

the corresponding probability a measurement of the observable  $A$  will yield the value  $a_m$  is

$$P(a_m) = \sum_{i=1}^{i=g_{a_m}} |\langle \alpha_m^{(i)} | \psi \rangle|^2. \quad (4)$$

(c) If  $A$  has a continuous spectrum (or if part of the spectrum of  $A$  is continuous), with

$$A|\alpha\rangle = \alpha|\alpha\rangle, \quad (5)$$

the probability a measurement of the physical observable,  $A$ , will yield a value between  $\alpha$  and  $\alpha + d\alpha$  is given by

$$P(\alpha)d\alpha = d\alpha |\langle \alpha | \psi \rangle|^2 \quad (6)$$

for the system specified by the state  $|\psi\rangle$ . Note: In the basis in which  $A$  is diagonal

$$A = \sum_{n,i} |\alpha_n^{(i)}\rangle a_n \langle \alpha_n^{(i)}| + \int d\alpha |\alpha\rangle \alpha \langle \alpha| \quad (7)$$

and

$$\begin{aligned} \langle \psi | A | \psi \rangle &= \sum_{n,i} a_n |\langle \alpha_n^{(i)} | \psi \rangle|^2 + \int d\alpha \alpha |\langle \alpha | \psi \rangle|^2 \\ &= \sum_n a_n P(a_n) + \int d\alpha \alpha P(\alpha). \end{aligned} \quad (8)$$

The operators

$$\sum_i |\alpha_m^{(i)}\rangle \langle \alpha_m^{(i)}|, \quad \text{or} \quad d\alpha |\alpha\rangle \langle \alpha|,$$

are projection operators onto  $a_m$  or  $\alpha$ , respectively.

IV. Immediately after a measurement of the physical observable,  $A$ , the state of the system is specified by a new state vector. If the system was originally specified by the state vector  $|\psi\rangle$ , and if the measurement of  $A$  performed on the system specified by  $|\psi\rangle$  yielded the specific value  $a_m$ , immediately after this measurement, the state of the system is specified by the new state vector

$$\frac{\sum_i |\alpha_m^{(i)}\rangle \langle \alpha_m^{(i)}| \psi}{\sqrt{\sum_j |\langle \alpha_m^{(j)} | \psi \rangle|^2}}.$$

For a nondegenerate  $a_n$ , on the other hand, the new state vector is simply  $|\alpha_n\rangle$ . The measurement of  $A$  disturbs the system! In the case of the two successive polarization filters of Chapter 17, after passing through the first filter, the state of the system was specified by  $|m\rangle$ . If a measurement of the polarization along the new direction  $z'$  then yielded the value  $\lambda_\alpha$ , the particle comes out of the second apparatus in the state  $|\alpha\rangle$ .

## B Time Evolution of a state $|\psi\rangle$

If at time  $t_0$  the state of the system is specified by  $|\psi(t_0)\rangle$ , what is the state of the system at a later time,  $t$ ; i.e., what is  $|\psi(t)\rangle$ ? If a measurement is made on the system of some observable  $A$  (or  $B$ , etc.), the time-evolution of the quantum system is noncausal. The measurement of  $A$  (between times  $t_0$  and  $t$ ) disturbs the system. The measurement process itself must be taken into account. If we enlarge the system to include the whole measurement apparatus, this larger system would have to be studied, and it may not be practical to consider this larger system. For an isolated system (undisturbed by an observer and his apparatus in the time interval from  $t_0$  to  $t$ ), however, the evolution in time from  $|\psi(t_0)\rangle$  to  $|\psi(t)\rangle$  is completely causal (though we are still tied to the probability description). The time evolution is given by

$$-\frac{\hbar}{i} \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi(t)\rangle. \quad (9)$$

The Hamiltonian will often not be an explicit function of the time, but we have here allowed for the possibility of an explicit time-dependence. We can also think of the  $|\psi(t)\rangle$  being produced by the action of a unitary operator acting on  $|\psi(t_0)\rangle$

$$|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle, \quad \text{with } U(t_0, t_0) = 1, \quad (10)$$

so

$$-\frac{\hbar}{i} \frac{d}{dt} U(t, t_0) |\psi(t_0)\rangle = H(t) U(t, t_0) |\psi(t_0)\rangle, \quad (11)$$

and because this is valid for any arbitrary  $|\psi(t_0)\rangle$ ,

$$-\frac{\hbar}{i} \frac{d}{dt} U(t, t_0) = H(t) U(t, t_0). \quad (12)$$

This equation has the solution

$$U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t dt' H(t') U(t', t_0). \quad (13)$$

If  $H$  is an explicit function of the time, it may be difficult to do the integral. If  $H$  is not an explicit function of the time, the equation for  $U$  can be integrated and yields

$$U(t, t_0) = e^{-\frac{i}{\hbar}(t-t_0)H}. \quad (14)$$

$U$  is unitary if  $H$  is hermitian,  $H^\dagger = H$ . The operator  $H$  is then the generator of this unitary operator, which now gives a shift in time or a “time-translation.” Recall the operator  $p_x$  was the generator,  $G$ , for a space translation in the  $x$ -direction. Now the time shift,  $(t - t_0)$ , has taken the place of the space shift,  $c_1$ , of Chapter 18. For an  $H$ , which is not an explicit function of time,

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}(t-t_0)H} |\psi(t_0)\rangle. \quad (15)$$

The description given here is the so-called *Schrödinger picture* of quantum theory, in which (a) the state vectors  $|\psi\rangle$  change with time, but (b) all physical observables  $A$ , such as  $p_x$ , or  $x$ , or functions of  $\vec{r}$ ,  $\vec{p}$ , such as  $H(\vec{p}, \vec{r})$ , are assumed to have no explicit time dependence.

An alternative point of view was taken by Heisenberg and is known by the name, the *Heisenberg picture*. Now, (a) state vectors are assumed constant in time, but (b) the physical observables are taken to vary with time. To make the transition from the Schrödinger picture to the Heisenberg picture, consider the expectation value of an operator,  $O(\vec{p}, \vec{r})$ , where we use the subscript,  $S$ , to designate this operator, *not* explicitly a function of  $t$ , i.e.,  $O = O_S$ , similarly for the time-dependent or Schrödinger state vector  $|\psi(t)\rangle = |\psi_S\rangle$ . Then,

$$\begin{aligned} \langle\psi(t)|O|\psi(t)\rangle &\equiv \langle\psi_S|O_S|\psi_S\rangle \\ &= \langle\psi(t_0)|U^\dagger(t, t_0)O U(t, t_0)|\psi(t_0)\rangle \equiv \langle\psi_H|O_H|\psi_H\rangle, \end{aligned} \quad (16)$$

where the subscript  $H$  now stands for Heisenberg. The time-independent state vector is  $|\psi(t_0)\rangle = |\psi_H\rangle$ , and the time-dependent Heisenberg operator,  $O_H$ , is given by

$$O_H = U^\dagger(t, t_0)O_S U(t, t_0). \quad (17)$$

Note,

$$\begin{aligned} -\frac{\hbar}{i} \frac{dO_H}{dt} &= \left( -\frac{\hbar}{i} \frac{dU^\dagger}{dt} \right) O_S U + U^\dagger O_S \left( -\frac{\hbar}{i} \frac{dU}{dt} \right) \\ &= -U^\dagger H O_S U + U^\dagger O_S H U \\ &= -(U^\dagger H U)(U^\dagger O_S U) + (U^\dagger O_S U)(U^\dagger H U) \\ &= -H O_H + O_H H, \end{aligned} \quad (18)$$

where we have used  $O_H = U^\dagger O_S U$  and that the Hamiltonian operator,  $H$ , commutes with  $U$ , which is a function only of pure numbers and the operator  $H$  itself. Thus,  $U^\dagger H U = H U^\dagger U = H$ . The time dependence of  $O_H$  is then given by the equation

$$-\frac{\hbar}{i} \frac{dO_H}{dt} = [O_H, H]. \quad (19)$$

This relation is known as the Heisenberg equation. Even in the Schrödinger picture, we sometimes introduce artificially an explicit time dependence, so  $O_S = O_S(t)$ . In that case, the corresponding equation would be

$$-\frac{\hbar}{i} \frac{dO_H}{dt} = [O_H, H] + \left( -\frac{\hbar}{i} \frac{\partial O}{\partial t} \right)_H, \quad \text{with} \quad \left( -\frac{\hbar}{i} \frac{\partial O}{\partial t} \right)_H = U^\dagger \left( -\frac{\hbar}{i} \frac{\partial O_S}{\partial t} \right) U. \quad (20)$$

In the Heisenberg picture, the kets and bras are time independent. We shall take matrix elements of eq. (19) (assuming that  $\frac{\partial O}{\partial t} = 0$ ) in the energy representation, i.e., between eigenstates of the Hamiltonian,  $|n\rangle$ , assuming for the moment  $H$  has only a discrete spectrum. Then, eq. (19) leads to

$$-\frac{\hbar}{i} \frac{d}{dt} \langle n | O_H(t) | m \rangle = \langle n | O_H(t) | m \rangle (E_m - E_n), \quad (21)$$

$$\frac{d(\langle n|O_H(t)|m\rangle)}{\langle n|O_H(t)|m\rangle} = +\frac{i}{\hbar}(E_n - E_m)dt, \quad (22)$$

$$\langle n|O_H(t)|m\rangle = \langle n|O|m\rangle e^{\frac{i}{\hbar}(E_n - E_m)t}, \quad (23)$$

where we have named the integration constant  $\langle n|O|m\rangle$ , which is time independent. The Heisenberg matrix elements,  $O_{nm} \equiv \langle n|O|m\rangle$ , are then just the  $\langle n|O_S|m\rangle$ . Eq. (23) was essentially the starting point in Heisenberg's thinking. He started with the Fourier time analysis of the classical quantity,  $O$ , and replaced the  $n^{th}$  overtone of the classical  $\omega$  with the two-index Bohr quantity  $\omega_{nm} = (E_n - E_m)/\hbar$ . Similarly, he replaced the  $n^{th}$  Fourier coefficient,  $O_n$ , in the Fourier time expansion with a two-index quantity he interpreted as the  $nm^{th}$  matrix element of  $O$ ,  $\langle n|O|m\rangle$ .

## C The Heisenberg Treatment of the One-Dimensional Harmonic Oscillator: Oscillator Annihilation and Creation Operators

Let us now briefly follow Heisenberg's analysis of one of his simplest examples, the 1-D harmonic oscillator. Again, we introduce scale factors to transform the physical coordinate, momentum, energy, and so on, to dimensionless  $x$ ,  $p_x$ , ...,  $x_{phys.} = x\sqrt{\hbar/m\omega_0}$ ,  $p_{phys.} = p_x\sqrt{\hbar m\omega_0}$ ,  $H_{phys.} = H\hbar\omega_0$ , so

$$H = \frac{1}{2}(p_x^2 + x^2). \quad (24)$$

Introduce the two operators

$$a = \frac{1}{\sqrt{2}}(x + ip_x), \quad a^\dagger = \frac{1}{\sqrt{2}}(x - ip_x). \quad (25)$$

From the commutation relation,  $[p_x, x] = -i$ , we get the commutator

$$[a, a^\dagger] = 1, \quad (26)$$

and the Hamiltonian can be expressed as

$$H = \frac{1}{2}(a^\dagger a + aa^\dagger) = (a^\dagger a + \frac{1}{2}). \quad (27)$$

It will be useful to name the operator  $a^\dagger a = N$ . Then, we have the family of three commutation relations

$$[N, a^\dagger] = +a^\dagger, \quad [N, a] = -a, \quad [a, a^\dagger] = 1. \quad (28)$$

These relations should be compared and contrasted with the standard angular momentum commutation relations

$$[L_0, L_+] = +L_+, \quad [L_0, L_-] = -L_-, \quad [L_-, L_+] = -2L_0. \quad (29)$$

The commutator algebra of  $a$ ,  $a^\dagger$ ,  $N$ , is known as the Heisenberg algebra. Note, in particular, the difference from the angular momentum [or SO(3)] algebra in the last entry. If the eigenvectors of the operator,  $N$ , are named  $|n\rangle$ , and its eigenvalues  $N_n$ , these  $|n\rangle$  are also the eigenvectors of  $H$ , because  $H = N + \frac{1}{2}$ ,

$$N_{\text{op.}}|n\rangle = N_n|n\rangle, \quad \text{and} \quad E_n = \hbar\omega_0(N_n + \frac{1}{2}), \quad (30)$$

or

$$(1) \quad a^\dagger a|n\rangle = N_n|n\rangle, \quad (2) \quad aa^\dagger|n\rangle = (N_n + 1)|n\rangle. \quad (31)$$

Acting with  $a$  on (1), and using  $aa^\dagger = N_{\text{op.}} + 1$ , we get

$$aa^\dagger(a|n\rangle) = N_n(a|n\rangle), \quad \text{or} \quad N_{\text{op.}}(a|n\rangle) = (N_n - 1)(a|n\rangle). \quad (32)$$

Similarly, acting with  $a^\dagger$  on (2), we get

$$a^\dagger a(a^\dagger|n\rangle) = (N_n + 1)(a^\dagger|n\rangle), \quad \text{or} \quad N_{\text{op.}}(a^\dagger|n\rangle) = (N_n + 1)(a^\dagger|n\rangle). \quad (33)$$

Eq. (32) tells us

$$\text{either } (a|n\rangle) = \text{const.}|(n - 1)\rangle, \quad \text{or} \quad (a|n\rangle) = 0. \quad (34)$$

Similarly, eq. (33) tells us

$$\text{either } (a^\dagger|n\rangle) = \text{const.'}|(n + 1)\rangle, \quad \text{or} \quad (a^\dagger|n\rangle) = 0, \quad (35)$$

where  $|(n \pm 1)\rangle$  are shorthand notation for the eigenvectors of  $N_{\text{op.}}$  with eigenvalues  $(N_n \pm 1)$ . Now we take the diagonal matrix element of the operator,  $N_{\text{op.}}$  (note the similarity of the procedure for the angular momentum algebra!),

$$\begin{aligned} N_n &= \langle n|a^\dagger a|n\rangle \\ &= \sum_k \langle n|a^\dagger|k\rangle \langle k|a|n\rangle \\ &= \sum_k |\langle k|a|n\rangle|^2 \\ &\geq 0. \end{aligned} \quad (36)$$

Thus,  $N_n$  is positive definite. Now, if  $(a|n\rangle)$  exists, repeat this process by taking the diagonal matrix element of  $N_{\text{op.}}$  between states  $|(n - 1)\rangle$ . We conclude  $(N_n - 1) \geq 0$ . We can repeat this process  $j$  times to conclude  $(N_n - j) \geq 0$ , if  $(a|n - j + 1\rangle) \neq 0$ . If  $N_n$  is positive, however, an integer  $j$  will eventually come, which is big enough such that  $(N_n - j)$  would be negative unless we hit a state  $|n_{\min.}\rangle$ , such that  $(a|n_{\min.}\rangle) = 0$ . For this state, eq. (31) tells us  $N_{n_{\min.}} = 0$ . Now, if we act on this state, with eigenvalue  $N_{n_{\min.}} = 0$ ,  $n$  times in succession with  $a^\dagger$ , we get a state with eigenvalue  $(0 + n)$ , i.e., with  $N_n = n$ . Also, continued operation with  $a^\dagger$  leaves the eigenvalue of  $N_{\text{op.}}$  positive, no upper bound to this discrete set of eigenvalues exists. Thus,

$$E_n = \hbar\omega_0(n + \frac{1}{2}). \quad (37)$$

All that remains is the job of calculating the matrix elements of  $x$  and  $p_x$ . From eq. (36)

$$\begin{aligned} N_n = n &= \sum_k |\langle k | a | n \rangle|^2 \\ &= |\langle (n-1) | a | n \rangle|^2, \end{aligned} \quad (38)$$

where we have assumed the states for this one-degree-of-freedom problem are nondegenerate, so there is just one state, with  $k = (n-1)$ . Except, for an arbitrary phase, we have determined the matrix element of the operator,  $a$ . Choosing the simplest (positive, real) value for this matrix element, we have

$$\langle (n-1) | a | n \rangle = \sqrt{n}. \quad (39)$$

Hermitian conjugation gives us

$$\langle n | a^\dagger | (n-1) \rangle = \sqrt{n}, \quad \text{or} \quad \langle (n+1) | a^\dagger | n \rangle = \sqrt{n+1}. \quad (40)$$

$a^\dagger$  is an oscillator quantum creation operator, and  $a$  is an oscillator quantum annihilation operator. Now, using

$$x = \frac{1}{\sqrt{2}}(a + a^\dagger), \quad \text{and} \quad p_x = \frac{i}{\sqrt{2}}(-a + a^\dagger), \quad (41)$$

we also get

$$\langle m | x | n \rangle = \frac{1}{\sqrt{2}} \left( \delta_{m(n-1)} \sqrt{n} + \delta_{m(n+1)} \sqrt{n+1} \right), \quad (42)$$

$$\langle m | p_x | n \rangle = \frac{1}{\sqrt{2}} \left( -i \delta_{m(n-1)} \sqrt{n} + i \delta_{m(n+1)} \sqrt{n+1} \right). \quad (43)$$

These relations are of course results we have obtained before; but the Heisenberg method of calculation required no knowledge of wave functions or differential equations. As before, we can build more complicated operators from powers of  $x$  and  $p_x$ , and then express any operator in Heisenberg (time-dependent) form

$$O_H(t) = \sum_{n,m} |n\rangle \langle n | O | m \rangle \langle m | e^{\frac{i}{\hbar}(E_n - E_m)t}. \quad (44)$$

For  $x$  and  $p_x$ , we could write the Heisenberg (time-dependent) form of these operators in terms of the Schrödinger (time-independent) oscillator quantum annihilation and creation operators,  $a$  and  $a^\dagger$ , as

$$\begin{aligned} x_H(t) &= \frac{1}{\sqrt{2}}(ae^{-i\omega_0 t} + a^\dagger e^{+i\omega_0 t}), \\ (p_x)_H(t) &= \frac{1}{\sqrt{2}}(-iae^{-i\omega_0 t} + ia^\dagger e^{+i\omega_0 t}), \end{aligned} \quad (45)$$

where we have used eq. (44) to get the time dependence, but have subsequently left off the unit operators,  $\sum_n |n\rangle \langle n| = 1$  and  $\sum_m |m\rangle \langle m| = 1$ .

## D Oscillator Coherent States

Remembering the physical displacement and momentum coordinates of the harmonic oscillator are related to the dimensionless  $x$  and  $p_x$  of the last section by  $q = \sqrt{\hbar/m\omega_0}x$  and  $p = \sqrt{\hbar m\omega_0}p_x$ , we can express the time-dependent displacement and momentum operators through eqs. (41) and (45) by

$$\begin{aligned} q(t) &= \sqrt{\frac{\hbar}{2m\omega_0}}(ae^{-i\omega_0 t} + a^\dagger e^{+i\omega_0 t}), \\ p(t) &= m\omega_0 \sqrt{\frac{\hbar}{2m\omega_0}}(-iae^{-i\omega_0 t} + ia^\dagger e^{+i\omega_0 t}). \end{aligned} \quad (46)$$

If we compare this with the classical solution for the harmonic oscillator,  $q(t) = q_0 \cos(\omega_0 t + \phi)$ , with

$$\begin{aligned} q(t) &= \left( \frac{q_0 e^{-i\phi}}{2} e^{-i\omega_0 t} + \frac{q_0 e^{i\phi}}{2} e^{+i\omega_0 t} \right), \\ p(t) &= m\omega_0 \left( -i \frac{q_0 e^{-i\phi}}{2} e^{-i\omega_0 t} + i \frac{q_0 e^{i\phi}}{2} e^{+i\omega_0 t} \right), \end{aligned} \quad (47)$$

we are led to the idea that it might be very useful to replace the eigenvectors,  $|n\rangle$ , of the harmonic oscillator hamiltonian (or the oscillator quantum number operator), with eigenvectors of the operator,  $a$  (or alternatively  $a^\dagger$ ), if we want to study the transition from the quantum oscillator to the classical oscillator. Moreover, we might expect the eigenvalue of the operator,  $a$ , to be given by a complex number, where the square of the absolute value of this number is related to the energy or the number of oscillator quanta, and the argument of this complex number is related to the classical phase. The new oscillator representation in terms of the eigenvectors of the oscillator annihilation operator,  $a$ , might be particularly useful if the physics of interest involves a statistical distribution of states with different numbers of oscillator quanta, particularly, if the average oscillator excitation number is large, as in the classical limit. Later, when we quantize the electromagnetic field (see Chapter 60), we shall write the hamiltonian of the electromagnetic field

$$H = \sum_{\vec{k}, \mu} \hbar\omega (a_{\vec{k}\mu}^\dagger a_{\vec{k}\mu} + \frac{1}{2})$$

in terms of an infinite number of oscillators with annihilation and creation operators,  $a_{\vec{k}\mu}$  and  $a_{\vec{k}\mu}^\dagger$ . These operators are interpreted as photon annihilation and creation operators, where the vector  $\vec{k}$  is the wave vector, corresponding to the circular frequency  $\omega = kc = |\vec{k}|c$ , and  $\mu$  is a polarization index for the photon. The generalization of the single-mode coherent state to be studied in this section to the multimode coherent state of the electromagnetic field will be useful in the study of optical beams whose proper quantum-mechanical description is given by a statistical distribution of quantum states with different numbers of oscillator quanta. (The seminal papers by R. J. Glauber on quantum optics and optical coherent states are all reprinted in an introduction to coherent states by John R.

Klauder and Bo-Sture Skagerstam, *Coherent States. Applications in Physics and Mathematical Physics*, Singapore: World Scientific, 1985.)

For the single-mode harmonic oscillator, two slightly different definitions of the coherent states can be found in the literature, to be denoted by  $|z\rangle$ , where  $z$  is a complex number giving the eigenvalue of the oscillator annihilation operator. In the first definition of the coherent state

$$|z\rangle_1 = e^{z^*a^\dagger - za}|0\rangle = U(z)|0\rangle, \quad (48)$$

where  $|0\rangle$ , the “vacuum state,” is the oscillator ground state and  $U(z)$  is a unitary operator, because

$$U(z)^\dagger = e^{-(z^*a^\dagger - za)} = U(-z) = U(z)^{-1}. \quad (49)$$

The noncommuting operators,  $A \equiv z^*a^\dagger$  and  $B = -za$ , have a very simple commutator,  $[A, B] = zz^*$ , a  $c$  number commuting with both  $A$  and  $B$ . In this very special case, when

$$[A, [A, B]] = 0 \quad \text{and} \quad [B, [A, B]] = 0, \quad (50)$$

we can write the operator relation

$$e^{(A+B)} = e^{-\frac{1}{2}[A,B]} e^A e^B, \quad (51)$$

as can be shown by direct verification. Note the so-called normal order of the operators on the right-hand side, with creation operators,  $a^\dagger$ , sitting to the left of annihilation operators,  $a$ . The above result leads to

$$|z\rangle_1 = e^{-\frac{1}{2}z^*z} e^{z^*a^\dagger} e^{-za}|0\rangle = e^{-\frac{1}{2}z^*z} e^{z^*a^\dagger}|0\rangle, \quad (52)$$

because  $a|0\rangle = 0$ . For some purposes, a somewhat simpler second definition of the coherent state may therefore be useful

$$|z\rangle_{II} = e^{z^*a^\dagger}|0\rangle, \quad (53)$$

which differs from the definition  $|z\rangle_1$  by the simple  $c$  number function,  $e^{-zz^*/2}$ . This second definition may be a particularly useful definition for generalized coherent states, such as the angular momentum coherent states to be introduced in the next section for which the commutator algebra no longer satisfies the simple relations of eq. (50). To avoid confusion, we will denote the complex number  $z$  in the two different definitions by two different symbols

$$\begin{aligned} |\alpha\rangle_1 &\equiv |\alpha\rangle = e^{-\frac{1}{2}\alpha^*\alpha} e^{\alpha^*a^\dagger}|0\rangle = e^{-\frac{1}{2}\alpha^*\alpha} \sum_{n=0} \frac{(\alpha^*)^n}{\sqrt{n!}} |n\rangle, \\ |\alpha\rangle_{II} &\equiv |\alpha\rangle = e^{z^*a^\dagger}|0\rangle = \sum_{n=0} \frac{(z^*)^n}{\sqrt{n!}} |n\rangle. \end{aligned} \quad (54)$$

Both are eigenvectors of the oscillator annihilation operator,  $a$ , with eigenvalue given by the complex number  $\alpha^*$  or  $z^*$ .

$$\begin{aligned} a|\alpha\rangle &= \alpha^*|\alpha\rangle, \\ a|z\rangle &= z^*|z\rangle. \end{aligned} \quad (55)$$

This follows, for the type II coherent state, from

$$a|z\rangle = ae^{z^*a^\dagger}|0\rangle = a\sum_{n=0}\frac{(z^*a^\dagger)^n}{n!}|0\rangle = z^*\sum_{n=1}\frac{(z^*a^\dagger)^{n-1}}{(n-1)!}|0\rangle = z^*e^{z^*a^\dagger}|0\rangle. \quad (56)$$

For the type I coherent state, the  $c$  number,  $e^{-\alpha\alpha^*/2}$ , is merely carried along in the analogous derivation.

The coherent states  $|\alpha\rangle$  (or  $|z\rangle$ ) then give us another continuous representation of an arbitrary state vector  $|\psi\rangle$  of a physical system. Besides the discrete oscillator quanta representation,  $\langle n|\psi\rangle$ , we already have two continuous representations, the coordinate representation  $\langle x|\psi\rangle$  and the momentum representation  $\langle p_x|\psi\rangle$ , where the operators  $x$  and  $p_x$  have a continuous range of eigenvalues from  $-\infty \rightarrow +\infty$ . We can now add the coherent state representation  $\langle \alpha|\psi\rangle$ , where  $\alpha$  is a complex number,

$$\alpha = \xi + i\eta = \rho e^{i\phi},$$

and  $\xi$  and  $\eta$  range from  $-\infty \rightarrow +\infty$ , and  $\rho$  ranges from  $0 \rightarrow \infty$  and  $\phi$  from  $0 \rightarrow 2\pi$ . Unlike  $\langle x|\psi\rangle$  and  $\langle p_x|\psi\rangle$ , however, which are orthonormal, continuous representations of  $|\psi\rangle$ , with

$$\langle x'|x\rangle = \delta(x' - x), \quad \langle p'_x|p_x\rangle = \delta(p'_x - p_x),$$

the scalar product  $\langle \alpha'|\alpha\rangle$  does not lead to  $\delta$ -functions. Instead,

$$\begin{aligned} \langle \alpha'|\alpha\rangle &= e^{-\frac{1}{2}|\alpha'|^2} e^{-\frac{1}{2}|\alpha|^2} \langle 0|e^{\alpha'^*a} e^{\alpha^*a^\dagger}|0\rangle = e^{-\frac{1}{2}|\alpha'|^2} e^{-\frac{1}{2}|\alpha|^2} \sum_{n,m} \frac{\alpha'^m}{\sqrt{m!}} \frac{\alpha^{*n}}{\sqrt{n!}} \langle m|n\rangle \\ &= e^{-\frac{1}{2}|\alpha'|^2} e^{-\frac{1}{2}|\alpha|^2} e^{\alpha'^*\alpha^*}, \end{aligned} \quad (57)$$

so  $\langle \alpha'|\alpha\rangle$  is a complicated function of  $\alpha$  and  $\alpha'$ , even though  $\langle \alpha|\alpha\rangle = 1$ . Also,

$$\langle z'|z\rangle = e^{z^*z^*}, \quad \text{with} \quad \langle z|z\rangle = e^{|z|^2} \neq 1. \quad (58)$$

The coherent states, however, are complete. In fact, with relations (57) or (58), in place of the Dirac  $\delta$  functions, the coherent states are overcomplete. The completeness can be seen from the existence of the unit operators. For the type I coherent state, the unit operator is

$$\mathbf{1} = \frac{1}{\pi} \int d^2\alpha |\alpha\rangle\langle\alpha| = \frac{1}{\pi} \int_{-\infty}^{\infty} d\xi \int_{-\infty}^{\infty} d\eta |\alpha\rangle\langle\alpha| = \frac{1}{\pi} \int_0^{\infty} \rho d\rho \int_0^{2\pi} d\phi |\alpha\rangle\langle\alpha|. \quad (59)$$

With the use of eq. (54), this unit operator transforms into

$$\begin{aligned} \mathbf{1} &= \frac{1}{\pi} \int d^2\alpha e^{-\alpha\alpha^*} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(\alpha^*)^n}{\sqrt{n!}} \frac{\alpha^m}{\sqrt{m!}} |n\rangle\langle m| \\ &= \sum_{n,m} \frac{1}{\pi} \int_0^{\infty} d\rho \frac{e^{-\rho^2} \rho^{n+m+1}}{\sqrt{n!m!}} \int_0^{2\pi} d\phi e^{i(m-n)\phi} |n\rangle\langle m| \\ &= \sum_{n,m} 2 \int_0^{\infty} d\rho \frac{e^{-\rho^2} \rho^{n+m+1}}{\sqrt{n!m!}} \delta_{nm} |n\rangle\langle m| = \sum_{n=0}^{\infty} 2 \int_0^{\infty} d\rho \frac{e^{-\rho^2} \rho^{2n+1}}{n!} |n\rangle\langle n| \end{aligned}$$

$$= \sum_{n=0}^{\infty} |n\rangle\langle n|, \quad (60)$$

where the completeness relation,  $\sum_n |n\rangle\langle n| = 1$ , was in fact proved in detail in Chapter 5, eq. (13), via

$$\sum_{n=0}^{\infty} \langle x' | n \rangle \langle n | x \rangle = \sum_{n=0}^{\infty} \psi_n(x') \psi_n^*(x) = \delta(x' - x) = \langle x' | x \rangle. \quad (61)$$

For the type II coherent state, conversely, the unit operator requires the Bargmann weighting factor,  $e^{-zz^*}$ , so

$$\begin{aligned} \mathbf{1} &= \frac{1}{\pi} \int d^2 z e^{-zz^*} |z\rangle\langle z| = \frac{1}{\pi} \int d^2 z e^{-zz^*} \sum_{n,m} \frac{z^{*n} z^m}{\sqrt{n!m!}} |n\rangle\langle m| \\ &= \sum_{n=0}^{\infty} |n\rangle\langle n|, \end{aligned} \quad (62)$$

as above.

The type II coherent state realization  $\langle z|\psi\rangle$  of an arbitrary state vector is simply the Bargmann transform of  $\psi(x)$ :  $\langle z|\psi\rangle = F(z)$ .

$$\langle z|\psi\rangle = \sum_{n=0}^{\infty} \langle n | \frac{z^n}{\sqrt{n!}} |\psi\rangle = \sum_{n=0}^{\infty} \frac{z^n}{\sqrt{n!}} \int_{-\infty}^{\infty} dx \psi_n^*(x) \psi(x) = \sum_{n=0}^{\infty} \frac{z^n}{\sqrt{n!}} c_n, \quad (63)$$

where  $\psi(x) = \langle x|\psi\rangle$  is the coordinate representation of  $|\psi\rangle$ , so

$$\langle z|\psi\rangle = \int dx A(x, z) \psi(x) = F(z),$$

where  $A(x, z)$  is the Bargmann kernel function with the simple expansion in terms of the *real*  $\psi_n(x)$  [see eq. (5) of chapter 5],

$$A(x, z) = \sum_{n=0}^{\infty} \psi_n(x) \frac{z^n}{\sqrt{n!}}.$$

We therefore again have two possible forms of the scalar product of two state vectors

$$\langle \psi_a | \psi_b \rangle = \int_{-\infty}^{\infty} dx \psi_a^*(x) \psi_b(x) = \frac{1}{\pi} \int d^2 z e^{-zz^*} F_a^*(z) F_b(z). \quad (64)$$

The complex  $k$  of Chapter 5 has here been renamed  $z$ , because  $k$  for the multi-mode electromagnetic oscillator is reserved for the wavenumber of the mode. Note, further, the natural appearance of the Bargmann measure,  $e^{-zz^*}/\pi$ , in the scalar product. Finally, the coherent state realizations  $F(z) = \langle z|\psi\rangle$  are analytic functions of  $z$ : We have mapped the coordinate functions,  $\sum_n \psi_n(x) c_n$ , into analytic functions,  $\sum_n (z^n / \sqrt{n!}) c_n$ , in a 2-D complex domain.

Let us examine some further properties of the coherent state  $|\alpha\rangle$ . From eq. (54),  $\langle n|\alpha\rangle = e^{-\frac{1}{2}\alpha^*\alpha} (\alpha^*)^n / \sqrt{n!}$ . The probability of finding the oscillator in the  $n^{\text{th}}$  level

in the coherent state  $|\alpha\rangle$  is, therefore,

$$P_n(\alpha) = \frac{e^{-|\alpha|^2} |\alpha|^{2n}}{n!}. \quad (65)$$

The expectation value of the oscillator quantum number operator in the state  $|\alpha\rangle$  is

$$\langle N \rangle = \langle \alpha | a^\dagger a | \alpha \rangle = \alpha \alpha^* = |\alpha|^2, \quad (66)$$

so the probability

$$P_n(\alpha) = \frac{e^{-\langle N \rangle} (\langle N \rangle)^n}{n!} \quad (67)$$

is given by the familiar Poisson distribution. We also have the expectation values

$$\begin{aligned} \langle \alpha | x | \alpha \rangle &= \sqrt{\frac{1}{2}} (\langle \alpha | a + a^\dagger | \alpha \rangle) = \sqrt{\frac{1}{2}} (\alpha^* + \alpha) = \sqrt{2}\xi, \\ \langle \alpha | x^2 | \alpha \rangle &= \frac{1}{2} \langle \alpha | (aa + a^\dagger a^\dagger + 2a^\dagger a + 1) | \alpha \rangle = \frac{1}{2} [(\alpha^* + \alpha)^2 + 1], \\ \langle \alpha | p_x | \alpha \rangle &= -i \sqrt{\frac{1}{2}} \langle \alpha | a - a^\dagger | \alpha \rangle = -i \sqrt{\frac{1}{2}} (\alpha^* - \alpha) = -\sqrt{2}\eta, \\ \langle \alpha | p_x^2 | \alpha \rangle &= \frac{1}{2} \langle \alpha | (-aa - a^\dagger a^\dagger + 2a^\dagger a + 1) | \alpha \rangle = \frac{1}{2} [1 - (\alpha^* - \alpha)^2], \end{aligned} \quad (68)$$

so

$$(\Delta x)_\alpha^2 = \frac{1}{2}, \quad (\Delta p_x)_\alpha^2 = \frac{1}{2}. \quad (69)$$

In the coherent state,  $|\alpha\rangle$ , we therefore have

$$\Delta p_x \Delta x = \frac{1}{2} \quad \text{and, thus,} \quad \Delta p \Delta q = \frac{\hbar}{2}, \quad (70)$$

where dimensionless  $x$  and  $p_x$  have been converted to physical  $q$  and  $p$ . The coherent state is therefore a state with the minimum possible uncertainty, despite the seemingly complicated probability distribution,  $P_n(\alpha)$ , spread over a range of states  $|n\rangle$  about the most likely  $n = \langle N \rangle = |\alpha|^2$ . To understand this, we note that the unitary operator,  $U(\alpha) = e^{(\alpha^* a^\dagger - \alpha a)}$ , shifts the operators,  $a$  and  $a^\dagger$ , hence,  $x$  and  $p_x$ , according to

$$U(\alpha)aU^{-1}(\alpha) = a - \alpha^*, \quad U(\alpha)a^\dagger U^{-1}(\alpha) = a^\dagger - \alpha, \quad (71)$$

where we have used

$$\sum_{n=0}^{\infty} [a, \frac{(\alpha a - \alpha^* a^\dagger)^n}{n!}] = -\alpha^* \sum_{n=1}^{\infty} \frac{(\alpha a - \alpha^* a^\dagger)^{n-1}}{(n-1)!}.$$

Eq. (71) thus leads to

$$\begin{aligned} U(\alpha)xU^{-1}(\alpha) &= x - \sqrt{\frac{1}{2}}(\alpha + \alpha^*) = (x - \sqrt{2}\xi), \\ U(\alpha)p_xU^{-1}(\alpha) &= p_x + i\sqrt{\frac{1}{2}}(\alpha^* - \alpha) = (p_x + \sqrt{2}\eta). \end{aligned} \quad (72)$$

$U(\alpha)$  is a displacement operator shifting coordinate,  $x$ , and momentum,  $p_x$ ,

$$x \rightarrow x - \sqrt{2}\Re(\alpha), \quad p_x \rightarrow p_x + \sqrt{2}\Im(\alpha).$$

Also, the eigenvalue equation,  $a|\alpha\rangle = \alpha^*|\alpha\rangle$ , leads to the following simple differential equations in coordinate and momentum space:

$$\begin{aligned} \frac{1}{\sqrt{2}}\left(x + \frac{d}{dx}\right)\langle x|\alpha\rangle &= \alpha^*\langle x|\alpha\rangle, \\ \frac{i}{\sqrt{2}}\left(\frac{d}{dp_x} + p_x\right)\langle p_x|\alpha\rangle &= \alpha^*\langle p_x|\alpha\rangle, \end{aligned} \quad (73)$$

with solutions

$$\begin{aligned} \langle x|\alpha\rangle &= \mathcal{N}e^{-\frac{1}{2}(x-\sqrt{2}\alpha^*)^2}, & \text{with } \mathcal{N} = e^{-\eta^2}/\pi^{\frac{1}{4}}, \\ \langle p_x|\alpha\rangle &= \mathcal{N}'e^{-\frac{1}{2}(p_x+i\sqrt{2}\alpha^*)^2}, & \text{with } \mathcal{N}' = e^{+\xi^2}/\pi^{\frac{1}{4}}, \end{aligned} \quad (74)$$

so

$$|\langle x|\alpha\rangle|^2 = \frac{1}{\sqrt{\pi}}e^{-(x-\sqrt{2}\xi)^2}, \quad |\langle p_x|\alpha\rangle|^2 = \frac{1}{\sqrt{\pi}}e^{-(p_x+\sqrt{2}\eta)^2}. \quad (75)$$

The minimum uncertainties for the coherent state can now be understood because these are the probabilities for the space and momentum distributions of a displaced oscillator in its  $n = 0$  lowest state, with a displacement  $+\sqrt{2}\Re(\alpha)$  in coordinate space and  $-\sqrt{2}\Im(\alpha)$  in momentum space. Moreover, such an oscillator wave packet will move with time *without* change of shape (see problems 10 and 11). This is the motion of a coherent wave packet.

Just as state vectors can be given in the coherent state representation,  $\langle\alpha|\psi\rangle$ , physical quantities represented by operators,  $O$ , can also be given in the coherent state representation. In the oscillator quantum number representation, we multiplied an operator,  $O$ , by unit operators on the left and on the right to yield,  $O = \sum_{n,m}|n\rangle\langle n|O|m\rangle\langle m|$ . Similarly, we could represent  $O$  by

$$O = \frac{1}{\pi^2}\int d^2\alpha \int d^2\beta |\alpha\rangle\langle\alpha|O|\beta\rangle\langle\beta|, \quad (76)$$

where  $|\alpha\rangle$  and  $|\beta\rangle$  are coherent states. Using eq. (54), we have

$$O = \frac{1}{\pi^2}\int d^2\alpha \int d^2\beta e^{-\frac{1}{2}(|\alpha|^2+|\beta|^2)}|\alpha\rangle\sum_{n,m}\left(\frac{\alpha^n}{\sqrt{n!}}\langle n|O|m\rangle\frac{\beta^{*m}}{\sqrt{m!}}\right)\langle\beta|. \quad (77)$$

The operator,  $O$ , in this form is two-sided, made up of operators,  $|\alpha\rangle\langle\beta|$ , involving two different coherent states. In our earlier continuous representations, such as the coordinate representation, e.g., operators were expressible in terms of functions of a single  $x$  and its derivative. In coordinate representation, e.g., an operator,  $O(x, p_x)$ , which is a function of the basic operators,  $x$  and  $p_x$ , was expressible as  $O(x, \frac{1}{i}\frac{\partial}{\partial x})$ , where we were able to use

$$\langle x'|O(x, p_x)|x\rangle = \delta(x' - x)O(x, \frac{1}{i}\frac{\partial}{\partial x}),$$

so  $O$  becomes expressible as a function of a single  $x$  and its derivative through the  $\delta$  function relation,  $\langle x'|x\rangle = \delta(x' - x)$ . Because this relation does not exist in the coherent state representation, the analogous operator relations must be handled

with some care. For the harmonic oscillator, an operator,  $O$ , can be expressed as a function of the basic operators,  $a^\dagger$  and  $a$ ,  $O(a^\dagger, a)$ . We want to express such an operator as a function of  $z$  and  $\partial/\partial z$ . We have purposely chosen  $z$  in place of  $\alpha$  because a type II coherent state will be somewhat simpler for this purpose. For type II coherent states,  $z$ -space realizations of state vectors,  $\langle z|\psi\rangle$ , are given by the Bargmann transforms,  $F(z) = \sum_n c_n z^n / \sqrt{n!}$ . The scalar product in the complex  $z$ -space involves the Bargmann measure,  $e^{-zz^*}/\pi$ . In this scalar product, the operator  $\partial/\partial z$  is the adjoint of the operator  $z$ . Given two Bargmann-space functions,

$$F_a(z) = \langle z|\psi_a\rangle = \sum_n a_n \frac{z^n}{\sqrt{n!}} \quad \text{and} \quad F_b(z) = \langle z|\psi_b\rangle = \sum_n b_n \frac{z^n}{\sqrt{n!}},$$

we have (using the orthonormality of the  $z^n / \sqrt{n!}$ )

$$\begin{aligned} \frac{1}{\pi} \int d^2z e^{-zz^*} F_a^*(z) \left( \frac{\partial}{\partial z} F_b(z) \right) &= \sum_{n=0} a_n^* b_{n+1} \sqrt{(n+1)} \\ &= \frac{1}{\pi} \int d^2z e^{-zz^*} \left( z F_a(z) \right)^* F_b(z). \end{aligned} \quad (78)$$

Also, from

$$z \left( \frac{z^n}{\sqrt{n!}} \right) = \sqrt{(n+1)} \left( \frac{z^{n+1}}{\sqrt{(n+1)!}} \right) \quad \text{and} \quad \frac{\partial}{\partial z} \left( \frac{z^n}{\sqrt{n!}} \right) = \sqrt{n} \left( \frac{z^{n-1}}{\sqrt{(n-1)!}} \right), \quad (79)$$

we have

$$\begin{aligned} \langle n' | z | n \rangle &= \sqrt{(n+1)} \delta_{n'(n+1)} = \langle n' | a^\dagger | n \rangle, \\ \langle n' | \frac{\partial}{\partial z} | n \rangle &= \sqrt{n} \delta_{n'(n-1)} = \langle n' | a | n \rangle. \end{aligned} \quad (80)$$

The  $z$ -space realizations of the operators,  $a^\dagger$  and  $a$ , are therefore

$$\gamma(a^\dagger) = z \quad \text{and} \quad \gamma(a) = \frac{\partial}{\partial z}. \quad (81)$$

A more complicated operator, such as  $x^2 = \frac{1}{2}(aa + a^\dagger a^\dagger + 2a^\dagger a + 1)$ , e.g., has the  $z$ -space realization

$$\gamma(x^2) = \frac{1}{2} \left( \frac{\partial^2}{\partial z^2} + z^2 + 2z \frac{\partial}{\partial z} + 1 \right).$$

Finally, with

$$\langle z|\psi\rangle = \langle 0|e^{za}|\psi\rangle = F(z)$$

$\langle z|\psi'\rangle$ , with  $|\psi'\rangle = O|\psi\rangle$ , is given by  $\langle 0|e^{za}O|\psi\rangle$ , which we want to write in the form  $\gamma(O)F(z)$ , where  $\gamma(O)$  is to be determined as a function of operators,  $z$ , and  $\partial/\partial z$ . For this purpose, we rewrite  $\langle z|O|\psi\rangle$  with the use of the unit operator,  $e^{-za}e^{za} = 1$ , as

$$\langle 0|e^{za}O|\psi\rangle = \langle 0|(e^{za}Oe^{-za})e^{za}|\psi\rangle$$

$$= \langle 0 | \left( O + z[a, O] + \frac{z^2}{2!} [a, [a, O]] + \dots \right) e^{za} |\psi\rangle, \quad (82)$$

where we have used eq. (23) of Chapter 16 (renaming  $i\epsilon \equiv z$ ) for the expansion of  $e^{za} O e^{-za}$ . In particular, with  $O = a$ , we have

$$\begin{aligned} \langle z|a|\psi\rangle &= \langle 0|ae^{za}\psi\rangle = \langle 0|\frac{\partial}{\partial z}e^{za}|\psi\rangle = \frac{\partial}{\partial z}\langle 0|e^{za}|\psi\rangle \\ &= \frac{\partial}{\partial z}\langle z|\psi\rangle, \end{aligned} \quad (83)$$

leading to

$$\gamma(a) = \frac{\partial}{\partial z}. \quad (84)$$

Similarly, with  $O = a^\dagger$ , we have

$$\langle z|a^\dagger|\psi\rangle = \langle 0|(a^\dagger + z)e^{za}|\psi\rangle = \langle 0|ze^{za}|\psi\rangle = z\langle z|\psi\rangle, \quad (85)$$

where we have used  $\langle 0|a^\dagger = (a|0)^\dagger = 0$ , leading again to

$$\gamma(a^\dagger) = z. \quad (86)$$

## E Angular Momentum Coherent States

Because we can make an analogy between the operators

$$a, a^\dagger, 1 = [a, a^\dagger] \quad \text{of the oscillator algebra and}$$

$$J_-, J_+, J_0 = -\frac{1}{2}[J_-, J_+] \quad \text{of the angular momentum algebra,}$$

it is possible to define angular momentum coherent states in analogy with the oscillator coherent states. Again, we will distinguish between two slightly different definitions. For the type I coherent state, using a complex variable  $\alpha$ , we define

$$|\alpha\rangle_I \equiv |\alpha\rangle = e^{\alpha^* J_- - \alpha J_+} |J, M = -J\rangle. \quad (87)$$

For the type II coherent state, using the complex variable  $z$ , we define

$$|z\rangle_{II} \equiv |z\rangle = e^{z^* J_-} |J, M = -J\rangle. \quad (88)$$

A generic  $|J, M\rangle$  has been used for the angular momentum eigenvectors, and the oscillator ground state,  $|0\rangle$ , has been replaced with the angular momentum eigenvector with the lowest possible eigenvalue of  $J_0, M = -J$ , so  $J_-|J, M = -J\rangle = 0$  in analogy with  $a|0\rangle = 0$ . For the type I coherent state, it will be useful to relate the complex number  $\alpha$  to the real angle variables  $\theta$  and  $\phi$ , via

$$-\alpha = \frac{\theta}{2} e^{i\phi},$$

where  $\theta, \phi$  are polar and azimuth angles giving the standard orientation of a unit vector  $\vec{r}/r$  in our 3-D world. With this choice of parameterization of the complex variable,  $\alpha$ , the type I coherent state becomes

$$\begin{aligned} |\alpha\rangle &= e^{-i\theta(-\sin\phi J_x + \cos\phi J_z)} |M = -J\rangle \\ &= e^{-i\theta(\vec{n}\cdot\vec{J})} |M = -J\rangle, \end{aligned} \quad (89)$$

where  $\vec{n}$  is a unit vector in the  $x, y$ -plane making an angle  $\phi$  with the  $y$ -axis and  $(\frac{\pi}{2} - \phi)$  with the negative  $x$ -axis; i.e.,  $\vec{n}$  is a unit vector in the direction of the  $y'$  axis after a rotation about the  $z$ -axis through an angle  $\phi$ . We shall return to the type I coherent state in chapter 29 after studying rotation operators in our 3-D world in greater generality.

For the type II coherent state, we can expand  $|z\rangle$  in terms of angular momentum eigenstates  $|JM\rangle$ , via

$$\begin{aligned} |z\rangle &= e^{z^* J_-} |M = -J\rangle = \sum_{n=0}^{2J} \frac{z^{*n}}{n!} (J_+)^n |M = -J\rangle \\ &= \sum_{n=0}^{2J} \frac{z^{*n}}{\sqrt{n!}} \sqrt{\frac{(2J)!}{(2J-n)!}} |M = -J+n\rangle. \end{aligned} \quad (90)$$

An arbitrary state vector  $|\psi\rangle$  in the subspace of Hilbert space appropriate to our angular momentum operator,  $\vec{J}$ , can now be specified through its  $z$ -space realization,  $\langle z|\psi\rangle$ ,

$$\begin{aligned} \langle z|\psi\rangle &= \langle M = -J | e^{zJ_-} |\psi\rangle = \sum_{n=0}^{2J} \frac{z^n}{\sqrt{n!}} \sqrt{\frac{(2J)!}{(2J-n)!}} \langle M = -J+n | \psi\rangle \\ &= \sum_{n=0}^{2J} \frac{z^n}{\sqrt{n!}} K_n \langle M = -J+n | \psi\rangle. \end{aligned} \quad (91)$$

Except for a new numerical factor,  $K_n$ , we have expanded the coherent state in terms of the orthonormal  $z$ -space oscillator basis. The orthonormality of the  $z^n/\sqrt{n!}$  requires the Bargmann weighting function  $e^{-zz^*}/\pi$  in the complex  $z$ -plane. We will therefore find it convenient to use the unit operator in the Bargmann form

$$1 = \frac{1}{\pi} \int d^2z e^{-zz^*} |z\rangle\langle z|$$

for  $z$ -space scalar products. We have thus mapped the angular momentum states onto oscillator states in the complex  $z$ -space realization. The oscillator excitation, however, is now limited to  $n \leq 2J$ . Also, the angular momentum coherent state  $|z\rangle$  is *not* an eigenvector of the operator  $J_-$  because of the additional  $n$ -dependent numerical factors,  $K$ .

To get the  $z$ -space realizations of operators, we use

$$\begin{aligned} \langle z|O|\psi\rangle &= \langle -J | e^{zJ_-} O |\psi\rangle = \langle -J | (e^{zJ_-} O e^{-zJ_-}) e^{zJ_-} |\psi\rangle \\ &= \langle -J | \left( O + z[J_-, O] + \frac{z^2}{2!} [J_-, [J_-, O]] + \dots \right) e^{zJ_-} |\psi\rangle, \end{aligned} \quad (92)$$

where we have used the abbreviation,  $|J, M = -J\rangle \equiv |-J\rangle$ , for the state of lowest possible  $M$ . Let us choose  $O = J_-, J_0, J_+$  in turn to get the  $z$ -space realizations of the angular momentum operators themselves.

$$\begin{aligned}\langle z|J_-|\psi\rangle &= \langle -J|J_-e^{zJ_-}|\psi\rangle = \langle -J|\frac{\partial}{\partial z}e^{zJ_-}|\psi\rangle = \frac{\partial}{\partial z}\langle -J|e^{zJ_-}|\psi\rangle \\ &= \frac{\partial}{\partial z}\langle z|\psi\rangle, \\ \langle z|J_0|\psi\rangle &= \langle -J|(J_0 + zJ_-)e^{zJ_-}|\psi\rangle = \langle -J|\left(-J + z\frac{\partial}{\partial z}\right)e^{zJ_-}|\psi\rangle, \\ &= \left(-J + z\frac{\partial}{\partial z}\right)\langle z|\psi\rangle; \\ \langle z|J_+|\psi\rangle &= \langle -J|(J_+ - 2J_0z - z^2J_-)e^{zJ_-}|\psi\rangle = \langle -J|\left(2Jz - z^2\frac{\partial}{\partial z}\right)e^{zJ_-}|\psi\rangle \\ &= \left(2Jz - z^2\frac{\partial}{\partial z}\right)\langle z|\psi\rangle,\end{aligned}\quad (93)$$

where we have used  $\langle -J|J_0 = (J_0 - J)^\dagger = -J\langle -J|$ , and  $\langle -J|J_+ = 0$ , via the hermitian conjugate of  $J_-| - J\rangle = 0$ . We have thus found  $z$ -space realizations of the operators,  $J_-, J_0, J_+$ ,

$$\begin{aligned}\Gamma(J_-) &= \frac{\partial}{\partial z}, \\ \Gamma(J_0) &= \left(-J + z\frac{\partial}{\partial z}\right), \\ \Gamma(J_+) &= z\left(2J - z\frac{\partial}{\partial z}\right).\end{aligned}\quad (94)$$

It is easy to verify these  $\Gamma(J_i)$  satisfy the angular momentum commutation rules, which of course is just a check of our arithmetic. In addition,

$$\Gamma(\vec{J}^2) = \frac{1}{2}[\Gamma(J_+)\Gamma(J_-) + \Gamma(J_-)\Gamma(J_+)] + \Gamma(J_0)^2 = J(J+1). \quad (95)$$

$\Gamma(J_+)$ , however, is not the adjoint of  $\Gamma(J_-)$  with respect to the Bargmann measure, where, as we have seen,  $\partial/\partial z$  is the adjoint of  $z$ . This is related to the fact that our  $z$ -space realization of the angular momentum operators is a nonunitary one. It is the reason why we have used  $\Gamma(J_i)$  for the above  $z$ -space realization of the  $J_i$ , reserving  $\gamma(J_i)$  for the unitary one. To calculate matrix elements of an operator,  $O$ , through its  $z$ -space realization, built from operators  $z$  and  $\partial/\partial z$ , we see from the expansion of  $\langle z|\psi\rangle$  of eq. (91) that such a  $\Gamma(O)$ , acting on the  $n^{\text{th}}$  term of the expansion will in general create Bargmann space orthonormal  $(z^{n'}/\sqrt{n'!})$  not multiplied by the proper  $K_{n'}$ . To attain the proper  $(K_{n'}z^{n'}/\sqrt{n'!})$ , we can multiply the resultant obtained from the action of  $\Gamma(O)$  by  $(K_{n'}^{-1} \times K_{n'}) = 1$  and thereby transform the nonunitary form of the operator,  $\Gamma(O)$ , into a unitary form, to be denoted by  $\gamma(O)$ , where

$$\gamma(O) = K^{-1}\Gamma(O)K = \left(\gamma(O^\dagger)\right)^\dagger, \quad (96)$$

thus making  $\gamma(O)$  unitary. The operators,  $K$ , are merely the command: Multiply an orthonormal Bargmann space function  $z^n/\sqrt{n!}$  by the appropriate factor,  $K_n$ .

For the most general,  $O$ , eq. (95) can be put in the form

$$\gamma(O) = K^{-1}\Gamma(O)K = (\gamma(O^\dagger))^\dagger = (K^{-1}\Gamma(O^\dagger)K)^\dagger = K^\dagger(\Gamma(O^\dagger))^\dagger(K^{-1})^\dagger, \quad (97)$$

or, via left-multiplication by  $K$  and right-multiplication by  $K^\dagger$ ,

$$\Gamma(O)KK^\dagger = KK^\dagger(\Gamma(O^\dagger))^\dagger. \quad (98)$$

For the specific operator,  $O = J_+$ , of the angular momentum algebra, eq. (96) becomes

$$\gamma(J_+) = K^{-1}\Gamma(J_+)K = (\gamma(J_-))^\dagger = K^\dagger(\Gamma(J_-))^\dagger(K^{-1})^\dagger, \quad (99)$$

and eq. (98) becomes

$$z(2J - z\frac{\partial}{\partial z})KK^\dagger = KK^\dagger\left(\frac{\partial}{\partial z}\right)^\dagger = KK^\dagger z. \quad (100)$$

In eq. (91), the factor  $K_n$  was evaluated from the known matrix elements of  $J_+$  acting  $n$  times in succession on the state  $|J, -J\rangle$ . If we had not had prior knowledge of these matrix elements, we could now evaluate these by using eq. (100) to first evaluate  $(KK^\dagger)_n$ . In particular, both the operator  $z$  and the operator  $\Gamma(J_+) = z(2J - z\partial/\partial z)$  convert a  $z$ -space function,  $z^n$ , into a  $z$ -space function,  $z^{n+1}$ , so eq. (100) becomes

$$z(2J - n)(KK^\dagger)_n = (KK^\dagger)_{n+1}z.$$

On the right-hand side of the equation, the action of  $KK^\dagger$  follows the action of the operator  $z$  and  $z\partial/\partial z(z^n) = n(z^n)$ . We therefore have

$$\frac{(KK^\dagger)_{n+1}}{(KK^\dagger)_n} = (2J - n).$$

Because the Bargmann state with  $n = 0$  has the same normalization as the angular momentum eigenstate,  $|J, M = -J\rangle$ , we have  $(KK^\dagger)_0 = 1$ . Iterating the above recursion relation for  $KK^\dagger$ , starting with  $n = 0$ , we obtain

$$(KK^\dagger)_n = 2J(2J - 1)\cdots(2J + 1 - n) = \frac{(2J)!}{(2J - n)!}.$$

The hermitian operator,  $KK^\dagger$ , must have real eigenvalues. In our special case,  $K$  is the simple command: Multiply  $(z^n/\sqrt{n!})$  by an  $n$ -dependent factor. We can make this renormalization factor real without loss of generality, so  $K_n$  becomes the real number

$$K_n = (K^\dagger)_n = \sqrt{\frac{(2J)!}{(2J - n)!}}. \quad (101)$$

We can therefore rederive the matrix elements of  $J_-$ ,  $J_0$ , and  $J_+$ . Eqs. (94) and (96) lead to

$$\langle n - 1 | J_- | n \rangle = (K^{-1})_{n-1}(n - 1 | \frac{\partial}{\partial z} | n)K_n = \sqrt{(2J + 1 - n)n}$$

$$\begin{aligned}
&= \sqrt{(J+1-M)(J+M)}, \\
\langle n|J_0|n\rangle n &= (K^{-1})_n(n|(-J+z\frac{\partial}{\partial z})|n)K_n = (-J+n) \\
&\quad = M, \\
\langle n+1|J_+|n\rangle &= (K^{-1})_{n+1}(n+1|z(2J-z\frac{\partial}{\partial z})|n)K_n \\
&= \sqrt{\frac{(2J-n-1)!}{(2J-n)!}}\sqrt{n+1}(2J-n) = \sqrt{(2J-n)(n+1)} \\
&= \sqrt{(J-M)(J+M+1)}, \tag{102}
\end{aligned}$$

where the Bargmann space matrix elements

$$(n'|\Gamma(O)|n) = \frac{1}{\pi} \int d^2z e^{-zz^*} \frac{z^{*n'}}{\sqrt{n'!}} \Gamma(O) \frac{z^n}{\sqrt{n!}}$$

have been denoted by round parentheses and we have used  $M = -J + n$  to express all matrix elements in their standard form.

Final Notes:

(1). The technique used here to derive the matrix elements of the angular momentum operators can be used to derive the matrix elements of more complicated families of operators with more complicated commutator algebras. For coherent state techniques of such generalized coherent states, see, e.g., A. Perelomov, *Generalized Coherent States and Their Applications*. Springer-Verlag, 1986, or K. T. Hecht, *The Vector Coherent State Method and its Application to Problems of Higher Symmetries*. Lecture Notes in Physics **290**. Springer-Verlag, 1987.

(2). The technique used here, which involved a mapping of angular momentum eigenstates onto orthonormal harmonic oscillator  $z$ -space Bargmann eigenstates,  $z^n/\sqrt{n!}$ , is useful if we have no a priori knowledge of the numerical values of the  $K$  operator or the  $KK^\dagger$  eigenvalues. Alternatively, we could have used a different  $z$ -space measure to make the  $(z^n/\sqrt{n!})K_n$  into an orthonormal set in the complex  $z$ -space domain. This would have involved a change of measure

$$\frac{1}{\pi} e^{-zz^*} \rightarrow \frac{(2J+1)}{\pi} \frac{1}{(1+zz^*)^{2J+2}},$$

as can be seen from the orthonormality integral

$$\begin{aligned}
&\frac{(2J+1)}{\pi} \int d^2z \frac{1}{(1+zz^*)^{2J+2}} \frac{z^{*m} K_m^*}{\sqrt{m!}} \frac{z^n K_n}{\sqrt{n!}} \\
&= \frac{(2J+1)}{\pi} \int_0^\infty \frac{d\rho \rho^{n+m+1}}{(1+\rho^2)^{2J+2}} \int_0^{2\pi} d\phi e^{i(n-m)\phi} \frac{K_m^* K_n}{\sqrt{m!n!}} \\
&= \delta_{nm} \frac{(2J+1)(2J)!}{n!(2J-n)!} 2 \int_0^\infty \frac{d\rho \rho^{2n+1}}{(1+\rho^2)^{2J+2}} = \delta_{nm}, \tag{103}
\end{aligned}$$

via the integral

$$2 \int_0^\infty \frac{d\rho \rho^{2n+1}}{(1+\rho^2)^{2J+2}} = \int_0^\infty \frac{d\tau \tau^n}{(1+\tau)^{2J+2}} = B(n+1, 2J+1-n)$$

$$= \frac{\Gamma(n+1)\Gamma(2J+1-n)}{\Gamma(2J+2)} = \frac{n!(2J-n)!}{(2J+1)!}, \quad (104)$$

where  $B(p, q)$  is the Beta function expressed by  $\Gamma$  functions and in terms of factorials because  $2J$  must be an integer.

## Problems

**23.** Given three hermitian operators,  $T_1, T_2, T_3$ , with commutation relations

$$[T_2, T_3] = iT_1, \quad [T_3, T_1] = iT_2, \quad [T_1, T_2] = -iT_3,$$

which differ from the angular momentum commutator algebra because of the minus sign in the last commutation relation! Show that the three  $T_j$  all commute with the operator

$$T^2 = T_3^2 - T_1^2 - T_2^2.$$

Again, note the minus signs and the difference from the angular momentum case. Convert the operators,  $T_j$ , to the new set

$$T_{\pm} = (T_1 \pm iT_2), \quad T_3 = T_0,$$

and show these equations satisfy the commutation relations

$$[T_0, T_{\pm}] = \pm T_{\pm}, \quad [T_+, T_-] = -2T_0.$$

Again, note the minus sign in the last commutation relation. Solve the simultaneous eigenvalue problem

$$\begin{aligned} T^2 |\lambda m\rangle &= \lambda |\lambda m\rangle = j(j+1) |\lambda m\rangle = j(j+1) |jm\rangle, \\ T_0 |\lambda m\rangle &= m |\lambda m\rangle = m |jm\rangle, \end{aligned} \quad (1)$$

where we have named  $\lambda = j(j+1)$ . (No implication exists that  $j$  be an integer or half-integer.) Show, in particular, that now:

(1) If  $T_3$  has positive eigenvalues, a minimum possible,  $m_{\min}$ , exists, such that

$$T_- |\lambda m_{\min}\rangle = 0, \quad m = m_{\min} + n, \quad \text{with } n = 0, 1, 2, \dots, \rightarrow \infty,$$

where  $m_{\min} = (j+1)$ .

(2) If  $T_3$  has negative eigenvalues, a maximum possible  $m_{\max} = -|m_{\max}|$  exists, such that

$$T_+ |\lambda m_{\max}\rangle = 0, \quad m = m_{\max} - n = -(|m_{\max}| + n), \quad \text{with } n = 0, 1, \dots, \rightarrow \infty,$$

where now  $m_{\max} = -(j+1)$  and we assume  $j$  is positive.

Find the nonzero matrix elements of  $T_+$  and  $T_-$ ,

$$\langle jm' | T_+ | jm \rangle = \langle j(m+1) | T_+ | jm \rangle,$$

$$\langle jm' | T_- | jm \rangle = \langle j(m-1) | T_- | jm \rangle,$$

and note the differences and similarities with the corresponding angular momentum case.

Note: The angular momentum operators,  $J_k$ , generate the group SO(3) (the special orthogonal transformations in three dimensions, with determinant = +1), in the case when  $j$  are integers, or SU(2) (the special unitary transformations in two dimensions) and in the case when  $j$  are half-integers. The three operators,  $T_k$ , on the other hand, generate the group SO(2,1). Note the two minus signs and the one plus sign in the operator  $\mathcal{T}^2$ .

### *Solution for Problem 23: The SO(2,1) Algebra*

The various commutator relations follow from the given commutation relations by simple commutator algebra. For example,

$$\begin{aligned}[T_3, \mathcal{T}^2] &= -T_1[T_3, T_1] - [T_3, T_1]T_1 - T_2[T_3, T_2] - [T_3, T_2]T_2 \\ &= -iT_1T_2 - iT_2T_1 + iT_2T_1 + iT_1T_2 = 0.\end{aligned}\quad (2)$$

We are interested in the simultaneous eigenvectors of the two commuting hermitian operators,  $T_3$  and  $\mathcal{T}^2$ ,

$$\begin{aligned}\mathcal{T}^2|\lambda m\rangle &= \lambda|\lambda m\rangle, \\ T_3|\lambda m\rangle &= m|\lambda m\rangle.\end{aligned}\quad (3)$$

Let us consider the new vectors,  $T_{\pm}|\lambda m\rangle$ . Acting on either of these with both  $\mathcal{T}^2$  and  $T_3$ , we get (with the use of the commutation relations),

$$\begin{aligned}\mathcal{T}^2(T_+|\lambda m\rangle) &= T_+\mathcal{T}^2|\lambda m\rangle = \lambda(T_+|\lambda m\rangle), \\ T_3(T_+|\lambda m\rangle) &= T_+T_3|\lambda m\rangle + T_+|\lambda m\rangle = (m+1)(T_+|\lambda m\rangle).\end{aligned}\quad (4)$$

Thus, if  $|\lambda m\rangle$  is simultaneously an eigenvector of  $\mathcal{T}^2$  and  $T_3$ , with eigenvalues  $\lambda$  and  $m$ , either  $(T_+|\lambda m\rangle)$  is simultaneously an eigenvector of  $\mathcal{T}^2$  and  $T_3$  with eigenvalues  $\lambda$  and  $(m+1)$  or  $(T_+|\lambda m\rangle) = 0$ . Similarly,

$$\begin{aligned}\mathcal{T}^2(T_-|\lambda m\rangle) &= T_-\mathcal{T}^2|\lambda m\rangle = \lambda(T_-|\lambda m\rangle), \\ T_3(T_-|\lambda m\rangle) &= T_-T_3|\lambda m\rangle - T_-|\lambda m\rangle = (m-1)(T_-|\lambda m\rangle).\end{aligned}\quad (5)$$

Thus, if  $|\lambda m\rangle$  is simultaneously an eigenvector of  $\mathcal{T}^2$  and  $T_3$ , with eigenvalues  $\lambda$  and  $m$ , either  $(T_-|\lambda m\rangle)$  is simultaneously an eigenvector of  $\mathcal{T}^2$  and  $T_3$  with eigenvalues  $\lambda$  and  $(m-1)$ ; or  $(T_-|\lambda m\rangle) = 0$ . To investigate these two possibilities, let us rewrite  $\mathcal{T}^2$

$$\begin{aligned}\mathcal{T}^2 &= T_3^2 - T_1^2 - T_2^2 = T_0^2 - \frac{1}{2}(T_+T_- + T_-T_+) = T_0^2 - T_+T_- - T_0 \\ &\quad = T_0^2 - T_-T_+ + T_0,\end{aligned}\quad (6)$$

$$\text{so } T_+T_- = T_0^2 - T_0 - \mathcal{T}^2$$

$$\text{and} \quad T_- T_+ = T_0^2 + T_0 - T^2. \quad (7)$$

Now, let us take the diagonal matrix element of these two relations between states with the same  $\lambda, m$ , assuming a state  $|\lambda m\rangle$  exists, viz., it leads to a square-integrable eigenfunction. First,

$$\begin{aligned} \langle \lambda m | T_+ T_- | \lambda m \rangle &= ((m^2 - m) - \lambda) \\ &= \sum_{m'} \langle \lambda m | T_+ | \lambda m' \rangle \langle \lambda m' | T_- | \lambda m \rangle \\ &= \sum_{m'} |\langle \lambda m' | T_- | \lambda m \rangle|^2 \geq 0, \end{aligned} \quad (8)$$

where we have used  $\langle \lambda m | T_+ | \lambda m' \rangle = \langle \lambda m' | T_- | \lambda m \rangle^*$  and have summed over a complete set of intermediate states. We must have  $m' = (m - 1)$ . By including a sum over states with  $m' = (m - 1)$ , we have allowed for the possibility more than one independent state with that restriction exists. Similarly, we have

$$\begin{aligned} \langle \lambda m | T_- T_+ | \lambda m \rangle &= ((m^2 + m) - \lambda) \\ &= \sum_{m'} |\langle \lambda m' | T_+ | \lambda m \rangle|^2 \geq 0. \end{aligned} \quad (9)$$

We have the two patently positive quantities of eqs. (7) and (8) only if the two functions,  $f(m) = ((m^2 - m) - \lambda)$  or  $((m^2 + m) - \lambda)$  are equal to or greater than zero. The two functions of  $m$ ,  $(m^2 \mp m)$ , have minima at  $m = \pm \frac{1}{2}$ , both with a minimum value of  $-\frac{1}{4}$ . Unlike the corresponding operator of the angular momentum algebra, with its slightly different commutation relations, the operator,  $T^2$ , is no longer a sum of positive hermitian operators. Thus, the eigenvalue,  $\lambda$ , could be either positive or negative. In particular, if  $\lambda < -\frac{1}{4}$ , the quantities  $((m^2 \mp m) - \lambda)$  are positive for all values of  $m$ , positive or negative. Thus, all values of  $\pm m$  are possible, and for any  $\lambda$ , such that  $\lambda < -\frac{1}{4}$ , we have a continuous spectrum of allowed values for both  $\lambda$  and  $m$ . Conversely, if  $\lambda > 0$ , and if an eigenvalue,  $m_0 > 0$  exists, such that  $((m_0^2 - m_0) - \lambda) > 0$ , the step-down action of  $n$  operations with  $T_-$  could eventually lead to an  $(m_0 - n)$  such that  $((m_0 - n)(m_0 - n - 1) - \lambda) < 0$ , and eq. (7) would lead to an inconsistency. A patently positive quantity on one side of eq. (7) would be equal to a negative quantity on the other side. Hence, our assumption of the existence of a square-integrable  $|\lambda m_0\rangle$  must have been incorrect. If  $m_0$ , however, is such that an integer  $n$  exists such that  $(m_0 - n) \equiv m_{\min.}$ , so

$$\left( T_- | \lambda m_{\min.} \rangle \right) = 0 \quad \text{and} \quad [m_{\min.}(m_{\min.} - 1) - \lambda] = 0, \quad (10)$$

an inconsistency never exists. If we name

$$\lambda = j(j + 1), \quad (11)$$

with  $j \geq 0$ , to be as close as possible to the language of the angular momentum algebra, the solution to  $[m_{\min.}(m_{\min.} - 1) - \lambda] = 0$  gives us  $m_{\min.} = (j + 1)$ . Only the positive root has meaning in this case. Also, the quantum number  $j$  is only a language to give us the eigenvalue  $\lambda$ . In this case,  $j$  may not be an integer or

half-integer. The actual values of  $m_{\min.} = (j + 1)$  and  $\lambda = j(j + 1)$  will depend on the detailed properties of the operators  $T^2$  and  $T_3$ , i.e., on the specific nature of the physics of the problem. If the nature of the problem is such that the eigenvalues of  $T^2$  and  $T_3$  must all be positive definite, we are done. The spectrum is given by

$$m = m_{\min.}, (m_{\min.} + 1), \dots, (m_{\min.} + n), \dots, \rightarrow \infty,$$

$$m = (j + 1), (j + 2), \dots, (j + 1 + n), \dots, \rightarrow \infty, \quad \text{with } \lambda = j(j + 1).$$

[The possible  $m$ -values can go to  $\infty$ . This follows because for  $m_{\min.} > 0$ , the quantity  $(m_{\min.}^2 + m_{\min.} - \lambda) = 2m_{\min.} > 0$  and thus  $[(m_{\min.} + n)(m_{\min.} + n + 1) - \lambda] > 0$  for any positive integer  $n$ , so the state  $(T_+|\lambda(m_{\min.} + n)\rangle)$  exists; i.e., the state  $|\lambda(m_{\min.} + n + 1)\rangle$  also leads to a square-integrable eigenfunction.]

Let us next examine the possibility the operators  $T^2$  and  $T_3$  are such that  $\lambda > 0$ , but  $m < 0$ . Now let us suppose some  $m_0 = -|m_0|$  exists; i.e., the state  $|\lambda, -|m_0|\rangle$  leads to square-integrable eigenfunctions. Now, if eq. (8) is satisfied for  $m = -|m_0|$ , i.e.,  $|m_0|(|m_0| + 1) - \lambda > 0$ , the state with  $m = (-|m_0| - n)$  leads to an  $m(m - 1) - \lambda = (|m_0| + n)(|m_0| + n + 1) - \lambda$  also  $> 0$ , so  $n$  actions with  $T_-$  would lead to another allowed state. However,  $n$  actions with the step-up operator,  $T_+$ , would lead to a state with  $m = -|m_0| + n$ , for which the function  $[(m^2 + m) - \lambda]$  of eq. (9) would lead to the value  $[(|m_0| - n)(|m_0| - n - 1) - \lambda]$ , which for large enough  $n$  could now be negative. Thus, eq. (9) would say that a patently positive quantity is equal to a function that can become a negative quantity for a large enough  $n$ . Now, a state  $|\lambda, -|m_0|\rangle$  can be an allowed state only if an integer  $n$  exists, such that  $m = (-|m_0| + n) \equiv m_{\max.}$  and

$$(T_+|\lambda m_{\max.}\rangle) = 0, \quad \text{so that } (m_{\max.}(m_{\max.} + 1) - \lambda) = 0, \quad (12)$$

where now  $m_{\max.}$  must be the negative root of the equation:  $(m_{\max.}(m_{\max.} + 1) - j(j + 1)) = 0$ ; that is,  $m_{\max.} = -\frac{1}{2} - \sqrt{\lambda + \frac{1}{4}} = -(j + 1)$ . In this case, therefore, the spectrum of possible  $m$ -values is

$$-\infty, \dots, -(j+1+n), \dots, -(j+2), -(j+1) = m_{\max.}, \quad \text{again with } \lambda = j(j+1).$$

Now, however, for general  $\lambda = j(j + 1) > 0$ , the two branches of allowed  $m$  values are unconnected, so the commutator algebra of the  $T_i$  does not lead to additional restrictions on  $\lambda$  and, hence,  $j$ . In particular,  $j$  need not be an integer or a half-integer. The physics of the operators  $T_3$ ,  $T^2$ , dictate the nature of the eigenvalues  $m$  and  $\lambda$ . Thus, for some physical applications for which the eigenvalues of  $T_3$  can be positive only, only the positive branch of allowed  $m$  values can exist.

