15

Addition of Angular Momenta

15.1. A Simple Example

Consider a system of two spin-1/2 particles (whose orbital degrees of freedom we ignore). If $\mathbf{S}_1$ and $\mathbf{S}_2$‡ are their spin operators, the two-particle Hilbert space $\mathbb{V}_{1\otimes 2}$ is spanned by the four vectors

$$|s_1m_1\rangle\otimes|s_2m_2\rangle\equiv|s_1m_1, s_2m_2\rangle \tag{15.1.1}$$

which obey

$$S_i^2|s_1m_1, s_2m_2\rangle=\hbar^2 s_i(s_i+1)|s_1m_1, s_2m_2\rangle \tag{15.1.2a}$$

$$S_{iz}|s_1m_1, s_2m_2\rangle=\hbar m_i|s_1m_1, s_2m_2\rangle \qquad (i=1, 2) \tag{15.1.2b}$$

Since $s_i=1/2$, and $m_i=\pm 1/2$ has freedom only in sign, let us use the compact notation $|++\rangle$, $|+-\rangle$, $|-+\rangle$, $|--\rangle$ to denote the states. For instance,

$$|+-\rangle=|s_1=\tfrac{1}{2}m_1=\tfrac{1}{2}, s_2=\tfrac{1}{2}m_2=-\tfrac{1}{2}\rangle \tag{15.1.3}$$

and so on. These four vectors form the *product* basis. They represent states that have well-defined values for the magnitude and z component of the individual spins.

Suppose now that we choose not to look at the individual spins but the system as a whole. What are the possible values for the magnitude and z component of the system spin, and what are the states that go with these values? This is a problem in *addition of angular momenta*, which is the topic of this chapter.

‡ In terms of the operators $\mathbf{S}_1^{(1)}$ and $\mathbf{S}_2^{(2)}$ which act on the one-particle spaces, $\mathbf{S}_1=\mathbf{S}_1^{(1)}\otimes I^{(2)}$ and $\mathbf{S}_2=I^{(1)}\otimes\mathbf{S}_2^{(2)}$.

Consider the operator

$$\mathbf{S}=\mathbf{S}_1+\mathbf{S}_2 \tag{15.1.4}$$

which we call the *total angular momentum operator*. That $\mathbf{S}$ is indeed the total angular momentum operator is supported by (1) our intuition; (2) the fact that it is the generator of rotation for the product kets, i.e., rotations of the whole system; (3) the fact that it obeys the commutation rules expected of a generator of rotations, namely,

$$[S_i, S_j]=\sum_k i\hbar\varepsilon_{ijk}S_k \tag{15.1.5}$$

as may be readily verified. *Our problem is to find the eigenvalues and eigenvectors of* S^2 *and* S_z. Consider first

$$S_z=S_{1z}+S_{2z} \tag{15.1.6}$$

which commutes with S_1^2, S_2^2, S_{1z}, and S_{2z}. We expect it to be diagonal in the product basis. This is readily verified:

$$\begin{aligned}
&S_z|++\rangle=(S_{1z}+S_{2z})|++\rangle=\left(\frac{\hbar}{2}+\frac{\hbar}{2}\right)|++\rangle \\
&S_z|+-\rangle=0|+-\rangle \\
&S_z|-+\rangle=0|-+\rangle \\
&S_z|--\rangle=-\hbar|--\rangle
\end{aligned} \tag{15.1.7}$$

Thus the allowed values for the total z component are $\hbar$, 0, and $-\hbar$.

By the method of images (or any other method)

$$S_z \xrightarrow[\text{product basis}]{} \hbar \begin{array}{c} \\ ++ \\ +- \\ -+ \\ -- \end{array} \begin{array}{c} \begin{array}{cccc} ++ & +- & -+ & -- \end{array} \\ \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \end{array} \tag{15.1.8}$$

Note that the eigenvalue $s_z=0$ is twofold degenerate, and the eigenspace is spanned by the vectors $|+-\rangle$ and $|-+\rangle$. If we form some linear combination, $\alpha|+-\rangle+\beta|-+\rangle$, we still get an eigenstate with $s_z=0$, but this state will not have definite values for S_{1z} and S_{2z} (unless α or $\beta=0$).

Consider next the operator

$$S^2=(\mathbf{S}_1+\mathbf{S}_2)\cdot(\mathbf{S}_1+\mathbf{S}_2)=S_1^2+S_2^2+2\mathbf{S}_1\cdot\mathbf{S}_2 \tag{15.1.9}$$

Although S^2 commutes with S_1^2 and S_2^2, it does not commute with S_{1z} and S_{2z} because of the $\mathbf{S}_1 \cdot \mathbf{S}_2$ term, which has S_{1x}, S_{1y}, etc. in it. By explicit computation,

$$S^2 \xrightarrow[\text{product basis}]{} \hbar^2 \begin{array}{c} \begin{matrix} ++ & +- & -+ & -- \end{matrix} \\ \begin{bmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{bmatrix} \end{array} \tag{15.1.10}$$

Thus we see that although $|++\rangle$ and $|--\rangle$ are eigenstates of $S^2[s(s+1)=2]$, the states of zero S_z, namely, $|+-\rangle$ and $|-+\rangle$, are not. However, the following linear combinations are:

$$\begin{aligned} &\frac{|+-\rangle + |-+\rangle}{2^{1/2}} \qquad (s=1) \\ &\frac{|+-\rangle - |-+\rangle}{2^{1/2}} \qquad (s=0) \end{aligned} \tag{15.1.11}$$

*Exercise 15.1.1.** Derive Eqs. (15.1.10) and (15.1.11). It might help to use

$$\mathbf{S}_1 \cdot \mathbf{S}_2 = S_{1z}S_{2z} + \tfrac{1}{2}(S_{1+}S_{2-} + S_{1-}S_{2+}) \tag{15.1.12}$$

This completes the solution to the problem we undertook. The allowed values for total spin are $s=1$ and 0, while the allowed values of s_z are $\hbar$, 0, and $-\hbar$. The corresponding eigenstates in the product basis are

$$\begin{aligned} &|s=1\ m=1, \quad s_1=1/2\ s_2=1/2\rangle = |++\rangle \\ &|s=1\ m=0, \quad s_1=1/2\ s_2=1/2\rangle = 2^{-1/2}[|+-\rangle + |-+\rangle] \\ &|s=1\ m=-1, s_1=1/2\ s_2=1/2\rangle = |--\rangle \\ &|s=0\ m=0, \quad s_1=1/2\ s_2=1/2\rangle = 2^{-1/2}[|+-\rangle - |-+\rangle] \end{aligned} \tag{15.1.13}$$

These vectors represent states with well-defined total angular momentum; they form the *total-s basis*. The three spin-1 states are called *triplets* and the solitary spin-0 state is called the *singlet*. The problem of adding angular momenta is essentially a change of basis, from one that diagonalizes $(S_1^2, S_2^2, S_{1z}, S_{2z})$ to one that diagonalizes (S^2, S_z, S_1^2, S_2^2). We can describe our findings symbolically as

$$1/2 \otimes 1/2 = 1 \oplus 0 \tag{15.1.14}$$

which means that the direct product of two spin-1/2 Hilbert spaces is a direct sum of a spin-1 space and a spin-0 space. The way the dimensionalities work out in

Eq. (15.1.14) is as follows:

$$\begin{aligned} &\text{left-hand side:} \quad (2s_1+1)(2s_2+1)=(2\times 1/2+1)(2\times 1/2+1)=4 \\ &\text{right-hand side:} \quad \sum_{s=0}^{1}(2s+1)=1+3=4 \end{aligned} \tag{15.1.15}$$

The decomposition of the direct product space into a sum over spaces with well-defined total spin can also be viewed this way. The rotation operators for the entire system will be 4×4 matrices in the product basis. These matrices are, however, reducible: by changing to the total-s basis, they may be block diagonalized into a 3×3 block (spin-1 sector) and a 1×1 block (spin-0 sector). The total-s basis is, however, irreducible; we cannot further subdivide the spin-1 space into parts that do not mix under rotations.

