PROBLEMS

8.1 Calculate the first order correction to the ground state energy of an anharmonic oscillator of mass m and angular frequency ω subjected to a potential $V(x) = 1/2\ m\omega^2x^2 + bx^4$, where b is a parameter independent of x. The ground state wave function is

$$\psi_0^0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

Solution. The first order correction to the ground state energy

$$E_0^{(1)} = \langle\psi_0^0|\, H'|\psi_0^0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} b \int_{-\infty}^{\infty} x^4 \exp\left(-\frac{m\omega x^2}{\hbar}\right) dx$$

Using the result given in the Appendix, we get

$$E_0^{(1)} = b\left(\frac{m\omega}{\pi\hbar}\right)^{1/2} 2\cdot\frac{3\sqrt{\pi}}{8}\left(\frac{\hbar}{m\omega}\right)^{5/2} = \frac{3b\hbar^2}{4m^2\omega^2}$$

8.2 A simple harmonic oscillator of mass m_0 and angular frequency ω is perturbed by an additional potential bx^3. Evaluate the second order correction to the ground state energy of the oscillator.

Solution. The second order correction to the ground state energy is given by

$$E_0^{(2)} = \sum_m{}' \frac{|\langle 0|H'|m\rangle|^2}{E_0^0 - E_m^0}, \qquad H' = bx^3$$

In terms of $a^\dagger$ and a,

$$x = \left(\frac{\hbar}{2m_0\omega}\right)^{1/2} (a + a^\dagger)$$

$$\langle 0|x^3|m\rangle = \left[\frac{\hbar}{2m_0\omega}\right]^{3/2} \langle 0|(a + a^\dagger)(a + a^\dagger)(a + a^\dagger)|m\rangle, \qquad m = 1, 2, 3, \ldots$$

$$= \left(\frac{\hbar}{2m_0\omega}\right)^{3/2} [\langle 0|aaa|3\rangle + \langle 0|aaa^\dagger + aa^\dagger a|1\rangle]$$

The other contributions vanish. For the nonvanishing contributions, we have

$$\langle 0|aaa|3\rangle = \sqrt{6}, \qquad \langle 0|aaa^\dagger + aa^\dagger a|1\rangle = 2 + 1 = 3$$

$$E_0^{(2)} = b^2\left(\frac{\hbar}{2m_0\omega}\right)^3 \left(\frac{6}{-3\hbar\omega} + \frac{9}{-\hbar\omega}\right) = -\frac{11b^2\hbar^2}{8m_0^3\omega^4}$$

8.3 Work out the splitting of the ^{1}P → ^{1}S transition of an atom placed in a magnetic field B along the z-axis.

Solution. For ^{1}P level, $S = 0$ and, therefore, the magnetic moment of the atom is purely orbital. The interaction energy between magnetic moment and the field is

$$H' = -\mu_z B = \frac{e}{2m_0} L_Z B$$

m_0 is the mass of electron and L_z is the z-component of the orbital angular momentum. The first order correction to energy of the ^1P state is

$$E^{(1)} = \left\langle lm \left| \left(\frac{e}{2m_0} \right) L_z B \right| lm \right\rangle = \frac{e\hbar}{2m_0} Bm_l, \qquad m_l = 1,\ 0,\ -1$$

The ^1P level thus splits into three levels as shown in Fig. 8.1. The ^1S level has neither orbital nor spin magnetic moment. Hence it is not affected by the field and the $^1P \to {}^1S$ transition splits into three lines.

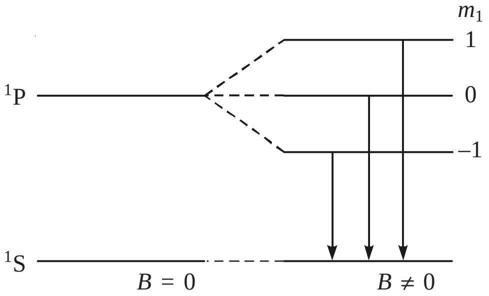


Fig. 8.1 Splitting of ^{1}P → ^{1}S transition of an atom in a magnetic field.

Note: (i) If the system has more than one electron, $l_z = (l_{1z} + l_{2z} + \cdots)$.
(ii) Splitting of a spectral line into three components in the presence of a magnetic field is an example of **normal Zeeman effect.**

8.4 The unperturbed wave functions of a particle trapped in an infinite square well of bottom a are $\psi_n^0 = (2/a)^{1/2} \sin (n\pi x/a)$. If the system is perturbed by raising the floor of the well by a constant amount V_0, evaluate the first and second order corrections to the energy of the nth state.

Solution. The first order correction to the energy of the nth state is

$$\langle \psi_n^0 | H' | \psi_n^0 \rangle = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0$$

Hence, the corrected energy levels are lifted by the amount V_0. The second order correction to the energy is

$$E_n^{(2)} = \sum_m{}' \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} = \sum_m{}' \frac{V_0^2 \, |\langle \psi_m^0 | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} = 0$$

The second order correction to the energy is zero.

8.5 A particle of mass m_0 and charge e oscillates along the x-axis in a one-dimensional harmonic potential with an angular frequency ω. If an electric field ε is applied along the x-axis, evaluate the first and second order corrections to the energy of the nth state.

Solution. The potential energy due to the field $\varepsilon = -e\varepsilon x$.
The perturbation $H' = -e\varepsilon x$.

$$\text{First order correction } E_n^{(1)} = -e\varepsilon \, \langle n | x | n \rangle$$

In terms of a and $a^\dagger$,

$$x = \left(\frac{\hbar}{2m_0\omega} \right)^{1/2} (a + a^\dagger)$$

$$E_n^{(1)} = -e\varepsilon\left(\frac{\hbar}{2m_0\omega}\right)^{1/2}\langle n|(a+a^\dagger)|n\rangle = 0$$

$$E_n^{(2)} = \sum_m{}' \frac{|\langle n|H'|m\rangle|^2}{E_n^0 - E_m^0}$$

$$\langle n|H'|m\rangle = -e\varepsilon\left(\frac{\hbar}{2m_0\omega}\right)^{1/2}\langle n|a+a^\dagger|m\rangle$$

Here, m can take all integral values except n. The nonvanishing elements correspond to $m = (n + 1)$ and $(n - 1)$. Hence,

$$E_n^{(2)} = e^2\varepsilon^2\frac{\hbar}{2m_0\omega}\left[\frac{(\sqrt{n+1})^2}{-\hbar\omega} + \frac{(\sqrt{n})^2}{\hbar\omega}\right] = -\frac{e^2\varepsilon^2}{2m_0\omega^2}$$

8.6 Evaluate the first and second order correction to the energy of the $n = 1$ state of an oscillator of mass m and angular frequency w subjected to a potential

$$V(x) = \frac{1}{2}m\omega^2x^2 + bx, \qquad bx \ll \frac{1}{2}m\omega^2x^2$$

Solution. The first order correction to energy for the $n = 1$ state is given by

$$E_1^{(1)} = \langle 1|bx|1\rangle = b\left(\frac{\hbar}{2m\omega}\right)^{1/2}\langle 1|(a+a^\dagger)|1\rangle$$

$$= b\left(\frac{\hbar}{2m\omega}\right)^{1/2}[\langle 1|a|1\rangle + \langle 1|a^\dagger|1\rangle] = 0$$

Since $a|n\rangle = \sqrt{n}\,|(n-1)\rangle$ and $a^\dagger|n\rangle = \sqrt{n+1}\,|(n+1)\rangle$,

$$E_1^{(2)} = b^2\left(\frac{\hbar}{2m\omega}\right)\sum{}'\frac{|\langle 1|(a+a^\dagger)|k\rangle|^2}{E_1^0 - E_k^0} = b^2\left(\frac{\hbar}{2m\omega}\right)\left[\frac{1}{E_1^0 - E_0^0} + \frac{2}{E_1^0 - E_2^0}\right]$$

$$= b^2\left(\frac{\hbar}{2m\omega}\right)\left(\frac{1}{\hbar\omega} - \frac{2}{\hbar\omega}\right) = -\frac{b^2}{2m\omega^2}$$

8.7 Calculate the ground state energy up to first order of the anharmonic oscillator having a potential energy $V = 1/2\, m\omega^2x^2 + ax^3$; $ax^3 \ll 1/2\, m\omega^2x^2$, where a is independent of x.

