# 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,

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

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 $|nlm_lm_s\rangle$ basis. Nonzero matrix elements are

$$\langle nlm_lm_s|L_z + 2S_z|nlm_lm_s\rangle = m_l + 2m_s. \tag{2}$$

Writing $\vec{L}\cdot\vec{S} = \frac{1}{2}(L_+S_- + L_-S_+) + L_0S_0$,

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

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

$$\vec{J} = \vec{L} + \vec{S}, \qquad \text{with} \qquad J_z = L_0 + S_0, \tag{4}$$

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-*

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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.,

$$\begin{aligned}&\langle nl, m_l' = (m_j \mp \tfrac{1}{2}), m_s = \pm\tfrac{1}{2}|\vec{L}\cdot\vec{S}|nl, m_l = (m_j \pm \tfrac{1}{2}), m_s = \mp\tfrac{1}{2}\rangle = \\ &\tfrac{1}{2}\sqrt{(l \pm m_j + \tfrac{1}{2})(l \mp m_j + \tfrac{1}{2})1\cdot 1} = \tfrac{1}{2}\sqrt{(l+\tfrac{1}{2})^2 - m_j^2}.\end{aligned} \tag{5}$$

In addition, we introduce the radial matrix element integral

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

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,

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

The $2 \times 2$ energy determinant leads to

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

or

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

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

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

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

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

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

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

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

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

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)

$$E^{(1)}_{nl}=\beta_{nl}\frac{l}{2}+\hbar\omega_L m_j\left(1+\frac{1}{(2l+1)}\right),\qquad \text{for}\quad j=(l+\tfrac{1}{2}),$$
$$E^{(1)}_{nl}=-\beta_{nl}\frac{(l+1)}{2}+\hbar\omega_L m_j\left(1-\frac{1}{(2l+1)}\right),\qquad \text{for}\quad j=(l-\tfrac{1}{2}).\tag{13}$$

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

$$E^{(1)}_{nl}=\hbar\omega_L(m_j\pm\tfrac{1}{2})\pm\frac{\beta_{nl}}{2}m_j-\frac{\beta_{nl}}{4}.\tag{14}$$