The total-s states have another property: they have definite symmetry under the exchange of the two particles. The triplets are symmetric and the singlet is antisymmetric. Now, the state vector for two identical spin-1/2 particles must be antisymmetric under the exchange of particle labels, i.e., under the exchange of their spin *and* orbital degrees of freedom. We already know that if Ω is some orbital operator (built out of coordinates and momenta), then

$$|\omega_1\omega_2, S\rangle = 2^{-1/2}[|\omega_1\omega_2\rangle + |\omega_2\omega_1\rangle]$$

and

$$|\omega_1\omega_2, A\rangle = 2^{-1/2}[|\omega_1\omega_2\rangle - |\omega_2\omega_1\rangle]$$

are symmetric and antisymmetric, respectively, under the exchange of the orbital variable. To form the complete state vector, we simply multiply orbital and spin states of *opposite* symmetry:

$$|\omega_1 m_1, \omega_2 m_2, A\rangle = \begin{cases} |\omega_1\omega_2, S\rangle \otimes \dfrac{|+-\rangle - |-+\rangle}{2^{1/2}} \\ |\omega_1\omega_2, A\rangle \otimes \begin{cases} |++\rangle \\ \dfrac{|+-\rangle + |-+\rangle}{2^{1/2}} \\ |--\rangle \end{cases} \end{cases} \tag{15.1.16}$$

These vectors provide a complete basis for the Hilbert space of two identical spin-1/2 particles. As an example, consider the ground state of the He atom, which has two electrons. In connection with the periodic table it was said that in this state of lowest energy, both electrons are in the lowest orbital state $|n=1, l=0, m=0\rangle$‡ and

‡ If we neglect interelectron forces, the states allowed to the electrons are hydrogenlike, in that they are labeled $|n, l, m\rangle$. But the energies and wave functions are obtained upon making the replacement $e^2 \to Ze^2 = 2e^2$.

have opposite spins. We can sharpen that statement now. The orbital part of the ground-state ket is just the direct product,

$$|\psi_o\rangle = |100\rangle \otimes |100\rangle \tag{15.1.17}$$

which is already symmetric. So the spin part must be

$$|\chi_s\rangle = 2^{-1/2}(|+-\rangle - |-+\rangle) \tag{15.1.18}$$

and so

$$|\psi_{\text{ground}}\rangle = |\psi_o\rangle \otimes |\chi_s\rangle \tag{15.1.19}$$

In this state, both the orbital and spin angular momenta are zero.

Let us now return to the problem of just the two spins (and no orbital coordinates). Now that we have two bases, which one should we use? The answer depends on the Hamiltonian. For instance, if the two spins only interact with an external field $\mathbf{B} = B_0\mathbf{k}$,

$$H = -(\gamma_1\mathbf{S}_1 + \gamma_2\mathbf{S}_2)\cdot\mathbf{B} = -B_0(\gamma_1 S_{1z} + \gamma_2 S_{2z}) \tag{15.1.20}$$

the product basis, which diagonalizes S_{1z} and S_{2z} is the obvious choice. (If, however, $\gamma_1 = \gamma_2$, then $H \propto S_z$, and we can use the total-s basis as well.) On the other hand, if the spins are mutually interacting and, say,

$$H = A\mathbf{S}_1\cdot\mathbf{S}_2 = \tfrac{1}{2}A(S^2 - S_1^2 - S_2^2) \tag{15.1.21}$$

the total-s basis diagonalizes H.

*Exercise 15.1.2.** In addition to the Coulomb interaction, there exists another, called the *hyperfine interaction*, between the electron and proton in the hydrogen atom. The Hamiltonian describing this interaction, which is due to the magnetic moments of the two particles is,

$$H_{hf} = A\mathbf{S}_1\cdot\mathbf{S}_2 \qquad (A > 0) \tag{15.1.22}$$

(This formula assumes the orbital state of the electron is $|1, 0, 0\rangle$.) The total Hamiltonian is thus the Coulomb Hamiltonian plus H_{hf}.

(1) Show that H_{hf} splits the ground state into two levels:

$$\begin{aligned} E_+ &= -\text{Ry} + \frac{\hbar^2 A}{4} \\ E_- &= -\text{Ry} - \frac{3\hbar^2 A}{4} \end{aligned} \tag{15.1.23}$$

and that corresponding states are triplets and singlet, respectively.

(2) Try to estimate the frequency of the emitted radiation as the atom jumps from the triplet to the singlet. To do so, you may assume that the electron and proton are two dipoles μ_e and μ_p separated by a distance a_0, with an interaction energy of the order‡

$$\mathscr{H}_{hf} \cong \frac{\mu_e \cdot \mu_p}{a_0^3}$$

Show that this implies that the constant in Eq. (15.1.22) is

$$A \sim \frac{2e}{2mc} \frac{(5.6)e}{2Mc} \frac{1}{a_0^3}$$

(where 5.6 is the g factor for the proton), and that

$$\Delta E = E_+ - E_- = A\hbar^2$$

is a correction of order $(m/M)\alpha^2$ relative to the ground-state energy. Estimate that the frequency of emitted radiation is a few tens of centimeters, using the mnemonics from Chapter 13. The measured value is 21.4 cm. This radiation, called the *21-cm line*, is a way to detect hydrogen in other parts of the universe.

(3) Estimate the probability ratio $P(\text{triplet})/P(\text{singlet})$ of hydrogen atoms in thermal equilibrium at room temperature.

15.2. The General Problem

Consider now the general problem of adding two angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$. What are the eigenvalues and eigenkets of J^2 and J_z, where $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$? One way to find out is to mimic the last section: construct the $(2j_1+1)\cdot(2j_2+1)$-dimensional matrices J^2 and J_z and diagonalize them. Now, J_z will be diagonal in the product basis itself, for

$$J_z|j_1 m_1, j_2 m_2\rangle = \hbar(m_1+m_2)|j_1 m_1, j_2 m_2\rangle \tag{15.2.1}$$

It will be a degenerate operator, for there are many ways to build up a total $m = m_1 + m_2$, except when $m = \pm(j_1+j_2)$ when both angular momenta have maximal projections up/down the z axis. For instance, if $m = j_1 + j_2 - 2$, there are three product kets: $(m_1 = j_1, m_2 = j_2 - 2)$, $(m_1 = j_1 - 1, m_2 = j_2 - 1)$, and $(m_1 = j_1 - 2, m_2 = j_2)$. In each of the degenerate eigenspaces of J_z, we must choose a basis that diagonalizes J^2 (and undiagonalizes J_{1z} and J_{2z}). We can do this by constructing the matrix J^2 and then diagonalizing it. But this can be a tedious business. (If you have done Exercise 15.1.1 you will know that the construction of S^2 is quite tedious even in this four-dimensional case.) There is, however, a more efficient alternative to be described now.

As a first step, we need to know the allowed values for j. Our intuition and our experience from the last section suggest that j can take on values $j_1 + j_2$,

‡ The description here is oversimplified; both $\mathscr{H}_{hf}$ and H_{hf} are rather tricky to derive. Our aim is just to estimate $|A|$ and not to get into its precise origin.

$j_1+j_2-1, \ldots, j_1-j_2$ (assuming $j_1 \geq j_2$).‡ Let us check this. The number of product kets is $(2j_1+1)\cdot(2j_2+1)$. This must equal the number of total-j kets. According to our conjecture, this number is

$$\sum_{j=j_1-j_2}^{j_1+j_2}(2j+1)=\sum_{j=0}^{j_1+j_2}(2j+1)-\sum_{j=0}^{j_1-j_2-1}(2j+1)=(2j_1+1)(2j_2+1) \qquad (15.2.2)$$

using the formula

$$\sum_{n=0}^{N} n=\frac{N(N+1)}{2}$$

We take this to be proof of our conjecture:

$$j_1 \otimes j_2=(j_1+j_2)\oplus(j_1+j_2-1)\oplus\cdots\oplus(j_1-j_2) \qquad (15.2.3)$$

In other words, the total-j kets are

$$|jm, j_1 j_2\rangle \quad \text{with} \quad j_1+j_2 \geq j \geq j_1-j_2, \qquad j \geq m \geq -j \qquad (15.2.4)$$

Let us write them in the form of an array:

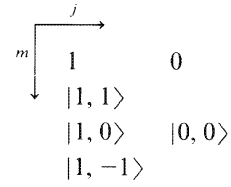
$$\begin{array}{c|lll}
 & j_1+j_2 & j_1+j_2-1 & \cdots \quad j_1-j_2 \\
 & |j_1+j_2, j_1+j_2\rangle & & \\
 & |j_1+j_2, j_1+j_2-1\rangle & |j_1+j_2-1, j_1+j_2-1\rangle & \\
 & |j_1+j_2, j_1+j_2-2\rangle & |j_1+j_2-1, j_1+j_2-2\rangle & |j_1-j_2, j_1-j_2\rangle \\
 & \vdots & \vdots & \cdots \quad \vdots \\
 & |j_1+j_2, -(j_1+j_2-2)\rangle & |j_1+j_2-1, -(j_1+j_2-2)\rangle & |j_1-j_2, -(j_1-j_2)\rangle \\
 & |j_1+j_2, -(j_1+j_2-1)\rangle & |j_1+j_2-1, -(j_1+j_2-1)\rangle & \\
 & |j_1+j_2, -(j_1+j_2)\rangle & &
\end{array} \qquad (15.2.5)$$

(Note that the labels $j_1 j_2$ are suppressed on the total-j kets. We shall do so frequently to simplify the notation.)