Solution. $E_0^{(1)} = \langle 0|ax^3|0\rangle$. The integrand of this integral is an odd function of x and, therefore, the first order correction to the ground state energy is zero.

8.8 Evaluate the first order correction to the energy of the nth state of the anharmonic oscillator having the potential energy

$$V = \frac{1}{2}m\omega^2x^2 + bx^4, \qquad bx^4 \ll \frac{1}{2}m\omega^2x^2$$

Solution.

$$E_n^{(1)} = \langle n|H'|n\rangle = b\langle n|x^4|n\rangle$$

$$= b\left(\frac{\hbar}{2m\omega}\right)^2 \langle n|(a+a^\dagger)(a+a^\dagger)(a+a^\dagger)(a+a^\dagger)|n\rangle$$

The six nonvanishing matrix elements are

1. $\langle n|(aaa^\dagger a^\dagger|n\rangle = (n+1)(n+2)$
2. $\langle n|(aa^\dagger aa^\dagger|n\rangle = (n+1)^2$
3. $\langle n|(aa^\dagger a^\dagger a\,|n\rangle = n(n+1)$
4. $\langle n|(a^\dagger aaa^\dagger\,|n\rangle = n(n+1)$
5. $\langle n|(a^\dagger aa^\dagger a|n\rangle = n^2$
6. $\langle n|(a^\dagger a^\dagger aa|n\rangle = n(n-1)$

Now,

$$E_n^{(1)} = b\left(\frac{\hbar}{2m\omega}\right)^2 [(n+1)(n+2) + (n+1)^2 + 2n(n+1) + n^2 + n(n-1)]$$

$$= 3b\left(\frac{\hbar}{2m\omega}\right)^2 (2n^2 + 2n + 1)$$

8.9 A simple harmonic oscillator of mass m and angular frequency ω is perturbed by an additional potential 1/2 bx^2. Obtain the first and second order corrections to the ground state energy.

Solution.

$$E_0^{(1)} = \frac{1}{2}b\langle 0|x^2|0\rangle = \frac{1}{2}b\left(\frac{\hbar}{2m\omega}\right)\langle 0|(a+a^\dagger)(a+a^\dagger)|0\rangle$$

$$= \frac{1}{2}b\left(\frac{\hbar}{2m\omega}\right)\langle 0|(aa^\dagger|0\rangle = \frac{b\hbar}{4m\omega}$$

$$E_0^{(2)} = \sum_n{}' \frac{|\langle 0|H'|n\rangle|^2}{E_0^0 - E_n^0}$$

$$\langle 0|H'|n\rangle = \frac{1}{2}b\left(\frac{\hbar}{2m\omega}\right)\langle 0|aa + aa^\dagger + a^\dagger a + a^\dagger a^\dagger|n\rangle, \qquad n \neq 0$$

$$= \frac{b\hbar}{4m\omega}\langle 0|aa|n\rangle, \qquad n = 2$$

$$= \frac{\sqrt{2}b\hbar}{4m\omega}$$

$$E_0^{(2)} = -\frac{2b^2\hbar^2}{16m^2\omega^2}\frac{1}{2\hbar\omega} = -\frac{b^2\hbar}{16m^2\omega^3} \qquad \text{since } E_0 - E_2 = -2\hbar\omega$$

8.10 A rotator having a moment of inertia I and an electric dipole moment μ executes rotational motion in a plane. Estimate the first and second order corrections to the energy levels when the rotator is acted on by an electric field ε in the plane of rotation.

Solution. The energy eigenvalues and eigenfunctions of a plane rotator (Problem 5.3) are

$$E_m = \frac{\hbar^2 m^2}{2I}, \qquad \psi(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi), \qquad m = 0, \pm 1, \pm 2, \ldots$$

The perturbation $H' = -\mu\varepsilon \cos\phi = -\dfrac{\mu\varepsilon}{2}(e^{i\phi} + e^{-i\phi})$

$$E_n^{(1)} = \langle n|H'|n\rangle = -\frac{\mu\varepsilon}{2\pi}\int_0^{2\pi} \cos\phi \, d\phi = 0$$

$$E_n^{(2)} = \sum_m{}' \frac{|\langle n|H'|m\rangle|^2}{E_n^0 - E_m^0}$$

$$\langle n|H'|m\rangle = -\frac{\mu\varepsilon}{4\pi}\int_0^{2\pi} e^{-in\phi}(e^{i\phi} + e^{-i\phi})\, e^{im\phi}\, d\phi$$

$$= -\frac{\mu\varepsilon}{4\pi}\left[\int_0^{2\pi} e^{i(m+1-n)\phi}\, d\phi + \int_0^{2\pi} e^{i(m-1-n)\phi}\, d\phi\right]$$

The integrals are finite when $m = n - 1$ (first one) and $m = n + 1$ (second one). Therefore,

$$E_n^{(2)} = \left(-\frac{\mu\varepsilon}{4\pi}\right)^2 \left[\frac{4\pi^2}{E_n^0 - E_{n-1}} + \frac{4\pi^2}{E_n^0 - E_{n+1}}\right]$$

$$= \left(-\frac{\mu\varepsilon}{4\pi}\right)^2 \frac{4\pi^2\, 2I}{\hbar^2}\left(\frac{1}{2n-1} - \frac{1}{2n+1}\right) = \frac{\mu^2\varepsilon^2 I}{\hbar^2(4n^2-1)}$$

8.11 The Hamiltonian matrix of a system is

$$H = \begin{pmatrix} 1 & \varepsilon & 0 \\ \varepsilon & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \qquad \varepsilon \ll 1$$

Find the energy eigenvalues corrected to first order in the perturbation. Also, find the eigenkets if the unperturbed eigenkets are $|\phi_1\rangle$, $|\phi_2\rangle$ and $|\phi_3\rangle$.