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

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

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

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

This equation leads to the normalized coefficients

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

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

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

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

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

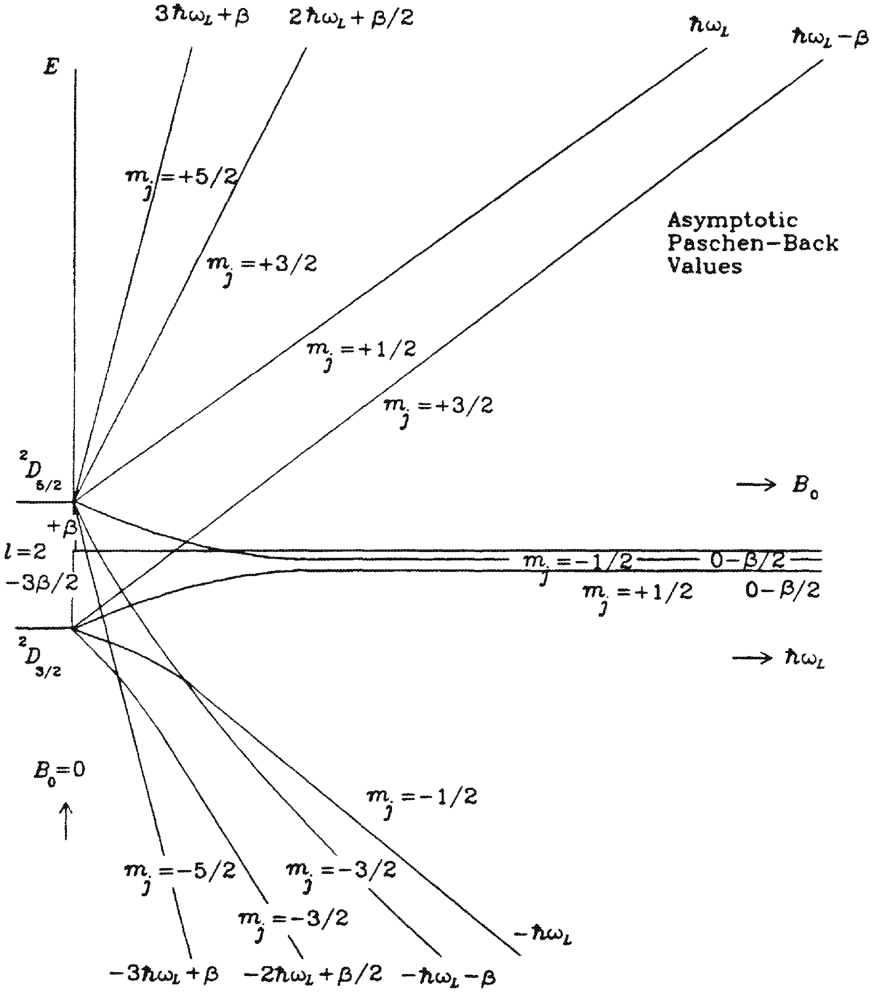

FIGURE 26.1. Magnetic field splitting of an alkali atom $^2D$ level.

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

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

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

$$\begin{array}{cc} & \begin{array}{cc} j=(l+\frac{1}{2}) & j=(l-\frac{1}{2}) \end{array} \\ \begin{array}{c} m_s=+\frac{1}{2} \\[2ex] m_s=-\frac{1}{2} \end{array} & \left( \begin{array}{cc} \sqrt{\frac{(l+\frac{1}{2}+m_j)}{(2l+1)}} & -\sqrt{\frac{(l+\frac{1}{2}-m_j)}{(2l+1)}} \\ \sqrt{\frac{(l+\frac{1}{2}-m_j)}{(2l+1)}} & \sqrt{\frac{(l+\frac{1}{2}+m_j)}{(2l+1)}} \end{array} \right). \end{array}$$

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

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

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

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) + V(r)$$

$$= -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V(r) + \frac{\hbar^2}{2\mu r^2}\left(\frac{(\vec{J}\cdot\vec{J})}{\hbar^2}\right).$$

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

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

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

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

the above Hamiltonian can be written as

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

where

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

with

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

(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

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

[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 *non*uniform electric field, $\vec{\mathcal{E}}$, so the zeroth-order rigid rotator solutions are perturbed by

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

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 $\vec{J}^2$ 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

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

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

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

Note,

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

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

$$E^{(0)}_{m_1 m_2} = \frac{\hbar^2}{2I_e}(m_1^2 + m_2^2), \qquad \text{with } \psi^{(0)}_{m_1 m_2}(\phi_1, \phi_2) = \frac{1}{2\pi}e^{im_1\phi_1}e^{im_2\phi_2},$$

with

$$m_1 = 0, \pm1, \pm2, \ldots, \qquad m_2 = 0, \pm1, \pm2, \ldots .$$

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 $\psi^{(0)}_{m_1 m_2}$, 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

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

with zeroth-order solutions

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

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

$$\langle (m_1+1)(m_2-1)|H^{(1)}|m_1 m_2\rangle = \tfrac{1}{2},$$
$$\langle (m_1-1)(m_2+1)|H^{(1)}|m_1 m_2\rangle = \tfrac{1}{2}. \qquad (3)$$

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

$$m_1, m_2 \rightarrow m_1', m_2' = (m_1+2), (m_2-2) \quad \text{or} \quad m_1, m_2 \quad \text{or} \quad (m_1-2), (m_2+2).$$