Our problem is to express each of these kets as a linear combination of product kets. To get an idea of how one goes about doing this, let us consider the problem

‡ There is no loss of generality, for we can always call the larger one j_1.

solved in the last section ($j_1 = j_2 = 1/2$). In this case the states are



Consider the *top state* in the first column, $|1, 1\rangle$, which has the largest possible z component. There is only one product state with the right value of m, namely, both spins up. So by inspection,

$$|1, 1\rangle = |{+}{+}\rangle$$

We can multiply the right-hand side by a phase factor, but we follow the convention, called the *Condon–Shortley convention*, in which the coefficient of this top state is chosen to be unity. Consider next the state below this one, namely, $|1, 0\rangle$. There are two product states with $m = 0$, namely, $|{+}{-}\rangle$ and $|{-}{+}\rangle$; and $|1, 0\rangle$ must be a linear combination of these. We find the combination as follows. We know that‡

$$S_-|1, 1\rangle = 2^{1/2}\hbar|1, 0\rangle$$

so that

$$|1, 0\rangle = \frac{1}{2^{1/2}\hbar} S_-|1, 1\rangle$$

But we do not want $|1, 0\rangle$ in terms of $|1, 1\rangle$, we want it in terms of the product kets. So we rewrite the right-hand side as

$$= \frac{1}{2^{1/2}\hbar}(S_{1-} + S_{2-})|{+}{+}\rangle = \frac{1}{2^{1/2}\hbar}(\hbar|{-}{+}\rangle + \hbar|{+}{-}\rangle)$$

so that

$$|1, 0\rangle = 2^{-1/2}(|{+}{-}\rangle + |{-}{+}\rangle)$$

in accordance with our earlier result.

The next state $|1, -1\rangle$ can be obtained by lowering this one more step in the above sense, or more simply by noting that there is only one ket with m maximally negative, namely, $|{-}{-}\rangle$. So

$$|1, -1\rangle = |{-}{-}\rangle$$

Our phase convention is such that this is what you would get if you lowered $|1, 0\rangle$.

‡ Recall $J_\pm|j, m\rangle = \hbar[(j \mp m)(j \pm m + 1)]^{1/2}|j, m \pm 1\rangle$.

This takes care of the $j=1$ states. Consider next $j=0$. The state $|0,0\rangle$ has $m=0$ and is also a linear combination of $|+-\rangle$ and $|-+\rangle$. We find the combination using two constraints: (1) The combination must be orthogonal to the one that forms the other state with $m=0$, namely, $|1,0\rangle$ and have real coefficients.‡ (2) The combination is normalized to unity. If we call the combination $\alpha|+-\rangle+\beta|-+\rangle$, these constraints tell us that

$$\alpha+\beta=0$$
$$\alpha^2+\beta^2=1$$

It follows that

$$|0,0\rangle=2^{-1/2}(|+-\rangle-|-+\rangle)$$

Note that we could still have multiplied the state by (-1). Our convention is as follows: in each column in Eq. (15.2.5) the top state is given the overall sign which makes the coefficient of the product ket with $m_1=j_1$ positive.

Let us now turn to the general problem, Eq. (15.2.5). Once again the top state in the first column, with m equal to its maximum value of j_1+j_2, can be built out of only one product ket, the one in which both angular momenta take on maximum possible projections along the z axis:

$$|j_1+j_2,j_1+j_2\rangle=|j_1j_1,j_2j_2\rangle \tag{15.2.6}$$

The other m states at this value of j are obtained by lowering. Let us consider going down just one step. Since

$$J_-|j_1+j_2,j_1+j_2\rangle=\hbar[2(j_1+j_2)]^{1/2}|j_1+j_2,j_1+j_2-1\rangle$$

we have, as in the spin-$(1/2\otimes 1/2)$ problem

$$\begin{aligned}
&|j_1+j_2,j_1+j_2-1\rangle \\
&\quad=\frac{1}{[2(j_1+j_2)]^{1/2}\hbar}\cdot(J_{1-}+J_{2-})|j_1j_1,j_2j_2\rangle \\
&\quad=\frac{1}{[2(j_1+j_2)]^{1/2}\hbar}[\hbar(2j_1)^{1/2}|j_1(j_1-1),j_2j_2\rangle+\hbar(2j_2)^{1/2}|j_1j_1,j_2(j_2-1)\rangle] \\
&\quad=\left(\frac{j_1}{j_1+j_2}\right)^{1/2}|j_1(j_1-1),j_2j_2\rangle+\left(\frac{j_2}{j_1+j_2}\right)^{1/2}|j_1j_1,j_2(j_2-1)\rangle
\end{aligned} \tag{15.2.7}$$

Proceeding in this manner we can get to the bottom state in the first column.§

Now for the top state in the second column. Since it has $m=j_1+j_2-1$, there are two product kets that are eligible to enter the linear combination; they are

‡ This is a matter of convention.

§ In practice one goes only to $m=0$. The states of negative m can be found using special properties of the expansion, to be discussed shortly.

$|j_1 j_1, j_2(j_2-1)\rangle$ and $|j_1(j_1-1), j_2 j_2\rangle$. The combination must be normalized to unity, be orthogonal to the other state formed out of these kets, namely, $|j_1+j_2, j_1+j_2-1\rangle$ [see Eq. (15.2.7)], and by convention have real coefficients. The answer is, by inspection,

$$|j_1+j_2-1, j_1+j_2-1\rangle = \left(\frac{j_1}{j_1+j_2}\right)^{1/2} |j_1 j_1, j_2(j_2-1)\rangle - \left(\frac{j_2}{j_1+j_2}\right)^{1/2} |j_1(j_1-1), j_2 j_2\rangle \tag{15.2.8}$$

The overall sign is fixed by requirement that the coefficient of the product ket with $m_1 = j_1$ be positive. Given the top state, the rest of the second column may be obtained by lowering. Let us go just one more column. The top state in the third column, $|j_1+j_2-2, j_1+j_2-2\rangle$, can be a superposition of three product kets. The three (real) coefficients are determined by these three requirements: orthogonality to the two preceding total-j kets of the same m, and unit normalization. It is clear that there are always enough constraints to determine the top states of each column, and once the top states are known, the rest follow by lowering.

Exercise 15.2.1. (1) Verify that $|j_1 j_1, j_2 j_2\rangle$ is indeed a state of $j = j_1 + j_2$ by letting $J^2 = J_1^2 + J_2^2 + 2J_{1z}J_{2z} + J_{1+}J_{2-} + J_{1-}J_{2+}$ act on it.

(2) (optional) Verify that the right-hand side of Eq. (15.2.8) indeed has angular momentum $j = j_1 + j_2 - 1$.

