Chapter 20
Addition of Angular Momenta, Clebsch-Gordan Coefficients, Vector and Tensor Operators, Wigner-Eckart Theorem

20.1 Addition of Angular Momenta and Clebsch-Gordan Coefficients

Now that we have seen how wave functions and state vectors are changed under symmetry operations, it is natural to ask how *operators* are transformed under the same operations. To do so, however, requires a slight digression. I first need to discuss the way in which angular momenta are coupled in quantum mechanics. I have already introduced the concept of coupling of orbital and spin angular momentum in Chap. 12, but want to generalize this to the coupling of any two angular momenta. For the moment let us consider two, *non-interacting* quantum systems having total angular momentum operator $\hat{J}_1$ associated with system 1 and total angular momentum operator $\hat{J}_2$ associated with system 2. Since the systems are non-interacting, the operators $\hat{J}_1$ and $\hat{J}_2$ commute and an eigenket for the combined system can be written as

$$|j_1, j_2; m_1, m_2\rangle = |j_1, m_1\rangle\, |j_2, m_2\rangle \tag{20.1}$$

which is a simultaneous eigenstate of the operators $\hat{J}_1^2, \hat{J}_2^2, \hat{J}_{1z}, \hat{J}_{2z}$.

If I form the operator

$$\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 \tag{20.2}$$

it is easy to prove that

$$\left[\hat{J}_x, \hat{J}_y\right] = i\hbar \hat{J}_z; \tag{20.3}$$

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the components of $\hat{J}$ satisfy the usual commutation laws for angular momenta. As a consequence, a simultaneous eigenket of $\hat{J}_1^2$, $\hat{J}_2^2$, $\hat{J}^2$, and $\hat{J}_z$ can also be written as $|j_1, j_2; j, m\rangle$,where j and m are the quantum numbers associated with $\hat{J}^2$ and $\hat{J}_z$. I want to relate the $|j_1, j_2; j, m\rangle$ eigenkets to the $|j_1, m_1\rangle\, |j_2, m_2\rangle$ eigenkets.

In effect, I need to see how the matrix elements of the sum operator, $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$, is related to those of the individual operators $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$. *Classically*, you know how to add two vectors $\mathbf{J}_1$ and $\mathbf{J}_2$ to get the sum vector $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$. You can prove easily that

$$|J_1 - J_2| \leq |\mathbf{J}_1 + \mathbf{J}_2| \leq J_1 + J_2. \tag{20.4}$$

Quantum-mechanically, we will find a similar condition. Classically, you can ask, "How many ways can we combine $\mathbf{J}_1 + \mathbf{J}_2$ to a given total value $\mathbf{J}$?" Clearly the z components must add, $J_{1z}+J_{2z} = J_z$. But even with this restriction there is an infinite number of ways to add the vectors together, provided they satisfy condition (20.4) with the $<$ rather than $\leq$ signs. [To see this, draw a triangle $\mathbf{J}_1 + \mathbf{J}_2 = \mathbf{J}$ in a plane. You can now rotate $\mathbf{J}_2$ around $\mathbf{J}_1$ keeping the angle between $\mathbf{J}_1$ and $\mathbf{J}_2$ constant. For each angle of rotation, $\mathbf{J}_1 + \mathbf{J}_2 = \mathbf{J}$.] At the extreme values, there is only one way to sum the vectors since they must be aligned. In quantum mechanics, there is also only one way to sum the vectors at the extreme values; however, for other than extreme values of J, there is always a *finite* rather than infinite number of ways to add the vectors to get the final vector, since angular momentum is quantized.

To relate the two bases I write

$$|j_1, j_2; j, m\rangle = \sum_{m_1, m_2} \langle j_1, j_2; m_1, m_2\, |j_1, j_2; j, m\rangle\, |j_1, j_2; m_1, m_2\rangle\,. \tag{20.5}$$

The coupling coefficients are written as

$$\langle j_1, j_2; m_1, m_2\, |j_1, j_2; j, m\rangle \equiv \langle j_1, j_2; m_1, m_2\, |j, m\rangle = \begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} \tag{20.6}$$

and are *Clebsch-Gordan coefficients.* Unconventionally, I use square brackets for the Clebsch-Gordan coefficients. The Clebsch-Gordan coefficients are given by a Mathematica function

$$\begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} = \text{ClebschGordan}\left[\{j_1, m_1\}, \{j_2, m_2\}, \{j_3, m_3\}\right]. \tag{20.7}$$

They are usually evaluated by noting first that

$$\begin{bmatrix} j_1 & j_2 & j_1 + j_2 \\ j_1 & j_2 & j_1 + j_2 \end{bmatrix} = 1 \tag{20.8}$$

(there is only one way to couple the vectors if they are aligned). One then operates with the ladder operator

$$\hat{J}_- = \hat{J}_x - i\hat{J}_y = \hat{J}_{1x} + \hat{J}_{2x} - i\left(\hat{J}_{1y} + \hat{J}_{2y}\right) = \hat{J}_{1-} + \hat{J}_{2-} \tag{20.9}$$

on Eq. (20.5) with $m = j$ to obtain a set of algebraic equations for the Clebsch-Gordan coefficients. For other values of $j \neq j_1 + j_2$ the ladder operators can be used to determine all the Clebsch-Gordan coefficients in terms of $\langle j_1 j_2, m_1 = j_1, m_2 = j - j_1 | j_1 j_2; j, j\rangle$, whose value is then fixed by normalization. The phase is chosen such that all the Clebsch-Gordan coefficients are real, implying that

$$\langle j_1, j_2; m_1, m_2 | j, m\rangle = \langle j, m | j_1, j_2; m_1, m_2\rangle . \tag{20.10}$$

In this way it is possible to get a closed form expression for all the Clebsch-Gordan coefficients in terms of a sum, which is the way Mathematica calculates these coefficients.[1] The Clebsch-Gordan coefficients are related to *3-J symbols* defined by

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} = \frac{(-1)^{j_1 - j_2 + m}}{\sqrt{2j+1}} \begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix}. \tag{20.11}$$

The 3-J symbols are, in some sense, symmetrized forms of the Clebsch-Gordan coefficients. In the "old days" one resorted to published tables of Clebsch-Gordan coefficients and 3-J symbols; now most symbolic mathematical programs have them as built-in functions. Mathematica subroutines for evaluating these functions are also listed on the book's web site.

I list some properties of Clebsch-Gordan coefficients and 3-J symbols:

$$\begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} \text{ is real;} \tag{20.12}$$

$$\begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} = 0 \quad \text{unless } m_1 + m_2 = m \text{ and } |j_2 - j_1| \leq j \leq j_1 + j_2; \tag{20.13}$$

$$\sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} \begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} \begin{bmatrix} j_1 & j_2 & j' \\ m_1 & m_2 & m' \end{bmatrix} = \delta_{j,j'} \delta_{m,m'}; \tag{20.14}$$

[1]See, for example, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N. J.,1960), Chap. 3.

$$\sum_{j=|j_2-j_1|}^{j_1+j_2} \sum_{m=-j}^{j} \begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} \begin{bmatrix} j_1 & j_2 & j \\ m_1' & m_2' & m \end{bmatrix} = \delta_{m_1,m_1'} \delta_{m_2,m_2'}; \tag{20.15}$$

$$\begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} = (-1)^{j_1+j_2-j} \begin{bmatrix} j_2 & j_1 & j \\ m_2 & m_1 & m \end{bmatrix} \tag{20.16a}$$

$$= (-1)^{j_1+j_2-j} \begin{bmatrix} j_1 & j_2 & j \\ -m_1 & -m_2 & -m \end{bmatrix} \tag{20.16b}$$

$$= (-1)^{j_1-j+m_2} \sqrt{\frac{2j+1}{2j_1+1}} \begin{bmatrix} j & j_2 & j_1 \\ m & -m_2 & m_1 \end{bmatrix} \tag{20.16c}$$

$$= (-1)^{j_2-j-m_1} \sqrt{\frac{2j+1}{2j_2+1}} \begin{bmatrix} j_1 & j & j_2 \\ -m_1 & m & m_2 \end{bmatrix}. \tag{20.16d}$$

Equation (20.13) is the quantum analogue of the restrictions encountered in the classical addition of angular momentum vectors.