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 |
|---|---|---|---|---|---|
| 0 | 1 | 0 | 0 | 0 | (1) |
| 1 | 4 | +1 | 0 | +1 | (2) |
| | | 0 | +1 | +1 | (2) |
| | | −1 | 0 | −1 | (2) |
| | | 0 | −1 | −1 | (2) |
| 2 | 4 | +1 | +1 | +2 | (1) |
| | | +1 | −1 | 0 | (3) |
| | | −1 | +1 | 0 | (3) |
| | | −1 | −1 | −2 | (1) |

| $\epsilon^{(0)}$ | $g_\epsilon$ | $m_1$ | $m_2$ | $M$ | type |
|---|---|---|---|---|---|
| 4 | 4 | +2 | 0 | +2 | (3) |
| | | 0 | +2 | +2 | (3) |
| | | −2 | 0 | −2 | (3) |
| | | 0 | −2 | −2 | (3) |
| 5 | 8 | +2 | +1 | +3 | (2) |
| | | +1 | +2 | +3 | (2) |
| | | −2 | −1 | −3 | (2) |
| | | −1 | −2 | −3 | (2) |
| | | +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

$$\epsilon^{(2)} = \frac{|\langle (m_1+1)(m_2-1)|H^{(1)}|m_1 m_2\rangle|^2}{(\epsilon^{(0)}_{m_1 m_2} - \epsilon^{(0)}_{(m_1+1)(m_2-1)})} + \frac{|\langle (m_1-1)(m_2+1)|H^{(1)}|m_1 m_2\rangle|^2}{(\epsilon^{(0)}_{m_1 m_2} - \epsilon^{(0)}_{(m_1-1)(m_2+1)})}.$$

Thus, for the state with $\epsilon^{(0)} = 0$,

$$\epsilon^{(2)} = \tfrac{1}{4}\Big(\frac{1}{(0-2)} + \frac{1}{(0-2)}\Big) = -\tfrac{1}{4}.$$

For the state with $\epsilon^{(0)} = 2$, $M = +2$; and similarly for $M = -2$,

$$\epsilon^{(2)} = \tfrac{1}{4}\Big(\frac{1}{(2-4)} + \frac{1}{(2-4)}\Big) = -\tfrac{1}{4}.$$

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 $M = -1$),

$$\epsilon^{(2)} = \tfrac{1}{4}\Big(\frac{1}{(5-13)} + \frac{1}{(5-1)}\Big) = +\tfrac{1}{32}.$$

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

$$\begin{array}{cc} & \begin{array}{cc} +1\;0 & 0+1 \end{array} \\ \begin{array}{c} +1\;0 \\ 0+1 \end{array} & \begin{pmatrix} -\epsilon^{(1)} & \frac{1}{2} \\ \frac{1}{2} & -\epsilon^{(1)} \end{pmatrix} \end{array},$$

with eigenvalues and eigenvectors, given by

$$\epsilon^{(1)} = +\tfrac{1}{2}; \quad |M = +1, (+)\rangle = \tfrac{1}{\sqrt{2}}\big(|+10\rangle + |0+1\rangle\big),$$

$$\epsilon^{(1)} = -\tfrac{1}{2}; \quad |M = +1, (-)\rangle = \tfrac{1}{\sqrt{2}}\big(|+10\rangle - |0+1\rangle\big),$$

where, now,

$$\epsilon^{(2)} = \sum_{m_1' m_2'}{}' \frac{|\langle m_1' m_2' | H^{(1)} | M = +1, (\pm)\rangle|^2}{(1 - \epsilon^{(0)}_{m_1' m_2'})}, \tag{4}$$

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,

$$\epsilon^{(2)}_{(\pm)} = |\tfrac{1}{2\sqrt{2}}|^2 \frac{1}{(1-5)} + |\pm \tfrac{1}{2\sqrt{2}}|^2 \frac{1}{(1-5)} = -\frac{1}{16},$$

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

$$\epsilon^{(2)}_{(\pm)} = |\frac{1}{2\sqrt{2}}|^2 \frac{1}{(5-9)} + |\pm \frac{1}{2\sqrt{2}}|^2 \frac{1}{(5-9)} = -\frac{1}{16}.$$