Let us now finally use eqs. (7) and (8) to find the matrix elements of the operators  $T_{\pm}$ . We shall look at the simple case, in which the states

$$|\lambda m_{\min.}\rangle \quad \text{or} \quad |\lambda m_{\max.}\rangle$$

are nondegenerate; i.e., the two relations

$$T_-|\lambda m_{\min.}\rangle = 0 \quad \text{and} \quad T_+|\lambda, -|m_{\max.}|\rangle = 0$$

are assumed to have only one allowed solution. This would of course be automatic if these two relations lead to first-order differential equations. In this case, action with  $T_+$  or  $T_-$ , respectively, would lead to a single (nondegenerate) state with the appropriate  $m$  value. Thus, all states in the ladder of either positive or negative  $m$  values might be expected to be nondegenerate, and the sums over  $m'$  in eqs. (8) and (9) would collapse to a single term with  $m' = (m - 1)$  or  $m' = (m + 1)$ , respectively. For branches of allowed  $m$  values, eq. (9) tells us

$$|\langle j(m+1)|T_+|jm\rangle|^2 = m(m+1) - j(j+1) = (m-j)(m+j+1). \quad (13)$$

This relation leads to no upper limit for positive  $m$  values with  $m \geq (j+1)$ , but leads to a zero matrix element for  $m = -(j+1)$  within the branch of negative  $m$  values. Similarly, eq. (8) leads to

$$|\langle j(m-1)|T_-|jm\rangle|^2 = m(m-1) - j(j+1) = (m+j)(m-j-1). \quad (14)$$

Now, no zero matrix elements exist for the negative branch with  $m \leq -(j+1)$ , but this matrix element is automatically zero if  $m = (j+1)$ . As for the corresponding angular momentum problem, eqs. (13) and (14) do not fix the phases of these matrix elements. If we choose these phases such that the matrix elements of  $T_+$ ,  $T_-$  are real, we have

$$\begin{aligned} \langle j(m+1)|T_+|jm\rangle &= \sqrt{(m-j)(m+j+1)}, \\ \langle j(m-1)|T_-|jm\rangle &= \sqrt{(m+j)(m-j-1)}. \end{aligned} \quad (15)$$

(In particular, these equations satisfy  $\langle jm'|T_-|jm\rangle = \langle jm|T_+|jm'\rangle^*$ .)

Final remark: The operators  $J_x = J_1$ ,  $J_y = J_2$ ,  $J_z = J_3$  of the angular-momentum algebra, which commute with the operator  $\vec{J}^2 = J_1^2 + J_2^2 + J_3^2$  are the generators of infinitesimal rotations in three-space about the  $x$ ,  $y$ , and  $z$  axes and thus connected with the group SO(3), the “special orthogonal group in three dimensions” (where the “special” means the  $3 \times 3$  orthogonal rotation matrices have determinant +1, leading to pure rotations and not including rotation reflections). The operators  $T_1$ ,  $T_2$ ,  $T_3$ , which commute with the operator,  $T^2 = T_3^2 - T_1^2 - T_2^2$ , conversely, are related in a similar way with a 3-D space with two space-like and one time-like dimension and thus connected with the group SO(2,1). As for the SO(3) group, most of the properties of the group SO(2,1) follow from the matrix elements of the  $T_i$ , which are now known to us.

Finally, the angular momentum operators,  $J_{\pm}$  are related to the ladder operators of case 3  $\mathcal{L}(m)$  of the factorization method, whereas the  $T_{\pm}$  of the SO(2,1) algebra are related to the ladder operators of case 4  $\mathcal{L}(m)$  of the factorization method.

Problems 24–26 give some actual physical examples of the SO(2,1) algebra. The signs of  $\lambda$  and  $m$  are usually dictated by the nature of the problem.

**24.** The 3-D harmonic oscillator via the SO(2,1) algebra. For the 3-D harmonic oscillator, define dimensionless quantities,  $\vec{r}$ ,  $H$ , etc., via

$$\vec{r}_{\text{phys.}} = \sqrt{\hbar/m\omega_0}\vec{r} \quad \text{and} \quad H_{\text{phys.}} = \hbar\omega_0 H; \dots .$$

Show that the three operators

$$T_1 = \frac{1}{4}(r^2 - \vec{p}^2) = \frac{1}{4}(r^2 + \nabla^2),$$

$$T_2 = -\frac{1}{4}(\vec{r} \cdot \vec{p} + \vec{p} \cdot \vec{r}) = \frac{i}{2}\left(r \frac{\partial}{\partial r} + \frac{3}{2}\right),$$

$$T_3 = \frac{1}{4}(r^2 + \vec{p}^2) = \frac{1}{4}(r^2 - \nabla^2),$$

where

$$\nabla^2 = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}\right) - \frac{\vec{L}^2}{r^2} = -p_r^2 - \frac{\vec{L}^2}{r^2}$$

[with  $\vec{L}^2$  given in terms of  $\theta, \phi$ -dependent operators through eq. (13) of Chapter 8] are hermitian with respect to the conventional volume element and satisfy the SO(2,1) commutation relations of problem 23.

Note that, with  $\psi = R(r)Y_{lm}(\theta, \phi)$ , the operator  $\nabla^2$  is hermitian with respect to the usual measure,  $r^2 \sin \theta$ ,

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_0^\infty dr r^2 \psi_2^*(\nabla^2 \psi_1) = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_0^\infty dr r^2 \psi_1^*(\nabla^2 \psi_2).$$

Also,

$$H = \frac{H_{\text{phys}}}{\hbar\omega_0} = \frac{1}{2}(r^2 - \nabla^2) = 2T_3 = 2T_0$$

with known (positive) eigenvalues,  $(N + \frac{3}{2})$ . Show that the functions

$$r^l e^{-\frac{1}{2}r^2} Y_{lm}(\theta, \phi)$$

satisfy the equations

$$T_-(r^l e^{-\frac{1}{2}r^2} Y_{lm}(\theta, \phi)) = 0 \quad \text{and} \quad T_0(r^l e^{-\frac{1}{2}r^2} Y_{lm}(\theta, \phi)) = \frac{1}{2}(l + \frac{3}{2})(r^l e^{-\frac{1}{2}r^2} Y_{lm}(\theta, \phi)),$$

so

$$m_{\min.} = \frac{1}{2}(l + \frac{3}{2}) \equiv (j + 1),$$

where  $m$  and  $j$  refer to the quantum numbers as defined in problem 23. ( $m$  and  $j$  are  $\frac{1}{4}$ -integers here!)

Use these results to show

$$E = \hbar\omega_0(l + 2n + \frac{3}{2}),$$

and the dimensionless operator  $r^2$  is given by

$$r^2 = 2T_0 + T_+ + T_-.$$

Find the nonzero matrix elements of  $r^2$  as functions of  $n$  and  $l$  or  $N$  and  $l$ . (Consult the results of problem 15.)

**25.** (a) For the SO(2,1) algebra with operators,  $T_-, T_+, T_0$ , satisfying the commutation relations

$$[T_0, T_{\pm}] = \pm T_{\pm} \quad \text{and} \quad [T_+, T_-] = -2T_0,$$

with eigenvalues  $(T_0)_{\text{eigen}} = m = m_{\min.} + n = (j + 1 + n)$ , where  $n = 0, 1, \dots, \rightarrow \infty$ , show that coherent state  $z$ -space realizations of these operators can be given by

$$\Gamma(T_-) = \frac{\partial}{\partial z}, \quad \Gamma(T_0) = j + 1 + z \frac{\partial}{\partial z},$$

$$\Gamma(T_+) = 2(j + 1)z + z^2 \frac{\partial}{\partial z}.$$

Find the eigenvalues,  $K_n$ , of the operator,  $K$ , which converts the above nonunitary  $\Gamma(T_i)$  into unitary  $\gamma(T_i)$  for this algebra, and rederive the general expressions found in problem 23 for the matrix elements of  $T_-, T_+, T_0$ , in a  $|jm\rangle$  basis.

(b) For the 1-D harmonic oscillator, the oscillator annihilation and creation operators,  $a_x, a_x^\dagger$ , expressed in terms of the dimensionless  $x$  and  $p_x$ , are

$$a_x = \frac{1}{\sqrt{2}}(x + ip_x) \quad \text{and} \quad a_x^\dagger = \frac{1}{\sqrt{2}}(x - ip_x).$$

Show that the three operators

$$T_+ = \frac{1}{4}a_x^\dagger a_x^\dagger, \quad T_- = \frac{1}{4}a_x a_x, \quad T_0 = \frac{1}{2}(a_x^\dagger a_x + \frac{1}{2}),$$

satisfy the SO(2,1) commutation relations

$$[T_0, T_{\pm}] = \pm T_{\pm} \quad \text{and} \quad [T_+, T_-] = -2T_0.$$

Show that the two oscillator states,  $|0\rangle$ , and  $|1\rangle = a_x^\dagger |0\rangle$ , satisfy

$$(1) : T_-|0\rangle = 0, \quad T_0|0\rangle = \frac{1}{4}|0\rangle,$$

$$(2) : T_-|1\rangle = 0, \quad T_0|1\rangle = \frac{3}{4}|1\rangle,$$

so  $m_{\min.} = \frac{1}{4}$  for case (1) and  $m_{\min.} = \frac{3}{4}$  for case (2). Use these results together with the results of problem 23, to calculate the matrix elements

$$\langle n' | a_x^\dagger a_x^\dagger | n \rangle,$$

$$\langle n' | a_x a_x | n \rangle.$$

**26.** For the hydrogen atom in stretched parabolic coordinates,  $\mu, \nu, \phi$  (see problem 6), the following operators are useful

$$T_1 = \frac{1}{4} \left( \frac{\partial^2}{\partial \mu^2} + \frac{1}{\mu} \frac{\partial}{\partial \mu} \right) - \frac{m^2}{4\mu^2} + \frac{\mu^2}{4},$$

$$T_2 = \frac{i}{2} \left( \mu \frac{\partial}{\partial \mu} + 1 \right),$$

$$T_3 = -\frac{1}{4} \left( \frac{\partial^2}{\partial \mu^2} + \frac{1}{\mu} \frac{\partial}{\partial \mu} \right) + \frac{m^2}{4\mu^2} + \frac{\mu^2}{4},$$

$$T'_1 = \frac{1}{4} \left( \frac{\partial^2}{\partial v^2} + \frac{1}{v} \frac{\partial}{\partial v} \right) - \frac{m^2}{4v^2} + \frac{v^2}{4},$$

$$T'_2 = \frac{i}{2} \left( v \frac{\partial}{\partial v} + 1 \right),$$

$$T'_3 = -\frac{1}{4} \left( \frac{\partial^2}{\partial v^2} + \frac{1}{v} \frac{\partial}{\partial v} \right) + \frac{m^2}{4v^2} + \frac{v^2}{4}.$$

Show that both the  $T_j$  and the  $T'_j$  satisfy the SO(2,1) commutation relations of problem 23. Show that the operators are hermitian with respect to the scalar product

$$\int_0^\infty d\mu \mu U_1^*(\mu) U_2(\mu) \quad \text{for the } T_j,$$

and with respect to the scalar product

$$\int_0^\infty dv v V_1^*(v) V_2(v) \quad \text{for the } T'_j.$$

Note: With  $\psi(\mu, v, \phi) = U(\mu)V(v)\Phi(\phi)$ , with  $\Phi_m(\phi) = e^{im\phi}/\sqrt{2\pi}$ , the standard scalar product would have been

$$\begin{aligned} \int d\vec{r} \psi_1^* \psi_2 &= \int_0^{2\pi} d\phi \int_0^\infty d\mu \int_0^\infty dv \frac{(\mu^2 + v^2)\mu v}{[-2\epsilon]^{\frac{3}{2}}} \\ &\quad U_1^*(\mu)V_1^*(v)\Phi_1^*(\phi)U_2(\mu)V_2(v)\Phi_2(\phi). \end{aligned}$$

Show how the Schrödinger equation for the hydrogenic atom can be rewritten in terms of the operators,  $T_j, T'_j$ . For this purpose, rewrite the Schrödinger equation

$$(H - \epsilon)\psi = 0,$$

or

$$\begin{aligned} -\frac{1}{2} \frac{(-2\epsilon)}{(\mu^2 + v^2)} \left( \frac{\partial^2}{\partial \mu^2} + \frac{1}{\mu} \frac{\partial}{\partial \mu} + \frac{\partial^2}{\partial v^2} + \frac{1}{v} \frac{\partial}{\partial v} + \left( \frac{1}{\mu^2} + \frac{1}{v^2} \right) \frac{\partial^2}{\partial \phi^2} \right) \psi \\ -\frac{2\sqrt{(-2\epsilon)}}{(\mu^2 + v^2)} \psi - \epsilon \psi = 0, \end{aligned}$$

by left-multiplying with  $\frac{1}{2}n^2(\mu^2 + v^2)$  to gain

$$-\frac{1}{4} \left( \frac{\partial^2}{\partial \mu^2} + \frac{1}{\mu} \frac{\partial}{\partial \mu} + \frac{\partial^2}{\partial v^2} + \frac{1}{v} \frac{\partial}{\partial v} + \left( \frac{1}{\mu^2} + \frac{1}{v^2} \right) \frac{\partial^2}{\partial \phi^2} \right) \psi$$

$$+ \frac{1}{4}(\mu^2 + v^2)\psi - \frac{1}{\sqrt{(-2\epsilon)}}\psi = 0.$$

Show

$$T^2 = T_3^2 - T_1^2 - T_2^2 = (T_3 - T_1)(T_3 + T_1) + [T_1, T_3] - T_2^2,$$

or

$$T^2 = (T_3 - T_1)(T_3 + T_1) - iT_2 - T_2^2 = \frac{(m^2 - 1)}{4}.$$

Similarly,

$$T'^2 = \frac{(m^2 - 1)}{4},$$

where  $m$  is the eigenvalue of the operator

$$\frac{1}{i} \frac{\partial}{\partial \phi}.$$

Show that for positive values of  $m$ :

$$(T_3)_{\text{eigen}} = \frac{1}{2} + \frac{1}{2}m + n_1, \quad n_1 = 0, 1, 2, \dots, \rightarrow \infty,$$

$$(T'_3)_{\text{eigen}} = \frac{1}{2} + \frac{1}{2}m + n_2, \quad n_2 = 0, 1, 2, \dots, \rightarrow \infty.$$

Find the corresponding ranges for  $(T_3)_{\text{eigen}}$  and  $(T'_3)_{\text{eigen}}$ , valid for negative values of  $m$ .

Find the energy,  $\epsilon$ , for the hydrogenic atom as a function of the quantum numbers,  $m, n_1, n_2$ .

In an  $|mn_1n_2\rangle$  basis, find expressions for the nonzero matrix elements of the dimensionless variables

$$(r + z) = \frac{\mu^2}{[-2\epsilon]^{\frac{1}{2}}} \quad \text{and} \quad (r - z) = \frac{v^2}{[-2\epsilon]^{\frac{1}{2}}}.$$

## **Part II**

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# Time-Independent Perturbation Theory

# 20

## Perturbation Theory

### A Introductory Remarks

If we have a Hamiltonian for which we cannot find exact eigenvalues and eigenvectors, we can in principle use the technique employed for the asymmetric rotator for more challenging problems. If for the moment  $|n\rangle$  is shorthand for the eigenvectors for a complete set of commuting operators, *including* the Hamiltonian in question, and  $|\alpha\rangle$  is shorthand for the eigenvectors of another complete set of commuting operators, spanning the same subspace of Hilbert space, but now *including* a simpler Hamiltonian,  $H_0$ , for which we *do* know the eigenvalues and eigenvectors, we can expand the unknown eigenvectors  $|n\rangle$  in terms of the known  $|\alpha\rangle$ . From a knowledge of the matrix elements,  $\langle\alpha'|H|\alpha\rangle$ , we can in principle diagonalize the matrix in this basis for  $H_0$  to find the eigenvalues and eigenvectors for the needed  $H$ . The difficulty, of course, is that in general this matrix will be infinite-dimensional. With modern computers, however, it may be possible to diagonalize this matrix in an  $N \times N$  limit, where  $N$  is taken to be a large number, and then test the possible convergence as  $N$  grows even larger. This method will be particularly successful if  $H$  differs from a known  $H_0$  by terms that can be classified by a parameter of smallness,  $\lambda$ , with  $\lambda \ll 1$ . Then, we can study the “corrections” to the eigenvalues and eigenvectors in a very systematic way as a power series in  $\lambda$ . This will be the first detailed study of the next chapter, which will include:

- (1) stationary-state or time-independent perturbation theory,
  - (a) Rayleigh–Schrödinger expansion,
  - (b) Wigner–Brillouin expansion.

This study will be in contrast to time-dependent perturbation theory, which will be covered in a later chapter; where we will make a similar expansion of the time-dependent integral of eq. (13) of Chapter 19. Other approximation techniques, also to be covered in later chapters, are the WKB or semiclassical approximation and variational methods.

The WKB approximation will be treated only after a long excursion on angular momentum theory, Part III of the course. Variational methods useful for the  $n$  electron atom will be discussed in Part IV of the course on systems of identical particles.

## B Transition Probabilities

Before proceeding with stationary-state perturbation theory, it will be advantageous to give a very brief first discussion of transition probabilities to answer the question: What is the probability an atomic system in an excited eigenstate,  $E_n$ , will make a transition to a lower state,  $E_m$ , through the spontaneous emission of a photon? To answer this question in a rigorous way, we will have to study both the atomic system and the electromagnetic field quantum mechanically; i.e., we would have to quantize the electromagnetic field and then study the interaction of the quantized electromagnetic field (photon) with the atomic system. Because we will save the study of time-dependent perturbation theory for a later chapter, we will do this in a rigorous fashion then. To have a formula for the transition probability for the spontaneous emission of a photon, however, let us give a very brief “plausibility” argument for the transition probability formula now. This will actually be the historically first (the so-called Bohr correspondence principle) argument for this formula. (Keep in mind, however, the rigorous derivation will come later. Historically, it also came later with a famous paper by Dirac on the quantization of the electromagnetic field.)

The Bohr argument goes as follows: Classically, a charged particle in motion will emit electromagnetic radiation only if the particle is accelerated. Quantitatively, the *classical* result is given by the Larmor formula, which calculates the energy loss per unit time of the charged particle (or a system of  $N$  charged particles) to the emission of electromagnetic radiation (in c.g.s. units),

$$-\frac{dE}{dt} = \frac{2e^2}{3c^3} \vec{a}^2 \quad \text{or} \quad -\frac{dE}{dt} = \frac{2}{3c^3} \sum_{i=1}^N (e_i \vec{a}_i)^2, \quad (1)$$

where  $\vec{a}_i$  is the acceleration vector of the  $i^{\text{th}}$  particle with charge  $e_i$ . The classical recipe for calculating this energy loss for a system of  $N$  moving particles involves the Fourier time analysis for the three components of the electric dipole moment

$$\sum_{i=1}^N e_i x_i = \sum_n \mu_n^{(x)} (e^{in\omega t} + e^{-in\omega t}),$$

$$\begin{aligned}\sum_{i=1}^N e_i y_i &= \sum_n^\infty \mu_n^{(y)} (e^{in\omega t} + e^{-in\omega t}), \\ \sum_{i=1}^N e_i z_i &= \sum_n^\infty \mu_n^{(z)} (e^{in\omega t} + e^{-in\omega t}),\end{aligned}\quad (2)$$

assuming for the moment the time-dependent functions are real. Then, according to classical theory, the frequencies radiated are the classical mechanical frequency and its overtones,  $\nu = \omega/2\pi$ , and  $n\nu$  (or in the case of multiple-periodic systems, the classical frequencies and their overtones or combination tones,  $n_1\nu_1 + n_2\nu_2$ , etc.). Taking the second time derivatives of the  $x_i$ ,  $y_i$ ,  $z_i$  of eq. (2), the classically predicted energy loss to the  $n^{\text{th}}$  overtone (time-averaged over one cycle) would have been

$$-\overline{\left[ \frac{dE}{dt} \right]_{nv}} = \frac{2}{3c^3} \times 2(n\omega)^4 \left( (\mu_n^{(x)})^2 + (\mu_n^{(y)})^2 + (\mu_n^{(z)})^2 \right). \quad (3)$$

Of course, this classical result is incorrect. This is what troubled Niels Bohr from 1913 to 1925. First, this result does not predict the observed frequencies. The hydrogen spectrum is *not* a fundamental frequency and its  $n$  overtones. Even worse, this classical result predicts the frequencies should change with time. As the system loses energy and the mechanical energy becomes more negative, the Kepler frequencies (or the Bohr “1913 frequencies”) would increase with time; the electron would spiral in to the proton and suffer a catastrophe in a time of the order of  $10^{-8}$  seconds. Bohr argued, however, the classically predicted frequency,  $n\omega$ , should be replaced by the Bohr frequency,  $\omega_{nm}$ , and the classically predicted Fourier coefficients,  $\mu_n^{(j)}$ , should be replaced by a two-index quantity,  $\mu_{nm}^{(j)}$ , which he identified with the Heisenberg matrix element. Thus,

$$\begin{array}{lll} \text{classical} & n\nu \rightarrow (E_n - E_m)/\hbar & \text{(Bohr)}, \\ \text{classical} & \mu_n^{(x)} \rightarrow \langle n | \mu_x | m \rangle & \text{(Heisenberg)}, \\ \text{classical} & \mu_n^{(y)} \rightarrow \langle n | \mu_y | m \rangle & \text{(Heisenberg)}, \\ \text{classical} & \mu_n^{(z)} \rightarrow \langle n | \mu_z | m \rangle & \text{(Heisenberg)}. \end{array} \quad (4)$$

This argument is the Bohr correspondence principle, which yields the result

$$-\overline{\left[ \frac{dE}{dt} \right]_{\nu_{nm}}} = \frac{64\pi^4}{3c^3} \nu_{nm}^4 \left[ |\langle n | \mu_x | m \rangle|^2 + |\langle n | \mu_y | m \rangle|^2 + |\langle n | \mu_z | m \rangle|^2 \right], \quad (5)$$

where the operators are  $\mu_x = \sum_i e_i x_i$ , and so on. To convert this principle to a transition probability, introduce the “Einstein  $A$ ,”

$$-\overline{\left[ \frac{dE}{dt} \right]_{\nu_{nm}}} = \hbar \nu_{nm} A_{n \rightarrow m} N_n, \quad (6)$$

where  $\hbar \nu_{nm}$  is the energy of the emitted photon,  $A_{n \rightarrow m}$ , gives the probability per unit time for the spontaneous emission of a photon with this frequency, and  $N_n$  is the number of atoms in the initial state,  $n$ . The transition probability per second the atom makes a transition from an excited state,  $n$ , to a lower state,  $m$ , is therefore

given in terms of the matrix elements of the three components of the electric dipole moment operator by

$$A_{n \rightarrow m} = \frac{64\pi^4}{3hc^3} v_{nm}^3 \left[ |\langle n | \mu_x | m \rangle|^2 + |\langle n | \mu_y | m \rangle|^2 + |\langle n | \mu_z | m \rangle|^2 \right]. \quad (7)$$

If the matrix elements of the three electric dipole moment components are all zero, the transition is “forbidden.” The correspondence principle argument then gives the correct result. A rigorous derivation will be given in a later chapter, when we shall quantize the electromagnetic field and introduce the interaction between the quantized electromagnetic field (photons) and the isolated atomic system. The above electric dipole result, however, is only the dominant term in an expansion involving a series in powers of  $a/\lambda$ , where  $a$  gives the size of the atomic system and  $\lambda$  is the wavelength of the emitted photon. Higher order terms will involve matrix elements of magnetic moment operators, electric quadrupole moment operators, and even higher magnetic and electric multipole moments. In nuclei, these higher order terms are often important.

Finally, we make a remark about induced absorption and emission processes. If the atomic system is in a beam or a bath of photons, the probability for induced absorption and emission processes is given by the “Einstein  $B$ ”s and by  $\rho(v_{nm})$ , the energy density of the electromagnetic radiation (photon beam). Through his study of the black-body radiation spectrum, Einstein found the relation

$$B_{m \rightarrow n} = B_{n \rightarrow m} = \frac{c^3}{8\pi h v_{nm}^3} A_{n \rightarrow m}, \quad (8)$$

where the probability per unit time of an induced absorption process is

$$\rho(v_{nm}) B_{m \rightarrow n} N_m, \quad (9)$$

and the probability per unit time of an induced emission process is

$$\rho(v_{nm}) B_{n \rightarrow m} N_n, \quad (10)$$

where  $\rho(v_{nm})$  is the energy per unit volume of the photon beam at the transition frequency, and  $N_n$  and  $N_m$  are the number of atoms in state  $n$  and  $m$ , respectively.

## Problems

**27.** Find the lifetime  $\tau$  in seconds of the 2p state of the hydrogen atom

$$\tau = \frac{1}{A_{2p \rightarrow 1s}},$$

where  $A_{2p \rightarrow 1s}$  is the Einstein  $A$  coefficient. Assume the three substates with  $m = 0, \pm 1$  are populated with equal probability initially.

**28.** For the diatomic molecule rigid rotator, the space-fixed components of the electric dipole moment operator are

$$\mu_x^{(el.)} = \mu_e \sin \theta \cos \phi, \quad \mu_y^{(el.)} = \mu_e \sin \theta \sin \phi, \quad \mu_z^{(el.)} = \mu_e \cos \theta,$$

where  $\mu_e$  is the permanent electric dipole moment of the molecule, oriented along the molecular symmetry axis. (Homonuclear diatomic molecules, such as H<sub>2</sub> or N<sub>2</sub>, have no permanent electric dipole moment. Their pure rotational transitions can therefore only be seen in Raman spectroscopy.)

Recall the rotational energies and wave functions are given by

$$E_J = \frac{\hbar^2}{2I_e} J(J+1), \quad \text{with } I_e = \mu r_e^2, \quad \psi_{JM}(\theta, \phi) = Y_{JM}(\theta, \phi).$$

Give a general formula for the energy loss per second for an emission line for a transition  $J \rightarrow (J-1)$ , assuming the molecule is in a gaseous sample in thermal equilibrium at temperature  $T$ , where the number of molecules in the state with energy  $E_J$  is

$$N_J = \frac{(2J+1)e^{-(E_J/kT)}}{\sum_J (2J+1)e^{-(E_J/kT)}} N_{\text{total}} \approx \frac{\hbar^2}{2I_e k T} (2J+1)e^{-(E_J/kT)} N_{\text{total}}.$$

For example, for the HBr molecule with  $r_e = 1.414 \times 10^{-8}$  cm, and  $\mu_e = e(0.17 \times 10^{-8}$  cm), make an estimate for the  $J = 3 \rightarrow 2$  transition in terms of the number of photons emitted per second. Your numerical answer should explain why such spectra are observed as absorption spectra rather than emission spectra. That is, the spontaneous emission process is very unlikely, so diatomic molecule rotational transitions are observed by utilizing the stimulated absorption and emission process for incident radiation of the appropriate frequency in the far infrared or microwave region. To come to the same conclusion, also calculate the lifetime in seconds of the first excited rotational state, with  $J = 1$ , and compare this result for the HBr molecule with the result of problem 27 for the first excited state of the hydrogen atom.

# 21

## Stationary-State Perturbation Theory

### A Rayleigh–Schrödinger Expansion

If a Hamiltonian,  $H$ , differs very little from a Hamiltonian,  $H_0$ , for which an exact solution is known, an expansion procedure may give a good approximation for the eigenvalues and eigenvectors of the full  $H$ . Many physically interesting problems, e.g., the Stark or Zeeman effects in an atom or a molecule, may involve a small perturbation of an exactly soluble problem. Let us assume the full Hamiltonian can be expanded about an  $H_0$ , with a known set of eigenvalues and eigenvectors, through a parameter of smallness,  $\lambda$ , with  $\lambda \ll 1$

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \lambda^3 H^{(3)} + \dots . \quad (1)$$

Sometimes, only a first-order term may exist, say, a perturbing potential,  $V$ . Then,

$$H = H^{(0)} + \lambda V, \quad \text{with} \quad H^{(2)} = H^{(3)} = \dots = 0. \quad (2)$$

We want a systematic solution to the problem

$$H|n\rangle = E_n|n\rangle, \quad (3)$$

assuming we know the solution

$$H^{(0)}|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle. \quad (4)$$

## B Case 1: Nondegenerate State

Let us first treat the simplest case in which the state  $|n^{(0)}\rangle$  is nondegenerate. We will expand both  $E_n$  and  $|n\rangle$  in a power series in  $\lambda$ .

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots, \quad (5)$$

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots \quad (6)$$

The equation,  $(H - E_n)|n\rangle = 0$ , or

$$\begin{aligned} & \left( (H^{(0)} - E_n^{(0)}) + \lambda (H^{(1)} - E_n^{(1)}) + \lambda^2 (H^{(2)} - E_n^{(2)}) + \dots \right) \\ & \times \left( |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots \right) = 0, \end{aligned} \quad (7)$$

can now be solved order by order, peeling off one term at a time. Thus,

$$\begin{aligned} \lambda^1 : \quad & (H^{(0)} - E_n^{(0)})|n^{(1)}\rangle + (H^{(1)} - E_n^{(1)})|n^{(0)}\rangle = 0, \\ \lambda^2 : \quad & (H^{(0)} - E_n^{(0)})|n^{(2)}\rangle + (H^{(1)} - E_n^{(1)})|n^{(1)}\rangle + (H^{(2)} - E_n^{(2)})|n^{(0)}\rangle = 0, \\ \vdots & \quad \vdots \quad \vdots \quad \vdots \\ \lambda^j : \quad & (H^{(0)} - E_n^{(0)})|n^{(j)}\rangle + (H^{(1)} - E_n^{(1)})|n^{(j-1)}\rangle + \dots \\ & \quad + (H^{(j)} - E_n^{(j)})|n^{(0)}\rangle = 0. \end{aligned} \quad (8)$$

To solve the first-order equation, first left-multiply this equation with  $\langle n^{(0)}|$ , to convert it to matrix element form:

$$\langle n^{(0)}|(H^{(0)} - E_n^{(0)})|n^{(1)}\rangle + \langle n^{(0)}|(H^{(1)} - E_n^{(1)})|n^{(0)}\rangle = 0. \quad (9)$$

The first term can be seen to be zero, because

$$\langle n^{(0)}|H^{(0)} - E_n^{(0)}|n^{(1)}\rangle = \langle n^{(1)}|H^{(0)\dagger} - E_n^{(0)}|n^{(0)}\rangle^* = 0, \quad (10)$$

via  $(H^{(0)} - E_n^{(0)})|n^{(0)}\rangle = 0$ . Eq. (9) then gives the first-order correction to the energy:

$$E_n^{(1)} = \langle n^{(0)}|H^{(1)}|n^{(0)}\rangle. \quad (11)$$

That is,  $E_n^{(1)}$  is given by the simple diagonal matrix element of  $H^{(1)}$ . For the first-order corrections to the state vector, consider the first-order equation

$$(H^{(0)} - E_n^{(0)})|n^{(1)}\rangle = -(H^{(1)} - E_n^{(1)})|n^{(0)}\rangle, \quad (12)$$

which is of the form,  $\mathcal{O}|n^{(1)}\rangle = |v\rangle$ , where the right-hand side is a known vector that can be calculated. In coordinate representation, this equation could be written in the form of an inhomogeneous differential equation for the unknown function,  $\psi_n^{(1)}(\vec{r})$ , with a known (calculable) function  $\phi_v(\vec{r}) = \langle \vec{r}|v\rangle$  on the right-hand side;

$$(H^{(0)} - E_n^{(0)})\psi_n^{(1)}(\vec{r}) = \phi_v(\vec{r}).$$

The solution is of the form: a particular solution of the inhomogeneous equation to which a solution of the homogeneous equation can be added. The latter is just

a solution of the zeroth order Schrödinger equation. In vector (ket) form, this equation is

$$|n^{(1)}\rangle = c_n^{(1)}|n^{(0)}\rangle + Q_n^{(0)}|n^{(1)}\rangle, \quad (13)$$

where the projection operator,

$$Q_n^{(0)} = 1 - P_n^{(0)} = 1 - |n^{(0)}\rangle\langle n^{(0)}| = \sum_{k \neq n} |k^{(0)}\rangle\langle k^{(0)}|, \quad (14)$$

projects onto the subspace of the Hilbert space excluding the state vector,  $|n^{(0)}\rangle$ . [The sum over  $k$  may have to include an integral, if the spectrum of  $H^{(0)}$  includes a continuum.] Now left-multiply eq. (11) with a specific  $\langle k^{(0)}| \neq \langle n^{(0)}|$  to yield

$$\langle k^{(0)}|(H^{(0)} - E_n^{(0)})|n^{(1)}\rangle = -\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle, \quad (15)$$

leading to

$$\langle k^{(0)}|n^{(1)}\rangle = \frac{\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})}, \quad (16)$$

so

$$|n^{(1)}\rangle = c_n^{(1)}|n^{(0)}\rangle + \sum_{k \neq n} |k^{(0)}\rangle \frac{\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}. \quad (17)$$

To determine  $c_n^{(1)}$ , normalize the state vector  $|n\rangle$  through first-order terms. With  $|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle$ , and  $|m\rangle = |m^{(0)}\rangle + \lambda|m^{(1)}\rangle$ ,

$$\begin{aligned} \langle m|n\rangle &= \delta_{mn} \\ &= \langle m^{(0)}|n^{(0)}\rangle + \lambda \left( \langle m^{(0)}|n^{(1)}\rangle + \langle n^{(0)}|m^{(1)*}\rangle \right) \\ &= \delta_{mn} \left( 1 + \lambda [c_n^{(1)} + c_m^{(1)*}] \right) \\ &\quad + \lambda \left( \frac{\langle m^{(0)}|H^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} + \frac{\langle n^{(0)}|H^{(1)}|m^{(0)}\rangle^*}{E_m^{(0)} - E_n^{(0)}} \right) \langle m^{(0)}|Q_n^{(0)}|n^{(0)}\rangle \\ &= \delta_{mn} \left( 1 + \lambda [c_n^{(1)} + c_n^{(1)*}] \right), \end{aligned} \quad (18)$$

where the  $\delta_{mn}$  term contributes only when  $n = m$ , whereas the second term, which could in principle have contributed when  $m \neq n$ , is automatically zero. Hence, we have orthonormality through first order in  $\lambda$ , provided  $c_n^{(1)} + c_n^{(1)*} = 0$ . The simplest choice is to make  $c_n^{(1)}$  real and, hence,  $c_n^{(1)} = 0$ . Therefore,

$$|n^{(1)}\rangle = \sum_{k \neq n} |k^{(0)}\rangle \frac{\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}. \quad (19)$$

We could also have written this in operator form, in terms of the projection operator,  $Q_n^{(0)}$ ,

$$|n^{(1)}\rangle = Q_n^{(0)} \frac{1}{(E_n^{(0)} - H^{(0)})} H^{(1)} |n^{(0)}\rangle. \quad (20)$$

Alternatively, using the properties of the projection operator

$$(Q_n^{(0)})^2 = Q_n^{(0)}, \quad [Q_n^{(0)}, H^{(0)}] = 0, \quad Q_n^{(0)}|n^{(0)}\rangle = 0, \quad (21)$$

we could also have written this as

$$|n^{(1)}\rangle = Q_n^{(0)} \frac{1}{E_n^{(0)} - H^{(0)}} Q_n^{(0)} H^{(1)} |n^{(0)}\rangle, \quad (22)$$

where the extra (redundant)  $Q_n^{(0)}$  has been added as a safety factor to make sure the inverse operator

$$\frac{1}{E_n^{(0)} - H^{(0)}}$$

has a meaning. Because this operator can never act on  $|n^{(0)}\rangle$ , either to the left or to the right, we will never be plagued by zero denominators. This operator is a function of  $H^{(0)}$  and can be thought of as being expanded in a Taylor series in  $H^{(0)}$ , where  $H^{(0)}$  acting on a  $|k^{(0)}\rangle$  will simply yield  $E_k^{(0)}|k^{(0)}\rangle$ .

## C Second-Order Corrections

To get the second-order corrections to the energy, let us (always the first step!) left-multiply the second-order equation by  $\langle n^{(0)}|$  to get

$$-\langle n^{(0)}|(H^{(0)} - E_n^{(0)})|n^{(2)}\rangle = \langle n^{(0)}|H^{(1)} - E_n^{(1)}|n^{(1)}\rangle + \langle n^{(0)}|H^{(2)}|n^{(0)}\rangle - E_n^{(2)}. \quad (23)$$

The left-hand side is again zero [think of “left action” of  $(H^{(0)} - E_n^{(0)})$  on  $\langle n^{(0)}|$ ], so, substituting for  $|n^{(1)}\rangle$  in the right-hand side,

$$E_n^{(2)} = \langle n^{(0)}|H^{(2)}|n^{(0)}\rangle + \sum_{k \neq n} \frac{\langle n^{(0)}|H^{(1)}|k^{(0)}\rangle \langle k^{(0)}|H^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}, \quad (24)$$

or

$$E_n^{(2)} = \langle n^{(0)}|H^{(2)}|n^{(0)}\rangle + \sum_{k \neq n} \frac{|\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle|^2}{E_n^{(0)} - E_k^{(0)}}. \quad (25)$$

This formula, together with the result for the first-order correction,  $E_n^{(1)}$ , eq. (11), was named by Fermi as “Golden Rule I.” (We shall meet an analogous “Golden Rule II” in time-dependent perturbation theory!), Fermi said most of the interesting results of quantum theory can be calculated with these Golden Rules. (Note also: If  $|n\rangle$  is the ground state of the system, the perturbations caused by the higher states will “push down” and lower the ground-state energy. The second term then has patently positive numerators and negative denominators.)

To obtain the second-order correction to the state vector,  $|n^{(2)}\rangle$ , we again decompose this into a part proportional to  $|n^{(0)}\rangle$  and a part orthogonal to  $|n^{(0)}\rangle$ ,

$$|n^{(2)}\rangle = c_n^{(2)}|n^{(0)}\rangle + Q_n^{(0)}|n^{(2)}\rangle. \quad (26)$$

The  $c_n^{(2)}$  will again be determined in the end to preserve orthonormality through second order. The piece  $Q_n^{(0)}|n^{(2)}\rangle$  can be determined from the second-order equation

$$(E_n^{(0)} - H^{(0)})|n^{(2)}\rangle = (H^{(1)} - E_n^{(1)})|n^{(1)}\rangle + (H^{(2)} - E_n^{(2)})|n^{(0)}\rangle \quad (27)$$

by inverting the operator, *after* action with the projection operator  $Q_n^{(0)}$ ,

$$\begin{aligned} & Q_n^{(0)}|n^{(2)}\rangle \\ &= Q_n^{(0)} \frac{1}{E_n^{(0)} - H^{(0)}} Q_n^{(0)} \left( (H^{(1)} - E_n^{(1)})|n^{(1)}\rangle + (H^{(2)} - E_n^{(2)})|n^{(0)}\rangle \right) \\ &= Q_n^{(0)} \frac{1}{E_n^{(0)} - H^{(0)}} Q_n^{(0)} (H^{(1)} - E_n^{(1)}) Q_n^{(0)} \frac{1}{E_n^{(0)} - H^{(0)}} Q_n^{(0)} H^{(1)} |n^{(0)}\rangle \\ &\quad + Q_n^{(0)} \frac{1}{E_n^{(0)} - H^{(0)}} Q_n^{(0)} H^{(2)} |n^{(0)}\rangle. \end{aligned} \quad (28)$$

Now, substituting for  $Q_n^{(0)}$ , in the form

$$Q_n^{(0)} = \sum_{k \neq n} |k^{(0)}\rangle \langle k^{(0)}| = \sum_{l \neq n} |l^{(0)}\rangle \langle l^{(0)}|, \quad (29)$$

and using the result,  $E_n^{(1)} = \langle n^{(0)}|H^{(1)}|n^{(0)}\rangle$ , we get

$$Q_n^{(0)}|n^{(2)}\rangle = \sum_{k \neq n} |k^{(0)}\rangle \langle k^{(0)}|n^{(2)}\rangle, \quad (30)$$

with

$$\begin{aligned} \langle k^{(0)}|n^{(2)}\rangle &= \sum_{l \neq n} \frac{\langle k^{(0)}|H^{(1)}|l^{(0)}\rangle \langle l^{(0)}|H^{(1)}|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})} \\ &\quad - \langle n^{(0)}|H^{(1)}|n^{(0)}\rangle \frac{\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})^2} \\ &\quad + \frac{\langle k^{(0)}|H^{(2)}|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})}. \end{aligned} \quad (31)$$

Now, we still need to evaluate  $c_n^{(2)} = \langle n^{(0)}|n^{(2)}\rangle$ , which is again chosen to normalize  $|n\rangle$  through second order. In calculating  $\langle n|n\rangle$  through second order, we get a contribution  $1 + c_n^{(2)} + c_n^{(2)*}$ , no contributions from  $\langle n^{(0)}|Q_n^{(0)}|n^{(2)}\rangle$ , but now a contribution from  $\langle n^{(1)}|n^{(1)}\rangle$ . Again, letting  $c_n^{(2)}$  be real, we get

$$c_n^{(2)} = -\frac{1}{2} \sum_{k \neq n} \frac{|\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle|^2}{(E_n^{(0)} - E_k^{(0)})^2}. \quad (32)$$

An alternative way to normalize the ket  $|n\rangle$  through some order, which may be particularly convenient if we want to go through some relatively high order in  $\lambda$ , would be to set all  $c_n^{(j)} = 0$  and then normalize the final result for  $|n^{(0)}\rangle + \sum_{j=1} \lambda^j Q_n^{(0)}|n^{(j)}\rangle$ . Through second order, this procedure would give the overall

normalization constant as

$$N_n = \frac{1}{\sqrt{1 + \lambda^2 \sum_{k \neq n} \frac{|\langle k^{(0)} | H^{(1)} | n^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})^2}}}. \quad (33)$$

When the square root is expanded in powers of  $\lambda^2$ , this result agrees with eq. (32).

By “turning the handle of the crank,” we can generalize the results of eq. (25) and (31) for second order to arbitrarily high order. Clearly, the results become more and more complicated.

## D The Wigner–Brillouin Expansion

This slightly different expansion becomes particularly useful in the special (but very common) case when  $H^{(1)} = V$  and  $H^{(2)} = H^{(3)} = \dots = 0$ , and particularly if we want to go to very high order. In the Wigner–Brillouin expansion, the needed  $E_n$  is at first not expanded. The equation to be solved by successive approximation is then

$$(E_n - H^{(0)})|n\rangle = \lambda V|n\rangle \quad (34)$$

and is to be solved by

$$|n\rangle = |n^{(0)}\rangle + Q_n^{(0)}|n\rangle, \quad (35)$$

with the state vector to be normalized in the very end. By inverting the operator  $(E_n - H^{(0)})$ , after multiplication of eq. (34) by  $Q_n^{(0)}$ , we get

$$Q_n^{(0)}|n\rangle = Q_n^{(0)} \frac{1}{E_n - H^{(0)}} Q_n^{(0)} \lambda V|n\rangle. \quad (36)$$

Now, we substitute for  $|n\rangle$  through eq. (35) and iterate this process over and over to get the expansion

$$\begin{aligned} Q_n^{(0)}|n\rangle &= Q_n^{(0)} \frac{1}{E_n - H^{(0)}} Q_n^{(0)} \lambda V|n^{(0)}\rangle \\ &+ Q_n^{(0)} \frac{1}{E_n - H^{(0)}} Q_n^{(0)} \lambda V Q_n^{(0)} \frac{1}{E_n - H^{(0)}} Q_n^{(0)} \lambda V|n^{(0)}\rangle \\ &+ Q_n^{(0)} \frac{1}{E_n - H^{(0)}} Q_n^{(0)} \lambda V Q_n^{(0)} \frac{1}{E_n - H^{(0)}} Q_n^{(0)} \lambda V \\ &\quad \times Q_n^{(0)} \frac{1}{E_n - H^{(0)}} Q_n^{(0)} \lambda V|n^{(0)}\rangle + \dots. \end{aligned} \quad (37)$$

To get an expression for the correction to the energy,  $(E_n - E_n^{(0)})$ , left-multiply eq. (34) by  $\langle n^{(0)} |$  to get

$$\langle n^{(0)} | (E_n - H^{(0)})|n\rangle = \langle n^{(0)} | \lambda V|n\rangle, \quad (38)$$

leading to

$$E_n - E_n^{(0)} = \langle n^{(0)} | \lambda V|n^{(0)}\rangle$$

$$\begin{aligned}
& + \sum_{k \neq n} \frac{\langle n^{(0)} | \lambda V | k^{(0)} \rangle \langle k^{(0)} | \lambda V | n^{(0)} \rangle}{(E_n - E_k^{(0)})} \\
& + \sum_{k \neq n} \sum_{l \neq n} \frac{\langle n^{(0)} | \lambda V | k^{(0)} \rangle \langle k^{(0)} | \lambda V | l^{(0)} \rangle \langle l^{(0)} | \lambda V | n^{(0)} \rangle}{(E_n - E_k^{(0)})(E_n - E_l^{(0)})} \\
& + \dots
\end{aligned} \tag{39}$$

Clearly, this can be generalized very easily to an arbitrarily high number of terms in the expansion in powers of  $\lambda$ . The unknown,  $E_n$ , for which we are solving, however, now appears in all energy denominators. To find this as a power series in  $\lambda$ , we must substitute

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \tag{40}$$

in all energy denominators. Then, expand these in powers of  $\lambda$  peeling off, first the first-order, then the second-order, and higher order terms. The final result will, of course, be the same as that given by the Rayleigh–Schrödinger expansion, but the simplicity of the first step may make the Wigner–Brillouin expansion useful in the case when very high orders are needed.

# 22

## Example 1: The Slightly Anharmonic Oscillator

In Chapter 15, we discussed the diatomic molecule, a complicated many-body system. At low energies, however, we can neglect specific treatment of the electron degrees of freedom. The electron cloud can in first approximation be taken as the source of a potential binding the two atomic nuclei into a nearly rigid, vibrating structure. The position of the atomic nuclei of the diatomic molecule in 3-D space can be described by the three coordinates:  $r$ , the radial distance between the two atomic nuclei, and  $\theta$ , and  $\phi$ , the two angles describing the orientation of the molecule axis in our 3-D space. The electron cloud gives rise to a potential (see Fig. 22.1) with a deep minimum at  $r = r_e$ , where  $r_e$  is the equilibrium distance between the two nuclei. For very small values of  $r$ , the potential becomes strongly repulsive and rises to  $\infty$ . For very large values of  $r$ , the potential approaches a constant value of  $V_{\text{diss.}}$ . If we can raise the energy above this value, i.e., if  $E > V_{\text{diss.}}$ , the molecule will dissociate into two atomic fragments. For  $E \ll V_{\text{diss.}}$ , however, the potential will be nearly parabolic and can be expanded about the value  $r = r_e$ ,

$$V(r) = V(r_e) + \frac{1}{2} \left( \frac{d^2 V}{dr^2} \right)_{r_e} (r - r_e)^2 + \frac{1}{3!} \left( \frac{d^3 V}{dr^3} \right)_{r_e} (r - r_e)^3 + \dots . \quad (1)$$

The Schrödinger equation for the wave function  $\psi(r, \theta, \phi) = u(r)Y_{lm}(\theta, \phi)$  separates approximately (for the vibration–rotation perturbations, see problem 30) into a radial equation describing the vibration of the molecule and an angular equation describing the rotation of the molecule (see Chapter 15). The 1-D radial equation can be described by the Hamiltonian

$$H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + V(r). \quad (2)$$

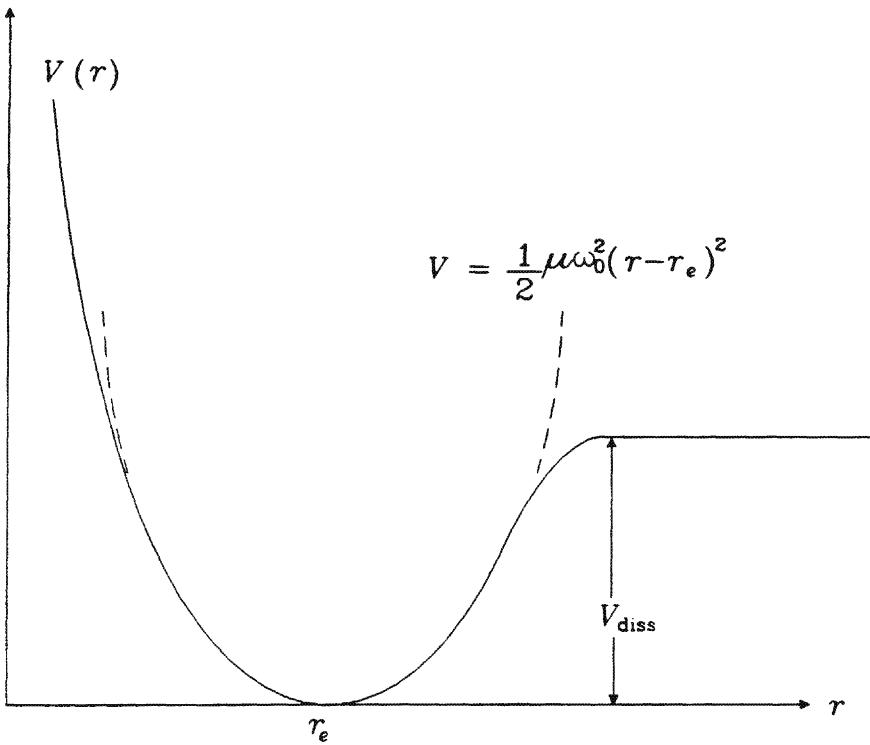


FIGURE 22.1. Diatomic molecule potential function.

For low-energy vibrational excitations,  $V(r)$  can be approximated by the first few terms of the above Taylor expansion. Then, if we replace the vibrational coordinate,  $(r - r_e)$ , by a dimensionless coordinate,  $x$ ,

$$(r - r_e) = \sqrt{\frac{\hbar}{\mu\omega_0}}x, \quad (3)$$

the vibrational Hamiltonian can be rewritten as

$$H = \hbar\omega_0 \left( \frac{1}{2} \left[ -\frac{d^2}{dx^2} + x^2 \right] + \lambda_3 x^3 + \lambda_4 x^4 \right), \quad (4)$$

with

$$\lambda_3 = \frac{1}{3\hbar\omega_0} \left( \frac{\hbar}{\mu\omega_0} \right)^{\frac{3}{2}} \left( \frac{d^3V}{dr^3} \right)_{r_e}, \quad \lambda_4 = \frac{1}{4\hbar\omega_0} \left( \frac{\hbar}{\mu\omega_0} \right)^2 \left( \frac{d^4V}{dr^4} \right)_{r_e}. \quad (5)$$

In most molecules  $\lambda_3 \ll 1$ , and  $\lambda_4 \simeq \text{order } (\lambda_3)^2$ . Thus, we can write the Hamiltonian of eq. (4)

$$\begin{aligned} H &= H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} \\ &= H^{(0)} + \hbar\omega_0 \lambda_3 x^3 + \hbar\omega_0 \lambda_4 x^4. \end{aligned} \quad (6)$$

The zeroth-order Hamiltonian is the simple 1-D harmonic oscillator Hamiltonian. Its eigenvectors are all nondegenerate, so we can use the machinery of stationary-state perturbation theory for an arbitrary nondegenerate state  $|n\rangle$ . We merely need to calculate the matrix elements of the two operators  $x^3$  and  $x^4$ . These operators follow by matrix multiplication from the simple (known) matrix elements of  $x$ . Calculating first the matrix elements of  $x^2$ , we can use these together with the matrix elements of  $x$  to evaluate all needed matrix elements. We list some of the needed results, as follows:

$$\begin{aligned}\langle n-2|x^2|n\rangle &= \frac{1}{2}\sqrt{n(n-1)} \\ \langle n+2|x^2|n\rangle &= \frac{1}{2}\sqrt{(n+1)(n+2)} \\ \langle n|x^2|n\rangle &= (n + \frac{1}{2}) \\ \langle m|x^2|n\rangle &= 0; \quad \text{for } m \neq n, (n \pm 2);\end{aligned}\tag{7}$$

$$\begin{aligned}\langle n-3|x^3|n\rangle &= \frac{1}{2}\sqrt{[n(n-1)(n-2)/2]} \\ \langle n+3|x^3|n\rangle &= \frac{1}{2}\sqrt{[(n+1)(n+2)(n+3)/2]} \\ \langle n-1|x^3|n\rangle &= \frac{3}{2}n\sqrt{[n/2]} \\ \langle n+1|x^3|n\rangle &= \frac{3}{2}(n+1)\sqrt{[(n+1)/2]} \\ \langle m|x^3|n\rangle &= 0; \quad \text{for } m \neq (n \pm 3), (n \pm 1).\end{aligned}\tag{8}$$

Through second order, we shall only need the diagonal matrix element of  $x^4$ . This matrix element has the value

$$\langle n|x^4|n\rangle = \frac{3}{2}(n^2 + n + \frac{1}{2}).\tag{9}$$

The terms cubic in  $x$  have no diagonal matrix elements. Therefore,  $H^{(1)}$  has no diagonal matrix element, and  $E_n^{(1)} = 0$ . The first correction to the energy is given by the second-order term

$$\begin{aligned}\lambda^2 E_n^{(2)} &= \langle n^{(0)}|H^{(2)}|n^{(0)}\rangle + \sum_{k \neq n} \frac{|\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle|^2}{(E_n^{(0)} - E_k^{(0)})} \\ &= \lambda_4 \langle n^{(0)}|\hbar\omega_0 x^4|n^{(0)}\rangle + \sum_{k \neq n} \frac{|\langle k^{(0)}|\lambda_3 \hbar\omega_0 x^3|n^{(0)}\rangle|^2}{\hbar\omega_0(n-k)} \\ &= \lambda_4 \hbar\omega_0 \frac{3}{2}(n^2 + n + \frac{1}{2}) + \frac{\lambda_3^2 \hbar\omega_0}{8} \left( \frac{9n^3}{+1} + \frac{9(n+1)^3}{-1} \right. \\ &\quad \left. + \frac{n(n-1)(n-2)}{+3} + \frac{(n+1)(n+2)(n+3)}{-3} \right).\end{aligned}\tag{10}$$

The final result gives

$$\lambda^2 E_n^{(2)} = \hbar\omega_0 \left[ \frac{3}{2}\lambda_4(n^2 + n + \frac{1}{2}) - \lambda_3^2(30n^2 + 30n + 11) \right].\tag{11}$$

We will also need the corrected state vectors. Often, it is sufficient to know these vectors to first order. For the slightly anharmonic oscillator, we have (to first order),

$$|n\rangle = |n^{(0)}\rangle + \lambda_3 \left( \sum_{k \neq n} |k^{(0)}\rangle \frac{\langle k^{(0)}|x^3|n^{(0)}\rangle}{(n-k)} \right)$$

$$\begin{aligned}
&= |n^{(0)}\rangle + \lambda_3 \left( |(n-3)^{(0)}\rangle \frac{\sqrt{n(n-1)(n-2)}}{6\sqrt{2}} \right. \\
&\quad - |(n+3)^{(0)}\rangle \frac{\sqrt{(n+3)(n+2)(n+1)}}{6\sqrt{2}} \\
&\quad \left. + |(n-1)^{(0)}\rangle \frac{3n\sqrt{n}}{2\sqrt{2}} - |(n+1)^{(0)}\rangle \frac{3(n+1)\sqrt{(n+1)}}{2\sqrt{2}} \right). \quad (12)
\end{aligned}$$

These corrected state vectors will be needed to calculate the corrections to the transition probabilities. For a diatomic molecule, the electric dipole moment along the direction of the molecular symmetry axis can be given by

$$\mu^{(el.)} = \mu_e + \left( \frac{d\mu}{dr} \right)_e (r - r_e) + \dots = \mu_e + e_{\text{eff.}} \sqrt{\frac{\hbar}{\mu\omega_0}} x + \dots, \quad (13)$$

where the dipole moment derivative is expressed in terms of an effective charge,  $e_{\text{eff.}}$ . Also, both the permanent electric dipole moment,  $\mu_e$ , and the effective charge (which gives the strength of the dipole moment change during the harmonic oscillation) are zero for a homonuclear diatomic molecule, such as  $H_2$ ,  $O_2$ , or  $N_2$ . Off-diagonal matrix elements of the electric dipole moment operator are given by

$$\langle m^{(0)} | \mu^{(el.)} | n^{(0)} \rangle = \delta_{m(n\pm 1)} e_{\text{eff.}} \sqrt{\frac{\hbar}{\mu\omega_0}} \langle m^{(0)} | x | n^{(0)} \rangle. \quad (14)$$

This equation leads to the zeroth-order vibrational selection rule,  $\Delta n = \pm 1$  and a zeroth-order transition probability given by the Einstein  $A$

$$A_{n \rightarrow (n-1)} = \frac{8\pi\omega_0^3}{3hc^3} e_{\text{eff.}}^2 \frac{\hbar}{\mu\omega_0} \frac{n}{2}. \quad (15)$$

If first-order anharmonic corrections are included in the state vector, the vibrational selection rule  $\Delta n = \pm 1$  is partially relaxed. For example, now transitions  $n \rightarrow (n-2)$  may become possible. If we write the analog of eq. (12) for the bra  $\langle (n-2) |$  through first order

$$\begin{aligned}
\langle (n-2) | &= \langle (n-2)^{(0)} | + \lambda_3 \left( \langle (n-3)^{(0)} | \frac{3(n-2)\sqrt{(n-2)}}{2\sqrt{2}} \right. \\
&\quad - \langle (n-1)^{(0)} | \frac{3(n-1)\sqrt{(n-1)}}{2\sqrt{2}} + \langle (n-5)^{(0)} | \frac{\sqrt{(n-2)(n-3)(n-4)}}{6\sqrt{2}} \\
&\quad \left. - \langle (n+1)^{(0)} | \frac{\sqrt{(n+1)n(n-1)}}{6\sqrt{2}} \right), \quad (16)
\end{aligned}$$

to first order in  $\lambda_3$ , the matrix element of  $\langle (n-2) | x | n \rangle$  gets contributions from the zeroth-order component of  $|n\rangle$  with the first-order components  $\langle (n-1)^{(0)} |$  and  $\langle (n+1)^{(0)} |$  of  $\langle (n-2) |$ , and from the zeroth-order component of  $\langle (n-2) |$  with the first-order components  $| (n-3)^{(0)} \rangle$  and  $| (n-1)^{(0)} \rangle$  of  $|n\rangle$ , leading to

$$\langle (n-2) | \mu^{(el.)} | n \rangle = e_{\text{eff.}} \sqrt{\frac{\hbar}{\mu\omega_0}} \lambda_3$$

$$\begin{aligned}
& \times \left( -\frac{3(n-1)\sqrt{(n-1)}}{2\sqrt{2}} \sqrt{\frac{n}{2}} - \frac{\sqrt{(n+1)n(n-1)}}{6\sqrt{2}} \sqrt{\frac{(n+1)}{2}} \right. \\
& \quad \left. + \frac{\sqrt{n(n-1)(n-2)}}{6\sqrt{2}} \sqrt{\frac{(n-2)}{2}} + \frac{3n\sqrt{n}}{2\sqrt{2}} \sqrt{\frac{(n-1)}{2}} \right) \\
& = e_{\text{eff.}} \sqrt{\frac{\hbar}{\mu\omega_0}} \lambda_3 \frac{1}{2} \sqrt{n(n-1)}. \tag{17}
\end{aligned}$$

This equation leads to the transition probability given by the Einstein  $A$

$$A_{n \rightarrow (n-2)} = \frac{8\pi(2\omega_0)^3}{3hc^3} e_{\text{eff.}}^2 \frac{\hbar}{\mu\omega_0} \lambda_3^2 \frac{n(n-1)}{4}. \tag{18}$$

This transition probability is weaker by a factor of  $\lambda_3^2$  compared with the zeroth-order allowed transition  $n \rightarrow (n-1)$ .

A number of remarks are in order: (1) The formula given here for the transition probabilities is for the true 1-D anharmonic oscillator. It therefore assumes the diatomic molecule remains oriented in a specific direction in space, say, the  $x$ -direction in a crystalline environment. In a free diatomic molecule, say, in a gaseous sample in a microwave wave guide, the molecule is of course free to both rotate and vibrate. To get the transition probabilities, we would need the matrix elements of

$$\mu_x^{(el.)} = \mu_r \sin \theta \cos \phi, \quad \mu_y^{(el.)} = \mu_r \sin \theta \cos \phi, \quad \mu_z^{(el.)} = \mu_r \cos \theta, \tag{19}$$

with radial part,  $\mu_r$ , given by eq. (13). The matrix elements given by eqs. (14) and (17) are just the radial (vibrational) part of the full electric dipole moment matrix element. This must be augmented by the angular (rotational) matrix elements of  $\sin \theta \cos \phi$ ,  $\sin \theta \sin \phi$ , and  $\cos \theta$ . These matrix elements were actually evaluated in Chapter 9. These matrix elements lead to the rotational selection rule,  $\Delta l = \pm 1$ . Therefore, the actual transition in a free diatomic molecule involves both a change in vibrational quantum number,  $\Delta n = \pm 1$ , and a change in the rotational quantum number,  $\Delta l = \pm 1$ , leading to a vibration–rotation rather than to a pure vibrational transition.

(2): The actual numerical values of a vibrational transition probability, such as that given by eq. (15), is very small, corresponding to inverse times of the order of seconds or minutes, compared with an atomic electronic transition probability corresponding to lifetimes of the order of  $10^{-8}$  seconds. Molecular vibrational or vibrational–rotational transitions are thus usually too weak to be seen in spontaneous emission. They are easily observed, however, in induced absorption processes, by placing the gaseous molecular sample in an electromagnetic beam of the appropriate infrared or microwave frequency. The transition probabilities will then be given by the Einstein  $B$  coefficients and the energy density of the incident beam. Because the Einstein  $B$  coefficients are proportional to the Einstein  $A$  coefficients, the results of this section will still be useful. Also, the induced emission probability for a transition  $n \rightarrow (n-1)$  will be less than the induced absorption probability for the transition  $(n-1) \rightarrow n$  if the number of molecules in the lower

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state,  $N_{(n-1)}$ , is greater than the number of molecules in the upper state,  $N_n$ , the usual situation for a gaseous sample in thermal equilibrium.

# Perturbation Theory for Degenerate Levels

## A Diagonalization of $H^{(1)}$ : Transformation to Proper Zeroth-Order Basis

Assume the eigenvector for the energy state with eigenvalue  $E_n$  is degenerate; i.e., assume  $g_n$  independent eigenvectors exist such that

$$H^{(0)}|nr^{(0)}\rangle = E_n^{(0)}|nr^{(0)}\rangle, \quad \text{with } r = 1, 2, \dots, g_n, \quad (1)$$

where the label  $r$  may just be an ordinal label identifying the different eigenvectors, or it may be a shorthand notation for additional quantum numbers. Clearly, our previous method might lead to difficulties, because now zeros could be in the energy denominators ( $E_n^{(0)} - E_k^{(0)}$ ). A state  $|k^{(0)}\rangle$  different from  $|nr^{(0)}\rangle$  could now include a state with the same zeroth-order energy. Note, however, if  $H^{(1)}$  is made diagonal within the  $g_n$ -dimensional subspace,  $|nr^{(0)}\rangle$ , with  $r = 1, 2, \dots, g_n$ , this difficulty will never arise. Therefore, the first step of the perturbation expansion will involve a transformation from the subbasis  $|nr^{(0)}\rangle$  to the new subbasis  $|nr'^{(0)}\rangle$ , with

$$|nr'^{(0)}\rangle = \sum_{r=1}^{g_n} |nr^{(0)}\rangle \langle nr^{(0)}|nr'^{(0)}\rangle = \sum_{r=1}^{g_n} |nr^{(0)}\rangle c_r, \quad (2)$$

such that

$$\langle ns'^{(0)}|H^{(1)}|nr'^{(0)}\rangle = \delta_{rs} E_{nr'}^{(1)}. \quad (3)$$

Rewriting the first-order equation of the perturbation expansion for the transformed state  $|nr'^{(0)}\rangle$  yields

$$(E_n^{(0)} - H^{(0)})|nr'^{(1)}\rangle = (H^{(1)} - E_n^{(1)})|nr'^{(0)}\rangle. \quad (4)$$

Left-multiplying by  $\langle nr'^{(0)}|$  leads to a zero for the left-hand side of this equation, so

$$\langle nr'^{(0)}|H^{(1)}|nr'^{(0)}\rangle - E_n^{(1)}\langle nr'^{(0)}|nr'^{(0)}\rangle = 0. \quad (5)$$

Introducing the unit operator  $\sum_s |ns^{(0)}\rangle\langle ns^{(0)}|$  for the subspace in question, we can transform this equation into

$$\sum_{s=1}^{g_n} \langle nr'^{(0)}|H^{(1)}|ns^{(0)}\rangle \langle ns^{(0)}|nr'^{(0)}\rangle = E_n^{(1)} \sum_{s=1}^{g_n} \delta_{rs} \langle ns^{(0)}|nr'^{(0)}\rangle, \quad (6)$$

or, in shorthand form, with  $\langle ns^{(0)}|nr'^{(0)}\rangle \equiv c_s$ ,

$$\sum_s (H_{rs}^{(1)} - E_n^{(1)}\delta_{rs})c_s = 0, \quad \text{with } r = 1, \dots, g_n. \quad (7)$$

This system of  $g_n$  linear equations will have a solution for the  $c_s$  if and only if the determinant of the coefficients is equal to zero

$$|H_{rs}^{(1)} - E_n^{(1)}\delta_{rs}| = 0. \quad (8)$$

This equation leads to an equation of degree  $g_n$  in the unknown  $E_n^{(1)}$  with  $g_n$  solutions  $E_{nr'}^{(1)}$ , such that

$$H^{(1)}|nr'^{(0)}\rangle = E_{nr'}^{(1)}|nr'^{(0)}\rangle, \quad \text{with } |nr'^{(0)}\rangle = \sum_s |ns^{(0)}\rangle c_s. \quad (9)$$

The first task in the case of degenerate-level perturbation theory then is to find those linear combinations of the zeroth-order eigenvectors  $|ns^{(0)}\rangle$  that diagonalize  $H^{(1)}$ . These so-called *proper* or *stabilized* zeroth-order eigenvectors will be the basis for the subsequent steps in the perturbation expansion. Three possibilities need to be considered.

## B Three Cases of Degenerate Levels

Case (1): The initial basis  $|nr^{(0)}\rangle$  may already be such that  $H^{(1)}$  is diagonal in this basis. (If higher order terms exist, such as  $H^{(2)}$ , we assume they are also diagonal in this basis.) This may not be such a fortuitous accident. Often, we choose the initial basis to be adapted to the symmetry of the problem. Both  $H^{(0)}$  and  $H^{(1)}$  may have symmetries that naturally lead to a *proper* choice of basis. The choice of this *proper* or *symmetry-adapted* basis may obviate the first step in degenerate-level perturbation theory, the diagonalization of  $H^{(1)}$  in the initial zeroth-order basis. Effectively, therefore, such a case can be treated by nondegenerate perturbation theory.

Other cases now exist in which the nondegenerate perturbation theory formulae of Chapter 21 are sufficient to some order in the parameter of smallness,  $\lambda$ . For example, suppose two (or more) degenerate states  $|nr^{(0)}\rangle$  and  $|ns^{(0)}\rangle$  are not connected with each other through second order. Assume they are connected with each other only in third order, either through the action of  $H^{(1)}$  three times, or through terms such as

$$\langle ns^{(0)}|H^{(1)}|n''u^{(0)}\rangle\langle n''u^{(0)}|H^{(1)}|n't^{(0)}\rangle\langle n't^{(0)}|H^{(1)}|nr^{(0)}\rangle$$

in the perturbation expansion (or similar terms combining a single action of both  $H^{(1)}$  and  $H^{(2)}$ ). In that case, if we are interested only in second-order corrections to the energy, the degenerate states  $|nr^{(0)}\rangle$  and  $|ns^{(0)}\rangle$  are effectively unconnected in second order and the nondegenerate perturbation theory formulae of Chapter 21 apply.

Case (2): The diagonalization of  $H^{(1)}$  in the initial zeroth-order basis may lead to a set of  $g_n$ -distinct eigenvalues  $E_{nr'}^{(1)}$ , with  $E_{nr'}^{(1)} \neq E_{ns'}^{(1)}$ , for  $r \neq s$ . In this case, the subsequent steps in the perturbation expansion closely parallel those for nondegenerate-level perturbation theory.

Case (3): The diagonalization of  $H^{(1)}$  may not remove the zeroth-order degeneracy completely. In this case, a special treatment is necessary. This treatment is similar to that discussed in a next chapter for two (or several) nearly (or precisely) degenerate levels, the toughest of all cases. Again, this case is not as uncommon as might have been thought. For example, the symmetries of  $H^{(0)}$  and  $H^{(1)}$  could be such that all matrix elements of  $H^{(1)}$  are zero in the  $|nr^{(0)}\rangle$  sub-basis. Perhaps the  $|nr^{(0)}\rangle$  all have the same parity and  $H^{(1)}$  has the opposite parity. In this case, we cannot diagonalize  $H^{(1)}$  to find the *proper* zeroth-order basis.

## C Higher Order Corrections with Proper Zeroth-Order Basis

Let us consider case (2). In this case, the first-order equation

$$(E_n^{(0)} - H^{(0)})|nr'^{(1)}\rangle = (H^{(1)} - E_{nr'}^{(1)})|nr'^{(0)}\rangle \quad (10)$$

leads to

$$\begin{aligned} Q_n^{(0)}|nr'^{(1)}\rangle &= Q_n^{(0)} \frac{1}{E_n^{(0)} - H^{(0)}} Q_n^{(0)} H^{(1)} |nr'^{(0)}\rangle \\ &= \sum_{k \neq n} \sum_s |ks^{(0)}\rangle \frac{\langle ks^{(0)}|H^{(1)}|nr'^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})}. \end{aligned} \quad (11)$$

Upon left-multiplication with  $\langle nr'^{(0)}|$ , the second-order equation

$$(E_n^{(0)} - H^{(0)})|nr'^{(0)}\rangle = (H^{(1)} - E_{nr'}^{(1)})|nr'^{(1)}\rangle + (H^{(2)} - E_{nr'}^{(2)})|nr'^{(0)}\rangle \quad (12)$$

leads to

$$0 = \sum_{k \neq n} \sum_s \frac{\langle nr'^{(0)} | H^{(1)} | ks^{(0)} \rangle \langle ks^{(0)} | H^{(1)} | nr'^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})} + \langle nr'^{(0)} | H^{(2)} | nr' \rangle - E_{nr'}^{(2)}, \quad (13)$$

so

$$E_{nr'}^{(2)} = \langle nr'^{(0)} | H^{(2)} | nr'^{(0)} \rangle + \sum_{k \neq n} \sum_s \frac{|\langle ks^{(0)} | H^{(1)} | nr'^{(0)} \rangle|^2}{(E_n^{(0)} - E_k^{(0)})}. \quad (14)$$

All steps in this and subsequent steps in the perturbation formalism parallel the earlier nondegenerate-state perturbation theory, except state vectors  $|n^{(0)}\rangle$  or their conjugate bras must be replaced by  $|nr'^{(0)}\rangle$  and the projection operators  $Q_n^{(0)}$  will have to include besides the sum over  $k \neq n$  a sum over the degeneracy label  $s$ . Note, in particular, that the states  $|ks^{(0)}\rangle$  need *not* be transformed to primed form.

## D Application 1: Stark Effect in the Diatomic Molecule Rigid Rotator

Let us consider a nonhomonuclear diatomic molecule, with a permanent electric dipole moment, which is perturbed by an external electric field,  $\vec{\mathcal{E}}$ . Let us consider only the lowest energies of this system, so the molecule can be considered as a rigid rotator, with zeroth-order energy eigenvalues and eigenfunctions (or eigenvectors)

$$E_l^{(0)} = \frac{\hbar^2}{2I_e} l(l+1), \quad Y_{lm}(\theta, \phi) = \langle \theta, \phi | lm \rangle, \quad (15)$$

with  $I_e = \mu r_e^2$  and

$$H^{(0)} |lm^{(0)}\rangle = E_l^{(0)} |lm^{(0)}\rangle, \quad \text{with } m = +l, \dots, -l. \quad (16)$$

The  $l^{th}$  level, thus, has a  $(2l+1)$ -fold degeneracy, the general degeneracy associated with rotationally invariant systems. In the presence of an external electric field,  $\vec{\mathcal{E}}$ , we must add a term

$$H^{(1)} = -\vec{\mu}^{(el.)} \cdot \vec{\mathcal{E}} = -\mu_e \cos \theta \mathcal{E}, \quad (17)$$

where we have assumed the electric field  $\vec{\mathcal{E}}$  is in the space-fixed  $z$  direction and the symmetry axis of the molecule makes a polar angle  $\theta$  with this  $z$  direction. This Stark perturbation (Stark effect) is often used to identify the  $l$  values of initial states in purely rotational transitions. To show  $H^{(1)}$  is a weak perturbation, assume the electric field is 1,000 Volts/cm, a strong field. The permanent electric dipole moments,  $\mu_e$ , of diatomic molecules are of order  $e \times 10^{-8}$  cm. Thus, even in this strong field,  $H^{(1)}$  can be expected to be of order  $10^{-5}$  eV. Take the HCl molecule as a specific example, so  $\mu \approx m_{\text{proton}}$ , with  $\mu c^2 \approx 10^9$  eV. Take  $r_e \approx 10^{-8}$  cm

(the precise value is known from the rotational spectrum to be  $1.2746 \times 10^{-8} \text{ cm}$ ). Then,

$$\frac{\hbar^2}{2\mu r_e^2} = \frac{(\hbar c)^2}{2(\mu c^2)r_e^2} \approx \frac{(1.973 \times 10^{-5} eV \text{ cm})^2}{2 \times 10^9 eV \times 10^{-16} \text{ cm}^2} \approx 2 \times 10^{-3} eV, \quad (18)$$

showing the Stark term,  $H^{(1)}$ , can indeed be treated as a perturbation. To calculate the matrix elements of  $H^{(1)}$ , recall (Chapter 9)

$$\cos \theta Y_{lm} = \sqrt{\frac{[(l+1)^2 - m^2]}{(2l+1)(2l+3)}} Y_{(l+1)m} + \sqrt{\frac{[l^2 - m^2]}{(2l+1)(2l-1)}} Y_{(l-1)m}, \quad (19)$$

so

$$\begin{aligned} \langle (l+1)m | \cos \theta | lm \rangle &= \sqrt{\frac{[(l+1)^2 - m^2]}{(2l+1)(2l+3)}}, \\ \langle (l-1)m | \cos \theta | lm \rangle &= \sqrt{\frac{[l^2 - m^2]}{(2l+1)(2l-1)}}. \end{aligned} \quad (20)$$

Our  $H^{(1)}$  does not have matrix elements diagonal in the quantum number,  $l$ . No first-order contribution to the Stark energy shift occurs. At first, it appears this belongs to case (3) of section B of this chapter and might require further treatment. All matrix elements of the perturbing Hamiltonian, however, are diagonal in  $m$ . States of a particular  $m$  are therefore completely unconnected from states of different  $m$ . We can therefore treat states of a particular  $m$  by themselves, as if they were unconnected from the rest, hence, by nondegenerate perturbation theory. This is of course connected to the symmetry of our Hamiltonian, even, including the full perturbation, our Hamiltonian has axial symmetry. Our zeroth-order state vectors, of good eigenvalue  $m$ , are automatically the *proper symmetry-adapted* zeroth-order state vectors. (If we had chosen to call the direction of the  $\vec{E}$  field the  $x$  rather than the  $z$  direction, our  $H^{(1)}$  would have been  $-\mu_e \sin \theta \cos \phi \vec{E}$ . If we had diagonalized this  $H^{(1)}$ , we would essentially have effected a rotation from our original  $x$  direction to a new  $z$  direction. By choosing our  $z$  rather than our  $x$  direction along the direction of the outside  $\vec{E}$ , our zeroth-order state vectors have automatically become the *proper* ones for the perturbation calculation.