Clebsch–Gordan (CG) Coefficients

The completeness of the product kets allows us to write the total-j kets as

$$|jm, j_1 j_2\rangle = \sum_{m_1, m_2} \sum |j_1 m_1, j_2 m_2\rangle \langle j_1 m_1, j_2 m_2 | jm, j_1 j_2\rangle$$

The coefficients of the expansion

$$\langle j_1 m_1, j_2 m_2 | jm, j_1 j_2\rangle \equiv \langle j_1 m_1, j_2 m_2 | jm\rangle$$

are called *Clebsch–Gordan coefficients* or *vector addition coefficients*. (Since the labels $j_1 j_2$ appear in the bra, we suppress them in the ket.) Here are some properties of these coefficients:

(1) $\langle j_1 m_1, j_2 m_2 | jm\rangle \neq 0$ only if $j_1 - j_2 \leq j \leq j_1 + j_2$ (15.2.9)

(This is called the *triangle inequality*, for geometrically it means that we must be able to form a triangle with sides j_1, j_2, and j).

(2) $\langle j_1 m_1, j_2 m_2 | jm\rangle \neq 0$ only if $m_1 + m_2 = m$ (15.2.10)

(3) they are real (conventional)

(4) $\langle j_1 j_1, j_2(j-j_1)|jj\rangle$ is positive (conventional)

(This condition fixes the overall sign in the expansion of each top state and was invoked in the preceding discussion.)

$$(5)\quad \langle j_1 m_1, j_2 m_2|jm\rangle = (-1)^{j_1+j_2-j}\langle j_1(-m_1), j_2(-m_2)|j(-m)\rangle \tag{15.2.11}$$

This relation halves the work we have to do: we start at the top state and work our way down to $m=0$ (or $1/2$ if j is half-integral). The coefficients for the negative m states are then determined by this relation.

*Exercise 15.2.2.** Find the CG coefficients of

(1) $\frac{1}{2}\otimes 1 = \frac{3}{2}\oplus\frac{1}{2}$

(2) $1\otimes 1 = 2\oplus 1\oplus 0$

Exercise 15.2.3. Argue that $\frac{1}{2}\otimes\frac{1}{2}\otimes\frac{1}{2} = \frac{3}{2}\oplus\frac{1}{2}\oplus\frac{1}{2}$.

If we assemble the CG coefficients into a matrix, we find it is orthogonal (real and unitary). This follows from the fact that it relates one orthonormal basis to another. If we invert the matrix, we can write the product kets in terms of total-j kets. The coefficients in this expansion are also CG coefficients:

$$\langle jm|j_1 m_1, j_2 m_2\rangle = \langle j_1 m_1, j_2 m_2|jm\rangle^* = \langle j_1 m_1, j_2 m_2|jm\rangle$$

because the CG coefficients are real. As an example, consider the $\frac{1}{2}\otimes\frac{1}{2}$ problem. There we have

$$\begin{matrix} |jm\rangle \\ \begin{bmatrix} |1,1\rangle \\ |1,0\rangle \\ |1,-1\rangle \\ |0,0\rangle \end{bmatrix} \end{matrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/2^{1/2} & 1/2^{1/2} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1/2^{1/2} & -1/2^{1/2} & 0 \end{bmatrix} \begin{matrix} |m_1 m_2\rangle \\ \begin{bmatrix} |{+}{+}\rangle \\ |{+}{-}\rangle \\ |{-}{+}\rangle \\ |{-}{-}\rangle \end{bmatrix} \end{matrix}$$

(Notice that the columns contain not the components of vectors, but the basis vectors themselves.) We can invert this relation to get

$$\begin{bmatrix} |{+}{+}\rangle \\ |{+}{-}\rangle \\ |{-}{+}\rangle \\ |{-}{-}\rangle \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/2^{1/2} & 0 & 1/2^{1/2} \\ 0 & 1/2^{1/2} & 0 & -1/2^{1/2} \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} |1,1\rangle \\ |1,0\rangle \\ |1,-1\rangle \\ |0,0\rangle \end{bmatrix}$$

Thus we can write

$$|+-\rangle = 2^{-1/2}(|1, 0\rangle + |0, 0\rangle)$$

etc. In practice one uses CG coefficients to go both ways, from the product to the total-j basis and vice versa.

Addition of L and S

Consider an electron bound to a proton in a state of orbital angular moment l. Since the electron has spin $1/2$, its total angular momentum $\mathbf{J}=\mathbf{L}+\mathbf{S}$ can have values of $j=l\pm 1/2$. We wish to express the total-j states in terms of product states $|lm_o, sm_s\rangle$.‡ Since $m_s=\pm 1/2$, at each m there will be at the most two eligible product kets.§ Let

$$|j=l+1/2, m\rangle = \alpha|l, m-1/2; 1/2, 1/2\rangle + \beta|l, m+1/2; 1/2, -1/2\rangle \tag{15.2.12}$$

$$|j=l-1/2, m\rangle = \alpha'|l, m-1/2; 1/2, 1/2\rangle + \beta'|l, m+1/2; 1/2, -1/2\rangle \tag{15.2.13}$$

The requirement that these states be orthonormal tells us that

$$\alpha^2+\beta^2=1 \tag{15.2.14}$$

$$\alpha'^2+\beta'^2=1 \tag{15.2.15}$$

$$\alpha\alpha'+\beta\beta'=0 \tag{15.2.16}$$

So we only need one more constraint, say the ratio α/β. We find it by demanding that

$$J^2|j=l+1/2, m\rangle = \hbar^2(l+1/2)(l+3/2)|j=l+1/2, m\rangle \tag{15.2.17}$$

Writing

$$J^2 = L^2+S^2+2L_zS_z+L_-S_++L_+S_- \tag{15.2.18}$$

we can deduce that

$$\frac{\beta}{\alpha}=\left(\frac{l+1/2-m}{l+1/2+m}\right)^{1/2} \tag{15.2.19}$$

‡ Here, m_o, m_s, and m stand for orbital, spin, and total projections along the z axis.

§ It might help to construct the table as in Eq. (15.2.5). It will contain just two columns, one for $j=l+1/2$ and one for $j=l-1/2$.

Given this, and our convention for the overall sign,

$$|j=l\pm 1/2, m\rangle = \frac{1}{(2l+1)^{1/2}}\left[\pm(l+1/2\pm m)^{1/2}|l, m-1/2; 1/2, 1/2\rangle\right.$$
$$\left.+(l+1/2\mp m)^{1/2}|l, m+1/2; 1/2, -1/2\rangle\right] \qquad (15.2.20)$$

[Notice that if $j=l+1/2$, $m=\pm(l+1/2)$; only one term survives with unit coefficient.] If the Hamiltonian contains just the Coulomb interaction, or, in addition, an interaction with a weak constant magnetic field, the product basis is adequate. The total-j basis will come in handy when we study the spin–orbit interaction [which involves the operator $\mathbf{L}\cdot\mathbf{S}=\frac{1}{2}(J^2-L^2-S^2)$] in Chapter 17.

Exercise 15.2.4. Derive Eqs. (15.2.19) and (15.2.20).

*Exercise 15.2.5.** (1) Show that $\mathbb{P}_1=\frac{3}{4}I+(\mathbf{S}_1\cdot\mathbf{S}_2)/\hbar^2$ and $\mathbb{P}_0=\frac{1}{4}I-(\mathbf{S}_1\cdot\mathbf{S}_2)/\hbar^2$ are projection operators, i.e., obey $\mathbb{P}_i\mathbb{P}_j=\delta_{ij}\mathbb{P}_j$ [use Eq. (14.3.39)].

(2) Show that these project into the spin-1 and spin-0 spaces in $\frac{1}{2}\otimes\frac{1}{2}=1\oplus 0$.

Exercise 15.2.6. Construct the project operators $\mathbb{P}_\pm$ for the $j=l\pm 1/2$ subspaces in the addition $\mathbf{L}+\mathbf{S}=\mathbf{J}$.

Exercise 15.2.7. Show that when we add j_1 to j_1, the states with $j=2j_1$ are symmetric. Show that the states with $j=2j_1=1$ are antisymmetric. (Argue for the symmetry of the top states and show that lowering does not change symmetry.) This pattern of alternating symmetry continues as j decreases, but is harder to prove.

The Modified Spectroscopic Notation

In the absence of spin, it is sufficient to use a single letter such as $s, p, d, \ldots$ to denote the (orbital) angular momentum of a particle. In the presence of spin one changes the notation as follows:

(1) Use capital letters $S, P, D, \ldots$ (let us call a typical letter L), to indicate the value of the orbital angular momentum.
(2) Append a *sub*script J to the right of L to indicate the j value.
(3) Append a *super*script $2S+1$ to the left of L to indicate the multiplicity due to spin projections.