Finally, for states of type (3), the matrix for $H' = UHU^{\dagger}$ with zeroth-order basis states $|m_1 m_2\rangle$ and $|(m_1 - 2)(m_2 + 2)\rangle$ now has the matrix elements

$$\langle m_1 m_2 | H' | m_1 m_2 \rangle = \sum_{m_1' m_2'}{}' \frac{|\langle m_1' m_2' | H^{(1)} | m_1 m_2 \rangle|^2}{(\epsilon^{(0)}_{m_1 m_2} - \epsilon^{(0)}_{m_1' m_2'})},$$

$$\langle m_1 m_2 | H' | (m_1 - 2)(m_2 + 2)\rangle = \langle (m_1 - 2)(m_2 + 2) | H' | m_1 m_2 \rangle =$$

$$\frac{\langle m_1 m_2|H^{(1)}|(m_1-1)(m_2+1)\rangle\langle(m_1-1)(m_2+1)|H^{(1)}|(m_1-2)(m_2+2)\rangle}{(\epsilon^{(0)}_{m_1m_2}-\epsilon^{(0)}_{(m_1-1)(m_2+1)})},$$

$$\langle(m_1-2)(m_2+2)|H'|(m_1-2)(m_2+2)\rangle=\sum_{m_1'm_2'}{}' \frac{|\langle m_1'm_2'|H^{(1)}|(m_1-2)(m_2+2)\rangle|^2}{(\epsilon^{(0)}_{m_1m_2}-\epsilon^{(0)}_{m_1'm_2'})},$$

where the primed sums again exclude the states with $\epsilon^{(0)}_{m_1'm_2'}=\epsilon^{(0)}_{m_1m_2}$.

For states with $\epsilon^{(0)}=2$, $M=0$, therefore, the matrix $(H'^{(2)}-\epsilon^{(2)})$ is

$$\begin{array}{cc} & \begin{array}{cc} +1-1 & \qquad\qquad -1+1 \end{array} \\ \begin{array}{c} +1-1 \\ -1+1 \end{array} & \begin{pmatrix} \frac{1}{4}\left(\frac{1}{(2-8)}+\frac{1}{(2-0)}\right)-\epsilon^{(2)} & \frac{1}{4}\frac{1}{(2-0)} \\ \frac{1}{4}\frac{1}{(2-0)} & \frac{1}{4}\left(\frac{1}{(2-8)}+\frac{1}{(2-0)}\right)-\epsilon^{(2)} \end{pmatrix} \end{array} =$$

$$\begin{array}{cc} & \begin{array}{cc} +1-1 & \quad -1+1 \end{array} \\ \begin{array}{c} +1-1 \\ -1+1 \end{array} & \begin{pmatrix} \frac{1}{12}-\epsilon^{(2)} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{12}-\epsilon^{(2)} \end{pmatrix} \end{array},$$

with eigenvalues and eigenvectors

$$\epsilon^{(2)}=+\frac{5}{24},\qquad |M=0(+)\rangle=\tfrac{1}{\sqrt{2}}(|+1,-1\rangle+|-1,+1\rangle),$$

$$\epsilon^{(2)}=-\frac{1}{24},\qquad |M=0(-)\rangle=\tfrac{1}{\sqrt{2}}(|+1,-1\rangle-|-1,+1\rangle).$$

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 (±) eigenvectors.

Through second order, therefore, the five lowest zeroth-order energy states of our problem are split into 11 energies, with