The second-order contributions to the energy are then simply

$$\begin{aligned} \lambda^2 E_{lm}^{(2)} &= \sum_{l'=\pm 1} \frac{|\langle l'm^{(0)} | H^{(1)} | lm^{(0)} \rangle|^2}{E_l^{(0)} - E_{l'}^{(0)}} = \frac{\mu_e^2 \mathcal{E}^2}{\hbar^2 / 2I_e} \\ &\times \left( \frac{[l^2 - m^2]/(2l+1)(2l-1)}{[l(l+1) - (l-1)l]} + \frac{[(l+1)^2 - m^2]/(2l+3)(2l+1)}{[l(l+1) - (l+1)(l+2)]} \right) \\ &= \frac{2I_e \mu_e^2 \mathcal{E}^2}{\hbar^2} \left( \frac{[l^2 - m^2]}{2l(2l+1)(2l-1)} - \frac{[(l+1)^2 - m^2]}{2(l+1)(2l+1)(2l+3)} \right) \\ &= \frac{2I_e \mu_e^2 \mathcal{E}^2}{\hbar^2} \frac{[l(l+1) - 3m^2]}{2l(l+1)(2l-1)(2l+3)}. \end{aligned} \quad (21)$$

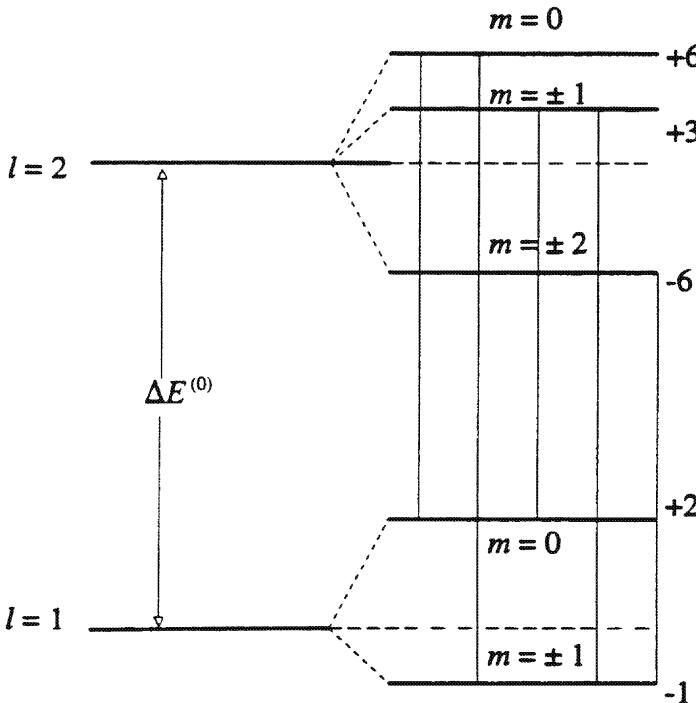


FIGURE 23.1. Second order Stark splitting of the  $l = 2$  and  $l = 1$  states of the diatomic molecule rigid rotator. The energy shifts are in units of  $[I_e \mu_e^2 \mathcal{E}^2 / \hbar^2 l(l+1)(2l-1)(2l+3)]$ .  $\Delta E^{(0)} = 2\hbar^2/I_e$ .

The Stark splitting of the  $l = 2$  and  $l = 1$  levels is shown in Fig. 23.1., where energy shifts are shown in units of  $(I_e \mu_e^2 \mathcal{E}^2 / \hbar^2 l(l+1)(2l-1)(2l+3))$ . Note that the  $l^{th}$  rotational level is split into only  $(l+1)$  levels since the second order energy shift depends only on  $m^2$ . The transition probabilities for the  $l = 2 \rightarrow l = 1$  transitions are now given by the matrix elements of

$$\mu_x^{(el.)} = \mu_e \sin \theta \cos \phi; \quad \mu_y^{(el.)} = \mu_e \sin \theta \sin \phi; \quad \mu_z^{(el.)} = \mu_e \cos \theta. \quad (22)$$

These lead to the selection rules,  $\Delta m = \pm 1$  for the x and y components, and  $\Delta m = 0$  for the z component. Thus the  $l = 2 \rightarrow l = 1$  transition is split into five components, corresponding to the transitions  $m = 2 \rightarrow 1, 1 \rightarrow 0, 1 \rightarrow 1, 0 \rightarrow 1, 0 \rightarrow 0$ . (Actually, the transition would be observed through an induced absorption process). The line pattern, including relative intensities, is shown in Fig. 23.2, where the shifts in frequency from the unperturbed frequency,  $(h/2\pi^2 I_e)$ , are given in units of  $\Delta = (I_e \mu_e^2 \mathcal{E}^2 / 2\pi\hbar^3 210)$ .

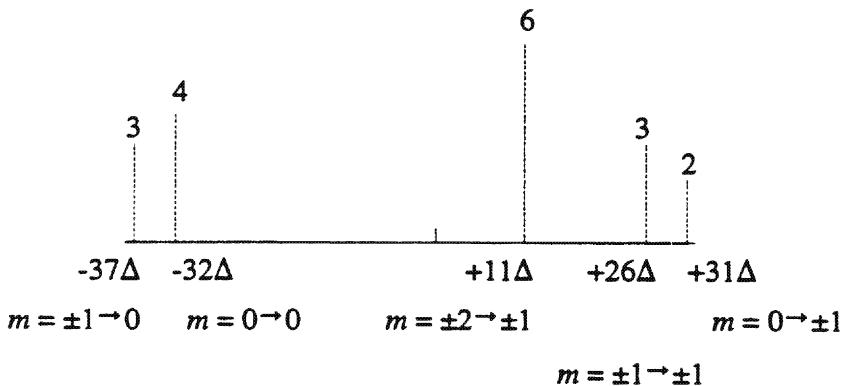


FIGURE 23.2. The Stark splitting of the  $l = 2 \rightarrow l = 1$  transition. The numbers above the lines give the relative intensities. Frequency shifts from the zeroth-order frequency are given in units of  $\Delta = (I_e \mu_e^2 \mathcal{E}^2 / 2\pi\hbar^3 210)$ .

## E Application 2: Stark Effect in the Hydrogen Atom

In an external electric field,  $\vec{\mathcal{E}}$ , the perturbing Hamiltonian is now

$$H^{(1)} = -(-e\vec{r}_1 + e\vec{r}_2) \cdot \vec{\mathcal{E}} = e(\vec{r}_1 - \vec{r}_2) \cdot \vec{\mathcal{E}} = ea_0 r \cos \theta \mathcal{E}, \quad (23)$$

where  $a_0$  is the Bohr radius and we have again introduced a dimensionless  $r$  via  $|\vec{r}_{\text{relative}}| = a_0 r$ . For an electric field  $\mathcal{E}$  of 1,000 Volts/cm,  $H^{(1)}$  is again of order  $10^{-5}$  eV, but now the zeroth-order energy is the Bohr energy  $\mu e^4 / \hbar^2 = 27$  eV, so  $|H^{(1)} / H^{(0)}| \ll 1$ , the ratio now being of order  $10^{-6}$ . Although the  $m$  quantum number is again a good quantum number to all orders, because the perturbation can not change  $m$ , several  $l$  values now exist for a given  $m$  [with the exception of the states with  $m = \pm(n - 1)$ ]. Let us take the four-fold degenerate state with  $n = 2$  as a special example. Now, a nonzero  $H^{(1)}$  matrix element connecting the  $m = 0$  states with  $l = 0$  and  $l = 1$  exists,

$$\begin{aligned} \langle nlm = 210 | \lambda H^{(1)} | nlm = 200 \rangle &= ea_0 \mathcal{E} \langle 210 | r \cos \theta | 200 \rangle \\ &= ea_0 \mathcal{E} I_{21,20}^{\text{rad.}} \frac{1}{\sqrt{3}}, \end{aligned} \quad (24)$$

where the angular part of the matrix element, with value  $1/\sqrt{3}$ , follows from eq. (19) and the radial part is given by

$$\begin{aligned} I_{21,20}^{\text{rad.}} &= \int_0^\infty dr r^2 R_{n=2,l=1}(r) r R_{n=2,l=0}(r) \\ &= \frac{1}{4\sqrt{3}} \int_0^\infty dr r^4 (1 - \frac{r}{2}) e^{-r} \\ &= \frac{1}{4\sqrt{3}} (4! - \frac{5!}{2}) = -3\sqrt{3}, \end{aligned} \quad (25)$$

leading to the  $4 \times 4$  matrix

$$\langle 2l'm | \lambda(H^{(1)} - E_{n=2}^{(1)}) | 2lm \rangle =$$

$$\begin{matrix} & 200 & 210 & 21+1 & 21-1 \\ \begin{matrix} 200 \\ 210 \\ 21+1 \\ 21-1 \end{matrix} & \begin{pmatrix} -\lambda E_2^{(1)} & -3ea_0\mathcal{E} & 0 & 0 \\ -3ea_0\mathcal{E} & -\lambda E_2^{(1)} & 0 & 0 \\ 0 & 0 & -\lambda E_2^{(1)} & 0 \\ 0 & 0 & 0 & -\lambda E_2^{(1)} \end{pmatrix} \end{matrix}$$

The energy determinant leads to the values  $\lambda E_2^{(1)} = +3ea_0\mathcal{E}$ ,  $-3ea_0\mathcal{E}$ , 0, and 0. The corresponding *proper* zeroth-order eigenvectors are

$$\begin{aligned} \text{For } +3ea_0\mathcal{E} : & \quad \frac{1}{\sqrt{2}}(|200\rangle - |210\rangle) \\ \text{For } -3ea_0\mathcal{E} : & \quad \frac{1}{\sqrt{2}}(|200\rangle + |210\rangle) \\ \text{For } 0 : & \quad |21+1\rangle \\ \text{For } 0 : & \quad |21-1\rangle. \end{aligned} \tag{26}$$

Because the first-order Stark effect in atomic hydrogen is very small, these first-order results may be sufficient. Because we have determined the *proper* zeroth-order eigenvectors, we could now use eq. (14) to calculate the Stark energy corrections to second order. The sum over states with  $k \neq n$ , however, is now a sum over an infinite number of discrete states and in fact includes a continuum sum (i.e., an integral) over the hydrogenic continuum states, because the operator  $r \cos \theta$  has nonzero matrix elements connecting a state  $nlm$  to states  $n'(l \pm 1)m$ , with *all* possible values of  $n' \neq n$ . (We shall find the stretched parabolic coordinates of problems 6 and 26 will give us an elegant way out of this computational difficulty; see problem 37.)

# 24

## The Case of Nearly Degenerate Levels

[Alternatively, the results of this section can also be used for precisely degenerate levels in case (3), when  $H^{(1)}$  does not remove the degeneracy and hence does not give the *proper* or *stabilized* zeroth-order state vectors.]

If for some specific pair of levels,  $n$  and  $m$ ,  $(E_n^{(0)} - E_m^{(0)})$  is accidentally very small (the case of an accidental near degeneracy), particularly if  $\langle m^{(0)} | H^{(1)} | n^{(0)} \rangle$  is of the same order of magnitude as  $(E_n^{(0)} - E_m^{(0)})$ , our perturbation theory formulae would give a very poor approximation for this pair of levels. A technique that can deal with this situation is the following: We shall make a unitary transformation on the original perturbed Hamiltonian,  $H$ , to transform it to a new Hamiltonian,  $H'$ , to eliminate the off-diagonal matrix elements that connect the nearly degenerate levels to all other levels, or at least make these off-diagonal matrix elements small enough in orders of powers of  $\lambda$ , so they will not contribute to the energies of states  $n$  and  $m$  to some particular order in  $\lambda$ . An elegant way to achieve this follows in the next section.

### A Perturbation Theory by Similarity Transformation

We shall try to find a unitary operator,  $U$ , generated by a hermitian operator,  $G$ , such that  $H$  is transformed into  $H'$

$$H' = UHU^\dagger = U(H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots)U^\dagger, \quad \text{with } U = e^{i\lambda G}, \quad (1)$$

where the parameter,  $\lambda$ , in  $U$  is the parameter of smallness in the perturbation expansion. (The eigenvalues of a hermitian operator are invariant to similarity

transformations.) In particular, if we succeed in choosing a  $G$  such that the first-order matrix elements of  $H'$  connecting states  $n$  and  $m$  to states  $k \neq n, m$  are all equal to zero, the  $2 \times 2$  matrix for  $H'$  in the  $n, m$  subspace will give us the energies correct to order  $\lambda^2$ . The surviving off-diagonal matrix elements (of order  $\lambda^2$ ) connecting states  $n$  and  $m$  to states  $k \neq n, m$  would contribute to the energies  $E_n$  and  $E_m$  only through their squares, divided by zeroth-order energy differences. The strategy then will be to find a  $G$  with matrix elements such that  $\langle k^{(0)} | H'^{(1)} | n^{(0)} \rangle = 0$ , and  $\langle k^{(0)} | H'^{(1)} | m^{(0)} \rangle = 0$  (with similar zeros for the transposed matrix elements of  $H'^{(1)}$ ) for all  $k \neq n, m$ .

$$\begin{aligned} H' &= (1 + i\lambda G - \frac{\lambda^2}{2} G^2 + \dots)(H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots) \\ &\quad \times (1 - i\lambda G - \frac{\lambda^2}{2} G^2 + \dots) \\ &= H^{(0)} + \lambda(H^{(1)} + i[G, H^{(0)}]) + \lambda^2(H^{(2)} + i[G, H^{(1)}] \\ &\quad - \frac{1}{2}[G, [G, H^{(0)}]]) + \dots \\ &= H^{(0)} + \lambda H'^{(1)} + \lambda^2 H'^{(2)} + \dots. \end{aligned} \quad (2)$$

Now, we shall choose  $G$  such that, with  $k \neq n, m$ ,

$$\begin{aligned} \langle k^{(0)} | H'^{(1)} | n^{(0)} \rangle &= \langle k^{(0)} | H^{(1)} | n^{(0)} \rangle + i \langle k^{(0)} | [G, H^{(0)}] | n^{(0)} \rangle = 0 \\ &= \langle k^{(0)} | H^{(1)} | n^{(0)} \rangle + i(E_n^{(0)} - E_k^{(0)}) \langle k^{(0)} | G | n^{(0)} \rangle. \end{aligned} \quad (3)$$

With a similar relation for the  $km^{\text{th}}$  matrix element, this equation leads to

$$\begin{aligned} \langle k^{(0)} | G | n^{(0)} \rangle &= i \frac{\langle k^{(0)} | H^{(1)} | n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})}, \quad \langle k^{(0)} | G | m^{(0)} \rangle = i \frac{\langle k^{(0)} | H^{(1)} | m^{(0)} \rangle}{(E_m^{(0)} - E_k^{(0)})}, \\ \langle n^{(0)} | G | k^{(0)} \rangle &= i \frac{\langle n^{(0)} | H^{(1)} | k^{(0)} \rangle}{(E_k^{(0)} - E_n^{(0)})}, \quad \langle m^{(0)} | G | k^{(0)} \rangle = i \frac{\langle m^{(0)} | H^{(1)} | k^{(0)} \rangle}{(E_k^{(0)} - E_m^{(0)})}. \end{aligned} \quad (4)$$

All remaining matrix elements of  $G$  will be set equal to zero. In particular,

$$\langle n^{(0)} | G | n^{(0)} \rangle = \langle m^{(0)} | G | m^{(0)} \rangle = \langle n^{(0)} | G | m^{(0)} \rangle = 0. \quad (5)$$

Now,

$$\begin{aligned} \langle n^{(0)} | H'^{(1)} | n^{(0)} \rangle &= \langle n^{(0)} | H^{(1)} | n^{(0)} \rangle \\ &+ i \sum_{k \neq n, m} \left[ \langle n^{(0)} | G | k^{(0)} \rangle \langle k^{(0)} | H^{(0)} | n^{(0)} \rangle - \langle n^{(0)} | H^{(0)} | k^{(0)} \rangle \langle k^{(0)} | G | n^{(0)} \rangle \right] \\ &= \langle n^{(0)} | H^{(1)} | n^{(0)} \rangle. \end{aligned} \quad (6)$$

Similarly,

$$\begin{aligned} \langle m^{(0)} | H'^{(1)} | m^{(0)} \rangle &= \langle m^{(0)} | H^{(1)} | m^{(0)} \rangle, \\ \langle n^{(0)} | H'^{(1)} | m^{(0)} \rangle &= \langle n^{(0)} | H^{(1)} | m^{(0)} \rangle. \end{aligned} \quad (7)$$

For

$$H'^{(2)} = H^{(2)} + i(GH^{(1)} - H^{(1)}G) - \frac{1}{2}(G^2H^{(0)} - 2GH^{(0)}G + H^{(0)}G^2), \quad (8)$$

let us first calculate the  $nm^{th}$  matrix element

$$\begin{aligned}
\langle n^{(0)} | H'^{(2)} | m^{(0)} \rangle &= \langle n^{(0)} | H^{(2)} | m^{(0)} \rangle \\
&+ i \sum_{k \neq n, m} \left[ \langle n^{(0)} | G | k^{(0)} \rangle \langle k^{(0)} | H^{(1)} | m^{(0)} \rangle - \langle n^{(0)} | H^{(1)} | k^{(0)} \rangle \langle k^{(0)} | G | m^{(0)} \rangle \right] \\
&- \frac{1}{2} \sum_{k \neq n, m} \left[ \langle n^{(0)} | G | k^{(0)} \rangle \langle k^{(0)} | G | m^{(0)} \rangle \langle m^{(0)} | H^{(0)} | m^{(0)} \rangle \right. \\
&- 2 \langle n^{(0)} | G | k^{(0)} \rangle \langle k^{(0)} | H^{(0)} | k^{(0)} \rangle \langle k^{(0)} | G | m^{(0)} \rangle \\
&\left. + \langle n^{(0)} | H^{(0)} | n^{(0)} \rangle \langle n^{(0)} | G | k^{(0)} \rangle \langle k^{(0)} | G | m^{(0)} \rangle \right] \\
&= \langle n^{(0)} | H^{(2)} | m^{(0)} \rangle + \sum_{k \neq n, m} \langle n^{(0)} | H^{(1)} | k^{(0)} \rangle \langle k^{(0)} | H^{(1)} | m^{(0)} \rangle \times \\
&\left[ \left( \frac{1}{(E_n^{(0)} - E_k^{(0)})} + \frac{1}{(E_m^{(0)} - E_k^{(0)})} \right) - \frac{1}{2} \left( \frac{E_m^{(0)} - 2E_k^{(0)} + E_n^{(0)}}{(E_n^{(0)} - E_k^{(0)})(E_m^{(0)} - E_k^{(0)})} \right) \right]. \quad (9)
\end{aligned}$$

Now, using the trivial identity

$$\frac{1}{(E_n^{(0)} - E_k^{(0)})} + \frac{1}{(E_m^{(0)} - E_k^{(0)})} = \frac{(E_n^{(0)} + E_m^{(0)} - 2E_k^{(0)})}{(E_n^{(0)} - E_k^{(0)})(E_m^{(0)} - E_k^{(0)})}, \quad (10)$$

and defining the average energy for the pair of levels  $\bar{E}_{n,m}^{(0)} = \frac{1}{2}(E_n^{(0)} + E_m^{(0)})$ , we obtain

$$\begin{aligned}
\langle n^{(0)} | H'^{(2)} | m^{(0)} \rangle &= \langle n^{(0)} | H^{(2)} | m^{(0)} \rangle \\
&+ \sum_{k \neq n, m} \langle n^{(0)} | H^{(1)} | k^{(0)} \rangle \langle k^{(0)} | H^{(1)} | m^{(0)} \rangle \frac{(\bar{E}_{n,m}^{(0)} - E_k^{(0)})}{(E_n^{(0)} - E_k^{(0)})(E_m^{(0)} - E_k^{(0)})}. \quad (11)
\end{aligned}$$

By setting  $m = n$  in this expression, we can also immediately get the matrix element  $\langle n^{(0)} | H'^{(2)} | n^{(0)} \rangle$ , and similarly by setting  $n = m$ , we get  $\langle m^{(0)} | H'^{(2)} | m^{(0)} \rangle$ . With these results, the  $2 \times 2$  submatrix of  $H'$  connecting the two states  $|n\rangle$  and  $|m\rangle$  is

$$\begin{pmatrix} H'_{nn} & H'_{nm} \\ H'_{mn} & H'_{mm} \end{pmatrix},$$

where, with an obvious shorthand matrix notation for the matrix elements, we have (through second order)

$$\begin{aligned}
H'_{nn} &= E_n^{(0)} + \lambda H_{nn}^{(1)} + \lambda^2 \left[ H_{nn}^{(2)} + \sum_{k \neq n, m} \frac{|H_{kn}^{(1)}|^2}{(E_n^{(0)} - E_k^{(0)})} \right] \\
H'_{nm} &= \lambda H_{nm}^{(1)} + \lambda^2 \left[ H_{nm}^{(2)} + \sum_{k \neq n, m} \frac{H_{nk}^{(1)} H_{km}^{(1)} (\bar{E}_{n,m}^{(0)} - E_k^{(0)})}{(E_n^{(0)} - E_k^{(0)})(E_m^{(0)} - E_k^{(0)})} \right] \\
H'_{mn} &= \lambda H_{mn}^{(1)} + \lambda^2 \left[ H_{mn}^{(2)} + \sum_{k \neq n, m} \frac{H_{mk}^{(1)} H_{kn}^{(1)} (\bar{E}_{n,m}^{(0)} - E_k^{(0)})}{(E_n^{(0)} - E_k^{(0)})(E_m^{(0)} - E_k^{(0)})} \right] \\
H'_{mm} &= E_m^{(0)} + \lambda H_{mm}^{(1)} + \lambda^2 \left[ H_{mm}^{(2)} + \sum_{k \neq n, m} \frac{|H_{km}^{(1)}|^2}{(E_m^{(0)} - E_k^{(0)})} \right]. \quad (12)
\end{aligned}$$

To get the energies to second order, it is now only necessary to diagonalize this  $2 \times 2$  matrix, leading to

$$E = E_{\pm} = \frac{1}{2} \left( (H'_{nn} + H'_{mm}) \pm \sqrt{(H'_{nn} - H'_{mm})^2 + 4|H'_{nm}|^2} \right). \quad (13)$$

This result is quite general. Note: If the two levels  $n$  and  $m$  are not nearly degenerate, the result applies for a *single* level, say, the  $n^{th}$  one, and in that case, we have simply regained the result of nondegenerate-level perturbation theory. The result also applies to a pair of exactly degenerate levels. In that case, with  $\bar{E}_{nm}^{(0)} = E_n^{(0)} = E_m^{(0)}$ , the off-diagonal matrix element has a term

$$\sum_{k \neq n,m} \frac{H_{nk}^{(1)} H_{km}^{(1)}}{(E_n^{(0)} - E_k^{(0)})}.$$

This equation will be important in case (3), in which  $H_{nm}^{(1)}$  is zero and does not remove the degeneracy in first order, and in the case in which  $H^{(1)}$  does not lead to the *proper* zeroth-order state vectors. Finally, the diagonal and off-diagonal matrix elements given by eq. (12) can be used in the case in which the degeneracy or near degeneracy is greater than two-fold.

## B An Example: Two Coupled Harmonic Oscillators with $\omega_1 \approx 2\omega_2$

Let us consider the Hamiltonian for two coupled nearly harmonic oscillators with cubic and quartic coupling terms

$$H = \frac{1}{2}\hbar\omega_1(p_x^2 + x^2) + \frac{1}{2}\hbar\omega_2(p_y^2 + y^2) + \lambda\hbar\omega_c xy^2 + \lambda^2(\hbar\omega_d x^4 + \hbar\omega_e y^4 + \hbar\omega_f x^2 y^2), \quad (14)$$

where  $x$ ,  $p_x$ ,  $y$ ,  $p_y$ , are dimensionless variables as for the 1-D oscillator. It is assumed  $\omega_1 \approx 2\omega_2$ . States with  $|n_1 n_2\rangle$  are then nearly degenerate with states  $|(n_1 - 1)(n_2 + 2)\rangle$ . Using matrix elements of  $x$ ,  $x^2$ ,  $x^4$  from earlier chapters, and combining these to yield, e.g.,

$$\langle(n_1 - 1)(n_2 + 2)|xy^2|n_1 n_2\rangle = \sqrt{\frac{n_1(n_2 + 1)(n_2 + 2)}{8}}, \quad (15)$$

we get, for the nearly degenerate levels  $n_1 n_2 = 10$  and  $n_1 n_2 = 02$ , the  $2 \times 2$  matrix for  $H'$ :

$$\begin{aligned} H'_{10,10} &= \frac{3}{2}\hbar\omega_1 + \frac{1}{2}\hbar\omega_2 - \lambda^2 \frac{(\hbar\omega_c)^2}{\hbar\omega_1} \left( \frac{1}{8} + \frac{\omega_1}{2(\omega_1 + 2\omega_2)} \right), \\ &\quad + \lambda^2 \frac{1}{4}(15\hbar\omega_d + 3\hbar\omega_e + 3\hbar\omega_f), \\ H'_{10,02} &= H'_{02,10} = \frac{1}{2}\lambda\hbar\omega_c, \\ H'_{02,02} &= \frac{1}{2}\hbar\omega_1 + \frac{5}{2}\hbar\omega_2 - \lambda^2 \frac{(\hbar\omega_c)^2}{\hbar\omega_1} \left( \frac{25}{8} + \frac{3\omega_1}{2(\omega_1 + 2\omega_2)} \right), \end{aligned}$$

$$+ \lambda^2 \frac{1}{4} (3\hbar\omega_d + 3\hbar\omega_e + 5\hbar\omega_f). \quad (16)$$

In particular, in this special example,  $H^{(1)}$  does not contribute a second-order term to  $H'_{nm}$ , but it does contribute to the two diagonal terms, via

$$\begin{aligned} & \sum_{k_1 k_2 \neq 10, 02} \frac{|\langle k_1 k_2 | H^{(1)} | 10 \rangle|^2}{(E_{10}^{(0)} - E_{k_1 k_2}^{(0)})} = \\ & \frac{|\langle 20 | H^{(1)} | 10 \rangle|^2}{-\hbar\omega_1} + \frac{|\langle 22 | H^{(1)} | 10 \rangle|^2}{(-\hbar\omega_1 - 2\hbar\omega_2)} + \frac{|\langle 00 | H^{(1)} | 10 \rangle|^2}{\hbar\omega_1} \\ & = \frac{(\hbar\omega_c)^2}{\hbar\omega_1} \left( \frac{1}{4} \frac{1}{(-1)} + \frac{1}{8} \frac{1}{(+1)} + \frac{1}{2} \frac{\omega_1}{(-(\omega_1 + 2\omega_2))} \right) \end{aligned} \quad (17)$$

and

$$\begin{aligned} & \sum_{k_1 k_2 \neq 10, 02} \frac{|\langle k_1 k_2 | H^{(1)} | 02 \rangle|^2}{(E_{02}^{(0)} - E_{k_1 k_2}^{(0)})} = \frac{|\langle 12 | H^{(1)} | 02 \rangle|^2}{-\hbar\omega_1} + \frac{|\langle 14 | H^{(1)} | 02 \rangle|^2}{(-\hbar\omega_1 - 2\hbar\omega_2)} \\ & = \frac{(\hbar\omega_c)^2}{\hbar\omega_1} \left( \frac{25}{8} \frac{1}{(-1)} + \frac{3}{2} \frac{\omega_1}{(-(\omega_1 + 2\omega_2))} \right). \end{aligned} \quad (18)$$

This example has been chosen as a simplified model for a real near degeneracy. The linear symmetrical CO<sub>2</sub> molecule, with an O-C-O configuration, has three vibrational frequencies, an in-phase and an out-of-phase stretching of the two CO bonds with frequencies, named  $\omega_1$  and  $\omega_3$ , and a two-fold degenerate oscillation in which the C atom moves in a direction perpendicular to the equilibrium line relative to the O-O group, where this two-fold degenerate frequency has been named  $\omega_2$ . For CO<sub>2</sub>, the three observed frequencies are

$$\frac{\hbar\omega_1}{hc} = 1351.2 \text{ cm}^{-1}, \quad \frac{\hbar\omega_2}{hc} = 672.2 \text{ cm}^{-1}, \quad \frac{\hbar\omega_3}{hc} = 2396.4 \text{ cm}^{-1}.$$

(In molecular spectroscopy, “frequencies” are usually given in “wavenumbers,” i.e., in  $\text{cm}^{-1}$ , in waves per centimeter.) Note that  $\hbar\omega_1 - 2\hbar\omega_2 = 6.8 \text{ cm}^{-1}$ . This difference is much less than the experimentally deduced coupling term  $\frac{1}{2}\hbar\omega_c = 50 \text{ cm}^{-1}$ . The problem of this near degeneracy was first solved by Fermi. The near degeneracy in CO<sub>2</sub> is known as the Fermi resonance. (Finally, we have made our simplified Hamiltonian such that  $V(y) = +V(-y)$ , so it mimicks the real potential of CO<sub>2</sub>.)

Finally, we need to have a more explicit expression for the perturbed state vectors  $|n\rangle$  and  $|m\rangle$ . We have converted  $H|n\rangle$  and  $H|m\rangle$  into  $UH|n\rangle = UHU^\dagger(U|n\rangle)$  and  $UH|m\rangle = UHU^\dagger(U|m\rangle)$ , where we now have  $H' = UHU^\dagger$  acting on  $|n^{(0)}\rangle = U|n\rangle$  (similar for  $U|m\rangle$ ). Thus, we have

$$|n\rangle = U^{-1}|n^{(0)}\rangle = (1 - i\lambda G - \frac{\lambda^2}{2}G^2)|n^{(0)}\rangle, \quad (19)$$

leading to

$$|n\rangle = |n^{(0)}\rangle - i\lambda \sum_{k \neq n, m} |k^{(0)}\rangle \langle k^{(0)}|G|n^{(0)}\rangle$$

$$\begin{aligned}
& - \frac{\lambda^2}{2} \sum_{k \neq n, m} \left( |n^{(0)}\rangle \langle n^{(0)}| G |k^{(0)}\rangle \langle k^{(0)}| G |n^{(0)}\rangle \right. \\
& \quad \left. + |m^{(0)}\rangle \langle m^{(0)}| G |k^{(0)}\rangle \langle k^{(0)}| G |n^{(0)}\rangle \right) \\
& = |n^{(0)}\rangle \left( 1 - \frac{\lambda^2}{2} \sum_{k \neq n, m} \frac{|\langle k^{(0)}| H^{(1)} |n^{(0)}\rangle|^2}{(E_n^{(0)} - E_k^{(0)})^2} \right) \\
& \quad + |m^{(0)}\rangle \left( -\frac{\lambda^2}{2} \sum_{k \neq n, m} \frac{\langle m^{(0)}| H^{(1)} |k^{(0)}\rangle \langle k^{(0)}| H^{(1)} |n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})(E_m^{(0)} - E_k^{(0)})} \right) \\
& \quad + \lambda \sum_{k \neq n, m} |k^{(0)}\rangle \frac{\langle k^{(0)}| H^{(1)} |n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})}, \tag{20}
\end{aligned}$$

with a similar expression for  $|m\rangle$ . The final expression for the eigenvectors associated with the energy eigenstates  $|E_{\pm}\rangle$  of eq. (13) will be

$$\begin{aligned}
|E_+\rangle &= c|n\rangle + s|m\rangle, \\
|E_-\rangle &= -s|n\rangle + c|m\rangle, \tag{21}
\end{aligned}$$

$$\text{with } \frac{c}{s} = \frac{H'_{nm}}{(E_+ - H'_{nn})}, \quad \text{with } c^2 + s^2 = 1. \tag{22}$$

# 25

## Magnetic Field Perturbations

So far, we have looked at a number of perturbation problems involving an external electric field,  $\vec{\mathcal{E}}$ . We would like to look at similar problems involving external magnetic fields.

### A The Quantum Mechanics of a Free, Charged Particle in a Magnetic Field

Classically, the Hamiltonian of a charged particle, of charge  $e$  and mass  $m$ , in a magnetic field,  $\vec{B}$ , derivable from a vector potential,  $\vec{A}$ , via  $\vec{B} = \text{curl} \vec{A}$ , is given by

$$H = \frac{1}{2m}(\vec{p} - \frac{e}{c}\vec{A}) \cdot (\vec{p} - \frac{e}{c}\vec{A}). \quad (1)$$

In a uniform field,  $\vec{B}_0$ , e.g., with  $\vec{A} = \frac{1}{2}[\vec{B}_0 \times \vec{r}]$ , the classical equations of motion in Hamiltonian formalism lead to

$$m \frac{d^2\vec{r}}{dt^2} = \frac{e}{c} [\vec{v} \times \vec{B}_0]. \quad (2)$$

The Schrödinger equation follows from eq. (1) via  $\vec{p} \rightarrow \frac{\hbar}{i}\vec{\nabla}$ . At first glance, this equation seems to be dependent on the choice of gauge of the vector potential. [With the choice of the so-called symmetric gauge for an electron in a uniform magnetic field in the z-direction, see eq. (15) below.] If  $\vec{A}$  gives rise to a magnetic induction  $\vec{B}$ , a vector potential  $\vec{A}'$  with  $\vec{A}' = \vec{A} + \vec{\nabla}f$ , where  $f$  is any function  $f(x, y, z)$ , will give rise to the same field  $\vec{B}$ . To keep the Schrödinger equation

form invariant to this gauge transformation, we must gauge not only  $\vec{A}$ , but the Schrödinger wave function as well. The quantum-mechanical form of eq. (1) is form invariant under the gauge transformation (see problem 3),

$$\begin{aligned}\vec{A} &\rightarrow \vec{A}' = \vec{A} + \vec{\nabla} f(x, y, z), \\ \psi &\rightarrow \psi' = \psi e^{\frac{i\epsilon}{\hbar c} f(x, y, z)}.\end{aligned}\quad (3)$$

## B Aharonov–Bohm Effect

The above gauge transformation was exploited by Bohm and Aharonov in a famous paper (Phys. Rev. **115** (1959) 485) to show that the quantum-mechanical wave function describing the motion of electrons can be influenced by the presence of magnetic fields, even if the electron trajectories are such that the electrons do not experience the Lorentz force  $\frac{e}{c}[\vec{v} \times \vec{B}]$ , if the trajectories are limited to regions in which  $\vec{B} = 0$ . They proposed the following experiment: An electron beam from an electron source is split into two identical beams, subsequently reflected from identical reflectors to end in a detector, as shown in Fig. 25.1. If the electrons in beam 1 are described by the wave function  $\psi_1$  and the electrons in beam 2 are described by the wave function  $\psi_2$ , the number of electrons arriving at the common detector will be proportional to  $|\psi_1 + \psi_2|^2$ . Bohm and Aharonov proposed to place a tightly wound, infinitely long solenoid of small radius,  $a$ , behind the screen. A magnetic field  $B_0$  exists *inside* the solenoid, parallel to the solenoid axis, but the field outside the solenoid is precisely zero. The electrons therefore traverse only regions of space where the  $\vec{B}$  field is precisely zero. (Of course, this infinitely long, tightly wound solenoid is a “theorist’s” solenoid, but it can be approximated very well in the actual experiment.) Because the electrons are always in regions of zero field, choose a gauge in which the vector potential  $\vec{A}'$  is also zero outside the solenoid; i.e., choose a gauge for which

$$\begin{aligned}\vec{A}' &= 0 = \vec{A} + \vec{\nabla} f(x, y, z) \\ \psi' &= \psi e^{\frac{i\epsilon}{\hbar c} f(x, y, z)}.\end{aligned}\quad (4)$$

Therefore, taking a line integral of  $\vec{A}'$  around the exterior contour shown in Fig. 25.1,

$$\begin{aligned}0 &= \oint \vec{A}' \cdot d\vec{l} + \oint \vec{\nabla} f \cdot d\vec{l} \\ &= \int_0^a r dr \int_0^{2\pi} d\phi [\vec{\nabla} \times \vec{A}] \cdot \vec{n} + \int_0^{2\pi} \frac{\partial f(r, \theta, \phi)}{r \partial \phi} r d\phi \\ &= B_0 \pi a^2 + (f(r, \theta, \phi = 2\pi) - f(r, \theta, \phi = 0)),\end{aligned}\quad (5)$$

where we have converted the first line integral to a surface integral via Stokes’s theorem. The unit vector  $\vec{n}$  is parallel to the solenoid axis. The above therefore leads to

$$B_0 \pi a^2 = -(f(2\pi) - f(0)).\quad (6)$$

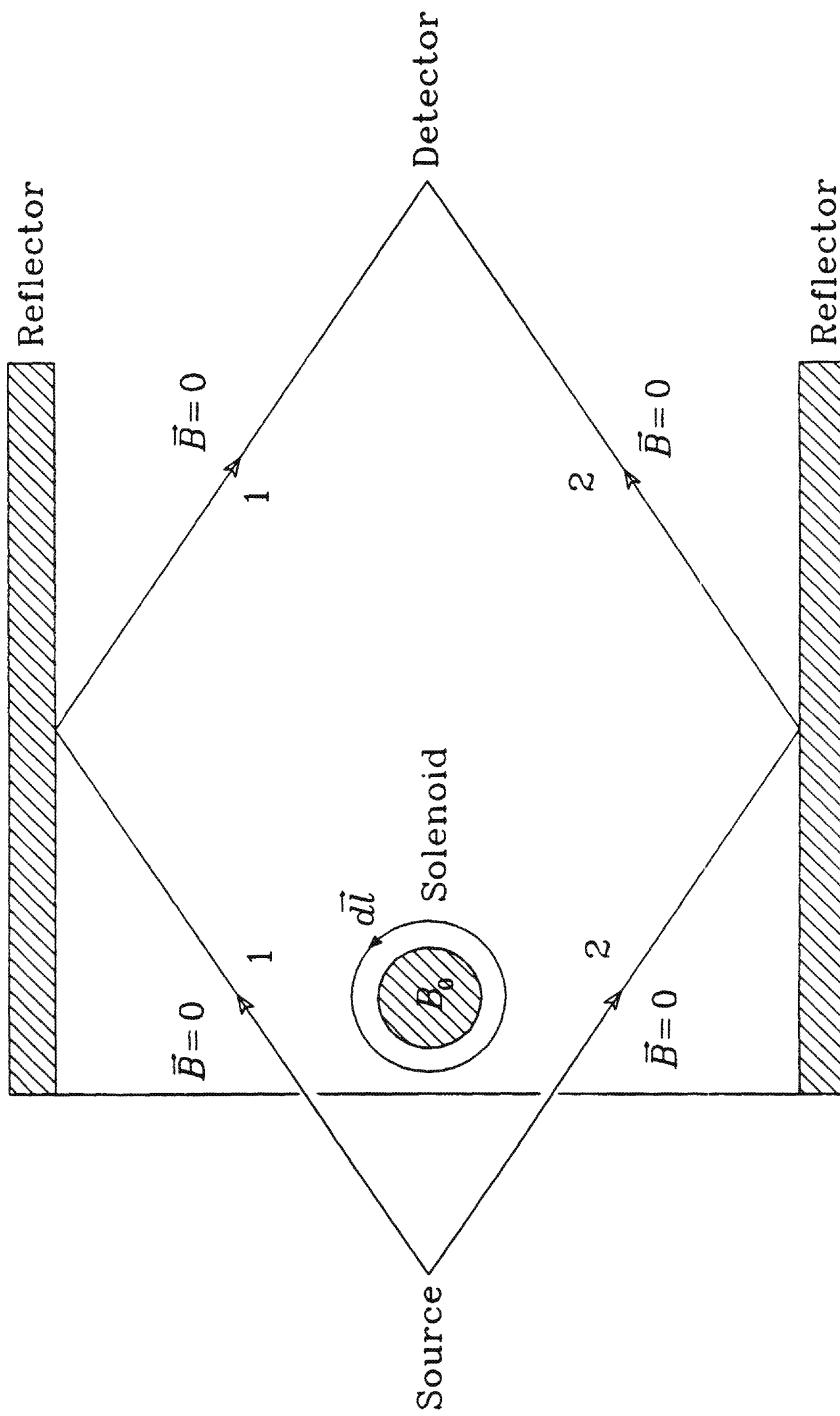


FIGURE 25.1. The Aharanov-Bohm effect

We have chosen a cylindrical coordinate system centered in the solenoid. The electrons traveling along trajectory 1 are, therefore, specified by

$$\psi_1 = \psi'_1 e^{-\frac{ie}{\hbar c} f(\phi=0)}, \quad (7)$$

so, at the detector,  $D$ ,

$$\psi_1 = \psi_D(\text{no field}) e^{-\frac{ie}{\hbar c} f(0)}. \quad (8)$$

Similarly, electrons traveling along trajectory 2 will, at the detector,  $D$ , be specified by the wave function

$$\psi_2 = \psi_D(\text{no field}) e^{-\frac{ie}{\hbar c} f(2\pi)}. \quad (9)$$

At the detector, therefore, the total wave function will be given by

$$\begin{aligned} \psi_1 + \psi_2 &= \psi_D(\text{no field}) e^{-\frac{ie}{\hbar c} f(0)} \left[ 1 + e^{-\frac{ie}{\hbar c} (f(2\pi) - f(0))} \right] \\ &= \psi_D(\text{no field}) e^{-\frac{ie}{\hbar c} f(0)} \left[ 1 + e^{+\frac{ie}{\hbar c} B_0 \pi a^2} \right]. \end{aligned} \quad (10)$$

The number of particles reaching the detector will then be proportional to

$$\begin{aligned} |\psi_D|^2 &= 2|\psi_D(\text{no field})|^2 \left[ 1 + \cos\left(\frac{eB_0\pi a^2}{\hbar c}\right) \right] \\ &= 4|\psi_D(\text{no field})|^2 \cos^2\left(\frac{eB_0\pi a^2}{2\hbar c}\right). \end{aligned} \quad (11)$$

That is, the number of particles arriving at the detector depends on the magnetic field strength in the solenoid, even though  $\vec{B} = 0$  in the region of the particle trajectories. The experiment has been done, both with long solenoids and with highly magnetized “magnetic whiskers.” Other experiments using the basic Bohm–Aharanov idea have also been successfully done. [For a review of experiments and ideas, see M. Peshkin and A. Tonomura, Lecture Notes in Physics **340**, Springer-Verlag (1989).]

## C Zeeman and Paschen–Back Effects in Atoms

We shall start by studying the perturbations of magnetic fields, both external and internal, on the energies of one-electron atoms. We shall start, however, with alkali atoms, Li, Na, K, Cs, or Rb. In these one-valence-electron atoms, the  $n^2$ -fold degeneracy of hydrogen is removed. Levels with different  $l$  have considerably different zeroth-order energies, each with a  $(2l+1)$ -fold degeneracy. The hydrogenic potential,  $V = -\frac{e^2}{r}$ , is replaced by

$$V(r) = -\frac{Z_{\text{eff.}}(r)e^2}{r}. \quad (12)$$

The  $Z_{\text{eff.}}(r)$  removes the degeneracy of levels with the same  $n$  but different  $l$ . In Na, e.g., with ground-state configuration  $(1s^2 2s^2 2p^6 3s)$ , the  $n = 3, l = 0, l = 1$ ,

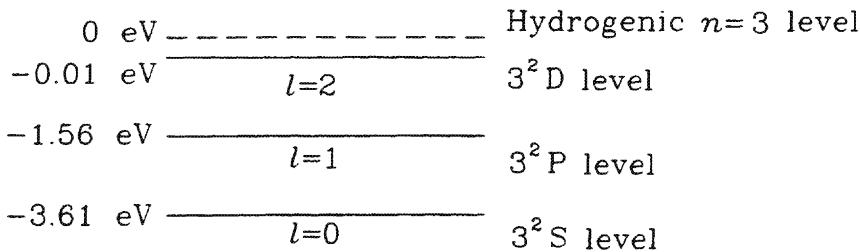


FIGURE 25.2. The Na-valence electron spectrum.

and  $l = 2$  valence electron levels ( $3^2 S$ ,  $3^2 P$ ,  $3^2 D$ ) are split in zeroth order, as shown in Fig. 25.2. The s ( $l = 0$ ) and p ( $l = 1$ ) orbits are penetrating orbits. They penetrate the spherically symmetric innershell electron cloud and see effectively a  $Z > 1$ ; hence, they lie at lower energy, with the s orbit having a considerably larger  $Z_{\text{eff}}$  than the p orbit. The d ( $l = 2$ ) electron spends most of its time outside the innershell electron cloud and thus sees an effective charge very nearly equal to  $(11 - 10) = 1$ . This level has been shifted to lower energy by only  $-0.01 \text{ eV}$ , relative to a purely hydrogenic value with  $Z = 1$ .

In a uniform, external magnetic field,  $\vec{B}_0$ , with  $\vec{A} = \frac{1}{2}[\vec{B}_0 \times \vec{r}]$  (where we have chosen a specific gauge, the so-called symmetric gauge), the Hamiltonian (ignoring for the moment the spin of the electron) has the form

$$H = \frac{1}{2m}(\vec{p} - \frac{e}{c}\vec{A}) \cdot (\vec{p} - \frac{e}{c}\vec{A}) + V(r). \quad (13)$$

Choosing  $\vec{B}_0$  along the  $z$ -direction, so

$$A_x = -\frac{1}{2}B_0y, \quad A_y = +\frac{1}{2}B_0x. \quad (14)$$

$$\begin{aligned} H &= \frac{p_x^2 + p_y^2 + p_z^2}{2m} - \frac{eB_0}{2mc}(xp_y - yp_x) + \frac{m}{2}\left(\frac{eB_0}{2mc}\right)^2(x^2 + y^2) + V(r) \\ &= \frac{p_x^2 + p_y^2}{2m} + \frac{m}{2}\omega_L^2(x^2 + y^2) + \hbar\omega_L L_z + \frac{p_z^2}{2m} + V(x, y, z), \end{aligned} \quad (15)$$

where we have used the Larmor frequency

$$\omega_L = \frac{|e|B_0}{2mc}, \quad \text{with } \hbar\omega_L = 5.8 \times 10^{-5} \frac{B_0}{\text{tesla}} \text{ eV},$$

and we have converted to a dimensionless, orbital angular momentum operator,  $L_z$ . (Remember the electron charge is negative.) For a free particle, with  $V(x, y, z) = 0$ ,  $L_z$  and  $p_z$  commute with the Hamiltonian of eq. (15) and can be replaced by their eigenvalues,  $m_l$ , and  $\hbar k_z$ . The problem of a free particle in a uniform magnetic field therefore reduces to a 2-D harmonic oscillator problem (see problem 42). For an atomic problem with a central  $V(r)$ , it will of course be useful to convert to spherical coordinates and dimensionless atomic units, with a physical  $\vec{r} = (x, y, z)$ ,

with  $|\vec{r}| = a_0 r$ , so

$$H = H^{(0)} + \hbar\omega_L L_z + \frac{1}{2} \frac{(\hbar\omega_L)^2}{(me^4/\hbar^2)} r^2 \sin^2 \theta. \quad (16)$$

$(\hbar\omega_L)/(\frac{me^4}{\hbar^2}) \approx 10^{-6}$  for a magnetic field of 1 tesla =  $10^4$  gauss, so the term proportional to  $\hbar\omega_L$ , the so-called paramagnetic term can be treated as  $H^{(1)}$ , whereas the term proportional to  $(\hbar\omega_L)^2$ , the diamagnetic term, can be treated as  $H^{(2)}$ . The paramagnetic term can be put in the form

$$H^{(1)} = -(\vec{\mu}_{\text{orbital}}^{(\text{magn.})} \cdot \vec{B}), \quad \text{with } \vec{\mu}_{\text{orbital}}^{(\text{magn.})} = \frac{e\hbar}{2mc} \vec{L}. \quad (17)$$

In 1924, when Uhlenbeck and Goudsmit postulated the existence of electron spin, with an associated spin magnetic moment, they added empirically a spin magnetic moment interaction to this paramagnetic term, but they found (empirically by fitting the predicted Zeeman spectra to the experimentally observed data) the gyromagnetic ratio for the spin magnetic moment requires an additional factor  $g_s = 2$  relative to that predicted for the orbital magnetic moment, so

$$\vec{\mu}_{\text{spin}}^{(\text{magn.})} = \frac{e\hbar}{2mc} g_s \vec{S}. \quad (18)$$

Although introduced empirically in 1924, the factor  $g_s = 2$  comes out automatically from the Dirac relativistic quantum theory of the electron. Thus,

$$H^{(1)} = -(\vec{\mu}_{\text{orbital}}^{(\text{magn.})} \cdot \vec{B}_0) - (\vec{\mu}_{\text{spin}}^{(\text{magn.})} \cdot \vec{B}_0) = \hbar\omega_L (L_z + 2S_z). \quad (19)$$

This perturbation has extremely simple matrix elements in the  $|nlm_l m_s\rangle$  basis, where we have added the eigenvalue  $m_s$  of the operator  $S_z$  to complete the basis, leading to the first-order magnetic field correction to the energy

$$E_{nlm_l m_s}^{(1)} = \hbar\omega_L (m_l + 2m_s). \quad (20)$$

This formula would be correct in the limit in which the external field  $\vec{B}_0$  is large compared with the internal atomic magnetic fields and their effects on the spin magnetic moment. We shall look at these effects next.

## D Spin-Orbit Coupling and Thomas Precession

Because of the motion of the valence electron, the electron sees an effective internal magnetic field that can interact with the spin magnetic moment of the electron. To first order in  $\frac{v}{c}$ , the magnetic field at the electron is

$$\vec{B} = \frac{1}{c} [\vec{\mathcal{E}} \times \vec{v}] = -\frac{1}{c} [\vec{\nabla} \Phi^{(\text{el.})} \times \frac{\vec{p}}{m}] = +\frac{1}{|e|mc} \frac{dV}{dr} \frac{1}{r} [\vec{r} \times \vec{p}], \quad (21)$$

where we have converted the electric scalar potential to the potential function  $V(r)$  and have used the fact that the electron charge is negative. We could of course also

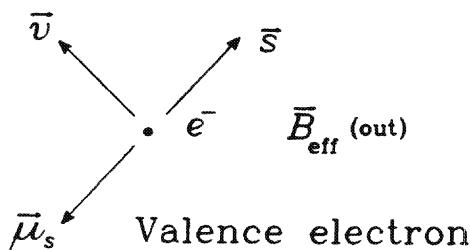
think of an observer “sitting on the electron” seeing the nuclear and innerelectron charge moving with a velocity  $-\vec{v}$  relative to the electron, therefore setting up a current giving rise to the magnetic field at the site of the electron (see Fig. 25.3). When the electron’s spin magnetic moment interacts with this internal magnetic field, we get a new contribution to the perturbed Hamiltonian of the one-electron atom

$$H_{\text{spin-orbit}}^{(1)} = -\vec{\mu}_s \cdot \vec{B} = +\frac{|e|\hbar g_s}{2mc} \frac{1}{r} \frac{dV}{dr} \frac{\hbar}{|e|mc} (\vec{S} \cdot \vec{L}) = \frac{\hbar^2}{m^2 c^2} \left( \frac{1}{r} \frac{dV}{dr} \right) (\vec{S} \cdot \vec{L}), \quad (22)$$

where  $\vec{L}$  and  $\vec{S}$  are dimensionless. Besides this magnetic spin-orbit term, a second purely relativistic correction term exists, the Thomas precession term, which has exactly the same form, but has an additional numerical factor of  $-\frac{1}{2}$ ,

$$H_{\text{Thomas}}^{(1)} = -\frac{1}{2} H_{\text{spin-orbit}}^{(1)}. \quad (23)$$

This purely relativistic term follows because two successive Lorentz transformations along different successive directions in the orbit are equivalent to a single Lorentz transformation plus a rotation in 3-D space. This rotation causes a precession of the intrinsic spin vector of the electron, the so-called Thomas precession,



Inner shell of electron cloud

FIGURE 25.3. Model of an alkali atom.

which cancels half of the magnetic spin orbit term. Thus,

$$H_{\text{spin-orbit}}^{(1)} + H_{\text{Thomas}}^{(1)} = \frac{\hbar^2}{2m^2c^2} \left( \frac{1}{r} \frac{dV}{dr} \right) (\vec{S} \cdot \vec{L}) = \frac{\hbar^2}{2m^2c^2} \left( \frac{\bar{Z}_{\text{eff.}} e^2}{r^3} \right) (\vec{S} \cdot \vec{L}), \quad (24)$$

where  $\bar{Z}_{\text{eff.}}(r) = Z_{\text{eff.}}(r) - r \frac{dZ_{\text{eff.}}}{dr}$  in an alkali atom; but  $\bar{Z}_{\text{eff.}}$  can be replaced by 1 in hydrogen. Converting the physical  $r$  in this equation to a dimensionless  $r$  via  $r_{\text{phys.}} = a_0 r$ , we have

$$H^{(1)} = \frac{1}{2} \frac{\left( \frac{me^4}{\hbar^2} \right)^2}{mc^2} \left( \frac{\bar{Z}_{\text{eff.}}}{r^3} \right) (\vec{S} \cdot \vec{L}) = \frac{1}{2} mc^2 \alpha^4 \left( \frac{\bar{Z}_{\text{eff.}}}{r^3} \right) (\vec{S} \cdot \vec{L}), \quad (25)$$

where  $r$ ,  $\vec{S}$ , and  $\vec{L}$  are now all dimensionless and  $\alpha$  is the fine structure constant. This term is of order

$$\frac{1}{mc^2} \left( \frac{me^4}{\hbar^2} \right)^2 = mc^2 \left( \frac{e^2}{\hbar c} \right)^4 = mc^2 \alpha^4 \approx 0.5 \text{ MeV} \left( \frac{1}{137} \right)^4 \approx 10^{-3} \text{ eV}. \quad (26)$$

To this order of magnitude, we must also consider the first-order relativistic mass correction. From

$$W = \sqrt{m_0^2 c^4 + p^2 c^2} = m_0 c^2 + \frac{p^2}{2m_0} - \frac{p^4}{8m_0^3 c^2} + \dots, \quad (27)$$

we get the relativistic mass correction to the kinetic energy term

$$W - m_0 c^2 = \frac{p^2}{2m_0} - \frac{1}{2m_0 c^2} \left( \frac{p^2}{2m_0} \right)^2 + \dots = \frac{p^2}{2m_0} - \frac{(E^{(0)} - V(r))^2}{2m_0 c^2} + \dots. \quad (28)$$

To get the hydrogen energies correct to order  $mc^2 \alpha^4$ , we must include this relativistic mass correction term along with the combined spin-orbit and Thomas term of eq. (25). This relativistic mass correction term, however, has been converted to a function of  $r$  only in the last form of eq. (28). In an alkali atom, therefore, it can be simply absorbed into the  $Z_{\text{eff.}}(r)/r$  term. This term merely establishes the zeroth-order energies of the separated  $l = 0, l = 1, l = 2, \dots$  terms. These terms are essentially taken from experiment and not calculated very precisely. We shall calculate accurately the splitting of such a  $2(l+1)$ -fold degenerate term into fine structure and Zeeman components, but take the zeroth-order positions of the different  $l$  levels from experiment. For the alkali atoms, therefore, this perturbation term can be absorbed into the zeroth-order terms.

# 26

## Fine Structure and Zeeman Perturbations in Alkali Atoms

We shall now look in detail at the fine structure (magnetic spin orbit + Thomas) and Zeeman perturbation terms; i.e., we shall diagonalize the first-order Hamiltonian,

$$H^{(1)} = \frac{mc^2\alpha^4}{2} \left( \frac{\vec{Z}_{\text{eff.}}(r)}{r^3} \right) (\vec{S} \cdot \vec{L}) + \hbar\omega_L(L_z + 2S_z), \quad (1)$$

in the  $2(2l + 1)$  degenerate subspace of a particular  $l$  sublevel of the valence  $n$  in an alkali atom. The fine structure term is of order  $10^{-3}$ eV, and the Zeeman term would be of this order of magnitude only for very strong fields, of the order of  $\sim 20$  tesla, but both terms are small compared with the zeroth-order separation of different  $l$  substates. (In Na, these terms were of the order of  $1 - 2$ eV.) Matrix elements are easy to calculate in the  $|nlm_l m_s\rangle$  basis. Nonzero matrix elements are

$$\langle nlm_l m_s | L_z + 2S_z | nlm_l m_s \rangle = m_l + 2m_s. \quad (2)$$

Writing  $\vec{L} \cdot \vec{S} = \frac{1}{2}(L_+ S_- + L_- S_+) + L_0 S_0$ ,

$$\begin{aligned} & \langle nlm_l m_s | \vec{L} \cdot \vec{S} | nlm_l m_s \rangle = m_l m_s, \\ & \langle nl(m_l + 1)(m_s - 1) | \vec{L} \cdot \vec{S} | nlm_l m_s \rangle \\ &= \frac{1}{2}\sqrt{(l - m_l)(l + m_l + 1)(s + m_s)(s - m_s + 1)}, \\ & \langle nl(m_l - 1)(m_s + 1) | \vec{L} \cdot \vec{S} | nlm_l m_s \rangle \\ &= \frac{1}{2}\sqrt{(l + m_l)(l - m_l + 1)(s - m_s)(s + m_s + 1)}, \end{aligned} \quad (3)$$

with  $s = \frac{1}{2}$ . Now, if we introduce

$$\vec{J} = \vec{L} + \vec{S}, \quad \text{with} \quad J_z = L_0 + S_0, \quad (4)$$

where  $J_z$  has eigenvalue  $m_j = m_l + m_s$ , all terms of our  $H^{(1)}$  do not change the quantum number  $m_j$ . (In passing, lowercase letters are usually used for *single-*

particle angular momentum quantum numbers.) Because the values  $m_j = l + \frac{1}{2}$  and  $m_j = -(l + \frac{1}{2})$  can each be made in only one way, whereas all other possible  $m_j$  values can be made in two ways, the full  $2(2l+1)$  matrix of  $H^{(1)}$  will split into  $2$  ( $1 \times 1$ ) and  $2l$  ( $2 \times 2$ ) submatrices. It is best to convert to  $m_j$  and  $m_s = \pm \frac{1}{2}$  in the matrix element expressions, so, e.g.,

$$\langle nl, m'_l = (m_j \mp \frac{1}{2}), m_s = \pm \frac{1}{2} | \vec{L} \cdot \vec{S} | nl, m_l = (m_j \pm \frac{1}{2}), m_s = \mp \frac{1}{2} \rangle = \frac{1}{2} \sqrt{(l \pm m_j + \frac{1}{2})(l \mp m_j + \frac{1}{2})} \cdot 1 \cdot 1 = \frac{1}{2} \sqrt{(l + \frac{1}{2})^2 - m_j^2}. \quad (5)$$

In addition, we introduce the radial matrix element integral

$$\frac{mc^2\alpha^4}{2} \int_0^\infty dr r^2 |R_{nl}(r)|^2 \frac{\bar{Z}_{\text{eff.}}(r)}{r^3} \equiv \beta_{nl}. \quad (6)$$

This number is common for all matrix elements of the full  $2(2l+1) \times 2(2l+1)$  matrix of  $H^{(1)}$ . The general  $2 \times 2$  submatrix for a given  $m_j$  is

$$\begin{pmatrix} H_{++} & H_{+-} \\ H_{-+} & H_{--} \end{pmatrix},$$

where we have used the subscript + for the state with  $m_s = +\frac{1}{2}$ , and  $m_l = m_j - \frac{1}{2}$ , and the subscript - for the state with  $m_s = -\frac{1}{2}$ , and  $m_l = m_j + \frac{1}{2}$ . In the matrix,

$$\begin{aligned} H_{++} &= \frac{1}{2} \beta_{nl} (m_j - \frac{1}{2}) + \hbar\omega_L (m_j + \frac{1}{2}), \\ H_{+-} &= H_{-+} = \frac{\beta_{nl}}{2} \sqrt{[(l + \frac{1}{2})^2 - m_j^2]}, \\ H_{--} &= -\frac{1}{2} \beta_{nl} (m_j + \frac{1}{2}) + \hbar\omega_L (m_j - \frac{1}{2}). \end{aligned} \quad (7)$$

The  $2 \times 2$  energy determinant leads to

$$E = \frac{1}{2} \left[ (H_{++} + H_{--}) \pm \sqrt{(H_{++} - H_{--})^2 + 4|H_{+-}|^2} \right], \quad (8)$$

or

$$E_{\pm}^{(1)} = \left( -\frac{\beta_{nl}}{4} + \hbar\omega_L m_j \right) \pm \frac{1}{2} \sqrt{\beta_{nl}^2 (l + \frac{1}{2})^2 + (\hbar\omega_L)^2 + 2m_j \beta_{nl} (\hbar\omega_L)}. \quad (9)$$

For the  $1 \times 1$  submatrices with  $m_j = \pm(l + \frac{1}{2})$ , the energies are given by the diagonal matrix elements

$$E^{(1)} = \beta_{nl} \frac{l}{2} \pm \hbar\omega_L (l + 1). \quad (10)$$

With no external magnetic field, i.e.,  $\hbar\omega_L = 0$ , we have

$$\begin{aligned} E_{nl}^{(1)} &= +\beta_{nl} \frac{l}{2} && \text{with } (2l+2)\text{-fold degeneracy} \\ &= -\beta_{nl} \frac{(l+1)}{2} && \text{with } 2l\text{-fold degeneracy.} \end{aligned} \quad (11)$$

These two levels correspond to the  $j$  values  $j = (l \pm \frac{1}{2})$ , respectively. With

$$\vec{J} = \vec{L} + \vec{S}, \quad \text{so} \quad \vec{L} \cdot \vec{S} = \frac{1}{2}(\vec{J} \cdot \vec{J} - \vec{L} \cdot \vec{L} - \vec{S} \cdot \vec{S}), \quad (12)$$

$\vec{L} \cdot \vec{S}$  has eigenvalues

$$\frac{1}{2}[j(j+1) - l(l+1) - \frac{3}{4}],$$

leading to the eigenvalue  $+\frac{1}{2}l$  for  $j = (l + \frac{1}{2})$ , and the eigenvalue  $-\frac{1}{2}(l+1)$  for  $j = (l - \frac{1}{2})$ .

For the weak-field case,  $\hbar\omega_L \ll \beta_{nl}$ , the energies are (expanding the square roots to first order)

$$\begin{aligned} E_{nl}^{(1)} &= \beta_{nl} \frac{l}{2} + \hbar\omega_L m_j \left(1 + \frac{1}{(2l+1)}\right), \quad \text{for } j = (l + \frac{1}{2}), \\ E_{nl}^{(1)} &= -\beta_{nl} \frac{(l+1)}{2} + \hbar\omega_L m_j \left(1 - \frac{1}{(2l+1)}\right), \quad \text{for } j = (l - \frac{1}{2}). \end{aligned} \quad (13)$$

For the huge field case, conversely, with  $\hbar\omega_L \gg \beta_{nl}$ ,

$$E_{nl}^{(1)} = \hbar\omega_L (m_j \pm \frac{1}{2}) \pm \frac{\beta_{nl}}{2} m_j - \frac{\beta_{nl}}{4}. \quad (14)$$

These energies are shown as a function of the external field strength,  $B_0$ , (or  $\hbar\omega_L$ ), for an  $l = 2$  state in Fig. 26.1.

Finally, we need to find the eigenvectors as linear combinations of the two states with  $m_s = +\frac{1}{2}$ ,  $m_l = (m_j - \frac{1}{2})$ , to be denoted by +, and  $m_s = -\frac{1}{2}$ ,  $m_l = (m_j + \frac{1}{2})$ , to be denoted by -. In particular, for the special case with  $B_0 = 0$  (hence,  $\hbar\omega_L = 0$ ), we get

$$[\frac{\beta_{nl}}{2}(m_j - \frac{1}{2}) - E^{(1)}]c_+ + \frac{\beta_{nl}}{2}\sqrt{(l + \frac{1}{2} + m_j)(l + \frac{1}{2} - m_j)}c_- = 0. \quad (15)$$

With  $E_{nl}^{(1)} = +\beta_{nl}l/2$ , for the state with  $j = (l + \frac{1}{2})$ , we get

$$\frac{c_+}{c_-} = \frac{\sqrt{(l + \frac{1}{2} + m_j)}}{\sqrt{(l + \frac{1}{2} - m_j)}}. \quad (16)$$

This equation leads to the normalized coefficients

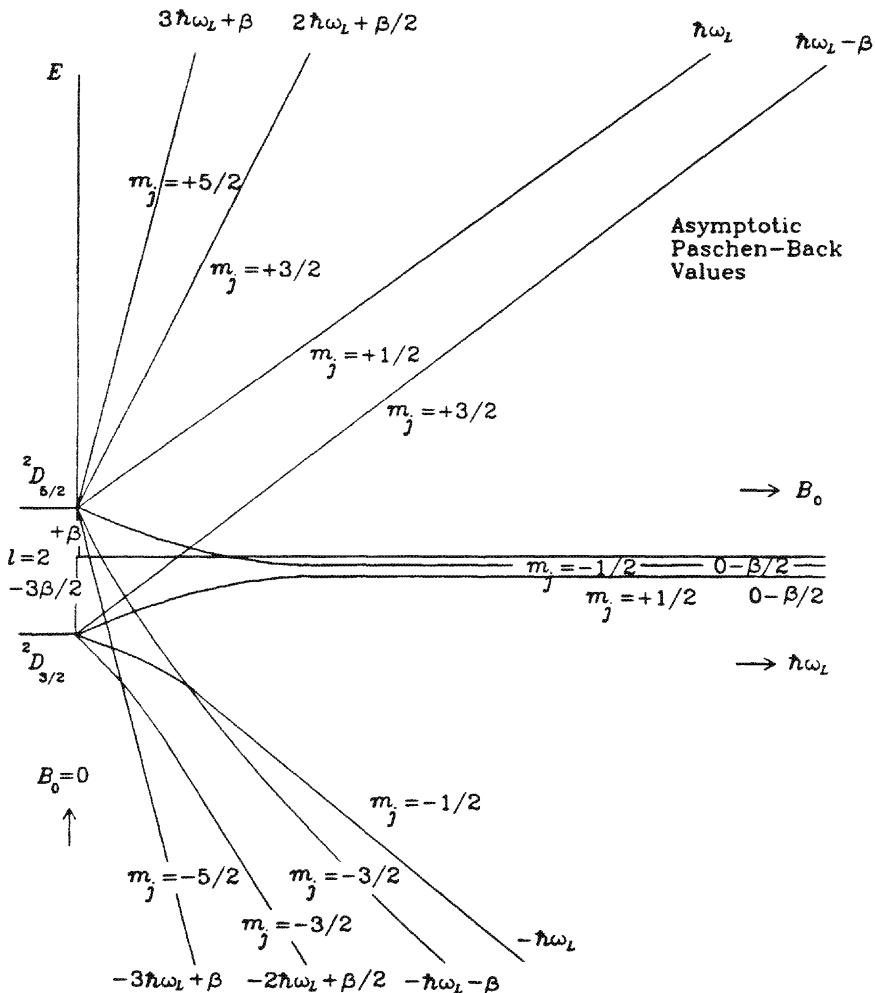
$$c_+ = \sqrt{\frac{(l + \frac{1}{2} + m_j)}{(2l+1)}}, \quad c_- = \sqrt{\frac{(l + \frac{1}{2} - m_j)}{(2l+1)}}. \quad (17)$$

With  $E_{nl} = -\beta_{nl}(l+1)/2$ , i.e., for the state with  $j = (l - \frac{1}{2})$ , we get in the same way

$$c_+ = -\sqrt{\frac{(l + \frac{1}{2} - m_j)}{(2l+1)}}, \quad c_- = \sqrt{\frac{(l + \frac{1}{2} + m_j)}{(2l+1)}}. \quad (18)$$

In this special case, we have calculated the transformation coefficients from a basis  $|nlm_ls_m\rangle$  that are eigenvectors of the four commuting operators

$$\vec{L} \cdot \vec{L}, \quad L_z, \quad \vec{S} \cdot \vec{S}, \quad S_z,$$

FIGURE 26.1. Magnetic field splitting of an alkali atom  $^2D$  level.

to a basis  $|nlsm_j\rangle$  that are eigenvectors of the four commuting operators

$$\vec{L} \cdot \vec{L}, \quad \vec{S} \cdot \vec{S}, \quad \vec{J} \cdot \vec{J}, \quad J_z;$$

that is, we have calculated the transformation coefficients

$$\langle lm_l sm_s | lsjm_j \rangle.$$

These are known as angular momentum coupling coefficients or Clebsch–Gordan coefficients. For the specific case with  $s = \frac{1}{2}$ , these coefficients are given by

$$m_s = +\frac{1}{2} \begin{pmatrix} j = (l + \frac{1}{2}) & j = (l - \frac{1}{2}) \\ \sqrt{\frac{(l+\frac{1}{2}+m_j)}{(2l+1)}} & -\sqrt{\frac{(l+\frac{1}{2}-m_j)}{(2l+1)}} \\ \sqrt{\frac{(l+\frac{1}{2}-m_j)}{(2l+1)}} & \sqrt{\frac{(l+\frac{1}{2}+m_j)}{(2l+1)}} \end{pmatrix}.$$

We shall study this type of transformation coefficient in a much more general way in the next chapter.

## Problems

**29.** For a Hamiltonian (with parameter  $\lambda \ll 1$ ),

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \lambda^3 H^{(3)},$$

(a) derive expressions for

$$E_n^{(3)} \quad \text{and} \quad Q_n^{(0)} |n^{(3)}\rangle$$

for a nondegenerate state,  $|n\rangle$ .

(b) Specialize the result of (a) to the Hamiltonian

$$H = H^{(0)} + \lambda V.$$

Use the Wigner–Brillouin expansion for this case, and verify the result of (a) as applied to this simpler case.

(c) For the Hamiltonian of (b), prove the second-order shift of the ground-state energy is bounded by

$$|E_{n=0}^{(2)}| \leq \frac{|\langle 0^{(0)} | V^2 | 0^{(0)} \rangle - (\langle 0^{(0)} | V | 0^{(0)} \rangle)^2|}{(E_{n=1}^{(0)} - E_{n=0}^{(0)})}.$$

Note,  $E_{n=0}^{(2)} \leq 0$ .

**30.** The vibrating–rotating diatomic molecule. The Hamiltonian for a vibrating–rotating diatomic molecule is given by

$$\begin{aligned} -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu r^2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) + V(r) \\ = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + V(r) + \frac{\hbar^2}{2\mu r^2} \left( \frac{(\vec{J} \cdot \vec{J})}{\hbar^2} \right). \end{aligned}$$

Assume  $V(r)$  can be approximated by the quadratic term

$$V(r) = \frac{\mu\omega^2}{2}(r - r_e)^2, \quad \text{with } (r - r_e) = \sqrt{\frac{\hbar}{\mu\omega}}x.$$

If the  $1/r^2$  term of the angular part is expanded as

$$\frac{1}{r^2} = \frac{1}{r_e^2} \left( 1 - 2\frac{(r - r_e)}{r_e} + 3\frac{(r - r_e)^2}{r_e^2} + \dots \right),$$

the above Hamiltonian can be written as

$$H = H_{\text{vibrator}}^{(0)} + H_{\text{rotator}}^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots,$$

where

$$H_{\text{vib.}}^{(0)} = \frac{\hbar\omega}{2} \left( -\frac{\partial^2}{\partial x^2} + x^2 \right), \quad H_{\text{rot.}}^{(0)} = \frac{\hbar^2}{2\mu r_e^2} \left( \frac{(\vec{J} \cdot \vec{J})}{\hbar^2} \right),$$

with

$$H^{(0)}|nJM\rangle = \left( \hbar\omega(n + \frac{1}{2}) + \frac{\hbar^2 J(J+1)}{2\mu r_e^2} \right) |nJM\rangle.$$

(Note: We have used capital letters,  $\vec{J}$ , and  $J, M$ , in place of the  $l, m$ , used earlier for the diatomic molecule rigid rotator. This is in agreement with the convention that lowercase letters are reserved for the single-particle angular momentum quantum numbers, whereas capital letters are used for the angular momentum quantum numbers of many-particle systems.) Take the parameter of smallness,  $\lambda$ , as

$$\lambda = \sqrt{\frac{\hbar^2}{2\mu r_e^2} \frac{1}{\hbar\omega}},$$

so the vibration–rotation interaction terms are perturbations, with

$$H^{(1)} = -\frac{\hbar^2}{2\mu r_e^2} 2\sqrt{2}x \left( \frac{(\vec{J} \cdot \vec{J})}{\hbar^2} \right), \quad H^{(2)} = \frac{\hbar^2}{2\mu r_e^2} 6x^2 \left( \frac{(\vec{J} \cdot \vec{J})}{\hbar^2} \right).$$

[To investigate the smallness of the parameter,  $\lambda$ , take the HCl molecule as a typical example. For HCl, (with Cl isotope 35),  $\hbar\omega = hc(2989.74\text{cm}^{-1})$ ;  $\hbar^2/(2\mu r_e^2) = hc(10.5909\text{cm}^{-1})$ , so  $\lambda = .06$ .]

Show that the  $|nJM\rangle$ , with  $\langle \vec{r} | nJM \rangle = \psi_n(x)Y_{JM}(\theta, \phi)$ , are “proper” zeroth-order eigenvectors, and find corrections to the zeroth-order energies, including terms of order  $\lambda^2(\hbar^2/2\mu r_e^2)$ .

Warning: We have taken as our zeroth-order Hamiltonian both the soluble vibrator and rotator Hamiltonians. Because their coefficients differ by the factor,  $\lambda^2$ , second-order perturbation theory will here give both terms of order  $\lambda^2(\hbar\omega)$  and terms of order  $\lambda^2(\hbar^2/2\mu r_e^2)$ .