Solution. The Hamiltonian matrix can be written as

$$H = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} + \begin{pmatrix} 0 & \varepsilon & 0 \\ \varepsilon & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{i}$$

In this form, we can identify the unperturbed part H^0 and the perturbation H' as

$$H^0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \qquad H' = \begin{pmatrix} 0 & \varepsilon & 0 \\ \varepsilon & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{ii}$$

The unperturbed energies are 1, 1, 2 units. The energy 1 units are two-fold degenerate. The secular determinant corresponding to H' is

$$\begin{vmatrix} -E^{(1)} & \varepsilon & 0 \\ \varepsilon & -E^{(1)} & 0 \\ 0 & 0 & -E^{(1)} \end{vmatrix} = 0 \quad \text{or} \quad E^{(1)^2} - \varepsilon^2 = 0 \ \text{ and } E^{(1)} = 0$$

where $E^{(1)}$ is the first order correction. The solution gives

$$E^{(1)} = \varepsilon, -\varepsilon, 0 \tag{iii}$$

Hence, the state $|\phi_3\rangle$ is not affected by the perturbation. The eigenkets corresponding to states 1 and 2 can easily be obtained. Let these states be

$$\phi_n' = c_1|\phi_1\rangle + c_2|\phi_2\rangle, \qquad n = 1, 2 \tag{iv}$$

The coefficients must obey the condition

$$-E^{(1)}c_1 + \varepsilon c_2 = 0 \tag{v}$$

For the eigenvalue $E^{(1)} = \varepsilon$, this equation reduces to

$$-\varepsilon c_1 + \varepsilon c_2 = 0 \quad \text{or} \quad c_1 = c_2$$

Normalization gives $c_1 = c_2 = 1/\sqrt{2}$. Hence,

$$\phi_1' = \frac{1}{\sqrt{2}}[|\phi_1\rangle + |\phi_2\rangle] \tag{vi}$$

With the value $E^{(1)} = -\varepsilon$, Eq. (v) reduces to

$$\varepsilon c_1 + \varepsilon c_2 = 0 \quad \text{or} \quad c_1 = -c_2$$

Normalization gives $c_1 = -c_2 = 1/\sqrt{2}$. This leads to

$$\phi_2' = \frac{1}{\sqrt{2}}[|\phi_1\rangle - |\phi_2\rangle] \tag{vii}$$

Thus, the corrected energies and eigenkets are

$$\begin{array}{ll} 1 + \varepsilon & \dfrac{1}{\sqrt{2}}[|\phi_1\rangle + |\phi_2\rangle] \\[2ex] 1 - \varepsilon & \dfrac{1}{\sqrt{2}}[|\phi_1\rangle - |\phi_2\rangle] \\[2ex] 2 & |\phi_3\rangle \end{array}$$

8.12 A rigid rotator in a plane is acted on by a perturbation represented by

$$H' = \frac{V_0}{2}(3\cos^2\phi - 1), \qquad V_0 = \text{constant}$$

Calculate the ground state energy up to the second order in the perturbation.

Solution. The energy eigenvalues and eigenfunctions of a plane rotator (refer Problem 5.3) are given by

$$E_m = \frac{m^2\hbar^2}{2I}, \qquad m = 0, \pm 1, \pm 2, \ldots$$

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi)$$

Except the ground state, all levels are doubly degenerate. The first order correction to the ground state energy is

$$\begin{aligned} E_0^{(1)} &= \langle\psi|H'|\psi\rangle = \left\langle\psi\left|\frac{V_0}{2}(3\cos^2\phi - 1)\right|\psi\right\rangle \\ &= \left\langle\psi\left|\frac{3V_0}{2}\cos^2\phi\right|\psi\right\rangle - \left\langle\psi\left|\frac{V_0}{2}\right|\psi\right\rangle \\ &= \frac{3}{4}V_0 - \frac{V_0}{2} = \frac{V_0}{4} \end{aligned}$$

The second order energy correction

$$E_0^{(2)} = \sum_m{}' \frac{|\langle 0|H'|m\rangle|^2}{E_0^0 - E_m^0}$$

$$\begin{aligned} \langle 0|H'|m\rangle &= \frac{V_0}{2}\int_0^{2\pi} \frac{1}{\sqrt{2\pi}}(3\cos^2\phi - 1)\frac{1}{\sqrt{2\pi}}\, e^{im\phi} d\phi \\ &= \frac{3V_0}{4\pi}\int_0^{2\pi} \cos^2\phi e^{im\phi}\, d\phi - \frac{V_0}{4\pi}\int_0^{2\pi} e^{im\phi}\, d\phi \end{aligned}$$

We can write $\cos^2\phi = (1 + \cos 2\phi)/2$. Also, the second integral vanishes. Hence,

$$\langle 0|H'|m\rangle = \frac{3V_0}{8\pi}\int_0^{2\pi} (1 + \cos 2\phi)e^{im\phi}\, d\phi = \frac{3V_0}{8\pi}\int_0^{2\pi} \cos 2\phi\, e^{im\phi}\, d\phi$$

since the other integral vanishes. Putting $\cos 2\phi$ in the exponential, we get

$$\begin{aligned} \langle 0|H'|m\rangle &= \frac{3V_0}{16\pi}\int_0^{2\pi} (e^{i2\phi} + e^{-i2\phi})e^{im\phi}\, d\phi \\ &= \frac{3V_0}{16\pi}\int_0^{2\pi} e^{i(m+2)\phi}\, d\phi + \frac{3V_0}{16\pi}\int_0^{2\pi} e^{i(m-2)\phi}\, d\phi \end{aligned}$$

The first integral is finite when $m = -2$, the second integral is finite when $m = +2$ and their values are equal to $3V_0/8$. $E_{\pm 2} = 2\hbar^2/I$, $E_0 = 0$. Hence,

$$E_0^0 - E_2^0 = E_0^0 - E_{-2}^0 = -\frac{2\hbar^2}{I}$$

Thus,

$$E_0^{(2)} = \frac{(3V_0 \mid 8)^2}{-2\hbar^2/I} + \frac{(3V_0 \mid 8)^2}{-2\hbar^2/I} = -\frac{9}{64}\,\frac{V_0^2 I}{\hbar^2}$$

8.13 A plane rigid rotator in the first excited state is subjected to the interaction

$$H' = \frac{V_0}{2}\,(3\cos^2\phi - 1)$$

where V_0 is constant. Calculate the energies to first order in H'.

Solution. For a plane rotator,

$$E_m = \frac{\hbar^2 m^2}{2I}, \qquad \psi(\phi) = \frac{1}{\sqrt{2\pi}}\,e^{im\phi}, \qquad m = 0, \pm 1, \pm 2, \ldots$$

Except the $m = 0$ state, all states are doubly degenerate. The energy and wave function of the first excited state are

$$E_{\pm 1} = \frac{\hbar^2}{2I}, \qquad \psi(\phi) = \frac{1}{\sqrt{2\pi}}\,e^{\pm i\phi}$$

The first order energy corrections are given by the roots of Eq. (8.6):

$$\begin{vmatrix} H'_{11} - E_1^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_1^{(1)} \end{vmatrix} = 0$$

$$H'_{11} = H'_{22} = \frac{1}{2\pi}\int_0^{2\pi} \frac{V_0}{2}\,(3\cos^2\phi - 1)\,d\phi$$

$$= \frac{V_0}{2\pi}\left[3\int_0^{2\pi}\cos^2\phi\,d\phi - \int_0^{2\pi} d\phi\right] = \frac{V_0}{2\pi}\,(3\pi - 2\pi) = \frac{V_0}{4}$$

$$H'_{12} = H'_{21} = \frac{1}{2\pi}\int_0^{2\pi} e^{-i\phi}\,\frac{V_0}{2}\,(3\cos^2\phi - 1)\,e^{-i\phi}\,d\phi = \frac{3V_0}{8}$$

The secular determinant takes the form

$$\begin{vmatrix} \dfrac{V_0}{4} - E_1^{(1)} & \dfrac{3V_0}{8} \\ \dfrac{3V_0}{8} & \dfrac{V_0}{4} - E_1^{(1)} \end{vmatrix} = 0$$

$$[E_1^{(1)}]^2 - \frac{V_0}{2}\,E_1^{(1)} - \frac{5V_0^2}{64} = 0$$

The roots of this equation are $-(V_0/8)$ and $-(5V_0/8)$. The corrected energies are

$$E = \frac{\hbar^2}{2I} + \frac{5V_0}{8} \quad \text{and} \quad \frac{\hbar^2}{2I} - \frac{V_0}{8}$$

8.14 A one-dimensional box of length a contains two particles each of mass m. The interaction between the particles is described by a potential of the type $V(x_1, x_2) = \lambda\delta(x_1 - x_2)$, which is the δ-Dirac delta function. Calculate the ground state energy to first order in λ.