$$\begin{aligned}
\epsilon&=0-\tfrac{1}{4}\lambda^2, && g_\epsilon=1,\\
\epsilon&=1+\tfrac{1}{2}\lambda-\tfrac{1}{16}\lambda^2, && g_\epsilon=2 \quad \text{with } M=\pm1,\\
\epsilon&=1-\tfrac{1}{2}\lambda-\tfrac{1}{16}\lambda^2, && g_\epsilon=2 \quad \text{with } M=\pm1,\\
\epsilon&=2-\tfrac{1}{4}\lambda^2, && g_\epsilon=2 \quad \text{with } M=\pm2,\\
\epsilon&=2+\tfrac{5}{24}\lambda^2, && g_\epsilon=1 \quad \text{with } M=0\ (+),\\
\epsilon&=2-\tfrac{1}{24}\lambda^2, && g_\epsilon=1 \quad \text{with } M=0\ (-),\\
\epsilon&=4+\tfrac{5}{24}\lambda^2, && g_\epsilon=2 \quad \text{with } M=\pm2,\\
\epsilon&=4-\tfrac{1}{24}\lambda^2, && g_\epsilon=2 \quad \text{with } M=\pm2,\\
\epsilon&=5+\tfrac{1}{2}\lambda-\tfrac{1}{16}\lambda^2, && g_\epsilon=2 \quad \text{with } M=\pm3,\\
\epsilon&=5-\tfrac{1}{2}\lambda-\tfrac{1}{16}\lambda^2, && g_\epsilon=2 \quad \text{with } M=\pm3,\\
\epsilon&=5+\tfrac{1}{32}\lambda^2, && g_\epsilon=4 \quad \text{with } (M=\pm1)^2.
\end{aligned} \tag{5}$$

Although the matrix elements of our $H^{(1)}$ were extremely simple in the $|m_1m_2\rangle$ 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 $(H' - \epsilon^{(0)}_{m_1(m_1+1)})$ is

$$(H' - \epsilon^{(0)}\mathbf{1}) = \begin{array}{c} \\ (m_1+1)m_1 \\ m_1(m_1+1) \end{array} \begin{array}{c} \begin{array}{cc} (m_1+1)m_1 & m_1(m_1+1) \end{array} \\ \begin{pmatrix} -\frac{1}{16}\lambda^2 & \frac{1}{2}\lambda \\ \frac{1}{2}\lambda & -\frac{1}{16}\lambda^2 \end{pmatrix} \end{array},$$

where we have used the fact that $\epsilon^{(0)}_{m_1(m_1+1)} - \epsilon^{(0)}_{(m_1-1)(m_1+2)} = -4$ 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 $(H' - \epsilon^{(0)}_{m_1(m_1+2)})$ is

$$(H' - \epsilon^{(0)}\mathbf{1}) = \begin{array}{c} \\ (m_1+2)m_1 \\ m_1(m_1+2) \end{array} \begin{array}{c} \begin{array}{cc} (m_1+2)m_1 & m_1(m_1+2) \end{array} \\ \begin{pmatrix} +\frac{1}{12}\lambda^2 & \frac{1}{8}\lambda^2 \\ +\frac{1}{8}\lambda^2 & +\frac{1}{12}\lambda^2 \end{pmatrix} \end{array},$$

where we have used the fact that $\epsilon^{(0)}_{m_1(m_1+2)} - \epsilon^{(0)}_{(m_1-1)(m_1+3)} = -6$ and $\epsilon^{(0)}_{m_1(m_1+2)} - \epsilon^{(0)}_{(m_1+1)(m_1+1)} = +2$, 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 $(H' - \epsilon^{(0)}_{m_1(m_1+n)})$, with $n \geq 3$, will factor into two $1 \times 1$ matrices

$$(H' - \epsilon^{(0)}\mathbf{1}) = \begin{array}{c} \\ (m_1+n)m_1 \\ m_1(m_1+n) \end{array} \begin{array}{c} \begin{array}{cc} (m_1+n)m_1 & m_1(m_1+n) \end{array} \\ \begin{pmatrix} +\frac{1}{4}\lambda^2\frac{1}{(n^2-1)} & 0 \\ 0 & +\frac{1}{4}\lambda^2\frac{1}{(n^2-1)} \end{pmatrix} \end{array},$$

again in agreement with our special case above, with $\epsilon^{(0)}_{-1,2} = 5$, 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

$$\phi = (\phi_1 - \phi_2), \qquad \Phi = \tfrac{1}{2}(\phi_1 + \phi_2). \tag{6}$$