Thus, for example

$$^{2S+1}L_J = {}^2P_{3/2}$$

denotes a state with $l=1$, $s=1/2$, $j=3/2$. For a single electron the $2S+1$ label is redundant and always equals 2. For a multielectron system, S and L stand

for total spin and total orbital angular momentum, and J for their sum. Thus in the ground state of He,

$$^{2S+1}L_J = {}^1S_0$$

15.3. Irreducible Tensor Operators

We have already discussed scalar and vector operators. A scalar operator S transforms like a scalar under rotations, i.e., remains invariant:

$$S \to S' = U^\dagger[R] S U[R] = S \tag{15.3.1}$$

By considering arbitrary infinitesimal rotations we may deduce that

$$[J_i, S] = 0$$

or in a form that will be used later

$$\begin{aligned} [J_+, S] &= 0 \\ [J_z, S] &= 0 \end{aligned} \tag{15.3.2}$$

Examples of S are rotationally invariant Hamiltonians such as the Coulomb or isotropic oscillator Hamiltonian. A vector operator $\mathbf{V}$ was defined as a collection of three operators (V_x, V_y, V_z) which transform as the components of a vector in $\mathbb{V}^3(R)$:

$$V_i \to V_i' = U^\dagger[R] V_i U[R] = \sum_j R_{ij} V_j \tag{15.3.3}$$

where R is the usual 3×3 rotation matrix. By considering infinitesimal rotations, we may deduce that [Eq. (12.4.14)]:

$$[V_i, J_j] = i\hbar \sum_k \varepsilon_{ijk} V_k \tag{15.3.4}$$

Let us rewrite Eq. (15.3.3) in an equivalent form. Replace R by $R^{-1} = R^T$ everywhere to get

$$U[R] V_i U^\dagger[R] = \sum_j R_{ji} V_j \tag{15.3.5}$$

Notice that we are summing now over the first index of R. This seems peculiar, for we are accustomed to the likes of Eq. (15.3.3) where the sum is over the second index. The relation of Eq. (15.3.3) to Eq. (15.3.5) is the following. Let $|1\rangle$, $|2\rangle$, and $|3\rangle$ be basis kets in $\mathbb{V}^3(R)$ and R a rotation operator on it. If $|V\rangle$ is some vector

with components $v_i = \langle i|V\rangle$, its rotated version $|V'\rangle = R|V\rangle$ has components

$$v_i' = \langle i|R|V\rangle = \sum_j \langle i|R|j\rangle\langle j|V\rangle = \sum_j R_{ij}v_j \tag{15.3.6}$$

If instead we ask what R does to the basis, we find $|i\rangle \to |i'\rangle = R|i\rangle$ where

$$|i'\rangle = R|i\rangle = \sum_j |j\rangle\langle j|R|i\rangle = \sum_j R_{ji}|j\rangle \tag{15.3.7}$$

Since $R_{ji} = (R^{-1})_{ij}$, we see that vector components and the basis vectors transform in "opposite" ways. Equation (15.3.3) defines a vector operator as one whose components transform under $V_i \to U^\dagger V_i U$ as do *components* of a vector $|V\rangle$ under $|V\rangle \to R|V\rangle$, while Eq. (15.3.5) defines it as one whose components V_i transform under $V_i \to UV_iU^\dagger$ as do the *kets* $|i\rangle$ under $|i\rangle \to R|i\rangle$. Both definitions are of course equivalent. The first played a prominent role in the past and the second will play a prominent role in what follows.

Tensor Operators

We know that a vector $|V\rangle$ is an element of $\mathbb{V}^3(R)$, i.e., may be written as

$$|V\rangle = \sum_{i=1}^{3} v_i|i\rangle \tag{15.3.8}$$

in terms of its components v_i and the basis kets $|i\rangle$. A *second-rank tensor* $|T^{(2)}\rangle$ is an element of the direct product space $\mathbb{V}^3(R)\otimes\mathbb{V}^3(R)$, spanned by the nine kets $|i\rangle\otimes|j\rangle$:

$$|T^{(2)}\rangle = \sum_{i=1}^{3}\sum_{j=1}^{3} t_{ij}|i\rangle\otimes|j\rangle \tag{15.3.9}$$

One refers to t_{ij} as the components of $|T^{(2)}\rangle$ in the basis $|i\rangle\otimes|j\rangle$.

As in the case of vectors, a tensor operator of rank 2 is a collection of nine operators T_{ij} which, under $T_{ij} \to U^\dagger T_{ij} U$, respond as do the tensor components t_{ij}, or, equivalently, under $T_{ij} \to UT_{ij}U^\dagger$, respond as do the basis kets $|i\rangle\otimes|j\rangle$. Tensors and tensor operators of rank $n > 2$ are defined in a similar way. (Note that a vector may be viewed as a tensor of rank 1.) We shall call these tensors *Cartesian tensors*.

Of greater interest to us are objects called *spherical tensor operators. A spherical tensor operator of rank k* has $2k+1$ components T_k^q, $q = +k, (k-1), \ldots, -k$, which,

under $T_k^q \to UT_k^q U^\dagger$ respond like the angular momentum eigenkets $|j=k, m=q\rangle = |kq\rangle$‡:

$$U[R]T_k^q U^\dagger[R] = \sum_{q'} D_{q'q}^{(k)} T_k^{q'} \tag{15.3.10}$$

Since the $2k+1$ kets $|kq\rangle$ transform irreducibly, so do the operators T_k^q. For this reason, they are also called *irreducible tensor operators.*

By considering infinitesimal rotations, we may deduce from Eq. (15.3.10) that (Exercise 15.3.1):

$$\begin{aligned} [J_\pm, T_k^q] &= \pm\hbar[(k \mp q)(k \pm q + 1)]^{1/2} T_k^{q\pm 1} \\ [J_z, T_k^q] &= \hbar q T_k^q \end{aligned} \tag{15.3.11}$$

Notice that commuting a J with T_k^q is like letting J act on the ket $|kq\rangle$.

Why are irreducible tensor operators interesting? Consider the effect of acting on a state $|\alpha lm\rangle$ with T_k^q. (Here α denotes labels besides angular momentum.) Let us rotate the resulting state and see what happens:

$$\begin{aligned} U[R]T_k^q|jm\rangle &= U[R]T_k^q U^\dagger[R]U[R]|jm\rangle \\ &= \sum_{q'} D_{q'q}^{(k)} T_k^{q'} \sum_{m'} D_{m'm}^{(j)} |jm'\rangle \\ &= \sum_{q'} \sum_{m'} D_{q'q}^{(k)} D_{m'm}^{(j)} T_k^{q'} |jm'\rangle \end{aligned} \tag{15.3.12}$$

We find that $T_k^q|jm\rangle$ responds to rotations like the product ket $|kq\rangle \otimes |jm\rangle$. *Thus, when we act on a state with T_k^q, we add angular momentum (k, q) to the state.* In other words, an irreducible tensor operator T_k^q imparts a definite amount of angular momentum (k, q) to the state it acts on. This allows us to say the following about matrix elements of T_k^q between angular momentum eigenstates:

$$\langle \alpha' j' m' | T_k^q | \alpha j m \rangle = 0 \quad \text{unless} \quad k + j \geq j' \geq |k - j|, \qquad m' = m + q \tag{15.3.13}$$

This is because $T_k^q|\alpha jm\rangle$ contains only those angular momenta that can be obtained by adding (k, q) and (j, m); so $|\alpha' j' m'\rangle$ is orthogonal to $T_k^q|jm\rangle$ unless (j', m') is one of the possible results of adding (k, q) and (j, m). Equation (15.3.13) is an example of a *selection rule.*

Let us consider some examples, starting with the tensor operator of rank 0. It has only one component T_0^0, which transforms like $|00\rangle$, i.e., remains invariant.