Solution. The interaction between the particles can be treated as the perturbation. The Hamiltonian without that will be the unperturbed part. Without the δ-potential

$$V(x_1, x_2) = \begin{cases} 0, & 0 \le x_1, x_2 \le a \\ \infty, & \text{Otherwise} \end{cases}$$

$$H_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx_1^2} - \frac{\hbar^2}{2m}\frac{d^2}{dx_2^2} + V(x_1, x_2)$$

From the results of an infinitely deep potential well, the energy and wave functions are

$$E_{nk} = \frac{\pi^2\hbar^2}{2ma^2}(n^2 + k^2), \qquad n, k = 1, 2, 3, \ldots$$

$$\psi_{nk}(x_1, x_2) = \psi_n(x_1)\psi_k(x_2) = \frac{2}{a}\sin\left(\frac{n\pi x_1}{a}\right)\sin\left(\frac{k\pi x_2}{a}\right)$$

For the ground state, $n = k = 1$, we have

$$E_{11}^0 = \frac{\pi^2\hbar^2}{ma^2}, \qquad \psi_{11}^0(x_1, x_2) = \frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)$$

$$H' = \lambda\delta(x_1 - x_2)$$

The first order correction to the ground state energy

$$\begin{aligned}
\Delta E &= \langle 11|H'|11\rangle \\
&= \left(\frac{2}{a}\right)^2 \int_0^a \int_0^a \lambda\delta(x_1 - x_2)\sin^2\left(\frac{\pi x_1}{a}\right)\sin^2\left(\frac{\pi x_2}{a}\right) dx_1 dx_2 \\
&= \left(\frac{2}{a}\right)^2 \lambda \int_0^a \sin^4\left(\frac{\pi x_1}{a}\right) dx_1 = \frac{4\lambda}{a^2}\,\frac{3}{8}\,a = \frac{3\lambda}{2a}
\end{aligned}$$

The corrected energy

$$E' = E_{11}^0 + \Delta E = \frac{\pi^2\hbar^2}{ma^2} + \frac{3\lambda}{2a}$$

8.15 Consider the infinite square well defined by

$$V(x) = 0 \quad \text{for} \quad 0 \le x < a$$

$V(x) = \infty$ otherwise

Using the first order perturbation theory, calculate the energy of the first two states of the potential well if a portion defined by $V(x) = V_0 x/a$, where V_0 is a small constant, with $0 \le x \le a$ being sliced off.

Solution. From Problem 4.1, the energy eigenvalues and eigenfunctions of the the unperturbed Hamiltonian are

$$E_n^0 = \frac{n^2\pi^2\hbar^2}{2ma^2}, \qquad \psi_n^0 = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}, \qquad n = 1, 2, 3, \ldots$$

The perturbation $H' = V_0 x/a$ which is depicted in Fig. 8.2.

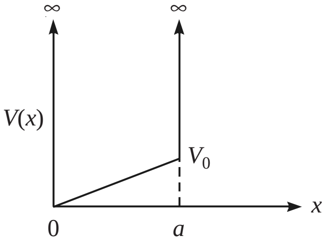


Fig. 8.2 Sliced infinite potential well.

The first order correction to the energy for the $n = 1$ state is

$$\left\langle \psi_1^0 \left| \frac{V_0 x}{a} \right| \psi_1^0 \right\rangle = \frac{V_0}{a}\frac{2}{a}\int_0^a x \sin^2\frac{\pi x}{a}\,dx$$

$$= \frac{2V_0}{a^2}\int_0^a \frac{x}{2}\left(1 - \cos\frac{2\pi x}{a}\right) dx$$

$$= \frac{2V_0}{a^2}\int_0^a \frac{x}{2}\,dx - \frac{2V_0}{a^2}\int_0^a \frac{x}{2}\cos\frac{2\pi x}{a}\,dx$$

$$= \frac{V_0}{2} + 0 = \frac{V_0}{2}$$

The first order correction to the $n = 2$ state is

$$\left\langle \psi_2^0 \left| \frac{V_0 x}{a} \right| \psi_2^0 \right\rangle = \frac{V_0}{a}\frac{2}{a}\int_0^a x \sin^2\frac{2\pi x}{a}\,dx = \frac{V_0}{2}$$

The corrected energies are

$$\frac{\pi^2\hbar^2}{2ma^2} + \frac{V_0}{2} \quad \text{and} \quad \frac{2\pi^2\hbar^2}{ma^2} + \frac{V_0}{2}$$

8.16 The energy levels of the one-electron atoms are doublets, except the s-states because of spin-orbit interaction. The spin-orbit Hamiltonian

$$H_{\text{so}} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\,\boldsymbol{L}\cdot\boldsymbol{S}$$

Treating H_{so} as a perturbation, evaluate the spin-orbit interaction energy. For hydrogenic atoms, assume that the expectation value is

$$\left\langle \frac{1}{r_3} \right\rangle = \frac{2z^3}{n^3 a_0^3\, l(l+1)(2l+1)}$$

where a_0 is the Bohr radius.

Solution. For the valence electron in a hydrogen-like atom, the potential

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \quad \text{or} \quad \frac{dV}{dr} = \frac{Ze^2}{4\pi\varepsilon_0 r^2} \tag{i}$$

Substituting the value of dV/dr, we get

$$H_{so} = \frac{Ze^2}{8\pi\varepsilon_0 m^2 c^2} \frac{\boldsymbol{L}\cdot\boldsymbol{S}}{r^3} \tag{ii}$$

Since $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$,

$$J^2 = L^2 + S^2 + 2\boldsymbol{L}\cdot\boldsymbol{S} \quad \text{or} \quad \boldsymbol{L}\cdot\boldsymbol{S} = \frac{J^2 - L^2 - S^2}{2} \tag{iii}$$

Using the basis $|lsjm\rangle$, the expectation value of $J^2 - L^2 - S^2$ is given by

$$\langle (J^2 - L^2 - S^2)\rangle = [j(j+1) - l(l+1) - s(s+1)]\hbar^2 \tag{iv}$$

Since the first order correction to the energy constitutes the diagonal matrix elements, substituting the values of $\langle 1/r^3\rangle$ and $\langle (J^2 - L^2 - S^2)\rangle$, we get

$$E_{so} = \frac{z^4 e^2 \hbar^2}{8\pi\varepsilon_0 m^2 c^2 a_0^3} \frac{j(j+1) - l(l+1) - s(s+1)}{n^3 l(l+1)(2l+1)} \tag{v}$$

The Bohr radius a_0 and the fine structure constant α are defined as

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}, \qquad \alpha = \frac{e^2}{4\pi\varepsilon_0 c\hbar} \tag{vi}$$

Using Eq. (vi), we get

$$E_{so} = \frac{z^4 e^2 \hbar^2}{8\pi\varepsilon_0 m^2 c^2 a_0^3} \frac{j(j+1) - l(l+1) - s(s+1)}{n^3 l(l+1)(2l+1)} \tag{vii}$$

This makes the state $j = l - (1/2)$ to have a lower energy than that with $j = l + (1/2)$.