We have made the Jacobian of this transformation equal to one. In the new variables, the Schrödinger equation is

$$\left[-\left(2\frac{\partial^2}{\partial\phi^2} + \frac{1}{2}\frac{\partial^2}{\partial\Phi^2}\right) + \lambda\cos\phi\right]\psi(\phi, \Phi) = \epsilon\psi(\phi, \Phi), \tag{7}$$

with zeroth-order solutions

$$\psi^{(0)}(\phi, \Phi) = \frac{1}{2\pi}e^{im\phi}e^{iM\Phi} \quad \text{and} \quad \epsilon^{(0)} = 2m^2 + \tfrac{1}{2}M^2. \tag{8}$$

From the inverse of the above transformation, we have

$$(m_1\phi_1 + m_2\phi_2) = \tfrac{1}{2}(m_1 - m_2)\phi + (m_1 + m_2)\Phi = m\phi + M\Phi. \tag{9}$$

Thus, $\quad m = \tfrac{1}{2}(m_1 - m_2) \quad$ and $\quad M = (m_1 + m_2)$,

So now $\quad m = 0, \pm\tfrac{1}{2}, \pm 1, \pm\tfrac{3}{2}, \pm 2, \ldots \quad$ and $\quad M = 0, \pm 1, \pm 2, \ldots.$

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

$$\psi^{(0)}_{\text{even}}(\phi) = \frac{1}{\sqrt{2\pi}} \text{ for } m = 0, \qquad \psi^{(0)}_{\text{even}}(\phi) = \frac{\cos m\phi}{\sqrt{\pi}} \text{ for } m = \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \ldots,$$

$$\psi^{(0)}_{\text{odd}}(\phi) = \frac{\sin m\phi}{\sqrt{\pi}} \quad \text{for } m = \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \ldots$$

(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 $(m-1) \leq 0$:

$$\begin{aligned} \langle (m+1), \text{even}|H^{(1)}|m, \text{even}\rangle &= \langle (m+1), \text{odd}|H^{(1)}|m, \text{odd}\rangle = \tfrac{1}{2}, \\ \langle (m-1), \text{even}|H^{(1)}|m, \text{even}\rangle &= \langle (m-1), \text{odd}|H^{(1)}|m, \text{odd}\rangle = \tfrac{1}{2}. \end{aligned} \qquad (10)$$

The additional special cases are

$$\begin{aligned} \langle 1, \text{even}|H^{(1)}|0, \text{even}\rangle &= \langle 0, \text{even}|H^{(1)}|1, \text{even}\rangle = \tfrac{1}{\sqrt{2}}, \\ \langle \tfrac{1}{2}, \text{even}|H^{(1)}|\tfrac{1}{2}, \text{even}\rangle &= +\tfrac{1}{2}, \\ \langle \tfrac{1}{2}, \text{odd}|H^{(1)}|\tfrac{1}{2}, \text{odd}\rangle &= -\tfrac{1}{2}. \end{aligned} \qquad (11)$$

All full matrix elements must be diagonal in $M$. Nondegenerate perturbation theory now gives

$$\begin{aligned} \epsilon_{m=0,\text{even},M} &= \epsilon^{(0)} - \tfrac{1}{4}\lambda^2 + \cdots, \\ \epsilon_{m=\frac{1}{2},\text{even},M} &= \epsilon^{(0)} + \tfrac{1}{2}\lambda - \tfrac{1}{16}\lambda^2 + \cdots, \\ \epsilon_{m=\frac{1}{2},\text{odd},M} &= \epsilon^{(0)} - \tfrac{1}{2}\lambda - \tfrac{1}{16}\lambda^2 + \cdots, \\ \epsilon_{m=1,\text{even},M} &= \epsilon^{(0)} + \tfrac{5}{24}\lambda^2 + \cdots, \\ \epsilon_{m=1,\text{odd},M} &= \epsilon^{(0)} - \tfrac{1}{24}\lambda^2 + \cdots, \\ \epsilon_{m=\frac{n}{2},\text{even},M} &= \epsilon^{(0)} + \tfrac{1}{4}\lambda^2 \tfrac{1}{(n^2-1)} + \cdots \quad \text{for } n \geq 3, \\ \epsilon_{m=\frac{n}{2},\text{odd},M} &= \epsilon^{(0)} + \tfrac{1}{4}\lambda^2 \tfrac{1}{(n^2-1)} + \cdots \quad \text{for } n \geq 3. \end{aligned} \qquad (12)$$