‡ Recall that

$$\begin{aligned} |kq\rangle \to U[R]|kq\rangle &= \sum_{k'} \sum_{q'} |k'q'\rangle\langle k'q'|U[R]|kq\rangle \\ &= \sum_{q'} D_{q'q}^{(k)} |kq'\rangle \end{aligned}$$

Thus T_0^0 is just a scalar operator S, discussed earlier. Our selection rule tells us that

$$\langle \alpha' j' m' | T_0^0 | \alpha j m \rangle = 0 \quad \text{unless} \quad j = j', \qquad m = m' \tag{15.3.14}$$

Consider next T_k^q ($q = 1, 0, -1$). Here we have three objects that go into each other under rotations. Since a vector operator $\mathbf{V}$ also has three components that transform irreducibly (why?) into each other, we conjecture that some linear combinations of the vector operator components should equal each T_k^q. In fact

$$\begin{aligned} T_1^{\pm 1} &= \mp \frac{V_x \pm i V_y}{2^{1/2}} \equiv V_1^{\pm 1} \\ T_1^0 &= V_z \equiv V_1^0 \end{aligned} \tag{15.3.15}‡$$

Given Eq. (15.3.4) and the above definitions, it may be readily verified that $V_1^{\pm 1}$ and V_1^0 obey Eq. (15.3.11) with $k = 1$, $q = \pm 1, 0$. The selection rule for, say, V_x is

$$\begin{aligned} \langle \alpha' j' m' | V_x | \alpha j m \rangle &= \langle \alpha' j' m' | \frac{V_1^{-1} - V_1^1}{2^{1/2}} | \alpha j m \rangle \\ &= 0 \quad \text{unless} \quad j + 1 \geq j' \geq |j - 1|, \qquad m' = m \pm 1 \end{aligned} \tag{15.3.16a}$$

and likewise

$$\begin{aligned} \langle \alpha' j' m' | V_z | \alpha j m \rangle &= \langle \alpha' j' m' | V_1^0 | \alpha j m \rangle \\ &= 0 \quad \text{unless} \quad j + 1 \geq j' \geq |j - 1|, \qquad m' = m \end{aligned} \tag{15.3.16b}$$

Once we go beyond rank 1, it is no longer possible to express Cartesian and spherical tensors *of the same rank* in terms of each other. A Cartesian tensor of rank n has 3^n components, whereas a spherical tensor of rank k has $(2k + 1)$ components. For $n = 0$ and $n = 1$, the Cartesian tensors happened to have the same number of components as spherical tensors of rank $k = 0$ and 1, respectively, and *also transformed irreducibly*. But consider higher ranks, say rank 2. The tensor T_2^q has *five* components that transform irreducibly. The tensor T_{ij} has *nine* components which transform reducibly, i.e., it is possible to form combinations of T_{ij} such that some of them never mix with others under rotations. There is one combination that is invariant, i.e., transforms like T_0^0; there are three combinations that transform like a vector or in light of Eq. (15.3.15) like T_1^q; and finally there are five that transform like T_2^q. We will see what these combinations are when we study the degeneracy of the isotropic oscillator of a few pages hence. Cartesian tensors of higher rank are likewise reducible. Let us now return to the selection rule, Eq. (15.3.13).

We can go a step further and relate the nonvanishing matrix elements. Consider the concrete example of R_1^q, the position operator in spherical form. We have

‡ In the special case $\mathbf{V} = \mathbf{J}$, $J_1^{\pm 1} = \mp (J_x \pm J_y)/2^{1/2} = \mp J_\pm / 2^{1/2}$ and $J_1^0 = J_z$.

(assuming no spin, so $\mathbf{J}=\mathbf{L}$)

$$\begin{aligned}
&\langle \alpha_2 l_2 m_2 | R_1^q | \alpha_1 l_1 m_1 \rangle \\
&= \int R^*_{\alpha_2 l_2}(r)\, Y^{m_2}_{l_2}{}^*(\theta,\phi) r \left(\frac{4\pi}{3}\right)^{1/2} Y_1^q R_{\alpha_1 l_1}(r)\, Y^{m_1}_{l_1}(\theta,\phi) r^2\, dr\, d\Omega \\
&= \left(\frac{4\pi}{3}\right)^{1/2} \int R^*_{\alpha_2 l_2} r R_{\alpha_1 l_1} r^2\, dr \cdot \int Y^{m_2}_{l_2}{}^* Y_1^q Y^{m_1}_{l_1}\, d\Omega \\
&= \langle \alpha_2 l_2 | \,|R_1|\, | \alpha_1 l_1 \rangle \cdot \langle l_2 m_2 | 1q, l_1 m_1 \rangle \qquad (15.3.17)\ddagger
\end{aligned}$$

where $\langle \alpha_2 l_2 | \,|R_1|\, | \alpha_1 l_1 \rangle$, the *reduced matrix element*, is independent of m_1, m_2, and q, which appear only in the CG coefficient, which is essentially the angular integral (up to a factor independent of m_1, m_2, and q).

This example illustrates a general result (not proven here):

$$\langle \alpha_2 j_2 m_2 | T_k^q | \alpha_1 j_1 m_1 \rangle = \langle \alpha_2 j_2 | \,|T_k|\, | \alpha_1 j_1 \rangle \cdot \langle j_2 m_2 | kq, j_1 m_1 \rangle \qquad (15.3.18)$$

This is called the *Wigner–Eckart* theorem. It separates the dependence of the matrix element on spatial orientation (on m_2, m_1, and q) from the rest. The former is expressed entirely in terms of the CG coefficients.

Exercise 15.3.1. (1) Show that Eq. (15.3.11) follows from Eq. (15.3.10) when one considers infinitesimal rotations. (Hint: $D^{(k)}_{q'q} = \langle kq' | I - (i\delta\boldsymbol{\theta}\cdot\mathbf{J})/\hbar | kq \rangle$. Pick $\delta\boldsymbol{\theta}$ along, say, the x direction and then generalize the result to the other directions.)

(2) Verify that the spherical tensor V_1^q constructed out of $\mathbf{V}$ as in Eq. (15.3.15) obeys Eq. (15.3.11).

Exercise 15.3.2. It is claimed that $\sum_q (-1)^q S_k^q T_k^{(-q)}$ is a scalar operator.

(1) For $k=1$, verify that this is just $\mathbf{S}\cdot\mathbf{T}$.

(2) Prove it in general by considering its response to a rotation. [Hint: $D^{(j)}_{-m,-m'} = (-1)^{m-m'} (D^{(j)}_{m,m'})^*$.]

Exercise 15.3.3. (1) Using $\langle jj | jj, 10 \rangle = [j/(j+1)]^{1/2}$ show that

$$\langle \alpha j | \,|J_1|\, | \alpha' j' \rangle = \delta_{\alpha\alpha'} \delta_{jj'} \hbar [j(j+1)]^{1/2}$$

(2) Using $\mathbf{J}\cdot\mathbf{A} = J_z A_z + \frac{1}{2}(J_- A_+ + J_+ A_-)$ (where $A_\pm = A_x \pm i A_y$) argue that

$$\langle \alpha' jm' | \mathbf{J}\cdot\mathbf{A} | \alpha jm \rangle = c \langle \alpha' j | \,|A|\, | \alpha j \rangle$$

where c is a constant independent of α, α' and $\mathbf{A}$. Show that $c = \hbar[j(j+1)]^{1/2} \delta_{m,m'}$.

(3) Using the above, show that

$$\langle \alpha' jm' | A^q | \alpha jm \rangle = \frac{\langle \alpha' jm | \mathbf{J}\cdot\mathbf{A} | \alpha jm \rangle}{\hbar^2 j(j+1)} \langle jm' | J^q | jm \rangle \qquad (15.3.19)$$

‡ Note that R_1^q is the tensor operator and $R_{\alpha l}(r)$ is the radial part of the wave function. We have also used Eq. (12.5.42) to obtain R_1^q.

*Exercise 15.3.4.** (1) Consider a system whose angular momentum consists of two parts $\mathbf{J}_1$ and $\mathbf{J}_2$ and whose magnetic moment is

$$\boldsymbol{\mu} = \gamma_1 \mathbf{J}_1 + \gamma_2 \mathbf{J}_2$$

In a state $|jm, j_1 j_2\rangle$ show, using Eq. (15.3.19), that

$$\langle \mu_x \rangle = \langle \mu_y \rangle = 0$$

$$\langle \mu_z \rangle = m\hbar \left[\frac{\gamma_1 + \gamma_2}{2} + \frac{(\gamma_1 - \gamma_2)}{2} \frac{j_1(j_1+1) - j_2(j_2+1)}{j(j+1)} \right]$$

(2) Apply this to the problem of a proton ($g = 5.6$) in a $^2P_{1/2}$ state and show that $\langle \mu_z \rangle = \pm 0.26$ nuclear magnetons.