The 3-J symbol,

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix},$$

vanishes unless $m_1 + m_2 + m = 0$ and $|j_2 - j_1| \leq j \leq j_1 + j_2$, it is invariant under a circular permutation of all columns, and it is multiplied by $(-1)^{j_1+j_2+j}$ under a permutation of any two columns or when the signs of all the m's are changed. Also

$$\begin{pmatrix} j_1 & j_2 & j \\ 0 & 0 & 0 \end{pmatrix} = 0 \quad \text{if } j_1 + j_2 + j \text{ is odd}, \tag{20.17}$$

as is the corresponding Clebsch-Gordan coefficient.

As an example, I can write

$$\begin{aligned}
|j_1 = 1, j_2 = 1; j = 1, m = 0\rangle &= \sum_{m_1,m_2} \begin{bmatrix} 1 & 1 & 1 \\ m_1 & m_2 & 0 \end{bmatrix} |j_1, j_2; m_1, m_2\rangle \\
&= \begin{bmatrix} 1 & 1 & 1 \\ 1 & -1 & 0 \end{bmatrix} |1,1;1,-1\rangle + \begin{bmatrix} 1 & 1 & 1 \\ 0 & 0 & 0 \end{bmatrix} |1,1;0,0\rangle \\
&\quad + \begin{bmatrix} 1 & 1 & 1 \\ 1 & -1 & 0 \end{bmatrix} |1,1;-1,1\rangle \\
&= \frac{1}{\sqrt{2}} |1,1;1,-1\rangle + 0\,|1,1;0,0\rangle - \frac{1}{\sqrt{2}} |1,1;-1,1\rangle .
\end{aligned} \tag{20.18}$$

The Clebsch-Gordan coefficients are very important in calculating transition rates. Often we look at transitions between two manifolds of atomic levels, each containing a number of magnetic sublevels (corresponding to different values of m). The ratio of the various transition rates between levels having different m's is equal to the square of the Clebsch-Gordan coefficients associated with the transition rates.

20.2 Vector and Tensor Operators

Some of you may have learned about *groups* in your mathematics courses. A group consists of a number of elements and some group operation. For example, all the real numbers form a group under addition since the addition of any two real numbers produces another real number which is a member of the group, there is an *identity element* zero, which when added to any real number produces the same number, and an *inverse* (the negative of a number) which, when added to an element gives the identity element $[x + (-x) = 0]$. This is not the course to go into elements of group theory as applied to quantum mechanics, but it is a powerful method. In fact I really only want to get to the Wigner-Eckart theorem, which offers a very useful method for evaluating matrix elements of operators or ratios of matrix elements of operators. To do this, I need to introduce the concept of an *irreducible tensor operator*.

Rotations also form a group, as do the rotation operators and the rotation matrices $\underset{\sim}{R}(\alpha, \beta, \gamma)$.[2] Any two successive rotations are equivalent to a single rotation. The identity element is no rotation at all (or a rotation of $2n\pi$ about an axis) and the inverse of a rotation is just the reverse rotation. However, you can convince yourself that if you perform rotations R_1 and then R_2 about different axes in three dimensions, it does not give the same result as if you reverse the order of the rotations. Rotations are said to form a *nonabelian group*. We have already seen that angular momentum is the generator of infinitesimal rotations. *The nonabelian nature of the rotation group can be linked to the fact that the different components of the angular momentum operator do not commute with one another*. In fact the commutation relations of the angular momentum operators are said to form an *algebra* (algebras have two operations) that determines the properties of the rotation group in the vicinity of the identity.

Why am I introducing these concepts? The reason is that the group structure of rotations is determined totally by the angular momentum operators. Thus we can define scalar, vector, and tensor operators under rotation in terms of their commutation relations with the angular momentum operators, as well as in the way they transform under rotation.

[2]The rotation matrices $\underset{\sim}{R}(\alpha, \beta, \gamma)$ form a group of orthogonal 3×3 matrices having determinant equal to $+1$, a group that is refered to as the special orthogonal group in three dimensions, SO(3). The group of unitary 2×2 matrices having determinant equal to $+1$, such as the $\mathcal{D}^{(1/2)}(\alpha, \beta, \gamma)$ matrices, is refered to as the special unitary group in two dimensions, SU(2).

A *scalar operator* $\hat{A}$ under rotation is one for which

$$\hat{A}_R = \hat{R}\hat{A}\hat{R}^\dagger = \hat{A}. \tag{20.19}$$

Consider an infinitesimal rotation $\delta\boldsymbol{\phi}$. When looking at the effects of rotation on kets that involve both orbital and spin angular momentum, rotation operators for *both* the spin and orbital angular momenta must be used. An appropriate rotation operator is

$$\hat{R}\left(\mathbf{u_n},\omega\right) = e^{-\frac{i}{\hbar}\omega\mathbf{u_n}\cdot\hat{\mathbf{L}}}e^{-\frac{i}{\hbar}\omega\mathbf{u_n}\cdot\hat{\mathbf{S}}} = e^{-\frac{i}{\hbar}\omega\mathbf{u_n}\cdot\hat{\mathbf{J}}}. \tag{20.20}$$

For an infinitesimal rotation $\delta\boldsymbol{\phi} = \mathbf{u_n}\delta\omega$,

$$\hat{R}\left(\delta\boldsymbol{\phi}\right) = e^{-i\delta\boldsymbol{\phi}\cdot\hat{\mathbf{J}}/\hbar} \approx \left(1 - \frac{i}{\hbar}\delta\boldsymbol{\phi}\cdot\hat{\mathbf{J}}\right). \tag{20.21}$$

Under this rotation, Eq. (20.19) becomes

$$\begin{aligned}\hat{A}_R &= \left(1 - \frac{i}{\hbar}\delta\boldsymbol{\phi}\cdot\hat{\mathbf{J}}\right)\hat{A}\left(1 + \frac{i}{\hbar}\delta\boldsymbol{\phi}\cdot\hat{\mathbf{J}}\right)\\ &\approx \hat{A} - \frac{i}{\hbar}\left[\begin{array}{c}\left(\delta\phi_x\hat{J}_x + \delta\phi_y\hat{J}_y + \delta\phi_z\hat{J}_z\right)\hat{A}\\ -\hat{A}\left(\delta\phi_x\hat{J}_x + \delta\phi_y\hat{J}_y + \delta\phi_z\hat{J}_z\right)\end{array}\right]\\ &= \hat{A} - \frac{i}{\hbar}\left\{\delta\phi_x\left[\hat{J}_x,\hat{A}\right] + \delta\phi_y\left[\hat{J}_y,\hat{A}\right] + \delta\phi_z\left[\hat{J}_z,\hat{A}\right]\right\} = \hat{A},\end{aligned} \tag{20.22}$$

where terms of order $(\delta\phi)^2$ have been neglected. For arbitrary $\delta\boldsymbol{\phi}$, the only way Eq. (20.22) can be satisfied is if

$$\left[\hat{A},\hat{\mathbf{J}}\right] = 0, \tag{20.23}$$

which is an alternative definition of a scalar operator under rotation. That is, either Eq. (20.19) or Eq. (20.23) can be used to define a scalar operator under rotation.