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

$$H^{(0)} = -\frac{\hbar^2}{2I_e}\frac{\partial^2}{\partial\phi^2}, \qquad \text{with } I_e = Mr_e^2,$$

with zeroth-order energies and eigenfunctions

$$E_m^{(0)} = \frac{\hbar^2}{2I_e}m^2, \qquad \text{and} \qquad \psi_m^{(0)}(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi},$$

with $m = 0, \pm 1, \pm 2, \ldots$. If this free rotational motion is perturbed by a potential of the form

$$V(\phi) = V_0\cos(2\phi), \qquad \text{with } V_0 = \lambda\frac{\hbar^2}{2I_e}, \quad \text{and } \lambda \ll 1,$$

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

$$E_{nj} = \frac{1}{2}\mu c^2\alpha^4\left(-\frac{1}{n^2} + \frac{\alpha^2}{n^3}\left[-\frac{1}{(j+\frac{1}{2})} + \frac{3}{4n}\right] + \cdots\right);$$

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

$$\left((-2\epsilon)\frac{2}{(\mu^2+\nu^2)}\left[-\frac{1}{4}\left(\frac{\partial^2}{\partial\mu^2} + \frac{1}{\mu}\frac{\partial}{\partial\mu} - \frac{m^2}{\mu^2}\right) - \frac{1}{4}\left(\frac{\partial^2}{\partial\nu^2} + \frac{1}{\nu}\frac{\partial}{\partial\nu} - \frac{m^2}{\nu^2}\right)\right] - \frac{2\sqrt{(-2\epsilon)}}{(\mu^2+\nu^2)} - \epsilon\right)\psi = 0. \tag{1}$$

For the hydrogen atom perturbed by a uniform external electric field, $\vec{\mathcal{E}}$, we have

$$H = H^{(0)} + \lambda z = H^{(0)} + \lambda\frac{(\mu^2 - \nu^2)}{2\sqrt{(-2\epsilon)}}, \qquad \text{with } \lambda = \frac{ea_0\mathcal{E}}{(me^4/\hbar^2)},$$

all in dimensionless units, so

$$(H^{(0)} + \lambda H^{(1)} - \epsilon)\psi = 0$$

becomes

$$\left((-2\epsilon)\frac{2}{(\mu^2+\nu^2)}\left[-\frac{1}{4}\left(\frac{\partial^2}{\partial\mu^2} + \frac{1}{\mu}\frac{\partial}{\partial\mu}\right) + \frac{m^2}{4\mu^2} - \frac{1}{4}\left(\frac{\partial^2}{\partial\nu^2} + \frac{1}{\nu}\frac{\partial}{\partial\nu}\right) + \frac{m^2}{4\nu^2}\right] - \frac{2\sqrt{(-2\epsilon)}}{(\mu^2+\nu^2)}\right.$$

$$+\lambda H^{(1)} - \epsilon\Big)\psi = 0. \tag{2}$$

Show, from the results of problem 26, we can rewrite this as

$$\left(T_3 + T_3' - \frac{1}{\sqrt{(-2\epsilon)}} + \lambda H^{(1)}\frac{(\mu^2+\nu^2)}{2(-2\epsilon)}\right)\psi = 0, \tag{3}$$

$$\text{with} \qquad \lambda H^{(1)}\frac{(\mu^2+\nu^2)}{2(-2\epsilon)} = \frac{\lambda}{4}\frac{(\mu^4-\nu^4)}{(-2\epsilon)^{\frac{3}{2}}}. \tag{4}$$