8.17 The spin -orbit interaction energy

$$E_{so} = \frac{z^4\alpha^4 mc^2}{2n^3} \frac{j(j+1) - l(l+1) - s(s+1)}{l(l+1)(2l+1)}$$

Calculate the doublet separation ΔE_{so} of states with the same n and l. Apply the result to the 2p state of hydrogen and obtain the doublet separation in units of eV.

Solution. For a given value of l, j can have the values $j = l + (1/2)$ and $j = l - (1/2)$. The difference in energy between these two is the doublet separation ΔE_{so}. Hence,

$$\Delta E_{so} = \frac{z^4\alpha^4 mc^2}{2n^3 l(l+1)(2l+1)}\left[\left(l+\frac{1}{2}\right)\left(l+\frac{3}{2}\right)-\left(l-\frac{1}{2}\right)\left(l+\frac{1}{2}\right)\right]$$

$$= \frac{z^4\alpha^4 mc^2\,(2l+1)}{2n^3 l(l+1)(2l+1)} = \frac{z^4\alpha^4 mc^2}{2n^3 l(l+1)}$$

For the 2p state of hydrogen, $n = 2$, $l = 1$, $z = 1$. So,

$$\Delta E_{so} = \frac{(9.1\times 10^{-31}\ \text{kg})\,(3\times 10^{8}\ \text{ms}^{-1})}{(137)^4 \times 2\times 2^3\times 2} = 7.265\times 10^{-24}\ \text{J}$$

$$= \frac{1.765\times 10^{-24}\ \text{J}}{1.6\times 10^{-19}\ \text{J/eV}} = 4.5\times 10^{-5}\ \text{eV}$$

8.18 The matrices for the unperturbed (H^0) and perturbation (H') Hamiltonians in the orthonormal basis $|\phi_1\rangle$ and $|\phi_2\rangle$ are

$$H^0 = \begin{pmatrix} E_o+\varepsilon & 0 \\ 0 & E_o-\varepsilon \end{pmatrix}, \qquad H' = \begin{pmatrix} 0 & A \\ A & 0 \end{pmatrix}$$

Determine (i) the first order correction to energy, (ii) second order correction to energy, and (iii) the wave function corrected to first order.

Solution.

(i) The first order correction to the energy is zero since the perturbation matrix has no diagonal element.

(ii) $$E_n^{(2)} = \sum_m \frac{|\langle n|H'|m\rangle|^2}{E_n^0 - E_m^0}, \qquad E_1^{(2)} = \frac{|\langle 1|H'|2\rangle|^2}{E_1^0 - E_2^0} = \frac{|A|^2}{2\varepsilon} = \frac{A^2}{2\varepsilon}$$

$$E_2^{(2)} = \frac{|\langle 2|H'|1\rangle|^2}{E_2^0 - E_1^0} = \frac{A^2}{-2\varepsilon}$$

$$E_1 = E_0 + \varepsilon + \frac{A^2}{2\varepsilon}, \qquad E_2 = E_0 - \varepsilon - \frac{A^2}{2\varepsilon}$$

The wave function corrected to first order is given by

$$\psi_n = \psi_n^0 + \sum_m \frac{\langle m|H'|n\rangle}{E_n^0 - E_m^0}\left|\psi_m^0\right\rangle$$

$$\psi_1 = |\phi_1\rangle + \frac{A}{E_1^0 - E_2^0}\left|\phi_2\right\rangle = |\phi_1\rangle + \frac{A}{2\varepsilon}\left|\phi_2\right\rangle$$

$$\psi_2 = |\phi_2\rangle - \frac{A}{2\varepsilon}\left|\phi_1\right\rangle$$

8.19 Given the matrix for H^0 and H':

$$H^0 = \begin{pmatrix} E_0 & 0 \\ 0 & E_0 \end{pmatrix}, \qquad H' = \begin{pmatrix} 0 & -A \\ -A & 0 \end{pmatrix}$$

In the orthonormal basis $|1\rangle$ and $|2\rangle$, determine (i) the energy eigenvalues, and (ii) energy eigenfunctions.

Solution. This is a case of degenerate states $|1\rangle$ and $|2\rangle$ with energy eigenvalue E_0. The secular determinant is, then,

$$\begin{vmatrix} -E^{(1)} & -A \\ -A & -E^{(1)} \end{vmatrix} = 0 \quad \text{or} \quad E^{(1)} = \pm A$$

The eigenfunctions corresponding to these eigenvalues are obtained by a linear combination of $|1\rangle$ and $|2\rangle$. Let the combination be $c_1|1\rangle + c_2|2\rangle$. For +A eigenvalue, the equation $(H'_{11} - E_1^{(1)})c_1 + H'_{12}c_2 = 0$ reduces to

$$-Ac_1 - Ac_2 = 0 \quad \text{or} \quad \frac{c_1}{c_2} = -1$$

Normalization gives $c_1 = 1/\sqrt{2}$, $c_2 = 1/\sqrt{2}$. Hence, the combination is $(|1\rangle - |2\rangle)/\sqrt{2}$. The other combination is $(|1\rangle + |2\rangle)/\sqrt{2}$. The energy eigenvalues and eigenfunctions are

$$E_0 + A \text{ and } (|1\rangle - |2\rangle)/\sqrt{2}$$

$$E_0 - A \text{ and } (|1\rangle + |2\rangle)/\sqrt{2}$$

8.20 Prove the Lande interval rule which states that in a given L-S term, the energy difference between two adjacent J-levels is proportional to the larger of the two values of J.

Solution. For a given L-S term the total orbital angular momentum J can have the values $J = L + S, L + S - 1, \ldots |L - S|$. The spin-orbit coupling energy E_{so}, Problem 8.16 for a given L-S term is

$$E_{so} = \text{constant } [J(J + 1) - L(L + 1) - S(S + 1)]$$

The energy difference between $J - 1$ and J levels is ΔE_{so} given by

$$\begin{aligned}\Delta E_{so} &= \text{constant } [J(J + 1) - L(L + 1) - S(S + 1) - J(J - 1) + L(L + \mathrm{S}) + S(S + 1)] \\ &= \text{constant} \times 2J\end{aligned}$$

That is, the energy difference between two adjacent J-levels is proportional to the larger of the two values of J.

8.21 An interaction of the nuclear angular momentum of an atom (I) with electronic angular momentum (J) causes a coupling of the $\boldsymbol{I}$ and $\boldsymbol{J}$ vectors: $\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}$. The interaction Hamiltonian is of the type $H_{\text{int}} = \text{constant } \boldsymbol{I} \cdot \boldsymbol{J}$. Treating this as a perturbation, evaluate the first order correction to the energy.