A *vector operator* or *tensor operator of rank 1* is defined as a set of *three* operators that transform as a Cartesian vector under a rotation as

$$\left(\hat{A}_R\right)_i = \hat{R}\hat{A}_i\hat{R}^\dagger = \sum_{j=1}^{3}\underline{R}_{ji}\hat{A}_j. \quad i = 1 - 3 \tag{20.24a}$$

$$\hat{\mathbf{A}}_R = \underline{R}^{-1}\hat{\mathbf{A}} = \underline{R}^T\hat{\mathbf{A}}, \tag{20.24b}$$

where $\underline{R}_{ji}$ is a matrix element of the (active) rotation matrix given by Eq. (19.78). Note the order *ji* of the indices—in other words, although constant vectors **f** transform under rotation as $\mathbf{f}' = \underset{\sim}{R}\mathbf{f}$, the vector operator $\hat{\mathbf{A}} = \left(\hat{A}_1, \hat{A}_2, \hat{A}_2\right)$ transforms as $\hat{\mathbf{A}}_R = \underset{\sim}{R}^T\hat{\mathbf{A}}$, where $\underset{\sim}{R}^T$ is the transpose of the rotation matrix.

To see that this works, let us rotate the *operator* $\hat{\mathbf{r}}$ by $\pi/2$ about the y axis. Under such a rotation we would expect the $\hat{x}$ component to transform into $-\hat{z}$, the $\hat{y}$ component to remain unchanged, and the $\hat{z}$ component to transform into $\hat{x}$. The rotation matrix in this case has Euler angles $\alpha = \gamma = 0$ and $\beta = \pi/2$, giving

$$\underset{\sim}{R}\left(0, \frac{\pi}{2}, 0\right) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}; \quad \underset{\sim}{R}^T\left(0, \frac{\pi}{2}, 0\right) = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}. \tag{20.25}$$

Then

$$\hat{\mathbf{r}}' = \begin{pmatrix} \hat{x}' \\ \hat{y}' \\ \hat{z}' \end{pmatrix} = \underset{\sim}{R}^T \begin{pmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{pmatrix} = \begin{pmatrix} -\hat{z} \\ \hat{y} \\ \hat{x} \end{pmatrix}, \tag{20.26}$$

as expected.

Equations (20.24) can be used to derive commutation relations of a vector operator with the angular momentum operator. To see this, I write the rotation matrix for an infinitesimal rotation. I consider a rotation of ϵ_x about the x axis, followed by a rotation of ϵ_y about the y axis and a rotation of ϵ_z about the z axis. Normally I would have to worry about the order of rotations since the rotation group is nonabelian. However, for *infinitesimal* rotations, the errors introduced by ignoring the order of the rotations are of second order in ϵ and can be neglected. The rotation matrix to first order in $\boldsymbol{\epsilon}$ is given by

$$\underset{\sim}{R}(\boldsymbol{\epsilon}) = \begin{pmatrix} 1 & -\epsilon_z & \epsilon_y \\ \epsilon_z & 1 & -\epsilon_x \\ -\epsilon_y & \epsilon_x & 1 \end{pmatrix}, \tag{20.27}$$

independent of the order of the rotations. Under such an infinitesmal rotation,

$$\begin{aligned} \left(\hat{A}_R\right)_i &= \hat{R}(\boldsymbol{\epsilon})\hat{A}_i\hat{R}^\dagger(\boldsymbol{\epsilon}) \\ &= \left(1 - \frac{i}{\hbar}\boldsymbol{\epsilon}\cdot\hat{\mathbf{J}}\right)\hat{A}_i\left(1 + \frac{i}{\hbar}\boldsymbol{\epsilon}\cdot\hat{\mathbf{J}}\right). \end{aligned} \tag{20.28}$$

Taking $i = 1 \equiv x$, I calculate

$$\begin{aligned} \left(\hat{A}_R\right)_x &\approx \hat{A}_x - \frac{i}{\hbar}\boldsymbol{\epsilon}\cdot\hat{\mathbf{J}}\hat{A}_x + \frac{i}{\hbar}\hat{A}_x\boldsymbol{\epsilon}\cdot\hat{\mathbf{J}} = \hat{A}_x - \frac{i}{\hbar}\boldsymbol{\epsilon}\cdot\left[\hat{\mathbf{J}},\hat{A}_x\right] \\ &= \hat{A}_x - \frac{i}{\hbar}\left(\epsilon_x\left[\hat{J}_x,\hat{A}_x\right] + \epsilon_y\left[\hat{J}_y,\hat{A}_x\right] + \epsilon_z\left[\hat{J}_z,\hat{A}_x\right]\right). \end{aligned} \tag{20.29}$$

On the other hand, it follows from Eqs. (20.24a) and (20.27) that the x-component of a vector operator must transform as

$$\begin{aligned}\left(\hat{A}_R\right)_x &= R_{11}(\boldsymbol{\epsilon})\hat{A}_x + R_{21}(\boldsymbol{\epsilon})\hat{A}_y + R_{31}(\boldsymbol{\epsilon})\hat{A}_z \\ &= \hat{A}_x + \epsilon_z\hat{A}_y - \epsilon_y\hat{A}_z. \end{aligned} \tag{20.30}$$

Equating coefficients of $\epsilon_x, \epsilon_y, \epsilon_z$ in Eqs. (20.29) and (20.30), I find that, if $\hat{A}$ is a vector operator, its x-component must satisfy the commutation relations

$$\left[\hat{J}_x, \hat{A}_x\right] = 0; \quad \left[\hat{J}_y, \hat{A}_x\right] = -i\hbar\hat{A}_z \quad \left[\hat{J}_z, \hat{A}_x\right] = i\hbar\hat{A}_y. \tag{20.31}$$

By considering cyclic permutations of x, y, z, I can generate the remaining commutation relations. According to this definition, $\hat{\mathbf{r}}$, $\hat{\mathbf{p}}$, and $\hat{\mathbf{J}}$ are vector operators. Equations (20.31) and their cyclical permutations provide an alternative way to define a vector operator.

I can extend this technique to consider tensor operators of rank two and beyond by combining vector operators of rank 1. For example, given two vector operators $\hat{\mathbf{A}}$ and $\hat{\mathbf{B}}$, a *tensor operator of rank 2* is defined as the set of *nine* operators $\hat{C}_{ij} = \hat{A}_i\hat{B}_j$ $(i, j = 1, 2, 3)$ that transform under rotation as

$$\left(\hat{C}_R\right)_{ij} = \hat{R}\hat{C}_{ij}\hat{R}^\dagger = \sum_{i',j'=1}^{3} \underline{R}_{i'i}\underline{R}_{j'j}\hat{C}_{i'j'}. \tag{20.32}$$

On the other hand, if I try to establish commutation relations of these tensor operators with the angular momentum operator, the results are not particularly useful.