To carry through the perturbation formalism, expand

$$\epsilon = \epsilon^{(0)} + \lambda\epsilon^{(1)} + \lambda^2\epsilon^{(2)} + \cdots = -\frac{1}{2n^2} + \lambda\epsilon^{(1)} + \lambda^2\epsilon^{(2)} + \cdots, \tag{5}$$

$$\begin{aligned}\frac{1}{\sqrt{(-2\epsilon)}} &= \frac{n}{\sqrt{1 - 2\lambda n^2\epsilon^{(1)} - 2\lambda^2 n^2\epsilon^{(2)} + \cdots}}\\ &= n + \lambda n^3\epsilon^{(1)} + \lambda^2[n^3\epsilon^{(2)} + \tfrac{3}{2}n^5(\epsilon^{(1)})^2] + \cdots,\end{aligned} \tag{6}$$

$$\frac{\lambda}{(-2\epsilon)^{\frac{3}{2}}} = \lambda n^3 + \lambda^2 3n^5\epsilon^{(1)} + \cdots, \tag{7}$$

and show eq. (3) can be rewritten as

$$\begin{aligned}\Bigg((T_3 + T_3' - n) + \lambda\Big[\tfrac{1}{4}n^3(\mu^4-\nu^4) - n^3\epsilon^{(1)}\Big] + \lambda^2\Big[\tfrac{1}{4}(\mu^4-\nu^4)3n^5\epsilon^{(1)}\\ - n^3\epsilon^{(2)} - \tfrac{3}{2}n^5\big(\epsilon^{(1)}\big)^2\Big] + \cdots\Bigg)\Big(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots\Big) = 0\end{aligned} \tag{8}$$

in analogy with the standard perturbation expansion

$$\begin{aligned}\Big((H^{(0)} - E_n^{(0)}) + \lambda(H^{(1)} - E_n^{(1)}) + \lambda^2(H^{(2)} - E_n^{(2)}) + \cdots\Big)\\ \times\Big(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots\Big) = 0.\end{aligned} \tag{9}$$

In eq. (8), the notation $|n^{(0)}\rangle$ is shorthand for $|mn_1n_2\rangle$ (see problem 26) with $n = (|m| + n_1 + n_2 + 1)$.

Express $\frac{1}{4}(\mu^4 - \nu^4)$ 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 $\epsilon^{(2)}_{n=1}$.

(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

$$H^{(0)} \to T_3 + T_3', \qquad E_n^{(0)} \to n,$$

$$H^{(1)} \to \tfrac{1}{4}(\mu^4 - \nu^4)n^3, \qquad E_n^{(1)} \to n^3\epsilon^{(1)}, \quad \text{etc.},$$

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

$$\sum_{n_1'} \sum_{n_2', n' \neq n} \frac{\langle m(n_1 + k)(n_2 - k)|H_{\text{eff.}}^{(1)}|mn_1'n_2'\rangle\langle mn_1'n_2'|H_{\text{eff.}}^{(1)}|mn_1n_2\rangle}{(n - n')},$$

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 $|mn_1n_2\rangle$ basis. Note: In the above, $H_{\text{eff.}}^{(1)} = \frac{1}{4}(\mu^4 - \nu^4)n^3$.

(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

$$\epsilon_n^{(1)} = \lambda \tfrac{3}{2} n(n_1 - n_2),$$

and

$$\epsilon_n^{(2)} = -\lambda^2 \frac{n^4}{8}\Big(34(n_1^2 + n_2^2 - n_1n_2) + 17(n_1 + n_2) + 18$$

$$+17m(n_1 + n_2 + 1) + 4m^2 - 27(n_1 - n_2)^2\Big),$$

or

$$\epsilon_n^{(2)} = -\lambda^2 \frac{n^4}{16}\Big(17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19\Big).$$