(3) For an electron in a $^2P_{1/2}$ state show that $\langle \mu_z \rangle = \pm \frac{1}{3}$ Bohr magnetons.

*Exercise 15.3.5.** Show that $\langle jm | T_k^q | jm \rangle = 0$ if $k > 2j$.

15.4. Explanation of Some "Accidental" Degeneracies

In this section the degeneracy of states of different l at a given value of n in the hydrogen atom and the isotropic oscillator (see Section 12.6) will be explained. But first let us decide what it means to explain any degeneracy. Consider for example the $(2l+1)$-fold degeneracy of the different m states at a given l in both these problems. We explain it in terms of the rotational invariance of the Hamiltonian as follows:

(1) For every rotation $R(\boldsymbol{\theta})$ on $\mathbb{V}^3(R)$ there exists a unitary operator $U[R]$ which rotates the vector operators

$$U^\dagger V_i U = \sum_j R_{ij} V_j \tag{15.4.1}$$

If the Hamiltonian depends only on the "lengths" of various vector operators like $\mathbf{P}$, $\mathbf{R}$, $\mathbf{L}$ etc., then it is rotationally invariant:

$$U^\dagger H U = H \tag{15.4.2}$$

i.e., rotations are symmetries of H. This is the case for the two problems in question.

(2) If we write this relation in infinitesimal form, we find

$$[H, L_i] = 0, \qquad i = 1, 2, 3 \tag{15.4.3}$$

where L_i are the generators of rotation. For every free parameter that defines a rotation (θ_x, θ_y, and θ_z) there is a corresponding generator. They are all conserved.

(3) From the three generators we construct the operator

$$L_- = L_x - iL_y \tag{15.4.4}$$

which lowers the m value:

$$L_-|l, m\rangle = c|l, m-1\rangle \tag{15.4.5}$$

Since $[L, H]=0$, the lowering operation does not change the energy.

This explains the degeneracy in m, for, starting with the state of highest m at a given l, we can go down all the way to the lowest m without changing the energy. (We can equally well work with L_+.)

Let us try to do the same for the two problems in question. We follow these steps:

Step (1): Identify symmetries of H besides rotational invariance.
Step (2): Find the generators of the symmetry transformations.
Step (3): Construct an operator from these generators that can change l by one unit in the case of hydrogen and two units in the case of the oscillator.

Hydrogen

Steps (1) and (2). Unfortunately the only obvious symmetry of the Coulomb Hamiltonian is rotational invariance. The additional symmetry, the one we are after, is very subtle and clearest in momentum space. We will not discuss it. But how then do we go to step (2)? The answer lies in the fact that the generators of the symmetry are conserved quantities. Now we have seen that the Coulomb problem admits an extra conserved quantity, the Runge–Lenz vector. Thus the three components of

$$\mathbf{N} = \frac{1}{2m}(\mathbf{P}\times\mathbf{L} - \mathbf{L}\times\mathbf{P}) - \frac{e^2\mathbf{R}}{(X^2+Y^2+Z^2)^{1/2}} \tag{15.4.6}$$

must be the generators of the additional symmetry transformations (or linear combinations thereof).

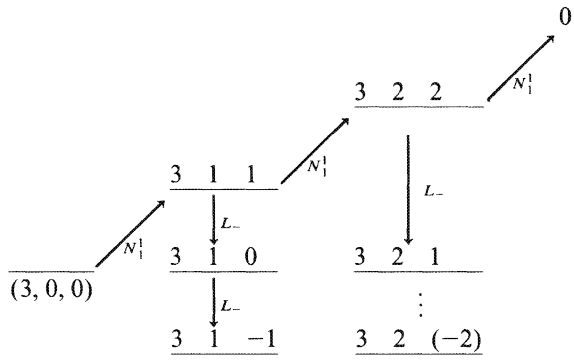
Step (3). Since we wish to talk about angular momentum let us write $\mathbf{N}$ in spherical form:

$$N_1^{\pm 1} = \mp\frac{N_x \pm iN_y}{2^{1/2}}$$
$$N_1^0 = N_z \tag{15.4.7}$$

Consider the state $|nll\rangle$ of the H-atom. Acting on it with N_1^1, we get another state of the same energy or same n (since $[H, N_1^1]=0$) but with higher angular momentum: $N_1^1|nll\rangle$ behaves as $|11\rangle\otimes|ll\rangle = |l+1, l+1\rangle$. So

$$N_1^1|n, l, l\rangle = c|n, l+1, l+1\rangle \tag{15.4.8}$$

(It will turn out that c vanishes when $l=l_{\max}=n-1$.) Using N_1^1 we can connect all the different l states at a given n, and using L_- we can connect all the m states at a given l. For example, at $n=3$ the network that connects degenerate states is as follows:



The Oscillator

Step (1). To find the extra symmetry of H, let us look at it again:

$$H=\frac{P_x^2+P_y^2+P_z^2}{2\mu}+\frac{1}{2}\mu\omega^2(X^2+Y^2+Z^2) \tag{15.4.9}$$

We say H is rotationally invariant because it depends only on the lengths squared of the (real) vectors $\mathbf{P}$ and $\mathbf{R}$. Let us now rewrite H in a way that reveals the extra symmetry. Define a *complex vector* (operator) whose real and imaginary parts are proportional to $\mathbf{R}$ and $\mathbf{P}$:

$$\mathbf{a}=\frac{1}{(2\mu\omega\hbar)^{1/2}}(\mu\omega\mathbf{R}+i\mathbf{P}) \tag{15.4.10}$$

and its adjoint, whose components are complex conjugates of those of $\mathbf{a}$:

$$\mathbf{a}^\dagger=\frac{1}{(2\mu\omega\hbar)^{1/2}}(\mu\omega\mathbf{R}-i\mathbf{P}) \tag{15.4.11}$$

The components of $\mathbf{a}$ and $\mathbf{a}^\dagger$ are just the lowering and raising operators for the x, y, and z oscillators. They obey

$$[a_i, a_j^\dagger]=\delta_{ij}$$

In terms of $\mathbf{a}$ and $\mathbf{a}^\dagger$,

$$H=\hbar\omega(\mathbf{a}^\dagger\cdot\mathbf{a}+3/2) \tag{15.4.12}$$

Thus we find that H is a function of the length squared of a *complex* three-dimensional vector $\mathbf{a}$. So it is invariant under "rotations" in $\mathbb{V}^3(C)$, i.e., under unitary transformations in $\mathbb{V}^3(C)$. Just as we denoted the rotations in $\mathbb{V}^3(R)$ by R, let us call these C.‡ For every "rotation" C (unitary transformation) in $\mathbb{V}^3(C)$, there will exist Hilbert space operators $U[C]$ which rotate the complex vector operator $\mathbf{a}$:

$$a_i\to a_i'=U^\dagger[C]a_iU[C]=\sum_j C_{ij}a_j \tag{15.4.13}$$

where C_{ij} are matrix elements of the unitary operator C in $\mathbb{V}^3(C)$. Since H depends only on the norm squared of $\mathbf{a}$,

$$U^\dagger[C]HU[C]=H \tag{15.4.14}$$

Step (2). How many generators of $U[C]$ are there and what are they? The answer to the first part is the number of parameters that define a rotation in $\mathbb{V}^3(C)$, i.e., the number of independent parameters in a 3×3 unitary matrix C. Now any such matrix can be written as

$$C=e^{i\Omega} \tag{15.4.15}$$

where Ω is a 3×3 Hermitian matrix. It is easy to see that Ω has three real diagonal elements and three independent complex off-diagonal elements. Thus it depends on nine real parameters. So there are nine conserved generators. What are they? Rather than deduce them (as we did the L's by considering the effect of infinitesimal rotations on ψ) we write down the nine conserved quantities by inspection. It is clear that in the oscillator case, the nine operators

$$T_{ij}=a_i^\dagger a_j \qquad (i,j=x,y,\text{ or }z) \tag{15.4.16}$$

are conserved. The proof is simple: a_j destroys a j quantum and $a_i^\dagger$ creates an i quantum and this leaves the energy invariant since the x, y, and z oscillators have the same ω (isotropy). To see what impact T_{ij} has on l degeneracy, we must decompose T_{ij} into its irreducible parts.