The reason for this is that the set of nine operators $\hat{C}_{ij} = \hat{A}_i\hat{B}_j$ do not constitute what is referred to as an *irreducible tensor operator*. To understand something about irreducible tensor operators, you need to know something about *representations* of groups. A matrix representation of a group is the assignment of a matrix to each group element. Clearly the rotation matrix is a three-dimensional representation of the rotation group. We say it is *isomorphic* to the rotation group since each element in the group corresponds to a single matrix. However, a representation of the group can also be the unit matrix in any number of dimensions—each group element is replaced by the unit matrix. This is referred to as a *homomorphism* since the same matrix corresponds to more than one group element.

The rotation matrices $\mathcal{D}^{(j)}_{mm'}(\alpha, \beta, \gamma)$ form a $(2j+1)$ *irreducible representation* of the rotation group. To understand what is meant by an irreducible representation, let me go back to coupling of two angular momenta, which I take for the sake of definiteness as $J_1 = J_2 = 1$. The eigenkets for these two independent angular momenta can be written in the direct product basis as

$$\left|j_1 = 1, j_2 = 1; m_1, m_2\right\rangle = \left|j_1, m_1\right\rangle \left|j_2, m_2\right\rangle . \tag{20.33}$$

Under rotation each of the eigenkets transforms separately and the resultant transformation matrix is a very complicated 9×9 matrix. However we know that we can couple these two angular momenta into states having $j = 0, 1, 2$ specified by the kets $\left|j_1, j_2; j, m\right\rangle$. Under rotation the *components of each value of j transform separately* such that the total transformation breaks down the 9×9 matrix into one that has a *block-diagonal* form with 1×1 $(j = 0)$, 3×3 $(j = 1)$, and 5×5 $(j = 2)$ sub-matrices along the diagonals. A matrix representation that is reduced to block diagonal form is called an irreducible representation.

This leads me to the definition of an *irreducible tensor of rank k* as a set of $(2k + 1)$ operators $\hat{T}_k^q$ that transform under rotations as

$$\left(\hat{T}_k^q\right)_R = \hat{R}\hat{T}_k^q\hat{R}^\dagger = \sum_{q'=-k}^{k} \mathcal{D}_{q'q}^{(k)} \hat{T}_k^{q'}, \tag{20.34}$$

where the $\mathcal{D}_{q'q}^{(k)}$ are elements of the rotation matrices defined by Eq. (19.49). I can use this equation to obtain commutation relations of the $\hat{T}_k^q$ with the angular momentum operators. For an infinitesimal rotation,

$$\left(\hat{T}_k^q\right)_R = \left(1 - \frac{i}{\hbar}\boldsymbol{\epsilon} \cdot \hat{\mathbf{J}}\right) \hat{T}_k^q \left(1 + \frac{i}{\hbar}\boldsymbol{\epsilon} \cdot \hat{\mathbf{J}}\right) = \sum_{q'=-k}^{k} \mathcal{D}_{q'q}^{(k)}(\boldsymbol{\epsilon}) \hat{T}_k^{q'}. \tag{20.35}$$

It is convenient to express the scalar product as

$$\boldsymbol{\epsilon} \cdot \hat{\mathbf{J}} = \frac{\epsilon_+ \hat{J}_- + \epsilon_- \hat{J}_+}{2} + \epsilon_z \hat{J}_z, \tag{20.36}$$

where

$$\epsilon_\pm = \epsilon_x \pm i\epsilon_x; \tag{20.37a}$$

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y. \tag{20.37b}$$

Then, by substituting

$$\mathcal{D}_{q'q}^{(k)}(\boldsymbol{\epsilon}) = \left\langle kq'\right| e^{-\frac{i}{\hbar}\boldsymbol{\epsilon}\cdot\hat{\mathbf{J}}} \left|kq\right\rangle \approx \left\langle kq'\right| \left(1 - \frac{i}{\hbar}\boldsymbol{\epsilon} \cdot \hat{\mathbf{J}}\right) \left|kq\right\rangle , \tag{20.38}$$

into Eq. (20.35), using the relationships

$$\hat{J}_\pm \left|kq\right\rangle = \hbar\sqrt{(k \mp q)(k \pm q + 1)} \left|kq \pm 1\right\rangle ; \tag{20.39a}$$

$$\hat{J}_z \left|kq\right\rangle = \hbar q \left|kq\right\rangle , \tag{20.39b}$$

derived in Chap. 11, and comparing coefficients of $\epsilon_{\pm}$ and ϵ_z in Eq. (20.35), I can obtain

$$\left[\hat{J}_z, \hat{T}_k^q\right] = \hbar q \hat{T}_k^q; \tag{20.40a}$$

$$\left[\hat{J}_{\pm}, \hat{T}_k^q\right] = \hbar \sqrt{(k \mp q)(k \pm q + 1)} \hat{T}_k^{q \pm 1}, \tag{20.40b}$$

which can serve as an alternative definition of an irreducible tensor of rank k under rotation.

What are some examples of irreducible tensor operators? Any scalar operator that commutes with $\hat{J}$ (such as $\hat{J}^2$) is an irreducible tensor of rank zero. It is not difficult to show that the components $\hat{A}_x, \hat{A}_y, \hat{A}_z$ of a vector operator do *not* form an irreducible tensor of rank 1. However it can be proven rather easily using Eq. (20.31) that the operators

$$A_1^{\pm 1} = \mp \frac{\hat{A}_x \pm i\hat{A}_y}{\sqrt{2}}; \qquad A_1^0 = \hat{A}_z \tag{20.41}$$

do form an irreducible tensor of rank 1 since they have the correct commutation relations with $\hat{J}$. Thus, if we have a vector operator, we can form an irreducible tensor of rank 1 from its components using Eq. (20.41).

Imagine there are two *commuting* vector operators $\hat{\mathbf{A}}$ and $\hat{\mathbf{B}}$. Then you can show (using the commutation relations of the components with the angular momentum operator) that the combination $\hat{\mathbf{A}} \cdot \hat{\mathbf{B}}$ is an irreducible tensor of rank 0, $\hat{\mathbf{A}} \times \hat{\mathbf{B}}$ is an irreducible tensor of rank 1, and

$$\begin{aligned} &\frac{1}{2}\left(\hat{A}_x\hat{B}_y + \hat{A}_y\hat{B}_x\right); \;\; \frac{1}{2}\left(\hat{A}_y\hat{B}_z + \hat{A}_z\hat{B}_y\right); \;\; \frac{1}{2}\left(\hat{A}_z\hat{B}_x + \hat{A}_x\hat{B}_z\right); \\ &\left(\hat{A}_x\hat{B}_x - \hat{A}_y\hat{B}_y\right); \;\; \left(2\hat{A}_z\hat{B}_z - \hat{A}_x\hat{B}_x - \hat{A}_y\hat{B}_y\right) \end{aligned} \tag{20.42}$$

form an irreducible tensor of rank 2 (quadrupole tensor).

The adjoint of an irreducible tensor operator $\left(\hat{T}^{(k)}\right)^{\dagger}$ of rank k can be defined as the set of operators $\left[\left(\hat{T}^{(k)}\right)^{\dagger}\right]_k^q$ for which

$$\left[\left(\hat{T}^{(k)}\right)^{\dagger}\right]_k^q = (-1)^q \left(\hat{T}_k^{-q}\right)^{\dagger}. \tag{20.43}$$

With this definition, any irreducible tensor of rank 1 formed from a Hermitian vector operator is also Hermitian. In addition, the $\hat{Y}_\ell^m(\theta, \phi)$ considered as *operators* in coordinate space form a Hermitian irreducible tensor operator of rank ℓ.