Solution. Though the unperturbed Hamiltonian has degenerate eigenvalues, one can avoid working with degenerate perturbation theory (refer Problem 8.16). The perturbing Hamiltonian

$$H' = \text{costant } \boldsymbol{I} \cdot \boldsymbol{J}$$

The first order correction to energy is the diagonal matrix element of $H' = \langle H' \rangle$ which can be obtained as

$$F^2 = (\boldsymbol{I} + \boldsymbol{J})^2 = I^2 + J^2 + 2\boldsymbol{I}\cdot\boldsymbol{J}$$

$$\boldsymbol{I}\cdot\boldsymbol{J} = \frac{F^2 - I^2 - J^2}{2}$$

$$\langle H' \rangle = \text{constant}\,[F(F+1) - I(I+1) - J(J+1)]\,\frac{\hbar^2}{2}$$

Hence, the first order correction

$$E^{(1)} = a\,[F(F+1) - I(I+1) - J(J+1)]$$

where a is a constant.

8.22 A particle in a central potential has an orbital angular momentum quantum number $l = 3$. If its spin $s = 1$, find the energy levels and degeneracies associated with the spin-orbit interaction.

Solution. The spin-orbit interaction

$$H_{\text{so}} = \xi(r)\,\boldsymbol{L}\cdot\boldsymbol{S}$$

where $\xi(r)$ is a constant. The total angular momentum

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} \quad \text{or} \quad \boldsymbol{L}\cdot\boldsymbol{S} = \frac{1}{2}(J^2 - L^2 - S^2)$$

Hence,

$$H_{\text{so}} = \frac{1}{2}\xi(r)\,(J^2 - L^2 - S^2)$$

In the $|jm_j ls\rangle$ basis, the first order correction

$$E_{\text{so}} = \left\langle jm_j ls \left| \frac{1}{2}\xi(r)\,(J^2 - L^2 - S^2) \right| jm_j ls \right\rangle$$

$$= \frac{1}{2}\xi(r)\,[j(j+1) - l(l+1) - s(s+1)]\,\hbar^2$$

Since $l = 3$ and $s = 1$, the possible values of j are 4, 3, 2. Hence

$$E_{\text{so}} = \begin{cases} 3\xi(r)\hbar^2, & j = 4 \\ -\xi(r)\hbar^2, & j = 3 \\ -4\xi(r)\hbar^2, & j = 2 \end{cases}$$

The degeneracy d is given by the $(2j + 1)$ value

$$d = \begin{cases} 9, & j = 4 \\ 7, & j = 3 \\ 5, & j = 2 \end{cases}$$

8.23 Consider the infinite square well

$$V(x) = 0 \quad \text{for } -a \le x \le a$$

$V(x) = \infty$ for $|x| > a$

with the bottom defined by $V(x) = V_0x/a$, where V_0 constant, being sliced off. Treating the sliced-off part as a perturbation to the regular infinite square well, evaluate the first order correction to the energy of the ground and first excited states.

Solution. For the regular infinite square well, the energy and eigenfunctions are given by Eqs. (4.2) and (4.3).

$$E_1^0 = \frac{\pi^2\hbar^2}{8ma^2}, \qquad \psi_1^0 = \frac{1}{\sqrt{a}}\cos\frac{\pi x}{2a}$$

$$E_2^0 = \frac{\pi^2\hbar^2}{2ma^2}, \qquad \psi_2^0 = \frac{1}{\sqrt{a}}\sin\frac{\pi x}{a}$$

The portion sliced off is illustrated in Fig. 8.3.

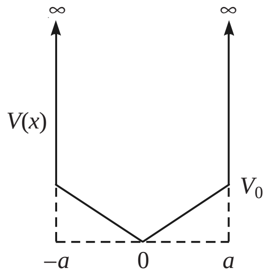


Fig. 8.3 Infinite square well with the bottom sliced off.

$$\text{Perturbation } H' = \frac{V_0x}{a}$$

The first order correction to the ground state energy is

$$E_1^{(1)} = \langle 1|H'|1\rangle = \frac{V_0}{a^2}\int_{-a}^{a} x\cos^2\frac{\pi x}{2a}\,dx = 0$$

since the integrand is odd. The first order correction to the first excited state is

$$E_2^{(1)} = \left\langle \psi_2^0 \left| \frac{V_0x}{a} \right| \psi_2^0 \right\rangle = \frac{V_0}{a^2}\int_{-a}^{a} x\sin^2\frac{\pi x}{a}\,dx = 0$$

since the integrand is odd.

8.24 Draw the energy levels, including the spin-orbit interaction for $n = 3$ and $n = 2$ states of hydrogen atom and calculate the spin-orbit doublet separation of the 2p, 3p and 3d states. The Rydberg constant of hydrogen is 1.097×10^7 m^{-1}.

Solution. Figure 8.4 represents the energy level for $n = 3$ and $n = 2$ states of hydrogen ($Z = 1$), including the spin-orbit interaction.

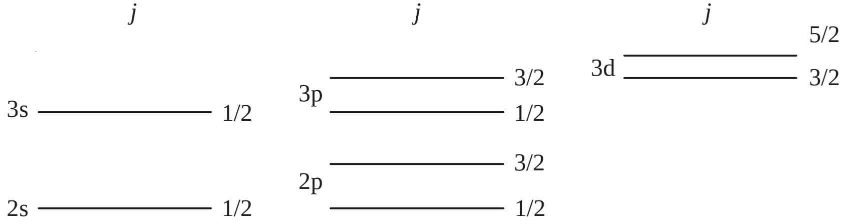


Fig. 8.4 Energy levels for $n = 3$ and $n = 2$ states of hydrogen.

The doublet separation

$$\Delta E = \frac{Z^4\alpha^2 R}{n^3 l(l+1)}$$

For the 2p state, $n = 2$, $l = 1$, and hence

$$(\Delta E)_{2\text{p}} = \frac{(1/137)^2(1.097\times 10^7\ \text{m}^{-1})}{8\times 2} = 36.53\ \text{m}^{-1}$$

For the 3p state, $n = 3$, $l = 1$, and so

$$(\Delta E)_{3\text{p}} = \frac{(1/137)^2(1.097\times 10^7\ \text{m}^{-1})}{27\times 2} = 10.82\ \text{m}^{-1}$$

For the 3d state $n = 3$, $l = 2$ and, therefore,

$$(\Delta E)_{3\text{d}} = \frac{(1/137)^2(1.097\times 10^7\ \text{m}^{-1})}{27\times 2\times 3} = 3.61\ \text{m}^{-1}$$

Note: The doublet separation decreases as l increases. The 2p doublet separation is greater than the 3p doublet which will be greater than the 4p separation (if evaluated), and so on. The d-electron doublet splitting are also similar.

8.25 A hydrogen atom in the ground state is placed in an electric field ε along the z-axis. Evaluate the first order correction to the energy.

Solution. Consider an atom situated at the origin. If $\boldsymbol{r}$ is the position vector of the electron, the dipole moment

$$\mu = -e\boldsymbol{r}$$

The additional potential energy in the electric field ε is $-\mu\cdot\varepsilon$, where θ is the angle between vectors $\boldsymbol{r}$ and ε. This energy can be treated as the perturbation

$$H' = er\,\varepsilon\cos\theta$$

The unperturbed Hamiltonian

$$H^0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

The unperturbed wave function

$$\psi_{100} = -\frac{1}{\pi^{1/2} a_0^{3/2}}\, e^{-r/a_0}$$

The first order correction to the energy

$$E_l^{(1)} = \langle 100 \,|\, er\varepsilon \cos\theta \,|100\rangle$$

The angular part of this equation is

$$\int_0^{\pi} \cos\theta \sin\theta \, d\theta = 0$$

i.e., the first order correction to the energy is zero.

