_1 \frac{1}{2}} \left(j_1 - \frac{1}{2}, j_1 - \frac{1}{2}; j_1, -\frac{1}{2} \right) &= \sqrt{\frac{2j_1}{2j_1 + 1}}, \\
C_{j_1 \frac{1}{2}} \left(j_1 - \frac{1}{2}, j_1 - \frac{1}{2}; j_1 - 1, \frac{1}{2} \right) &= \frac{-1}{\sqrt{2j_1 + 1}}.
\end{aligned} \tag{7.25}$$

You can look up tables of Clebsch–Gordan coefficients in textbooks and online, but you should learn to love them and practice deriving some!

Example 7.2.3 (Application to hydrogen energy levels). An important application of this general story arises in the analysis of atoms. Let us start with a single-electron atom (a.k.a., a Hydrogen-like atom). We model this as an electron moving in an external Coulomb potential, and you have studied the corresponding stationary state wave functions in **All Quantum Theory**. However, the electron has intrinsic spin $1/2$, so we should really think of its Hilbert space as being the tensor product

$$\mathcal{H}_{\text{electron}} \cong L^2(\mathbb{R}^3) \otimes \mathcal{H}_{\text{spin } 1/2}. \tag{7.26}$$

A general state in the electron Hilbert space will then consist of *two wavefunctions*, one for each of the possible internal spin states

$$|\psi\rangle = |\psi_+ \otimes +\frac{1}{2}\rangle + |\psi_- \otimes -\frac{1}{2}\rangle, \tag{7.27}$$

where $|\pm\frac{1}{2}\rangle$ are the $m_s = \pm\frac{1}{2}$ intrinsic spin eigenstates for, say, the S_3 operator, and $\psi_{\pm}(\mathbf{x})$ give the wave functions for the situation that the electron has $m_s = \pm\frac{1}{2}$. In non-relativistic quantum mechanics, the Schrödinger equation does not mix the two m -values, so the component wave functions $\psi_{\pm}(\mathbf{x})$ must both individually satisfy the same Schrodinger equation.⁴⁵

If we take the wavefunctions $\psi_{\pm}(\mathbf{x})$ to be the stationary state wave functions you met for the Hydrogen atom previously, we end up with stationary states that we write as

$$|n, \ell, m_{\ell}; m_s\rangle = f_{n\ell}(r) Y_{\ell}^{m_{\ell}}(\theta, \varphi) \otimes |m_s\rangle, \tag{7.28}$$

where on the right we have separated out the explicit wave function part in front and left only the intrinsic spin state in the ket. Here, as elsewhere, the $Y_{\ell}^{m_{\ell}}(\theta, \varphi)$ are the spherical harmonics with eigenvalues $\hbar^2 \ell(\ell + 1)$ for L^2 and $\hbar m_{\ell}$ for L_3 , and $f_{n\ell}(r)$ is a (particular) polynomial in r of degree $n - 1$ multiplied by $\exp(-Zr/na_0)$. These states simultaneously diagonalise L^2 , S^2 , L_3 , S_3 , and H , with energy

$$E_n = \frac{E_0}{n^2}, \quad E_0 = -\frac{Z^2 q_e^2}{2a_0}. \tag{7.29}$$

The energy eigenstates depend only on the *principal quantum number*, n , and for a given n there are states with $\ell = 0, \dots, n - 1$, and for each ℓ there are $2\ell + 1$ different values of m_{ℓ} . Each such wave function also occurs twice, once for each of the two values of m_s . Adding everything up, there is a degeneracy of $2n^2$ for the energy level E_n .