20.3 Wigner-Eckart Theorem

I now state the Wigner-Eckart theorem without proof (a proof is given in the Appendix). The matrix elements of an irreducible tensor operator can be written as

$$\begin{aligned}\langle \alpha jm| \hat{T}_k^q \left|\alpha' j' m'\right\rangle &= \frac{1}{\sqrt{2j+1}} \begin{bmatrix} j' & k & j \\ m' & q & m \end{bmatrix} \langle \alpha j \| \, T^{(k)} \left\| \alpha' j' \right\rangle \\ &= (1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \langle \alpha j \| \, T^{(k)} \left\| \alpha' j' \right\rangle \end{aligned} \tag{20.44}$$

where $\langle \alpha j \| \, T^{(k)} \left\| \alpha' j' \right\rangle$ is referred to as a *reduced matrix element* and α and α' are additional quantum numbers (such as n in the hydrogen atom). The matrix element of an irreducible operator is a product of a term that is independent of q, m, and m', multiplied by a Clebsch-Gordan coefficient. This theorem is extremely useful since it lets you calculate matrix elements of different components of a vector or tensor operator in terms of one quantity which itself must be calculated explicitly. Some authors use a different form for Eq. (20.44) (e.g., they omit the $1/\sqrt{2j+1}$ factor), but the form I use is the most common.

As a first example, let me consider a matrix element of the operator $\hat{\mathbf{r}}$ in the $|\alpha \ell m\rangle$ basis. I will need to evaluate matrix elements of this type when I look at atom–field interactions that are proportional to $\hat{\mathbf{r}} \cdot \mathbf{E}$, where $\mathbf{E}$ is the electric field. From the definitions (20.41), I can write

$$\hat{x} = \frac{\hat{T}_1^{-1} - \hat{T}_1^1}{\sqrt{2}}; \tag{20.45a}$$

$$\hat{y} = -\frac{\hat{T}_1^{-1} + \hat{T}_1^1}{\sqrt{2}i}; \tag{20.45b}$$

$$\hat{z} = \hat{T}_1^0, \tag{20.45c}$$

so

$$\begin{aligned}\langle \alpha \ell m| \, \hat{x} \left|\alpha' \ell' m'\right\rangle &= - \langle \alpha \ell m| \left(\frac{\hat{T}_1^1 - \hat{T}_1^{-1}}{\sqrt{2}} \right) \left|\alpha' \ell' m'\right\rangle \\ = -\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2\ell+1}} &\left(\begin{bmatrix} \ell' & 1 & \ell \\ m' & 1 & m \end{bmatrix} - \begin{bmatrix} \ell' & 1 & \ell \\ m' & -1 & m \end{bmatrix} \right) \langle \alpha \ell \| \, r^{(1)} \left\| \alpha' \ell' \right\rangle ; \end{aligned} \tag{20.46a}$$

$$\begin{aligned}\langle \alpha \ell m| \, \hat{y} \left|\alpha' \ell m'\right\rangle &= - \langle \alpha \ell m| \left(\frac{\hat{T}_1^1 + \hat{T}_1^{-1}}{\sqrt{2}i} \right) \left|\alpha' \ell' m'\right\rangle \\ -\frac{1}{\sqrt{2}i} \frac{1}{\sqrt{2\ell+1}} &\left(\begin{bmatrix} \ell' & 1 & \ell \\ m' & 1 & m \end{bmatrix} + \begin{bmatrix} \ell' & 1 & \ell \\ m' & -1 & m \end{bmatrix} \right) \langle \alpha \ell \| \, r^{(1)} \left\| \alpha' \ell' \right\rangle ; \end{aligned} \tag{20.46b}$$

$$\langle \alpha \ell m| \, \hat{z} \left|\alpha' \ell m'\right\rangle = \frac{1}{\sqrt{2\ell+1}} \begin{bmatrix} \ell' & 1 & \ell \\ m' & 0 & m \end{bmatrix} \langle \alpha \ell \| \, r^{(1} \left\| \alpha' \ell' \right\rangle . \tag{20.46c}$$

Note that the reduced matrix element, $\langle\alpha\ell\|\, r^{(1}\, \|\alpha'\ell'\rangle$, can be calculated from the last of these equations as

$$\langle\alpha\ell|\, |r^{(1)}|\, \left|\alpha'\ell'\right\rangle = \frac{\sqrt{2\ell+1}}{\begin{bmatrix}\ell' & 1 & \ell\\ m & 0 & m\end{bmatrix}} \int d\mathbf{r}\psi^*_{\alpha\ell m}(\mathbf{r}) z \psi_{\alpha'\ell' m}(\mathbf{r}), \tag{20.47}$$

using any value of m you choose. The *ratio* of matrix elements depends solely on the Clebsch-Gordan coefficients. This is useful in calculating *branching ratios* for transitions originating on different degenerate (or nearly-degenerate) sublevels in a given energy manifold of levels.

As a second example, consider matrix elements of $\hat{J}$ itself. Following the same steps that led to Eq. (20.47), I can calculate

$$\begin{aligned}\langle\alpha j\|\, J^{(1)}\, \left\|\alpha' j'\right\rangle &= \frac{\sqrt{2j+1}}{\begin{bmatrix}j' & 1 & j\\ m & 0 & m\end{bmatrix}} \langle\alpha j m|\, \hat{J}_z \left|\alpha' j' m\right\rangle \\ &= \frac{\sqrt{2j+1}m\hbar}{\begin{bmatrix}j & 1 & j\\ m & 0 & m\end{bmatrix}} \delta_{j,j'}\delta_{\alpha,\alpha'}\end{aligned} \tag{20.48}$$

Taking $m = j$, I find

$$\begin{aligned}\langle\alpha j\|\, J^{(1)}\, \left\|\alpha' j'\right\rangle &= \frac{\sqrt{2j+1}j\hbar}{\begin{bmatrix}j & 1 & j\\ j & 0 & j\end{bmatrix}} \delta_{j,j'}\delta_{\alpha,\alpha'} = \frac{\sqrt{2j+1}j\hbar}{\sqrt{j}/\sqrt{j+1}} \delta_{j,j'}\delta_{\alpha,\alpha'} \\ &= \hbar\sqrt{j\,(2j+1)\,(j+1)}\delta_{j,j'}\delta_{\alpha,\alpha'}.\end{aligned} \tag{20.49}$$

Further examples will be given when I discuss the Zeeman effect in the next chapter.