**31.** A diatomic molecule rigid rotator with a permanent electric dipole moment along the molecule axis is placed in a *nonuniform* electric field,  $\vec{\mathcal{E}}$ , so the zeroth-order rigid rotator solutions are perturbed by

$$\lambda H^{(1)} = -\vec{\mu}^{(\text{el.})} \cdot \vec{\mathcal{E}} = 2k \sin^2 \theta \sin 2\phi, \quad \text{with } k = \lambda \left( \frac{\hbar^2}{2I_e} \right); \quad \lambda \ll 1.$$

For the states with  $J = 0$ , and  $J = 1$ , find the perturbed energies correct to order  $\lambda^2(\hbar^2/2I_e)$ , and show how the  $J = 0 \rightarrow J = 1$  absorption transition is split by this

perturbation. Give the relative intensities of the Stark fine structure components of this transition. (Calculate relative intensities only in dominant, zeroth-order approximation.)

**32.** A diatomic molecule rigid rotator with a permanent electric dipole moment is placed in a uniform electric field in the  $x$ -direction, so

$$\lambda H^{(1)} = -\vec{\mu}^{(\text{el.})} \cdot \vec{\mathcal{E}} = -\mu_e^{(\text{el.})} |\mathcal{E}| \sin \theta \cos \phi.$$

Because the Stark energy is independent of the direction of the electric field, you know the result for the second-order energy correction (see Chapter 23). To test yourself on your knowledge of perturbation theory, find the second-order corrections for the energies of the  $J = 1$  states by using the above  $H^{(1)}$  and a zeroth-order basis in which  $\hat{J}^2$  and  $J_z$ , perpendicular to the direction of  $\vec{\mathcal{E}}$ , are diagonal. This method is admittedly the hard way to do an easy problem. The  $|JM^{(0)}\rangle$  are now not proper zeroth-order eigenvectors, because the above  $H^{(1)}$  now connects states with different  $M$ . Also,  $H^{(1)}$  now does not remove the zeroth-order degeneracy in first order. We are therefore dealing with case (3), as enumerated in Chapter 23. Hint: The best way to solve such a problem is with the use of our formulae for three nearly degenerate (or exactly degenerate) states and diagonalize the  $3 \times 3 H'$ -matrix for  $J = 1$  which to order  $\lambda^2$  is effectively disconnected from states with  $J' \neq J$ .

**33.** For a slightly asymmetric rotator, with

$$H = H^{(0)} + \lambda H^{(1)} = \frac{1}{2}(a+b)\hat{P}^2 + \frac{1}{2}(2c-a-b)P_{z'}^2 + \frac{1}{4}(a-b)(P'_+ P'_+ + P'_- P'_-),$$

use the parameter of smallness,  $\lambda \ll 1$ ,

$$\lambda = \frac{(a-b)}{(2c-a-b)}, \quad \text{with } \lambda H^{(1)} = \frac{1}{4}(2c-a-b)\lambda(P'_+ P'_+ + P'_- P'_-).$$

Note,

$$E_{JK}^{(0)} = \frac{1}{2} \left[ (a+b)J(J+1) + (2c-a-b)K^2 \right].$$

To order  $\lambda^2$ , zeroth-order states with  $K = 0$  and  $|K| \geq 3$  can be treated by nondegenerate perturbation theory. These states effectively belong to case (1), as enumerated in Chapter 23. For these states, find  $E_{JK}$  correct to second order as general functions of  $J$  and  $K$ . For states with  $|K| = 1$  and  $|K| = 2$ , use degenerate-level perturbation theory. Show, in particular, states with  $|K| = 1$  belong to case (2), as enumerated in Chapter 23, but states with  $|K| = 2$  belong to case (3). For the latter, therefore, use the treatment for two nearly (or exactly) degenerate levels to find the energies correct to order  $\lambda^2$ . Use the results of problems 20 and 21 to expand the exact expressions for these energies in powers of  $\lambda$  for states with  $J = 2$  and  $J = 3$  to compare with the perturbation theory results. Also, verify your perturbation theory results give the correct values for  $J = 1$ .

**34.** Two identical diatomic units on opposite ends of a long-chain molecule are constrained to move on identical parallel circles of equal radius, but are almost

free to rotate on these circles of equal radius, so they are subject to a Hamiltonian

$$H = H^{(0)} + \lambda H^{(1)} = -\frac{\hbar^2}{2I_e} \left( \frac{\partial^2}{\partial \phi_1^2} + \frac{\partial^2}{\partial \phi_2^2} \right) + V_0 \cos(\phi_1 - \phi_2),$$

where  $I_e$  is a constant and  $V_0 = \lambda(\hbar^2/2I_e)$ , with  $\lambda \ll 1$ , so the  $V_0$  term can be treated as a perturbation. The zeroth-order solutions are

$$E_{m_1 m_2}^{(0)} = \frac{\hbar^2}{2I_e} (m_1^2 + m_2^2), \quad \text{with } \psi_{m_1 m_2}^{(0)}(\phi_1, \phi_2) = \frac{1}{2\pi} e^{im_1 \phi_1} e^{im_2 \phi_2},$$

with

$$m_1 = 0, \pm 1, \pm 2, \dots, \quad m_2 = 0, \pm 1, \pm 2, \dots.$$

Enumerate all states with zeroth-order energies,  $E^{(0)} \leq 5(\hbar^2/2I_e)$ , and find their degeneracies. Indicate which states belong to cases (1), (2), or (3) of degenerate-state perturbation theory, and find the perturbed energies for the above states correct to order  $\lambda^2(\hbar^2/2I_e)$ . [An alternative method of solution: Make use of the symmetry of the Hamiltonian to find the *proper* zeroth-order wave functions as linear combinations of the above  $\psi_{m_1 m_2}^{(0)}$ , and show that these *proper* zeroth-order wave functions reduce the calculation of the degenerate states to case (1) automatically.]

### Solution for Problem 34

The Schrödinger equation in the dimensionless quantities,  $\epsilon = E/(\hbar^2/2I_e)$  and  $\lambda = V_0/(\hbar^2/2I_e)$ , has the simple form

$$-\left( \frac{\partial^2}{\partial \phi_1^2} + \frac{\partial^2}{\partial \phi_2^2} \right) \psi(\phi_1, \phi_2) + \lambda \cos(\phi_1 - \phi_2) \psi(\phi_1, \phi_2) = \epsilon \psi(\phi_1, \phi_2), \quad (1)$$

with zeroth-order solutions

$$\psi^{(0)}(\phi_1, \phi_2) = \frac{1}{2\pi} e^{im_1 \phi_1} e^{im_2 \phi_2}, \quad \text{with } \epsilon^{(0)} = (m_1^2 + m_2^2). \quad (2)$$

The needed matrix elements of  $H^{(1)} = \cos(\phi_1 - \phi_2)$  are extremely simple in this basis. The only nonzero matrix elements are

$$\begin{aligned} \langle (m_1 + 1)(m_2 - 1) | H^{(1)} | m_1 m_2 \rangle &= \frac{1}{2}, \\ \langle (m_1 - 1)(m_2 + 1) | H^{(1)} | m_1 m_2 \rangle &= \frac{1}{2}. \end{aligned} \quad (3)$$

All other matrix elements are zero. Note:  $H^{(1)}$  is diagonal in the quantum number  $M = (m_1 + m_2)$ , so this quantum number is conserved to all orders of the perturbation. We list in the table below the possible quantum numbers  $m_1, m_2, M$ , as well as the perturbation type and the total degeneracy number,  $g_\epsilon$ , for all states with  $\epsilon^{(0)} \leq 5$ . Degeneracies of 4 and 8 are common to most of the  $\epsilon^{(0)}$  for this problem. Because  $H^{(1)}$ , however, does not connect states of different total  $M$ , most of the states of this system are effectively doubly degenerate or nondegenerate.

Among the states with a single  $m_1, m_2$ -combination for a fixed  $M$  are the states with  $\epsilon^{(0)} = 2$  and  $M = +2$ , or  $M = -2$ , as well as the ground state. Also, a

double action with  $H^{(1)}$  on a state  $|m_1 m_2\rangle$  can convert it only to states with  $m_1, m_2 \rightarrow m'_1, m'_2 = (m_1 + 2), (m_2 - 2)$  or  $m_1, m_2$  or  $(m_1 - 2), (m_2 + 2)$ .

Therefore, states such as the pair of states with  $\epsilon^{(0)} = 5, M = +1$ , with  $m_1, m_2 = +2, -1$ , or  $-1, +2$ , with  $\Delta m_1, \Delta m_2 = -3, +3$ , are unconnected through second order and can thus effectively be treated as if they were nondegenerate (if only corrections through second order are significant). These states are therefore listed as belonging to type (1), using the characterization of degenerate states given in Chapter 23. For type (1) states, the  $m_1, m_2$  basis is effectively the *proper* basis, and the states can be treated as if they were nondegenerate.

$\epsilon^{(0)}$	$g_\epsilon$	$m_1$	$m_2$	$M$	type	$\epsilon^{(0)}$	$g_\epsilon$	$m_1$	$m_2$	$M$	type
0	1	0	0	0	(1)	4	4	+2	0	+2	(3)
1	4	+1	0	+1	(2)			0	+2	+2	(3)
		0	+1	+1	(2)			-2	0	-2	(3)
		-1	0	-1	(2)			0	-2	-2	(3)
		0	-1	-1	(2)	5	8	+2	+1	+3	(2)
2	4	+1	+1	+2	(1)			+1	+2	+3	(2)
		+1	-1	0	(3)			-2	-1	-3	(2)
		-1	+1	0	(3)			-1	-2	-3	(2)
		-1	-1	-2	(1)			+2	-1	+1	(1)
								-1	+2	+1	(1)
								-2	+1	-1	(1)
								+1	-2	-1	(1)

Doubly degenerate states with a  $\Delta m_1, \Delta m_2 = \pm 1, \mp 1$ , conversely, have their degeneracy removed in first order. For such states, diagonalization of  $H^{(1)}$  to find the  $\epsilon^{(1)}$  will also yield the *proper* linear combinations of the zeroth-order eigenvectors to carry forward the higher order perturbations. Such states are characterized as type (2) according to the catalog of Chapter 23.

Finally, doubly degenerate states with a  $\Delta m_1, \Delta m_2$  of  $\pm 2, \mp 2$  have their degeneracy removed only in second order. Such states are best treated by transforming the  $2 \times 2$  Hamiltonian matrix  $H$  into a new  $H' = UHU^\dagger$ , as in Chapter 24 [see, in particular, eq. (12) of Chapter 24]. These are states characterized as type (3) in Chapter 23.

For states of type (1), we get the second-order corrections,  $\epsilon^{(2)}$ , via

$$\epsilon^{(2)} = \frac{|\langle (m_1 + 1)(m_2 - 1)|H^{(1)}|m_1 m_2\rangle|^2}{(\epsilon_{m_1 m_2}^{(0)} - \epsilon_{(m_1 + 1)(m_2 - 1)}^{(0)})} + \frac{|\langle (m_1 - 1)(m_2 + 1)|H^{(1)}|m_1 m_2\rangle|^2}{(\epsilon_{m_1 m_2}^{(0)} - \epsilon_{(m_1 - 1)(m_2 + 1)}^{(0)})}.$$

Thus, for the state with  $\epsilon^{(0)} = 0$ ,

$$\epsilon^{(2)} = \frac{1}{4} \left( \frac{1}{(0 - 2)} + \frac{1}{(0 - 2)} \right) = -\frac{1}{4}.$$

For the state with  $\epsilon^{(0)} = 2, M = +2$ ; and similarly for  $M = -2$ ,

$$\epsilon^{(2)} = \frac{1}{4} \left( \frac{1}{(2 - 4)} + \frac{1}{(2 - 4)} \right) = -\frac{1}{4}.$$

For the state with  $\epsilon^{(0)} = 5, m_1, m_2 = +2, -1, M = +1$  (similarly for the other state with  $M = +1$ , and the two states with  $M = -1$ ),

$$\epsilon^{(2)} = \frac{1}{4} \left( \frac{1}{(5-13)} + \frac{1}{(5-1)} \right) = +\frac{1}{32}.$$

For states of type (2), we first diagonalize  $H^{(1)}$ . For example, for the states with  $\epsilon^{(0)} = 1, M = +1$ , the  $2 \times 2$  matrix for  $(H^{(1)} - \epsilon^{(1)})$  is

$$\begin{array}{ccccc} & +1 & 0 & 0 & +1 \\ +1 & 0 & \left( \begin{array}{cc} -\epsilon^{(1)} & \frac{1}{2} \\ \frac{1}{2} & -\epsilon^{(1)} \end{array} \right), \\ 0 & +1 & & & \end{array}$$

with eigenvalues and eigenvectors, given by

$$\epsilon^{(1)} = +\frac{1}{2}; \quad |M = +1, (+)\rangle = \frac{1}{\sqrt{2}}(|+10\rangle + |0+1\rangle),$$

$$\epsilon^{(1)} = -\frac{1}{2}; \quad |M = +1, (-)\rangle = \frac{1}{\sqrt{2}}(|+10\rangle - |0+1\rangle),$$

where, now,

$$\epsilon^{(2)} = \sum'_{m'_1 m'_2} \frac{|\langle m'_1 m'_2 | H^{(1)} | M = +1, (\pm) \rangle|^2}{(1 - \epsilon_{m'_1 m'_2}^{(0)})}, \quad (4)$$

and the primed sum excludes the states with  $\epsilon^{(0)} = 1$ . For the  $M = +1$  state, therefore,  $m'_1 m'_2$  can only take the values  $m'_1 m'_2 = +2, -1$  [with only the  $+10$  piece of  $|M = +1(\pm)\rangle$  contributing to the matrix element], and  $m'_1 m'_2 = -1, +2$ , [with only the  $0 + 1$  piece of  $|M = +1(\pm)\rangle$  contributing to the matrix element]. Thus,

$$\epsilon_{(\pm)}^{(2)} = |\pm \frac{1}{2\sqrt{2}}|^2 \frac{1}{(1-5)} + |\pm \frac{1}{2\sqrt{2}}|^2 \frac{1}{(1-5)} = -\frac{1}{16},$$

with the same result for the two states with  $M = -1$ . The  $2 \times 2$  matrix  $(H^{(1)} - \epsilon^{(1)})$ , has exactly the same form for any pair of states of type (2), so  $\epsilon^{(1)} = \pm \frac{1}{2}$  for all type (2) states. For states with  $\epsilon^{(0)} = 5, M = +3$ , we have

$$\epsilon_{(\pm)}^{(2)} = |\pm \frac{1}{2\sqrt{2}}|^2 \frac{1}{(5-9)} + |\pm \frac{1}{2\sqrt{2}}|^2 \frac{1}{(5-9)} = -\frac{1}{16}.$$

Finally, for states of type (3), the matrix for  $H' = U H U^\dagger$  with zeroth-order basis states  $|m_1 m_2\rangle$  and  $|(m_1 - 2)(m_2 + 2)\rangle$  now has the matrix elements

$$\langle m_1 m_2 | H' | m_1 m_2 \rangle = \sum'_{m'_1 m'_2} \frac{|\langle m'_1 m'_2 | H^{(1)} | m_1 m_2 \rangle|^2}{(\epsilon_{m_1 m_2}^{(0)} - \epsilon_{m'_1 m'_2}^{(0)})},$$

$$\langle m_1 m_2 | H' | (m_1 - 2)(m_2 + 2) \rangle = \langle (m_1 - 2)(m_2 + 2) | H' | m_1 m_2 \rangle =$$

$$\frac{\langle m_1 m_2 | H^{(1)} | (m_1 - 1)(m_2 + 1) \rangle \langle (m_1 - 1)(m_2 + 1) | H^{(1)} | (m_1 - 2)(m_2 + 2) \rangle}{(\epsilon_{m_1 m_2}^{(0)} - \epsilon_{(m_1 - 1)(m_2 + 1)}^{(0)})},$$

$$\langle (m_1 - 2)(m_2 + 2) | H' | (m_1 - 2)(m_2 + 2) \rangle = \sum_{m'_1 m'_2}' \frac{|\langle m'_1 m'_2 | H^{(1)} | (m_1 - 2)(m_2 + 2) \rangle|^2}{(\epsilon_{m'_1 m'_2}^{(0)} - \epsilon_{(m_1 - 1)(m_2 + 1)}^{(0)})},$$

where the primed sums again exclude the states with  $\epsilon_{m'_1 m'_2}^{(0)} = \epsilon_{m_1 m_2}^{(0)}$ .

For states with  $\epsilon^{(0)} = 2, M = 0$ , therefore, the matrix  $(H'^{(2)} - \epsilon^{(2)})$  is

$$\begin{aligned} &+1 - 1 && -1 + 1 \\ &+1 - 1 \left( \begin{array}{cc} \frac{1}{4} \left( \frac{1}{(2-8)} + \frac{1}{(2-0)} \right) - \epsilon^{(2)} & \frac{1}{4} \frac{1}{(2-0)} \\ \frac{1}{4} \frac{1}{(2-0)} & \frac{1}{4} \left( \frac{1}{(2-8)} + \frac{1}{(2-0)} \right) - \epsilon^{(2)} \end{array} \right) = \\ &+1 - 1 && -1 + 1 \\ &+1 - 1 \left( \begin{array}{cc} \frac{1}{12} - \epsilon^{(2)} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{12} - \epsilon^{(2)} \end{array} \right), \end{aligned}$$

with eigenvalues and eigenvectors

$$\epsilon^{(2)} = +\frac{5}{24}, \quad |M = 0(+)\rangle = \frac{1}{\sqrt{2}}(|+1, -1\rangle + |-1, +1\rangle),$$

$$\epsilon^{(2)} = -\frac{1}{24}, \quad |M = 0(-)\rangle = \frac{1}{\sqrt{2}}(|+1, -1\rangle - |-1, +1\rangle).$$

Finally, for type (3) states with  $\epsilon^{(0)} = 4$  and  $M = +2$ , (or  $M = -2$ ), we also have  $\epsilon^{(2)} = +5/24, -1/24$ , with similar ( $\pm$ ) eigenvectors.

Through second order, therefore, the five lowest zeroth-order energy states of our problem are split into 11 energies, with

$$\begin{aligned} \epsilon &= 0 - \frac{1}{4}\lambda^2, & g_\epsilon &= 1, \\ \epsilon &= 1 + \frac{1}{2}\lambda - \frac{1}{16}\lambda^2, & g_\epsilon &= 2 \quad \text{with } M = \pm 1, \\ \epsilon &= 1 - \frac{1}{2}\lambda - \frac{1}{16}\lambda^2, & g_\epsilon &= 2 \quad \text{with } M = \pm 1, \\ \epsilon &= 2 - \frac{1}{4}\lambda^2, & g_\epsilon &= 2 \quad \text{with } M = \pm 2, \\ \epsilon &= 2 + \frac{5}{24}\lambda^2, & g_\epsilon &= 1 \quad \text{with } M = 0 (+), \\ \epsilon &= 2 - \frac{1}{24}\lambda^2, & g_\epsilon &= 1 \quad \text{with } M = 0 (-), \\ \epsilon &= 4 + \frac{5}{24}\lambda^2, & g_\epsilon &= 2 \quad \text{with } M = \pm 2, \\ \epsilon &= 4 - \frac{1}{24}\lambda^2, & g_\epsilon &= 2 \quad \text{with } M = \pm 2, \\ \epsilon &= 5 + \frac{1}{2}\lambda - \frac{1}{16}\lambda^2, & g_\epsilon &= 2 \quad \text{with } M = \pm 3, \\ \epsilon &= 5 - \frac{1}{2}\lambda - \frac{1}{16}\lambda^2, & g_\epsilon &= 2 \quad \text{with } M = \pm 3, \\ \epsilon &= 5 + \frac{1}{32}\lambda^2, & g_\epsilon &= 4 \quad \text{with } (M = \pm 1)^2. \end{aligned} \tag{5}$$

Although the matrix elements of our  $H^{(1)}$  were extremely simple in the  $|m_1 m_2\rangle$  basis, the method seems to be somewhat complicated because we had to pay attention to the perturbation type. Note, We could have written, however, a general

matrix for the transformed Hamiltonian,  $H' = UHU^\dagger$ , for which the  $2 \times 2$  matrix for the general case would split into two  $1 \times 1$  matrices for states of type (1) (see e.g., the states with  $\epsilon^{(0)} = 5, M = +1$ ). Also, by including the off-diagonal matrix elements of  $H^{(1)}$ , the full  $2 \times 2$  matrix for  $H'$  at once gives both the eigenvalues through second order and the eigenvectors as the correct linear combination of the zeroth-order state vectors. For example, for the most general case of type (2), the  $2 \times 2$  matrix for  $(H' - \epsilon_{m_1(m_1+1)}^{(0)})$  is

$$(H' - \epsilon^{(0)}\mathbf{1}) = \begin{pmatrix} (m_1 + 1)m_1 & m_1(m_1 + 1) \\ m_1(m_1 + 1) & \begin{pmatrix} -\frac{1}{16}\lambda^2 & \frac{1}{2}\lambda \\ \frac{1}{2}\lambda & -\frac{1}{16}\lambda^2 \end{pmatrix} \end{pmatrix},$$

where we have used the fact that  $\epsilon_{m_1(m_1+1)}^{(0)} - \epsilon_{(m_1-1)(m_1+2)}^{(0)} = -4$  is independent of  $m_1$ . The above matrix leads to the eigenvalues  $\pm\frac{1}{2}\lambda - \frac{1}{16}\lambda^2$ , with eigenvectors

$$\frac{1}{\sqrt{2}}(|(m_1 + 1)m_1\rangle \pm |m_1(m_1 + 1)\rangle),$$

as seen in the special cases above.

Similarly, for the most general case of type (3), the  $2 \times 2$  matrix for  $(H' - \epsilon_{m_1(m_1+2)}^{(0)})$  is

$$(H' - \epsilon^{(0)}\mathbf{1}) = \begin{pmatrix} (m_1 + 2)m_1 & m_1(m_1 + 2) \\ m_1(m_1 + 2) & \begin{pmatrix} +\frac{1}{12}\lambda^2 & \frac{1}{8}\lambda^2 \\ +\frac{1}{8}\lambda^2 & +\frac{1}{12}\lambda^2 \end{pmatrix} \end{pmatrix},$$

where we have used the fact that  $\epsilon_{m_1(m_1+2)}^{(0)} - \epsilon_{(m_1-1)(m_1+3)}^{(0)} = -6$  and  $\epsilon_{m_1(m_1+2)}^{(0)} - \epsilon_{(m_1+1)(m_1+1)}^{(0)} = +2$ , are both independent of  $m_1$ . Diagonalization of this matrix leads to eigenvalues,  $(\frac{1}{12} \pm \frac{1}{8})\lambda^2$ , with eigenvectors

$$\frac{1}{\sqrt{2}}(|m_1(m_1 + 2)\rangle \pm |(m_1 + 2)m_1\rangle),$$

as seen in the special type (3) cases above.

The general  $2 \times 2$  matrix for  $(H' - \epsilon_{m_1(m_1+n)}^{(0)})$ , with  $n \geq 3$ , will factor into two  $1 \times 1$  matrices

$$(H' - \epsilon^{(0)}\mathbf{1}) = \begin{pmatrix} (m_1 + n)m_1 & m_1(m_1 + n) \\ m_1(m_1 + n) & \begin{pmatrix} +\frac{1}{4}\lambda^2 \frac{1}{(n^2-1)} & 0 \\ 0 & +\frac{1}{4}\lambda^2 \frac{1}{(n^2-1)} \end{pmatrix} \end{pmatrix},$$

again in agreement with our special case above, with  $\epsilon_{-1,2}^{(0)} = 5$ , with  $n = 3$ . In this case, the degeneracy is not removed through second order. The *proper* linear combination of zeroth-order state vectors would be discovered only in higher order of perturbation theory

### Alternative Method: Symmetry-Adapted Eigenfunctions

Although the diagonalization of the  $H'$  matrices is extremely simple, the question arises: Is there a simpler way of discovering the *proper* linear combination of zeroth-order state vectors that would automatically reduce the problem to nondegenerate perturbation theory. In general, degeneracies (unless “accidental”) arise because of some underlying symmetry. Sometimes, of course, this symmetry may be very sophisticated and not so easy to discover. Therefore, if we have used the wrong coordinates for our Schrödinger equation (which are not “symmetry adapted”), we may have missed some of the simplicity of the problem. Conversely, if we start with symmetry-adapted or *proper* zeroth-order wave functions or state vectors, the perturbation problem may be reduced to nondegenerate perturbation theory, in spite of the degeneracies of the zeroth-order problem. In our simple example, we have not at all made use of the fact that the perturbing potential is an *even* function of the relative coordinate,  $(\phi_1 - \phi_2)$ . It will therefore be useful to transform from the “single-particle” coordinates,  $\phi_1, \phi_2$ , to the relative coordinate  $(\phi_1 - \phi_2)$ , and a “center of mass” coordinate,  $\Phi$ , via the transformation

$$\phi = (\phi_1 - \phi_2), \quad \Phi = \frac{1}{2}(\phi_1 + \phi_2). \quad (6)$$

We have made the Jacobian of this transformation equal to one. In the new variables, the Schrödinger equation is

$$\left[ -\left( 2 \frac{\partial^2}{\partial \phi^2} + \frac{1}{2} \frac{\partial^2}{\partial \Phi^2} \right) + \lambda \cos \phi \right] \psi(\phi, \Phi) = \epsilon \psi(\phi, \Phi), \quad (7)$$

with zeroth-order solutions

$$\psi^{(0)}(\phi, \Phi) = \frac{1}{2\pi} e^{im\phi} e^{iM\Phi} \quad \text{and} \quad \epsilon^{(0)} = 2m^2 + \frac{1}{2} M^2. \quad (8)$$

From the inverse of the above transformation, we have

$$(m_1 \phi_1 + m_2 \phi_2) = \frac{1}{2}(m_1 - m_2)\phi + (m_1 + m_2)\Phi = m\phi + M\Phi. \quad (9)$$

Thus,  $m = \frac{1}{2}(m_1 - m_2)$  and  $M = (m_1 + m_2)$ ,

So now  $m = 0, \pm \frac{1}{2}, \pm 1, \pm \frac{3}{2}, \pm 2, \dots$  and  $M = 0, \pm 1, \pm 2, \dots$

The above exponentials,  $e^{im\phi}$ , however, are not yet symmetry adapted. We need to replace them with functions that are even or odd functions of  $\phi$ , viz., with

$$\psi_{\text{even}}^{(0)}(\phi) = \frac{1}{\sqrt{2\pi}} \quad \text{for } m = 0, \quad \psi_{\text{even}}^{(0)}(\phi) = \frac{\cos m\phi}{\sqrt{\pi}} \quad \text{for } m = \frac{1}{2}, 1, \frac{3}{2}, 2, \dots,$$

$$\psi_{\text{odd}}^{(0)}(\phi) = \frac{\sin m\phi}{\sqrt{\pi}} \quad \text{for } m = \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$$

(We have now restricted the quantum number  $m$  such that  $m \geq 0$ .) Because our perturbing Hamiltonian is independent of  $\Phi$ , it again conserves the quantum number,  $M$ . Because it is an even function of  $\phi$ , it cannot connect even functions to

odd functions. The only non-zero matrix elements of  $H^{(1)}$  are now, first for  $m > 0$ , but excluding cases for which  $(m - 1) \leq 0$ :

$$\begin{aligned}\langle (m+1), \text{even} | H^{(1)} | m, \text{even} \rangle &= \langle (m+1), \text{odd} | H^{(1)} | m, \text{odd} \rangle = \frac{1}{2}, \\ \langle (m-1), \text{even} | H^{(1)} | m, \text{even} \rangle &= \langle (m-1), \text{odd} | H^{(1)} | m, \text{odd} \rangle = \frac{1}{2}.\end{aligned}\quad (10)$$

The additional special cases are

$$\begin{aligned}\langle 1, \text{even} | H^{(1)} | 0, \text{even} \rangle &= \langle 0, \text{even} | H^{(1)} | 1, \text{even} \rangle = \frac{1}{\sqrt{2}}, \\ \langle \frac{1}{2}, \text{even} | H^{(1)} | \frac{1}{2}, \text{even} \rangle &= +\frac{1}{2}, \\ \langle \frac{1}{2}, \text{odd} | H^{(1)} | \frac{1}{2}, \text{odd} \rangle &= -\frac{1}{2}.\end{aligned}\quad (11)$$

All full matrix elements must be diagonal in  $M$ . Nondegenerate perturbation theory now gives

$$\begin{aligned}\epsilon_{m=0,\text{even},M} &= \epsilon^{(0)} - \frac{1}{4}\lambda^2 + \dots, \\ \epsilon_{m=\frac{1}{2},\text{even},M} &= \epsilon^{(0)} + \frac{1}{2}\lambda - \frac{1}{16}\lambda^2 + \dots, \\ \epsilon_{m=\frac{1}{2},\text{odd},M} &= \epsilon^{(0)} - \frac{1}{2}\lambda - \frac{1}{16}\lambda^2 + \dots, \\ \epsilon_{m=1,\text{even},M} &= \epsilon^{(0)} + \frac{5}{24}\lambda^2 + \dots, \\ \epsilon_{m=1,\text{odd},M} &= \epsilon^{(0)} - \frac{1}{24}\lambda^2 + \dots, \\ \epsilon_{m=\frac{n}{2},\text{even},M} &= \epsilon^{(0)} + \frac{1}{4}\lambda^2 \frac{1}{(n^2-1)} + \dots \quad \text{for } n \geq 3, \\ \epsilon_{m=\frac{n}{2},\text{odd},M} &= \epsilon^{(0)} + \frac{1}{4}\lambda^2 \frac{1}{(n^2-1)} + \dots \quad \text{for } n \geq 3.\end{aligned}\quad (12)$$

In particular, the eigenvalue for  $m = 1$  for the even case gets contributions from off-diagonal elements with  $m = 0$  missing for the odd case. It is also easy to show that  $\lambda^3$  terms contribute only to the energies of states with  $m = \frac{1}{2}$  and  $m = \frac{3}{2}$ , with contributions  $\mp \frac{1}{128}\lambda^3$  for the even (odd) states with  $m = \frac{1}{2}$ , but  $\pm \frac{1}{128}\lambda^3$  for the even (odd) states with  $m = \frac{3}{2}$ .

**35.** An atom of mass  $M$  in a long complicated molecule is constrained to move on a circle of radius,  $r_e$ , but is essentially free to move on this circle, with Hamiltonian

$$H^{(0)} = -\frac{\hbar^2}{2I_e} \frac{\partial^2}{\partial \phi^2}, \quad \text{with } I_e = Mr_e^2,$$

with zeroth-order energies and eigenfunctions

$$E_m^{(0)} = \frac{\hbar^2}{2I_e} m^2, \quad \text{and} \quad \psi_m^{(0)}(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi},$$

with  $m = 0, \pm 1, \pm 2, \dots$ . If this free rotational motion is perturbed by a potential of the form

$$V(\phi) = V_0 \cos(2\phi), \quad \text{with } V_0 = \lambda \frac{\hbar^2}{2I_e}, \quad \text{and } \lambda \ll 1,$$

find corrections to the energy good through order  $\lambda^2(\hbar^2/2I_e)$ . Pay particular attention to the  $|m|$  values that may require special treatment. [Footnote: In this case, some  $|m|$  values belonging to cases (2) or (3) will exist. We could again

have reduced all calculations to case (1) by making use of the symmetry of the Hamiltonian to find *proper* symmetry-adapted zeroth-order wave functions.]

**36.** (a) For the hydrogen atom,  $Z = 1$ , find the perturbation corrections to the energy to order,  $mc^2\alpha^4$ , caused by the magnetic spin orbit, Thomas ( $\vec{l} \cdot \vec{s}$ ) term, and the relativistic mass correction to the kinetic energy, but no external magnetic fields, as a function of  $n, l, j$ , and show

$$E_{nj} = \frac{1}{2}\mu c^2\alpha^4 \left( -\frac{1}{n^2} + \frac{\alpha^2}{n^3} \left[ -\frac{1}{(j + \frac{1}{2})} + \frac{3}{4n} \right] + \dots \right);$$

that is, show the states with the same  $j$  but different  $l$  are still degenerate. Here,  $\alpha$  is the fine structure constant. Use the results of problem 18 to get some of the needed matrix elements. Show  $|nljm_j\rangle$  are the *proper* zeroth-order states and use these for the calculation. [Footnote: For the states with  $l = 0, j = (l + \frac{1}{2}) = \frac{1}{2}$ , your method of calculation may not be rigorously correct, because it will involve a factor  $(l/l) = (0/0)$ . The rigorous derivation of this case will have to wait for Dirac theory, Chapter 74, and the so-called Darwin term.]

(b) Repeat for the once-ionized helium atom (one-electron atom with  $Z = 2$ ). The helium nucleus, unlike the proton, has no nuclear spin, hence, no nuclear magnetic moment and no so-called hyperfine perturbation terms. In this case, find the additional first-order energy perturbation caused by a uniform external magnetic field,  $B_0$ , assuming  $\hbar\omega_L \ll mc^2\alpha^4$ . For the special case,  $n = 2$ , calculate, in addition, corrections of order  $(\hbar\omega_L)^2/mc^2\alpha^4$ .

**37.** The perturbed hydrogen atom in stretched parabolic coordinates: Stark effect.

In stretched parabolic coordinates, we showed in problem 6  $(H^{(0)} - \epsilon)\psi = 0$  can be rewritten as

$$\left( (-2\epsilon) \frac{2}{(\mu^2 + \nu^2)} \left[ -\frac{1}{4} \left( \frac{\partial^2}{\partial \mu^2} + \frac{1}{\mu} \frac{\partial}{\partial \mu} - \frac{m^2}{\mu^2} \right) - \frac{1}{4} \left( \frac{\partial^2}{\partial \nu^2} + \frac{1}{\nu} \frac{\partial}{\partial \nu} - \frac{m^2}{\nu^2} \right) \right] - \frac{2\sqrt{(-2\epsilon)}}{(\mu^2 + \nu^2)} - \epsilon \right) \psi = 0. \quad (1)$$

For the hydrogen atom perturbed by a uniform external electric field,  $\vec{\mathcal{E}}$ , we have

$$H = H^{(0)} + \lambda z = H^{(0)} + \lambda \frac{(\mu^2 - \nu^2)}{2\sqrt{(-2\epsilon)}}, \quad \text{with } \lambda = \frac{ea_0\mathcal{E}}{(me^4/\hbar^2)},$$

all in dimensionless units, so

$$(H^{(0)} + \lambda H^{(1)} - \epsilon)\psi = 0$$

becomes

$$\left( (-2\epsilon) \frac{2}{(\mu^2 + \nu^2)} \left[ -\frac{1}{4} \left( \frac{\partial^2}{\partial \mu^2} + \frac{1}{\mu} \frac{\partial}{\partial \mu} \right) + \frac{m^2}{4\mu^2} - \frac{1}{4} \left( \frac{\partial^2}{\partial \nu^2} + \frac{1}{\nu} \frac{\partial}{\partial \nu} \right) + \frac{m^2}{4\nu^2} \right] - \frac{2\sqrt{(-2\epsilon)}}{(\mu^2 + \nu^2)} \right) \psi = 0$$

$$+ \lambda H^{(1)} - \epsilon \Big) \psi = 0. \quad (2)$$

Show, from the results of problem 26, we can rewrite this as

$$\left( T_3 + T'_3 - \frac{1}{\sqrt{(-2\epsilon)}} + \lambda H^{(1)} \frac{(\mu^2 + v^2)}{2(-2\epsilon)} \right) \psi = 0, \quad (3)$$

$$\text{with } \lambda H^{(1)} \frac{(\mu^2 + v^2)}{2(-2\epsilon)} = \frac{\lambda}{4} \frac{(\mu^4 - v^4)}{(-2\epsilon)^{\frac{3}{2}}}. \quad (4)$$

To carry through the perturbation formalism, expand

$$\epsilon = \epsilon^{(0)} + \lambda \epsilon^{(1)} + \lambda^2 \epsilon^{(2)} + \dots = -\frac{1}{2n^2} + \lambda \epsilon^{(1)} + \lambda^2 \epsilon^{(2)} + \dots, \quad (5)$$

$$\begin{aligned} \frac{1}{\sqrt{(-2\epsilon)}} &= \frac{n}{\sqrt{1 - 2\lambda n^2 \epsilon^{(1)} - 2\lambda^2 n^2 \epsilon^{(2)} + \dots}} \\ &= n + \lambda n^3 \epsilon^{(1)} + \lambda^2 [n^3 \epsilon^{(2)} + \frac{3}{2} n^5 (\epsilon^{(1)})^2] + \dots, \end{aligned} \quad (6)$$

$$\frac{\lambda}{(-2\epsilon)^{\frac{3}{2}}} = \lambda n^3 + \lambda^2 3n^5 \epsilon^{(1)} + \dots, \quad (7)$$

and show eq. (3) can be rewritten as

$$\begin{aligned} &\left( (T_3 + T'_3 - n) + \lambda \left[ \frac{1}{4} n^3 (\mu^4 - v^4) - n^3 \epsilon^{(1)} \right] + \lambda^2 \left[ \frac{1}{4} (\mu^4 - v^4) 3n^5 \epsilon^{(1)} \right. \right. \\ &\quad \left. \left. - n^3 \epsilon^{(2)} - \frac{3}{2} n^5 (\epsilon^{(1)})^2 \right] + \dots \right) \left( |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots \right) = 0 \end{aligned} \quad (8)$$

in analogy with the standard perturbation expansion

$$\begin{aligned} &\left( (H^{(0)} - E_n^{(0)}) + \lambda (H^{(1)} - E_n^{(1)}) + \lambda^2 (H^{(2)} - E_n^{(2)}) + \dots \right) \\ &\quad \times \left( |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots \right) = 0. \end{aligned} \quad (9)$$

In eq. (8), the notation  $|n^{(0)}\rangle$  is shorthand for  $|mn_1 n_2\rangle$  (see problem 26) with  $n = (|m| + n_1 + n_2 + 1)$ .

Express  $\frac{1}{4}(\mu^4 - v^4)$  in terms of the operators,  $T_3$ ,  $T_+$ ,  $T_-$ , and  $T'_3$ ,  $T'_+$ ,  $T'_-$ .

(a) Derive the expression for the first-order Stark energy

$$\epsilon^{(1)} = \frac{3}{2} n(n_1 - n_2).$$

(b) For the nondegenerate ground state, with  $n = 1$ , ( $m = n_1 = n_2 = 0$ ), find the second-order Stark correction; i.e., calculate  $\epsilon_{n=1}^{(2)}$ .

(c) States with  $|m| = (n - 1)$  (arbitrary  $n$ ) can also be treated by nondegenerate perturbation theory, and find  $\epsilon^{(2)}$  for such states as a function of  $n$ .

[Footnote: The evaluation of  $E_n^{(2)}$  by standard perturbation theory, using eq. (1) in the conventional  $|n^{(0)}\rangle = |nlm\rangle$  basis, would have required an infinite sum over discrete states with  $n' \neq n$  and an integral over the continuum states of the hydrogen atom, even to obtain the simple ground state,  $n = 1$ , result of (b).]

**38.** The Stark effect in the hydrogen atom for degenerate levels (arbitrary  $n, m$ ) in stretched parabolic coordinates.

(a) Using the parallel between

$$H^{(0)} \rightarrow T_3 + T'_3, \quad E_n^{(0)} \rightarrow n,$$

$$H^{(1)} \rightarrow \frac{1}{4}(\mu^4 - v^4)n^3, \quad E_n^{(1)} \rightarrow n^3\epsilon^{(1)}, \quad \text{etc.,}$$

found in problem 37, make the parallel of the unitary transformation  $UHU^\dagger = H'$ , such that the  $(n - |m|)$ -fold degenerate states for fixed  $n$  and  $m$  (taking  $m \geq 0$  without loss of generality) are “unhooked” from states with  $n' \neq n$  to within second order in  $\lambda$  (cf., Chapter 24).

(b) Show that sums such as

$$\sum_{n'_1} \sum_{n'_2, n' \neq n} \frac{\langle m(n_1 + k)(n_2 - k) | H_{\text{eff.}}^{(1)} | mn'_1 n'_2 \rangle \langle mn'_1 n'_2 | H_{\text{eff.}}^{(1)} | mn_1 n_2 \rangle}{(n - n')},$$

with  $k = \pm 1, \pm 2$  are zero, so, effectively, to second order in  $\lambda$ , we can get  $\epsilon_n^{(2)}$  from the diagonal matrix elements of  $H'_{\text{eff.}}$  in the  $|mn_1 n_2\rangle$  basis. Note: In the above,  $H_{\text{eff.}}^{(1)} = \frac{1}{4}(\mu^4 - v^4)n^3$ .

(c) Calculate the Stark energy corrections,  $\epsilon_n^{(1)}$ ,  $\epsilon_n^{(2)}$ , as functions of  $m, n_1, n_2$ , for an arbitrary excited state of hydrogen. In particular, show

$$\epsilon_n^{(1)} = \lambda \frac{3}{2} n(n_1 - n_2),$$

and

$$\begin{aligned} \epsilon_n^{(2)} = -\lambda^2 \frac{n^4}{8} & \left( 34(n_1^2 + n_2^2 - n_1 n_2) + 17(n_1 + n_2) + 18 \right. \\ & \left. + 17m(n_1 + n_2 + 1) + 4m^2 - 27(n_1 - n_2)^2 \right), \end{aligned}$$

or

$$\epsilon_n^{(2)} = -\lambda^2 \frac{n^4}{16} \left( 17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19 \right).$$

## **Part III**

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# Angular Momentum Theory

# Angular Momentum Coupling Theory

In the last chapter, we calculated (for the special case  $s = \frac{1}{2}$ ) the transformation coefficient  $\langle nlm_lsm_s | nlsjm_j \rangle = \langle nlsjm_j | nlm_lsm_s \rangle^*$  from a basis  $|nlm_lsm_s\rangle$  in which  $L_z$  and  $S_z$  are diagonal, which was a good basis for the case in which the external  $B_0$  field was the dominant perturbation, to the basis  $|nlsjm_j\rangle$ , the proper basis in the limit  $B_0 = 0$  in which the  $(\vec{L} \cdot \vec{S})$  term is the dominant perturbation and in which the operators  $(\vec{J} \cdot \vec{J})$  and  $J_z$  are diagonal. This was a special case of an important and common problem, met in many applications of quantum theory.

Given two commuting angular momentum operators,  $\vec{J}_1$  and  $\vec{J}_2$ , each with standard angular momentum commutation relations, i.e., with

$$[\vec{J}_1, \vec{J}_2] = 0, \quad \text{and} \\ [J_0, J_{\pm}] = \pm J_{\pm}, \quad [J_+, J_-] = 2J_0, \quad \text{for both } \vec{J}_1, \vec{J}_2. \quad (1)$$

We construct the coupled angular momentum vector

$$\vec{J} = \vec{J}_1 + \vec{J}_2, \quad (2)$$

which also satisfies the standard angular momentum commutation relations of eq. (1). We will often need to make the transformation from the  $|j_1 m_1 j_2 m_2\rangle$  basis, where these are simultaneously eigenvectors of the four commuting operators

$$(\vec{J}_1 \cdot \vec{J}_1), \quad (J_1)_z, \quad (\vec{J}_2 \cdot \vec{J}_2), \quad (J_2)_z,$$

to the  $|j_1 j_2 jm\rangle$  basis, where these are simultaneously eigenvectors of the four commuting operators

$$(\vec{J}_1 \cdot \vec{J}_1), \quad (\vec{J}_2 \cdot \vec{J}_2), \quad (\vec{J} \cdot \vec{J}), \quad J_z.$$

The possible  $m$  values are

$$\begin{aligned} m_1 &= j_1, (j_1 - 1), (j_1 - 2), \dots, -j_1, \\ m_2 &= j_2, (j_2 - 1), (j_2 - 2), \dots, -j_2, \\ m &= j, (j - 1), (j - 2), \dots, -j, \end{aligned} \quad (3)$$

where  $m$  is an additive quantum number

$$m = m_1 + m_2. \quad (4)$$

First, we need to find the possible  $j$  values for a given  $j_1, j_2$ . We shall name the  $j_1, j_2$ , such that  $j_1 \geq j_2$ . To find the possible values of  $j$ , we simply count the number of occurrences for each possible value of  $m$ .

The maximum possible  $m$  value is  $m = j_1 + j_2$ , which can be made in only one way, with  $m_1 = j_1$  and  $m_2 = j_2$ . Hence, one  $j$  value must exist with  $j = j_1 + j_2$ .

There are two ways of making  $m = (j_1 + j_2 - 1)$ ; either with  $m_1 = j_1, m_2 = (j_2 - 1)$ , or with  $m_1 = (j_1 - 1), m_2 = j_2$ . One linear combination of these two states will be the state with  $j = j_1 + j_2$  and  $m = (j_1 + j_2 - 1)$ . The other linear combination of these two states must be a state with  $m = j = (j_1 + j_2 - 1)$ . Thus, one  $j$  value must exist with  $j = (j_1 + j_2 - 1)$ .

There are three ways of making states with  $m = (j_1 + j_2 - 2)$ , viz., with  $m_1, m_2 = j_1, (j_2 - 2), (j_1 - 1), (j_2 - 1)$ , or  $(j_1 - 2), j_2$ . One linear combination of these three states is needed to make the state with  $j = j_1 + j_2$  and  $m = (j_1 + j_2 - 2)$ . A second linear combination of these three states is needed to make the state with  $j = (j_1 + j_2 - 1)$  and  $m = (j_1 + j_2 - 2)$ . This leaves one linear combination to make a single state with  $m = j = (j_1 + j_2 - 2)$ , so one  $j$  value exists with  $j = (j_1 + j_2 - 2)$ .

This process can be continued for  $k \leq 2j_2$  (recall we chose  $j_1 \geq j_2$ ), so that there are  $(k + 1)$  ways of making states with  $m = (j_1 + j_2 - k)$ . Of these,  $k$  linear combinations are needed to make the states with this  $m$  value, but with one of the allowed  $j$  values with  $j > (j_1 + j_2 - k)$ , leaving but a single linear combination of these states with  $m = j = (j_1 + j_2 - k)$ , so a single  $j$  value exists with  $(j_1 + j_2 - k)$ .

This process quits with  $k = 2j_2$ . For  $k \geq 2j_2$  and  $m \geq 0$ , there are only  $(2j_2 + 1)$  ways of making the  $m$  value  $m = (j_1 + j_2 - k)$  with  $k \geq 2j_2$ , and all  $(2j_2 + 1)$  independent linear combinations of these states are needed to make the states with  $j \geq (j_1 - j_2)$ , so no new  $j$  values arise, with  $j < (j_1 - j_2)$ . Finally, symmetry exists between the positive and negative  $m$  values.

Thus, the possible  $j$  values are

$$(j_1 + j_2), (j_1 + j_2 - 1), (j_1 + j_2 - 2), \dots, |(j_1 - j_2)|,$$

with each  $j$  value occurring once only. The total number of states is

$$\begin{aligned} \sum_{|j_1-j_2|}^{(j_1+j_2)} (2j+1) &= \sum_{k=0}^{k=2j_2} [2(j_1 + j_2 - k) + 1] \\ &= (2j_2 + 1)(2j_1 + 2j_2 + 1) - 2 \frac{(2j_2 + 1)2j_2}{2} \\ &= (2j_1 + 1)(2j_2 + 1), \end{aligned} \quad (5)$$

as it should be.

## A General Properties of Vector Coupling Coefficients

We shall need the transformation coefficients of the unitary transformation

$$|j_1 j_2 jm\rangle = \sum_{m_1, (m_2)} |j_1 m_1 j_2 m_2\rangle \langle j_1 m_1 j_2 m_2 | j_1 j_2 jm\rangle, \quad (6)$$

where  $\langle j_1 m_1 j_2 m_2 | j_1 j_2 jm\rangle$  is the unitary transformation matrix, which could be written as,

$$U_{m_1 m_2, jm},$$

where the row label is given by  $m_1 m_2$ , and the column label is specified by  $jm$ . We sum over both  $m_1$  and  $m_2$  in eq. (6), but  $m$  is fixed and because  $m = m_1 + m_2$ ,  $m_2$  is determined by  $m_1$  and  $m$ , so it gets “dragged along” in the sum. This is why we have put  $m_2$  in parentheses in the summation symbol. Because  $j_1$  and  $j_2$  is common to both bases, the unitary transformation coefficient is often abbreviated by

$$\langle j_1 m_1 j_2 m_2 | jm\rangle.$$

It is known as a “Clebsch–Gordan coefficient,” or as a “Wigner coefficient,” or as a “vector coupling coefficient.” Slightly different notations are used by different people. Other commonly used notations are  $\langle j_1 j_2 m_1 m_2 | jm\rangle$  (note the different order of the labels in the left-hand side), or  $C_{m_1 m_2 m}^{j_1 j_2 j}$ , or several others.

The inverse of the above transformation, eq. (6), is in Dirac notation

$$|j_1 m_1 j_2 m_2\rangle = \sum_j |j_1 j_2 jm\rangle \langle j_1 j_2 jm | j_1 m_1 j_2 m_2\rangle, \quad (7)$$

where the summation is one over  $j$  only, because  $m$  is fixed by the fixed values of  $m_1$  and  $m_2$  and

$$\begin{aligned} \langle j_1 j_2 jm | j_1 m_1 j_2 m_2\rangle &= (U^{-1})_{jm, m_1 m_2} = (U_{m_1 m_2, jm})^* \\ &= \langle j_1 m_1 j_2 m_2 | j_1 j_2 jm\rangle^* = \langle j_1 m_1 j_2 m_2 | jm\rangle^*. \end{aligned} \quad (8)$$

The Clebsch–Gordan coefficients can all be made real. (This is the “world” standard to which everyone adheres!) Therefore, the complex conjugate sign is not needed for the inverse transformation, and we can write the inverse transformation, in terms of the Clebsch–Gordan coefficient notation, as

$$|j_1 m_1 j_2 m_2\rangle = \sum_j |j_1 j_2 jm\rangle \langle j_1 m_1 j_2 m_2 | jm\rangle. \quad (9)$$

(From the point of view of the Dirac notation, the transformation coefficient appears to have bra and ket inverted. This inversion is because we have made use of the unitary property of this *real* transformation coefficient. We shall always write the Clebsch–Gordan coefficient in the Dirac-like notation, but with the  $m_1$ ,  $m_2$

labels always on the left!) Using the unitary property of this real transformation coefficient, we get the: Orthogonality relations of the Clebsch–Gordan coefficients:

$$\sum_{m_1, (m_2)} \langle j_1 m_1 j_2 m_2 | jm \rangle \langle j_1 m_1 j_2 m_2 | j'm' \rangle = \delta_{jj'} \delta_{mm'},$$

$$\sum_j \langle j_1 m_1 j_2 m_2 | jm \rangle \langle j_1 m'_1 j_2 m'_2 | jm \rangle = \delta_{m_1 m'_1} \delta_{m_2 m'_2}. \quad (10)$$

## B Methods of Calculation

For  $j_2 = \frac{1}{2}$ , we have already found one method: diagonalize the operator  $(\vec{J}_1 \cdot \vec{J}_2)$  in the  $|j_1 m_1 j_2 m_2\rangle$  basis. For  $j_2 \geq 1$ , however, this method would lead to a diagonalization of  $3 \times 3, 4 \times 4, \dots$ , matrices. Hence, we shall look for better methods. One of these methods involves recursion formulae for the Clebsch–Gordan coefficients. We shall derive a recursion formula for the Clebsch–Gordan coefficients by acting on the state vector  $|j_1 j_2 jm\rangle$  with the operator,

$$J_+ = (J_1)_+ + (J_2)_+,$$

$$J_+ |j_1 j_2 jm\rangle = \sum_{m'_1, (m'_2)} \left( (J_1)_+ + (J_2)_+ \right) |j_1 m'_1 j_2 m'_2\rangle \langle j_1 m'_1 j_2 m'_2 | jm \rangle, \quad (11)$$

or

$$\begin{aligned} & \sqrt{(j-m)(j+m+1)} |j_1 j_2 j(m+1)\rangle \\ &= \sum_{m'_1, (m'_2)} \left( \sqrt{(j_1 - m'_1)(j_1 + m'_1 + 1)} |j_1(m'_1 + 1) j_2 m'_2\rangle \right. \\ & \quad \left. + \sqrt{(j_2 - m'_2)(j_2 + m'_2 + 1)} |j_1 m'_1 j_2(m'_2 + 1)\rangle \right) \langle j_1 m'_1 j_2 m'_2 | jm \rangle. \end{aligned} \quad (12)$$

Now, expanding  $|j_1 j_2 j(m+1)\rangle$  on the left-hand side of this relation, and renaming the dummy summation indices  $m'_1, m'_2 = (m_1 - 1), m_2$  in the first term of the right-hand side, and making the change  $m'_1, m'_2 = m_1, (m_2 - 1)$  in the second term of the right-hand side, we get

$$\begin{aligned} & \sqrt{(j-m)(j+m+1)} \sum_{m_1, (m_2)} |j_1 m_1 j_2 m_2\rangle \langle j_1 m_1 j_2 m_2 | j(m+1) \rangle \\ &= \sum_{m_1, (m_2)} |j_1 m_1 j_2 m_2\rangle \left( \sqrt{(j_1 - m_1 + 1)(j_1 + m_1)} (j_1(m_1 - 1) j_2 m_2 | jm \rangle \right. \\ & \quad \left. + \sqrt{(j_2 - m_2 + 1)(j_2 + m_2)} (j_1 m_1 j_2(m_2 - 1) | jm \rangle) \right). \end{aligned} \quad (13)$$

Now, with left-multiplication by a  $\langle j_1 m_1 j_2 m_2 |$  with a specific, fixed  $m_1$  and  $m_2$ , this equation is converted to the recursion relation, as follows.

Recursion Formula I:

$$\sqrt{(j-m)(j+m+1)} \langle j_1 m_1 j_2 m_2 | j(m+1) \rangle$$

$$= \sqrt{(j_1 + m_1)(j_1 - m_1 + 1)}(j_1(m_1 - 1)j_2m_2|jm\rangle \\ + \sqrt{(j_2 + m_2)(j_2 - m_2 + 1)}(j_1m_1j_2(m_2 - 1)|jm\rangle). \quad (14)$$

For states with  $m = j$ , this three-term recursion formula is reduced to a two-term recursion formula, which leads to

$$\frac{\langle j_1(m_1 - 1)j_2m_2|jj\rangle}{\langle j_1m_1j_2(m_2 - 1)|jj\rangle} = -\sqrt{\frac{(j_2 + m_2)(j_2 - m_2 + 1)}{(j_1 + m_1)(j_1 - m_1 + 1)}}. \quad (15)$$

We can use this successively, starting with  $m_1 = j_1$ , and, hence,  $m_2 = j - j_1 + 1$ , to relate

$$\langle j_1m_1j_2(m_2 = j - m_1)|jj\rangle \quad \text{to} \quad \langle j_1j_1j_2(j - j_1)|jj\rangle,$$

and, thus, get

$$\begin{aligned} & \frac{\langle j_1m_1j_2(j - m_1)|jj\rangle}{\langle j_1j_1j_2(j - j_1)|jj\rangle} \\ &= (-1)^{j_1-m_1} \sqrt{\frac{(j_2 + j - j_1 + 1)(j_2 + j - j_1 + 2) \cdots (j_2 + j - m_1)}{2j_1(2j_1 - 1) \cdots (j_1 + m_1 + 1)}} \\ & \times \sqrt{\frac{(j_2 - j + j_1)(j_2 - j + j_1 - 1) \cdots (j_2 - j + m_1 + 1)}{1 \cdot 2 \cdots (j_1 - m_1)}} \\ &= (-1)^{j_1-m_1} \sqrt{\frac{(j_2 + j - m_1)!}{(j_2 + j - j_1)!} \frac{(j_2 - j + j_1)!}{(j_2 - j + m_1)!} \frac{(j_1 + m_1)!}{2j_1!(j_1 - m_1)!}}. \end{aligned} \quad (16)$$

Now we can calculate  $|\langle j_1j_1j_2(j - j_1)|jj\rangle|$  by using the orthonormality

$$\sum_{m_1} |\langle j_1m_1j_2(j - m_1)|jj\rangle|^2 = 1. \quad (17)$$

To do the sum, we will need an addition theorem for binomial coefficients

$$\sum_{m_1} \frac{(a + m_1)!(b - m_1)!}{(c + m_1)!(d - m_1)!} = \frac{(a + b + 1)!(a - c)!(b - d)!}{(c + d)!(a + b - c - d + 1)!}. \quad (18)$$

Because this relation will only give us the absolute value of the starting coefficient  $\langle j_1j_1j_2(j - j_1)|jj\rangle$ , its phase must be chosen. The choice universally accepted, the so-called Condon and Shortley phase convention, is the following: This starting coefficient is chosen to be real and positive. Then,

$$\langle j_1j_1j_2(j - j_1)|jj\rangle = \sqrt{\frac{2j_1!(2j + 1)!}{(j_1 + j_2 + j + 1)!(j_1 - j_2 + j)!}}, \quad (19)$$

and, finally,

$$\langle j_1m_1j_2(j - m_1)|jj\rangle = (-1)^{j_1-m_1} \times \sqrt{\frac{(j_1 + m_1)!(j_2 + j - m_1)!(j_1 + j_2 - j)!(2j + 1)!}{(j_1 - m_1)!(j_2 - j + m_1)!(j_2 - j_1 + j)!(j_1 - j_2 + j)!(j_1 + j_2 + j + 1)!}}. \quad (20)$$

Now we need to calculate coefficients with  $m < j$ . We can accomplish this by deriving a recursion formula that steps down in  $m$ . By repeating the steps of eqs. (11)–(14) by acting on the coupled state  $|j_1 j_2 j m\rangle$  with the step-down operator  $J_- = (J_1)_- + (J_2)_-$ , we arrive at the analogue of eq. (14) as follows.

Recursion Formula II:

$$\begin{aligned} & \sqrt{(j+m)(j-m+1)} \langle j_1 m_1 j_2 m_2 | j(m-1) \rangle \\ &= \sqrt{(j_1 - m_1)(j_1 + m_1 + 1)} \langle j_1 (m_1 + 1) j_2 m_2 | jm \rangle \\ &+ \sqrt{(j_2 - m_2)(j_2 + m_2 + 1)} \langle j_1 m_1 j_2 (m_2 + 1) | jm \rangle. \end{aligned} \quad (21)$$

Repeated application of this recursion formula II will give us the coefficients with arbitrary  $m$ , starting with the known coefficient with  $m = j$ . In practice, the most widely used tables are those in which one of the angular momenta is reasonably small, say,  $j_2 = \frac{1}{2}, 1, \frac{3}{2}, 2$ . (See problem 39.) To calculate some of these it will be useful to first study the symmetries of the Clebsch–Gordan coefficients.

# Symmetry Properties of Clebsch–Gordan Coefficients

Clebsch–Gordan coefficients in which the three angular momenta,  $j_1$ ,  $j_2$ , and  $j \equiv j_3$ , are reordered may be simply related to each other. The most trivial case involves the exchange of the order of the quantum numbers,  $j_1 m_1$  and  $j_2 m_2$ . The state vector  $|j_1 m_1 j_2 m_2\rangle$  is a direct product of two vectors involving separate subspaces of the full Hilbert space, or in terms of the coordinate representation, the wave function  $\psi_{j_1 m_1} \psi_{j_2 m_2}$  is a product of functions involving different variables. For example,  $\psi_{j_1 m_1}$  might be a function of orbital variables and  $\psi_{j_2 m_2}$  might be a function of spin variables. Thus, the product of these two functions should not depend on the order in which we write the two functions. Therefore, when we expand this product function in terms of the total angular momentum eigenfunctions  $\Psi_{j_1 j_2 j_m}$ , the result must be independent of the order in which we write the original product function,  $\psi_{j_1 m_1} \psi_{j_2 m_2}$ , or  $\psi_{j_2 m_2} \psi_{j_1 m_1}$ , with the possible exception of an overall phase factor. This phase factor comes in because our phase convention fixing the overall sign of the Clebsch–Gordan coefficients gives preference to the angular momenta sitting in the number 1 and number 3 positions of the Clebsch–Gordan coefficient. Thus,  $\langle j_1 j_1 j_2 m_2 | j_3 j_3 \rangle$  must be positive by our phase convention. Similarly,  $\langle j_2 j_2 j_1 m_1 | j_3 j_3 \rangle$  must also be positive. On the contrary, the Clebsch–Gordan coefficient  $\langle j_1 m_1 j_2 j_2 | j_3 j_3 \rangle$  has the sign  $(-1)^{j_1 - m_1}$  with  $m_1 = j_3 - j_2$ . Hence, its sign is  $(-1)^{j_1 + j_2 - j_3}$ . Thus, the coefficients in which the order of  $j_1$  and  $j_2$  is exchanged will differ by this phase factor for all possible  $m$ 's. Thus, we have our first symmetry property:

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle = (-1)^{j_1 + j_2 - j_3} \langle j_2 m_2 j_1 m_1 | j_3 m_3 \rangle. \quad (1)$$

Next, if we rearrange the vector addition equation,

$$\vec{J}_1 + \vec{J}_2 = \vec{J}_3, \quad (2)$$

to read

$$\vec{J}_3 - \vec{J}_2 = \vec{J}_1, \quad (3)$$

we can see that the Clebsch–Gordan coefficient  $\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle$  must be related to the coefficient  $\langle j_3 m_3 j_2 - m_2 | j_1 m_1 \rangle$ . In particular, if we make the substitution  $j_1 m_1 \leftrightarrow j_3 m_3$  and  $m_2 \rightarrow -m_2$  in recursion formula I (or II), we obtain recursion formula II (or I), provided the transformed coefficients are related to the original ones via a phase factor proportional to  $(-1)^{m_2}$  and an  $m$ -independent factor; i.e., we expect

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle = (-1)^{m_2} K(j_1, j_2, j_3) \langle j_3 m_3 j_2 - m_2 | j_1 m_1 \rangle, \quad (4)$$

where  $K(j_1, j_2, j_3)$  is the  $m$ -independent overall factor. This factor can be determined via the orthonormality of the Clebsch–Gordan coefficients

$$\begin{aligned} \sum_{m_3} \sum_{m_1, (m_2)} |\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle|^2 &= \sum_{m_3} 1 = (2j_3 + 1) \\ &= \sum_{m_1} \sum_{m_3, (m_2)} |K(j_1, j_2, j_3)|^2 |\langle j_3 m_3 j_2 - m_2 | j_1 m_1 \rangle|^2 = \sum_{m_1} |K(j_1, j_2, j_3)|^2 \\ &= (2j_1 + 1) |K(j_1, j_2, j_3)|^2. \end{aligned} \quad (5)$$

Thus,

$$K(j_1, j_2, j_3) = (-1)^{\phi(j_1, j_2, j_3)} \sqrt{\frac{(2j_3 + 1)}{(2j_1 + 1)}}, \quad (6)$$

where the  $j_i$ -dependent phase  $\phi$  can be determined because the coefficients with both  $m_1 = j_1$  and  $m_3 = j_3$  and hence  $m_2 = j_3 - j_1$  must both be positive, and hence  $\phi = j_1 - j_3$ . Thus, we get a second symmetry property

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle = (-1)^{j_1 - j_3 + m_2} \sqrt{\frac{(2j_3 + 1)}{(2j_1 + 1)}} \langle j_3 m_3 j_2 - m_2 | j_1 m_1 \rangle. \quad (7)$$

By combining this symmetry property with the first one,  $(1 \leftrightarrow 2)$  exchange, we get

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle = (-1)^{j_2 + m_2} \sqrt{\frac{(2j_3 + 1)}{(2j_1 + 1)}} \langle j_2 - m_2 j_3 m_3 | j_1 m_1 \rangle. \quad (8)$$

This process is a cyclic exchange of the type  $123 \rightarrow (-2)31$ . If we follow this by the cyclic exchange  $(-2)31 \rightarrow (-3)1(-2)$  and subsequently by the cyclic exchange  $(-3)1(-2) \rightarrow (-1)(-2)(-3)$ , we obtain

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle = (-1)^{j_1 + j_2 - j_3} \langle j_1 - m_1 j_2 - m_2 | j_3 - m_3 \rangle, \quad (9)$$

where we have used the identity  $j_1 + m_1 + j_2 + m_2 + j_3 + m_3 = j_1 + j_2 + j_3 + 2m_3$ , and  $j_1 + j_2 + j_3 + 2m_3 = j_1 + j_2 - j_3 + \text{even integer}$ , because  $2j_3 + 2m_3$  is always an even integer. (Either  $j_3$  and  $m_3$  are both integers or are both  $\frac{1}{2}$ -integers.)

We have now derived several symmetry properties, involving interchanges such as  $123 \rightarrow 213$ , or cyclic interchanges such as  $123 \rightarrow (-2)31$ , or changes of sign in all  $m$ 's,  $123 \rightarrow (-1)(-2)(-3)$ . Twelve such symmetry properties exist altogether. These properties are much easier to remember by introducing the 3-j symbol, defined by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix} = \frac{(-1)^{j_1-j_2+m_3}}{\sqrt{(2j_3+1)}} \langle j_1 m_1 | j_2 m_2 | j_3 m_3 \rangle. \quad (10)$$

This 3-j symbol has the following symmetry properties: The 3-j symbol is invariant under any even permutation of columns. The 3-j symbol changes sign by the factor  $(-1)^{j_1+j_2+j_3}$  under either an odd permutation of columns or under the transformation  $m_i \rightarrow -m_i$  for all  $i = 1, 2, 3$ .

Although the symmetry properties are easier to remember in terms of the 3-j symbol, this symbol does not have simple orthonormality properties. The orthonormality relations for the Clebsch-Gordan coefficients are so useful most authors prefer to use the Clebsch-Gordan coefficients.

References: several little books on angular momentum coupling in quantum mechanics exist: (1) D. M. Brink and G. R. Satchler. *Angular Momentum*. Oxford: Clarendon Press, 1968; (2) M. E. Rose. *Elementary Theory of Angular Momentum*. New York: John Wiley, 1957; (3) A. R. Edmonds. *Angular Momentum in Quantum Mechanics*. Princeton University Press, 1974.

Tables: *The 3-j and 6-j Symbols*. M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten. Cambridge, Mass.: MIT Press, 1959. *Tables of Clebsch-Gordan Coefficients*, Peking: Science Press, 1965.

TABLE 28.1.  $\langle j_1 m_1 | j_2 m_2 | jm \rangle$ 

$j =$	$m_2 = +\frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j_1 + \frac{1}{2}$	$\sqrt{\frac{(j_1+m+\frac{1}{2})}{(2j_1+1)}}$	$\sqrt{\frac{(j_1-m+\frac{1}{2})}{(2j_1+1)}}$
$j_1 - \frac{1}{2}$	$-\sqrt{\frac{(j_1-m+\frac{1}{2})}{(2j_1+1)}}$	$\sqrt{\frac{(j_1+m+\frac{1}{2})}{(2j_1+1)}}$

TABLE 28.2.  $\langle j_1 m_1 | j_2 m_2 | jm \rangle$ 

$j =$	$m_2 = +1$	$m_2 = 0$	$m_2 = -1$
$j_1 + 1$	$\sqrt{\frac{(j_1+m)(j_1+m+1)}{(2j_1+1)(2j_1+2)}}$	$\sqrt{\frac{(j_1-m+1)(j_1+m+1)}{(2j_1+1)(j_1+1)}}$	$\sqrt{\frac{(j_1-m)(j_1-m+1)}{(2j_1+1)(2j_2+2)}}$
$j_1$	$-\sqrt{\frac{(j_1+m)(j_1-m+1)}{2j_1(j_1+1)}}$	$\frac{m}{\sqrt{j_1(j_1+1)}}$	$\sqrt{\frac{(j_1-m)(j_1+m+1)}{2j_1(j_1+1)}}$
$j_1 - 1$	$\sqrt{\frac{(j_1-m)(j_1-m+1)}{2j_1(2j_1+1)}}$	$-\sqrt{\frac{(j_1-m)(j_1+m)}{j_1(2j_1+1)}}$	$\sqrt{\frac{(j_1+m+1)(j_1+m)}{2j_1(2j_1+1)}}$

The most useful Clebsch-Gordan coefficients are those in which one of the angular momenta, say,  $j_2$ , are small. Such coefficients, with  $j_2 \leq 4$ , can be found in general algebraic form in the last reference (Peking: Science Press, 1965). Coefficients with  $j_2 = \frac{1}{2}$  and  $j_2 = 1$  are appended.

# Invariance of Physical Systems Under Rotations

Before going further with our study of angular momentum, it will be advantageous to study the general behavior of physical systems under rotations in our 3-D space. If a state vector which describes the state of a physical system is specified by  $|\psi\rangle$ , the state vector for the rotated system will be specified by  $|\psi_{\text{rot.}}\rangle = R|\psi\rangle$ . (We use the subscript, rot., in place of a prime, which is often used for the rotated state, because primes are also often used on quantum labels.) The operator,  $R$ , is the operator that rotates the system. Recall from the theory of translation operators, two possible points of view exist for such operators: (1) The active point of view, in which  $R$  is used to rotate the system. (2) The passive point of view, in which the system is left unchanged and  $R$  is used to rotate the coordinate system (in the opposite sense) to view the system from a rotated reference frame. We shall use the active point of view in this chapter.

The operator  $R$  is a linear, unitary operator:

$$R^{-1} = R^\dagger, \quad (1)$$

$$R(\lambda_1|\psi_1\rangle + \lambda_2|\psi_2\rangle) = \lambda_1(R|\psi_1\rangle) + \lambda_2(R|\psi_2\rangle). \quad (2)$$

Also, note the following properties.

$$1. \text{ If } |\psi\rangle \rightarrow |\psi_{\text{rot.}}\rangle = R|\psi\rangle, \quad \text{then } \langle\psi| \rightarrow \langle\psi_{\text{rot.}}| = \langle\psi|R^\dagger. \quad (3)$$

$$2. \text{ If } |\chi\rangle = O|\psi\rangle, \quad \text{then } |\chi_{\text{rot.}}\rangle = R|\chi\rangle = ROR^\dagger(R|\psi\rangle), \\ \text{so } O_{\text{rot.}} = ROR^\dagger. \quad (4)$$

If  $[R, O] = 0$ , then  $O_{\text{rot.}} = O$ , and if  $O$  is hermitian,  $O_{\text{rot.}}$  is hermitian. Also, if  $\langle \chi | \psi \rangle$  are observable amplitudes, then

$$3. \quad \langle \chi_{\text{rot.}} | \psi_{\text{rot.}} \rangle = \langle \chi | R^\dagger R | \psi \rangle = \langle \chi | \psi \rangle. \quad (5)$$

Matrix elements of operators are also invariant:

$$4. \quad \langle \chi_{\text{rot.}} | O_{\text{rot.}} | \psi_{\text{rot.}} \rangle = \langle \chi | O | \psi \rangle. \quad (6)$$

Relations among operators are preserved under rotations:

$$5. \quad \text{If } [A, B] = iC, \quad \text{then } [A_{\text{rot.}}, B_{\text{rot.}}] = iC_{\text{rot.}}. \quad (7)$$

## A Rotation Operators

We shall begin by studying a single-particle system and assume for the moment that the particle has no spin. We shall construct the rotation operator for a rotation through an angle,  $\alpha$ , about a specific axis. We shall also take the  $z$  axis of our coordinate system along the direction of the rotation axis. Then, in analogy with the translation operator,  $T = e^{-\frac{i}{\hbar} c_1 p_z}$ , we shall try

$$R_z(\alpha) = e^{-\frac{i}{\hbar} \alpha L_z^{\text{phys.}}} = e^{-i\alpha L_z}, \quad (8)$$

where we have converted the physical angular momentum operator ( $z$  component) into the dimensionless  $L_z$  in the last step. To study the action of  $R_z(\alpha)$  on a general  $|\psi\rangle$ , expand  $|\psi\rangle$  in terms of angular momentum eigenfunctions.

$$\begin{aligned} |\psi\rangle &= \sum_{nlm} |nlm\rangle \langle nlm| \psi \rangle \quad \text{or} \\ \langle \vec{r} | \psi \rangle &= \psi(r, \theta, \phi) = \sum_{nlm} \langle \vec{r} | nlm \rangle \langle nlm | \psi \rangle \\ &= \sum_{nlm} R_{nl}(r) \Theta_{lm}(\theta) \frac{e^{im\phi}}{\sqrt{2\pi}} c_{nlm}. \end{aligned} \quad (9)$$

Then,

$$\begin{aligned} |\psi_{\text{rot.}}\rangle &= R|\psi\rangle = \sum_{nlm} e^{-i\alpha L_z} |nlm\rangle \langle nlm| \psi \rangle = \sum_{nlm} e^{-i\alpha m} |nlm\rangle \langle nlm| \psi \rangle \\ \text{or } \langle \vec{r} | \psi_{\text{rot.}} \rangle &= \psi_{\text{rot.}}(r, \theta, \phi) = \sum_{nlm} R_{nl}(r) \Theta_{lm}(\theta) e^{im(\phi-\alpha)} \frac{c_{nlm}}{\sqrt{2\pi}}. \end{aligned} \quad (10)$$

Thus,

$$\psi_{\text{rot.}}(r, \theta, \phi) = \psi(r, \theta, \phi_{\text{rot.}}) = \psi(r, \theta, \phi - \alpha). \quad (11)$$

We see (Fig. 29.1), if the original  $\psi(r, \theta, \phi)$  has a maximum at some angle  $\phi = \phi_0$ , the rotated wave function,  $\psi_{\text{rot.}}$ , has a maximum where  $(\phi - \alpha) = \phi_0$ , that is, where  $\phi = \phi_0 + \alpha$ . In other words, the physical system has been rotated in the positive sense through an angle  $\alpha$ . Note: The prime is often used to designate  $\phi_{\text{rot.}}$ , i.e.,  $\phi_{\text{rot.}} \equiv \phi' = (\phi - \alpha)$ , and note the last minus sign.

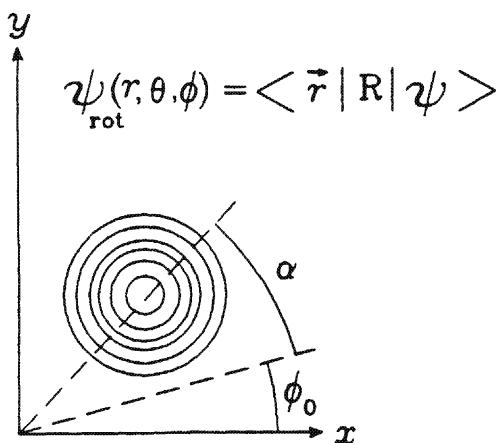
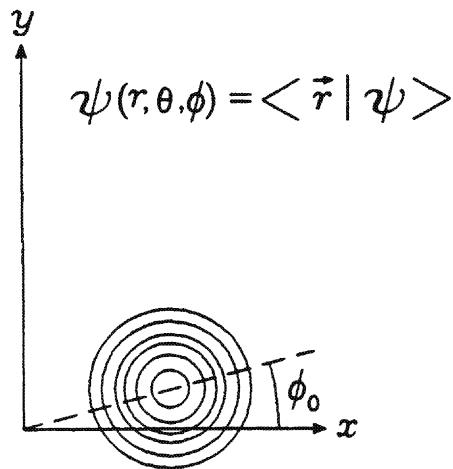


FIGURE 29.1. The rotation operation,  $e^{-i\alpha L_2}$ .