Now for various purposes (we will see more on this in future chapters) it can prove useful to adopt a basis of states that diagonalises the total angular momentum operator J^2 (where $\mathbf{J} = \mathbf{L} + \mathbf{S}$). Following our previous discussion of addition of angular momentum, we can find a basis of states that does this with eigenvalue $j(j + 1)\hbar^2$, where $j = \ell \pm \frac{1}{2}$ (or $j = \frac{1}{2}$ if $\ell = 0$). These are given by the linear combinations,

$$|n, \ell, j, m_j\rangle = \sum_{\substack{m_{\ell}, m_s \\ m_{\ell} + m_s = m_j}} C_{\ell, \frac{1}{2}}(j, m_j; m_{\ell}, m_s) |n, \ell, m_{\ell}; m_s\rangle. \tag{7.30}$$

⁴⁵In a relativistic setting, the usual Schrödinger equation is replaced by the *Dirac equation*, which does mix up the different spin states. This is beyond the scope of our course.

where $C_{\ell, \frac{1}{2}}(j, m_j; m_\ell, m_s)$ are of course the Clebsch–Gordan coefficients. This gives us a basis of stationary states that are eigenvectors for H, L^2, J^2 , and J_3 , the latter with eigenvalue m_j , but not for L_3 and S_3 .

There is a standard nomenclature for the electron stationary states in this basis. The set of states with given values of n, ℓ , and j are known as $n\ell_j$ orbitals. For historical reasons, instead of writing the numerical value for $\ell = 0, 1, 2, 3, 4, \dots$, one normally substitutes the letters s, p, d, f, g, \dots respectively (continuing alphabetically). Each such orbital contains $2j + 1$ states with $m_j = -j, -j + 1, \dots, j - 1, j$. So, for example:

- For all n , we have the $\ell = 0$ states (s orbitals) which appear only in the orbital $ns_{\frac{1}{2}}$ with the two states corresponding to $m_j = m_s = \pm\frac{1}{2}$.
- For $n \geq 2$ we can have $\ell = 1$ states (p orbitals) which arise in the configuration $np_{\frac{1}{2}}$ with two states or $np_{\frac{3}{2}}$ with four states, giving a total of 6 states for the np orbitals.
- In general, we have orbits $n\ell_{\ell \pm \frac{1}{2}}$ with $n \geq \ell + 1$, and a similar counting for the $n\ell$ type of energy level gives a total of $2(\ell - \frac{1}{2}) + 1 + 2(\ell + \frac{1}{2}) + 1 = 4\ell + 2$ states.

Remark 7.2.4. While we have reorganised the Hydrogen stationary states so as to diagonalise the total angular momentum operator, it may not yet be clear that this is a superior basis to choose. We will see in some examples in the next chapter that when we start considering *corrections* to the Hydrogen atom Hamiltonian arising from more subtle physical effects, these will often lead to a preference for one basis over another.

7.3 Irreducible tensor operators and the Wigner–Eckart theorem

Just as the Hilbert space of a rotational system can be organised in terms of the action of the angular momentum operators, so too can many *operators* in such systems. It then turns out that the matrix elements of operators with definite angular momentum properties (the so-called *irreducible tensor operators*, see below) are controlled by the same rules of addition of angular momentum that we have just developed.

We define an action of the rotation group on operators by conjugation by the corresponding unitaries,

$$A \xrightarrow{R} A' = U(R)AU(R)^* . \quad (7.31)$$

This definition is arranged so that under a combined action of rotations on states and operators, matrix elements remain fixed. (The idea is that if we simultaneously rotate the state of our system and the measuring apparatus (the operators), then the corresponding measurements/matrix elements should be invariant.)

$$\langle \psi | A | \varphi \rangle \xrightarrow{R} \langle U(R)\psi | A' | U(R)\varphi \rangle = \langle \psi | U(R)^* U(R) A U(R) U(R) | \varphi \rangle = \langle \psi | A | \varphi \rangle . \quad (7.32)$$