Let me return briefly to the reduced matrix elements, which can be calculated using Eq. (20.44). You might ask about the relationship between $\langle\alpha j\|\, T^{(k)}\, \|\alpha' j'\rangle$ and $\langle\alpha' j'\|\, T^{(k)}\, \|\alpha j\rangle$. To examine this relationship, I use Eqs. (20.43) and (20.44) to write

$$\begin{aligned}&\left\langle\alpha' j' m'\right| \left[\left(\hat{T}^{(k)}\right)^\dagger\right]^{-q}_k |\alpha j m\rangle = \frac{1}{\sqrt{2j'+1}} \begin{bmatrix}j & k & j'\\ m & -q & m'\end{bmatrix} \left\langle\alpha' j'\right\| \left(\hat{T}^{(k)}\right)^\dagger \|\alpha j\rangle \\ &= (-1)^q \left\langle\alpha' j' m'\right| \left(\hat{T}^q_k\right)^\dagger |\alpha j m\rangle = (-1)^q \langle\alpha j m|\, \hat{T}^q_k \left|\alpha' j' m'\right\rangle^* .\end{aligned} \tag{20.50}$$

By combining this equation with Eqs. (20.44) and (20.16d), I obtain

$$\langle\alpha j\|\, T^{(k)}\, \left\|\alpha' j'\right\rangle = (-1)^{j-j'} \left\langle\alpha' j'\right\| \left(\hat{T}^{(k)}\right)^\dagger \|\alpha j\rangle^* . \tag{20.51}$$

For any Hermitian vector operator $\hat{\mathbf{V}}$, it then follows that

$$\langle \alpha j \| V^{(1)} \| \alpha' j' \rangle = (-1)^{j-j'} \langle \alpha' j' \| V^{(1)} \| \alpha j \rangle^* . \tag{20.52}$$

As a simple example, consider matrix elements of the position operator between eigenkets $|n\ell m\rangle$ of the hydrogen atom. In that case, the matrix elements vanish unless $\ell = \ell' \pm 1$ and

$$\langle n\ell \| r^{(1)} \| n', \ell' \pm 1 \rangle = -\langle n', \ell' \pm 1 \| r^{(1)} \| n\ell \rangle , \tag{20.53}$$

where $r^{(1)}$ is an irreducible tensor having components given by Eqs. (20.45). The fact that the reduced matrix element is real can be deduced from Eq. (20.44) using $q = 0$.

20.4 Summary

Several topics were covered in this chapter. Coupling of angular momentum in quantum mechanics can be formulated in terms of the Clebsch-Gordan or 3-J symbols. In contrast to classical coupling of two vectors, there are only discrete ways in which angular momentum can be coupled in quantum mechanics. The definition of vector and tensor operators under rotation was introduced and related to the commutation relations of the operators with the angular momentum operators. It turned out to be useful to introduce a new class of operators, irreducible tensor operators, that transformed under rotation in terms of the irreducible representations of the rotation group, that is, the $\mathcal{D}^{(k)}_{q'q}$. A matrix element of an irreducible tensor operators could be expressed as a product of a Clebsch-Gordan coefficients multiplied by a reduced matrix element that is independent of the magnetic quantum numbers, a result embodied in the Wigner-Eckart theorem.

20.5 Appendix: Proof of the Wigner-Eckart Theorem

Consider

$$\widetilde{|jm\rangle} = \sum_{m',q} \hat{T}^q_k \, |\alpha' j' m'\rangle \begin{bmatrix} k & j' & j \\ q & m' & m \end{bmatrix}, \tag{20.54}$$

where $\hat{T}^q_k$ is an irreducible tensor operator. The ket $\widetilde{|jm\rangle}$ is an implicit function of j', k, and α' (α' represents an additional quantum number such as energy). You can show that $\widetilde{|jm\rangle}$ is an eigenket of $\hat{J}^2$ and $\hat{J}_z$ by using the commutation relations between the irreducible tensor operator $\hat{T}_k^q$ and $\hat{J}$. For example,

$$\begin{aligned}\hat{J}_z \widetilde{|jm\rangle} &= \hat{J}_z \sum_{m',q} \hat{T}_k^q \left|\alpha' j' m'\right\rangle \begin{bmatrix} k & j' & j \\ q & m' & m \end{bmatrix} \\ &= \sum_{m',q} \begin{bmatrix} k & j' & j \\ q & m' & m \end{bmatrix} \left(\left[\hat{J}_z, \hat{T}_k^q\right] + \hat{T}_k^q \hat{J}_z \right) \left|\alpha' j' m'\right\rangle \\ &= \hbar \sum_{m',q} \begin{bmatrix} k & j' & j \\ q & m' & m \end{bmatrix} \left(q + m'\right) \hat{T}_k^q \left|\alpha' j' m'\right\rangle \\ &= m\hbar \sum_{m',q} \begin{bmatrix} k & j' & j \\ q & m' & m \end{bmatrix} \hat{T}_k^q \left|\alpha' j' m'\right\rangle = m\hbar \widetilde{|jm\rangle},\end{aligned} \tag{20.55}$$

since the Clebsch-Gordan coefficients vanish unless $(q + m') = m$. However, although different $\widetilde{|jm\rangle}$ are orthogonal ($\widetilde{\langle jm}\widetilde{|j'm'\rangle}$ vanishes unless $j = j'$ and $m = m'$), the $\widetilde{\langle jm}\widetilde{|jm\rangle}$ are not normalized, $\widetilde{\langle jm}\widetilde{|jm\rangle} \neq 1$.

I expand $\widetilde{|jm\rangle}$ in the $|\alpha j' m'\rangle$ basis as

$$\widetilde{|jm\rangle} = \sum_{\alpha, j', m'} \left\langle \alpha j' m' \middle| \widetilde{jm} \right\rangle \left|\alpha j' m'\right\rangle. \tag{20.56}$$

Since both $\widetilde{|jm\rangle}$ and $|\alpha j' m'\rangle$ are simultaneous eigenkets of $\hat{J}^2$ and $\hat{J}_z$, the coupling coefficients $\langle \alpha j' m' | \widetilde{jm}\rangle$ vanish unless $j = j'$, $m = m'$;

$$\widetilde{|jm\rangle} = \sum_{\alpha} \langle \alpha jm | \widetilde{jm}\rangle \, |\alpha jm\rangle \, . \tag{20.57}$$

If you act on both sides of this equation with $\hat{J}_+$ you will find that

$$\widetilde{|jm+1\rangle} = \sum_{\alpha} \langle \alpha jm | \widetilde{jm}\rangle \, |\alpha j, m+1\rangle \, ; \tag{20.58}$$

however, from Eq. (20.56) it follows that

$$\widetilde{|j, m+1\rangle} = \sum_{\alpha} \langle \alpha j, m+1 | \widetilde{j, m+1}\rangle \, |\alpha j, m+1\rangle \, . \tag{20.59}$$

By comparing Eqs. (20.58) and (20.59), you see that the coupling coefficients $\langle \alpha jm | \widetilde{jm}\rangle$ *must be independent of* m.

I now invert Eq. (20.54),

$$\hat{T}_k^q \left|\alpha' j' m'\right\rangle = \sum_{j'',m''} \begin{bmatrix} k & j' & j'' \\ q & m' & m'' \end{bmatrix} \widetilde{|j''m''\rangle}$$

$$= \sum_{\alpha'',j'',m''} \begin{bmatrix} k & j' & j'' \\ q & m' & m'' \end{bmatrix} \langle \alpha j'' m'' | \widetilde{j''m''}\rangle |\alpha'' j'' m''\rangle, \tag{20.60}$$

multiply on the left by $\langle \alpha jm|$, and use Eq. (20.16a) to obtain

$$\langle \alpha jm| \hat{T}_k^q \left|\alpha' j' m'\right\rangle = \frac{1}{\sqrt{2j+1}}(-1)^{k-j'+j} \begin{bmatrix} k & j' & j \\ q & m' & m \end{bmatrix} \langle \alpha j \| \, T^{(k)} \, \| \alpha' j' \rangle$$

$$= \frac{1}{\sqrt{2j+1}} \begin{bmatrix} j' & k & j \\ m' & q & m \end{bmatrix} \langle \alpha j \| \, T^{(k)} \, \| \alpha' j' \rangle, \tag{20.61}$$

where

$$\frac{1}{\sqrt{2j+1}}(-1)^{k-j'+j} \langle \alpha j \| \, T^{(k)} \, \| \alpha' j' \rangle = \langle \alpha jm| \widetilde{jm}\rangle \tag{20.62}$$

is independent of m, but still depends on α' and j' and the properties of $T^{(k)}$ [recall that $\widetilde{|j'm'\rangle}$, as defined by Eq. (20.54) is an implicit function of j', k and α']. The choice of writing this is somewhat arbitrary, but the result states that the matrix element of an irreducible tensor operator is equal to the product of a Clebsch-Gordan coefficient and a term that is independent of m, m', q.