Next, we shall look at a single-particle system, but now we assume the particle is a spin  $\frac{1}{2}$ -particle, like the electron. Because spin and orbital operators commute, we shall try

$$R = R_L R_S, \quad (12)$$

with

$$R_S(\alpha) = e^{-i\alpha S_z} = e^{-i\frac{\alpha}{2}\sigma_z}. \quad (13)$$

Now, using  $\sigma_z^2 = 1$ , we get

$$R_S(\alpha) = \cos\left(\frac{\alpha}{2}\right) \times 1 - i \sin\left(\frac{\alpha}{2}\right)\sigma_z, \quad (14)$$

or

$$R_S(\alpha) = \begin{pmatrix} e^{-i\frac{\alpha}{2}} & 0 \\ 0 & e^{+i\frac{\alpha}{2}} \end{pmatrix}, \quad (15)$$

leading to

$$(\sigma_z)_{\text{rot.}} = R_S(\alpha)\sigma_z R_S^\dagger(\alpha) = \sigma_z, \quad (16)$$

because  $R_S$  commutes with  $\sigma_z$ . Similarly,

$$(\sigma_x)_{\text{rot.}} = \begin{pmatrix} e^{-i\frac{\alpha}{2}} & 0 \\ 0 & e^{+i\frac{\alpha}{2}} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} e^{+i\frac{\alpha}{2}} & 0 \\ 0 & e^{-i\frac{\alpha}{2}} \end{pmatrix}. \quad (17)$$

Carrying out the matrix multiplication, this equation leads to

$$(\sigma_x)_{\text{rot.}} = \cos \alpha \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \sin \alpha \begin{pmatrix} 0 & -i \\ +i & 0 \end{pmatrix}, \quad (18)$$

or

$$(\sigma_x)_{\text{rot.}} = \cos \alpha \sigma_x + \sin \alpha \sigma_y, \quad (19)$$

and, similarly,

$$(\sigma_y)_{\text{rot.}} = -\sin \alpha \sigma_x + \cos \alpha \sigma_y. \quad (20)$$

Thus, the rotation operator  $R_S(\alpha)$  rotates the  $\vec{\sigma}$  vector properly. Note: This  $\vec{\sigma}$  vector is part of the physical system. Finally, if we combine the orbital and spin operators, we get

$$R_z(\alpha) = R_L(\alpha)R_S(\alpha) = e^{-i\alpha(L_z+S_z)} = e^{-i\alpha J_z} \quad (21)$$

for a single particle with spin. The generator of the rotation about an axis is the component of the total angular momentum operator along that axis. This result holds equally well for a many-particle system or any general system, provided  $J_z$  is the  $z$  component of the *total* angular momentum vector.

## B General Rotations, $R(\alpha, \beta, \gamma)$

The most general rotation will be parameterized by the three Euler angles,  $\alpha$ ,  $\beta$ , and  $\gamma$ , and will be built from the three successive rotations as follows.

The first rotation through the angle  $\alpha$  about the original space-fixed  $z$  axis will take the  $(x, y, z)$  coordinate system to a rotated  $(x_1, y_1, z_1)$  system, with  $z_1 = z$ .

The second rotation through an angle  $\beta$  about the new  $y_1$  axis will take the  $(x_1, y_1, z_1)$  coordinate system to a new  $(x_2, y_2, z_2)$  system, with  $y_2 = y_1$ .

The third rotation through an angle  $\gamma$  about the  $z_2$  axis will take the  $(x_2, y_2, z_2)$  coordinate system to the final rotated  $(x', y', z')$  system, with  $z' = z_2$ .

We shall think of the coordinate systems as being attached to our physical system. Thus, the general rotation can be expressed through

$$R(\alpha, \beta, \gamma) = e^{-i\gamma J_z'} e^{-i\beta J_{z1}} e^{-i\alpha J_z}, \quad (22)$$

where this is not a very handy form because the three generators of the unitary transformations,  $R(\alpha)$ ,  $R(\beta)$ , and  $R(\gamma)$ , are expressed in terms of angular momentum components along three different coordinate systems. Using  $O_{\text{rot.}} = R O R^\dagger$ , however, and noting the operator  $J_{y1}$  is reached from  $J_y$  via the rotation  $R(\alpha)$ , we have

$$e^{-i\beta J_{y1}} = R(\alpha) e^{-i\beta J_y} R(\alpha)^\dagger = e^{-i\alpha J_z} e^{-i\beta J_y} e^{+i\alpha J_z}. \quad (23)$$

Similarly, noting the operator  $J_{z'} = J_{z2}$  is reached from  $J_{z1}$  via the rotation  $R(\beta)$ , we have

$$e^{-i\gamma J_{z'}} = R(\beta) e^{-i\gamma J_{z1}} R(\beta)^\dagger. \quad (24)$$

Thus, we can write

$$R(\alpha, \beta, \gamma) = R(\beta) e^{-i\gamma J_{z1}} R(\beta)^\dagger R(\beta) e^{-i\alpha J_z} = R(\beta) e^{-i\gamma J_{z1}} e^{-i\alpha J_z}. \quad (25)$$

Now, noting  $J_{z1} = J_z$ , the two rotation operators on the extreme right commute with each other, and we can write

$$R(\alpha, \beta, \gamma) = e^{-i\beta J_{z1}} R(\alpha) e^{-i\gamma J_z} = R(\alpha) e^{-i\beta J_y} R(\alpha)^\dagger R(\alpha) e^{-i\gamma J_z}. \quad (26)$$

This process leads to the final result,

$$R(\alpha, \beta, \gamma) = e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z}. \quad (27)$$

Now, all generators are expressed with respect to components along the original axes, but seemingly the order of the rotations is “backwards,” we start on the right with the  $\gamma$  rotation, followed by  $\beta$ , and last the  $\alpha$ -term.

## C Transformation of Angular Momentum Eigenvectors or Eigenfunctions

Having derived a useful expression for the most general rotation operator, we can now give an expression for a rotated state vector that is an eigenvector of both  $\vec{J}^2$  and  $J_z$  (and other operators commuting with these two), in terms of the original eigenvectors of this type

$$|(JM)_{\text{rot.}}\rangle = R(\alpha, \beta, \gamma)|JM\rangle = \sum_{\mu} |J\mu\rangle \langle J\mu| R(\alpha, \beta, \gamma) |JM\rangle, \quad (28)$$

where, for simplicity of notation, we have omitted all quantum numbers other than  $J$  and  $M$  (associated with the remaining operators). Also, the matrix elements of operators,  $J_z$  and  $J_y$  are diagonal in the quantum number  $J$ . Thus, the  $J$  sum disappears from the unit operator,  $\sum_{J,\mu} |J\mu\rangle \langle J\mu|$ . The rotation matrix is usually

denoted by the symbol  $D$  (for the German word “Darstellung,” or representation), because this rotation matrix is an irreducible representation matrix of the rotation group  $SO(3)$  for integral angular momenta or the unitary group  $SU(2)$  for  $\frac{1}{2}$ -integral spins.

$$\langle JM|e^{-i\alpha J_z}e^{-i\beta J_y}e^{-i\gamma J_z}|JM\rangle = D_{\mu M}^J(\alpha, \beta, \gamma)^*. \quad (29)$$

The  $*$  is added so the simple exponential factors have + signs; (but this notation is not universal!)

$$D_{\mu M}^J(\alpha, \beta, \gamma) = e^{+i\mu\alpha} d_{\mu M}^J(\beta) e^{+iM\gamma}, \quad (30)$$

where

$$d_{\mu M}^J(\beta) = \langle JM|e^{-i\beta J_y}|JM\rangle \quad (31)$$

is a *real* function of  $\beta$ , because the matrix elements of  $iJ_y$  are always real in the standard angular momentum conventions. (Therefore, no  $*$  was needed on the  $d$  function.)

We can also convert eq. (28) into an equation for angular-momentum eigenfunctions

$$\begin{aligned} \langle \vec{r}|(JM)_{\text{rot.}} \rangle &= (\psi_{\text{rot.}})_{JM}(r, \theta, \phi, \vec{\sigma}) = \psi_{JM}(r, \theta', \phi', \vec{\sigma}') \\ &= \sum_{\mu} \psi_{J\mu}(r, \theta, \phi, \vec{\sigma}) D_{\mu M}^J(\alpha, \beta, \gamma)^*, \end{aligned} \quad (32)$$

where we have now used primed angles for the angles in the rotated angular momentum eigenfunction. Recall  $\theta', \phi' = \theta, (\phi - \alpha)$  for the simple  $z$  rotation with  $\beta = 0, \gamma = 0$ . In general,  $\theta', \phi'$  are complicated functions of  $\theta, \phi, \alpha, \beta, \gamma$ . We can write the inverse of this transformation

$$\psi_{JM}(r, \theta, \phi, \vec{\sigma}) = \sum_{\mu} \psi_{J\mu}(r, \theta', \phi', \vec{\sigma}') ((D^{-1})_{\mu M}^J)^*. \quad (33)$$

Now, making use of the unitary property of the  $D$  matrix,

$$\psi_{JM}(r, \theta, \phi, \vec{\sigma}) = \sum_{\mu} D_{M\mu}^J(\alpha, \beta, \gamma) \psi_{J\mu}(r, \theta', \phi', \vec{\sigma}'). \quad (34)$$

The job of calculating the  $d_{\mu M}^J(\beta)$  of eq. (31) remains. For the smallest  $J$  values, this process is quite straightforward. For example, for  $J = \frac{1}{2}$ , with

$$\mathbf{1} = \sigma_y^2 = \sigma_y^4 = \dots, \quad \sigma_y = \sigma_y^3 = \sigma_y^5 \dots, \quad (35)$$

so

$$e^{-i\frac{\beta}{2}\sigma_y} = \sum_n \left( \frac{-i\beta}{2} \right)^n \frac{(\sigma_y)^n}{n!} = \mathbf{1} \cos\left(\frac{\beta}{2}\right) - i\sigma_y \sin\left(\frac{\beta}{2}\right). \quad (36)$$

Substituting the matrices

$$\mathbf{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \text{and} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ +i & 0 \end{pmatrix}, \quad (37)$$

we get the  $2 \times 2 d$  matrix

$$d_{m'm}^{\frac{1}{2}}(\beta) = \begin{pmatrix} \cos \frac{\beta}{2} & -\sin \frac{\beta}{2} \\ +\sin \frac{\beta}{2} & \cos \frac{\beta}{2} \end{pmatrix}. \quad (38)$$

Similarly, for  $J = 1$ , using the  $3 \times 3$  matrix relations in this case,

$$J_y = \begin{pmatrix} 0 & \frac{-i}{\sqrt{2}} & 0 \\ \frac{+i}{\sqrt{2}} & 0 & \frac{-i}{\sqrt{2}} \\ 0 & \frac{+i}{\sqrt{2}} & 0 \end{pmatrix} = J_y^3 = J_y^5 = \dots, \quad (39)$$

and

$$J_y^2 = \begin{pmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} = J_y^4 = J_y^6 = \dots, \quad (40)$$

we get

$$e^{-i\beta J_y} = \mathbf{1} - i J_y \sin \beta + J_y^2 (\cos \beta - 1), \quad (41)$$

leading to

$$d_{M'M}^{J=1} = \begin{pmatrix} \frac{1+\cos \beta}{2} & -\frac{\sin \beta}{\sqrt{2}} & \frac{1-\cos \beta}{2} \\ \frac{\sin \beta}{\sqrt{2}} & \cos \beta & -\frac{\sin \beta}{\sqrt{2}} \\ \frac{1-\cos \beta}{2} & \frac{\sin \beta}{\sqrt{2}} & \frac{1+\cos \beta}{2} \end{pmatrix}. \quad (42)$$

For higher values of  $J$ , this direct method of calculating the  $d$  matrices will of course become more and more difficult, and we shall have to find a better method.

## D General Expression for the Rotation Matrices

Although we know the matrix elements of  $J_y = -\frac{i}{2}(J_+ - J_-)$ , the calculation of  $(J_y)^n$  (in the expansion of the exponential  $e^{-i\beta J_y}$ ) is complicated because of the noncommutability of the operators  $J_+$  and  $J_-$ . The calculation of the  $d$  matrix would be straightforward if we could restructure the rotation operator in the form,

$$e^{\beta_+ J_+} e^{\beta_0 J_0} e^{\beta_- J_-}, \quad \text{or} \quad e^{\gamma_- J_-} e^{\gamma_0 J_0} e^{\gamma_+ J_+}.$$

In principle, the transformation of an operator product of the form  $e^A e^B$  into the form  $e^C$ , where  $A$  and  $B$  are noncommuting operators (or their matrix realizations) can be achieved by the so-called Baker–Campbell–Hausdorff relation

$$\begin{aligned} e^A e^B &= e^C, \quad \text{with} \\ C &= A + B + \frac{1}{2}[A, B] + \frac{1}{12}([A, [A, B]] + [B, [B, A]]) + \dots, \end{aligned} \quad (43)$$

where the  $\dots$  involves triple and quadruple and ever higher commutators of the operators  $A$  and  $B$ . The Baker–Campbell–Hausdorff expansion is very useful in cases in which the multiple commutators are all zero, say, after the second or third term. For the angular momentum algebra, unfortunately, the series is an infinite

one, with ever more complicated coefficients. The desired final result, however, depends only on the angular momentum commutator algebra. The coefficients,  $\beta_{\pm}$ ,  $\beta_0$ , or  $\gamma_{\pm}$ ,  $\gamma_0$ , depend only on the commutator algebra of  $J_+$ ,  $J_-$ , and  $J_0$ , not on the quantum number,  $J$ . It will therefore be sufficient to use the simplest nontrivial representation of the rotation operator, viz., the representation for  $J = \frac{1}{2}$ , where we deal with extremely simple  $2 \times 2$  matrices. It will be useful to solve a slightly more general problem, and “disentangle” the more general operator,  $(a_+ J_+ + a_0 J_0 + a_- J_-)$  through

$$e^{(a_+ J_+ + a_0 J_0 + a_- J_-)} = e^{b_+ J_+} e^{(ln b_0) J_0} e^{b_- J_-} = e^{c_- J_-} e^{(lnc_0) J_0} e^{c_+ J_+}. \quad (44)$$

(We have renamed  $\beta_0 = ln b_0$ ,  $\beta_{\pm} = b_{\pm}$ , for convenience, similarly for the  $\gamma_{\pm}$ ,  $\gamma_0$ . Now,

$$\text{for } J = \frac{1}{2},$$

$$J_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad J_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad J_0 = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}, \quad (45)$$

so  $(J_+)^n$  and  $(J_-)^n$ , with  $n \geq 2$ , are all null matrices. With

$$(a_+ J_+ + a_0 J_0 + a_- J_-) = \begin{pmatrix} \frac{1}{2} a_0 & a_+ \\ a_- & -\frac{1}{2} a_0 \end{pmatrix} \equiv \mathbf{a}, \quad \text{we have} \quad (46)$$

$$\mathbf{a}^2 = \begin{pmatrix} (\frac{1}{4} a_0^2 + a_+ a_-) & 0 \\ 0 & (\frac{1}{4} a_0^2 + a_+ a_-) \end{pmatrix} = a^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = a^2 \mathbf{1}, \quad (47)$$

and with  $\mathbf{a}^{2n} = a^{2n} \mathbf{1}$  and  $\mathbf{a}^{2n+1} = a^{2n} \mathbf{a}$ , we have

$$e^{(a_+ J_+ + a_0 J_0 + a_- J_-)} = \begin{pmatrix} \cosh a + \frac{1}{2} \frac{a_0}{a} \sinh a & \frac{a_+}{a} \sinh a \\ \frac{a_-}{a} \sinh a & \cosh a - \frac{1}{2} \frac{a_0}{a} \sinh a \end{pmatrix} \equiv \cosh a \mathbf{1} + \frac{\sinh a}{a} \mathbf{a}. \quad (48)$$

[The scalar  $a$  is defined through  $a^2 = (\frac{1}{4} a_0^2 + a_+ a_-)$ .] Similarly,

$$e^{b_+ J_+} e^{(ln b_0) J_0} e^{b_- J_-} = \frac{1}{\sqrt{b_0}} \begin{pmatrix} (b_0 + b_+ b_-) & b_+ \\ b_- & 1 \end{pmatrix}, \quad (49)$$

and

$$e^{c_- J_-} e^{(lnc_0) J_0} e^{c_+ J_+} = \sqrt{c_0} \begin{pmatrix} 1 & c_+ \\ c_- & (\frac{1}{c_0} + c_+ c_-) \end{pmatrix}. \quad (50)$$

Now, the coefficients  $b_{\pm}$ ,  $b_0$  or  $c_{\pm}$ ,  $c_0$  can be evaluated in terms of the  $a_{\pm}$ ,  $a_0$  by comparing eqs. (49) or (50) with eq. (48). We are interested in the rotation operator,  $e^{-i\beta J_z} = e^{-\frac{1}{2}\beta(J_+ - J_-)}$ . In our special case, therefore,  $a_{\pm} = \mp \frac{1}{2}\beta$ ,  $a_0 = 0$ . For this case, we have

$$b_{\pm} = \mp \tan \frac{\beta}{2}, \quad b_0 = \frac{1}{\cos^2(\frac{\beta}{2})}, \quad c_{\pm} = \mp \tan \frac{\beta}{2}, \quad c_0 = \cos^2(\frac{\beta}{2}), \quad (51)$$

so

$$\begin{aligned} e^{-i\beta J_z} &= e^{+\tan \frac{\beta}{2} J_-} (\cos^2(\frac{\beta}{2}))^{J_0} e^{-\tan \frac{\beta}{2} J_+} \\ &= e^{-\tan \frac{\beta}{2} J_+} \frac{1}{(\cos^2(\frac{\beta}{2}))^{J_0}} e^{+\tan \frac{\beta}{2} J_-}. \end{aligned} \quad (52)$$

With the first form of this result, we can write

$$\begin{aligned} d_{M'M}^J(\beta) &= \langle JM' | e^{+\tan \frac{\beta}{2} J_-} (\cos^2(\frac{\beta}{2}))^{J_0} e^{-\tan \frac{\beta}{2} J_+} | JM \rangle \\ &= \sum_n \frac{(\tan \frac{\beta}{2})^{M+n-M'} (\cos \frac{\beta}{2})^{2(M+n)} (-\tan \frac{\beta}{2})^n}{n!(M+n-M')!} \\ &\times \langle JM' | (J_-)^{M+n-M'} (J_+)^n | JM \rangle, \end{aligned} \quad (53)$$

where both  $n$  and  $M + n - M'$  must be positive integers (including zero) and restrictions on magnetic quantum numbers limit the sum over  $n$  to a sum from  $n \geq (M' - M)$  to  $n \leq (J - M)$  for the case  $M' - M \geq 0$ , and to a sum from  $n = 0$  to  $n \leq (J - M)$  for the case  $M' - M < 0$ . Using the simple known matrix elements of  $J_{\pm}$ , with

$$(J_+)^n |JM\rangle = \sqrt{\frac{(J-M)!(J+M+n)!}{(J-M-n)!(J+M)!}} |J(M+n)\rangle \quad \text{and} \quad (54)$$

$$(J_-)^{M+n-M'} |J(M+n)\rangle = \sqrt{\frac{(J+M+n)!(J-M')!}{(J+M')!(J-M-n)!}} |JM'\rangle. \quad (55)$$

We therefore get

$$\begin{aligned} d_{M'M}^J(\beta) &= \left[ \frac{(J-M)!(J-M')!}{(J+M)!(J+M')!} \right]^{\frac{1}{2}} \sum_n (-1)^n \\ &\times \frac{(J+M+n)!}{(J-M-n)!(M+n-M')!n!} (\cos \frac{\beta}{2})^{M+M'} (\sin \frac{\beta}{2})^{M-M'+2n}, \end{aligned} \quad (56)$$

where the sum over  $n$  ranges from  $n = \max.[0, M' - M]$  to  $n = (J - M)$ . In the very special case  $M = J$ , the integer  $n$  is restricted to  $n = 0$ , and

$$d_{M'J}^J(\beta) = \left[ \frac{(2J)!}{(J+M')!(J-M')!} \right]^{\frac{1}{2}} (\cos \frac{\beta}{2})^{J+M'} (\sin \frac{\beta}{2})^{J-M'}. \quad (57)$$

In the further special case  $M = -J$ , it will be useful to rename the summation index  $n = n' + J + M'$ , so eq. (56) yields

$$\begin{aligned} d_{M' - J}^J(\beta) &= (-1)^{J+M'} \left[ \frac{2J!}{(J+M')!(J-M')!} \right]^{\frac{1}{2}} (\cos \frac{\beta}{2})^{-J+M'} (\sin \frac{\beta}{2})^{J+M'} \\ &\times \sum_{n'=0}^{J-M'} \frac{(J-M')!(-1)^{n'}}{(J-M'-n')!n'!} (\sin^2 \frac{\beta}{2})^{n'} \end{aligned}$$

$$= (-1)^{J+M'} \left[ \frac{(2J)!}{(J+M'!)(J-M'!)!} \right]^{\frac{1}{2}} (\cos \frac{\beta}{2})^{J-M'} (\sin \frac{\beta}{2})^{J+M'}, \quad (58)$$

where we have used the binomial expansion of  $(1 - \sin^2(\beta/2))^{J-M'}$ .

## E Rotation Operators and Angular Momentum Coherent States

In Chapter 19, we defined two slightly different types of angular momentum coherent states  $|\alpha\rangle$  and  $|z\rangle$ , giving us two slightly different continuous representations of state vectors  $|\psi\rangle$  of our 3-D world in terms of functions of the complex variables,  $\alpha$  and  $z$ , where these complex numbers are related to the orientation of the physical system in our 3-D world. We are now in a position to see the relationship between these type I and type II coherent states. Such angular coherent states will again be very useful for physical systems best described through a statistical distribution of states with different orientations in our laboratory.

The type I coherent state was defined through

$$|\alpha\rangle = e^{\alpha^* J_+ - \alpha J_-} |J, M = -J\rangle = e^{-i\theta(\vec{J} \cdot \vec{n})} |J, M = -J\rangle, \quad (59)$$

where the complex variable,  $\alpha$ , is related to the angles  $\theta, \phi$  through  $\alpha = -(\theta/2)e^{i\phi}$ , so the unit vector,  $\vec{n}$ , lies in the  $x, y$ -plane and is rotated forward from the laboratory  $y$  axis through an angle  $\phi$ . The coherent state  $|\alpha\rangle$  can thus be expressed through a rotation operator, with Euler angles,  $\phi, \theta$ , and  $\gamma = 0$ :

$$|\alpha\rangle \equiv |\alpha(\theta, \phi)\rangle = R(\phi, \theta, 0) |J, M = -J\rangle. \quad (60)$$

We can therefore expand the type I angular coherent state through

$$\begin{aligned} |\alpha(\theta, \phi)\rangle &= \sum_{M=-J}^{+J} |JM\rangle D_{M,-J}^J(\phi, \theta, 0)^* \\ &= \sum_{M=-J}^{+J} |JM\rangle c_{J,M} (-1)^{J+M} \left(\sin \frac{\theta}{2}\right)^{J+M} \left(\cos \frac{\theta}{2}\right)^{J-M} e^{-iM\phi} \\ &= \sum_{M=-J}^{+J} |JM\rangle c_{J,M} \frac{(-1)^{J+M} \left(\tan \frac{\theta}{2}\right)^{J+M}}{\left(1 + \tan^2 \frac{\theta}{2}\right)^J} e^{-iM\phi}, \\ \text{with } c_{J,M} &= \sqrt{\frac{(2J)!}{(J+M)!(J-M)!}}, \end{aligned} \quad (61)$$

where we have used eq. (58) of the last section and the trivial identity,

$$\cos^2 \frac{\theta}{2} = (1 + \tan^2 \frac{\theta}{2})^{-1}.$$

The above expansion suggests the unit operator appropriate for this type of coherent state is

$$\begin{aligned} 1 &= \frac{(2J+1)}{4\pi} \int \int d\Omega |\alpha(\theta, \phi)\rangle \langle \alpha(\theta, \phi)| \\ &= \sum_{M,M'} \frac{(2J+1)}{4\pi} \int \int d\Omega D_{M,-J}^J(\phi, \theta, 0)^* D_{M',-J}^J(\phi, \theta, 0) |JM\rangle \langle JM'| \\ &= \sum_M |JM\rangle \langle JM|, \end{aligned} \quad (62)$$

where  $d\Omega = \sin \theta d\theta d\phi$ . The angular ranges in the integrals have their usual values, and we have made use of the orthonormality integral

$$\int \int d\Omega D_{M,\mu}^J(\phi, \theta, 0)^* D_{M',\mu'}^{J'}(\phi, \theta, 0) = \delta_{JJ'} \delta_{MM'} \delta_{\mu\mu'} \frac{4\pi}{(2J+1)}. \quad (63)$$

[The derivation of this integral is given in detail through eq. (30) of the next chapter; note the D functions with Euler angle  $\gamma = 0$  are of course independent of this third angle.]

The type II angular momentum coherent state, conversely, was defined by

$$\begin{aligned} |z\rangle &= e^{z^* J_+} |J, -J\rangle = \sum_{n=0}^{2J} \frac{z^{*n}}{\sqrt{n!}} \sqrt{\frac{(2J)!}{(2J-n)!}} |J, M = -J+n\rangle \\ &= \sum_{M=-J}^{+J} (z^*)^{J+M} \sqrt{\frac{(2J)!}{(J+M)!(J-M)!}} |JM\rangle. \end{aligned} \quad (64)$$

In Chapter 19, it was shown that the  $z$  space functions

$$\frac{z^n}{\sqrt{n!}} \sqrt{\frac{(2J)!}{(2J-n)!}}$$

formed an orthonormal set with respect to the measure

$$\frac{(2J+1)}{\pi} \frac{d^2 z}{(1 + zz^*)^{2J+2}}.$$

We can now complete our discussion of these angular momentum coherent states by showing explicitly the relationship between the two types of coherent states. Eq. (61) could have been obtained directly by putting the operator  $e^{\alpha^* J_+ - \alpha J_-}$  into normal ordered form through the comparison of eqs. (49) and (48) of the last section, yielding

$$\begin{aligned} |\alpha\rangle &= e^{b_+ J_+} \frac{1}{\left(\cos^2 \frac{\theta}{2}\right)^{J_0}} e^{b_- J_-} | -J\rangle \\ &= e^{b_+ J_+} \left(\cos^2 \frac{\theta}{2}\right)^J | -J\rangle, \end{aligned}$$

$$\text{with } b_{\pm} = \mp \tan \frac{\theta}{2} e^{\mp i\phi}. \quad (65)$$

Expansion of the exponential  $e^{b_+ J_+}$  again leads to eq. (61), but the present form suggests a change from the complex variable,  $\alpha$ , to the new complex variable  $z$ , where

$$z = \rho e^{i\phi} = -\tan \frac{\theta}{2} e^{i\phi},$$

so

$$|\alpha\rangle = e^{\bar{z}^* J_+} \frac{1}{(1 + zz^*)^J} | -J \rangle. \quad (66)$$

Also, with

$$\rho^2 = zz^* = \tan^2 \frac{\theta}{2},$$

we have

$$\sin \theta d\theta d\phi = 4\rho d\rho d\phi \frac{1}{(1 + \rho^2)^2}.$$

With this relation and eq. (66), the unit operator can be transformed into

$$\begin{aligned} & \frac{(2J+1)}{4\pi} \int \int d\Omega |\alpha\rangle \langle \alpha| \\ &= \frac{(2J+1)}{\pi} \int_0^{2\pi} d\phi \int_0^\infty \frac{d\rho \rho}{(1+\rho^2)^2} \frac{e^{\bar{z}^* J_+}}{(1+\rho^2)^J} | -J \rangle \langle -J | \frac{e^{z J_-}}{(1+\rho^2)^J} \\ &= \frac{(2J+1)}{\pi} \int \frac{d^2 z}{(1+zz^*)^{2J+2}} |z\rangle \langle z|. \end{aligned} \quad (67)$$

This relation is precisely the unit operator needed for the type II coherent states,  $|z\rangle$ , with a measure making the  $z$  space functions

$$\frac{z^n}{\sqrt{n!}} \sqrt{\frac{(2J)!}{(2J-n)!}}$$

into an orthonormal set, as shown in Chapter 19.

## The Clebsch–Gordan Series

For a system built from state vectors,  $|j_1 m_1\rangle$  and  $|j_2 m_2\rangle$  express the angular momentum–coupled state vector  $|j_1 j_2 jm\rangle$  for the rotated system in terms of the uncoupled state vectors, also in the rotated system

$$\begin{aligned} |(j_1 j_2 jm)_{\text{rot.}}\rangle &= \sum_{m_1, (m_2)} |(j_1 m_1)_{\text{rot.}}\rangle |(j_2 m_2)_{\text{rot.}}\rangle \langle j_1 m_1 j_2 m_2 | jm \rangle \\ &= \sum_{\mu} |j_1 j_2 j \mu\rangle D_{\mu m}^{j*} \\ &= \sum_{m_1, (m_2)} \sum_{\mu_1, (\mu_2)} |j_1 \mu_1\rangle |j_2 \mu_2\rangle D_{\mu_1 m_1}^{j_1*} D_{\mu_2 m_2}^{j_2*} \langle j_1 m_1 j_2 m_2 | jm \rangle. \end{aligned} \quad (1)$$

Now, expanding

$$|j_1 \mu_1\rangle |j_2 \mu_2\rangle = \sum_{j'} |j_1 j_2 j' \mu\rangle \langle j_1 \mu_1 j_2 \mu_2 | j' \mu \rangle, \quad (2)$$

left-multiplying by  $\langle j_1 j_2 j \mu |$ , and using the orthonormality of the coupled vectors  $\langle j_1 j_2 j \mu |$  and  $|j_1 j_2 j' \mu\rangle$ , we get (after complex conjugation of this equation, using the reality of the Clebsch–Gordan coefficients)

$$D_{\mu m}^j = \sum_{m_1, (m_2)} \sum_{\mu_1, (\mu_2)} D_{\mu_1 m_1}^{j_1} D_{\mu_2 m_2}^{j_2} \langle j_1 m_1 j_2 m_2 | jm \rangle \langle j_1 \mu_1 j_2 \mu_2 | j \mu \rangle. \quad (3)$$

This relation is the so-called Clebsch–Gordan series. This relation could be used in a build-up process to calculate the  $D$  functions for  $j = \frac{3}{2}$  from the known  $D$  functions for  $j = 1$  and  $j = \frac{1}{2}$ , and so on for  $D$  functions of higher  $j$  values.

Finally, from the inverse of the process used here, we get the second relation

$$D_{\mu_1 m_1}^{j_1} D_{\mu_2 m_2}^{j_2} = \sum_j D_{\mu m}^j \langle j_1 m_1 j_2 m_2 | jm \rangle \langle j_1 \mu_1 j_2 \mu_2 | j \mu \rangle. \quad (4)$$

## A Addition Theorem for Spherical Harmonics

Let us replace the angular momentum eigenfunctions  $\psi_{jm}(r, \theta, \phi, \vec{\sigma})$  by the spherical harmonics,  $Y_{lm}(\theta, \phi)$  and use the general rotation relation

$$Y_{lm}(\theta', \phi') = \sum_{\mu} Y_{l\mu}(\theta, \phi) D_{\mu m}^l(\alpha, \beta, \gamma)^*. \quad (5)$$

Suppose we have two particles, with position vectors  $\vec{r}_1 = (r_1, \theta_1, \phi_1)$  and  $\vec{r}_2 = (r_2, \theta_2, \phi_2)$ , (see Fig. 30.1), we first note

$$\sum_m Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) = \mathcal{I}, \quad (6)$$

where  $\mathcal{I}$  is a rotationally invariant quantity, depending only on the relative position of the two particles.

$$\begin{aligned} & \sum_m Y_{lm}^*(\theta'_1, \phi'_1) Y_{lm}(\theta'_2, \phi'_2) = \\ & \sum_m \sum_{\mu v} Y_{l\mu}^*(\theta_1, \phi_1) D_{\mu m}^l(\alpha, \beta, \gamma) Y_{lv}(\theta_2, \phi_2) D_{vm}^l(\alpha, \beta, \gamma)^*. \end{aligned} \quad (7)$$

Now, using the unitarity of the  $D$  functions,

$$\sum_m D_{\mu m}^l D_{vm}^{l*} = \delta_{\mu v}, \quad (8)$$

we have

$$\sum_m Y_{lm}^*(\theta'_1, \phi'_1) Y_{lm}(\theta'_2, \phi'_2) = \sum_{\mu} Y_{l\mu}^*(\theta_1, \phi_1) Y_{l\mu}(\theta_2, \phi_2) = \mathcal{I}. \quad (9)$$

To evaluate the invariant, choose the  $x'$ ,  $y'$ ,  $z'$  coordinate system, such that  $\theta'_1 = 0$ ; i.e., choose the  $z'$  axis along  $\vec{r}_1$ . Then,

$$Y_{lm}(0, \phi'_1) = \delta_{m0} \sqrt{\frac{(2l+1)}{4\pi}} \left( P_l(\cos 0) \right) = \delta_{m0} \sqrt{\frac{(2l+1)}{4\pi}}, \quad (10)$$

so

$$\mathcal{I} = \sqrt{\frac{(2l+1)}{4\pi}} Y_{l0}(\theta'_2 = \theta_{12}, 0) = \frac{(2l+1)}{4\pi} P_l(\cos \theta_{12}), \quad (11)$$

and

$$\sum_m Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) = \frac{(2l+1)}{4\pi} P_l(\cos \theta_{12}). \quad (12)$$

That is, this invariant is expressed in terms of the Legendre polynomial, expressed in terms of the angle  $\theta_{12}$  between the two vectors  $\vec{r}_1$  and  $\vec{r}_2$ .

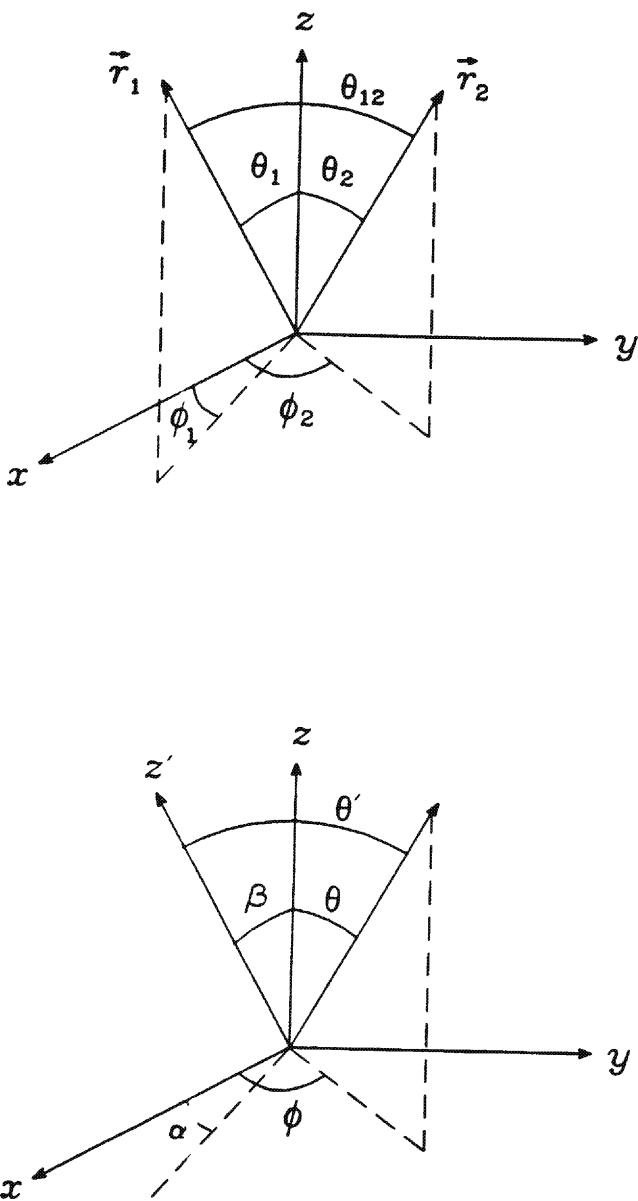


FIGURE 30.1.

By renaming  $\theta_2, \phi_2 = \theta, \phi$ , and  $\theta_1, \phi_1 = \beta, \alpha$ , and  $\theta_{12} = \theta'$ , i.e., by thinking of a single particle located at  $\vec{r}_2 \equiv (r, \theta, \phi)$  relative to the  $x, y, z$  coordinate system, while  $\vec{r}_2 \equiv (r, \theta', \phi')$  relative to the  $x', y', z'$  coordinate system, we can rewrite eq. (11) as

$$Y_{l0}(\theta', \phi') = \sqrt{\frac{4\pi}{(2l+1)}} \mathcal{I} = \sum_m \sqrt{\frac{4\pi}{(2l+1)}} Y_{lm}^*(\beta, \alpha) Y_{lm}(\theta, \phi). \quad (13)$$

Comparing this equation with

$$Y_{l0}(\theta', \phi') = \sum_m Y_{lm}(\theta, \phi) D_{m0}^{l*}(\alpha, \beta, 0), \quad (14)$$

we get

$$D_{m0}^l(\alpha, \beta, 0) = \sqrt{\frac{4\pi}{(2l+1)}} Y_{lm}(\beta, \alpha). \quad (15)$$

Also, using the unitarity of the  $D_{\mu m}^l$ , and writing the inverse to the Euler rotation transformation  $(\alpha, \beta, \gamma)$  as  $(-\gamma, -\beta, -\alpha)$ ,

$$\begin{aligned} D_{0m}^l(0, \beta, \gamma) &= D_{m0}^{l*}(-\gamma, -\beta, 0) = \sqrt{\frac{4\pi}{(2l+1)}} Y_{lm}^*(-\beta, -\gamma) \\ &= (-1)^m \sqrt{\frac{4\pi}{(2l+1)}} Y_{lm}(\beta, \gamma), \end{aligned} \quad (16)$$

so

$$D_{0m}^l(0, \beta, \gamma) = (-1)^m \sqrt{\frac{4\pi}{(2l+1)}} Y_{lm}(\beta, \gamma). \quad (17)$$

## B Integrals of $D$ Functions

We shall evaluate the following very useful integral:

$$\begin{aligned} I &= \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} d\alpha d\beta \sin \beta d\gamma D_{\mu_3 m_3}^{j_3*} D_{\mu_1 m_1}^{j_1} D_{\mu_2 m_2}^{j_2} \\ &= \int \int \int d\Omega_{\alpha\beta\gamma} D_{\mu_3 m_3}^{j_3*} D_{\mu_1 m_1}^{j_1} D_{\mu_2 m_2}^{j_2}. \end{aligned} \quad (18)$$

To evaluate this integral, let us use eq. (4)

$$D_{\mu_1 m_1}^{j_1} D_{\mu_2 m_2}^{j_2} = \sum_j \langle j_1 m_1 j_2 m_2 | jm \rangle \langle j_1 \mu_1 j_2 \mu_2 | j \mu \rangle D_{\mu m}^j \quad (19)$$

and the relation

$$D_{\mu_3 m_3}^{j_3*} = \left( e^{i\mu_3 \alpha} d_{\mu_3 m_3}^{j_3}(\beta) e^{im_3 \gamma} \right)^* = e^{-i\mu_3 \alpha} d_{\mu_3 m_3}^{j_3}(\beta) e^{-im_3 \gamma}, \quad (20)$$

where we have used the reality of the  $d$  function. In addition the  $d$  functions have the property

$$d_{\mu_3 m_3}^{j_3}(\beta) = (-1)^{\mu_3 - m_3} d_{-\mu_3, -m_3}^{j_3}(\beta). \quad (21)$$

For the values of  $j = \frac{1}{2}$  and  $j = 1$ , this equation follows by inspection, (see Chapter 29). For values of  $j \geq \frac{3}{2}$ , this equation follows from the build-up relation, eq. (3), and the fact that sign change under the transformation  $m_i \rightarrow -m_i$  in the  $m_i$ -dependent Clebsch–Gordan coefficient is balanced by the same sign change under the transformation  $\mu_i \rightarrow -\mu_i$  in the  $\mu_i$ -dependent Clebsch–Gordan coefficient. Our integral can then be transformed into

$$\begin{aligned} I &= \int \int \int d\Omega_{\alpha\beta\gamma} D_{\mu_3 m_3}^{j_3*} D_{\mu_1 m_1}^{j_1} D_{\mu_2 m_2}^{j_2} = \sum_j \langle j_1 m_1 j_2 m_2 | jm \rangle \langle j_1 \mu_1 j_2 \mu_2 | j \mu \rangle \\ &\times (-1)^{\mu_3 - m_3} \int \int \int d\Omega_{\alpha\beta\gamma} D_{-\mu_3, -m_3}^{j_3} D_{\mu\mu}^j. \end{aligned} \quad (22)$$

Using the Clebsch–Gordan series once more on the product of two  $D$  functions in our integral, we obtain

$$\begin{aligned} I &= \sum_j \sum_{j'} \langle j_1 m_1 j_2 m_2 | jm \rangle \langle j_1 \mu_1 j_2 \mu_2 | j \mu \rangle (-1)^{\mu_3 - m_3} \langle j \mu j_3 - \mu_3 | j' \mu - \mu_3 \rangle \\ &\times \langle jm j_3 - m_3 | j' m - m_3 \rangle \int \int \int d\Omega_{\alpha\beta\gamma} D_{\mu - \mu_3, m - m_3}^{j'}. \end{aligned} \quad (23)$$

Now, we can use explicitly

$$\begin{aligned} \int \int \int d\Omega_{\alpha\beta\gamma} D_{\mathcal{M}M}^L &= \int_0^{2\pi} d\alpha e^{iM\alpha} \int_0^{2\pi} d\gamma e^{iM\gamma} \int_0^\pi d\beta \sin \beta d_{\mathcal{M}M}^L \\ &= 2\pi \delta_{\mathcal{M}0} 2\pi \delta_{M0} \int_0^\pi d\beta \sin \beta d_{00}^L(\beta). \end{aligned} \quad (24)$$

We also use

$$d_{00}^L(\beta) = \sqrt{\frac{4\pi}{(2L+1)}} Y_{L0}(\beta, -) \quad \text{and} \quad Y_{00} = \frac{1}{\sqrt{4\pi}} \quad (25)$$

to get

$$\begin{aligned} \int \int \int d\Omega_{\alpha\beta\gamma} D_{\mathcal{M}M}^L &= \\ 2\pi \delta_{\mathcal{M}0} \delta_{M0} &\int_0^{2\pi} d\gamma \int_0^\pi d\beta \sin \beta \left( \sqrt{\frac{4\pi}{(2L+1)}} Y_{L0} \right) \left( \sqrt{4\pi} Y_{00}^* \right) \\ &= 8\pi^2 \delta_{\mathcal{M}0} \delta_{M0} \delta_{L0}, \end{aligned} \quad (26)$$

where we have made use of the orthonormality of the spherical harmonics. Thus, in eq. (23), we must have  $j' = 0$ ,  $\mu - \mu_3 = 0$ , and  $m - m_3 = 0$ . This result simplifies two of the Clebsch–Gordan coefficients. From the symmetry property

(123)  $\rightarrow$  (3 – 21) of the Clebsch–Gordan coefficients, we get

$$\langle jmj_3 - m_3|00\rangle = \frac{(-1)^{j-m_3}\langle 00j_3m_3|jm\rangle}{\sqrt{(2j+1)}} = \frac{(-1)^{j_3-m_3}}{\sqrt{(2j_3+1)}}\delta_{jj_3}\delta_{mm_3}. \quad (27)$$

Similarly,

$$\langle j\mu j_3 - \mu_3|00\rangle = \frac{(-1)^{\mu_3-j_3}}{\sqrt{(2j_3+1)}}\delta_{jj_3}\delta_{\mu\mu_3}. \quad (28)$$

With all of these relations, we get our final very simple result

$$\int \int \int d\Omega_{\alpha\beta\gamma} D_{\mu_3m_3}^{j_3*} D_{\mu_1m_1}^{j_1} D_{\mu_2m_2}^{j_2} = 8\pi^2 \frac{\langle j_1\mu_1j_2\mu_2|j_3\mu_3\rangle \langle j_1m_1j_2m_2|j_3m_3\rangle}{(2j_3+1)}. \quad (29)$$

A special case follows from the above by setting  $j_2 = \mu_2 = m_2 = 0$ . This leads to the orthonormality integral for the  $D$  functions

$$\int \int \int d\Omega_{\alpha\beta\gamma} D_{\mu m}^{j*} D_{\mu' m'}^{j'} = \frac{8\pi^2}{(2j+1)}\delta_{jj'}\delta_{\mu\mu'}\delta_{mm'}. \quad (30)$$

Another important special case follows by setting  $\mu_1 = 0, \mu_2 = 0, \mu_3 = 0$ , and now setting  $j_i = l_i$ , where  $l_i$  denotes the angular momentum quantum number is an integer. Using our result,

$$D_{m0}^l(\alpha, \beta, \gamma) = \sqrt{\frac{4\pi}{(2l+1)}} Y_{lm}(\beta, \alpha),$$

we get as a special case of the above

$$\begin{aligned} & \int_0^{2\pi} d\alpha \int_0^\pi d\beta \sin \beta Y_{l_3m_3}^* Y_{l_1m_1} Y_{l_2m_2} \\ &= \sqrt{\frac{(2l_1+1)(2l_2+1)}{(2l_3+1)4\pi}} \langle l_1m_1l_2m_2|l_3m_3\rangle \langle l_10l_20|l_30\rangle. \end{aligned} \quad (31)$$

We could also write this formula as

$$\langle nl'm'|Y_{l_0m_0}|nlm\rangle = \sqrt{\frac{(2l+1)(2l_0+1)}{(2l'+1)4\pi}} \langle lm_l m_0|l'm'\rangle \langle l_0l_20|l'0\rangle. \quad (32)$$

In earlier chapters, we worked hard to calculate these matrix elements for the special case with  $l_0 = 1$ . Now, everything follows from a knowledge of Clebsch–Gordan coefficients. Eqs. (31) and (32) tell us in particular these matrix elements are zero, unless  $l, l_0, l'$  satisfy the triangle condition of angular momentum addition, i.e., unless  $l' = |l - l_0|, |l - l_0| + 1, \dots, (l + l_0)$ . Also, these matrix elements are zero unless  $l + l_0 - l' = \text{even integer}$ . This parity selection rule follows because

$$\langle l_10l_20|l_30\rangle = (-1)^{l_1+l_2-l_3} \langle l_10l_20|l_30\rangle \quad (33)$$

a special case of the symmetry property

$$\langle j_1 - m_1j_2 - m_2|j_3 - m_3\rangle = (-1)^{j_1+j_2-j_3} \langle j_1m_1j_2m_2|j_3m_3\rangle. \quad (34)$$

Because the parity of the spherical harmonics,  $Y_{lm}$ , is given by  $(-1)^l$ , operators of odd parity can connect levels of even parity only to levels of odd parity and vice versa, whereas operators of even parity must preserve the parity of the states. In terms of the polar and azimuth angles,  $\theta, \phi$ , the space inversion operation can be achieved by the transformation  $\theta, \phi \rightarrow (\pi - \theta), (\phi + \pi)$ . The parity of the spherical harmonics follows from

$$Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi). \quad (35)$$

The result of eq. (31) or (32) can be generalized to a much wider class of operators, which transform under rotations in our three-space like the spherical harmonics. These operators are named spherical tensor operators and will be the subject of the next chapter. Their matrix elements between the appropriate angular momentum eigenstates can be shown to have a form similar to that of eq. (31).

## Problems

**39.** Calculate the Clebsch–Gordan coefficients,  $\langle j_1 m_1 | j m \rangle$ , for the three values,  $m_2 = +1, 0, -1$ , and  $j = (j_1 + 1), j_1, (j_1 - 1)$ , as functions of  $j_1$  and  $m$ . Calculate first the coefficients  $\langle j_1 m_1 | j - m | 1 - m_2 \rangle$  with  $m_2 = 0, +1$  from the known coefficients with  $m_2 = -1$ . [See eq. (20) of Chapter 27 for the latter.] Then use symmetry properties of the Clebsch–Gordan coefficients to relate these coefficients to  $\langle j_1 m_1 | j m \rangle$ .

**40.** Calculate  $D_{\mu m}^{\frac{3}{2}}(\alpha, \beta, \gamma)$  from a knowledge of  $d_{\mu_1 m_1}^{\frac{1}{2}}(\beta)$  and  $d_{\mu_2 m_2}^1(\beta)$  and the Clebsch–Gordan series.

A beam of particles with spin  $s = \frac{3}{2}$  is polarized by a filter so the particles are in a state with  $m_s = +\frac{3}{2}$ , with respect to the beam axis. If there are  $N$  (particles/cm<sup>2</sup> sec.) in the beam, how many particles will pass through a second filter set for  $m_s = +\frac{1}{2}$ , but with its axis rotated about a direction perpendicular to the beam through an angle of  $30^\circ$ ?

**41.** The 2-D isotropic harmonic oscillator and the D functions.

The eigenvectors  $|n_1 n_2\rangle$  of the 2-D isotropic harmonic oscillator Hamiltonian  $H = \hbar\omega_0(\frac{1}{2}p_x^2 + \frac{1}{2}x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}y^2)$ , with  $H|n_1 n_2\rangle = \hbar\omega_0(n_1 + n_2 + 1)|n_1 n_2\rangle$ , can be expressed in terms of oscillator creation operators

$$a_x^\dagger = \sqrt{\frac{1}{2}}(x - ip_x); \quad a_y^\dagger = \sqrt{\frac{1}{2}}(y - ip_y),$$

by

$$|n_1 n_2\rangle = \frac{(a_x^\dagger)^{n_1}}{\sqrt{n_1!}} \frac{(a_y^\dagger)^{n_2}}{\sqrt{n_2!}} |00\rangle.$$

Show that the operators,  $\Lambda_i$ , defined by

$$\Lambda_i = \frac{1}{2} (a_x^\dagger - a_y^\dagger)(\sigma_i) \begin{pmatrix} a_x \\ a_y \end{pmatrix},$$

where  $\sigma_i$  are  $2 \times 2$  Pauli spin matrices, satisfy standard angular momentum commutation relations, such that, if we define

$$\Lambda_{\pm} = (\Lambda_1 \pm i\Lambda_2), \quad \Lambda_0 = \Lambda_3,$$

$$[\Lambda_0, \Lambda_{\pm}] = \pm \Lambda_{\pm}, \quad [\Lambda_+, \Lambda_-] = 2\Lambda_0,$$

with

$$\Lambda_+ = a_x^\dagger a_y, \quad \Lambda_- = a_y^\dagger a_x, \quad \Lambda_0 = \frac{1}{2}(a_x^\dagger a_x - a_y^\dagger a_y).$$

Show that the  $|n_1 n_2\rangle$  are eigenvectors of the operators  $\vec{\Lambda}^2$  and  $\Lambda_0$ ,  $|\Lambda M_{\Lambda}\rangle$ , with

$$\Lambda = \frac{1}{2}(n_1 + n_2), \quad M_{\Lambda} = \frac{1}{2}(n_1 - n_2).$$

We therefore have

$$a_x^\dagger |0\rangle = |\Lambda = \frac{1}{2}, M_{\Lambda} = +\frac{1}{2}\rangle, \quad a_y^\dagger |0\rangle = |\Lambda = \frac{1}{2}, M_{\Lambda} = -\frac{1}{2}\rangle,$$

and

$$e^{-i\beta\Lambda_2} a_x^\dagger |0\rangle = \sum_{\bar{M}_{\Lambda}} |\frac{1}{2} \bar{M}_{\Lambda}\rangle d_{\bar{M}_{\Lambda}, +\frac{1}{2}}^{\frac{1}{2}}(\beta) = \left( a_x^\dagger \cos\left(\frac{\beta}{2}\right) + a_y^\dagger \sin\left(\frac{\beta}{2}\right) \right) |0\rangle,$$

$$e^{-i\beta\Lambda_2} a_y^\dagger |0\rangle = \sum_{\bar{M}_{\Lambda}} |\frac{1}{2} \bar{M}_{\Lambda}\rangle d_{\bar{M}_{\Lambda}, -\frac{1}{2}}^{\frac{1}{2}}(\beta) = \left( -a_x^\dagger \sin\left(\frac{\beta}{2}\right) + a_y^\dagger \cos\left(\frac{\beta}{2}\right) \right) |0\rangle.$$

If we now rename

$$\Lambda \rightarrow j, \quad M_{\Lambda} \rightarrow m, \quad \text{so} \quad n_1 = j + m; \quad n_2 = j - m,$$

we have

$$e^{-i\beta\Lambda_2} |n_1 n_2\rangle = \sum_{\bar{n}_1, \bar{n}_2} |\bar{n}_1 \bar{n}_2\rangle d_{\frac{1}{2}(\bar{n}_1 - \bar{n}_2), \frac{1}{2}(n_1 - n_2)}^{\frac{1}{2}(n_1 + n_2)}(\beta),$$

or

$$e^{-i\beta\Lambda_2} |jm\rangle = \sum_{m'} |jm'\rangle d_{m', m}^j(\beta) \\ = \frac{\left( a_x^\dagger \cos\left(\frac{\beta}{2}\right) + a_y^\dagger \sin\left(\frac{\beta}{2}\right) \right)^{j+m}}{\sqrt{(j+m)!}} \frac{\left( -a_x^\dagger \sin\left(\frac{\beta}{2}\right) + a_y^\dagger \cos\left(\frac{\beta}{2}\right) \right)^{j-m}}{\sqrt{(j-m)!}} |0\rangle.$$

Use this expression to derive a general expression for the  $d$  function:

$$d_{m', m}^j(\beta) = \sqrt{\frac{(j+m')!(j-m')!}{(j+m)!(j-m)!}} \sum_{\alpha} \frac{(-1)^{j-m-\alpha} (j+m)!(j-m)!}{(m+m'+\alpha)!(j-m'-\alpha)!\alpha!(j-m-\alpha)!} \\ \times \left( \sin\left(\frac{\beta}{2}\right) \right)^{2j-2\alpha-m-m'} \left( \cos\left(\frac{\beta}{2}\right) \right)^{2\alpha+m+m'}.$$

- 42.** Show that the Hamiltonian for an electron in a uniform external magnetic field,  $\vec{B}_0$ , in the  $z$  direction, with  $A_x = -\frac{1}{2}y_{\text{phys.}}B_0$ ,  $A_y = \frac{1}{2}x_{\text{phys.}}B_0$ , can be written in terms of dimensionless  $x$  and  $y$ , defined by

$$x_{\text{phys.}} = x\sqrt{\frac{\hbar}{m\omega_L}}, \quad y_{\text{phys.}} = y\sqrt{\frac{\hbar}{m\omega_L}}, \quad \text{with } \omega_L = \frac{|e|B_0}{2mc},$$

as

$$H = \hbar\omega_L \left( (a_x^\dagger a_x + a_y^\dagger a_y + 1) + i(a_y^\dagger a_x - a_x^\dagger a_y) \right) + \frac{p_z^2}{2m},$$

where

$$a_x = \sqrt{\frac{1}{2}}(x + ip_x), \quad a_x^\dagger = \sqrt{\frac{1}{2}}(x - ip_x),$$

$$a_y = \sqrt{\frac{1}{2}}(y + ip_y), \quad a_y^\dagger = \sqrt{\frac{1}{2}}(y - ip_y),$$

are 1-D harmonic oscillator annihilation and creation operators. Use the commutator algebra of the operators,  $\Lambda_+ = a_x^\dagger a_y$ ,  $\Lambda_- = a_y^\dagger a_x$ , and  $\Lambda_0 = \frac{1}{2}(a_x^\dagger a_x - a_y^\dagger a_y)$  (see problem 41) and standard angular momentum theory results to find the energy eigenvalues for  $H(x, y)$ . In particular, find the degeneracy,  $g_n$ , for the  $n^{\text{th}}$  level, with energy  $E_n$ .

For this purpose, use a basis in which the operators  $\vec{\Lambda}^2$  and  $\Lambda_2$ , rather than the conventional  $\Lambda^2$  and  $\Lambda_3$ , are diagonal. Also, the full energy includes a contribution from the free particle motion in the  $z$  direction,

$$E_{\text{total}} = E_n + \frac{\hbar^2 k^2}{2m}, \quad \text{with } k = 0 \rightarrow \infty,$$

where  $\hbar^2 k^2$  gives the eigenvalue of  $p_z^2$ . Also, try to give an explanation for the value of the degeneracy,  $g_n$ , in terms of the possible classical orbits of the electron.

# Spherical Tensor Operators

From the previous discussion, it is clear it would be advantageous to give vectors, such as  $\vec{r}$ , not in Cartesian component, but in spherical component form. Recalling

$$\begin{pmatrix} rY_{1+1} \\ rY_{10} \\ rY_{1-1} \end{pmatrix} = \sqrt{\frac{3}{4\pi}} \times \begin{pmatrix} -\frac{1}{\sqrt{2}}r \sin \theta e^{+i\phi} \\ r \cos \theta \\ +\frac{1}{\sqrt{2}}r \sin \theta e^{-i\phi} \end{pmatrix} = \sqrt{\frac{3}{4\pi}} \times \begin{pmatrix} -\frac{1}{\sqrt{2}}(x + iy) \\ z \\ +\frac{1}{\sqrt{2}}(x - iy) \end{pmatrix},$$

it will be useful to write the vector  $\vec{r}$  in terms of the spherical components  $(r_{+1}, r_0, r_{-1})$ , with

$$r_{+1} = -\frac{1}{\sqrt{2}}(x + iy), \quad r_0 = z, \quad r_{-1} = +\frac{1}{\sqrt{2}}(x - iy). \quad (1)$$

Note, in particular, the differences between  $r_{+1}$  and  $r_+ = (x + iy)$ , and  $r_{-1}$  and  $r_- = (x - iy)$ . Before generalizing this vector result to higher rank tensor components in spherical form, let us look at second rank tensors,  $T_{ij}$ , in Cartesian component form. Write the general second rank tensor in terms of a symmetric, traceless part,  $S_{ij}$ , an antisymmetric part,  $A_{ij}$ , and the trace  $\sum_\alpha T_{\alpha\alpha}$ .

$$\begin{aligned} T_{ij} &= \left( \frac{1}{2}(T_{ij} + T_{ji}) - \frac{1}{3}\delta_{ij} \sum_\alpha T_{\alpha\alpha} \right) + \frac{1}{2}(T_{ij} - T_{ji}) + \frac{1}{3}\delta_{ij} \sum_\alpha T_{\alpha\alpha} \\ &= S_{ij} + A_{ij} + \frac{1}{3}\delta_{ij} \sum_\alpha T_{\alpha\alpha}, \end{aligned} \quad (2)$$

where  $S_{ij} = S_{ji}$  and  $\sum_\alpha S_{\alpha\alpha} = 0$ , and  $A_{ij} = -A_{ji}$ . Under this decomposition of the nine components of the tensor, the  $9 \times 9$  rotation matrix  $O_{ij,\alpha\beta}$  that gives the rotated tensor components  $T'_{ij}$  in terms of the original  $T_{\alpha\beta}$  via

$$T'_{ij} = \sum_{\alpha, \beta} O_{ij,\alpha\beta} T_{\alpha\beta} \quad (3)$$

will split into three submatrices. The five independent components of the traceless, symmetric tensor,  $S_{ij}$ , transform only among themselves. The three components of the antisymmetric tensor,  $A_{ij}$ , will transform only among themselves, and the trace of the tensor is a rotationally invariant quantity. The five independent components of  $S_{ij}$  transform like the five components of a spherical harmonic,  $Y_{2m}$ . The three components of  $A_{ij}$  transform like the three components of a vector. We can see this at once if we build the tensor  $T_{ij}$  from two vectors  $(x, y, z)$  and  $(X, Y, Z)$ , with  $A_{12} = (xY - yX)$ ,  $A_{31} = (zX - xZ)$ , and  $A_{23} = (yZ - zY)$ , where these are the  $z$ ,  $y$ , and  $x$  components of the vector product  $\vec{r} \times \vec{R}$ . The trace of the tensor transforms like the spherical harmonic  $Y_{00}$ . We have thus succeeded in finding second rank tensor components that transform like spherical harmonics, with  $l = 2, 1$ , and  $0$ . As we go to higher rank tensors, this type of decomposition will become more difficult. For example, the 27 components of a third rank tensor will have 10 totally symmetric components. These components could be split further into seven components that transform like spherical harmonics, with  $l = 3$ , and three components that transform like the three components of a spherical harmonic, with  $l = 1$ . A single, totally antisymmetric tensor component exists, which is rotationally invariant; i.e., it transforms like a  $Y_{00}$ . The 16 remaining components of mixed symmetry could be split into two sets of five components that transform like spherical harmonics with  $l = 2$  and two sets of three components that transform like spherical harmonics, with  $l = 1$ .

## A Definition: Spherical Tensors

The set of  $(2k + 1)$  components of a spherical tensor  $T_q^k$  with  $q = +k, (k - 1), \dots, -k$  and  $k = \text{integer or } \frac{1}{2}\text{-integer}$  are a set of  $(2k + 1)$  operators that under rotations transform like the components of an angular momentum eigenfunction,  $\psi_{kq}$ . Recalling  $O_{\text{rot.}} = ROR^{-1}$ ,

$$(T_q^k)_{\text{rot.}} = R(\alpha, \beta, \gamma)T_q^kR^{-1}(\alpha, \beta, \gamma) = \sum_{v=-k}^k T_v^k D_{vq}^{k*}(\alpha, \beta, \gamma). \quad (4)$$

## B Alternative Definition

The components of a spherical tensor can also be defined through their commutator relations with the components of the total angular momentum vector of the system on which the tensor components act. In particular,

$$\begin{aligned} [J_0, T_q^k] &= q T_q^k, \\ [J_{\pm}, T_q^k] &= \sqrt{(k \mp q)(k \pm q + 1)} T_{(q \pm 1)}^k, \end{aligned} \quad (5)$$

where this definition essentially just involves infinitesimal rotation operators in place of the finite rotation operators of eq. (4). Let  $R$  correspond to an infinitesimal

rotation about the  $z$ ,  $x$ ,  $y$  axes. For example, with

$$R = e^{-i\alpha J_z}, \quad \text{and with} \quad \alpha \ll 1, \quad (6)$$

we get

$$\begin{aligned} RT_q^k R^{-1} &= (1 - i\alpha J_z + \dots) T_q^k (1 + i\alpha J_z + \dots) = T_q^k - i\alpha [J_z, T_q^k] + \dots \\ &= \sum_v D_{vq}^{k*} T_q^k = \delta_{vq} (1 - i\alpha q + \dots) T_q^k, \end{aligned} \quad (7)$$

where we have used

$$D_{vq}^{k*} = \langle kv | e^{-i\alpha J_z} | kq \rangle = \delta_{vq} (1 - i\alpha q + \dots), \quad (8)$$

thus leading to the first relation,  $[J_z, T_q^k] = q T_q^k$ . Similarly, combining infinitesimal rotations about the  $x$  and  $y$  axes, we are lead to the remaining two relations of eq. (5). We can use these relations to show the  $r_q$  of eq.(1) are spherical tensor components of rank  $k = 1$ . We can build higher rank spherical tensors from spherical vectors like these by a build-up process.

## C Build-up Process

If  $V_{q_1}^{k_1}$  and  $U_{q_2}^{k_2}$  are spherical tensors,  $T_q^k$ , defined by

$$T_q^k = \sum_{q_1, (q_2)} V_{q_1}^{k_1} U_{q_2}^{k_2} \langle k_1 q_1 k_2 q_2 | kq \rangle, \quad (9)$$

are spherical tensors of rank  $k$ . This relation follows from

$$\begin{aligned} RT_q^k R^{-1} &= \sum_{q_1, q_2} RV_{q_1}^{k_1} R^{-1} RU_{q_2}^{k_2} R^{-1} \langle k_1 q_1 k_2 q_2 | kq \rangle \\ &= \sum_{q_1, q_2} \sum_{q'_1, q'_2} V_{q'_1}^{k_1} U_{q'_2}^{k_2} D_{q'_1 q_1}^{k_1*} D_{q'_2 q_2}^{k_2*} \langle k_1 q_1 k_2 q_2 | kq \rangle \\ &= \sum_j \sum_{q'_1 q'_2} V_{q'_1}^{k_1} U_{q'_2}^{k_2} \left( \sum_{q_1, q_2} \langle k_1 q_1 k_2 q_2 | kq \rangle \langle k_1 q_1 k_2 q_2 | jq \rangle \right) \langle k_1 q'_1 k_2 q'_2 | jq' \rangle D_{q'_1 q'_2}^{j*} \\ &= \sum_j \sum_{q'_1 q'_2} V_{q'_1}^{k_1} U_{q'_2}^{k_2} (\delta_{jk}) \langle k_1 q'_1 k_2 q'_2 | jq' \rangle D_{q'_1 q'_2}^{j*} \\ &= \sum_{q'_1 q'_2} V_{q'_1}^{k_1} U_{q'_2}^{k_2} \langle k_1 q'_1 k_2 q'_2 | kq' \rangle D_{q'_1 q'_2}^{k*} = \sum_{q'} T_{q'}^k D_{q' q}^{k*}. \end{aligned} \quad (10)$$

We shall often also use the shorthand notation

$$T_q^k = \sum_{q_1, (q_2)} V_{q_1}^{k_1} U_{q_2}^{k_2} \langle k_1 q_1 k_2 q_2 | kq \rangle \equiv [V^{k_1} \times U^{k_2}]_q^k. \quad (11)$$

Let us now use this build-up process to construct tensors from two vectors each of spherical rank,  $l = 1$ . Let us choose the coordinate vector of eq. (1), with  $r_q = (r_{+1}, r_0, r_{-1})$ , and as our second vector, the momentum vector with spherical

components  $p_q = (p_{+1}, p_0, p_{-1})$ , and let us construct the spherical tensors

$$T_q^k = \sum_{q_1 q_2} r_{q_1} p_{q_2} \langle 1q_1 1q_2 | kq \rangle, \quad (12)$$

with  $k = 0, 1, 2$ . With  $k = 0$ , using

$$\langle 1q_1 1 - q_1 | 00 \rangle = \frac{1}{\sqrt{3}}(-1)^{1-q_1}, \quad (13)$$

we get

$$\begin{aligned} T_0^0 &= -\frac{1}{\sqrt{3}} \sum_q (-1)^q r_{+q} p_{-q} = -\frac{1}{\sqrt{3}} (\vec{r} \cdot \vec{p}) \\ &= -\frac{1}{\sqrt{3}} \left( \frac{1}{2}(x + iy)(p_x - ip_y) + \frac{1}{2}(x - iy)(p_x + ip_y) + zp_z \right). \end{aligned} \quad (14)$$

Note,

$$(\vec{r} \cdot \vec{p}) = \sum_q (-1)^q r_q^1 p_{-q}^1. \quad (15)$$

We can now generalize this scalar product to the more general scalar product of two tensors of rank  $k$ ,

$$(T^k \cdot T^k) = \sum_m (-1)^m T_m^k T_{-m}^k. \quad (16)$$

We shall continue by constructing next the coupled spherical tensor operator, constructed from the vectors  $\vec{r}$  and  $\vec{p}$  to make the spherical tensor of rank  $l = 1$ ,

$$T_q^1 = [r^1 \times p^1]_q^1. \quad (17)$$

$$\begin{aligned} T_{+1}^1 &= \langle 1110 | 11 \rangle r_{+1} p_0 + \langle 1011 | 11 \rangle r_0 p_{+1} \\ &= \frac{1}{\sqrt{2}} r_{+1} p_0 + (-\frac{1}{\sqrt{2}}) r_0 p_{+1} \\ &= -\frac{1}{2}(x + iy)p_z + \frac{1}{2}z(p_x + ip_y) = \frac{i}{\sqrt{2}} \left( -\frac{1}{\sqrt{2}}(L_x + iL_y) \right). \end{aligned} \quad (18)$$

In general,

$$[r^1 \times p^1]_m^1 = \frac{i}{\sqrt{2}} L_m, \quad \text{with } m = +1, 0, -1. \quad (19)$$

Also, in general,

$$\begin{aligned} [V^1 \times U^1]_{+1}^1 &= \frac{1}{2}(V_0 U_+ - V_+ U_0), \\ [V^1 \times U^1]_0^1 &= -\frac{1}{2\sqrt{2}}(V_+ U_- - V_- U_+), \\ [V^1 \times U^1]_{-1}^1 &= \frac{1}{2}(V_0 U_- - V_- U_0), \end{aligned} \quad (20)$$

where  $V_+ = (V_x + iV_y)$ ,  $V_- = (V_x - iV_y)$ . Note again the difference from the spherical components  $V_{+1} = -\frac{1}{\sqrt{2}}V_+$  and  $V_{-1} = +\frac{1}{\sqrt{2}}V_-$ . Finally, we build a spherical tensor of rank  $l = 2$  from two vectors. The results for the five components are

$$[V^1 \times U^1]_{+2}^2 = \frac{1}{2}V_+ U_+,$$

$$\begin{aligned}
[V^1 \times U^1]_{+1}^2 &= -\frac{1}{2}(V_0 U_+ + V_+ U_0), \\
[V^1 \times U^1]_0^2 &= -\frac{1}{\sqrt{6}} \left[ \frac{1}{2}(V_+ U_- + V_- U_+) - 2V_0 U_0 \right], \\
[V^1 \times U^1]_{-1}^2 &= \frac{1}{2}(V_0 U_- + V_- U_0), \\
[V^1 \times U^1]_{-2}^2 &= \frac{1}{2}V_- U_-. \tag{21}
\end{aligned}$$

## The Wigner–Eckart Theorem

The Wigner–Eckart theorem gives the  $M$  dependence of matrix elements of spherical tensor operators in a basis of good angular momentum. If  $J$  and  $M$  are the angular momentum quantum numbers for the total angular momentum operator appropriate for the space of a particular  $T_q^k$ ,

$$\langle \alpha' J' M' | T_q^k | \alpha J M \rangle = F(\alpha, J, k, \alpha', J') \langle JM k q | J' M' \rangle, \quad (1)$$

where  $\alpha$  is shorthand for all quantum numbers other than  $J, M$ , the total angular momentum quantum numbers for the system. The factor  $F(\alpha, J, k, \alpha', J')$  is independent of the quantum numbers  $M, q, M'$ . The dependence on  $M, q, M'$  sits solely in the Clebsch–Gordan coefficient. The factor  $F(\alpha, J, k, \alpha', J')$  is usually written in terms of the so-called “double-barred” or “reduced” matrix element,

$$F(\alpha, J, k, \alpha', J') = \frac{\langle \alpha' J' \| T^k \| \alpha J \rangle}{\sqrt{(2J'+1)}}, \quad (2)$$

so

$$\langle \alpha' J' M' | T_q^k | \alpha J M \rangle = \frac{\langle \alpha' J' \| T^k \| \alpha J \rangle}{\sqrt{(2J'+1)}} \langle JM k q | J' M' \rangle. \quad (3)$$

The factor  $1/\sqrt{(2J'+1)}$  is factored out of the  $M, q, M'$ -independent factor for convenience. (It makes the absolute value of the reduced or double-barred matrix element invariant to bra, ket interchange). Also, the Wigner–Eckart theorem greatly reduces the labor of calculating matrix elements. We need to choose only one (convenient!) set  $M, q, M'$  to calculate the full matrix element. The rest then follow through the Clebsch–Gordan coefficient. A very important special case is the one for rotationally invariant or scalar,  $k = 0$ , operators. Because  $\langle JM00 | J' M' \rangle =$

$1\delta_{JJ'}\delta_{MM'}$ , the matrix element of a scalar ( $k = 0$ ) operator is *independent* of  $M$ . The important case is that of a Hamiltonian operator of an isolated system. Because the properties of the system cannot depend on the orientation of the frame of reference from which it is viewed, the Hamiltonian must be a spherical tensor of rank  $l = 0$ . The energies will be independent of the quantum number  $M$ . The  $(2J + 1)$ -fold degeneracy of the energy levels can be removed only through the action of external perturbations. More important for calculational purposes, we can choose any convenient  $M$ , such as  $M = J$ , to calculate the energies of the isolated (unperturbed) system.

We now briefly give a few double-barred matrix elements of some simple operators. The “extra”  $\sqrt{(2J' + 1)}$  factor, part of the definition of the double barred matrix element, leads to the fact that the reduced matrix element of the simple unit operator is not unity.

$$\langle J' \parallel 1 \parallel J \rangle = \sqrt{(2J + 1)}\delta_{JJ'}. \quad (4)$$

For brevity of notation, we omit the additional quantum numbers  $\alpha$ . Next, from the matrix element

$$\langle JM | J_0 | JM \rangle = M, \quad (5)$$

and the value of the Clebsch–Gordan coefficient,

$$\langle JM 10 | JM \rangle = \frac{M}{\sqrt{J(J + 1)}}, \quad (6)$$

we get the double-barred matrix element for  $\vec{J} = J^{k=1}$ :

$$\langle J' \parallel J^1 \parallel J \rangle = \sqrt{(2J + 1)J(J + 1)}\delta_{JJ'}. \quad (7)$$

As a third example, from our result for the matrix element of  $Y_{l_0 m_0}$  in an orbital angular momentum basis, we can read off at once (from eq. (32) of Chapter 30)

$$\langle l' \parallel Y^{l_0} \parallel l \rangle = \sqrt{\frac{(2l + 1)(2l_0 + 1)}{4\pi}} \langle l 0 l_0 0 | l' 0 \rangle. \quad (8)$$

Before proving the Wigner–Eckart theorem, let us give a useful, special case as follows.

## A Diagonal Matrix Elements of Vector Operators

The matrix element of any vector operator,  $\vec{V} = V_q^1$ , *diagonal* in  $J$ , is given by

$$\langle \alpha' J(M + q) | V_q | \alpha JM \rangle = \frac{1}{J(J + 1)} \langle \alpha' J(M + q) | (\vec{V} \cdot \vec{J}) J_q | \alpha JM \rangle. \quad (9)$$

(The theorem does *not* apply, however, to matrix elements off-diagonal in  $J$ , which may also be nonzero!). To prove the theorem, we make repeated use of the Wigner–Eckart theorem

$$\langle \alpha' J(M + q) | (\vec{V} \cdot \vec{J}) J_q | \alpha JM \rangle =$$

$$\begin{aligned}
& \sum_m (-1)^m \langle \alpha' J(M+q) | V_{-m} | \alpha J(M+m+q) \rangle \\
& \times \langle \alpha J(M+m+q) | J_m | \alpha J(M+q) \rangle \langle \alpha J(M+q) | J_q | \alpha JM \rangle \\
& = \sum_m (-1)^m \frac{\langle \alpha' J \| V^1 \| \alpha J \rangle}{\sqrt{(2J+1)}} \langle J(M+m+q) 1 - m | J(M+q) \rangle \\
& \times \langle J(M+q) 1 m | J(M+m+q) \rangle \sqrt{J(J+1)} \langle JM 1 q | J(M+q) \rangle \sqrt{J(J+1)} \\
& = J(J+1) \sum_m \left( \langle J(M+m+q) 1 - m | J(M+q) \rangle \right)^2 \\
& \quad \times \langle JM 1 q | J(M+q) \rangle \frac{\langle \alpha' J \| V^1 \| \alpha J \rangle}{\sqrt{(2J+1)}} \\
& = J(J+1) \langle JM 1 q | J(M+q) \rangle \frac{\langle \alpha' J \| V^1 \| \alpha J \rangle}{\sqrt{(2J+1)}} \\
& = J(J+1) \langle \alpha' J(M+q) | V_q^1 | \alpha JM \rangle,
\end{aligned} \tag{10}$$

where we have used  $(-1)^{2m} = +1$  and have done the  $m$  sum using the orthonormality of the Clebsch–Gordan coefficients.