From this we can infer the transformation of an operator under an infinitesimal rotation, which is formulated in terms of the angular momentum operators,

$$U(R)AU(R)^* \approx (1 - \frac{i\varepsilon}{\hbar} \boldsymbol{\omega} \cdot \mathbf{J})A(1 + \frac{i\varepsilon}{\hbar} \boldsymbol{\omega} \cdot \mathbf{J}) \approx A - \frac{i\varepsilon}{\hbar} [\boldsymbol{\omega} \cdot \mathbf{J}, A] . \quad (7.33)$$

Thus we identify the infinitesimal transformation $\delta_\omega A$ of an operator A with the commutator with the angular momentum operators,

$$\delta_\omega A = -\frac{i}{\hbar} [\boldsymbol{\omega} \cdot \mathbf{J}, A] . \quad (7.34)$$

7.3.1 Vector operators

A number of operators that appear frequently in rotational systems have good reason to transform nicely under rotations. In particular, the position operators \mathbf{X} or the momentum operators \mathbf{P} should, in principle, *transform as vectors under rotations*. More precisely, they will transform according to,⁴⁶

$$U(R)\mathbf{V}U(R)^* = R^{-1}\mathbf{V} , \quad U(R)(\mathbf{n} \cdot \mathbf{V})U(R)^* = (R\mathbf{n}) \cdot \mathbf{V} , \quad (7.35)$$

⁴⁶The R^{-1} rather than R here is coming from the same place as the R^{-1} appearing in the action of rotations on wavefunctions.

Notice that with this definition, if we act with rotations on the *states* of a system while leaving the (vector) operators fixed,⁴⁷ then we have

$$\langle \psi | \mathbf{V} | \varphi \rangle \xrightarrow{R} \langle \psi | U(R)^* \mathbf{V} U(R) | \varphi \rangle = \langle \psi | U(R^{-1}) \mathbf{V} U(R^{-1})^* | \varphi \rangle = R \langle \psi | \mathbf{V} | \varphi \rangle , \quad (7.36)$$

so our measured expectation values/matrix elements transform by the rotation matrix R . Working infinitesimally, we have

$$\delta_{\omega}(\mathbf{n} \cdot \mathbf{V}) = (\boldsymbol{\omega} \wedge \mathbf{n}) \cdot \mathbf{V} , \quad (7.37)$$

so in terms of angular momentum operators, we have

$$[\boldsymbol{\omega} \cdot \mathbf{J}, \mathbf{n} \cdot \mathbf{V}] = i\hbar(\boldsymbol{\omega} \wedge \mathbf{n}) \cdot \mathbf{V} . \quad (7.38)$$

we recognise this as the component-free expression for the commutation relations for the angular momentum operators, with some \mathbf{J} 's replaced by \mathbf{V} 's. Indeed working in components, we arrive at the following definition.

Definition 7.3.1. A *vector operator* is any triple of operators \mathbf{V} in a rotational system that obey the commutation relations

$$[J_i, V_j] = i \sum_k \varepsilon_{ijk} V_k . \quad (7.39)$$

As an examples, we have (by direct computation) that the position, momentum, and angular momentum operators are all vector operators in this sense. More generally, operators can transform as irreducible representations (of arbitrary spin) of the rotation group/angular momentum operators. We make the following definition.

Definition 7.3.2. An *irreducible tensor operator operator of spin k* is a $(2k+1)$ -tuple of operators $T_q^{(k)}$ for $q = -k, -k+1, \dots, k-1, k$ in a rotational system that obey the commutation relations

$$\begin{aligned} [J_3, T_q^{(k)}] &= \hbar q T_q^{(k)} , \\ [J_{\pm}, T_q^{(k)}] &= \hbar \sqrt{k(k+1) - q(q \pm 1)} T_{q \pm 1}^{(k)} . \end{aligned} \quad (7.40)$$

Note that for the case $k = 1$, the basis $T_q^{(1)}$ is related to the Cartesian basis according to

$$T_0^{(1)} = V_3 , \quad T_{\pm 1}^{(1)} = \mp \frac{V_1 \pm iV_2}{\sqrt{2}} , \quad (7.41)$$

and with this change of basis the commutation relations in (7.39) and (7.40) coincide. The key result that motivates our definition of general tensor operators is the following theorem, which allows for a drastic simplification in the computation of matrix elements of tensor operators.