8.26 A particle of mass *m* moves in an infinite one-dimensional box of bottom *a* with a potential dip as defined by

$$V(x) = \infty \qquad \text{for } x < 0 \text{ and } x > a$$

$$V(x) = -V_0 \qquad \text{for } 0 < x < \frac{a}{3}$$

$$V(x) = 0 \qquad \text{for } \frac{a}{3} < x < a$$

Find the first order energy of the ground state.

Solution. For a particle in the infinite potential well (Fig. 8.5) defined by $V(x) = 0$ for $0 < x < a$ and $V(x) = \infty$ otherwise, the energy eigenvalues and eignfunctions are

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}, \qquad \psi_n = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}, \qquad n = 1,\ 2.\ 3,\ \ldots$$

The perturbation $H' = -V_0$, $0 < x < (a/3)$. Hence, the first order energy correction to the ground state is

$$E^{(1)} = -\frac{2}{a}V_0 \int_0^{a/3} \sin^2\frac{\pi x}{a}\, dx$$

$$= -\frac{2}{a}V_0 \int_0^{a/3} \frac{1}{2}\left(1 - \cos\frac{2\pi x}{a}\right) dx$$

$$-\frac{a}{3} = -\frac{V_0}{a}[x]_0^{a/3} + \frac{V_0}{a}\frac{a}{2\pi}\left[\sin\frac{2\pi x}{a}\right]_0^{a/3}$$

$$= -\frac{V_0}{3} + \frac{V_0}{4\pi} \times 0.866 = -0.264\, V_0$$

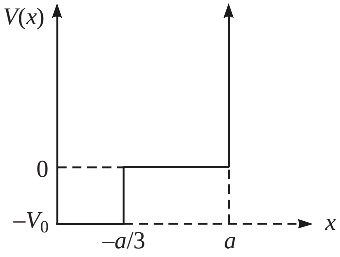


Fig. 8.5 Infinite square well with potential dip.

The energy of the ground state corrected to first order is

$$E = \frac{\pi^2\hbar^2}{2ma^2} - 0.264V_0$$

8.27 A particle of mass m moves in a one-dimensional potential well defined by

$$V(x) = \begin{cases} 0 & \text{for } -2a < x < -a \text{ and } a < x < 2a \\ \infty & \text{for } x > 2a \text{ and } x < -2a \\ V_0 & \text{for } -a < x < a \end{cases}$$

Treating V_0 for $-a < x < a$ as perturbation on the flat bottom box $V(x) = 0$ for $-2a < x < 2a$ and $V(x) = \infty$ otherwise, calculate the energy of the ground state corrected up to first order.

Solution. The unperturbed energy and wave function of the ground state is

$$E_1^0 = \frac{\pi^2 \hbar^2}{32 m a^2}$$

$$\psi_1^0 = \frac{1}{\sqrt{2a}} \cos \frac{\pi x}{4a}$$

The first order correction to the energy

$$E^{(1)} = \frac{V_0}{2a} \int_{-a}^{a} \cos^2 \frac{\pi x}{4a}\, dx = \frac{V_0}{2a} \int_{-a}^{a} \frac{1}{2}\left(1 + \cos \frac{\pi x}{2a}\right) dx$$

$$= \frac{V_0}{4a} (x)_{-a}^{a} + \frac{V_0}{4a} \frac{2a}{\pi} \left(\sin \frac{\pi x}{2a}\right)_{-a}^{a}$$

$$= \frac{V_0}{2} + \frac{V_0}{\pi} = V_0 \left(\frac{1}{2} + \frac{1}{\pi}\right)$$

The corrected ground state energy

$$E_1 = \frac{\pi^2 \hbar^2}{32 m a^2} + V_0 \left(\frac{1}{2} + \frac{1}{\pi}\right)$$

8.28 A particle of mass m moves in an infinite one dimensional box of bottom $2a$ with a potential dip as defined by

$V(x) = \infty$ for $x < -a$ and $x > a$

$V(x) = -V_0$ for $-a < x < -\frac{a}{3}$

$V(x) = 0$ for $-\frac{a}{3} < x < a$

Find the energy of the ground state corrected to first order.

Solution. The unperturbed part of the Hamiltonian is that due to a particle in an infinite potential defined by $V(x)$ for $-a < x < a$ and $V(x) = \infty$ otherwise. The unperturbed ground state energy and eignfunctions are

$$E_1 = \frac{\pi^2 \hbar^2}{8 m a^2}, \qquad \psi_1 = \frac{1}{\sqrt{a}} \cos \frac{\pi x}{2a}$$

The perturbation $H' = -V_0$, $-a < x < -(a/3)$. The first order correction is

$$
\begin{aligned}
E^{(1)} &= -\frac{V_0}{a}\int_{-a}^{-a/3}\cos^2\frac{\pi x}{2a}\,dx = -\frac{V_0}{2a}\int_{-a}^{-a/3}\left(1+\cos\frac{\pi x}{a}\right)dx \\
&= -\frac{V_0}{a}(x)_{-a}^{-a/3} - \frac{V_0}{2a}\,\frac{a}{\pi}\left(\sin\frac{\pi x}{a}\right)_{-a}^{-a/3} \\
&= -\frac{V_0}{3}+\frac{V_0}{2\pi}\sin 60° = -\frac{V_0}{3}+\frac{V_0}{2\pi}\times 0.866 \\
E_1^{(1)} &= 0.195V_0
\end{aligned}
$$

The ground state energy corrected to first order is

$$E = \frac{\pi^2\hbar^2}{8ma^2} - 0.195V_0$$

8.29 A hydrogen atom in the first excited state is placed in a uniform electric field ε along the positive z-axis. Evaluate the second order correction to the energy. Draw an energy level diagram illustrating the different states in the presence of the field. Given

$$\psi_{200} = \frac{1}{\pi^{1/2}}\left(\frac{1}{2a_0}\right)^{3/2}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}$$

$$\psi_{210} = \frac{1}{\pi^{1/2}}\left(\frac{1}{2a_0}\right)^{5/2} re^{-r/2a_0}\cos\theta$$

$$\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}}$$

Solution. The first excited state ($n = 2$) is four-fold degenerate. The possible (l, m) values are (0,0), (1,0), (1,1) and (1,–1). The four degerate states are $|nlm\rangle$: $|200\rangle$, $|210\rangle$, $|211\rangle$, and $|21, -1\rangle$. The additional potential energy in the field can be taken as the perturbation, i.e.,

$$H' = er\varepsilon\cos\theta \tag{i}$$

The energy of the $n = 2$ state, E_2^0 is the unperturbed energy. Out of the 12 off-diagonal elements, in 10 we have the factor

$$\int_0^{2\pi} e^{i(m'-m)\phi}\,d\phi$$

which is equal to zero if $m' \neq m$. Only two off-diagonal elements will be nonvanishing; these are

$$
\begin{aligned}
\langle 200|er\varepsilon\cos\theta|210\rangle &= \frac{e\varepsilon}{16\pi a_0^4}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\left(1-\frac{r}{2a_0}\right)r^4e^{-r/a_0}\cos^2\theta\sin\theta\,dr\,d\theta\,d\phi \\
&= \frac{e\varepsilon 2\pi}{16\pi a_0^4}\int_0^{\pi}\cos^2\theta\sin\theta\,d\theta\int_0^{\infty}\left(r^4-\frac{r^5}{2a_0}\right)e^{-r/a_0}\,dr \qquad \text{(ii)}
\end{aligned}
$$