## B Proof of the Wigner–Eckart Theorem

To derive the Wigner–Eckart theorem, consider the ket

$$\sum_{M,(q)} T_q^k | \alpha JM \rangle \langle JM k q | J' M' \rangle \equiv | \gamma \rangle, \tag{11}$$

where the ket  $| \gamma \rangle$  is a function of the quantum numbers  $J'$ ,  $M'$ , as well as  $\alpha$ ,  $J$ , and  $k$ . First, this ket is an eigenvector of the angular momentum operators with eigenvalues,  $J'$ ,  $M'$ . To show this, act on  $| \gamma \rangle$  first with  $J_+$  (subsequently with  $J_-$  and  $J_0$ ).

$$\begin{aligned}
J_+ | \gamma \rangle &= \sum_{M,(q)} J_+ T_q^k | \alpha JM \rangle \langle JM k q | J' M' \rangle \\
&= \sum_{M,(q)} \left( T_q^k J_+ + [J_+, T_q^k] \right) | \alpha JM \rangle \langle JM k q | J' M' \rangle.
\end{aligned} \tag{12}$$

From the spherical tensor character of  $T_q^k$ , we have

$$[J_+, T_q^k] = \sqrt{(k-q)(k+q+1)} T_{q+1}^k, \tag{13}$$

so

$$\begin{aligned}
J_+ | \gamma \rangle &= \sum_{M,(q)} \left( \sqrt{(J-M)(J+M+1)} \langle JM k q | J' M' \rangle T_q^k | \alpha J(M+1) \rangle \right. \\
&\quad \left. + \sqrt{(k-q)(k+q+1)} \langle JM k q | J' M' \rangle T_{q+1}^k | \alpha JM \rangle \right).
\end{aligned} \tag{14}$$

Now, rename the dummy summation indices as follows: In the first term, change  $M \rightarrow (M-1)$ ; in the second term, change  $q \rightarrow (q-1)$ , noting, however,  $M'$  is

a fixed number, so

$$J_+|\gamma\rangle = \sum_{M,(q)} \left( \sqrt{(J-M+1)(J+M)} \langle J(M-1)kq|J'M' \right. \\ \left. + \sqrt{(k-q+1)(k+q)} \langle JMk(q-1)|J'M' \rangle \right) T_q^k |\alpha JM\rangle. \quad (15)$$

The terms in large parentheses can be replaced, using recursion formula I for Clebsch–Gordan coefficients (eq. (14) of Chapter 27), to yield

$$J_+|\gamma\rangle = \sqrt{(J'-M')(J'+M'+1)} \sum_{M,(q)} T_q^k |\alpha JM\rangle \langle JMkq|J'(M'+1)\rangle; \quad (16)$$

i.e., the vector  $|\gamma\rangle$  with eigenvalues  $J'$ ,  $M'$  has been converted to a new vector  $|\gamma'\rangle$  in which the eigenvalue  $M'$  has been replaced by  $(M'+1)$ , all other labels, such as  $\alpha$ ,  $J$ ,  $K$ ,  $J'$ , being the same. In addition, the numerical multiplicative factor is the standard matrix element of the operator  $J_+$  acting on an eigenvector with quantum numbers  $J'$ ,  $M'$ . Similarly,

$$J_-|\gamma\rangle = \sqrt{(J'+M')(J'-M'+1)} \sum_{M,(q)} T_q^k |\alpha JM\rangle \langle JMkq|J'(M'-1)\rangle, \quad (17)$$

and

$$J_0|\gamma\rangle = M' \sum_{M,(q)} T_q^k |\alpha JM\rangle \langle JMkq|J'M'\rangle. \quad (18)$$

Thus, the ket  $|\gamma\rangle$  is an angular momentum eigenvector with eigenvalues  $J'$ ,  $M'$ , which is also dependent on the labels  $(\alpha, J, k)$ ,

$$|\gamma\rangle = |(\alpha, J, k)J'M'\rangle. \quad (19)$$

Therefore,

$$\langle \alpha'' J'' M'' | \gamma \rangle = \delta_{J' J''} \delta_{M' M''} F(\alpha, J, k; \alpha'', J''), \quad (20)$$

or (using barred labels for the summed quantum numbers),

$$\sum_{\bar{M}, \bar{q}} \langle \alpha'' J'' M'' | T_{\bar{q}}^k |\alpha J \bar{M}\rangle \langle J \bar{M} k \bar{q} | J'M' \rangle = \delta_{J' J''} \delta_{M' M''} F(\alpha, J, k; \alpha'', J''). \quad (21)$$

Multiplying both sides of this equation by  $\langle JMkq|J'M'\rangle$ , summing over  $J'$ , and using the orthogonality for Clebsch–Gordan coefficients, yields

$$\begin{aligned} & \sum_{\bar{M}, \bar{q}} \left( \sum_{J'} \langle J \bar{M} k \bar{q} | J'M' \rangle \langle JMkq | J'M' \rangle \right) \langle \alpha'' J'' M'' | T_{\bar{q}}^k |\alpha J \bar{M}\rangle \\ &= \sum_{\bar{M}, \bar{q}} \delta_{M \bar{M}} \delta_{q \bar{q}} \langle \alpha'' J'' M'' | T_{\bar{q}}^k |\alpha J \bar{M}\rangle \\ &= \sum_{J'} \delta_{J' J''} \delta_{M' M''} F(\alpha, J, k; \alpha'', J'') \langle JMkq | J'M' \rangle, \end{aligned} \quad (22)$$

leading to the desired result

$$\langle \alpha'' J'' M'' | T_q^k |\alpha JM\rangle = F(\alpha, J, k; \alpha'', J'') \langle JMkq | J'' M'' \rangle. \quad (23)$$

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## Nuclear Hyperfine Structure in One-Electron Atoms

We shall use the magnetic nuclear hyperfine structure calculation in one-electron atoms to illustrate how the Wigner–Eckart theorem can be exploited in actual calculations. So far, we have calculated the perturbed one-electron spectrum (in hydrogen or in alkali atoms) only under the assumption the nucleus (the proton in hydrogen or the alkali atomic nucleus) have a charge but no magnetic properties. Because the proton has a spin (with spin quantum number  $\frac{1}{2}$ ), it also has a magnetic moment, similarly for alkali atoms. The spin of the stable isotope of Na, e.g., is  $\frac{3}{2}$ , and hence, it also has a nuclear magnetic moment. These nuclear magnetic moments will have a magnetic interaction with the spin magnetic moment of the electron. In addition, the motion of the electron relative to the nucleus will set up an effective magnetic field at the nucleus (proportional to the orbital angular momentum of the electron). The magnetic moment of the nucleus will also lead to a  $-(\vec{\mu}^{\text{magn.}} \cdot \vec{B})$  magnetic interaction caused by this field. These magnetic interactions of nuclear origin will give rise to the so-called hyperfine structure splitting of the  $nlsj$  states of the one-electron atoms. If we call the electron magnetic moment  $\vec{\mu}_s$  and the nuclear magnetic moment  $\vec{\mu}_I$ ,

$$\vec{\mu}_s = \frac{e\hbar}{2mc} 2\vec{s} = -\frac{|e\hbar|}{2mc} 2\vec{s}, \quad \vec{\mu}_I = \frac{|e\hbar|}{2Mc} g_I \vec{I}, \quad (1)$$

where we use the vector,  $\vec{I}$ , for the nuclear spin operator, with quantum number,  $I$ , e.g.,  $I = \frac{1}{2}$  for the proton,  $I = \frac{3}{2}$  for  $^{23}\text{Na}$ . Also,  $m$  is the electron mass, whereas  $M$  is the proton mass. (Even in the Na nucleus, the magnetic moment is caused by the last odd valence proton in the nucleus, so it is the proton mass in the so-called nuclear magneton,  $\frac{|e\hbar|}{2Mc}$ , which gives a natural measure for nuclear magnetic moments.) The  $g$  factor for the nuclear magnetic moment is not simply equal to

2.0, as for the point electron (as follows from Dirac theory), but is “anomalous,” e.g.,  $g_I = 2 \times 2.793$  for the proton. This “anomalous” factor is now rather well understood in terms of the quark structure of the nucleon.

The magnet–magnet interaction between the magnetic moments of the electron and the nucleus is given by [see, e.g., J. D. Jackson, 2<sup>nd</sup> ed., eq. (5.73)]

$$\begin{aligned} H_{\text{magn. magn.}} &= \left( \left[ (\vec{\mu}_s \cdot \vec{\mu}_I) - 3\left(\frac{\vec{r}}{r} \cdot \vec{\mu}_s\right)\left(\frac{\vec{r}}{r} \cdot \vec{\mu}_I\right) \right] \frac{1}{r^3} - \frac{8\pi}{3} (\vec{\mu}_s \cdot \vec{\mu}_I) \delta(\vec{r}) \right) \\ &= \frac{e^2 \hbar^2}{2mMc^2} g_I \left( \left[ -(\vec{s} \cdot \vec{I}) + 3\left(\frac{\vec{r}}{r} \cdot \vec{s}\right)\left(\frac{\vec{r}}{r} \cdot \vec{I}\right) \right] \frac{1}{r^3} + \frac{8\pi}{3} (\vec{s} \cdot \vec{I}) \delta(\vec{r}) \right), \end{aligned} \quad (2)$$

including the delta-function term that comes into play only if the two magnets can be on top of each other. This so-called contact term, (part of *classical* electrodynamics according to J. D. Jackson, *Classical Electrodynamics*, New York: John Wiley, 1967), comes into play only in atomic s-states,  $l = 0$  states, where the electron has a finite probability of sitting “on” the nucleus. The additional  $-(\vec{\mu}_I \cdot \vec{B}_{\text{eff.}})$  term, with

$$\vec{B}_{\text{eff.}} = \frac{e}{cr^3} [\vec{r} \times \frac{\vec{p}}{m}] = -\frac{|e|\hbar}{mcr^3} \vec{l}, \quad (3)$$

caused by the effective magnetic field of the moving electron at the nucleus, leads to an additional interaction term

$$H_{\text{orb. nucl. magn.}} = \frac{e^2 \hbar^2}{2mMc^2} g_I (\vec{l} \cdot \vec{I}) \frac{1}{r^3}. \quad (4)$$

In these relations, the quantity  $r$  is  $r_{\text{phys.}} = a_0 r$ , where the last  $r$  is our usual dimensionless  $r$ . In terms of this dimensionless  $r$ , the combined magnetic interactions give

$$H_{\text{int.}} = \frac{mc^2 \alpha^4}{2} \frac{m}{M} g_I \left( \left[ -(\vec{s} \cdot \vec{I}) + 3\left(\frac{\vec{r}}{r} \cdot \vec{s}\right)\left(\frac{\vec{r}}{r} \cdot \vec{I}\right) \right] \frac{1}{r^3} + \frac{8\pi}{3} (\vec{s} \cdot \vec{I}) \delta(\vec{r}) + (\vec{l} \cdot \vec{I}) \frac{1}{r^3} \right), \quad (5)$$

where we have also used

$$\delta(a_0 \vec{r}) = \frac{1}{a_0^3} \delta(\vec{r}), \quad (6)$$

and  $\alpha = (1/137)$  is the fine structure constant. This hyperfine structure term is  $\frac{m}{M} g_I$  times the fine structure term. Now, express the magnetic moment–magnetic moment interaction in terms of spherical tensor operators. In terms of the coupled spherical tensors, defined by

$$[V^{k_1} \times U^{k_2}]_q^k \equiv \sum_{q_1, q_2} V_{q_1}^{k_1} U_{q_2}^{k_2} \langle k_1 q_1 k_2 q_2 | k q \rangle, \quad (7)$$

we need the spherical tensors  $[r^1 \times r^1]_q^2 \equiv r_q^2$ , and  $[s^1 \times I^1]_q^2$ . These have spherical components

$$r_{\pm 2}^2 = \frac{1}{2}(x \pm iy)^2, \quad r_{\pm 1}^2 = \mp z(x \pm iy), \quad r_0^2 = \frac{1}{\sqrt{6}}(2z^2 - x^2 - y^2), \quad (8)$$

and

$$\begin{aligned} [s^1 \times I^1]_{\pm 2}^2 &= \frac{1}{2}s_{\pm}I_{\pm}; & [s^1 \times I^1]_{\pm 1}^2 &= \mp \frac{1}{2}(s_{\pm}I_0 + s_0I_{\pm}), \\ [s^1 \times I^1]_0^2 &= -\frac{1}{\sqrt{6}}\left(\frac{1}{2}(s_+I_- + s_-I_+) - 2s_0I_0\right). \end{aligned} \quad (9)$$

Also,  $r_q^2$  can be expressed in terms of standard spherical harmonics by

$$r_q^2 = r^2 \sqrt{\frac{8\pi}{15}} Y_{2,q}(\theta, \phi). \quad (10)$$

In terms of these spherical tensors of rank,  $k = 2$ , the magnetic dipole–magnetic dipole interaction term can be expressed through

$$\begin{aligned} \left(-(\vec{s} \cdot \vec{I}) + 3(\vec{s} \cdot \frac{\vec{r}}{r})(\vec{I} \cdot \frac{\vec{r}}{r})\right) &= 3\sqrt{\frac{8\pi}{15}} \sum_q (-1)^q Y_{2,q} [s^1 \times I^1]_{-q}^2 \\ &= 3\sqrt{\frac{8\pi}{15}} (Y^2 \cdot [s^1 \times I^1]^2), \end{aligned} \quad (11)$$

where the dot in the last form stands for the generalized scalar product of two spherical tensors each of spherical rank 2. This type of interaction is therefore sometimes called a “tensor” interaction, but the term is somewhat of a misnomer. The full interaction is a scalar, a rotationally invariant  $k = 0$  spherical tensor, but the term “tensor” is used because it involves the scalar product of two spherical tensors each of spherical rank 2. Because we want to calculate matrix elements of this interaction in an  $|n|[l \times s]j \times I]FM_F\rangle$  basis, corresponding to the vector coupling

$$(\vec{l} + \vec{s}) + \vec{I} = \vec{j} + \vec{I} = \vec{F} \quad (12)$$

basis, rather than a

$$\vec{l} + (\vec{s} + \vec{I}) = \vec{l} + \vec{S} = \vec{F} \quad (13)$$

basis, we need to tailor the magnet–magnet interaction to the coupling scheme of eq. (12), where  $\vec{l}$  and  $\vec{s}$  are coupled to resultant  $\vec{j}$ , which is then coupled to the nuclear spin  $\vec{I}$  to resultant total angular momentum  $\vec{F}$ . The form of eq. (11) is tailored more to the coupling scheme of eq. (13), where the electron spin,  $\vec{s}$ , and the nuclear spin,  $\vec{I}$ , are coupled to total spin  $\vec{S}$ , which is then coupled with  $\vec{l}$  to resultant total angular momentum  $\vec{F}$ . By rearranging the order of the couplings, we can also express the magnet–magnet interaction through

$$\begin{aligned} \left(-(\vec{s} \cdot \vec{I}) + 3(\vec{s} \cdot \frac{\vec{r}}{r})(\vec{I} \cdot \frac{\vec{r}}{r})\right) \\ = -\sqrt{8\pi}([Y^2 \times s^1]^1 \cdot I^1) = -\sqrt{8\pi} \sum_q (-1)^q [Y^2 \times s^1]_q^1 I_{-q}^1. \end{aligned} \quad (14)$$

As a specific example, we shall now calculate the hyperfine splitting of the  $2p_{\frac{3}{2}}$ , i.e., the  $n = 2, l = 1, j = \frac{3}{2}$ , fine structure level of hydrogen. Because the proton

has a spin  $I = \frac{1}{2}$ , this level will be split into two hyperfine components, with quantum numbers  $F = 2$  and  $F = 1$ . Because the contact term, with the delta function, can contribute only in  $s$  states, with  $l = 0$ , for which the electron has a nonzero probability of being on the proton, this term cannot contribute to the  $p$ -state hyperfine splitting. Thus, both the nonzero terms have a  $\frac{1}{r^3}$  radial dependence and lead to the radial integral

$$\beta_{\text{h.f.s.}} = \frac{mc^2}{2} \alpha^4 \frac{m}{M} g_I \int_0^\infty dr r^2 |R_{nl}(r)|^2 \frac{1}{r^3}. \quad (15)$$

This hyperfine structure integral,  $\beta_{\text{h.f.s.}} = \frac{m}{M} g_I \beta_{nl}$ , where  $\beta_{nl} = \beta_{\text{f.s.}}$  gives the strength of the fine structure splitting.

We shall now exploit the Wigner–Eckart theorem in two ways: (1) Because  $H_{\text{int.}}$  is a  $k = 0$  scalar operator, it will be sufficient to calculate the diagonal matrix element of this interaction for states with  $M_F = F$ . (2) In addition, the calculation can be reduced to a calculation of the reduced or double-barred matrix elements of the two operators,  $[Y^2 \times s^1]_q^1$  and  $l_q^1$ , in the  $|n[l \times s]jm_j\rangle$  basis. The needed matrix elements of  $l_q^1$  are very simple and can then be combined with these after application of the Wigner–Eckart theorem. To calculate the double-barred matrix elements of  $[Y^2 \times s^1]^1$  and  $l^1$ , let us use the state with  $m_j = +j = +\frac{3}{2}$ ,

$$|[l = 1 \times s = \frac{1}{2}]j = \frac{3}{2} m_j = +\frac{3}{2}\rangle = |l = 1 \ m_l = +1 \ s = \frac{1}{2} \ m_s = +\frac{1}{2}\rangle, \quad (16)$$

for the calculation, so

$$\begin{aligned} & \langle j = m_j = \frac{3}{2} | [Y^2 \times s^1]_0^1 | j = m_j = \frac{3}{2} \rangle = \langle \frac{3}{2} \frac{3}{2} 10 | \frac{3}{2} \frac{3}{2} \rangle \frac{\langle \frac{3}{2} | [Y^2 \times s^1]^1 | \frac{3}{2} \rangle}{\sqrt{4}} \\ &= \langle l = m_l = 1, s = m_s = \frac{1}{2} | [Y^2 \times s^1]_0^1 | l = 1 m_l = 1, s = m_s = \frac{1}{2} \rangle \\ &= \langle 1 + 1 \frac{1}{2} + \frac{1}{2} | Y_{20} s_0 | 1 + 1 \frac{1}{2} + \frac{1}{2} \rangle \langle 2010 | 10 \rangle \\ &= \langle 1 \ m_l = +1 | Y_{20} | 1 \ m_l = +1 \rangle \langle +\frac{1}{2} | 2010 | 10 \rangle \\ &= \sqrt{\frac{3 \cdot 5}{3 \cdot 4\pi}} \langle 1120 | 11 \rangle \langle 1020 | 10 \rangle \langle 2010 | 10 \rangle \langle +\frac{1}{2} | \\ &= \frac{1}{5} \sqrt{\frac{1}{8\pi}}, \end{aligned} \quad (17)$$

where only the  $Y_{20}s_0$  component of  $[Y^2 \times s^1]_0^1$  contributes to our matrix element because it is diagonal in *both*  $m_l$  and  $m_s$ . This simplification is related to our “clever” choice of  $m_j = +\frac{3}{2}$  in the full matrix element. In the above, we have used eq. (32) of Chapter 30 for the matrix element of  $Y_{20}$  and the values of the Clebsch–Gordan coefficients

$$\begin{aligned} \langle 2010 | 10 \rangle &= \langle 1020 | 10 \rangle = -\sqrt{\frac{2}{5}}, \\ \langle 1120 | 11 \rangle &= +\sqrt{\frac{1}{10}}. \end{aligned} \quad (18)$$

Finally, using

$$\langle \frac{3}{2} \frac{3}{2} 10 | \frac{3}{2} \frac{3}{2} \rangle = \sqrt{\frac{3}{5}} \quad (19)$$

for the first step in eq. (17), we get the desired reduced matrix element

$$\langle \frac{3}{2} \| [Y^2 \times s^1]^1 \| \frac{3}{2} \rangle = \frac{1}{\sqrt{30\pi}}. \quad (20)$$

Similarly, we can get the reduced matrix element of  $l_q^1$  from

$$\begin{aligned} \langle j = \frac{3}{2} \ m_j = +\frac{3}{2} | l_0^1 | j = \frac{3}{2} \ m_j = +\frac{3}{2} \rangle &= \langle \frac{3}{2} \frac{3}{2} 10 | \frac{3}{2} \frac{3}{2} \rangle \frac{\langle \frac{3}{2} \| l^1 \| \frac{3}{2} \rangle}{\sqrt{4}} \\ &= \langle l = 1 \ m_l = +1 \ s = m_s = \frac{1}{2} | l_0 | l = 1 \ m_l = +1 \ s = m_s = \frac{1}{2} \rangle \\ &= +1, \end{aligned} \quad (21)$$

so

$$\langle \frac{3}{2} \| l^1 \| \frac{3}{2} \rangle = 2\sqrt{\frac{5}{3}}. \quad (22)$$

Although the calculation of this reduced matrix element in the state with  $j = (l + \frac{1}{2})$  was extremely trivial, we note an alternative method that might be useful for states with  $j = (l - \frac{1}{2})$  or for states with  $s > \frac{1}{2}$  and several possible  $j$  values. From eq. (9) of Chapter 32, we could also have written

$$\begin{aligned} \langle [l \times s]j \| \vec{l} \| [l \times s]j \rangle &= \frac{\langle [l \times s]j \| (\vec{l} \cdot \vec{j})\vec{j} \| [l \times s]j \rangle}{j(j+1)} \\ &= \frac{[j(j+1) + l(l+1) - s(s+1)]}{2j(j+1)} \langle j \| \vec{j} \| j \rangle \\ &= \frac{1}{2}[j(j+1) + l(l+1) - s(s+1)] \sqrt{\frac{(2j+1)}{j(j+1)}}, \end{aligned} \quad (23)$$

where we have used eq. (7) of Chapter 32 for the reduced matrix element of  $\vec{j} \equiv j^1$ , and have also used

$$(\vec{l} \cdot \vec{j}) = (\vec{l} \cdot (\vec{l} + \vec{s})) = (\vec{l} \cdot \vec{l}) + (\vec{l} \cdot \vec{s}), \quad (24)$$

with

$$(\vec{l} \cdot \vec{s}) = \frac{1}{2}[(\vec{j} \cdot \vec{j}) - (\vec{l} \cdot \vec{l}) - (\vec{s} \cdot \vec{s})]. \quad (25)$$

With  $l = 1$ ,  $s = \frac{1}{2}$ , and  $j = \frac{3}{2}$ , this relation immediately gives the result of eq. (22). Now that we have the reduced matrix elements of  $[Y^2 \times s^1]^1$  and  $l^1 \equiv \vec{l}$ , we can calculate the matrix elements of  $H_{\text{int}}$  in the needed states with  $M_F = F$ . First, for  $F = 2$ , with

$$|[j \times I]F \ M_F\rangle = |[\frac{3}{2} \times \frac{1}{2}]F = 2 \ M_F = +2\rangle = |j = m_j = \frac{3}{2} \ I = M_I = \frac{1}{2}\rangle, \quad (26)$$

we get

$$\begin{aligned}
& \langle F = M_F = 2 | H_{\text{int.}} | F = M_F = 2 \rangle = \beta_{\text{h.f.s.}}(-\sqrt{8\pi}) \\
& \times \langle F = M_F = 2 | ([Y_2 \times s^1]^1 \cdot I^1) + (\vec{I} \cdot \vec{I}) | F = M_F = 2 \rangle \\
& = \beta_{\text{h.f.s.}} \left( -\sqrt{8\pi} \langle j = m_j = \frac{3}{2} | [Y^2 \times s^1]_0^1 | j = m_j = \frac{3}{2} \rangle \right. \\
& \quad \left. + \langle j = m_j = \frac{3}{2} | l_0 | j = m_j = \frac{3}{2} \rangle \right) \langle I = M_I = \frac{1}{2} | I_0 | I = M_I = \frac{1}{2} \rangle \\
& = \beta_{\text{h.f.s.}} \left( -\sqrt{8\pi} \frac{\left(\frac{3}{2}\right) \| [Y^2 \times s^1]^1 \| \frac{3}{2}}{\sqrt{4}} + \frac{\left(\frac{3}{2}\right) \| l^1 \| \frac{3}{2}}{\sqrt{4}} \right) \langle \frac{3}{2} \frac{3}{2} 10 | \frac{3}{2} \frac{3}{2} \rangle (+\frac{1}{2}) \\
& = \beta_{\text{h.f.s.}} \left( -\sqrt{8\pi} \frac{1}{2\sqrt{30\pi}} + 2\sqrt{\frac{5}{3}} \cdot \frac{1}{2} \right) \sqrt{\frac{3}{5}} (+\frac{1}{2}) \\
& = \beta_{\text{h.f.s.}} \left( -\frac{1}{5} + 1 \right) (+\frac{1}{2}) = \frac{2}{5} \beta_{\text{h.f.s.}}. \tag{27}
\end{aligned}$$

For the state with  $F = 1$ , the calculation is somewhat more complicated. We shall again choose the state with  $M_F = F$  to do the calculation, where now

$$\begin{aligned}
| [j = \frac{3}{2} \times I = \frac{1}{2}] F = M_F = 1 \rangle &= \sum_{m_J M_I} |\frac{3}{2} m_J \frac{1}{2} M_I \rangle \langle \frac{3}{2} m_J \frac{1}{2} M_I | 11 \rangle \\
&= |\frac{3}{2} + \frac{3}{2} \frac{1}{2} - \frac{1}{2} \rangle \langle \frac{3}{2} + \frac{3}{2} \frac{1}{2} - \frac{1}{2} | 1 + 1 \rangle + |\frac{3}{2} + \frac{1}{2} \frac{1}{2} + \frac{1}{2} \rangle \langle \frac{3}{2} + \frac{1}{2} \frac{1}{2} + \frac{1}{2} | 1 + 1 \rangle \\
&= |\frac{3}{2} + \frac{3}{2} \frac{1}{2} - \frac{1}{2} \rangle \frac{\sqrt{3}}{2} + |\frac{3}{2} + \frac{1}{2} \frac{1}{2} + \frac{1}{2} \rangle (-\frac{1}{2}). \tag{28}
\end{aligned}$$

Calculating first the matrix element for the  $([Y^2 \times s^1]^1 \cdot I^1)$  term, we get

$$\begin{aligned}
& \langle [\frac{3}{2} \times \frac{1}{2}] F = 1 \ M_F = 1 | ([Y^2 \times s^1]^1 \cdot I^1) | [\frac{3}{2} \times \frac{1}{2}] F = 1 \ M_F = 1 \rangle \\
& = \frac{3}{4} \langle \frac{3}{2} + \frac{3}{2} \frac{1}{2} - \frac{1}{2} | [Y^2 \times s^1]_0^1 \ I_0 | \frac{3}{2} + \frac{3}{2} \frac{1}{2} - \frac{1}{2} \rangle \\
& + \frac{1}{4} \langle \frac{3}{2} + \frac{1}{2} \frac{1}{2} + \frac{1}{2} | [Y^2 \times s^1]_0^1 \ I_0 | \frac{3}{2} + \frac{1}{2} \frac{1}{2} + \frac{1}{2} \rangle \\
& - \frac{\sqrt{3}}{4} \langle \frac{3}{2} + \frac{3}{2} \frac{1}{2} - \frac{1}{2} | (-[Y^2 \times s^1]_{+1}^1 \ I_{-1}) | \frac{3}{2} + \frac{1}{2} \frac{1}{2} + \frac{1}{2} \rangle \\
& - \frac{\sqrt{3}}{4} \langle \frac{3}{2} + \frac{1}{2} \frac{1}{2} + \frac{1}{2} | (-[Y^2 \times s^1]_{-1}^1 \ I_{+1}) | \frac{3}{2} + \frac{3}{2} \frac{1}{2} - \frac{1}{2} \rangle, \tag{29}
\end{aligned}$$

where the state vectors in the four terms are given in the  $|j \ m_J \ I \ M_I\rangle$  basis. Noting the matrix elements of the spherical components of  $\vec{I}$  are given by

$$\langle \frac{1}{2} M_I | I_0 | \frac{1}{2} M_I \rangle = M_I \quad \text{and} \quad \langle \frac{1}{2} \pm \frac{1}{2} | I_{\pm} | \frac{1}{2} \mp \frac{1}{2} \rangle = \mp \frac{1}{\sqrt{2}}, \tag{30}$$

and using the Wigner–Eckart theorem for the matrix elements of the operators  $[Y^2 \times s^1]_q^1$  in the  $|j \ m_J\rangle$  basis, we get

$$\begin{aligned}
& -\sqrt{8\pi} \langle [\frac{3}{2} \times \frac{1}{2}] F = M_F = 1 | ([Y^2 \times s^1]^1 \cdot I^1) | [\frac{3}{2} \times \frac{1}{2}] F = M_F = 1 \rangle \\
& = -\sqrt{8\pi} \left[ \frac{3}{4} \langle \frac{3}{2} \frac{3}{2} 10 | \frac{3}{2} \frac{3}{2} \rangle (-\frac{1}{2}) + \frac{1}{4} \langle \frac{3}{2} \frac{1}{2} 10 | \frac{3}{2} \frac{1}{2} \rangle (+\frac{1}{2}) \right. \\
& \quad \left. + \frac{\sqrt{3}}{4} \langle \frac{3}{2} \frac{1}{2} 1 + 1 | \frac{3}{2} \frac{3}{2} \rangle (\frac{1}{\sqrt{2}}) + \frac{\sqrt{3}}{4} \langle \frac{3}{2} \frac{3}{2} 1 - 1 | \frac{3}{2} \frac{1}{2} \rangle (-\frac{1}{\sqrt{2}}) \right] \frac{1}{\sqrt{4}} \langle \frac{3}{2} \| [Y^2 \times s^1]^1 \| \frac{3}{2} \rangle
\end{aligned}$$

$$\begin{aligned}
&= -\sqrt{8\pi} \left[ \frac{3}{4} \sqrt{\frac{3}{5}} (-\frac{1}{2}) + \frac{1}{4} \frac{1}{\sqrt{15}} (+\frac{1}{2}) \right. \\
&\quad \left. + \frac{\sqrt{3}}{4} (-\sqrt{\frac{2}{5}})(\frac{1}{\sqrt{2}}) + \frac{\sqrt{3}}{4} (+\sqrt{\frac{2}{5}})(-\frac{1}{\sqrt{2}}) \right] \frac{1}{\sqrt{4}} \frac{1}{\sqrt{30\pi}} \\
&= +\frac{1}{6}. \tag{31}
\end{aligned}$$

The matrix element of the  $(\vec{l} \cdot \vec{I})$  term differs from this matrix element only by the ratio of the reduced matrix elements, which is a factor of  $-5$ . Thus,

$$\langle F = M_F = 1 | H_{\text{int.}} | F = M_F = 1 \rangle = \beta_{\text{h.f.s.}} (\frac{1}{6} - \frac{5}{6}) = -\frac{2}{3} \beta_{\text{h.f.s.}}. \tag{32}$$

Thus, the hyperfine levels of the hydrogen  $2p_{\frac{3}{2}}$  fine structure level, with  $F = 2$  and  $F = 1$  are shifted by  $+\frac{2}{3}\beta_{\text{h.f.s.}}$  and  $-\frac{2}{3}\beta_{\text{h.f.s.}}$ , leading to a splitting of  $\frac{16}{15}\beta_{\text{h.f.s.}}$ . We leave as an exercise the splitting for the  $2p_{\frac{1}{2}}$  fine structure level with a shift of  $+\frac{2}{3}\beta_{\text{h.f.s.}}$  for the  $F = 1$  hyperfine level and a shift of  $-2\beta_{\text{h.f.s.}}$  for the  $F = 0$  hyperfine level.

## Problems

- 43.** In a one-electron atom, such as sodium, find the relative intensities for the transitions,  $n[l\frac{1}{2}]j \rightarrow n'[(l-1)\frac{1}{2}]j'$  for the four possibilities:  $j = (l \pm \frac{1}{2})$ ;  $j' = (l-1) \pm \frac{1}{2}$ . Express your answers in terms of general functions of  $l$ . Show first that

$$\sum_{\alpha=x,y,z} |\langle n'l'\frac{1}{2}j'm' | \mu_{\alpha}^{(\text{el.})} | nl\frac{1}{2}jm \rangle|^2 = \sum_{q=\pm 1,0} |\langle n'l'\frac{1}{2}j'm' | \mu_q^{(\text{el.})} | nl\frac{1}{2}jm \rangle|^2,$$

where  $\mu_q^{(\text{el.})}$  are spherical components of the electric dipole moment operator. Also, show that

$$\sum_{m,q,m'} |\langle n'l'\frac{1}{2}j'm' | \mu_q^{(\text{el.})} | nl\frac{1}{2}jm \rangle|^2 = |\langle n'l'\frac{1}{2}j' | \vec{\mu}^{(\text{el.})} | nl\frac{1}{2}j \rangle|^2,$$

so only the reduced (or double-barred) matrix elements of  $\vec{\mu}^{(\text{el.})}$ , a spherical tensor of rank 1, need to be calculated. Also, use the fact that the  $m$  sublevels of the initial state are all populated with an equal probability of  $1/(2j+1)$ .

- 44.** In an atom with an atomic nucleus, with a nuclear spin,  $I \geq 1$ , a hyperfine interaction exists, caused by the electrostatic interaction between the nuclear electric quadrupole moment and the atomic electrons. In a one-electron atom, such as Na, this interaction gives rise to a hyperfine perturbation

$$H_{\text{int.}} = -e^2 \sum_m (-1)^m Q_{2,m} \sqrt{\frac{4\pi}{5}} Y_{2,-m}(\theta, \phi) \frac{1}{r^3},$$

where the  $Q_{2,m}$  are the (spherical) laboratory components of the nuclear quadrupole operator, a spherical tensor of rank 2, and  $r, \theta, \phi$  give the position of the valence electron. The  $^{23}_{11}\text{Na}_{12}$  nucleus has a spin  $I = \frac{3}{2}$  and a nuclear quadrupole moment,  $Q = 0.14$  barns ( $1 \text{ barn} \equiv 10^{-24} \text{ cm}^2$ ). “The” nuclear quadrupole moment,  $Q$ , is defined as

$$\begin{aligned} Q &= 2\langle IM_I = I | Q_{2,0} | IM_I = I \rangle = 2\langle II20 | II \rangle \frac{\langle I \| Q_2 \| I \rangle}{\sqrt{(2I+1)}} \\ &= 2\sqrt{\frac{I(2I-1)}{(2I+1)(I+1)(2I+3)}} \langle I \| Q_2 \| I \rangle. \end{aligned}$$

We can evaluate the reduced matrix element of  $Q_2$  in terms of the experimental  $Q$  through this relation. Also,  $Q$  is related to the nuclear charge density,  $\rho_{\text{nuc.}}$ , through

$$Q = \frac{1}{|e|} \int d\vec{r}_{\text{nuc.}} r_{\text{nuc.}}^2 (3 \cos^2 \theta_{\text{nuc.}} - 1) \rho_{\text{nuc.}},$$

so  $Q$  has the dimension  $\text{cm}^2$ , because the charge  $|e|$  is factored out in the definition.

Calculate the hyperfine splitting caused by this perturbation for the  $3p_{\frac{3}{2}}$  and  $3p_{\frac{1}{2}}$  levels of the Na atom. Show, in particular, the  $F=1, 2$  hyperfine levels for  $p_{\frac{1}{2}}$  are not affected by this perturbation, whereas the  $p_{\frac{3}{2}}$  state is split into hyperfine sublevels with  $F = 0, 1, 2, 3$ . Show, however, the  $F=1$  and  $F=3$  sublevels remain (accidentally) degenerate. Express the hyperfine splitting in terms of  $Q$  and the quantity

$$\beta_{nl} = \frac{me^4}{\hbar^2} \alpha^2 \int_0^\infty dr r^2 |R_{nl}(r)|^2 \frac{1}{r^3},$$

where  $r$  is the dimensionless radial coordinate measured in atomic units.

**45.** The hyperfine splitting of the  $1s_{\frac{1}{2}}$  ground state of the hydrogen atom arises solely through the delta function contact term of

$$H_{\text{h.f.int.}} = \frac{mc^2 \alpha^4}{2} \frac{m}{M} g_I \left( \left[ -(\vec{s} \cdot \vec{l}) + 3\left(\frac{\vec{r}}{r} \cdot \vec{s}\right)\left(\frac{\vec{r}}{r} \cdot \vec{l}\right) \right] \frac{1}{r^3} + \frac{8\pi}{3} (\vec{s} \cdot \vec{l}) \delta(\vec{r}) + (\vec{l} \cdot \vec{l}) \frac{1}{r^3} \right).$$

Calculate the hyperfine splitting of the hydrogen atom ground state. Find the numerical value of the energy difference between the  $F = 1$  and  $F = 0$  hyperfine sublevels. (Recall  $g_I = 2 \times 2.793$  for the proton.)

**46.** In a diatomic molecule with one atomic nucleus with a spin,  $I \geq 1$ , a hyperfine interaction exists through the electrostatic interaction between the nuclear electric quadrupole moment and the electric field at the nucleus caused by the molecular electrons and the second nuclear charge. This interaction gives rise to a quadrupole hyperfine perturbation

$$H_{\text{h.f.int.}} = eq \sum_m (-1)^m Q_{2,m} Y_{2,-m}(\theta, \phi) \sqrt{\frac{4\pi}{5}},$$

where  $Q_{2,m}$  are the (spherical) laboratory components of the nuclear quadrupole operator (see problem 44) and the angles  $\theta, \phi$  give the orientation in the laboratory of the diatomic molecule symmetry axis. The number,  $eq$ , gives the  $\theta, \phi$ -independent part of the molecular matrix element of the inhomogeneous electric field at the nucleus, using the molecular electronic wave function. Here,  $e$  is the electronic charge, and  $q$  is a commonly used notation. Assume the nuclear spin is  $I = 1$ . Find the hyperfine splitting of the first excited rotational state with  $J = 1$  and zeroth-order rotational wave function,  $\psi_{JM}^{\text{rot}} = Y_{J=1,M}(\theta, \phi)$ , as a function of  $eq$  and  $Q$ , where  $Q$  is “the” nuclear quadrupole moment, as defined in problem 44. That is, find the splitting of the rotational level with  $J = 1$  into hyperfine levels with  $F = 0, 1, 2$ , where  $\vec{F} = \vec{J} + \vec{I}$ .

**47.** A diatomic molecule rigid rotator with zeroth-order rotational energies,  $\hbar^2 J(J+1)/(2\mu r_e^2)$ , and zeroth-order rotational eigenfunctions,  $Y_{JM}(\theta, \phi)$ , has atomic nuclei with nuclear spins,  $I_1 = \frac{3}{2}$  and  $I_2 = \frac{1}{2}$ . Assume the nuclei have no electric quadrupole moments, so the hyperfine interaction is caused by a magnet-magnet type interaction leading to an interaction Hamiltonian of the form

$$H_{\text{int.}} = a(\vec{I}_1 \cdot \vec{I}_2) + b \left[ 3\left(\vec{I}_1 \cdot \frac{\vec{r}}{r}\right)\left(\vec{I}_2 \cdot \frac{\vec{r}}{r}\right) - (\vec{I}_1 \cdot \vec{I}_2) \right],$$

where  $\vec{r}$  is the vector pointing from nucleus 2 to nucleus 1, with angular coordinates,  $\theta, \phi$ , and  $a$  and  $b$  are constants. Assume, however,  $a \gg b$  [but both  $a, b \ll \hbar^2/(2\mu r_e^2)$ ]. For these values of the constants, the  $|(J[I_1 I_2]I)FM_F\rangle$  basis is a good basis for the hyperfine structure calculation. Here,  $\vec{I}_1 + \vec{I}_2 = \vec{I}$ , where  $\vec{I}$  is the total nuclear spin vector, and  $\vec{J} + \vec{I} = \vec{F}$ , where  $\vec{F}$  is the total angular momentum vector. Find the hyperfine energies as functions of  $a$  and  $b$  for the rotational state with  $J = 1$  and hyperfine multiplet with  $I = 1, F = 0, 1, 2$ , and  $I = 2, F = 1, 2, 3$ .

# 34

## Angular Momentum Recoupling: Matrix Elements of Coupled Tensor Operators in an Angular Momentum Coupled Basis

In Chapter 33, we evaluated the matrix elements of a vector-coupled spherical tensor of type  $[U^{k_1} \times V^{k_2}]_q^k$  in terms of the reduced matrix elements of both  $U^{k_1}$  and  $V^{k_2}$  in the appropriate angular momentum-coupled basis,

$$\langle [j'_1 \times j'_2]J'M' | [U^{k_1} \times V^{k_2}]_q^k | [j_1 \times j_2]JM \rangle,$$

where we managed to simplify the calculation by judicious use of the Wigner-Eckart theorem and convenient choices of magnetic quantum numbers. In some cases, however, the calculation still involved fairly tedious  $m$  sums of expressions involving products of Clebsch-Gordan coefficients. It is the purpose of this chapter to show matrix elements of the above type can be expressed in terms of so-called angular momentum recoupling coefficients. Because values of these recoupling coefficients are available through tabulations or computer codes, and in many cases through algebraic expressions, it will be valuable to study these recoupling coefficients.

### A The Recoupling of Three Angular Momenta: Racah Coefficients or 6-j Symbols

So far, we have studied transformations of states involving two commuting angular momentum operators from a basis

$|j_1 m_1 j_2 m_2\rangle$  simultaneous eigenvectors of  $\vec{j}_1^2, j_{1z}, \vec{j}_2^2, j_{2z}$ ,

to a basis with good total angular momentum,  $\vec{J} = \vec{j}_1 + \vec{j}_2$ ,

$$|j_1 j_2 JM\rangle \text{ simultaneous eigenvectors of } \vec{j}_1^2, \vec{j}_2^2, \vec{J}^2, J_z.$$

For states involving three commuting angular momentum operators, we require six angular momentum quantum numbers, hence, six commuting operators, e.g.,

$$\vec{j}_1^2, j_{1z}, \vec{j}_2^2, j_{2z}, \vec{j}_3^2, j_{3z},$$

for a complete specification of the basis:

$$|j_1 m_1 j_2 m_2 j_3 m_3\rangle.$$

As for the case of two angular momenta, it will often be advantageous to use a basis with good total angular momentum in which  $\vec{J}^2$  is diagonal. Now, however, the five commuting operators  $\vec{j}_1^2, \vec{j}_2^2, \vec{j}_3^2, \vec{J}^2$ , and  $J_z = j_{1z} + j_{2z} + j_{3z}$  will be insufficient. A sixth operator is needed. To find this sixth operator, we could couple to total  $\vec{J}$  in two ways

$$\begin{aligned} \vec{J} &= (\vec{j}_1 + \vec{j}_2) + \vec{j}_3 = \vec{j}_{12} + \vec{j}_3 \\ &= j_1 + (j_2 + j_3) = \vec{j}_1 + \vec{J}_{23}, \end{aligned} \quad (1)$$

and use the eigenvectors of the six commuting operators

$$\vec{j}_1^2, \vec{j}_2^2, \vec{j}_3^2, \vec{j}_{12}^2, \vec{J}^2, J_z :$$

$$|[j_1 j_2] J_{12} j_3] JM\rangle,$$

where we first couple the two angular momenta  $\vec{j}_1, \vec{j}_2$  to a state with good  $\vec{j}_{12}^2$ , or alternatively, we could use the eigenvectors of the six commuting operators

$$\vec{j}_1^2, \vec{j}_2^2, \vec{j}_3^2, \vec{j}_{23}^2, \vec{J}^2, J_z :$$

$$|[j_1 [j_2 j_3] J_{23}] JM\rangle,$$

where we couple the angular momentum  $\vec{j}_1$  to a state in which  $\vec{j}_2$  and  $\vec{j}_3$  have been coupled to a state of good  $\vec{j}_{23}^2$ . The transformation from the one basis to the other must be unitary

$$\begin{aligned} &|[j_1 j_2] J_{12} j_3] JM\rangle \\ &= \sum_{J_{23}} |[j_1 [j_2 j_3] J_{23}] JM\rangle \langle [j_1 [j_2 j_3] J_{23}] JM| |[j_1 j_2] J_{12} j_3] JM\rangle \\ &= \sum_{J_{23}} |[j_1 [j_2 j_3] J_{23}] JM\rangle U(j_1 j_2 J_{12}; J_{12} J_{23}), \end{aligned} \quad (2)$$

where we have renamed the unitary transformation coefficient a  $U$  coefficient,

$$\langle [j_1 [j_2 j_3] J_{23}] JM | |[j_1 j_2] J_{12} j_3] JM\rangle = U(j_1 j_2 J_{12}; J_{12} J_{23}) \equiv U_{J_{12} J_{23}}(j_1 j_2 J_{12}), \quad (3)$$

where we have anticipated this unitary transformation is independent of the magnetic quantum number  $M$ . It is a matrix element of the unit operator, a spherical tensor of rank 0, in the total angular momentum basis, hence,  $M$ -independent by

the Wigner–Eckart theorem. The rather strange order of the angular momentum quantum numbers is that first introduced by Racah through his  $W$  coefficient, related to the above  $U$  coefficient via

$$U(j_1 j_2 J j_3; J_{12} J_{23}) = \sqrt{(2J_{12} + 1)(2J_{23} + 1)} W(j_1 j_2 J j_3; J_{12} J_{23}). \quad (4)$$

Finally, we have indicated this unitary transformation could be expressed through the elements of a matrix with row index  $J_{12}$  and column index  $J_{23}$ , where the matrix elements are functions of the quantum numbers  $j_1, j_2, J, j_3$ , common to both bases. The unitary character of the transformation gives us

$$U_{J_{23} J_{12}}^{-1} = U_{J_{12} J_{23}}^* = U_{J_{12} J_{23}}. \quad (5)$$

Because the  $U$  coefficients can be expressed in terms of Clebsch–Gordan coefficients, which are real, the  $U$  coefficients are real, so the  $*$  has been omitted in the last step, and the inverse matrix is given by the transposed matrix,  $U^{-1} = \tilde{U}$ . Therefore,

$$\begin{aligned} |[j_1 [j_2 j_3] J_{23}] JM\rangle &= \sum_{J_{12}} U_{J_{23} J_{12}}^{-1} |[[j_1 j_2] J_{12} j_3] JM\rangle \\ &= \sum_{J_{12}} U_{J_{12} J_{23}} |[[j_1 j_2] J_{12} j_3] JM\rangle \\ &= \sum_{J_{12}} U(j_1 j_2 J j_3; J_{12} J_{23}) |[[j_1 j_2] J_{12} j_3] JM\rangle. \end{aligned} \quad (6)$$

Because the signs of angular momentum–coupled functions depend on the order of the couplings, it is important to keep the order of the various couplings, as indicated by the order of the angular momentum couplings inside the [ ] brackets. For this purpose a pictorial representation of eqs. (2) and (6) is also useful. See Figs. 34.2(a) and (b), where the arrow also helps to indicate the order of the couplings. See also Figs. 34.1(a) and (b) for a pictorial representation of the coupling of two angular momenta.

## B Relations between $U$ Coefficients and Clebsch–Gordan Coefficients

By expanding the angular momentum coupled states of eqs. (2) and (6) in terms of uncoupled states via the appropriate Clebsch–Gordan coefficients, we can express the  $U$  coefficients in terms of sums of products of Clebsch–Gordan coefficients. Thus,

$$\begin{aligned} |[[j_1 j_2] J_{12} j_3] JM\rangle &= \sum_{m_1 m_2 m_3} |j_1 m_1\rangle |j_2 m_2\rangle |j_3 m_3\rangle \langle j_1 m_1 j_2 m_2| J_{12} M_{12}\rangle \langle J_{12} M_{12} j_3 m_3| JM\rangle \\ &= \sum_{m_1 m_2 m_3} |j_1 m_1\rangle \sum_{J'_{23}} |[j_2 j_3] J'_{23} M_{23}\rangle \langle j_2 m_2 j_3 m_3| J'_{23} M_{23}\rangle \\ &\quad \times \langle j_1 m_1 j_2 m_2| J_{12} M_{12}\rangle \langle J_{12} M_{12} j_3 m_3| JM\rangle \end{aligned}$$

$$\begin{aligned}
 \left| \begin{array}{c} j_2 \\ j_1 \end{array} \right\rangle \langle JM | &= \sum_{m_1(m_2)} \left| \begin{array}{c} jm_1 \\ jm_2 \end{array} \right\rangle \langle jm_1, jm_2 | JM \rangle \\
 \left| \begin{array}{c} j_1 \\ j_2 \end{array} \right\rangle \langle JM | &= (-1)^{j_1 + j_2 - J} \left| \begin{array}{c} j_2 \\ j_1 \end{array} \right\rangle \langle JM |
 \end{aligned}$$

FIGURE 34.1. Coupling of two angular momenta.

$$\begin{aligned}
 & \left| \begin{array}{c} j_2 \\ j_1 \\ \hline j_3 \end{array} \right\rangle = \sum_{J_{23}} \left| \begin{array}{c} j_2 \\ j_1 \\ \hline J_{23} \end{array} \right\rangle U(j_1 j_2 J_{23}; J_{12} J_{23}) \\
 & \left| \begin{array}{c} j_2 \\ j_1 \\ \hline j_3 \end{array} \right\rangle = \sum_{J_{12}} \left| \begin{array}{c} j_2 \\ j_1 \\ \hline J_{12} \end{array} \right\rangle U(j_1 j_2 J_{12}; J_{12} J_{23}) \\
 & \left| \begin{array}{c} j_2 \\ j_1 \\ \hline j_3 \end{array} \right\rangle = \left| \begin{array}{c} j_2 \\ j_1 \\ \hline J_M \end{array} \right\rangle
 \end{aligned}$$

Diagram illustrating the recoupling of three angular momenta. Each diagram shows three vectors (j1, j2, j3) forming a triangle, with a fourth vector (JM or J12 or J23) originating from the vertex opposite the triangle. The JM diagram has an arrow pointing to the right.

FIGURE 34.2. Recoupling of three angular momenta.

$$= \sum_{m_1 m_2 m_3} \sum_{J'_{23}} |[j_1 [j_2 j_3] J'_{23}] J' M\rangle \langle j_1 m_1 J'_{23} M_{23} | J' M\rangle \\ \times \langle j_2 m_2 j_3 m_3 | J'_{23} M_{23}\rangle \langle j_1 m_1 j_2 m_2 | J_{12} M_{12}\rangle \langle J_{12} M_{12} j_3 m_3 | J M\rangle. \quad (7)$$

Now, left-multiplying this relation by  $\langle [j_1 [j_2 j_3] J'_{23}] J M |$  and using,

$$\langle [j_1 [j_2 j_3] J'_{23}] J M | [j_1 [j_2 j_3] J'_{23}] J' M\rangle = \delta_{J'_{23} J_{23}} \delta_{J' J}, \quad (8)$$

in the last step of the above relation, we are led to

$$U(j_1 j_2 J j_3; J_{12} J_{23}) = \sum_{m_1 m_2 m_3} \langle j_1 m_1 j_2 m_2 | J_{12} M_{12}\rangle \\ \times \langle J_{12} M_{12} j_3 m_3 | J M\rangle \langle j_1 m_1 J_{23} M_{23} | J M\rangle \langle j_2 m_2 j_3 m_3 | J_{23} M_{23}\rangle \quad (9)$$

where it is important to remember  $M$  is fixed at some specific value,  $M = m_1 + m_2 + m_3$ , when taking the  $m_i$  sums, so that there are essentially only two  $m_i$  sums to perform. A second relation can be obtained from

$$|j_1 m_1\rangle |[j_2 j_3] J_{23} M_{23}\rangle = \sum_j |[j_1 [j_2 j_3] J_{23}] J M\rangle \langle j_1 m_1 J_{23} M_{23} | J M\rangle \\ = \sum_j \sum_{J_{12}} |[j_1 j_2] J_{12} j_3\rangle J M U(j_1 j_2 J j_3; J_{12} J_{23}) \langle j_1 m_1 J_{23} M_{23} | J M\rangle \\ = \sum_{m_2} |j_1 m_1\rangle |j_2 m_2\rangle |j_3 m_3\rangle \langle j_2 m_2 j_3 m_3 | J_{23} M_{23}\rangle \\ = \sum_{m_2} \sum_{J'_{12}} \sum_{J'} |[j_1 j_2] J'_{12} j_3\rangle J' M \langle j_1 m_1 j_2 m_2 | J'_{12} M_{12}\rangle \\ \times \langle J'_{12} M_{12} j_3 m_3 | J' M\rangle \langle j_2 m_2 j_3 m_3 | J_{23} M_{23}\rangle. \quad (10)$$

Now, using the orthonormality of the states

$$\langle [j_1 j_2] J_{12} j_3 | [j_1 j_2] J'_{12} j_3\rangle = \delta_{J_{12} J'_{12}} \delta_{J J'}, \quad (11)$$

we get

$$U(j_1 j_2 J j_3; J_{12} J_{23}) \langle j_1 m_1 J_{23} M_{23} | J M\rangle = \\ \sum_{m_2} \langle j_1 m_1 j_2 m_2 | J_{12} M_{12}\rangle \langle J_{12} M_{12} j_3 m_3 | J M\rangle \langle j_2 m_2 j_3 m_3 | J_{23} M_{23}\rangle. \quad (12)$$

In this relation,  $m_1$ ,  $M_{23}$ , and  $M$ , are all fixed. Because the right-hand side, therefore, involves only a single  $m$  sum, this relation is particularly useful for the evaluation of  $U$  coefficients.

Finally, we get a third relation, by starting with

$$|j_1 m_1 j_2 m_2 j_3 m_3\rangle = \\ \sum_{J_{12}} \sum_j |[j_1 j_2] J_{12} j_3\rangle J M \langle j_1 m_1 j_2 m_2 | J_{12} M_{12}\rangle \langle J_{12} M_{12} j_3 m_3 | J M\rangle \\ = \sum_{J_{23}} \sum_{J'} |[j_1 [j_2 j_3] J_{23}] J' M\rangle \langle j_2 m_2 j_3 m_3 | J_{23} M_{23}\rangle \langle j_1 m_1 J_{23} M_{23} | J' M\rangle \\ = \sum_{J'_{12}} \sum_{J'_{23}} |[j_1 j_2] J'_{12} j_3\rangle J' M \langle j_1 m_1 J_{23} M_{23} | J' M\rangle \\ \times \langle j_2 m_2 j_3 m_3 | J_{23} M_{23}\rangle \langle j_1 m_1 J_{23} M_{23} | J' M\rangle, \quad (13)$$

leading to

$$\langle j_1 m_1 j_2 m_2 | J_{12} M_{12} \rangle \langle J_{12} M_{12} j_3 m_3 | JM \rangle = \sum_{J_{23}} U(j_1 j_2 J j_3; J_{12} J_{23}) \langle j_2 m_2 j_3 m_3 | J_{23} M_{23} \rangle \langle j_1 m_1 J_{23} M_{23} | JM \rangle. \quad (14)$$

In this relation, all the  $m_i$  and, hence, the  $M_{ij}$  and  $M$  are fixed.

All three relations, eqs. (9), (12), and (14) may be useful in the evaluation of  $U$  coefficients.

As a very simple example, let us evaluate the  $U$  coefficients for the case  $j_1 = l, j_2 = \frac{1}{2}, j_3 = \frac{1}{2}$ . This recoupling coefficient might be needed in two-electron configurations in which one electron has arbitrary orbital angular momentum,  $l$ , whereas the second electron is an  $s$  electron with  $l = 0$ . Here, a  $U$  coefficient is needed in the transformation from  $LS$  to  $jj$  coupling and has the form  $U(l \frac{1}{2} J \frac{1}{2}; JS)$ , where  $S$  is the total two-electron spin and  $J$  is the total angular momentum quantum number. Here,  $J$  can have the values  $l + 1, l$ , and  $l - 1$ . With  $J = l + 1$ , however,  $S$  is fixed uniquely at  $S = 1$ , and  $j$  is fixed uniquely at  $j = (l + \frac{1}{2})$ . The  $U$  transformation matrix is a  $1 \times 1$  matrix. For any  $1 \times 1$  transformation, the  $U$  coefficient has the value +1. Thus,

$$U(l \frac{1}{2} (l + 1) \frac{1}{2}; (l + \frac{1}{2}) 1) = +1. \quad (15)$$

Similarly,

$$U(l \frac{1}{2} (l - 1) \frac{1}{2}; (l - \frac{1}{2}) 1) = +1. \quad (16)$$

When  $J = l$ , however,  $S$  has the two possible values,  $S = 0, 1$ , and  $j$  has the two possible values  $j = (l + \frac{1}{2}), (l - \frac{1}{2})$ . In this case, the  $U$  transformation matrix is a  $2 \times 2$  matrix. With the simple table of Clebsch–Gordan coefficients of Chapter 28, eqs. (9) or (12) yield

$$U(l \frac{1}{2} l \frac{1}{2}; JS) = \begin{aligned} j &= (l + \frac{1}{2}) \begin{pmatrix} S = 0 & S = 1 \\ \sqrt{\frac{l+1}{2l+1}} & \sqrt{\frac{l}{2l+1}} \end{pmatrix} \\ j &= (l - \frac{1}{2}) \begin{pmatrix} S = 0 & S = 1 \\ -\sqrt{\frac{l}{2l+1}} & \sqrt{\frac{l+1}{2l+1}} \end{pmatrix}. \end{aligned} \quad (17)$$

## C Alternate Forms for the Recoupling Coefficients for Three Angular Momenta

The recoupling coefficients for three commuting angular momentum operators were first introduced by Racah through his  $W$  coefficient. The relation between the Racah  $W$  coefficient and the unitary  $U$  coefficient has been given in eq. (4). Because the Clebsch–Gordan coefficients are subject to  $2 \times 3!$  symmetry relations most easily expressed via the 3-j symbol (see Chapter 28) there will of course be similar symmetry relations for the  $U$  coefficients. To see the symmetry relations most easily, without factors of  $\sqrt{(2J + 1)}$  or complicated phase factors, it is useful

to introduce the so-called 6-j coefficient or 6-j symbol, conventionally written between curly brackets in two rows,

$$U(j_1 j_2 J j_3; J_{12} J_{23}) = (-1)^{j_1+j_2+j_3+J} \sqrt{(2J_{12} + 1)(2J_{23} + 1)} \left\{ \begin{matrix} j_1 & j_2 & J_{12} \\ j_3 & J & J_{23} \end{matrix} \right\}. \quad (18)$$

The 6-j symbol must satisfy four angular momentum addition triangle relations: The three angular momenta in the first row must satisfy an angular momentum addition triangle relation. Any angular momentum quantum number from the first row satisfies such a triangle relation with two partners from the second row, which must lie in columns different from the column of the symbol in the first row. The 6-j symbol is invariant under the following symmetry transformations:

(1) The 6-j symbol is invariant under any permutation of columns (i.e., six symmetry operations).

(2) The 6-j symbol is invariant under an exchange of the  $j$ 's in rows 1 and 2 for any two columns:

$$\left\{ \begin{matrix} a & b & c \\ d & e & f \end{matrix} \right\} = \left\{ \begin{matrix} d & e & c \\ a & b & f \end{matrix} \right\} = \left\{ \begin{matrix} a & e & f \\ d & b & c \end{matrix} \right\} = \left\{ \begin{matrix} d & b & f \\ a & e & c \end{matrix} \right\}. \quad (19)$$

In actual calculations, the unitary form of the recoupling coefficients is often the most useful. In order to make use of its symmetry properties, however, it is clearly advantageous to convert it to 6-j form first. As a simple application of such symmetry properties, let us evaluate the  $U$  coefficient in which the quantum number,  $J_{23} = 0$ , and therefore  $J = j_1$ , and  $j_3 = j_2$ . If one of the labels,  $j_1, j_2, j_3$ , or  $J$ , has the value zero, the  $U$  matrix is a  $1 \times 1$  matrix and the  $U$  coefficient has the value +1. Therefore,

$$\begin{aligned} U(j_1 j_2 j_1 j_2; J_{12} 0) &= \sqrt{(2J_{12} + 1)}(-1)^{2j_1+2j_2} \left\{ \begin{matrix} j_1 & j_2 & J_{12} \\ j_2 & j_1 & 0 \end{matrix} \right\} \\ &= \sqrt{(2J_{12} + 1)}(-1)^{2j_1+2j_2} \left\{ \begin{matrix} J_{12} & j_1 & j_2 \\ 0 & j_2 & j_1 \end{matrix} \right\} \\ &= \sqrt{\frac{(2J_{12} + 1)}{(2j_1 + 1)(2j_2 + 1)}}(-1)^{j_1+j_2-J_{12}} (U(J_{12} j_1 j_2 0; j_2 j_1) = +1). \end{aligned} \quad (20)$$

Therefore,

$$U(j_1 j_2 j_1 j_2; J_{12} 0) = (-1)^{j_1+j_2-J_{12}} \sqrt{\frac{(2J_{12} + 1)}{(2j_1 + 1)(2j_2 + 1)}}. \quad (21)$$

Similarly,

$$U(j_1 j_1 j_2 j_2; 0 J_{23}) = (-1)^{j_1+j_2-J_{23}} \sqrt{\frac{(2J_{23} + 1)}{(2j_1 + 1)(2j_2 + 1)}}. \quad (22)$$

## D Matrix Element of $(U^k(1) \cdot V^k(2))$ in a Vector-Coupled Basis

To illustrate the usefulness of the recoupling coefficients of Racah type, let us calculate the matrix element of a scalar operator of type

$$(U^k(1) \cdot V^k(2)) = \sum_q (-1)^q U_q^k(1) V_{-q}^k(2) \quad (23)$$

in a  $[[j_1 j_2]JM]$  basis, where  $U_q^k(1)$  are spherical tensors of rank  $k$  built from operators acting in the space of variables of type (1)  $\equiv (\vec{r}_1, \vec{\sigma}_1, \dots)$ , similarly for  $V_{-q}^k(2)$  and space (2) and where the vectors  $|j_1 m_1\rangle$  are angular momentum eigenvectors for the subspace (1), similarly for  $|j_2 m_2\rangle$  and space (2). That is, we want to calculate matrix elements of type

$$\langle [j'_1 j'_2]JM | (U^k(1) \cdot V^k(2)) | [j_1 j_2]JM \rangle.$$

These are matrix elements of the type met in Chapter 33. For simplicity, we have left off additional quantum numbers that may be needed for a full specification of the states in question. Expanding the angular momentum coupled states in ket and bra and using the Wigner–Eckart theorem to express the matrix elements of  $U_q^k(1)$  and  $V_{-q}^k(2)$  in terms of their reduced matrix elements, we have

$$\begin{aligned} & \langle [j'_1 j'_2]JM | (U^k(1) \cdot V^k(2)) | [j_1 j_2]JM \rangle = \\ & \sum_q \sum_{m_1(m_2)} \sum_{m'_1(m'_2)} \langle j_1 m_1 j_2 m_2 | JM \rangle \langle j'_1 m'_1 j'_2 m'_2 | JM \rangle \langle j_1 m_1 k q | j'_1 m'_1 \rangle \\ & \times \frac{\langle j'_1 \| U^k(1) \| j_1 \rangle}{\sqrt{(2j'_1 + 1)}} (j_2 m_2 k - q | j'_2 m'_2 \rangle) (-1)^q \frac{\langle j'_2 \| V^k(2) \| j_2 \rangle}{\sqrt{(2j'_2 + 1)}}. \end{aligned} \quad (24)$$

Now, let us use a symmetry property of the Clebsch–Gordan coefficients to reexpress

$$\langle j_2 m_2 k - q | j'_2 m'_2 \rangle = (-1)^{k-q} \sqrt{\frac{(2j'_2 + 1)}{(2j_2 + 1)}} \langle k q j'_2 m'_2 | j_2 m_2 \rangle. \quad (25)$$

The above matrix element then can be rewritten as

$$\begin{aligned} & \langle [j'_1 j'_2]JM | (U^k(1) \cdot V^k(2)) | [j_1 j_2]JM \rangle = (-1)^k \frac{\langle j'_1 \| U^k(1) \| j_1 \rangle \langle j'_2 \| V^k(2) \| j_2 \rangle}{\sqrt{(2j'_1 + 1)(2j'_2 + 1)}} \\ & \times \sum_q \sum_{m_1(m_2)} \sum_{m'_1(m'_2)} \langle j_1 m_1 k q | j'_1 m'_1 \rangle \langle j'_1 m'_1 j'_2 m'_2 | JM \rangle \\ & \times \langle j_1 m_1 j_2 m_2 | JM \rangle \langle k q j'_2 m'_2 | j_2 m_2 \rangle. \end{aligned} \quad (26)$$

Comparing the sum over  $q, m_1, m'_1$  of the product of the four Clebsch–Gordan coefficients in the last lines with eq. (9), the identification of the six angular momenta in these Clebsch–Gordan coefficients with those of eq. (9) yields

$$\sum_{q, m_1, m'_1} \langle j_1 m_1 k q | j'_1 m'_1 \rangle \langle j'_1 m'_1 j'_2 m'_2 | JM \rangle \langle j_1 m_1 j_2 m_2 | JM \rangle \langle k q j'_2 m'_2 | j_2 m_2 \rangle$$

$$= U(j_1 k J j'_2; j'_1 j_2), \quad (27)$$

so

$$\begin{aligned} & \langle [j'_1 j'_2] JM | (U^k(1) \cdot V^k(2)) | [j_1 j_2] JM \rangle \\ &= (-1)^k \frac{\langle j'_1 \| U^k(1) \| j_1 \rangle \langle j'_2 \| V^k(2) \| j_2 \rangle}{\sqrt{(2j'_1 + 1)(2j_2 + 1)}} U(j_1 k J j'_2; j'_1 j_2) \\ &= (-1)^{j_1 + j'_1 + J} \langle j'_1 \| U^k(1) \| j_1 \rangle \langle j'_2 \| V^k(2) \| j_2 \rangle \left\{ \begin{array}{ccc} j_1 & k & j'_1 \\ j'_2 & J & j_2 \end{array} \right\}. \end{aligned} \quad (28)$$

## E Recoupling of Four Angular Momenta: 9-j Symbols

In a two-electron configuration of an atom, we may be interested in a transformation from an  $LS$ -coupled basis to a  $jj$ -coupled basis,

$$|[l_1 l_2] L [s_1 s_2] S] JM \rangle \longrightarrow |[l_1 s_1] j_1 [l_2 s_2] j_2] JM \rangle.$$

This is a special case (with  $s_1 = s_2 = \frac{1}{2}$ ) of a recoupling of four angular momenta;  $j_1, j_2, j_3, j_4$ , if we name  $j_1 \equiv l_1$ ,  $j_2 \equiv l_2$ , and  $j_3 \equiv s_1$ ,  $j_4 \equiv s_2$ . We need the transformation from a basis in which  $J_{12}$  and  $J_{34}$  are good quantum numbers to a basis in which  $J_{13}$  and  $J_{24}$  are good quantum numbers

$$\begin{aligned} & |[[j_1 j_2] J_{12} [j_3 j_4] J_{34}] JM \rangle = \sum_{J_{13} J_{24}} |[[j_1 j_3] J_{13} [j_2 j_4] J_{24}] JM \rangle \\ & \quad \langle [[j_1 j_3] J_{13} [j_2 j_4] J_{24}] JM | [[j_1 j_2] J_{12} [j_3 j_4] J_{34}] JM \rangle \\ &= \sum_{J_{13} J_{24}} |[[j_1 j_3] J_{13} [j_2 j_4] J_{24}] JM \rangle \ U \left( \begin{array}{ccc} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{array} \right). \end{aligned} \quad (29)$$

See Fig. 34.3 for a pictorial representation of this relation. The  $U(\dots)$  symbol involving the nine  $j$ 's is again a unitary transformation matrix, again independent of  $M$ ; now with row and column indices specified by two quantum numbers each,

$$U \left( \begin{array}{ccc} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{array} \right) = U_{J_{12} J_{34}, J_{13} J_{24}}. \quad (30)$$

For example, with  $j_1 \equiv l_1 = 1$ ,  $j_2 \equiv l_2 = 2$ , and  $j_3 \equiv s_1 = \frac{1}{2}$ ,  $j_4 \equiv s_2 = \frac{1}{2}$ , and resultant total  $J = 1$ , this would be a  $3 \times 3$  transformation matrix, where the row labels  $J_{12} J_{34} \equiv LS$  have the three possible values 10, 11, 21, and the column labels  $J_{13} J_{24} \equiv jj'$  have the three possible values  $\frac{1}{2}\frac{3}{2}, \frac{3}{2}\frac{3}{2}, \frac{3}{2}\frac{5}{2}$ . Because the above matrix is again both unitary and real, we have

$$(U^{-1})_{J_{13} J_{24}, J_{12} J_{34}} = U_{J_{12} J_{34}, J_{13} J_{24}}. \quad (31)$$

Therefore, the inverse transformation is given by

$$|[[j_1 j_3] J_{13} [j_2 j_4] J_{24}] JM \rangle$$

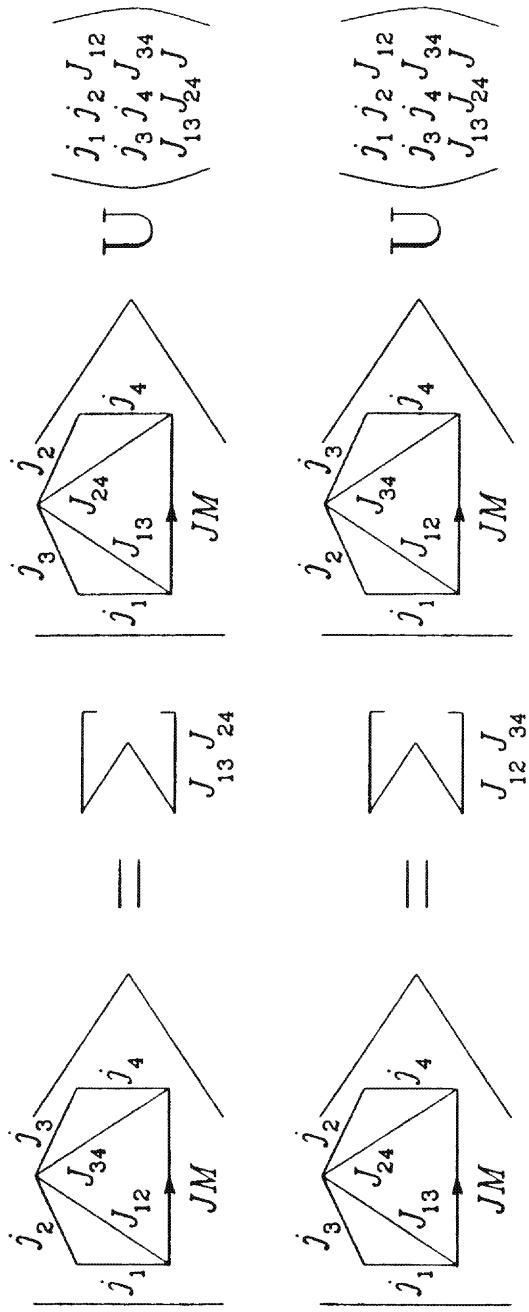


FIGURE 34.3. Recoupling of four angular momenta

$$= \sum_{J_{12}J_{34}} |[[j_1 j_2] J_{12} [j_3 j_4] J_{34}] JM\rangle U \begin{pmatrix} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{pmatrix}. \quad (32)$$

See Fig. 34.3(b). In the arrangement of the positions of the nine  $j$ 's in the  $U(\dots)$  symbol, each row and each column corresponds to a coupling of two angular momenta to a resultant. The 9-j  $U$  coefficient can thus be expressed in terms of sums over products of six Clebsch–Gordan coefficients

$$U \begin{pmatrix} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{pmatrix} =$$

$$\sum_{m_i} \langle j_1 m_1 j_2 m_2 | J_{12} M_{12} \rangle \langle j_3 m_3 j_4 m_4 | J_{34} M_{34} \rangle \langle J_{12} M_{12} J_{34} M_{34} | JM \rangle \\ \times \langle j_1 m_1 j_3 m_3 | J_{13} M_{13} \rangle \langle j_2 m_2 j_4 m_4 | J_{24} M_{24} \rangle \langle J_{13} M_{13} J_{24} M_{24} | JM \rangle, \quad (33)$$

where the sum is over all  $m_i$ , but with  $M = m_1 + m_2 + m_3 + m_4$  fixed at a specific value. Clearly, the symmetry properties of the Clebsch–Gordan coefficients will again lead to many symmetry properties of the unitary 9-j transformation coefficients. These will again have their simplest form not in terms of the unitary 9-j transformation coefficients, but in terms of the so-called 9-j symbol, always written in curly brackets, which is defined by

$$U \begin{pmatrix} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{pmatrix} = \sqrt{(2J_{12} + 1)(2J_{34} + 1)(2J_{13} + 1)(2J_{24} + 1)} \left\{ \begin{array}{ccc} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{array} \right\}. \quad (34)$$

This  $\{\dots\}$  9-j symbol has the following symmetry properties:

- (1) The 9-j symbol is invariant under any even permutation of rows or columns.
- (2) The 9-j symbol is invariant under reflection in either diagonal.
- (3) The 9-j symbol changes sign by the factor,  $(-1)^{j_1+j_2+j_3+j_4+J_{12}+J_{34}+J_{13}+J_{24}+J}$ , involving all nine  $j$ 's, under any odd permutation of rows or columns.