Theorem 7.3.3 (Wigner–Eckart). The matrix elements of an irreducible tensor operator of spin k with respect to angular momentum eigenstates are given by

$$\langle \alpha; J, M | T_q^{(k)} | \beta; j, m \rangle = C_{j,k}(J, M; m, q) \langle \alpha; J || T^{(k)} || \beta; j \rangle . \quad (7.42)$$

Here α and β represent additional labels on the states that are not affected by the action of angular momentum operators. The double-bracketed object $\langle \alpha; J || T^{(k)} || \beta; j \rangle$ on the right hand side is called the *reduced matrix element*, and is some number that doesn't depend on the labels m, M , and q .

The punchline here is that by symmetry, the matrix elements of tensor operators between definite angular momentum states are determined entirely up to a single constant for each choice of the three angular momentum multiplets being coupled (two irreps as states and the choice of tensor operator), with the dependence on the particular states/elements of the angular momentum multiplets being entirely encoded in Clebsch–Gordan coefficients. In practice, the overall constant can then usually be evaluated by making a convenient choice of M, m , and q .

⁴⁷We think of this as rotating the state of our system while leaving the measuring apparatus/laboratory equipment fixed

Proof. We consider the following matrix elements:

$$\langle \alpha; J, M | [J_{\pm}, T_q^{(k)}] | \beta; j, m \rangle = \hbar \sqrt{k(k+1) - q(q \pm 1)} \langle \alpha; J, M | T_{q \pm 1}^{(k)} | \beta; j, m \rangle, \quad (7.43)$$

which we can also rewrite by acting with the J_{\pm} operators in the commutators to the left and to the right on the states, which yields

$$\hbar \sqrt{J(J+1) - M(M \mp 1)} \langle \alpha; J, M \mp 1 | T_q^{(k)} | \beta; j, m \rangle - \hbar \sqrt{j(j+1) - m(m \pm 1)} \langle \alpha; J, M | T_q^{(k)} | \beta; j, m \pm 1 \rangle. \quad (7.44)$$

Now observe that for the Clebsch–Gordan coefficients, we have

$$\begin{aligned} \langle J, M | J_{\pm} | j_1, m_1; j_2, m_2 \rangle &= \hbar \sqrt{j_1(j_1+1) - m_1(m_1 \pm 1)} \langle J, M | j_1, m_1 \pm 1; j_2, m_2 \rangle \\ &\quad + \hbar \sqrt{j_2(j_2+1) - m_2(m_2 \pm 1)} \langle J, M | j_1, m_1; j_2, m_2 \pm 1 \rangle \\ &= \hbar \sqrt{J(J+1) - M(M \mp 1)} \langle J, M \mp 1 | j_1, m_1; j_2, m_2 \rangle. \end{aligned} \quad (7.45)$$

Comparing the two sets of relations, we find that we have *identical recursion relations* with the relation

$$(J, M, j, m, k, q) \leftrightarrow (J, M, j_1, m_1, j_2, m_2).$$

These recursion relations allow to determine both the Clebsch–Gordan coefficients (with fixed J, j_1, j_2) and our matrix elements (with fixed α, β, J, k, j) by homogeneous linear relations in terms of a single coefficient/matrix element. The two sets of numbers thus must agree up to an overall rescaling. ■

The Wigner–Eckart theorem tells us that the rules for addition of angular momentum also constrain the possible matrix elements of tensor operators in rotational systems. For example, for a vector operator like \mathbf{X} , \mathbf{P} , or even \mathbf{J} itself, matrix elements can only be non-zero between states whose total angular momentum differs by at most one! This is an important selection rule in many applications, for example in atomic physics.