Consider first the combination

$$\text{Tr } T=T_{xx}+T_{yy}+T_{zz}=a_x^\dagger a_x+a_y^\dagger a_y+a_z^\dagger a_z=\mathbf{a}^\dagger\cdot\mathbf{a} \tag{15.4.17}$$

This is clearly a scalar, i.e., transforms like T_0^0. The fact that it commutes with H does not explain the degeneracy in l because it "carries" no angular momentum. In fact $\mathbf{a}^\dagger\cdot\mathbf{a}$ is just H up to a scale factor and an additive constant.

‡ We should really be calling these U. But that will complicate the notation.

Consider next the three antisymmetric combinations

$$\begin{aligned} T_{xy}-T_{yx}&=a_x^\dagger a_y-a_y^\dagger a_x=(\mathbf{a}^\dagger\times\mathbf{a})_z\\ T_{yz}-T_{zy}&=(\mathbf{a}^\dagger\times\mathbf{a})_x\\ T_{zx}-T_{xz}&=(\mathbf{a}^\dagger\times\mathbf{a})_y \end{aligned} \tag{15.4.18}$$

These clearly transform as a vector $\mathbf{V}=\mathbf{a}^\dagger\times\mathbf{a}$. There seems to be a problem here. Suppose we form the operator $V_1^1=-(V_x+iV_y)/2^{1/2}$. Then we expect

$$V_1^1|nll\rangle=c|n,l+1,l+1\rangle \tag{15.4.19}$$

as in Eq. (15.4.8). This would mean that states differing by *one* unit in l are degenerate. But we know from Section 12.6 that states differing by *two* units in l are degenerate. So how do we get out of the fix? To find out, you must work out any one of the components of the operator $\mathbf{V}=\mathbf{a}^\dagger\times\mathbf{a}$ in terms of $\mathbf{R}$ and $\mathbf{P}$. If you do, you will see that c in Eq. (15.4.19) is really zero, and the paradox will be resolved.

We are now left with $9-1-3=5$ degrees of freedom out of the original nine T_{ij}'s. We argue that these must transform *irreducibly*. Why? Suppose the contrary is true. Then it must be possible to form irreducible tensors with fewer than five components out of these residual degrees of freedom. The only possibilities are tensors with 1 or 3 components, that is to say, scalars or vectors. But we know that given two vectors $\mathbf{a}^\dagger$ and $\mathbf{a}$ we can form only one scalar, $\mathbf{a}^\dagger\cdot\mathbf{a}$ and only one vector $\mathbf{a}^\dagger\times\mathbf{a}$, both of which we have already used up. So we are driven to the conclusion that the five residual degrees of freedom are linear combinations of some T_2^q. One usually refers to this object as the *quadrupole tensor* Q_2^q. All we need here is the component Q_2^2, since

$$Q_2^2|nll\rangle=c|n,l+2,l+2\rangle \tag{15.4.20}$$

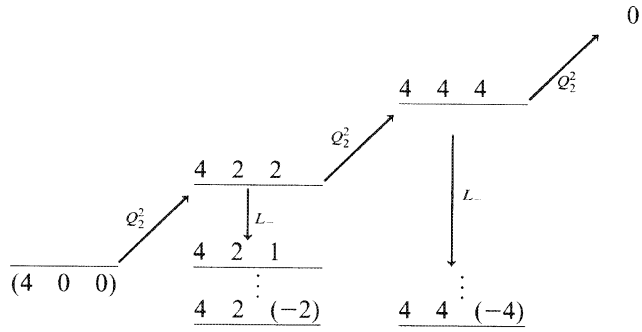
which explains the degeneracy in l at each n. (When $l=n=l_{\max}$, c vanishes.)

Let us explicitly construct the operator Q_2^2 in terms of $a_i^\dagger a_j$ to gain some experience. Now $\mathbf{a}$ and $\mathbf{a}^\dagger$ are vector operators from which we can form the tensor operators a_1^q and $(a^\dagger)_1^q$ which behave like $|1,q\rangle$. The product $a_i^\dagger a_j$ then behaves like the direct product of (linear combinations) of two spin-1 objects. Since Q_2^2 behaves like $|22\rangle$ and since $|22\rangle=|11\rangle\otimes|11\rangle$, we deduce that

$$\begin{aligned} Q_2^2&=(a^\dagger)_1^1(a_1^1)\\ &=\left(\frac{a_x^\dagger+ia_y^\dagger}{2^{1/2}}\right)\left(\frac{a_x+ia_y}{2^{1/2}}\right)\\ &=\tfrac{1}{2}[a_x^\dagger a_x-a_y^\dagger a_y+i(a_x^\dagger a_y+a_y^\dagger a_x)] \end{aligned} \tag{15.4.21}$$

Other components of Q_2^q may be constructed by similar techniques. (It is just a matter of adding angular momenta $1\otimes1$ to get 2.) Starting with the smallest value

of l at each n (namely, 0 or 1), we can move up in steps of 2 until we reach $l=n$, at which point c in Eq. (15.4.20) will vanish. The network for $n=4$ is shown below:



This completes the explanation of the degeneracy of the oscillator.

The Free-Particle Solutions

We examine the free-particle solutions from Section 12.6 in the light of the preceding discussion. Here again we have a case where states with different l, in fact an infinite number of them, are degenerate at each energy $E=\hbar^2k^2/2\mu$. This degeneracy is, however, not "accidental," since the extra symmetry of the free-particle Hamiltonian, namely, translational invariance, is obvious. We therefore have a conserved vector operator $\mathbf{P}$ from which we can form P_+,‡ which can raise l and m by one unit. Thus, given the state with $l=m=0$, we can move up in l using

$$|kll\rangle = c(P_+)^l|k00\rangle \tag{15.4.22}$$

where c is some normalization constant.

Recall that in the coordinate basis it was easy to find

$$|k00\rangle \rightarrow \psi_{k00} = \frac{U_0(\rho)}{\rho} Y_0^0 \tag{15.4.23}$$

where $\rho=kr$, and $U_0(\rho)$ is $\sin\rho$ or $-\cos\rho$ (regular or irregular solutions). It is easy to verify that

$$\begin{aligned} P_+|k00\rangle &\xrightarrow[\text{basis}]{\text{coordinate}} -i\hbar(x+iy)\frac{1}{r}\cdot\frac{d}{dr}\left[\frac{U_0(\rho)}{\rho}\right]Y_0^0 \\ &= C_1(x+iy)\frac{1}{\rho}\frac{d}{d\rho}\left[\frac{U_0(\rho)}{\rho}\right] \end{aligned} \tag{15.4.24}$$

‡ $P_+=P_x+iP_y$ is, up to a scale factor $(-2^{1/2})$ which does not change its rotational properties, just P_1^1.

where C_1 has absorbed all the factors that have no ρ dependence. If we operate once again with P_+ and use $[P_+, R_+]=0$ (where $R_+=R_x+iR_y\propto R_1^1$), we get

$$(P_+)^2|k00\rangle\rightarrow C_2(x+iy)^2\left(\frac{1}{\rho}\frac{\partial}{\partial\rho}\right)^2\frac{U_0(\rho)}{\rho} \tag{15.4.25}$$

and so finally

$$\begin{aligned}(P_+)^l|k00\rangle\rightarrow\psi_{kll}&=C_l(x+iy)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\frac{U_0(\rho)}{\rho}\\&=\tilde{C}_l(\sin\theta)^l e^{il\phi}\rho^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\frac{U_0(\rho)}{\rho}\\&=\tilde{\tilde{C}}_l Y_l^l\rho^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\frac{U_0(\rho)}{\rho}\\&=R_l Y_l^l\end{aligned} \tag{15.4.26}$$

where

$$R_l=\tilde{\tilde{C}}_l\rho^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\frac{U_0(\rho)}{\rho}=\tilde{\tilde{C}}_l\rho^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l R_0(\rho) \tag{15.4.27}$$

This agrees with Eq. (12.6.29) if we set $\tilde{\tilde{C}}_l=(-1)^l$.