20.6 Problems

1. In qualitative terms, to what do the Clebsch-Gordan coefficients correspond? What does it mean to say that an operator is a scalar or vector operator under rotation? What does it mean to say that a set of operators is an irreducible tensor operator under rotation? Under a rotation about the z axis by 2π, what happens to the rotation operator?, to the spin-rotation operator?

2. Write a subroutine that will let you calculate $|j_1 j_2; jm\rangle$ in terms of $|j_1 m_1; j_2 m_2\rangle$ and the Clebsch-Gordan coefficients. (Use the Clebsch-Gordan function in Mathematica or some equivalent function). Obtain the solution for $|j_1 = 1, j_2 = 3; j = 2, m = 1\rangle$.

3. Prove that

$$\begin{bmatrix} j_1 & j_2 & j_1 + j_2 \\ j_1 & j_2 & j_1 + j_2 \end{bmatrix} = 1.$$

Derive the orthogonality relation for the Clebsch-Gordan coefficients,

$$\sum_{m_1=-j_1}^{j_1}\sum_{m_2=-j_2}^{j_2}\begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix}\begin{bmatrix} j_1 & j_2 & j' \\ m_1 & m_2 & m' \end{bmatrix} = \delta_{j,j'}\delta_{m,m'}.$$

Prove that

$$|j_1 m_1; j_2 m_2\rangle = \sum_{j=|j_2-j_1|}^{j_1+j_2}\sum_{m=-j}^{j}\begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix}|j_1 j_2; jm\rangle$$

and derive the orthogonality relation

$$\sum_{j=|j_2-j_1|}^{j_1+j_2}\sum_{m=-j}^{j}\begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix}\begin{bmatrix} j_1 & j_2 & j \\ m_1' & m_2' & m \end{bmatrix} = \delta_{m_1,m_1'}\delta_{m_2,m_2'}.$$

4. Evaluate

$$\frac{\langle 3,2,2|\,\hat{p}_x\,|2,1,1\rangle}{\langle 3,2,0|\,\hat{p}_y\,|2,1,-1\rangle},$$

where the states $|n\ell m\rangle$ are eigenkets of the hydrogen atom. Note: You do not have to evaluate any integrals in this problem.

5. Sodium atoms have a single valence electron. In the ground state, $L = 0$ (writing $L = 0$ is actually a convention corresponding to $\ell = 0$), while in the first excited state, $L = 1$. What are the possible values for J in the ground state and first excited state? Sodium has a *nuclear* spin quantum number $I = 3/2$. The nuclear spin couples with the angular momentum $\mathbf{J}$ to give a total angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{I}$. For each of the J states in the ground and first excited states, calculate the possible values for the total angular momentum quantum number F. States having different F are split in energy by the *hyperfine* interaction of the spin of the electron with the spin of the nucleus. What are the various fine and hyperfine frequency separations in the 3S (ground state) and 3P (first excited state) states of sodium?

6–7. Calculate the effect of a rotation with Euler angles ($\alpha = 0, \beta = \pi/2, \gamma = 0$) on the hydrogen eigenket $\left|n = 2, \ell = 1, j = 1/2, m_j = 1/2\right\rangle$ and obtain an expression for the wave function of the rotated state.

8. Suppose that angular momentum operators are defined such that $\hat{\mathbf{K}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$. By operating with the operators $\hat{K}_\pm = \hat{J}_{1\pm} + \hat{J}_{2\pm}$ on the state

$$|j_1 j_2; KQ\rangle = \sum_{m_1,m_2}\begin{bmatrix} j_1 & j_2 & K \\ m_1 & m_2 & Q \end{bmatrix}|j_1 m_1\rangle\,|j_2 m_2\rangle$$

prove the recursion relation

$$\sqrt{(K\mp Q)(K\pm Q+1)}\begin{bmatrix} j_1 & j_2 & K \\ m_1 & m_2 & Q\pm 1\end{bmatrix}$$
$$=\sqrt{(j_1\mp(m_1\mp 1))(j_1\pm(m_1\mp 1)+1)}\begin{bmatrix} j_1 & j_2 & K \\ m_1\mp 1 & m_2 & Q\end{bmatrix}$$
$$+\sqrt{(j_2\mp(m_2\mp 1))(j_2\pm(m_2\mp 1)+1)}\begin{bmatrix} j_1 & j_2 & K \\ m_1 & m_2\mp 1 & Q\end{bmatrix}.$$

9–10. In Chap. 11, I showed that any operator in Dirac notation could be expanded in terms of a complete set of basis operators $|\alpha\rangle\langle\beta|$. If the eigenkets are specified as $|jm\rangle$, then a complete set of basis operators can be specified by $\underline{\mathrm{u}}(j_1m_1;j_2m_2)=|j_1m_1\rangle\langle j_2m_2|$. The $\underline{\mathrm{u}}(j_1m_1;j_2m_2)$ do *not* constitute a set of irreducible tensor basis operators.

(a) Prove that the set of basis operators defined by

$$\underline{\mathrm{u}}_Q^K(j_1,j_2)=\sum_{m_1,m_2}(-1)^{j_2-m_2}\begin{bmatrix} j_1 & j_2 & K \\ m_1 & -m_2 & Q\end{bmatrix}|j_1m_1\rangle\langle j_2m_2|$$

do form an irreducible tensor of rank K by showing they obey Eqs. (20.39).

(b) Prove that these operators are orthogonal in the sense that

$$\mathrm{Tr}\left(\underline{\mathrm{u}}_Q^K(j_1,j_2)\left[\underline{\mathrm{u}}_{Q'}^{K'}(j_1',j_2')\right]^\dagger\right)=\delta_{j_1,j_1'}\delta_{j_2,j_2'}\delta_{K,K'}\delta_{Q,Q'}.$$

(c) As a consequence, an arbitrary operator $\underline{\mathrm{A}}$ can be expanded in terms of its irreducible tensor components as

$$\underline{\mathrm{A}}=\sum_{j_1,j_2,K,Q}A_Q^K(j_1,j_2)\,\underline{\mathrm{u}}_Q^K(j_1,j_2).$$

Show that the expansion coefficients $A_Q^K(j_1,j_2)$ are given by

$$A_Q^K(j_1,j_2)=\mathrm{Tr}\left(\underline{\mathrm{A}}\left[\underline{\mathrm{u}}_Q^K(j_1,j_2)\right]^\dagger\right)$$
$$=\sum_{m_1,m_2}(-1)^{j_2-m_2}\begin{bmatrix} j_1 & j_2 & K \\ m_1 & -m_2 & Q\end{bmatrix}\langle j_1m_1|\hat{A}|j_2m_2\rangle.$$

The use of an irreducible tensor basis for operators is useful since the components transform in a simple way under rotation.