The 9-j transformation coefficients can be expressed in terms of products of 6-j  $U$  coefficients. For example,

$$|[[j_1 j_2] J_{12} [j_3 j_4] J_{34}] JM\rangle \\ = \sum_{J_{234}} |[j_1 [j_2 [j_3 j_4] J_{34}] J_{234}] JM\rangle U(j_1 j_2 J J_{34}; J_{12} J_{234}) \\ = \sum_{J_{234}} (-1)^{j_3+j_4-J_{34}} |[j_1 [j_2 [j_4 j_3] J_{34}] J_{234}] JM\rangle U(j_1 j_2 J J_{34}; J_{12} J_{234}) \\ = \sum_{J_{234}} \sum_{J_{24}} (-1)^{j_3+j_4-J_{34}} |[j_1 [[j_2 j_4] J_{24} j_3] J_{234}] JM\rangle \\ \times U(j_2 j_4 J_{234} j_3; J_{24} J_{34}) U(j_1 j_2 J J_{34}; J_{12} J_{234}) \\ = \sum_{J_{234}} \sum_{J_{24}} (-1)^{j_3+j_4-J_{34}} (-1)^{j_3+J_{24}-J_{234}} |[j_1 [j_3 [j_2 j_4] J_{24}] J_{234}] JM\rangle \\ \times U(j_2 j_4 J_{234} j_3; J_{24} J_{34}) U(j_1 j_2 J J_{34}; J_{12} J_{234})$$

$$\begin{aligned}
 & \left| \begin{array}{c} j_2 \\ | \\ j_1 & J_{12} \\ | & | \\ j_3 & J_{34} \\ | & | \\ j_4 \\ \hline JM \end{array} \right\rangle = \sum_{J_{234}} \left| \begin{array}{c} j_2 \\ | \\ j_1 & J_{234} \\ | & | \\ j_3 & J_{34} \\ | & | \\ j_4 \\ \hline JM \end{array} \right\rangle \cup \left( j_1 j_2 J J_{34}; J_{12} J_{234} \right) \\
 & = \sum_{J_{234}} (-1)^{j_3 + j_4 - J_{34}} \left| \begin{array}{c} j_2 \\ | \\ j_1 & J_{234} \\ | & | \\ j_3 & J_{34} \\ | & | \\ j_4 \\ \hline JM \end{array} \right\rangle \cup \left( j_1 j_2 J J_{34}; J_{12} J_{234} \right) \\
 & = \sum_{J_{234}} \sum_{J_{24}} (-1)^{j_3 + j_4 - J_{34}} \left| \begin{array}{c} j_2 \\ | \\ j_1 & J_{24} \\ | & | \\ j_3 & J_{234} \\ | & | \\ j_4 \\ \hline JM \end{array} \right\rangle \\
 & \quad \times \cup \left( j_2 j_4 J_{234} j_3; J_{24} J_{34} \right) \cup \left( j_1 j_2 J J_{34}; J_{12} J_{234} \right) \\
 & = \sum_{J_{234}} \sum_{J_{24}} (-1)^{j_3 + j_4 - J_{34}} (-1)^{j_3 + J_{24} - J_{234}} \left| \begin{array}{c} j_3 \\ | \\ j_1 & J_{24} \\ | & | \\ j_2 & J_{234} \\ | & | \\ j_4 \\ \hline JM \end{array} \right\rangle \\
 & \quad \times \cup \left( j_2 j_4 J_{234} j_3; J_{24} J_{34} \right) \cup \left( j_1 j_2 J J_{34}; J_{12} J_{234} \right) \\
 & = \sum_{J_{234}} \sum_{J_{24}} \sum_{J_{13}} (-1)^{2j_3 + j_4 - J_{34} + J_{24} + J_{234}} \left| \begin{array}{c} j_3 \\ | \\ j_1 & J_{24} \\ | & | \\ j_2 & J_{13} \\ | & | \\ j_4 \\ \hline JM \end{array} \right\rangle \\
 & \quad \times \cup \left( j_2 j_4 J_{234} j_3; J_{24} J_{34} \right) \cup \left( j_1 j_2 J J_{34}; J_{12} J_{234} \right) \cup \left( j_1 j_3 J J_{24}; J_{13} J_{234} \right)
 \end{aligned}$$

FIGURE 34.4. Pictorial version of eq. (35).

$$\begin{aligned}
 & = \sum_{J_{234}} \sum_{J_{24}} \sum_{J_{13}} (-1)^{2j_3 + j_4 - J_{34} - J_{234} + J_{24}} [[j_1 j_3] J_{13} [j_2 j_4] J_{24}] J M \rangle \\
 & \quad \times U(j_2 j_4 J_{234} j_3; J_{24} J_{34}) U(j_1 j_2 J J_{34}; J_{12} J_{234}) U(j_1 j_3 J J_{24}; J_{13} J_{234}) \\
 & = \sum_{J_{13}, J_{24}} [[j_1 j_3] J_{13} [j_2 j_4] J_{24}] J M \rangle U \begin{pmatrix} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{pmatrix}. \tag{35}
 \end{aligned}$$

The various steps in this relation are easier to follow in a pictorial representation. See Fig. 34.4. Comparing the last two lines of this relation, we get

$$U \begin{pmatrix} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{pmatrix} =$$

$$\begin{aligned} & \sum_{J_{234}} (-1)^{2j_3+j_4-J_{34}-J_{234}+J_{24}} U(j_2 j_4 J_{234} j_3 : J_{24} J_{34}) \\ &= \sum_{J_{234}} \frac{\times U(j_1 j_2 J J_{34}; J_{12} J_{234}) U(j_1 j_3 J J_{24}; J_{13} J_{234})}{(-1)^{2J_{234}} (2J_{234} + 1) \sqrt{(2J_{12} + 1)(2J_{34} + 1)(2J_{13} + 1)(2J_{24} + 1)}} \\ & \quad \times \left\{ \begin{array}{ccc} j_2 & j_4 & J_{24} \\ j_3 & J_{234} & J_{34} \end{array} \right\} \left\{ \begin{array}{ccc} j_1 & j_2 & J_{12} \\ J_{34} & J & J_{234} \end{array} \right\} \left\{ \begin{array}{ccc} j_1 & j_3 & J_{13} \\ J_{24} & J & J_{234} \end{array} \right\}. \end{aligned} \quad (36)$$

This relation is particularly useful if one of the angular momenta has the value zero. For example, if  $j_2 = 0$ . Then, with  $J_{24} = j_4$  and  $J_{234} = J_{34}$ , we have  $U(0 j_4 J_{34} j_3; j_4 J_{34}) = +1$  and with  $J_{12} = j_1$  and again  $J_{234} = J_{34}$ , we have  $U(j_1 0 J J_{34}; j_1 J_{34}) = +1$ . The above relation collapses to

$$U \left( \begin{array}{ccc} j_1 & 0 & j_1 \\ j_3 & j_4 & J_{34} \\ J_{13} & j_4 & J \end{array} \right) = U(j_1 j_3 J j_4; J_{13} J_{34}). \quad (37)$$

This relation can also be seen directly from the pictorial representation of Fig. 34.5, from which we see the triangle, coupling  $j_1$  with 0 to resultant  $j_1$ , rides along on the back of a single Racah type of recoupling transformation involving the recoupling of  $j_1$ ,  $j_3$ , and  $j_4$ . Similarly, we have

$$U \left( \begin{array}{ccc} j_1 & j_2 & J_{12} \\ j_3 & 0 & j_3 \\ J_{13} & j_2 & J \end{array} \right) = (-1)^{j_1+j-J-J_{12}-J_{13}} U(j_2 j_1 J j_3; J_{12} J_{13}). \quad (38)$$

See also Fig. 34.6.

## F Matrix Element of a Coupled Tensor Operator, $[U^{k_1}(1) \times V^{k_2}(2)]_q^k$ in a Vector-Coupled Basis

To appreciate how the 9-j transformation coefficient can facilitate calculations in an angular momentum coupled basis, let us calculate the matrix element of a vector-coupled tensor operator,

$$[U^{k_1}(1) \times V^{k_2}(2)]_q^k = \sum_{q_1(q_2)} \langle k_1 q_1 k_2 q_2 | k q \rangle U_{q_1}^{k_1}(1) V_{q_2}^{k_2}(2), \quad (39)$$

in a  $[(j_1 j_2) JM]$  basis, where again, the  $U_{q_1}^{k_1}(1)$  are spherical tensors of rank  $k_1$  acting on variables of type (1) and where the  $|j_1 m_1\rangle$  are angular momentum eigenvectors of the space (1), similarly for  $V_{q_2}^{k_2}(2)$  and the  $|j_2 m_2\rangle$  and space (2). The needed matrix element can be expressed in terms of a reduced matrix element via the Wigner–Eckart theorem and can be expanded in terms of Clebsch–Gordan coefficients via

$$\begin{aligned} & \langle [j'_1 j'_2] J' M' | [U^{k_1}(1) \times V^{k_2}(2)]_q^k | [j_1 j_2] JM \rangle \\ &= \langle JM k q | J' M' \rangle \frac{\langle [j'_1 j'_2] J' | [U^{k_1}(1) \times V^{k_2}(2)]^k | [j_1 j_2] J \rangle}{\sqrt{(2J'+1)}} \end{aligned}$$

$$\begin{aligned}
 & U(j_1 j_3 J \quad j_4; J_{13} J_{34}) \\
 & \quad \left| \begin{array}{c} j_3 \\ j_1 \\ j_1 \\ j_4 \end{array} \right\rangle \quad JM \\
 & = \quad \left[ \begin{array}{c} \diagup \\ \diagdown \end{array} \right]_{J_{13}} \\
 & \quad \left| \begin{array}{c} j_3 \\ J_{34} \\ j_1 \\ j_1 \\ j_4 \end{array} \right\rangle \quad JM
 \end{aligned}$$

FIGURE 34.5. Pictorial version of Eq. (37).

$$\begin{aligned}
& \left| \begin{array}{c} j_2 \\ j_1 \\ \hline J_{12} \\ JM \end{array} \right\rangle \left| \begin{array}{c} j_3 \\ 0 \\ \hline JM \end{array} \right\rangle = (-1)^{j_1 + j_2 - J_{12}} \left| \begin{array}{c} j_1 \\ j_2 \\ \hline J_{12} \\ JM \end{array} \right\rangle \left| \begin{array}{c} j_3 \\ 0 \\ \hline JM \end{array} \right\rangle \\
& = (-1)^{j_1 + j_2 - J_{12}} \left| \begin{array}{c} j_1 \\ j_2 \\ \hline J_{12} \\ JM \end{array} \right\rangle \left| \begin{array}{c} j_3 \\ 0 \\ \hline JM \end{array} \right\rangle (+1) \\
& = (-1)^{j_1 + j_2 - J_{12}} \sum_{J_{13}} \left| \begin{array}{c} j_1 \\ j_2 \\ \hline J_{13} \\ JM \end{array} \right\rangle \left| \begin{array}{c} j_3 \\ 0 \\ \hline JM \end{array} \right\rangle \cup (j_2 j_1 J j_3; J_{12} J_{13}) \\
& = (-1)^{j_1 + j_2 - J_{12}} \sum_{J_{13}} (-1)^{J - j_2 - J_{13}} \left| \begin{array}{c} j_3 \\ j_1 \\ \hline J_{13} \\ JM \end{array} \right\rangle \left| \begin{array}{c} j_2 \\ 0 \\ \hline JM \end{array} \right\rangle \cup (j_2 j_1 J j_3; J_{12} J_{13}) \\
& = \sum_{J_{13}} (-1)^{j_1 + J - J_{12} - J_{13}} \left| \begin{array}{c} j_3 \\ j_1 \\ \hline J_{13} \\ JM \end{array} \right\rangle \left| \begin{array}{c} j_2 \\ 0 \\ \hline JM \end{array} \right\rangle (+1) \cup (j_2 j_1 J j_3; J_{12} J_{13})
\end{aligned}$$

FIGURE 34.6. Pictorial version of eq. (38).

$$\begin{aligned}
& = \sum_{m_1 m'_1 q_1} \langle j_1 m_1 j_2 m_2 | JM \rangle \langle j'_1 m'_1 j'_2 m'_2 | J' M' \rangle \langle k_1 q_1 k_2 q_2 | kq \rangle \\
& \times \langle j_1 m_1 k_1 q_1 | j'_1 m'_1 \rangle \frac{\langle j'_1 \| U^{k_1} \| j_1 \rangle}{\sqrt{(2j_1 + 1)}} \langle j_2 m_2 k_2 q_2 | j'_2 m'_2 \rangle \frac{\langle j'_2 \| V^{k_2} \| j_2 \rangle}{\sqrt{(2j_2 + 1)}}, \quad (40)
\end{aligned}$$

where the magnetic quantum numbers,  $M$ ,  $q$ , and  $M'$  are fixed at specific values. If we multiply this equation by  $\langle JM kq | J' M' \rangle$ , and, keeping  $M'$  fixed, sum over all possible values of  $M$  and  $q = (M' - M)$ , the orthogonality relation,

$$\sum_{M, (q)} \langle JM kq | J' M' \rangle^2 = 1,$$

will pick out the reduced matrix element for our coupled tensor operator

$$\begin{aligned}
& \frac{\langle [j'_1 j'_2] J' \| [U^{k_1}(1) \times V^{k_2}(2)]^k \| [j_1 j_2] J \rangle}{\sqrt{(2J' + 1)}} \\
& = \frac{\langle j'_1 \| U^{k_1} \| j_1 \rangle}{\sqrt{(2j'_1 + 1)}} \frac{\langle j'_2 \| V^{k_2} \| j_2 \rangle}{\sqrt{(2j'_2 + 1)}}
\end{aligned}$$

$$\begin{aligned} & \times \sum_{m_1, m'_1, q_1, q_2} \langle j_1 m_1 j_2 m_2 | JM \rangle \langle j'_1 m'_1 j'_2 m'_2 | J' M' \rangle \langle k_1 q_1 k_2 q_2 | kq \rangle \\ & \times \langle j_1 m_1 k_1 q_1 | j'_1 m'_1 \rangle \langle j_2 m_2 k_2 q_2 | j'_2 m'_2 \rangle \langle JM kq | J' M' \rangle. \end{aligned} \quad (41)$$

The  $m$  sums over the product of the six Clebsch–Gordan coefficients is over all  $m$ 's except that  $M' = m_1 + m_2 + q_1 + q_2$  is fixed. This is precisely the  $m$  sum of eq. (33) which yields a single unitary 9-j transformation coefficient. Thus,

$$\begin{aligned} & \frac{\langle [j'_1 j'_2] J' \| [U^{k_1}(1) \times V^{k_2}(2)]^k \| [j_1 j_2] J \rangle}{\sqrt{(2J'+1)}} \\ & = \frac{\langle j'_1 \| U^{k_1} \| j_1 \rangle}{\sqrt{(2j'_1+1)}} \frac{\langle j'_2 \| V^{k_2} \| j_2 \rangle}{\sqrt{(2j'_2+1)}} U \begin{pmatrix} j_1 & j_2 & J \\ k_1 & k_2 & k \\ j'_1 & j'_2 & J' \end{pmatrix}. \end{aligned} \quad (42)$$

This “grand result” illustrates the full power of the angular momentum recoupling theory and shows how the 9-j transformation coefficients can be put to good use. In special cases, the 9-j transformation coefficients will collapse to a 6-j  $U$  coefficient. For example, if the tensor operator acts only in the subspace of type (1), then  $V_{q_2}^{k_2} \rightarrow 1$ , and we can set  $k_2 = 0$ . Eq. (38) then tells us

$$\begin{aligned} & \frac{\langle [j'_1 j'_2] J' \| U^{k_1}(1) \| [j_1 j_2] J \rangle}{\sqrt{(2J'+1)}} \\ & = \frac{\langle j'_1 \| U^{k_1} \| j_1 \rangle}{\sqrt{(2j'_1+1)}} (-1)^{j_1 + J' - J - j'_1} U(j_2 j_1 J' k_1; J j'_1), \end{aligned} \quad (43)$$

where we have also used

$$\langle j'_2 \| 1 \| j_2 \rangle = \delta_{j_2 j'_2} \sqrt{(2j'_2+1)}.$$

An example of this would be the matrix element of an electric dipole moment operator, which is independent of spin variables, in an  $|[ls]jm_j\rangle$  basis

$$\frac{\langle [l's] j' \| \vec{\mu}^{(\text{el.})} \| [ls] j \rangle}{\sqrt{(2j'+1)}} = \frac{\langle l' \| \vec{\mu}^{(\text{el.})} \| l \rangle}{\sqrt{(2l'+1)}} (-1)^{l-l'+j'-j} U(\tfrac{1}{2} l j' 1; j l'). \quad (44)$$

Another special case would be the case of a scalar operator, with  $k = 0$ , hence  $k_2 = k_1$ , and  $J' = J$ . We leave it as an exercise in the symmetry properties of the 9-j symbol to show our general result of eq. (42) then collapses to the result already derived in eq. (28). Recall  $(U^k \cdot V^k) = (-1)^k [(2k+1)^\frac{1}{2} [U^k \times V^k]]_0^0$ .

Although tabulations of 9-j symbols are not readily available, computer codes are easy to construct. For tabulations of 6-j symbols, see the references to tabulations at the end of Chapter 28. For algebraic expressions for 6-j symbols with at least one  $j \leq 2$ , see the references at the end of Chapter 28.

## G An Application: The Nuclear Hyperfine Interaction in a One-Electron Atom Revisited

In Chapter 33, we calculated the nuclear hyperfine interaction in a one-electron atom with the use of a few Wigner coefficients by making judicious use of the Wigner–Eckart theorem. In particular, we calculated the nuclear hyperfine splitting of a one-electron  $p_{3/2}$  state, where our nucleus had a nuclear spin  $I = \frac{1}{2}$  as in hydrogen, and we also quoted the result for the partner  $p_{1/2}$  state. We can now repeat this calculation in a much more general way by making full use of the angular momentum recoupling machinery of this addendum.

The nuclear hyperfine interaction for a hydrogenic  $s$ -state, with  $l = 0$ , was given in Chapter 33 as

$$H_{\text{h.f.int}} = \frac{mc^2\alpha^4}{2} \frac{m}{M} g_I \frac{8\pi}{3} (\vec{s} \cdot \vec{I}) \delta(\vec{r}). \quad (45)$$

For a hydrogenic state with  $l \neq 0$ , conversely, it was shown to be

$$H_{\text{h.f.int}} = \frac{mc^2\alpha^4}{2} \frac{m}{M} g_I \left[ \frac{1}{r^3} \left( (\vec{l} \cdot \vec{I}) - \sqrt{8\pi} ([Y^2 \times s^1]^1 \cdot I^1) \right) \right], \quad (46)$$

[see eqs. (5) and (14) of Chapter 33]. If we define the needed hydrogenic integrals via

$$\begin{aligned} \beta'_{\text{h.f.s.}}(l=0) &= \frac{mc^2\alpha^4}{2} \frac{m}{M} g_I \int d\vec{r} |\psi(\vec{r})_{n00}|^2 \frac{8\pi}{3} \delta(\vec{r}) = \frac{mc^2\alpha^4}{2} \frac{m}{M} g_I \frac{2}{3} |R_{n0}(0)|^2, \\ \beta_{\text{h.f.s.}}(l \neq 0) &= \frac{mc^2\alpha^4}{2} \frac{m}{M} g_I \int_0^\infty dr r^2 |R_{nl}(r)|^2 \frac{1}{r^3}, \end{aligned} \quad (47)$$

then we have an effective hyperfine interaction Hamiltonian that can be written

$$\begin{aligned} H_{\text{h.f.int}} &= \beta_{\text{h.f.s.}} \left[ (\vec{l} \cdot \vec{I}) - \sqrt{8\pi} ([Y^2 \times s^1]^1 \cdot I^1) \right], & \text{for } l \neq 0; \\ H_{\text{h.f.int}} &= \beta'_{\text{h.f.s.}} (\vec{s} \cdot \vec{I}), & \text{for } l = 0. \end{aligned} \quad (48)$$

All terms in these electron-nuclear spin interactions are of the form  $(U^{k=1}(1) \cdot V^{k=1}(2))$ , where the space (1) is that of the electron and includes both electron orbital and electron spin variables, whereas the space (2) is that of the nuclear intrinsic variables characterized by the nuclear spin vector,  $\vec{I}$ . We will of course need the coupling scheme  $\vec{l} + \vec{s} = \vec{j}$  for the electron variables, and we will assume the fine structure splitting is much greater than the hyperfine structure splitting, so  $j$  is a good quantum number. Finally, we will couple electron  $\vec{j}$  with the nuclear spin,  $\vec{I}$ , to resultant total angular momentum,  $\vec{F}$ :  $\vec{j} + \vec{I} = \vec{F}$ . All of the needed matrix elements are then given in terms of electron reduced matrix elements, the nuclear spin reduced matrix element, and a single 6-j symbol by formula (28) of this chapter. For example,

$$\langle [ls]jI]FM_F|(\vec{l} \cdot \vec{I})|[ls]jI]FM_F\rangle$$

$$= (-1)^{j+l+F} \langle [ls]j \parallel \vec{l} \parallel [ls]j \rangle \langle I \parallel \vec{I} \parallel I \rangle \begin{Bmatrix} j & 1 & j \\ l & F & I \end{Bmatrix}, \quad (49)$$

with similar expressions for matrix elements of the operators ( $\vec{s} \cdot \vec{I}$ ) and ( $[Y^2 \times s^1]^1 \cdot \vec{I}$ ). The reduced matrix elements of the electronic operators,  $\vec{l}$ ,  $\vec{s}$ , and  $[Y^2 \times s^1]^1_q$  in the  $|[ls]jm_j\rangle$  basis of the  $\vec{l} + \vec{s} = \vec{j}$ -coupled scheme are all given through formula (42) of this chapter. For example,

$$\frac{\langle [ls]j \parallel \vec{s} \parallel [ls]j \rangle}{\sqrt{(2j+1)}} = \frac{\langle l \parallel 1 \parallel l \rangle}{\sqrt{(2l+1)}} \frac{\langle s \parallel \vec{s} \parallel s \rangle}{\sqrt{(2s+1)}} U \begin{pmatrix} l & \frac{1}{2} & j \\ 0 & 1 & 1 \\ l & \frac{1}{2} & j \end{pmatrix}. \quad (50)$$

Because we are interested in the reduced matrix element of  $\vec{s}$  mainly for states with orbital angular momentum,  $l = 0$ , the needed unitary 9-j coefficient, with all zeros in the first column, corresponds to a  $1 \times 1$  unitary transformation and thus has the value, +1. The reduced matrix elements for the unit operator and the angular momentum vector operator are given for any angular momentum basis by eqs. (4) and (7) of Chapter 32. Thus,

$$\langle l \parallel 1 \parallel l \rangle = \sqrt{(2l+1)}, \quad \langle s \parallel \vec{s} \parallel s \rangle = \sqrt{(2s+1)s(s+1)} = \sqrt{\frac{3}{2}};$$

so, with  $[ls]j = [0\frac{1}{2}]_2^{\frac{1}{2}}$

$$\langle [0\frac{1}{2}]_2^{\frac{1}{2}} \parallel \vec{s} \parallel [0\frac{1}{2}]_2^{\frac{1}{2}} \rangle = \sqrt{\frac{3}{2}}.$$

Similarly,

$$\begin{aligned} \frac{\langle [ls]j \parallel \vec{l} \parallel [ls]j \rangle}{\sqrt{(2j+1)}} &= \frac{\langle l \parallel \vec{l} \parallel l \rangle}{\sqrt{(2l+1)}} \frac{\langle s \parallel 1 \parallel s \rangle}{\sqrt{(2s+1)}} U \begin{pmatrix} l & \frac{1}{2} & j \\ 1 & 0 & 1 \\ l & \frac{1}{2} & j \end{pmatrix} \\ &= \sqrt{l(l+1)} U(\frac{1}{2}lj1; jl), \end{aligned} \quad (51)$$

where we have used eq. (38) to convert the unitary 9-j coefficient with one zero to a unitary Racah coefficient. This can be read from tables of 6-j symbols. For  $l = 1$ , this  $U$  coefficient has the values:  $\sqrt{\frac{5}{6}}$  for  $j = \frac{3}{2}$ , and  $\sqrt{\frac{2}{3}}$  for  $j = \frac{1}{2}$ . Therefore,

$$\langle [1\frac{1}{2}]_2^3 \parallel \vec{l} \parallel [1\frac{1}{2}]_2^3 \rangle = 2\sqrt{\frac{5}{3}}; \quad \langle [1\frac{1}{2}]_2^1 \parallel \vec{l} \parallel [1\frac{1}{2}]_2^1 \rangle = 2\sqrt{\frac{2}{3}}.$$

Finally,

$$\langle [ls]j \parallel [Y^2 \times s^1]^1 \parallel [ls]j \rangle = \sqrt{(2j+1)} \frac{\langle l \parallel Y^2 \parallel l \rangle}{\sqrt{(2l+1)}} \frac{\langle \frac{1}{2} \parallel \vec{s} \parallel \frac{1}{2} \rangle}{\sqrt{2}} U \begin{pmatrix} l & \frac{1}{2} & j \\ 2 & 1 & 1 \\ l & \frac{1}{2} & j \end{pmatrix}, \quad (52)$$

where the reduced matrix element of  $Y^2$  was given in Chapter 32. It has the value

$$\frac{\langle l \parallel Y^2 \parallel l \rangle}{\sqrt{(2l+1)}} = \sqrt{\frac{5}{4\pi}} \langle l020|l0 \rangle = -\frac{1}{\sqrt{2\pi}} \quad \text{for } l = 1.$$

The unitary 9-j coefficients above can be given in terms of 6-j symbols through eq. (36). For  $l = 1$ , and both  $j = \frac{3}{2}$  and  $j = \frac{1}{2}$ , the sum over  $J_{234}$  in this relation

collapses to a single term:  $J_{234}$  has the unique value  $\frac{3}{2}$ . The above 9-j  $U$  coefficients have the values  $-1/(3\sqrt{5})$  and  $+(2/3)$  for  $j = \frac{3}{2}$  and  $j = \frac{1}{2}$ , respectively. Thus,

$$\langle [1\frac{1}{2}] \frac{3}{2} \| [Y^2 \times s^1]^1 \| [1\frac{1}{2}] \frac{3}{2} \rangle = \frac{1}{\sqrt{30\pi}}, \quad \langle [1\frac{1}{2}] \frac{1}{2} \| [Y^2 \times s^1]^1 \| [1\frac{1}{2}] \frac{1}{2} \rangle = -\frac{1}{\sqrt{3\pi}}.$$

With these electron reduced matrix elements, together with the nuclear spin reduced matrix element,

$$\langle I \| \vec{I} \| I \rangle = \sqrt{(2I+1)I(I+1)}, \quad (53)$$

the nuclear hyperfine interaction in a one-electron atom is then given by, first for the case  $l \neq 0$ ,

$$\begin{aligned} \langle [[ls]jI]FM_F | H_{\text{h.f.int.}} | [[ls]jI]FM_F \rangle &= \beta_{\text{h.f.s.}} \sqrt{(2I+1)I(I+1)} \\ &\times \left[ \langle [ls]j \| \vec{l} \| [ls]j \rangle - \sqrt{8\pi} \langle [ls]j \| [Y^2 \times s^1]^1 \| [ls]j \rangle \right] \\ &\times (-1)^{j+I+F} \left\{ \begin{array}{ccc} j & 1 & j \\ I & F & I \end{array} \right\}, \end{aligned} \quad (54)$$

and for the case,  $l = 0$ , with  $j = \frac{1}{2}$ ,

$$\begin{aligned} \langle [[ls]jI]FM_F | H_{\text{h.f.int.}} | [[ls]jI]FM_F \rangle &= \beta'_{\text{h.f.s.}} \sqrt{(2I+1)I(I+1)} \\ &\times \langle [ls]j \| \vec{s} \| [ls]j \rangle (-1)^{j+I+F} \left\{ \begin{array}{ccc} j & 1 & j \\ I & F & I \end{array} \right\}. \end{aligned} \quad (55)$$

For the cases,  $l = 1$  and  $l = 0$ , with  $I = \frac{1}{2}$ , we will need the 6-j symbols

$$\begin{aligned} \left\{ \begin{array}{ccc} \frac{3}{2} & 1 & \frac{3}{2} \\ \frac{1}{2} & 2 & \frac{1}{2} \end{array} \right\} &= \frac{1}{2\sqrt{10}}, & \left\{ \begin{array}{ccc} \frac{3}{2} & 1 & \frac{3}{2} \\ \frac{1}{2} & 1 & \frac{1}{2} \end{array} \right\} &= \frac{\sqrt{5}}{6\sqrt{2}}, \\ \left\{ \begin{array}{ccc} \frac{1}{2} & 1 & \frac{1}{2} \\ \frac{1}{2} & 1 & \frac{1}{2} \end{array} \right\} &= \frac{1}{6}, & \left\{ \begin{array}{ccc} \frac{1}{2} & 1 & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \end{array} \right\} &= \frac{1}{2}, \end{aligned}$$

so, with  $l = 1$ , and both  $I = \frac{1}{2}$  and  $s = \frac{1}{2}$ ,

$$\begin{aligned} \langle [[1s]jI]FM_F | H_{\text{h.f.int.}} | [[1s]jI]FM_F \rangle &= +\frac{2}{5}\beta_{\text{h.f.s.}} \text{ for } j = \frac{3}{2}, \quad F = 2, \\ \langle [[1s]jI]FM_F | H_{\text{h.f.int.}} | [[1s]jI]FM_F \rangle &= -\frac{2}{3}\beta_{\text{h.f.s.}} \text{ for } j = \frac{3}{2}, \quad F = 1, \\ \langle [[1s]jI]FM_F | H_{\text{h.f.int.}} | [[1s]jI]FM_F \rangle &= +\frac{2}{3}\beta_{\text{h.f.s.}} \text{ for } j = \frac{1}{2}, \quad F = 1, \\ \langle [[1s]jI]FM_F | H_{\text{h.f.int.}} | [[1s]jI]FM_F \rangle &= -2\beta_{\text{h.f.s.}} \text{ for } j = \frac{1}{2}, \quad F = 0, \end{aligned} \quad (56)$$

and for  $l = 0$  states,

$$\begin{aligned} \langle [[0s]sI]FM_F | H_{\text{h.f.int.}} | [[0s]sI]FM_F \rangle &= +\frac{1}{4}\beta'_{\text{h.f.s.}}, \quad \text{for } F = 1, \\ \langle [[0s]sI]FM_F | H_{\text{h.f.int.}} | [[0s]sI]FM_F \rangle &= -\frac{3}{4}\beta'_{\text{h.f.s.}}, \quad \text{for } F = 0. \end{aligned} \quad (57)$$

# 35

## Perturbed Coulomb Problems via SO(2,1) Algebra

### A Perturbed Coulomb Problems: The Conventional Approach with its Infinite Sums and Continuum Integrals: An Example: The Second-Order Stark Effect of the Hydrogen Atom Ground State

So far, we have not solved many perturbed Coulomb problems by conventional perturbation theory, that is, by the conventional radial and angular functions. The difficulty here is that perturbation terms which are functions of the radial coordinate,  $r$ , lead to an infinite number of nonzero matrix elements, connecting a bound state of definite,  $n$ , to all other bound states, as well as to the full spectrum of continuum states. The complete set of states includes both the bound states and the continuum states. The unit operator in this conventional basis is given by

$$1 = \sum_{n=1}^{\infty} \sum_{l,m} |nlm\rangle \langle nlm| + \int d\Omega_k \int_0^{\infty} dk k^2 |\vec{k}\rangle \langle \vec{k}|, \quad (1)$$

where the continuum states are the continuum solutions of the Coulomb problem, with energy,  $\hbar^2 k^2 / (2\mu)$ , which in the limit  $k \rightarrow \infty$  go over to plane wave states  $\rightarrow \langle \vec{r}|\vec{k}\rangle = e^{i\vec{k}\cdot\vec{r}} / (2\pi)^{\frac{3}{2}}$ . (These continuum Coulomb states will be discussed in detail in Chapter 42 in connection with our study of scattering theory.)

To illustrate the difficulties with the conventional radial Coulomb functions, let us look at a very simple perturbation problem: the second-order Stark effect of the

hydrogen atom ground state. The Hamiltonian is

$$H = H^{(0)} + H^{(1)} = H_{\text{Coulomb}} - e\mathcal{E}r \cos \theta, \quad (2)$$

where  $\vec{\mathcal{E}}$  is the external electric field in the  $z$  direction. Conventional second-order perturbation theory gives

$$E_{n=1,l=0,m=0}^{(2)} = \sum_{n=2}^{\infty} \frac{|\langle n|H^{(1)}|100\rangle|^2}{(E_1^{(0)} - E_n^{(0)})} + \int d\Omega_k \int_0^{\infty} dk k^2 \frac{|\langle \vec{k}|H^{(1)}|100\rangle|^2}{[E_1^{(0)} - \frac{\hbar^2 k^2}{2\mu}]}. \quad (3)$$

The needed matrix element between the hydrogen ground state and an arbitrary discrete excited state will be calculated later in this chapter. It is

$$\langle nlm|H^{(1)}|100\rangle = -\delta_{l1}\delta_{m0}e\mathcal{E}a_0 2^4 n^3 \frac{(n-1)^{n-3}}{(n+1)^{n+3}} \left[ \frac{(n+1)n(n-1)}{3} \right]^{\frac{1}{2}}. \quad (4)$$

The needed matrix element between the hydrogenic ground state and a continuum state will be calculated in the mathematical appendix to Chapter 42. It is

$$\begin{aligned} \langle \vec{k}|H^{(1)}|100\rangle &= -\delta_{l1}\delta_{m0}e\mathcal{E} \frac{a_0^{\frac{5}{2}}}{(2\pi)^{\frac{1}{2}}} \frac{4\pi}{\sqrt{3}} Y_{lm}(\theta_k, \phi_k) \\ &\times \left[ \frac{(\gamma^2 + 1)2\pi\gamma}{(1 - e^{-2\gamma\pi})} \right]^{\frac{1}{2}} \frac{8i\gamma^5}{(\gamma^2 + 1)^3} e^{-2\gamma \tan^{-1}(1/\gamma)}, \end{aligned} \quad (5)$$

where  $\gamma$  is the Coulomb parameter

$$\gamma = \frac{1}{ka_0}, \quad a_0 = \frac{\hbar^2}{Z\mu e^2}, \quad (6)$$

and  $\vec{k}$  is given by its magnitude,  $k$ , and direction specified by polar and azimuthal angles,  $\theta_k$ ,  $\phi_k$ . With these results, the second-order correction to the energy is

$$\begin{aligned} E^{(2)} &= -\left(\frac{e^2 a_0^2 \mathcal{E}^2}{\mu Z^2 e^4 / \hbar^2}\right) \left( \sum_{n=2}^{\infty} \frac{2^9 n^9 (n-1)^{2n-6}}{3 (n+1)^{2n+6}} \right. \\ &+ \int d\Omega_k Y_{10}^*(\theta_k, \phi_k) Y_{10}(\theta_k, \phi_k) \frac{512}{3} \int_0^{\infty} d\gamma \frac{\gamma^9}{(\gamma^2 + 1)^6} \frac{e^{-4\gamma \tan^{-1}(1/\gamma)}}{(1 - e^{-2\gamma\pi})} \Big) \\ &= -\left(\frac{e^2 a_0^2 \mathcal{E}^2}{\mu Z^2 e^4 / \hbar^2}\right) \left( \sum_{n=2}^{\infty} \frac{2^9 n^9 (n-1)^{2n-6}}{3 (n+1)^{2n+6}} + .418371 \right) \\ &= -\left(\frac{e^2 a_0^2 \mathcal{E}^2}{\mu Z^2 e^4 / \hbar^2}\right) 2.25, \end{aligned} \quad (7)$$

where the  $\gamma$  integral is best done numerically, and, as we shall see, the final result is given, in the appropriate units, by  $-(9/4)$ , exactly. The infinite discrete sum converges quite rapidly. For example, the first five terms, through  $n = 6$ , give 1.792758, or a total of 2.211129 with the continuum contribution, which is within 1.7% of the exact result. We shall see in this chapter, however, we can arrive at the exact final result very simply by a perturbation expansion requiring a discrete sum of just two terms.

## B The Runge–Lenz Vector as an $\ell$ Step Operator and the SO(4) Algebra of the Coulomb Problem

Before introducing the operators of an SO(2,1) algebra, which will be used to simplify the perturbation expansions for a perturbed Coulomb problem, let us look first at the commutator algebra of the quantum-mechanical operators arising from the known classical integrals for the Coulomb potential, the orbital angular momentum vector,  $\vec{L}$ , and the Runge–Lenz vector,  $\vec{\mathcal{R}}$ . It will be convenient to express all operators in dimensionless quantities through atomic units. Thus,

$$\begin{aligned}\vec{r}_{\text{phys.}} &= a_0 \vec{r}, & \vec{p}_{\text{phys.}} &= \frac{\hbar}{a_0} \vec{p}, & \vec{L}_{\text{phys.}} &= \hbar \vec{L}, & \text{with } a_0 &= \frac{\hbar^2}{Z\mu e^2}, \\ H_{\text{phys.}} &= \frac{Z^2 \mu e^4}{\hbar^2} H, & E_{\text{phys.}} &= \frac{Z^2 \mu e^4}{\hbar^2} \epsilon.\end{aligned}\quad (8)$$

In these units, the Runge–Lenz vector (see problems 13 and 19) is

$$\vec{\mathcal{R}} = \frac{1}{2} \left( [\vec{p} \times \vec{L}] - [\vec{L} \times \vec{p}] \right) - \frac{\vec{r}}{r} = \vec{r}(\vec{p} \cdot \vec{p}) - \vec{p}(\vec{r} \cdot \vec{p}) - \frac{\vec{r}}{r}, \quad (9)$$

with the properties

$$(\vec{\mathcal{R}} \cdot \vec{\mathcal{R}}) = 2H(\vec{L} \cdot \vec{L} + 1) + 1, \quad (10)$$

and

$$\vec{\mathcal{R}} \cdot \vec{L} = \vec{L} \cdot \vec{\mathcal{R}} = 0. \quad (11)$$

It was useful to define

$$\vec{V} = \frac{\vec{\mathcal{R}}}{\sqrt{(-2\epsilon)}} = n \vec{\mathcal{R}},$$

valid for negative-energy bound states. With this definition, eq. (10) becomes

$$(\vec{V} \cdot \vec{V}) + (\vec{L} \cdot \vec{L}) + 1 = \frac{1}{(-2\epsilon)} = n^2, \quad (12)$$

and the commutator algebra of the operators,  $\vec{V}$ ,  $\vec{L}$ , is given by

$$[L_j, L_k] = i\epsilon_{jka} L_a, \quad [L_j, V_k] = i\epsilon_{jka} V_a, \quad [V_j, V_k] = i\epsilon_{jka} L_a. \quad (13)$$

If we define  $L_{jk} = -L_{kj}$ , with  $j, k = 1, \dots, 4$  through

$$\begin{aligned}L_{jk} &= \frac{1}{i} \left( x_j \frac{\partial}{\partial x_k} - x_k \frac{\partial}{\partial x_j} \right), & \text{with } L_1 &= L_{23}, \quad L_2 = L_{31}, \quad L_3 = L_{12}, \\ \text{and } V_j &= L_{j4},\end{aligned}\quad (14)$$

the six operators,  $\vec{L}$ ,  $\vec{V}$ , satisfy the same commutation relations as the six  $L_{jk}$ ; i.e., the six operators,  $\vec{L}$ ,  $\vec{V}$ , constitute infinitesimal rotation generators in an abstract 4-D space; i.e., they generate an SO(4) group, with a subgroup, SO(3), generated by the three components of  $\vec{L}$ .

It is useful to define the vector operators,  $\vec{M}$  and  $\vec{N}$ , through

$$\vec{M} = \frac{1}{2}(\vec{L} + \vec{V}), \quad \vec{N} = \frac{1}{2}(\vec{L} - \vec{V}), \quad (15)$$

where these operators satisfy the commutation relations of two *commuting* angular momentum operators

$$[M_j, M_k] = i\epsilon_{jka}M_a, \quad [N_j, N_k] = i\epsilon_{jka}N_a, \quad [M_j, N_k] = 0. \quad (16)$$

Eqs. (11) and (12) then lead to

$$\begin{aligned} (\vec{M}^2 - \vec{N}^2) &= \frac{1}{2}(\vec{L} \cdot \vec{V} + \vec{V} \cdot \vec{L}) = 0, \\ (\vec{M}^2 + \vec{N}^2) &= \frac{1}{2}(n^2 - 1). \end{aligned} \quad (17)$$

If the eigenvalues of the operators  $\vec{M}^2$  and  $\vec{N}^2$  are denoted by  $j_1(j_1 + 1)$  and  $j_2(j_2 + 1)$ , respectively, these relations require

$$j_1 = j_2 = \frac{1}{2}(n - 1). \quad (18)$$

These angular momentum quantum numbers can thus be integral or half-integral. Two commuting angular momentum operators of this type generate a group which is a direct product of two SU(2) groups:  $SU(2) \times SU(2)$ . Because  $\vec{L} = (\vec{M} + \vec{N})$ , and we want to construct states of good orbital angular momentum, we want to use the vector-coupled basis  $|[j_1 \times j_2]lm\rangle = |[\frac{1}{2}(n-1) \times \frac{1}{2}(n-1)]lm\rangle$ , which is an eigenvector simultaneously of  $\vec{L}^2$ ,  $L_0$ , and  $H$ , the latter with eigenvalue,  $\epsilon = -1/2n^2$ . The quantum number,  $n$ , also gives the eigenvalues of  $\vec{M}^2$  and  $\vec{N}^2$ . Angular momentum vector coupling rules tell us the possible quantum numbers  $l$  range from 0, 1, . . . to (n-1).

To understand the significance of the vector  $\vec{V} = (\vec{M} - \vec{N})$ , let us rewrite

$$\vec{V} = n\left(\vec{r}(\vec{p} \cdot \vec{p} - \frac{1}{r}) - \vec{p}(\vec{r} \cdot \vec{p})\right)$$

in terms of spherical coordinates,  $r, \theta, \phi$ . It will be sufficient to choose one component, e.g., the  $z$  component, which then has the form

$$\begin{aligned} \frac{V_0}{n} &= r \cos \theta \left( -\frac{\partial^2}{\partial r^2} - \frac{2}{r} \frac{\partial}{\partial r} + \frac{l(l+1)}{r^2} - \frac{1}{r} \right) \\ &\quad + \left( \cos \theta \left( \frac{\partial}{\partial r} \right) + \frac{\sin \theta e^{i\phi}}{2r} L_- - \frac{\sin \theta e^{-i\phi}}{2r} L_+ \right) \left( r \frac{\partial}{\partial r} \right). \end{aligned} \quad (19)$$

Using the known matrix elements of  $L_{\pm}$  and of  $\cos \theta$  and  $\sin \theta e^{\pm i\phi}$ , see e.g., eqs. (42)–(44) of Chapter 9, we see that action of this operator on a Coulomb eigenfunction yields

$$\begin{aligned} V_0 R_{nl}(r) Y_{lm}(\theta, \phi) &= \\ n(l+1) &\left[ \left( -\frac{\partial}{\partial r} + \frac{l}{r} - \frac{1}{(l+1)} \right) R_{nl}(r) \right] \sqrt{\frac{[(l+1)^2 - m^2]}{(2l+1)(2l+3)}} Y_{(l+1)m} \\ &\quad + nl \left[ \left( +\frac{\partial}{\partial r} + \frac{(l+1)}{r} - \frac{1}{l} \right) R_{nl}(r) \right] \sqrt{\frac{[l^2 - m^2]}{(2l+1)(2l-1)}} Y_{(l-1)m}. \end{aligned} \quad (20)$$

Rewriting the radial function in terms of the one-dimensionalized radial function,  $R_{nl}(r) = u_{nl}(r)/r$ , and introducing the Clebsch–Gordan coefficients,  $\langle lm10|(l \pm 1)m\rangle$  (see the table at the end of Chapter 28), this can be rewritten as

$$\begin{aligned}
V_0 R_{nl}(r) Y_{lm}(\theta, \phi) &= \\
n(l+1) \frac{1}{r} \left[ \left( -\frac{\partial}{\partial r} + \frac{(l+1)}{r} - \frac{1}{(l+1)} \right) u_{nl}(r) \right] & \\
\times \sqrt{\frac{(l+1)}{(2l+3)}} \langle lm10|(l+1)m\rangle Y_{(l+1)m} & \\
-nl \frac{1}{r} \left[ \left( +\frac{\partial}{\partial r} + \frac{l}{r} - \frac{1}{l} \right) u_{nl}(r) \right] \sqrt{\frac{l}{(2l-1)}} \langle lm10|(l-1)m\rangle Y_{(l-1)m} & \\
= n(l+1) \frac{1}{r} \left( O_+(l+1) u_{nl}(r) \right) \sqrt{\frac{(l+1)}{(2l+3)}} \langle lm10|(l+1)m\rangle Y_{(l+1)m} & \\
-nl \frac{1}{r} \left( O_-(l) u_{nl}(r) \right) \sqrt{\frac{l}{(2l-1)}} \langle lm10|(l-1)m\rangle Y_{(l-1)m}, & \quad (21)
\end{aligned}$$

where the operators  $O_+(l+1)$  and  $O_-(l)$  are the  $l$  step operators introduced in Chapter 10 to construct the radial Coulomb eigenfunctions. Finally, using the operators,  $\mathcal{O}_+(l+1)$  and  $\mathcal{O}_-(l)$ , which construct normalized radial functions [see eq. (13) of Chapter 10], we have

$$\begin{aligned}
V_0 \left[ \frac{1}{r} u_{nl}(r) \right] Y_{lm}(\theta, \phi) &= \\
\sqrt{(l+1)[n^2 - (l+1)^2]} \frac{1}{r} \mathcal{O}_+(l+1) u_{nl}(r) \frac{\langle lm10|(l+1)m\rangle}{\sqrt{(2l+3)}} Y_{(l+1)m} & \\
-\sqrt{l[n^2 - l^2]} \frac{1}{r} \mathcal{O}_-(l) u_{nl}(r) \frac{\langle lm10|(l-1)m\rangle}{\sqrt{(2l-1)}} Y_{(l-1)m}, & \quad (22)
\end{aligned}$$

where  $(1/r)[\mathcal{O}_+(l+1)u_{nl}(r)]$  gives the normalized  $R_{n(l+1)}(r)$ , and similarly for  $(1/r)[\mathcal{O}_-(l)u_{nl}(r)]$ . Recalling the definition of the reduced matrix elements

$$\langle nl'm | V_0 | nlm \rangle = \frac{\langle lm10|l'm\rangle}{\sqrt{(2l'+1)}} \langle nl' \| \vec{V} \| nl \rangle,$$

we see

$$\begin{aligned}
\langle n(l+1) \| \vec{V} \| nl \rangle &= \sqrt{(l+1)[n^2 - (l+1)^2]}, \\
\langle n(l-1) \| \vec{V} \| nl \rangle &= -\sqrt{l[n^2 - l^2]}. \quad (23)
\end{aligned}$$

These equations give the only nonzero matrix elements of  $\vec{V}$ . We note that the properly normalized Runge–Lenz vector operator gives the  $l$  step operators in the subspace of a definite principal quantum number,  $n$ . Because the components of  $\vec{L}$  furnish the  $m$  step operators for a fixed  $l$ ; the operators  $\vec{V}$  and  $\vec{L}$  can serve to construct all  $n^2$  states of a definite  $n$ , starting with the maximum possible  $l = m = (n-1)$ .

Although we have achieved our aim of finding the meaning of  $\vec{V}$ , we could have arrived at the above reduced matrix elements of  $\vec{V}$  by using the angular momen-

tum-coupled basis  $|[\frac{1}{2}(n-1) \times \frac{1}{2}(n-1)]lm\rangle$ , in which the angular momentum eigenvectors of  $\vec{M}$  are coupled to the angular momentum eigenvectors of  $\vec{N}$  to resultant good orbital angular momentum of definite  $l, m$ . With  $\vec{L} = \vec{M} + \vec{N}$ , and  $\vec{V} = \vec{M} - \vec{N}$ , the reduced matrix elements of  $\vec{L}$  and  $\vec{V}$  follow from the reduced matrix elements of  $\vec{M}$  and  $\vec{N}$  via a simple unitary 9-j coefficient [see eq. (42) of Chapter 34]. Recall the vector  $\vec{M}$  is a spherical tensor of spherical rank 1 in the  $\vec{M}$  space, but because it does not act on the  $\vec{N}$  space, it can be thought of as multiplied by the number 1, a spherical tensor of rank 0 in the  $\vec{N}$  space. Thus,

$$\begin{aligned} & \langle [j_1 j_2]l' | \vec{M} \pm \vec{N} | [j_1 j_2]l \rangle \\ & \equiv \langle [\frac{1}{2}(n-1) \quad \frac{1}{2}(n-1)]l' | \vec{M} \pm \vec{N} | [\frac{1}{2}(n-1) \quad \frac{1}{2}(n-1)]l \rangle \\ & = \frac{1}{2}\sqrt{(2l'+1)(n-1)(n+1)} \left[ U \begin{pmatrix} \frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l \\ 1 & 0 & 1 \\ \frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l' \end{pmatrix} \right. \\ & \quad \left. \pm U \begin{pmatrix} \frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l \\ 0 & 1 & 1 \\ \frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l' \end{pmatrix} \right] \\ & = \frac{1}{2}\sqrt{(2l'+1)(n-1)(n+1)} \left( 1 \pm (-1)^{l'+l} \right) \\ & \quad \times \left[ U \begin{pmatrix} \frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l \\ 1 & 0 & 1 \\ \frac{1}{2}(n-1) & \frac{1}{2}(n-1) & l' \end{pmatrix} \right], \end{aligned} \quad (24)$$

where we have used the reduced matrix elements,

$$\langle j' | 1 | j \rangle = \delta_{jj'}\sqrt{(2j+1)}, \quad \langle j' | \vec{J} | j \rangle = \delta_{jj'}\sqrt{(2j+1)j(j+1)},$$

valid for any angular momentum operator [see eqs. (4) and (7) of Chapter 32], where now  $\vec{J}$  is either  $\vec{M}$  or  $\vec{N}$  and  $j = \frac{1}{2}(n-1)$  for both. In the last step of the above equation, we have also used a symmetry property of the 9-j coefficient, involving interchange of columns 1 and 2. Finally, the unitary 9-j coefficient with one angular momentum,  $j_4$ , of zero can be replaced by a unitary Racah coefficient [see eq. (38) of Chapter 34], to yield

$$\begin{aligned} & \langle [\frac{1}{2}(n-1) \quad \frac{1}{2}(n-1)]l' | \vec{M} \pm \vec{N} | [\frac{1}{2}(n-1) \quad \frac{1}{2}(n-1)]l \rangle = \\ & \frac{1}{2}\sqrt{(2l'+1)(n-1)(n+1)}(-1)^{l'-l}U(\frac{1}{2}(n-1)\frac{1}{2}(n-1)l'1; l\frac{1}{2}(n-1)) \\ & \quad \times \left( 1 \pm (-1)^{l'+l} \right). \end{aligned} \quad (25)$$

We see at once  $\vec{L} = \vec{M} + \vec{N}$  has only diagonal matrix elements with  $l' = l$ , whereas  $\vec{V} = \vec{M} - \vec{N}$  has zero diagonal matrix element with  $l' = l$ . (This can, of course, also be seen from the negative parity of the operator  $\vec{V}$ .) The Racah coefficients, with one  $j = 1$ , are tabulated as algebraic functions of the possible angular momentum quantum numbers (see the angular momentum references at the end of Chapter 28). Putting in these values, we obtain the above results for  $\langle nl' | \vec{V} | nl \rangle$ , and the expected

$$\langle nl' | \vec{L} | nl \rangle = \delta_{ll'}\sqrt{(2l+1)l(l+1)}. \quad (26)$$

## C The SO(2,1) Algebra

So far, the six operators,  $\vec{V}$  and  $\vec{L}$ , can be used to generate the states and matrix elements in the  $n^2$ -dimensional subspace of a definite bound state of the hydrogen atom. To obtain general expressions for the matrix elements of radial functions, we still need to construct operators that can raise or lower the principal quantum number,  $n$ . For this purpose, we introduce the three operators, useful also for general central force potentials,

$$\begin{aligned} T_1 &= \frac{1}{2} \left( r p_r^2 + \frac{l(l+1)}{r} - r \right) \\ T_2 &= r p_r \\ T_3 &= \frac{1}{2} \left( r p_r^2 + \frac{l(l+1)}{r} + r \right), \end{aligned} \quad (27)$$

with

$$p_r = \frac{1}{i} \left( \frac{\partial}{\partial r} + \frac{1}{r} \right), \quad (28)$$

where  $r$  is again the dimensionless  $r = r_{\text{phys.}}/a_0$ . These  $T_i$  satisfy the SO(2,1) commutation relations

$$[T_1, T_2] = -iT_3, \quad [T_2, T_3] = iT_1, \quad [T_3, T_1] = iT_2, \quad (29)$$

or in terms of  $T_{\pm} = (T_1 \pm iT_2)$

$$[T_3, T_{\pm}] = \pm T_{\pm}, \quad \text{but} \quad [T_+, T_-] = -2T_3. \quad (30)$$

Except for one minus sign, these operators would be standard angular momentum operators. (The eigenvectors and operator matrix elements of these  $T_i$  were studied in problem 23.) These  $T_i$ , however, are hermitian operators not with respect to the standard volume element measure,  $d\Omega dr r^2$ , but instead with respect to the measure,  $d\Omega dr r$ . For example,

$$\begin{aligned} &\int \int d\Omega \int_0^\infty dr r \psi_1^* (T_2 \psi_2) = \int \int d\Omega \int_0^\infty dr r \psi_1^* \frac{1}{i} \left( r \frac{\partial}{\partial r} + 1 \right) \psi_2 \\ &= \int \int d\Omega \left( \frac{1}{i} r^2 \psi_1^* \psi_2 |_0^\infty + \left( - \int_0^\infty dr \psi_2 \frac{1}{i} \frac{\partial}{\partial r} (r^2 \psi_1^*) + \int_0^\infty dr \psi_2 \frac{r}{i} \psi_1^* \right) \right) \\ &= - \int \int d\Omega \left( \int_0^\infty dr \psi_2 \frac{r}{i} \psi_1^* + \int_0^\infty dr r^2 \psi_2 \frac{1}{i} \frac{\partial \psi_1^*}{\partial r} \right) \\ &= \int \int d\Omega \left( \int_0^\infty dr r \psi_2 (T_2 \psi_1) \right)^*. \end{aligned} \quad (31)$$

The three  $T_i$  commute with the generalized  $\vec{T}^2$  or SO(2,1) Casimir operator,  $\mathcal{C}$ , defined by

$$\begin{aligned} \mathcal{C} &= T_3^2 - T_1^2 - T_2^2 = (T_3 - T_1)(T_3 + T_1) - [T_3, T_1] - T_2^2 \\ &= r^2 p_r^2 + l(l+1) - i r p_r - (r p_r)(r p_r) = l(l+1). \end{aligned} \quad (32)$$

In a basis in which both  $\mathcal{C}$  and  $T_3$  are diagonal,

$$\mathcal{C}|ql\rangle = l(l+1)|ql\rangle,$$

$$T_3 = q|ql\rangle, \quad (33)$$

the spectrum of allowed  $q$  values is given by a ladder of values starting with a minimum  $q$  value (see problem 23)

$$q = q_{\min} + n_r = (l + 1) + n_r, \quad \text{with } n_r = 0, 1, 2, \dots, \infty, \quad (34)$$

so the eigenvalue,  $q$ , of the operator  $T_3$  can be identified with the principal quantum number  $n = l + 1 + n_r$ , and the nonzero matrix elements of  $\vec{T}$  are given by

$$\begin{aligned} (ql|T_3|ql) &= q = n, \\ ((q - 1)l|T_-|ql) &= \sqrt{(q + l)(q - l - 1)}, \\ ((q + 1)l|T_+|ql) &= \sqrt{(q - l)(q + l + 1)}. \end{aligned} \quad (35)$$

(See problem 23.) Note:  $T_-$  annihilates the state with  $q = (l + 1)$ , and  $T_+$  can act as step-up operator to create states with  $q = n > (l + 1)$ .

## D The Dilation Property of the Operator, $T_2$

For the ordinary angular momentum algebra, the operator  $e^{i\phi L_2}$  acted as a rotation operator. For the SO(2,1) algebra, the corresponding operator,  $e^{iaT_2}$ , acts as a dilation operator. Here, the parameter,  $a$ , like  $\phi$ , is a real number. This dilation or stretching property follows because  $e^{iaT_2}$  acting on an arbitrary function of  $r$  yields

$$e^{iaT_2} F(r) = e^{a(r \frac{d}{dr} + 1)} F(r) = e^a F(e^a r). \quad (36)$$

This relation follows if  $F(r)$  can be expanded in an infinite series,

$$F(r) = c_0 + \sum_{n=1}^{\infty} (c_{-n}/r^n + c_n r^n),$$

because

$$e^{ar \frac{d}{dr}} r^{\pm n} = \sum_k \frac{a^k}{k!} \left( r \frac{d}{dr} \right)^k r^{\pm n} = \left( \sum_k \frac{(\pm an)^k}{k!} \right) r^{\pm n} = e^{\pm an} r^{\pm n} = \left( e^a r \right)^{\pm n}. \quad (37)$$

We shall also need the transformation of operators,  $O$ , via the unitary operator,  $e^{iaT_2}$

$$e^{iaT_2} O e^{-iaT_2} = \sum_n \frac{(ia)^n}{n!} [T_2, [T_2, [T_2, \dots [T_2, O] \dots]]]_n, \quad (38)$$

where the expansion is in terms of the  $n^{\text{th}}$  commutator of  $T_2$  with the operator,  $O$  (for a derivation, see eqs. (23)–(25) of Chapter 16). For example, if  $O = T_3$ , we see that

$$[T_2, [T_2, [T_2, \dots [T_2, T_3] \dots]]]^{2n+1} = i^{2n+1} T_1, \quad (39)$$

for a commutator with an odd number of  $T_2$ 's, whereas

$$[T_2, [T_2, [T_2, \dots [T_2, T_3] \dots]]]^{2n} = i^{2n} T_3, \quad (40)$$

for a commutator with an even number of  $T_2$ 's. We therefore obtain

$$e^{iaT_2} T_3 e^{-iaT_2} = \cosh aT_3 - \sinh aT_1, \quad (41)$$

and, similarly,

$$e^{iaT_2} T_1 e^{-iaT_2} = \cosh aT_1 - \sinh aT_3. \quad (42)$$

Also, with  $r = T_3 - T_1$ ,

$$e^{iaT_2} r e^{-iaT_2} = e^a r, \quad (43)$$

and

$$e^{iaT_2} p_r e^{-iaT_2} = e^{-a} p_r. \quad (44)$$

From these last two relations, the dilation transformation properties of simple functions of  $r$  and  $p_r$  can be obtained.

## E The Zeroth-Order Energy Eigenvalue Problem for the Hydrogen Atom: Stretched States

The zeroth-order hydrogen atom eigenvalue problem can be written in terms of the  $\text{SO}(2,1)$  operators  $T_i$ . Keeping in mind the natural measure for these operators is  $d\Omega dr$  (rather than the conventional  $d\Omega dr r^2$ ), the zeroth-order energy eigenvalue problem can be rewritten as

$$\begin{aligned} 0 &= \int d\vec{r} \Psi^* (H - \epsilon) \Psi \\ &= \int \int d\Omega \int_0^\infty dr r \Psi^* (rH - r\epsilon) \Psi \\ &= \int \int d\Omega \int_0^\infty dr r \Psi^* \left( \frac{1}{2} \left( rp_r^2 + \frac{\vec{L}^2}{r} \right) - 1 - r\epsilon \right) \Psi \\ &= \int \int d\Omega \int_0^\infty dr r \Psi^* \left( \frac{1}{2} r \left( -\frac{\partial^2}{\partial r^2} - \frac{2}{r} \frac{\partial}{\partial r} + \frac{l(l+1)}{r^2} \right) - 1 - r\epsilon \right) \Psi \\ &= \int \int d\Omega \int_0^\infty dr r \Psi^* \left( \frac{1}{2} (T_3 + T_1) - \epsilon (T_3 - T_1) - 1 \right) \Psi. \end{aligned} \quad (45)$$

Although we have succeeded in rewriting the operator  $r(H - \epsilon)$  in terms of the generators  $T_3$  and  $T_1$ , these cannot be made simultaneously diagonal. To eliminate the unwanted  $T_1$ , we shall stretch the states  $\Psi$  with the dilation operator. By inserting unit operators, expressed through  $1 = e^{-iaT_2} e^{iaT_2}$ , in the appropriate places, the above eigenvalue integral can be rewritten as

$$\begin{aligned} 0 &= \int d\vec{r} \Psi^* (H - \epsilon) \Psi \\ &= \int \int d\Omega \int_0^\infty dr r \left( e^{iaT_2} \Psi \right)^* \left[ e^{iaT_2} \left( \frac{1}{2} (T_3 + T_1) \right) \right. \\ &\quad \left. e^{-iaT_2} \Psi \right] \end{aligned}$$

$$\begin{aligned}
& -\epsilon(T_3 - T_1) - 1 \Big] e^{-iaT_2} \Big] \Big( e^{iaT_2} \Psi \Big) \\
& = \int_0^\infty dr r \Big( e^{iaT_2} R_{nl}(r) \Big)^* \Big( \Big[ (\frac{1}{2} - \epsilon) \cosh a - (\frac{1}{2} + \epsilon) \sinh a \Big] T_3 \\
& + \Big[ (\frac{1}{2} + \epsilon) \cosh a - (\frac{1}{2} - \epsilon) \sinh a \Big] T_1 - 1 \Big) \Big( e^{iaT_2} R_{nl}(r) \Big), \quad (46)
\end{aligned}$$

where we have assumed the angular part of  $\Psi$  is a spherical harmonic of definite  $l$  and  $m$ . By choosing the real number,  $a$ , such that the coefficient of the  $T_1$  term in the last line of the above relation is set equal to zero, the radial part of  $(e^{iaT_2} \Psi)$  will have been transformed into an eigenfunction of  $T_3$  and  $\mathcal{C}$ . This result is achieved by choosing the parameter,  $a$ , such that

$$\Big[ (\frac{1}{2} + \epsilon) \cosh a - (\frac{1}{2} - \epsilon) \sinh a \Big] = 0, \quad (47)$$

which, for bound states, with negative  $\epsilon$ , leads to

$$e^{2a} = -\frac{1}{2\epsilon} = +n^2, \quad (48)$$

so

$$e^a = n \quad \text{and} \quad \Big[ (\frac{1}{2} - \epsilon) \cosh a - (\frac{1}{2} + \epsilon) \sinh a \Big] = \frac{1}{n} \quad (49)$$

for a bound state with  $\epsilon = -1/2n^2$ . The above eigenvalue equation then becomes

$$\begin{aligned}
0 &= \int \int d\Omega \int_0^\infty dr r \Psi^*(rH - r\epsilon)\Psi \\
&= \int_0^\infty dr r \Big( e^{iaT_2} R_{nl}(r) \Big)^* \Big( \frac{1}{n} T_3 - 1 \Big) \Big( e^{iaT_2} R_{nl}(r) \Big) \\
&= |\mathcal{N}|^2 \int_0^\infty dr r \psi_{ql}^* \Big( \frac{1}{n} T_3 - 1 \Big) \psi_{ql}, \quad (50)
\end{aligned}$$

which leads to the eigenvalue equation

$$(T_3 - n)\psi_{ql} = (q - n)\psi_{ql} = 0, \quad (51)$$

so  $q$  can be identified with the conventional principal quantum number,  $n$ . We previously found that  $q = q_{\min.} + n_r = (l+1) + n_r$ , which agrees with this result. In the above, we have named the stretched state

$$\Big( e^{iaT_2} R_{nl}(r) \Big) = \mathcal{N} \psi_{ql}, \quad (52)$$

where  $\psi_{q=n,l}$  is the normalized eigenfunction of the hermitian operator  $T_3$  and the full 3-D function  $\psi_{nl}(r)Y_{lm}(\theta, \phi) \equiv \Psi_{nlm}(\vec{r})$  is normalized with the new measure  $d\Omega dr r$ . Because of this change of measure, the normalization is not preserved by the unitary dilation operator  $e^{iaT_2}$ . The normalization factor,  $\mathcal{N}$ , can be derived from

$$1 = \int_0^\infty dr r^2 R_{nl}(r)^* R_{nl}(r)$$

$$\begin{aligned}
&= \int_0^\infty dr r \left( e^{iaT_2} R_{nl}(r) \right)^* \left( e^{iaT_2} r e^{-iaT_2} \right) \left( e^{iaT_2} R_{nl}(r) \right) \\
&= \int_0^\infty dr r \mathcal{N}^* \psi_{nl}^*(r) (nr) \mathcal{N} \psi_{nl}(r) = |\mathcal{N}|^2 \int_0^\infty dr r \psi_{nl}^*(r) n(T_3 - T_1) \psi_{nl}(r) \\
&= |\mathcal{N}|^2 n^2 \int_0^\infty dr r \psi_{nl}(r)^* \psi_{nl}(r) = |\mathcal{N}|^2 n^2,
\end{aligned} \tag{53}$$

where we have used the eigenvalue eq. (51) and the fact that  $T_1$  has no matrix elements diagonal in  $n$ . We can therefore choose

$$\mathcal{N} = \frac{1}{n}. \tag{54}$$

Henceforth, we shall use the notations,

$$\psi_{q=n,l}(r), \quad \text{or } \Psi_{q=n,lm}(\vec{r}) = \psi_{q=n,l}(r) Y_{lm}(\theta, \phi),$$

for the normalized stretched eigenfunctions and retain the  $R_{nl}(r)Y_{lm}(\theta, \phi)$  for the conventional normalized bound-state eigenfunctions. To avoid confusion between the two conventions, we shall use caret notation for state vectors and matrix elements for the conventional hydrogenic states, but will use round parentheses for the state vectors and matrix elements of the stretched states. Thus, for an operator,  $O$ , a function of  $\vec{r}$  and/or  $\vec{p}$ ,

$$\int \int d\Omega \int_0^\infty dr r^2 (R_{n'l'}(r) Y_{l'm'}(\theta, \phi))^* O R_{nl}(r) Y_{lm}(\theta, \phi) \equiv \langle n'l'm' | O | nlm \rangle, \tag{55}$$

but for the analogous operator,  $\tilde{O} \equiv e^{iaT_2} O e^{-iaT_2}$ ,

$$\int \int d\Omega \int_0^\infty dr r \Psi_{n'l'm'}^*(\vec{r} \tilde{O}) \Psi_{nlm} \equiv \langle n'l'm' | (\tilde{O}) | nlm \rangle. \tag{56}$$

[We have already anticipated this change of notation in our discussion of the matrix elements of the SO(2,1) operators  $T_i$  in eq. (35), where we have used round parentheses.] We can construct the explicit functional dependence of the  $\psi_{ql}(r)$ , via the explicit relation,  $T_-|q = q_{\min.} = (l+1), l\rangle = 0$ , and subsequent successive action with  $T_+$ . Using

$$T_\pm = (T_1 \pm i T_2) = (T_1 - T_3) \pm iT_2 + T_3 = -r \pm \left( r \frac{\partial}{\partial r} + 1 \right) + T_3, \tag{57}$$

the relation

$$\begin{aligned}
T_-|q = q_{\min.} = (l+1), l\rangle &= 0 && \text{leads to} \\
\left( -r - r \frac{\partial}{\partial r} - 1 + (l+1) \right) \psi_{q=(l+1),l}(r) &= 0,
\end{aligned} \tag{58}$$

so

$$r \frac{d\psi_{(l+1),l}}{dr} = (l-r)\psi_{(l+1),l}, \tag{59}$$

with solution (normalized with the measure  $drr$ ),

$$\psi_{q=(l+1),l}(r) = \frac{2^{l+1}}{\sqrt{(2l+1)!}} r^l e^{-r}. \quad (60)$$

States with values of  $q > q_{\min}$  can be obtained with successive action of  $T_+$ , with

$$\begin{aligned} |(q+1)l\rangle &= \frac{1}{\sqrt{(q-l)(q+l+1)}} T_+ |ql\rangle \\ \psi_{(q+1)l}(r) &= \frac{1}{\sqrt{(q-l)(q+l+1)}} \left( r \frac{d}{dr} - r + q + 1 \right) \psi_{ql}(r), \end{aligned} \quad (61)$$

or

$$\begin{aligned} \psi_{ql}(r) &= \left[ \frac{1}{1 \cdot 2 \cdots (q-l-1) \cdot (2l+2)(2l+3) \cdots (q+l)} \right]^{\frac{1}{2}} \left( r \frac{d}{dr} - r + q \right) \\ &\quad \times \left( r \frac{d}{dr} - r + q - 1 \right) \cdots \left( r \frac{d}{dr} - r + l + 3 \right) \left( r \frac{d}{dr} - r + l + 2 \right) \psi_{q=(l+1)l}(r) \\ &= \sqrt{\frac{(2l+1)!}{(q+l)!(q-l-1)!}} \left( r \frac{d}{dr} - r + q \right) \left( r \frac{d}{dr} - r + q - 1 \right) \cdots \\ &\quad \cdots \left( r \frac{d}{dr} - r + l + 3 \right) \left( r \frac{d}{dr} - r + l + 2 \right) \psi_{q=(l+1)l}(r). \end{aligned} \quad (62)$$

Using the identity

$$\left( r \frac{d}{dr} - r + \alpha \right) \psi(r) = e^r \left( r \frac{d}{dr} + \alpha \right) e^{-r} \psi(r), \quad (63)$$

and the fact that  $(r \frac{d}{dr} + \alpha)$  commutes with  $(r \frac{d}{dr} + \beta)$ , the function  $\psi_{ql}(r)$  can be rewritten (note the reversal of the operator order),

$$\begin{aligned} \psi_{ql}(r) &= \sqrt{\frac{(2l+1)!}{(q+l)!(q-l-1)!}} e^r \left( r \frac{d}{dr} + l + 2 \right) \left( r \frac{d}{dr} + l + 3 \right) \cdots \\ &\quad \cdots \left( r \frac{d}{dr} + q - 1 \right) \left( r \frac{d}{dr} + q \right) e^{-r} \psi_{q=(l+1)l}(r) \\ &= \sqrt{\frac{(2l+1)!}{(q+l)!(q-l-1)!}} e^r \frac{1}{r^{l+1}} \frac{d}{dr} r^{l+2} \frac{d}{dr} \cdots \frac{d}{dr} r^{q-1} \frac{d}{dr} r^q e^{-r} \\ &\quad \times \frac{2^{l+1}}{\sqrt{(2l+1)!}} r^l e^{-r}, \end{aligned} \quad (64)$$

where we have made repeated use of the operator identity

$$\left( r \frac{d}{dr} + \alpha \right) = \frac{1}{r^{\alpha-1}} \frac{d}{dr} r^\alpha, \quad (65)$$

with  $\alpha = l+2, l+3, \dots, \alpha = q$ . Simplifying, the above equation leads to the expression

$$\psi_{q,l}(r) = \frac{2^{l+1}}{\sqrt{(q+l)!(q-l-1)!}} e^r \frac{1}{r^{l+1}} \frac{d^{q-l-1}}{dr^{q-l-1}} \left( r^{q+l} e^{-2r} \right). \quad (66)$$

As a final remark to this section, we note that the stretched states with  $q = n$ , eigenstates of the operator,  $T_3$ , apply to the bound states of the hydrogen atom only, with negative  $\epsilon$ . For the continuum states with  $\epsilon > 0$ , the requirement,  $e^{2a} = -(1/2\epsilon)$  of eq. (48) cannot be met with a real value for  $a$ , and hence a unitary stretching operator  $e^{iaT_2}$ . In this case, however,  $e^a$  can be chosen such that the stretched states are eigenstates of the operator,  $T_1$ , by choosing a real parameter,  $a$ , such that the coefficient of  $T_3$  in eq. (46) is set equal to zero, viz.,

$$\left(\frac{1}{2} - \epsilon\right) \cosh a - \left(\frac{1}{2} + \epsilon\right) \sinh a = 0, \quad (67)$$

leading to

$$e^{2a} = +\frac{1}{2\epsilon} = \frac{1}{(ka_0)^2} = \gamma^2, \quad (68)$$

where  $\gamma$  is the Coulomb parameter introduced in eq. (6). Now the zeroth order equation becomes

$$\begin{aligned} \left(\frac{1}{\gamma} T_1 - 1\right) \left(e^{iaT_2} R_{\gamma,l}(r)\right) &= 0, \\ (T_1 - \gamma) \mathcal{N}_\gamma \psi_{\gamma,l}(r) &= 0. \end{aligned} \quad (69)$$

The important point, however, is the following. The states  $\psi_{nl}(r)$  and the  $\psi_{\gamma,l}(r)$  belong to different irreducible representations of the SO(2,1) group. Each forms a complete set of its own. Perturbation theory for the bound states will not connect the  $\psi_{nl}$  to the  $\psi_{\gamma,l}$ .