11. Suppose that angular momentum operators are defined such that $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$. By operating with the rotation operator on the state

$$|j_1 j_2; jm\rangle = \sum_{m_1, m_2} \begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} |j_1 m_1\rangle \, |j_2 m_2\rangle$$

prove the *decomposition relation*

$$\begin{aligned} \mathcal{D}^{(j)}_{mm'}(\alpha, \beta, \gamma) = & \sum_{\substack{m_1, m_2 \\ m_1', m_2'}} \begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} \begin{bmatrix} j_1 & j_2 & j \\ m_1' & m_2' & m' \end{bmatrix} \\ & \times \mathcal{D}^{(j_1)}_{m_1 m_1'}(\alpha, \beta, \gamma) \, \mathcal{D}^{(j_2)}_{m_2 m_2'}(\alpha, \beta, \gamma) \, . \end{aligned}$$

12. For a rotation specified by the rotation operator $\hat{R}(\alpha, \beta, \gamma)$, find the transformed angular momentum operator

$$\hat{\mathbf{L}}_R(\alpha, \beta, \gamma) = \hat{R}(\alpha, \beta, \gamma) \, \hat{\mathbf{L}} \hat{R}^{-1}(\alpha, \beta, \gamma) \, .$$

If

$$\begin{aligned} \mathbf{B} &= B_x \mathbf{u}_x + B_y \mathbf{u}_y + B_z \mathbf{u}_z \\ &= B\left(\sin\theta_B \cos\phi_B \mathbf{u}_x + \sin\theta_B \sin\phi_B \mathbf{u}_y + \cos\theta_B \mathbf{u}_z\right), \end{aligned}$$

is a constant vector having polar angles (θ_B, ϕ_B), prove that an interaction Hamiltonian of the form $\hat{H} = \alpha \hat{\mathbf{L}} \cdot \mathbf{B}$, where α is a constant, is transformed into

$$\hat{H}_R = \alpha \hat{\mathbf{L}}_R(0, -\theta_B, -\phi_B) \cdot \mathbf{B} = \hat{L}_z B$$

under the action of the rotation operator $\hat{R}(0, -\theta_B, -\phi_B)$; in other words, in the transformed Hamiltonian, it is as if the vector $\mathbf{B}$ lies along the z-axis, even though this constant vector is unaffected by the transformation (recall that only *operators* are transformed under quantum transformations).

13–14. If a constant magnetic field induction $\mathbf{B}$ is applied to a hydrogen atom, there is an extra interaction term in the Hamiltonian of the form

$$\hat{H}' = \frac{e}{2m_e} \hat{\mathbf{L}} \cdot \mathbf{B},$$

where m_e is the electron mass and spin has been neglected. I have already shown that, if the quantization axis is taken along the field direction, the eigenkets are unchanged and each ℓ level is split into $(2\ell + 1)$ equally spaced levels separated in frequency by $\omega = qB/2m_e$. Sometimes it is more convenient to take the quantization axis along a different direction (e.g., along the polarization vector of an optical field that is also present). Evaluate the matrix elements $\langle n\ell m| \hat{H}' |n'\ell' m'\rangle$ for a magnetic field induction

$$\begin{aligned}\mathbf{B} &= B_x + B_y\mathbf{u}_y + B_z\mathbf{u}_z \\ &= B\left(\sin\theta\cos\phi\mathbf{u}_x + \sin\theta\sin\phi\mathbf{u}_y + \cos\theta\mathbf{u}_z\right),\end{aligned}$$

where θ and ϕ are the polar angles of the field. Explicitly diagonalize the $\ell = 1$ submatrix to obtain the changes in the energy produced by the field and the new eigenkets.

The $\mathcal{D}^{(\ell)}(\alpha,\beta,\gamma)$ matrices can be used to get a *general* expression for the new eigenkets. Under a rotation $(0,-\theta_B,-\phi_B)$ the eigenkets transform as

$$|\ell m\rangle_R' = \hat{R}(0,-\theta_B,-\phi_B)\,|\ell m\rangle'.$$

But we have seen in the previous problem that such a transformation produces an effective interaction in which the field is along the z-direction; that is, the transformed kets are simply the *standard* kets when the quantization axis is taken along the z-axis, $|\ell m\rangle_R' = |\ell m\rangle$, which implies that

$$|\ell m\rangle = \hat{R}(0,-\theta_B,-\phi_B)\,|\ell m\rangle'.$$

Invert this equation to prove that

$$|\ell m\rangle' = \sum_{m'} \mathcal{D}^{(\ell)}_{m'm}(\phi_B,\theta_B,0)\left|\ell m'\right\rangle,$$

the eigenkets for which the quantization axis is along the field can be obtained from the standard kets by rotation that takes the z-axis into the field direction. Check to see if your result for $\ell = 1$ agrees with that obtained by direct diagonalization. The result derived is quite general for any Euler angles (α,β,γ); that is, the eigenkets relative to a quantization axis defined by the Euler angles (α,β,γ) are given by

$$|\ell m\rangle' = \sum_{m'} \mathcal{D}^{(\ell)}_{m'm}(\alpha,\beta,\gamma)\left|\ell m'\right\rangle.$$

15–16. For two irreducible tensor operators, $\hat{T}_k^q(1)$ and $\hat{T}_k^q(2)$, associated with two *separate* atoms, you can form a set of irreducible tensor operators as

$$\hat{T}_K^Q(k_1,k_2) = \sum_{q_1,q_2}\begin{bmatrix} k_1 & k_2 & K \\ q_1 & q_2 & Q\end{bmatrix}\hat{T}_{k_1}^{q_1}(1)\hat{T}_{k_2}^{q_2}(2).$$

An interaction potential $\hat{V}$ connecting the two atoms can then be expanded as

$$\hat{V} = \sum_{q_1,q_2} A(k_1 q_1, k_2 q_2) \hat{T}_{k_1}^{q_1}(1) \hat{T}_{k_2}^{q_2}(2)$$
$$= \sum_{K,Q} A_K^Q(k_1, k_2) \hat{T}_K^Q(k_1, k_2).$$

As a specific example, take $\hat{V}$ as the dipole–dipole interaction between the atoms,

$$\hat{V} = \frac{1}{4\pi\epsilon_0} \frac{\hat{\mathbf{p}}_e(1) \cdot \hat{\mathbf{p}}_e(2) - 3\left[\hat{\mathbf{p}}_e(1) \cdot \mathbf{u}_R\right]\left[\hat{\mathbf{p}}_e(2) \cdot \mathbf{u}_R\right]}{R^3},$$

where $\hat{\mathbf{p}}_e(j)$ is the electric dipole moment operator of atom j and $\mathbf{u}_R$ is a unit vector in the direction of the interatomic separation $\mathbf{R}$ from atom 1 to atom 2. Choose a coordinate system in which atom 1 is located at the origin and θ and ϕ are the polar angles of $\mathbf{R}$. For this interaction, prove that

$$A_K^Q(k_1, k_2) = -3 \frac{(4\pi)^{1/2}}{\epsilon_0 R^3} \left(\frac{2}{15}\right)^{1/2} \left[Y_2^Q(\theta, \phi)\right]^* \delta_{k_1,1} \delta_{k_2,1} \delta_{K,2},$$

provided $\hat{T}_{k_1}^{q_1}(j)$ is taken to be an irreducible tensor component of the electric dipole operator of atom j. In this form, both the expansion coefficients $A_K^Q(k_1, k_2)$ and the irreducible tensor operators $\hat{T}_K^Q(k_1, k_2)$ have simple transformation properties under rotation. Explain on physical grounds why the $K = 0$ component (which must be invariant under rotation) and the $K = 1$ component (which is odd under parity) must vanish.