## F Perturbations of the Coulomb Problem

For a perturbed hydrogenic atom problem, it will be useful to transcribe the Schrödinger equation for the full Hamiltonian into the stretched-state basis. The SO(2,1) basis will be particularly useful for spherically symmetric perturbations, where  $l$  and  $m$  will be good quantum numbers to all orders. In that case [case (1) of Chapter 23], the spherical,  $nlm$ , is the symmetry adapted or proper basis; and therefore nondegenerate perturbation theory can be used. No connections exist from  $lm$  to states with  $l' \neq l$ ,  $m' \neq m$ . For that case, the Schrödinger equation for the full Hamiltonian

$$\begin{aligned} 0 &= r(H - \epsilon)R_{nl}(r) \\ &= r \left[ (H^{(0)} + H^{(1)} + H^{(2)} + \dots) - (\epsilon^{(0)} + \epsilon^{(1)} + \epsilon^{(2)} + \dots) \right] R_{nl}(r) \\ &= \left( \left[ \frac{1}{2}(rp_r^2 + \frac{l(l+1)}{r}) - 1 - r\epsilon^{(0)} \right] \right. \\ &\quad \left. + \left[ (rH^{(1)} - r\epsilon^{(1)}) + (rH^{(2)} - r\epsilon^{(2)}) + \dots \right] \right) R_{nl}(r) \end{aligned} \quad (70)$$

can be transcribed to stretched form by acting on the above with  $e^{iaT_2}$  to obtain

$$\begin{aligned} 0 &= e^{iaT_2} \left( \left[ \frac{1}{2}(T_3 + T_1) - 1 - (T_3 - T_1)\epsilon^{(0)} \right] + \left[ (T_3 - T_1)(H^{(1)} - \epsilon^{(1)}) \right. \right. \\ &\quad \left. \left. + (T_3 - T_1)(H^{(2)} - \epsilon^{(2)}) + \dots \right] \right) e^{-iaT_2} (e^{iaT_2} R_{nl}) \\ &= \frac{\mathcal{N}}{n} \left( (T_3 - n) + n \left[ n(T_3 - T_1)(\tilde{H}^{(1)} - \epsilon^{(1)} + \tilde{H}^{(2)} - \epsilon^{(2)} + \dots) \right] \right) \psi_{ql} \quad (71) \end{aligned}$$

where

$$\tilde{H}^{(i)} = e^{iaT_2} H^{(i)} e^{-iaT_2}, \quad (72)$$

and the  $\psi_{ql}$  are expanded in terms of the zeroth-order eigenfunctions of  $T_3$ ,

$$T_3 \psi_{ql}^{(0)} = q \psi_{ql}^{(0)} = n \psi_{q=n,l}^{(0)}, \quad (73)$$

where now eq. (71) can be written as

$$\left[ (T_3 - n) + (H_{\text{eff.}}^{(1)} - \epsilon_{\text{eff.}}^{(1)}) + (H_{\text{eff.}}^{(2)} - \epsilon_{\text{eff.}}^{(2)}) + \dots \right] (\psi_{nl}^{(0)} + \psi_{nl}^{(1)} + \psi_{nl}^{(2)} + \dots) = 0. \quad (74)$$

Here,

$$H_{\text{eff.}}^{(i)} = n^2 (T_3 - T_1) \tilde{H}^{(i)}, \quad \epsilon_{\text{eff.}}^{(i)} = n^2 (T_3 - T_1) \epsilon^{(i)}. \quad (75)$$

Straightforward generalization of Rayleigh–Schrödinger perturbation theory in terms of the zeroth-order eigenfunctions of  $T_3$  (rather than  $H^{(0)}$ ), now yields

$$(\psi_{nl}^{(0)} | \epsilon_{\text{eff.}}^{(1)} | \psi_{nl}^{(0)}) = n^3 \epsilon_{nl}^{(1)} = (\psi_{nl}^{(0)} | H_{\text{eff.}}^{(1)} | \psi_{nl}^{(0)}), \quad (76)$$

$$\psi_{nl}^{(1)} = \sum_{q \neq n} c_{ql}^{(1)} \psi_{ql}^{(0)}, \quad \text{with } c_{ql}^{(1)} = \frac{(\psi_{ql}^{(0)} | (H_{\text{eff.}}^{(1)} - \epsilon_{\text{eff.}}^{(1)}) | \psi_{nl}^{(0)})}{(n - q)}, \quad (77)$$

and

$$\begin{aligned} (\psi_{nl}^{(0)} | \epsilon_{\text{eff.}}^{(2)} | \psi_{nl}^{(0)}) &= n^3 \epsilon_{nl}^{(2)} = (\psi_{nl}^{(0)} | H_{\text{eff.}}^{(2)} | \psi_{nl}^{(0)}) \\ &+ \sum_{q \neq n} \frac{(\psi_{nl}^{(0)} | (H_{\text{eff.}}^{(1)} - \epsilon_{\text{eff.}}^{(1)}) | \psi_{ql}^{(0)}) (\psi_{ql}^{(0)} | (H_{\text{eff.}}^{(1)} - \epsilon_{\text{eff.}}^{(1)}) | \psi_{nl}^{(0)})}{(n - q)}. \end{aligned} \quad (78)$$

Once the number,  $\epsilon_n^{(1)}$ , has been calculated, the matrix elements of  $\epsilon_{\text{eff.}}^{(1)}$  can be calculated, but this operator now has off-diagonal connections through the  $T_1$  part of the operator  $(T_3 - T_1)$ .

For nonspherically symmetric perturbations, the results of eqs. (76) through (78) will still apply for the nondegenerate case, e.g., for the hydrogenic ground state,  $n = 1$ , or for axially symmetric perturbations for the special states with  $l = (n - 1)$  and  $m = \pm(n - 1)$ , provided the  $\psi_{ql}^{(0)}$  of eqs. (76)–(78) are replaced with the full stretched state,  $\Psi_{nlm}^{(0)}$ . In addition, the sums over  $q \neq n$  will have to include sums over states with  $l' \neq l$ , and possibly  $m' \neq m$ . For the general degenerate states, it

is best to parallel the treatment of the degenerate case of Chapter 24 and first make a similarity transformation of the operator

$$\left[ (T_3 - n) + (H_{\text{eff.}}^{(1)} - \epsilon_{\text{eff.}}^{(1)}) + \dots \right]$$

via a unitary operator,  $e^{i\lambda G}$ , where now

$$\begin{aligned} (n'l'm'|G|nlm) &= \frac{-i}{(n' - n)} (n'l'm'|H_{\text{eff.}}^{(1)} - \epsilon_{\text{eff.}}^{(1)}|nlm) \quad \text{for } n' \neq n, \\ (nlm|G|n'l'm') &= \frac{-i}{(n - n')} (nlm|H_{\text{eff.}}^{(1)} - \epsilon_{\text{eff.}}^{(1)}|n'l'm') \quad \text{for } n' \neq n, \\ (nl'm'|G|nlm) &= (nlm|G|nl'm') = 0; \quad \text{for all } l', m' \text{ if } n' = n. \end{aligned} \quad (79)$$

This process leads to a matrix in the  $n$  subspace that is the analog of eq. (12) of Chapter 24, if the  $H^{(i)}$  there are replaced by  $H_{\text{eff.}}^{(i)} - \epsilon_{\text{eff.}}^{(i)}$ , and the  $E_n^{(0)}$  and  $E_{q \neq n}^{(0)}$  of Chapter 24 are now replaced by  $n$  and  $q$ . The pure numbers  $\epsilon_n^{(1)}$  may first have to be determined by diagonalizing this matrix in first order in  $\lambda$ , but the  $\epsilon_{\text{eff.}}^{(1)}$  contributes to the off-diagonal sums in second order through its  $(T_3 - T_1)$  factor.

The greatest usefulness of the stretched spherical hydrogenic basis comes into play with spherically symmetric perturbations.

## G An Application: Coulomb Potential with a Perturbing Linear Potential: Charmonium

A Coulomb potential with a linear confining potential may have some useful applications. The charmed quark-charmed antiquark two-body system has particles heavy enough so that nonrelativistic quantum theory may be a very good approximation. The bound states of this system have been described by an attractive  $1/r$  color-electric potential augmented by a linear confining potential. For the deeply bound states, where the  $1/r$  potential predominates, the linear (repulsive) confining potential may be treated as a perturbation. We then have a perturbed Coulomb problem with

$$H^{(1)} = V^{(1)}(r) = +\lambda r, \quad H^{(2)} = 0, \quad (80)$$

where we assume  $\lambda \ll 1$  and  $r$  is again a dimensionless  $r$ . Also,  $\lambda > 0$ . Now,

$$H_{\text{eff.}}^{(1)} = \lambda n^3 (T_3 - T_1)^2, \quad \epsilon_{\text{eff.}}^{(i)} = n^2 (T_3 - T_1) \epsilon_n^{(i)}. \quad (81)$$

By rewriting

$$(T_3 - T_1) = T_3 - \frac{1}{2}(T_+ + T_-) \quad \text{and} \quad (82)$$

$$\begin{aligned} (T_3 - T_1)^2 &= T_3^2 + \frac{1}{4}(T_+T_- + T_-T_+) - T_+(T_3 + \frac{1}{2}) - T_-(T_3 - \frac{1}{2}) \\ &\quad + \frac{1}{4}T_+T_+ + \frac{1}{4}T_-T_- \\ &= \frac{3}{2}T_3^2 - \frac{1}{2}l(l+1) - T_+(T_3 + \frac{1}{2}) - T_-(T_3 - \frac{1}{2}) \\ &\quad + \frac{1}{4}T_+T_+ + \frac{1}{4}T_-T_-, \end{aligned} \quad (83)$$

we can use the simple matrix elements of  $T_3$ ,  $T_{\pm}$  to obtain, via eq. (76),

$$\epsilon_n^{(1)} = \lambda \left[ \frac{3}{2}n^2 - \frac{1}{2}l(l+1) \right], \quad (84)$$

and via eq. (78),

$$\begin{aligned} n^3 \epsilon_n^{(2)} &= \\ &\frac{1}{(-1)} \left[ \left( -n^3 \lambda (n + \frac{1}{2}) + \frac{1}{2}n^2 \epsilon_n^{(1)} \right) \sqrt{(n-l)(n+l+1)} \right]^2 \\ &+ \frac{1}{(+1)} \left[ \left( -n^3 \lambda (n - \frac{1}{2}) + \frac{1}{2}n^2 \epsilon_n^{(1)} \right) \sqrt{(n+l)(n-l-1)} \right]^2 \\ &+ \frac{1}{(-2)} \left[ \frac{1}{4} \lambda n^3 \sqrt{(n+1-l)(n+2+l)(n-l)(n+1+l)} \right]^2 \\ &+ \frac{1}{(+2)} \left[ \frac{1}{4} \lambda n^3 \sqrt{(n-1+l)(n-2-l)(n+l)(n-1-l)} \right]^2 \\ &= -\lambda^2 \frac{1}{8} n^5 (7n^4 + 5n^2 - 3l^2(l+1)^2), \end{aligned} \quad (85)$$

leading to

$$\epsilon = -\frac{1}{2n^2} + \lambda \left[ \frac{3}{2}n^2 - \frac{1}{2}l(l+1) \right] - \lambda^2 \frac{1}{8} n^2 [7n^4 + 5n^2 - 3l^2(l+1)^2] + \dots \quad (86)$$

## H Matrix Elements of the Vector Operators, $\vec{r}$ and $r\vec{p}$ , in the Stretched Basis

In the last example, all of the needed matrix elements involved merely matrix elements of the  $SO(2,1)$  generators,  $T_i$ . For spherically nonsymmetric perturbations, however, we will encounter spherical tensors of higher rank that can change the quantum numbers  $l$  and  $m$ . The basic operators, from which more complicated ones can be built, are the vector operators,  $\vec{r}$  and  $\vec{p}$ . So far, the only  $l$  step operators we have met are the components of the Runge–Lenz vector, which left the principal quantum number,  $n$ , invariant. Conversely, the ladder operators,  $T_{\pm}$ , of  $SO(2,1)$  could change only the  $n$  quantum number within a ladder of a definite  $l$ . The general vector operator, such as  $\vec{r}$  and  $\vec{p}$ , can change both  $n$  and  $l$ .

Recall, first, the Runge–Lenz vector, in the form of the vector,  $\vec{V}$ , is given by

$$\begin{aligned} \vec{V} &= \frac{1}{\sqrt{(-2\epsilon)}} \left[ \vec{r} \left( \frac{1}{2}(\vec{p} \cdot \vec{p}) \right) - \vec{p}(\vec{r} \cdot \vec{p}) + \vec{r} \left[ \frac{1}{2}(\vec{p} \cdot \vec{p}) - \frac{1}{r} \right] \right] \\ &= n \left[ \vec{r} \left[ \frac{1}{2}(\vec{p} \cdot \vec{p}) \right] - \vec{p}(\vec{r} \cdot \vec{p}) + \vec{r} \left( \frac{-1}{2n^2} \right) \right], \end{aligned} \quad (87)$$

where this has been put into the most convenient form for conversion into its stretched counterpart,  $\tilde{\vec{V}} \equiv \vec{A}$ ,

$$\tilde{\vec{V}} = e^{iaT_2} \vec{V} e^{-iaT_2} \equiv \vec{A} = n \left[ n\vec{r} \frac{(\vec{p} \cdot \vec{p})}{2n^2} - \frac{\vec{p}}{n}(n\vec{r} \cdot \frac{\vec{p}}{n}) + n\vec{r} \left( \frac{-1}{2n^2} \right) \right]$$

$$\equiv \vec{A} = \vec{r}\left(\frac{1}{2}(\vec{p} \cdot \vec{p})\right) - \vec{p}(\vec{r} \cdot \vec{p}) - \frac{1}{2}\vec{r}. \quad (88)$$

Because

$$\begin{aligned} & \int d\Omega \int_0^\infty dr r^2 (R_{nl'} Y_{l'm'})^* V_\mu R_{nl} Y_{lm} \\ &= \int d\Omega \int_0^\infty dr r \left(\frac{\psi_{nl'}}{n} Y_{l'm'}\right)^* \left(e^{iaT_2} r e^{-iaT_2}\right) \tilde{V}_\mu \frac{\psi_{nl}}{n} Y_{lm} \\ &= \int d\Omega \int_0^\infty dr r \left(\frac{\psi_{nl'}}{n} Y_{l'm'}\right)^* \left(n(T_3 - T_1)\right) \tilde{V}_\mu \frac{\psi_{nl}}{n} Y_{lm} \\ &= \int d\Omega \int_0^\infty dr r (\psi_{nl'} Y_{l'm'})^* \tilde{V}_\mu \psi_{nl} Y_{lm}, \end{aligned} \quad (89)$$

where we have used  $T_3 \psi_{nl'} = n \psi_{nl'}$  and the fact that  $T_1$  has no matrix elements diagonal in  $n$ ,

$$\langle nl'm' | V_\mu | nlm \rangle = \langle nl'm' | A_\mu | nlm \rangle. \quad (90)$$

The reduced matrix elements of  $\vec{A}$  in the stretched basis are therefore the same as the reduced matrix elements of  $\vec{V}$  in the conventional basis.

$$\begin{aligned} (nl| \vec{A} | nl) &= \sqrt{(l+1)[n^2 - (l+1)^2]} \\ (nl| \vec{A} | nl) &= -\sqrt{l[n^2 - l^2]} \\ (nl| \vec{A} | nl) &= 0. \end{aligned} \quad (91)$$

In addition, the commutator algebra of the six operators  $\vec{L}$  and  $\vec{A}$  is the same as that of  $\vec{L}$  and  $\vec{V}$ . Also, because  $\vec{L}$  are functions only of  $\theta, \phi$  and  $\partial/\partial\theta, \partial/\partial\phi$ ,

$$[T_2, L_j] = 0, \quad \text{for } j = 1, 2, 3. \quad (92)$$

Finally,

$$\begin{aligned} [T_2, A_j] &= [\frac{1}{i} \left(r \frac{\partial}{\partial r} + 1\right), \frac{1}{2} x_j ((\vec{p} \cdot \vec{p}) - 1) - p_j (\vec{r} \cdot \vec{p})] \\ &= i \left(\frac{1}{2} x_j (\vec{p} \cdot \vec{p}) - p_j (\vec{r} \cdot \vec{p}) + \frac{1}{2} x_j\right) = i B_j, \end{aligned} \quad (93)$$

where we have introduced the vector,  $\vec{B}$ , given by

$$\begin{aligned} \vec{B} &= \left(\frac{1}{2}\vec{r}(\vec{p} \cdot \vec{p}) - \vec{p}(\vec{r} \cdot \vec{p}) + \frac{1}{2}\vec{r}\right), \\ \text{while } \vec{A} &= \left(\frac{1}{2}\vec{r}(\vec{p} \cdot \vec{p}) - \vec{p}(\vec{r} \cdot \vec{p}) - \frac{1}{2}\vec{r}\right). \end{aligned} \quad (94)$$

In particular,

$$\vec{r} = \vec{B} - \vec{A}, \quad (95)$$

and we have expressed the needed vector,  $\vec{r}$ , in terms of operators which make it convenient to calculate its matrix elements in the stretched hydrogenic basis. In particular, from the commutator

$$[T_2, A_3] = i B_3, \quad \text{or} \quad B_3 = \frac{1}{2}[(T_- - T_+), A_3], \quad (96)$$

we get the matrix elements (in the stretched basis!),

$$\begin{aligned} (n'l'm|B_3|nlm) &= (n'l'|\vec{B}|nl) \frac{\langle lm|10|l'm\rangle}{\sqrt{(2l'+1)}} \\ &= \frac{1}{2} \left[ (n'l'm|(T_- - T_+)|nl'm)(nl'|\vec{A}|nl) \right. \\ &\quad \left. - (n'l'|\vec{A}|nl')(n'l'm|(T_- - T_+)|nlm) \right] \frac{\langle lm|10|l'm\rangle}{\sqrt{(2l'+1)}}. \end{aligned} \quad (97)$$

$\vec{A}$  can change only  $l \rightarrow (l \pm 1)$ , but keeps  $n$  invariant, whereas  $T_\pm$  changes only  $n \rightarrow (n \pm 1)$  but keeps  $l$  invariant. The sum over intermediate states in the above relation has thus collapsed to a single term for each of the four possible  $n'l'$  values of  $(n \pm 1)(l \pm 1)$ . In addition, because  $\vec{r} = \vec{B} - \vec{A}$ , and because the nonzero matrix elements of  $\vec{A}$  are restricted to  $n', l' = n, (l \pm 1)$ , we can obtain the reduced matrix elements of  $\vec{r}$  in the stretched basis by combining the above relation with the known matrix elements of  $\vec{A}$  to yield

$$\begin{aligned} ((n+1)(l+1)|\vec{r}|nl) &= +\frac{1}{2}\sqrt{(l+1)(n+l+1)(n+l+2)} \\ (n(l+1)|\vec{r}|nl) &= -\sqrt{(l+1)(n+l+1)(n-l-1)} \\ ((n-1)(l+1)|\vec{r}|nl) &= +\frac{1}{2}\sqrt{(l+1)(n-l-1)(n-l-2)} \\ ((n+1)(l-1)|\vec{r}|nl) &= -\frac{1}{2}\sqrt{l(n-l+1)(n-l)} \\ (n(l-1)|\vec{r}|nl) &= +\sqrt{l(n+l)(n-l)} \\ ((n-1)(l-1)|\vec{r}|nl) &= -\frac{1}{2}\sqrt{l(n+l-1)(n+l)}. \end{aligned} \quad (98)$$

Because  $\vec{r}$  can be combined with itself or with functions of  $r = (T_3 - T_1)$ , we can use the above matrix elements to gain the matrix elements of more complicated functions of  $\vec{r}$  and  $r$ . To get reduced matrix elements of  $\vec{p}$ , we note that

$$[T_3, B_3] = -irp_3. \quad (99)$$

This simple commutator can thus be used to generate matrix elements of a new vector,

$$r\vec{p} \equiv \vec{C}. \quad (100)$$

This relation is ideal for matrix elements in the stretched hydrogenic basis, because the needed vector  $\vec{p}$  in the conventional basis will lead to matrix elements of  $r\vec{p}$  in the stretched basis. The commutator relation  $rp_3 = +i[T_3, B_3]$  leads at once to

$$\begin{aligned} (n'l'm|rp_3|nlm) &= +i(n'-n)(n'l'm|B_3|nlm), \\ (n'l'|\vec{r}\vec{p}|nl) &= +i(n'-n)(n'l'|\vec{B}|nl). \end{aligned} \quad (101)$$

We have now met four vector operators,  $\vec{L}$ ,  $\vec{A}$ ,  $\vec{B}$ ,  $\vec{C}$ , and the three components  $T_j$ . We have already seen  $\vec{L}$  and  $\vec{A}$  form the six components of a 4-D angular momentum algebra, if we identify  $A_j = L_{j4}$ . If we further identify  $B_j = L_{j5}$ , and

$C_j = L_{j6}$ , and  $T_2 = L_{45}$ ,  $T_1 = L_{46}$ ,  $T_3 = L_{56}$ , so, with  $j, k = 1, \dots, 6$ ,

$$L_{jk} = \begin{pmatrix} 0 & L_3 & -L_2 & A_1 & B_1 & C_1 \\ -L_3 & 0 & L_1 & A_2 & B_2 & C_2 \\ L_2 & -L_1 & 0 & A_3 & B_3 & C_3 \\ -A_1 & -A_2 & -A_3 & 0 & T_2 & T_1 \\ -B_1 & -B_2 & -B_3 & -T_2 & 0 & T_3 \\ -C_1 & -C_2 & -C_3 & -T_1 & -T_3 & 0 \end{pmatrix}, \quad (102)$$

where the  $L_{jk} = -L_{kj}$  are “angular momentum” operators in a (4+2)-dimensional space, with commutation relations

$$[L_{ab}, L_{ac}] = i g_{aa} L_{bc}, \quad \text{with } g_{aa} = +1 \text{ for } a = 1, 2, 3, 4,$$

$$g_{55} = g_{66} = -1. \quad (103)$$

These 15 operators generate the group SO(4,2). We will not, however, need to make use of the detailed properties of this relatively complicated group! In order to solve hydrogenic perturbation problems, it will be sufficient for us to know the matrix elements of  $\vec{L}$ , including the  $m$  step operators  $L_{\pm}$ , of  $\vec{A}$  that are the  $l$  step operators for a fixed  $n$ , of  $T_{\pm}$  that are the  $n$  step operators for a fixed  $l$ , and, finally, of the vector operators  $\vec{r} = \vec{B} - \vec{A}$ , and  $r \vec{p} = \vec{C}$ . We have now achieved this goal.

## I Second-Order Stark Effect of the Hydrogen Ground State Revisited

Let us now reexamine the second-order Stark effect in the ground state of the hydrogen atom by using the stretched hydrogenic basis. The perturbing Hamiltonian can be written as

$$H^{(1)} = -\lambda r \cos \theta, \quad (103)$$

where  $r$  is now dimensionless and  $\lambda = (ea_0\mathcal{E})/(Ze^2/a_0)$  is also dimensionless. In the ground state with  $n = 1, l = 0$ , no diagonal matrix element exists, so  $\epsilon_{n=1}^{(1)} = 0$ . We therefore have  $\epsilon_{\text{eff.}}^{(1)} = 0$ , and, with  $n = 1$ ,

$$H_{\text{eff.}}^{(1)} = -\lambda(T_3 - T_1)\vec{r}_0 = -\lambda(T_3 - \frac{1}{2}T_+ - \frac{1}{2}T_-)\vec{r}_0. \quad (104)$$

From our tabulation of reduced matrix elements of  $\vec{r}$ ,

$$(n'10|\vec{r}_0|n = 1, l = 0, m = 0) = \frac{\langle 0010|10\rangle}{\sqrt{3}}(n'1||\vec{r}||10) = \frac{1}{\sqrt{3}}\delta_{n'2}\sqrt{\frac{3}{2}}. \quad (105)$$

Combining this with the matrix elements of  $T_3, T_{\pm}$ , we have

$$\begin{aligned} (210|H_{\text{eff.}}^{(1)}|100) &= -\lambda\sqrt{2}, \\ (310|H_{\text{eff.}}^{(1)}|100) &= +\lambda\sqrt{\frac{1}{2}}. \end{aligned} \quad (106)$$

The generalization of eq. (78) for the 3-D stretched basis then gives

$$\epsilon^{(2)} = -\lambda^2 \left[ \frac{2}{(2-1)} + \frac{1}{2} \frac{1}{(3-1)} \right] = -\lambda^2 \frac{9}{4}, \quad (107)$$

in agreement with the result of eq. (7), but now from the simple addition of two terms (no infinite sums over a set of discrete states and no integrals over a continuum!).

## J The Calculation of Off-Diagonal Matrix Elements via the Stretched Hydrogenic Basis

We have seen how use of the stretched basis greatly simplifies calculations for a specific bound state. The stretched hydrogenic basis may also be used to simplify off-diagonal matrix elements for transitions between different bound states. An example is the electric dipole moment matrix element between different hydrogen bound states. In eq. (4), we used the matrix element of  $r \cos \theta$  between a  $p$ -state of arbitrary  $n$  and the ground state. This process requires the calculation of the conventional matrix element

$$\langle 100 | r \cos \theta | n10 \rangle = \frac{1}{\sqrt{3}} \int_0^\infty dr r^3 R_{n=1,l=0}^*(r) R_{n,l=1}(r).$$

Let us transcribe this equation into the stretched basis for the state with arbitrary  $n$ , via

$$\begin{aligned} & \int_0^\infty dr r^3 R_{n=1,l=0}^*(r) R_{n,l=1}(r) \\ &= \int_0^\infty dr r \left( e^{iaT_2} R_{10}(r) \right)^* \left( e^{iaT_2} r^2 e^{-iaT_2} \right) \left( e^{iaT_2} R_{n1}(r) \right) \\ &= \int_0^\infty dr r \left( e^{iaT_2} R_{10}(r) \right)^* n^2 r^2 \frac{1}{n} \psi_{q=n,l=1} \\ &= \int_0^\infty dr r \left( n2e^{-nr} \right)^* nr^2 \frac{2^2}{\sqrt{(n+1)!(n-2)!}} \frac{e^r}{r^2} \frac{d^{n-2}}{dr^{n-2}} \left( r^{n+1} e^{-2r} \right), \end{aligned} \quad (109)$$

where, with  $e^a = n$ , we have used, see eq. (36),

$$e^{iaT_2} R_{10}(r) = e^a R_{10}(e^a r) = n R_{10}(nr),$$

for the 1s state of the left-hand side, and have substituted the general derivative expression for the stretched state,  $\psi_{n,1}(r)$ , derived in eq. (66). We therefore have

$$\langle 100 | r \cos \theta | n10 \rangle = \frac{2^3 n^2}{(n-2)! \sqrt{3(n+1)n(n-1)}} \int_0^\infty dr r e^{-(n-1)r} \frac{d^{n-2}}{dr^{n-2}} \left( r^{n+1} e^{-2r} \right). \quad (110)$$

The last integral is performed by integrating by parts  $(n-2)$  times to yield

$$\int_0^\infty dr r e^{-(n-1)r} \frac{d^{n-2}}{dr^{n-2}} \left( r^{n+1} e^{-2r} \right) = \int_0^\infty dr (n-1)^{n-2} r^{n+2} e^{-(n+1)r}$$

$$-(n-2) \int_0^\infty dr (n-1)^{n-3} r^{n+1} e^{-(n+1)r} = \frac{(n-1)^{n-3}}{(n+1)^{n+3}} (n+1)! 2n, \quad (111)$$

leading to the final result

$$\langle 100 | r \cos \theta | nl = 10 \rangle = \frac{(n-1)^{n-3}}{(n+1)^{n+3}} 2^4 n^3 \sqrt{\frac{(n+1)n(n-1)}{3}}. \quad (112)$$

## K Final Remarks

As we have seen, the techniques introduced in this chapter are particularly useful for spherically symmetric perturbations of the hydrogenic atom. For nonspherically symmetric perturbations, the stretched hydrogenic basis can be used to get second-order results, but the solution for the final eigenvalues and eigenvectors still requires the diagonalization of some finite-dimensional matrices. For axially symmetric perturbations, parabolic coordinates are more convenient. We have seen in problem 26 that stretched parabolic coordinates,  $\mu, v$ , can be expressed in term of two commuting  $SO(2,1)$  groups with generators,  $T_i$  and  $T'_i$ . The zeroth-order hydrogen problem is then transformed into an eigenvalue equation of the form

$$(T_3 + T'_3) \psi_{n_1, m}(\mu) \psi_{n_2, m}(v) e^{\pm im\phi} = \left[ \left( \frac{1}{2}(m+1) + n_1 \right) + \left( \frac{1}{2}(m+1) + n_2 \right) \right] \psi_{n_1, m}(\mu) \psi_{n_2, m}(v) e^{\pm im\phi}, \quad (113)$$

with  $(n_1 + n_2 + m + 1) = n$ , where  $n$  is the usual principal quantum number. The Stark effect has been solved to second order for arbitrary,  $n$ , using this  $SO(2, 1) \times SO(2, 1)$  basis in problem 38.

A very good reference for the use of the stretched spherical basis for hydrogenic perturbation problems is: *Lie Algebraic Methods and their Applications to Simple Quantum Systems*; B. G. Adams, J. Cizek and J. Paldus, Advances in Quantum Chemistry **19** (1988) 1; and Barry G. Adams, *Algebraic Approach to Simple Quantum Systems*, New York: Springer-Verlag, 1994. For a detailed use of the stretched parabolic coordinates, see D. Delande and J. C. Gay, J. Phys. B: At. Mol. Phys. **17** (1984) L335.

## Problems

- 48.** Use the stretched spherical basis to show the conventional diagonal matrix element of  $r^2$  is given by

$$\langle nlm | r^2 | nlm \rangle = \frac{5}{2} n^4 - \frac{3}{2} n^2 l(l+1) + \frac{1}{2} n^2.$$

- 49.** Assume the attractive Coulombic ( $1/r$ ) potential for a two-body nonrelativistic system is perturbed by a quadratic repulsive term, with  $H^{(1)} = +\lambda r^2$ , where  $\lambda \ll 1$  and  $r$  is dimensionless. Show that the energy through second order

is given by

$$\epsilon = -\frac{1}{2n^2} + \lambda \left( \frac{5}{2}n^4 - \frac{3}{2}n^2l(l+1) + \frac{1}{2}n^2 \right)$$

$$-\lambda^2 \frac{n^6}{16} \left( 143n^4 + 345n^2 + 28 - 90n^2l(l+1) - 21l^2(l+1)^2 - 126l(l+1) \right).$$

**50.** Use the stretched hydrogenic functions to show the conventional matrix element of the electric dipole moment between the  $2s$  state and an arbitrary  $p$  state is given by

$$\langle 200|r \cos \theta|n10\rangle = \sqrt{\frac{(n+1)n(n-1)}{2 \cdot 3}} \frac{2^9 n^3 (n-2)^{n-3}}{(n+2)^{n+3}}.$$

**51.** Write the dilation operator,  $e^{iaT_2} = e^{\frac{1}{2}a(T_+ - T_-)}$ , in its “disentangled” forms. In particular, show that

$$e^{iaT_2} = e^{-\tanh \frac{a}{2} T_-} (\cosh^2 \frac{a}{2})^{T_0} e^{+\tanh \frac{a}{2} T_+},$$

$$e^{iaT_2} = e^{+\tanh \frac{a}{2} T_+} \frac{1}{(\cosh^2 \frac{a}{2})^{T_0}} e^{-\tanh \frac{a}{2} T_-}.$$

Hint: Use (1) the corresponding result for the angular momentum operators of SO(3) (see Chapter 29); (2) the fact that the operators  $T_3, iT_+, iT_-$  of SO(2,1) have formally the same commutation relations as the operators  $J_3, J_+, J_-$  of SO(3); and (3) the fact that the disentanglement relations depend only on the commutator algebra of the operators. Use these relations to rederive the result of eq. (112), without the use of the explicit functional forms of the radial functions, by relating the conventional matrix element  $\langle n10|r \cos \theta|100\rangle$  to its stretched form

$$\begin{aligned} \langle n10|r \cos \theta|100\rangle &= \frac{1}{n} (\Psi_{n10}|e^{iaT_2}r(\vec{r})_0|\Psi_{100}) \\ &= \frac{1}{n\sqrt{2}} (\Psi_{n10}|e^{+\frac{(n-1)}{(n+1)}T_+} \left[ \frac{4n}{(n+1)^2} \right]^{T_3} e^{-\frac{(n-1)}{(n+1)}T_-} \left( T_3 - \frac{1}{2}(T_+ + T_-) \right)|\Psi_{210}), \end{aligned}$$

where we have used  $\vec{r}_0|\Psi_{100}\rangle = \frac{1}{\sqrt{2}}|\Psi_{210}\rangle$ , and  $\tanh \frac{a}{2} = (n-1)/(n+1)$ ,  $\cosh^2 \frac{a}{2} = (n+1)^2/4n$ .

# 36

## The WKB Approximation

Although this perturbation technique (due to Wentzel, Kramers, and Brillouin) has practical value essentially only for 1-D problems (or for problems separable into one-dimensionalized problems), it is of considerable interest through its connection with classical physics and the “old” (pre-1925) quantum theory. It is not only of historical theoretical importance, however. It can be very useful for problems involving quantum-mechanical tunneling.

For a one-dimensionalized Schrödinger equation, we have

$$\frac{d^2u}{dx^2} + \frac{2\mu}{\hbar^2}(E - V(x))u(x) = 0, \quad (1)$$

or

$$\frac{d^2u}{dx^2} + \frac{P^2(x)}{\hbar^2}u(x) = 0, \quad (2)$$

where  $P(x)$  is the “local” ( $x$ -dependent) momentum of the particle. Thus if  $V(x)$  were constant over a small range of  $x$  values,  $P$  would be the momentum of the particle in this range of  $x$  values. The WKB technique uses  $\hbar$  as an expansion parameter; that is, it uses an expansion in powers of  $\hbar$  that should therefore be valid in the classical limit  $\hbar \rightarrow 0$ . In particular, solutions are sought of the form

$$u(x) = e^{\frac{i}{\hbar}S(x)} = e^{\frac{i}{\hbar}\left(S_0(x) + \hbar S_1(x) + \hbar^2 S_2(x) + \dots\right)}, \quad (3)$$

so

$$u' = \frac{i}{\hbar}(S'_0 + \hbar S'_1 + \hbar^2 S'_2 + \dots)e^{\frac{i}{\hbar}S(x)}, \quad (4)$$

$$u'' = \left[ -\frac{1}{\hbar^2} (S'_0 + \hbar S'_1 + \hbar^2 S'_2 + \dots)^2 + \frac{i}{\hbar} (S''_0 + \hbar S''_1 + \hbar^2 S''_2 + \dots) \right] e^{\frac{i}{\hbar} S(x)}. \quad (5)$$

Substituting this relation into the Schrödinger equation, and picking off terms of order  $\frac{1}{\hbar^2}$ , of order  $\frac{1}{\hbar}$ , and of successively smaller order in powers of  $\hbar$ , we get (first) from the term of order  $\frac{1}{\hbar^2}$ :

$$-(S'_0)^2 + P^2(x) = 0, \quad (6)$$

$$\frac{dS_0}{dx} = \pm P(x), \quad S_0(x) = \pm \int_{\text{const.}}^x d\xi P(\xi). \quad (7)$$

Next, the term of order  $\frac{1}{\hbar}$  leads to

$$iS''_0 - 2S'_0 S'_1 = 0, \quad S'_1 = \frac{i}{2} \frac{S''_0}{S'_0} = \frac{i}{2} \frac{d}{dx} \ln S'_0, \quad (8)$$

leading to

$$S_1(x) = \frac{i}{2} \ln P(x), \quad \text{or} \quad e^{iS_1} = \frac{1}{\sqrt{P(x)}}. \quad (9)$$

In the next approximation, terms of order 1 in the powers of  $\hbar$  development lead to

$$iS''_1 - (S'_1)^2 - 2S'_0 S''_2 = 0, \quad (10)$$

$$S'_2 = \frac{i}{2} \frac{S''_1}{S'_0} - \frac{(S'_1)^2}{2S'_0} = -\frac{1}{4} \frac{S'''_0}{(S'_0)^2} + \frac{3}{8} \frac{(S''_0)^2}{(S'_0)^3} = -\frac{1}{4} \left( \frac{S''_0}{(S'_0)^2} \right)' - \frac{1}{8} \frac{(S''_0)^2}{(S'_0)^3}, \quad (11)$$

so

$$S_2 = -\frac{1}{4} \left( \frac{\frac{dP}{dx}}{P^2} \right) - \frac{1}{8} \int_{\text{const.}}^x d\xi \frac{\left( \frac{dP}{d\xi} \right)^2}{P^3(\xi)}, \quad (12)$$

or

$$S_2 = \frac{1}{4} \frac{\mu \frac{dV}{dx}}{[2\mu(E - V(x))]^{\frac{3}{2}}} - \frac{1}{8} \int_{\text{const.}}^x d\xi \frac{\mu^2 (\frac{dV}{d\xi})^2}{[2\mu(E - V(\xi))]^{\frac{5}{2}}}. \quad (13)$$

The second approximation function,  $S_2(x)$ , is usually neglected. We see, from its specific form, that this may be justified, provided  $V(x)$  is a mildly varying function of  $x$ , i.e.,  $|\frac{dV}{dx}|$  is small, and provided  $x$  is not near a classical turning point for which we would have  $(E - V(x)) = 0$ , hence, a zero in the denominator of the function  $S_2(x)$ . Assuming  $S_2$  can be neglected, we still have to consider two different types of solutions.

1. For  $(E - V(x)) > 0$ , for classically allowed regions, we have oscillatory solutions

$$u(x) = \frac{C}{\sqrt{P(x)}} \cos \left( \frac{1}{\hbar} \int_{x_2}^x d\xi P(\xi) + \alpha \right), \quad (14)$$

where we have assumed  $x > x_2$ ,  $x_2$  is a left classical turning point (see Fig. 36.1), and  $C$  and  $\alpha$  are integration constants.

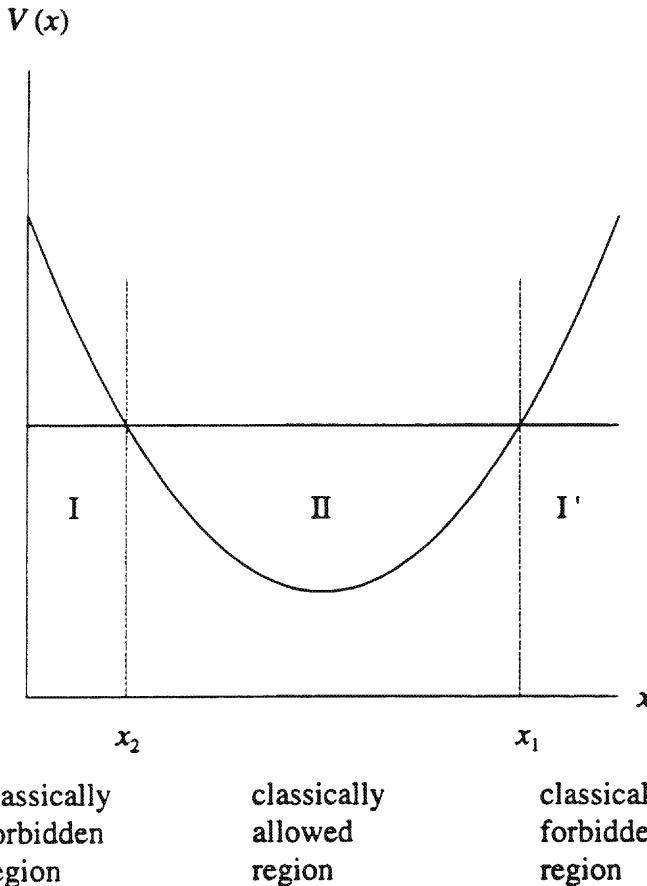


FIGURE 36.1.

2. For  $(E - V(x)) < 0$ , for classically forbidden regions, we have exponential solutions. These solutions are best put in the form

$$u(x) = \frac{A}{\sqrt{|P(x)|}} e^{+\frac{1}{\hbar} \int_{x_1}^x d\xi |P(\xi)|} + \frac{B}{\sqrt{|P(x)|}} e^{-\frac{1}{\hbar} \int_{x_1}^x d\xi |P(\xi)|}, \quad \text{for } x > x_1, \quad (15)$$

or

$$u(x) = \frac{A}{\sqrt{|P(x)|}} e^{+\frac{1}{\hbar} \int_{x_2}^x d\xi |P(\xi)|} + \frac{B}{\sqrt{|P(x)|}} e^{-\frac{1}{\hbar} \int_{x_2}^x d\xi |P(\xi)|}, \quad \text{for } x < x_2. \quad (16)$$

Even to this order, the WKB solutions blow up at the classical turning points. As  $x \rightarrow x_1$ , or  $x \rightarrow x_2$ ,  $P(x) \rightarrow 0$ , and the WKB solutions go to  $\infty$ . The exact solutions, however, have no remarkable behavior or singularities there. We need an expression that gives a continuous  $u(x)$  valid for all regions. We need to relate the integration constants,  $C, \alpha$ , from the oscillatory solutions to the  $A, B$  from

the exponential solutions. In square well problems, we had a similar situation, in which we used boundary conditions at discontinuities of the potential to find  $C$ ,  $\alpha$  as functions of  $A$ ,  $B$ . Unfortunately, it is precisely at the classical turning points, where  $u_{\text{WKB}}$  breaks down and becomes invalid (see Fig. 36.2). The problem was solved by Kramers through his connection formulae. In the vicinity of the classical turning points,  $x_1$ ,  $x_2$ , a good approximation to an exact solution can be found and this approximation can be used to make the connection between the exponential and the oscillatory WKB approximate solutions. For this purpose, it is sufficient to consider  $\frac{dV}{dx}$  to be constant over a small range of  $x$  near  $x = x_1$ , or near  $x = x_2$ , and use the exact solution for this straight-line potential of fixed slope to fit onto the oscillatory solution on one side and the exponential one on the other. The details involve Bessel functions with index  $n = \pm \frac{1}{3}$ . The details of the derivation will be given in an appendix.

## A The Kramers Connection Formulae

At a left turning point (see Fig. 36.1),  $x = x_2$ , a decreasing exponential solution connects onto an oscillatory solution according to

$$\frac{1}{\sqrt{|P(x)|}} e^{-\frac{i}{\hbar} \int_x^{x_2} d\xi |P(\xi)|} \leftrightarrow \frac{2}{\sqrt{P(x)}} \cos \left[ \frac{1}{\hbar} \int_{x_2}^x d\xi P(\xi) - \frac{\pi}{4} \right], \quad (17)$$

whereas an increasing exponential solution connects onto an oscillatory one according to

$$\frac{1}{\sqrt{|P(x)|}} e^{+\frac{i}{\hbar} \int_x^{x_2} d\xi |P(\xi)|} \leftrightarrow \frac{1}{\sqrt{P(x)}} \cos \left[ \frac{1}{\hbar} \int_{x_2}^x d\xi P(\xi) + \frac{\pi}{4} \right]. \quad (18)$$

At a right turning point,  $x = x_1$ , the decreasing exponential solution connects onto an oscillatory solution according to

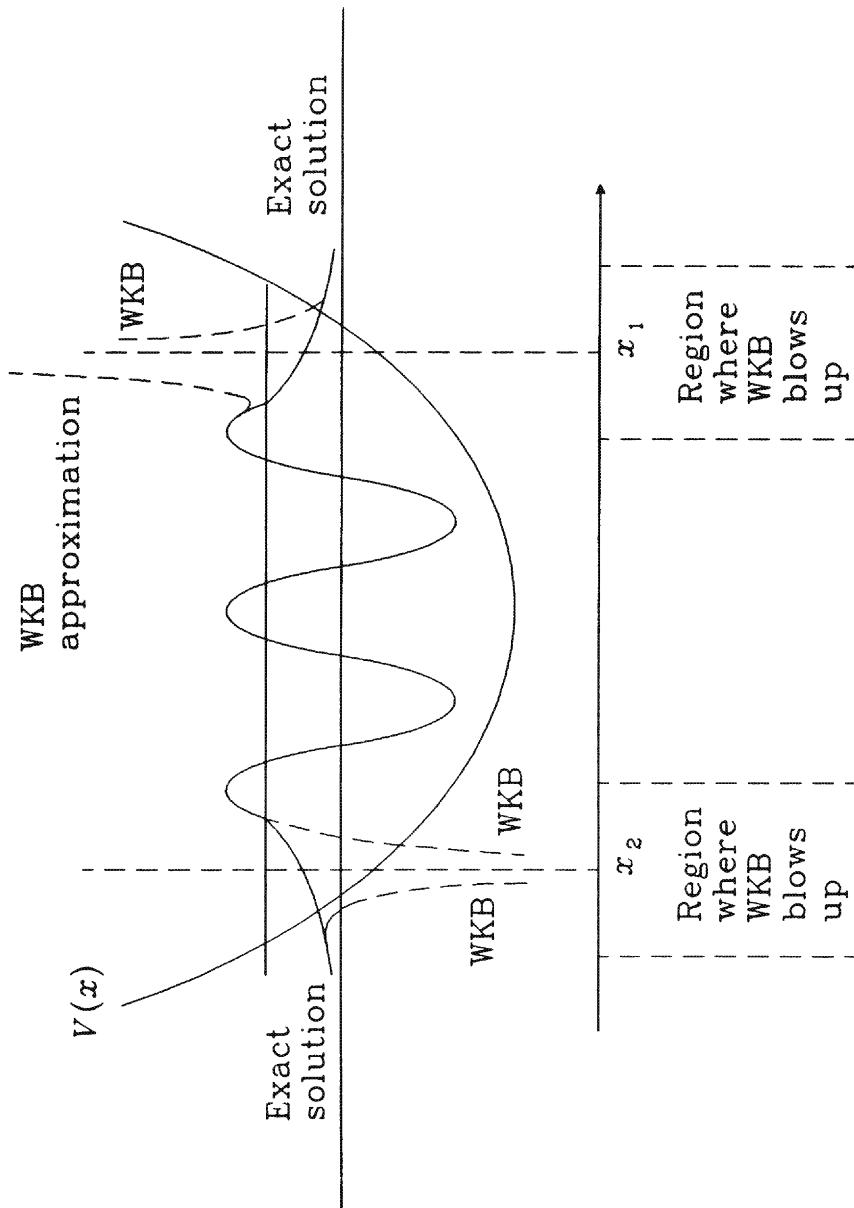
$$\frac{1}{\sqrt{|P(x)|}} e^{-\frac{i}{\hbar} \int_{x_1}^x d\xi |P(\xi)|} \leftrightarrow \frac{2}{\sqrt{P(x)}} \cos \left[ \frac{1}{\hbar} \int_x^{x_1} d\xi P(\xi) - \frac{\pi}{4} \right], \quad (19)$$

whereas the increasing exponential solution connects onto an oscillatory one according to

$$\frac{1}{\sqrt{|P(x)|}} e^{+\frac{i}{\hbar} \int_{x_1}^x d\xi |P(\xi)|} \leftrightarrow \frac{1}{\sqrt{P(x)}} \cos \left[ \frac{1}{\hbar} \int_x^{x_1} d\xi P(\xi) + \frac{\pi}{4} \right]. \quad (20)$$

## B Appendix: Derivation of the Connection Formulae

In the vicinity of a classical turning point (let us choose a left turning point  $x = x_2$ ), let us assume the potential function varies smoothly so the function  $V(x)$  can be approximated by a straight line over the region where the WKB approximation is not valid. Thus, for the left turning point,  $x = x_2$ , we will assume  $u_{\text{WKB}}(x)$  is

FIGURE 36.2. WKB and exact solutions for a  $V(x)$  with one classically allowed region.

a good approximation for  $x < x_2 - \frac{\Delta}{2}$  (in the exponential region I), and again for  $x > x_2 + \frac{\Delta}{2}$  (in the oscillatory region II). We will also assume in the region,  $x_2 - \frac{\Delta}{2} < x < x_2 + \frac{\Delta}{2}$ , the potential  $V(x)$  can be approximated by a straight line, so in this region

$$\frac{2\mu}{\hbar^2}(E - V(x)) = c^2(x - x_2), \quad \text{where } c^2 = \frac{2\mu}{\hbar^2} \left| \frac{dV}{dx} \right|_{x=x_2}. \quad (21)$$

The strategy is then the following: Find an exact solution to the equation

$$u'' + c^2(x - x_2)u(x) = 0, \quad (22)$$

valid in the region near  $x = x_2$  (where the WKB solution blows up), and continue this solution into region II where it matches the oscillatory WKB solution for  $x - x_2$  sufficiently large and also continue it to the left into region I where now for  $x_2 - x$  sufficiently large it matches the exponential WKB solution. It will be convenient to introduce new dependent and new independent variables for eq. (22).

In particular, in region I, for  $x < x_2$ , introduce

$$y = \frac{1}{\hbar} \int_x^{x_2} d\xi |P(\xi)| = c \int_x^{x_2} d\xi \sqrt{(x_2 - \xi)} = \frac{2}{3}c(x_2 - x)^{\frac{3}{2}}. \quad (23)$$

Similarly, in region II, for  $x > x_2$ , introduce

$$y = \frac{1}{\hbar} \int_{x_2}^x d\xi P(\xi) = c \int_{x_2}^x d\xi \sqrt{(\xi - x_2)} = \frac{2}{3}c(x - x_2)^{\frac{3}{2}}. \quad (24)$$

These relations lead to

$$\frac{du}{dx} = -c(x_2 - x)^{\frac{1}{2}} \frac{du}{dy}, \quad \text{for region I}, \quad (25)$$

$$\frac{du}{dx} = +c(x - x_2)^{\frac{1}{2}} \frac{du}{dy}, \quad \text{for region II}. \quad (26)$$

This process transforms the equation  $u'' + c^2(x - x_2)u = 0$  into

$$\pm c^2(x_2 - x) \left( \frac{d^2u}{dy^2} + \frac{1}{3y} \frac{du}{dy} \mp u \right) = 0, \quad (27)$$

for regions I (upper signs) and II (lower signs), respectively. Now we will make the further change of dependent variable,

$$u(y) = y^{\frac{1}{3}}v(y), \quad (28)$$

in both cases, leading to the new equations

$$y^2 \frac{d^2v}{dy^2} + y \frac{dv}{dy} + \left[ \mp y^2 - \left( \frac{1}{3} \right)^2 \right] v(y) = 0, \quad (29)$$

where upper (and lower) signs again refer to regions I (and II). This equation is the Bessel equation with index  $n^2 = (\frac{1}{3})^2$  of the variable  $y$  for region II, and the variable  $iy$  for region I. Thus,

$$v_I(y) = A_+ J_{+\frac{1}{3}}(iy) + A_- J_{-\frac{1}{3}}(iy) = A_+ I_{+\frac{1}{3}}(y) + A_- I_{-\frac{1}{3}}(y)$$

$$v_{II}(y) = B_+ J_{+\frac{1}{3}}(y) + B_- J_{-\frac{1}{3}}(y), \quad (30)$$

or

$$\begin{aligned} u_I(y) &= A_+ y^{\frac{1}{3}} I_{+\frac{1}{3}}(y) + A_- y^{\frac{1}{3}} I_{-\frac{1}{3}}(y) \\ u_{II}(y) &= B_+ y^{\frac{1}{3}} J_{+\frac{1}{3}}(y) + B_- y^{\frac{1}{3}} J_{-\frac{1}{3}}(y), \end{aligned} \quad (31)$$

where the arbitrary constants,  $A_+$ ,  $A_-$ ,  $B_+$ ,  $B_-$ , must still be chosen to make  $u$  and its first derivative continuous at  $y = 0$ , ( $x = x_2$ ). We therefore need the behavior of the Bessel function near  $y = 0$ . From

$$J_n(y) = \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \frac{1}{\Gamma(n+k+1)} \left(\frac{y}{2}\right)^{n+2k}, \quad (32)$$

we have near  $y = 0$

$$J_{\pm\frac{1}{3}}(y) = I_{\pm\frac{1}{3}}(y) = \frac{1}{\Gamma(\pm\frac{1}{3} + 1)} \left(\frac{y}{2}\right)^{\pm\frac{1}{3}} + \dots . \quad (33)$$

Therefore, near  $x = x_2$ , after transforming back to functions of  $x$ ,

$$\begin{aligned} u_I(x) &= \frac{A_+ (\frac{1}{2})^{\frac{1}{3}} (\frac{2c}{3})^{\frac{2}{3}}}{\Gamma(\frac{4}{3})} (x_2 - x)^{\frac{1}{3}} + \frac{A_- (\frac{1}{2})^{-\frac{1}{3}}}{\Gamma(\frac{2}{3})} + \dots, \\ u_{II}(x) &= \frac{B_+ (\frac{1}{2})^{\frac{1}{3}} (\frac{2c}{3})^{\frac{2}{3}}}{\Gamma(\frac{4}{3})} (x - x_2)^{\frac{1}{3}} + \frac{B_- (\frac{1}{2})^{-\frac{1}{3}}}{\Gamma(\frac{2}{3})} + \dots. \end{aligned} \quad (34)$$

Now, the requirement

$$u_I(x_2) = u_{II}(x_2) \quad \text{leads to} \quad B_- = A_-, \quad (35)$$

whereas

$$\left[ \frac{du_I}{dx} \right]_{x=x_2} = \left[ \frac{du_{II}}{dx} \right]_{x=x_2} \quad \text{leads to} \quad B_+ = -A_+. \quad (36)$$

Next, we want to continue these solutions to large values of  $y$ , far enough from the turning point,  $y = 0$ , so they may match the WKB solutions. For this purpose, we will attempt to use the asymptotic expansions of the Bessel functions, valid for large values of  $y$ . [Actual experience, that is, a look at the exact plots of  $J_n(y)$ , shows  $y$  does not have to be very large for these asymptotic expressions to be surprisingly good approximations.] For  $J_n(y)$ , as  $y \rightarrow \text{large}$ ,

$$J_n(y) \rightarrow \sqrt{\frac{2}{\pi y}} \cos(y - [n + \frac{1}{2}] \frac{\pi}{2}). \quad (37)$$

Thus,

$$J_{\pm\frac{1}{3}}(y) \rightarrow \sqrt{\frac{2}{\pi y}} \cos(y - \frac{\pi}{4} \mp \frac{\pi}{6}), \quad (38)$$

whereas

$$I_{\pm \frac{1}{3}}(y) \rightarrow \frac{1}{\sqrt{2\pi y}} \left( e^y + e^{-y} e^{-(\frac{1}{2} \pm \frac{1}{3})i\pi} \right), \quad (39)$$

but for large values of  $y$ ,  $e^{-y}$  is completely negligible compared with  $e^{+y}$ . The  $e^{-y}$  term comes into play only for the difference  $(I_{+\frac{1}{3}} - I_{-\frac{1}{3}})$  for which the  $e^y$  terms cancel. For this difference, as  $y \rightarrow$  large,

$$(I_{+\frac{1}{3}} - I_{-\frac{1}{3}}) \rightarrow \frac{1}{\sqrt{2\pi y}} e^{-y} \left( e^{-\frac{5i\pi}{6}} - e^{-\frac{i\pi}{6}} \right) = -\sqrt{\frac{2}{\pi y}} e^{-y} \cos \frac{\pi}{6}. \quad (40)$$

Otherwise,

$$I_{\pm \frac{1}{3}} \rightarrow \frac{1}{\sqrt{2\pi y}} e^{+y}. \quad (41)$$

Now, with the  $B_{\pm}$  determined from the boundary conditions at  $x = x_2$ , we have

$$\text{In region I : } u_I(y) = y^{\frac{1}{3}} (A_+ I_{+\frac{1}{3}}(y) + A_- I_{-\frac{1}{3}}(y)). \quad (42)$$

$$\text{In region II : } u_{II}(y) = y^{\frac{1}{3}} (-A_+ J_{+\frac{1}{3}}(y) + A_- J_{-\frac{1}{3}}(y)). \quad (43)$$

Let us now for a first choice pick  $A_+ = -A_-$ . Then,

$$u_I(y) = -y^{\frac{1}{3}} A_- (I_{+\frac{1}{3}}(y) - I_{-\frac{1}{3}}(y)) \rightarrow \frac{A_-}{y^{\frac{1}{6}}} \sqrt{\frac{2}{\pi}} e^{-y} \cos \frac{\pi}{6}. \quad (44)$$

Similarly, with this choice of constants,

$$\begin{aligned} u_{II}(y) &\rightarrow \frac{A_-}{y^{\frac{1}{6}}} \sqrt{\frac{2}{\pi}} \left( \cos(y - \frac{\pi}{4} - \frac{\pi}{6}) + \cos(y - \frac{\pi}{4} + \frac{\pi}{6}) \right) \\ &= \frac{A_-}{y^{\frac{1}{6}}} \sqrt{\frac{2}{\pi}} \left[ \cos(y - \frac{\pi}{4}) \right] 2 \cos \frac{\pi}{6}. \end{aligned} \quad (45)$$

Thus, with this choice of constants, viz.  $A_+ = -A_-$ , we get

$$\text{in I } \frac{e^{-y}}{y^{\frac{1}{6}}} \leftarrow u(y) \rightarrow \frac{2}{y^{\frac{1}{6}}} \cos(y - \frac{\pi}{4}) \text{ in II.} \quad (46)$$

Now, substituting the values for  $y$  for regions I and II, through eqs. (23) and (24), with (21), we can translate this equation into the connection formula

$$\frac{1}{\sqrt{|P(x)|}} e^{-\frac{1}{\hbar} \int_x^{x_2} d\xi |P(\xi)|} \rightarrow \frac{2}{\sqrt{P(x)}} \cos \left[ \frac{1}{\hbar} \int_{x_2}^x d\xi P(\xi) - \frac{\pi}{4} \right]. \quad (47)$$

This relation gives us one of the connection formulae for a left turning point.

To get the second connection formula, choose  $A_+ = A_-$ . Then, we have

$$u_I(y) = A_+ y^{\frac{1}{3}} (I_{+\frac{1}{3}} + I_{-\frac{1}{3}}) \rightarrow \frac{A_+}{\sqrt{2\pi}} \frac{1}{y^{\frac{1}{6}}} 2e^y, \quad (48)$$

and

$$\begin{aligned} u_{II}(y) &= A_+ y^{\frac{1}{3}} (-J_{+\frac{1}{3}} + J_{-\frac{1}{3}}) \\ &\rightarrow A_+ \frac{1}{y^{\frac{1}{6}}} \sqrt{\frac{2}{\pi}} \left( -\cos(y - \frac{\pi}{4} - \frac{\pi}{6}) + \cos(y - \frac{\pi}{4} + \frac{\pi}{6}) \right) \\ &= \frac{A_+}{y^{\frac{1}{6}}} \sqrt{\frac{2}{\pi}} \cos(y + \frac{\pi}{4}). \end{aligned} \quad (49)$$

Thus, with this choice of constants, we are led to

$$\text{in I } \frac{A_+}{y^{\frac{1}{6}}} \sqrt{\frac{2}{\pi}} e^{+y} \leftarrow u(y) \rightarrow \frac{A_+}{y^{\frac{1}{6}}} \sqrt{\frac{2}{\pi}} \cos(y + \frac{\pi}{4}) \text{ in II.} \quad (50)$$

Substituting for the values of  $y$  in regions I and II, this relation translates into the second connection formula at the left turning point,  $x_2$ ,

$$\frac{1}{\sqrt{|P(x)|}} e^{+\frac{1}{\hbar} \int_{x_2}^x d\xi |P(\xi)|} \leftrightarrow \frac{1}{\sqrt{P(x)}} \cos \left[ \frac{1}{\hbar} \int_{x_2}^x d\xi P(\xi) + \frac{\pi}{4} \right]. \quad (51)$$

Derivations for the connection formulae at a right turning point,  $x_1$ , go in precisely parallel fashion.

# Applications of the WKB Approximation

## A The Wilson–Sommerfeld Quantization Rules of the Pre-1925 Quantum Theory

To show how the WKB approximation is used, let us first derive the energies for a potential with one minimum, with a single left and a single right turning point. In region I, with  $x < x_2$ , the solution must be restricted to one with a decreasing exponential only. In region I,

$$u_I(x) = \frac{A}{\sqrt{|P(x)|}} e^{-\frac{1}{\hbar} \int_{x_2}^x d\xi |P(\xi)|}. \quad (1)$$

This relation will connect in region II, where  $x > x_2$ , onto the oscillatory solution

$$u_{II}(x) = \frac{2A}{\sqrt{|P(x)|}} \cos \left[ \frac{1}{\hbar} \int_{x_2}^x d\xi P(\xi) - \frac{\pi}{4} \right]. \quad (2)$$

This formula can be rewritten as

$$u_{II}(x) = \frac{2A}{\sqrt{|P(x)|}} \cos \left[ \left( \frac{1}{\hbar} \int_{x_2}^{x_1} d\xi P(\xi) - \frac{\pi}{2} \right) - \left( \frac{1}{\hbar} \int_x^{x_1} d\xi P(\xi) - \frac{\pi}{4} \right) \right]. \quad (3)$$

In region  $I'$ , with  $x > x_1$ , we must again have a purely decreasing exponential solution

$$u_{I'}(x) = \frac{B}{\sqrt{|P(x)|}} e^{-\frac{1}{\hbar} \int_{x_1}^x d\xi |P(\xi)|}. \quad (4)$$

This relation will connect in region II, with  $x < x_1$ , onto

$$u_{II}(x) = \frac{2B}{\sqrt{P(x)}} \cos \left[ \frac{1}{\hbar} \int_x^{x_1} d\xi P(\xi) - \frac{\pi}{4} \right]. \quad (5)$$

Now, comparing the two expressions for  $u_{II}(x)$ , these match, if  $|A| = |B|$ , and if

$$\frac{1}{\hbar} \int_{x_2}^{x_1} d\xi P(\xi) - \frac{\pi}{2} = n\pi. \quad (6)$$

We can rewrite this as

$$\frac{1}{\pi} \int_{x_2}^{x_1} d\xi P(\xi) \equiv \frac{1}{2\pi} \oint d\xi P(\xi) = \hbar(n + \frac{1}{2}), \quad (7)$$

where  $\oint$  is used to indicate the integral over one complete classical cycle of the classical orbit, starting at  $x_2$ , proceeding to  $x_1$ , and then back again to  $x_2$ . This quantity, using a generalized momentum, is known as the action variable, and usually denoted by  $J$  in classical mechanics. It is a function of the energy,  $E$ .

$$J(E) = \frac{1}{2\pi} \oint d\xi P(\xi) = \hbar(n + \frac{1}{2}). \quad (8)$$

This is the Wilson–Sommerfeld quantization rule, a generalization of the Planck quantization rule, which goes all the way back to the birth of the quantum theory.

For the simple 1-D harmonic oscillator, e.g., with  $\mu = m$ , and  $V(x) = \frac{1}{2}m\omega_0^2x^2$ ,

$$\begin{aligned} J(E) &= \frac{1}{\pi} \int_{-x_0}^{+x_0} d\xi \sqrt{2m(E - \frac{1}{2}m\omega_0^2\xi^2)} = \frac{1}{\pi} m\omega_0 \int_{-x_0}^{+x_0} d\xi \sqrt{(x_0^2 - \xi^2)} \\ &= \frac{1}{\pi} m\omega_0 x_0^2 \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} d\phi \cos^2 \phi = \frac{1}{2} m\omega_0 x_0^2 = \frac{E}{\omega_0}, \end{aligned} \quad (9)$$

where we have used,  $E = \frac{1}{2}m\omega_0^2x_0^2$ , in the first step, and have used the substitution,  $\xi = x_0 \sin \phi$ , in the integral. Thus, for the 1-D harmonic oscillator

$$J(E) = \frac{E}{\omega_0} = \hbar(n + \frac{1}{2}), \quad (10)$$

giving the exact quantum-mechanical result,  $E = \hbar\omega_0(n + \frac{1}{2})$ . For other simple problems, the integrals for  $J(E)$  are a little more challenging but can be done in closed form. For the hydrogen atom, e.g., with  $V(r) = -Ze^2/r + \hbar^2l(l+1)/2\mu r^2$ , leading to

$$J(E) = \frac{Ze^2 \sqrt{\mu}}{\sqrt{(-2E)}} - \hbar\sqrt{l(l+1)} = \hbar(n_r + \frac{1}{2}), \quad (11)$$

or

$$\frac{Ze^2 \sqrt{\mu}}{\sqrt{(-2E_{\text{WKB}})}} = \hbar(n_r + \frac{1}{2} + \sqrt{l(l+1)}). \quad (12)$$

This WKB result is to be compared with the exact quantum-mechanical result, which could be put in the form

$$\frac{Ze^2\sqrt{\mu}}{\sqrt{(-2E)}} = \hbar\left(n_r + \frac{1}{2} + \sqrt{(l + \frac{1}{2})^2}\right), \quad (13)$$

so the WKB expression for the energy,  $E$ , goes over to the exact result in the limit  $(l^2 + l) \rightarrow (l + \frac{1}{2})^2 = (l^2 + l + \frac{1}{4})$ , certainly valid in the limit of large quantum numbers,  $l$ , for which the classical orbit description begins to have some meaning.

Similarly, for the 3-D harmonic oscillator,

$$J(E) = \frac{E}{2\omega_0} - \frac{\hbar\sqrt{l(l+1)}}{2} = \hbar\left(n_r + \frac{1}{2}\right), \quad (14)$$

leads to

$$E_{\text{WKB}} = \hbar\omega_0(2n_r + 1 + \sqrt{l(l+1)}), \quad (15)$$

which again leads to the exact result

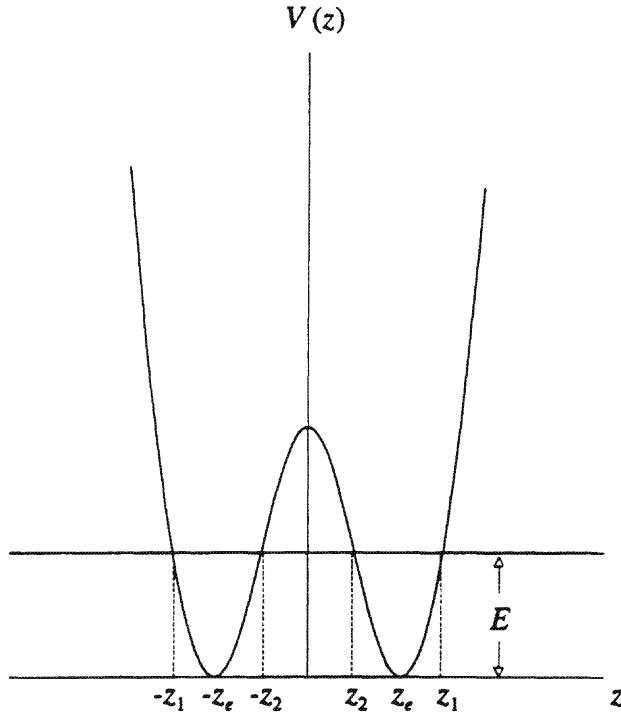
$$E = \hbar\omega_0(2n_r + l + \frac{3}{2}), \quad (16)$$

if, again,  $l(l+1)$  is replaced by  $(l + \frac{1}{2})^2$ , valid for large values of  $l$ .

## B Application 2: The Two-Minimum Problem: The Inversion Splitting of the Levels of the Ammonia Molecule

In the vibrational spectrum of the ammonia molecule,  $\text{NH}_3$ , one degree of freedom exists, which corresponds to the motion of the N atom relative to the  $\text{H}_3$  symmetrical triangle. This degree of freedom can be approximated by  $z$ , the distance of the N atom above (or below) the  $\text{H}_3$  plane. The potential,  $V(z)$ , has the the symmetrical double minimum form shown in Fig. 37.1. Classically, the N atom would lie either above the  $\text{H}_3$  plane and undergo a vertical oscillation about its upper equilibrium configuration at  $z = +z_e$ , or alternately it might lie below the  $\text{H}_3$  plane and undergo an oscillation about its lower equilibrium configuration at  $z = -z_e$ . Quantum mechanically, of course, the N atom can tunnel from the upper minimum to the lower one, leading to a doubling of the vibrational energy levels, with one eigenfunction being an even function of  $z$ , the second an odd function of  $z$ . We have already seen the energy splitting,  $\Delta E$ , is related to the frequency with which the N atom tunnels back and forth from one minimum to the other. The reduced mass for this degree of freedom is  $3m_H m_N / (3m_H + m_N)$ .

Because  $V(-z) = V(z)$ , we expect the one-dimensionalized wave functions,  $u(z)$ , to be either even or odd functions of  $z$ . Thus in the central exponential region, region I, with  $-z_2 < z < +z_2$ , we would expect  $u(z)$  to be either a hyperbolic

FIGURE 37.1. The  $\text{NH}_3$  inversion potential for the coordinate,  $z$ .

cosine or hyperbolic sine type function,

$$u_I(z) = \frac{A}{2\sqrt{|P(z)|}} \left[ e^{+\frac{1}{\hbar} \int_0^z d\xi |P(\xi)|} \pm e^{-\frac{1}{\hbar} \int_0^z d\xi |P(\xi)|} \right]. \quad (17)$$

We will find it convenient to use

$$\int_0^{z_2} d\xi \dots = \int_0^z d\xi \dots + \int_z^{z_2} d\xi \dots \quad \text{to rewrite}$$

$$\begin{aligned} u_I(z) &= \frac{A}{2\sqrt{|P(z)|}} \left[ e^{\frac{1}{\hbar} \int_0^{z_2} d\xi |P(\xi)|} e^{-\frac{1}{\hbar} \int_z^{z_2} d\xi |P(\xi)|} \right. \\ &\quad \left. \pm e^{-\frac{1}{\hbar} \int_0^{z_2} d\xi |P(\xi)|} e^{+\frac{1}{\hbar} \int_z^{z_2} d\xi |P(\xi)|} \right] \\ &= \frac{A}{2\sqrt{|P(z)|}} \left[ \frac{1}{Q} e^{-\frac{1}{\hbar} \int_z^{z_2} d\xi |P(\xi)|} \pm Q e^{+\frac{1}{\hbar} \int_z^{z_2} d\xi |P(\xi)|} \right], \end{aligned} \quad (18)$$

where we have named

$$Q \equiv e^{-\frac{1}{\hbar} \int_0^{z_2} d\xi |P(\xi)|}. \quad (19)$$

For energies,  $E$ , far below the maximum of the central potential hill this exponential quantity,  $Q \ll 1$ . Now the function  $u_I$  for the central exponential region is in a

form in which we can make the connection to region II, the upper oscillatory region of our potential. With the connection formulae for a left turning point, this would connect onto

$$\begin{aligned} u_{II}(z) &= \frac{A}{2\sqrt{P(z)}} \left( \frac{2}{Q} \cos \left[ \frac{1}{\hbar} \int_{z_2}^z d\xi P(\xi) - \frac{\pi}{4} \right] \pm Q \cos \left[ \frac{1}{\hbar} \int_{z_2}^z d\xi P(\xi) + \frac{\pi}{4} \right] \right) \\ &= \frac{A}{2\sqrt{P(z)}} \left( \frac{2}{Q} \cos \left[ \frac{1}{\hbar} \int_{z_2}^z d\xi P(\xi) - \frac{\pi}{4} \right] \mp Q \sin \left[ \frac{1}{\hbar} \int_{z_2}^z d\xi P(\xi) - \frac{\pi}{4} \right] \right) \\ &= \frac{AR}{2\sqrt{P(z)}} \cos \left[ \left( \frac{1}{\hbar} \int_{z_2}^z d\xi P(\xi) - \frac{\pi}{4} \right) \pm \delta \right], \end{aligned} \quad (20)$$

$$\text{where } \tan \delta = \frac{Q^2}{2}, \quad \text{and} \quad R = \sqrt{Q^2 + \left( \frac{2}{Q} \right)^2}. \quad (21)$$

Also,  $\tan \delta \approx \delta$ , because we expect  $Q^2 \ll 1$ . It will be convenient, for purposes of making the connection to the right exponential region, with  $z > z_1$ , to reexpress this WKB solution for the oscillatory region II as

$$u_{II}(z) = \frac{AR}{2\sqrt{P(z)}} \cos \left( \left[ \frac{1}{\hbar} \int_{z_2}^{z_1} d\xi P(\xi) - \frac{\pi}{2} \pm \delta \right] - \left[ \frac{1}{\hbar} \int_z^{z_1} d\xi P(\xi) - \frac{\pi}{4} \right] \right). \quad (22)$$

Finally, in the exponential region  $I'$ , with  $z > z_1$ , the solution must be an exponentially decreasing function as we penetrate further into the classically forbidden region,

$$u_{I'}(z) = \frac{B}{\sqrt{|P(z)|}} e^{-\frac{1}{\hbar} \int_{z_1}^z d\xi |P(\xi)|}. \quad (23)$$

This solution connects onto an oscillatory solution in region II of the form

$$u_{II}(z) = \frac{2B}{\sqrt{P(z)}} \cos \left[ \frac{1}{\hbar} \int_z^{z_1} d\xi P(\xi) - \frac{\pi}{4} \right]. \quad (24)$$

We get a match with the earlier form for  $u_{II}(z)$ , if  $|2B| = \frac{1}{2}|AR|$ , and if

$$\frac{1}{\hbar} \int_{z_2}^{z_1} d\xi P(\xi) - \frac{\pi}{2} \pm \delta = n\pi, \quad (25)$$

or

$$\frac{1}{\pi} \int_{z_2}^{z_1} d\xi P(\xi) = \hbar(n + \frac{1}{2}) \mp \frac{\delta\hbar}{\pi}. \quad (26)$$

The left-hand side gives the action integral  $J(E)$  for the upper potential minimum at the energy  $E$  appropriate for the even (or odd) solution for the full problem. If the energy,  $E$ , is far below the central potential maximum, the potential in the vicinity of the potential minimum between  $+z_2$  and  $+z_1$  can be approximated by a parabola, with  $J(E) = E/\omega_0$ . With  $E = E^{(0)} + \Delta E$ , we get

$$J(E) = J(E^{(0)}) + \left( \frac{\partial J}{\partial E} \right)_0 \Delta E + \dots = \hbar(n + \frac{1}{2}) + \frac{1}{\omega_0} \Delta E + \dots \quad (27)$$

Therefore, eq. (26) can be put in the form

$$J(E) = \hbar(n + \frac{1}{2}) + \frac{\Delta E}{\omega_0} = \hbar(n + \frac{1}{2}) \mp \frac{\delta\hbar}{\pi}. \quad (28)$$

With  $\delta \approx \tan \delta = \frac{1}{2} Q^2$ , this equation leads to

$$\Delta E = \mp \frac{\hbar\omega_0}{2\pi} Q^2, \quad (29)$$

where the upper (lower) signs refer to the even (odd) solutions. The even functions lie at lower energies. Finally,

$$Q^2 = e^{-2\frac{1}{\hbar} \int_0^{z_2} d\xi |P(\xi)|} = e^{-\frac{1}{\hbar} \int_{-z_2}^{+z_2} d\xi |P(\xi)|} \quad (30)$$

is a function of  $E$ . However, for energy levels far below the central potential maximum, the energy splitting is very small compared with  $E_n^{(0)} = \hbar\omega_0(n + \frac{1}{2})$ , so we can express the energy splitting of the  $n^{\text{th}}$  vibrational state by

$$\Delta E_n = \Delta E_{\text{odd}} - \Delta E_{\text{even}} = \frac{\hbar\omega_0}{\pi} Q_n^2 = \frac{\hbar\omega_0}{\pi} e^{-\frac{1}{\hbar} \int_{-z_2}^{+z_2} d\xi \sqrt{2\mu(V(\xi) - E_n^{(0)})}}. \quad (31)$$

We have seen previously the exponential,

$$e^{-G}, \quad \text{with} \quad G = \frac{1}{\hbar} \int_{-z_2}^{+z_2} d\xi \sqrt{2\mu(V(\xi) - E_n^{(0)})}, \quad (32)$$

is related to the probability the N atom tunnel through the central potential maximum. In Chapter 6, we showed the frequency with which the N atom tunnels back and forth from one potential minimum to the other is given by

$$\nu_{\text{tunneling}} = \frac{\Delta E}{2\pi\hbar} = \frac{\nu_0}{\pi} e^{-G}. \quad (33)$$

The factor,  $\nu_0$ , the oscillator frequency in a single well, gives the frequency with which the N atom hits the potential barrier. The probability the N atom tunnel through the barrier is thus given by  $e^{-G}/\pi$ . The factor  $e^{-G}$  is known as the Gamow factor, because Gamow first discussed the tunneling phenomenon in connection with  $\alpha$  decay in a heavy nucleus (see also problem 8).

## Problems

**52.** In certain quark models, a linear confinement potential is used for heavy quarks, such as the charmed or  $b$  quarks, for which nonrelativistic quantum theory is approximately valid. The one-dimensionalized radial wave equation for such a quark would be

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2} (E - V_{\text{eff.}}(r)) u(r) = 0,$$

with

$$V_{\text{eff.}}(r) = kr, \quad \text{for } r \geq 0, \quad k = \text{positive constant},$$