The integral in θ is very straightforward. The integral in the variable r can be evaluated with the data given. Then,

$$\int_0^{\pi} \cos^2\theta \sin\theta \, d\theta = \frac{2}{3} \tag{iii}$$

$$\int_0^{\infty} \left(r^4 - \frac{r^5}{2a_0} \right) e^{-r/a_0} \, dr = -36a_0^5 \tag{iv}$$

Substituting these integrals in Eq. (ii), we get

$$\langle 200 | H' | 210 \rangle = \frac{e\varepsilon}{8a_0^4} \times \frac{2}{3} (36a_0^5) = -3ea_0\varepsilon \tag{v}$$

Then the perturbation matrix is

$$\begin{array}{c c} (nlm) \rightarrow & \begin{array}{cccc} (200) & (210) & (211) & (21,-1) \end{array} \\ \downarrow & \\ \begin{array}{c} (200) \\ (210) \\ (211) \\ (21,-1) \end{array} & \begin{bmatrix} 0 & -3ea_0\varepsilon & 0 & 0 \\ -3ea_0\varepsilon & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \end{array} \tag{vi}$$

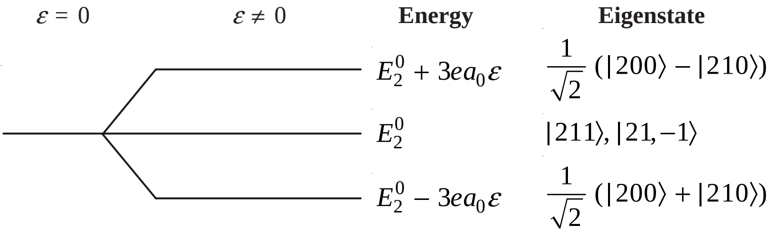
and the secular determinant is

$$\begin{vmatrix} -E_2^{(1)} & -3ea_0\varepsilon & 0 & 0 \\ -3ea_0\varepsilon & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} = 0 \tag{vii}$$

The four roots of this determinant are $3ea_0\varepsilon$, $-3ea_0\varepsilon$, 0 and 0. The states $|200\rangle$ and $|210\rangle$ are affected by the electric field, whereas the states $|211\rangle$ and $|21, -1\rangle$ are not. Including the correction, the energy of the states are

$$E_2^0 - 3ea_0\varepsilon, \qquad E_2^0 \text{ and } E_2^0 + 3ea_0\varepsilon$$

This is illustrated below (The eigenstates are also noted these).



Note: The electric field has affected the energy means that the atom has a permanent magnetic moment. The states $|211\rangle$ and $|21, -1\rangle$ do not possess dipole moment and therefore do not have first order interaction.

8.30 The ground state of the Hydrogen atom is split by the hyperfine interaction. Work out the interaction energy using first order perturbation theory and indicate the level diagram.

Solution. Hyperfine interaction is one that takes place between the electronic angular momentum and the nuclear spin angular momentum. Hydrogen atom in the ground state has no orbital angular momentum. Hence the electronic angular momentum is only due to electron spin and the interaction is simply between the intrinsic angular momenta of the electron ($\mathbf{S}_e$) and proton ($\mathbf{S}_p$); both are spin-half particles. The resultant angular momentum

$$\boldsymbol{I} = \boldsymbol{S}_e + \boldsymbol{S}_p$$

$$\boldsymbol{S}_e \cdot \boldsymbol{S}_p = \frac{1}{2}(I^2 - S_e^2 - S_p^2)$$

Since both are spin half particles, the possible values of I are 0 and 1. $I = 0$ corresponds to a singlet state and $I = 1$ to a triplet state.

$$\langle \boldsymbol{S}_e \cdot \boldsymbol{S}_p \rangle = \frac{1}{2}\left[I(I+1) - \frac{1}{2} \times \frac{3}{2} - \frac{1}{2} \times \frac{3}{2}\right]\hbar^2$$

$$= \begin{cases} -\dfrac{3}{4}\hbar^2, & I = 0 \text{ (singlet state)} \\ \dfrac{1}{4}\hbar^2, & I = 1 \text{ (triplet state)} \end{cases}$$

The hyperfine interaction causes the ground state to split into two, a singlet ($I = 0$) and a triplet ($I = 1$), see Fig. 8.6.

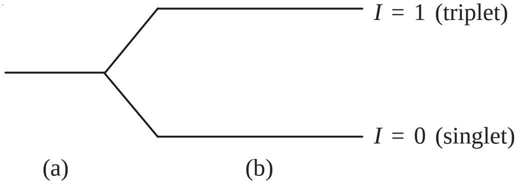


Fig. 8.6 Energy level: (a) without hyperfine interaction; (b) with hyperfine interaction.

8.31 Consider an atomic electron with angular momentum quantum number $l = 3$, placed in a magnetic field of 2 T along the z-direction. Into how many components does the energy level of the atom split. Find the separation between the energy levels.

Solution. For $l = 3$, m can have the values 3, 2, 1, 0, –1, –2, –3. The interaction Hamiltonian $H' = -\boldsymbol{\mu} \cdot \boldsymbol{B}$, where $\boldsymbol{\mu}$ is the magnetic moment of the electron which is given by

$$\boldsymbol{\mu} = -\frac{e}{2m_0}\boldsymbol{L}$$

Here, $\boldsymbol{L}$ is the orbital angular momentum of the electron and m_0 is its rest mass.

$$H' = \frac{e}{2m_0}\, \boldsymbol{L}\cdot\boldsymbol{B} = \frac{eB}{2m_0}\, L_z$$

In the $|lm\rangle$ basis, the energy

$$E = \frac{eB}{2m_0} m\hbar = \frac{e\hbar}{2m_0} Bm = \mu_B Bm$$

where μ_B is the Bohr magneton which has a value of 9.27×10^{-24} J/T. Since m can have seven values, the energy level splits into seven. The energies of these seven levels are

$$3\mu_B B, \quad 2\mu_B B, \quad 1\mu_B B, \quad 0, \quad -1\mu_B B, \quad -2\mu_B B, \quad -3\mu_B B$$

The lines are equally spaced and the separation between any two is

$$\mu_B B = (9.27 \times 10^{-24}\ \text{J/T}) \times 2T$$
$$= 18.54 \times 10^{-24}\ \text{J}$$

8.32 A system described by the Hamiltonian $H = \alpha L^2$, where L^2 is the square of the angular momentum and α is a constant, exhibits a line spectrum where the line A represents transition from the second excited state to the first excited state. The system is now placed in an external magnetic field and the Hamiltonian changes to $H = \alpha L^2 + \beta L_z$, where L_z is the z-component of the angular momentum. How many distinct lines will the original line A split into?

Solution. The Hamiltonian $H = \alpha L^2$. The eigenkets are $|lm\rangle$, $l = 0, 1, 2, \ldots$, $m = 0, \pm 1, \pm 2, \ldots$ The first excited state is $l = 1$, $m = 0, \pm 1$. The second excited state is $l = 2$, $m = 0, \pm 1, \pm 2$. In the presence of magnetic field, $H = \alpha L^2 + \beta L_z$. The perturbation $H' = \beta L_z$.

$$\text{First order correction} = \langle lm|\beta L_z|lm\rangle$$
$$= \beta m\hbar \text{ for a given value of } l$$

For the first excited state,

$$\beta m\hbar = \beta\hbar,\ 0,\ -\beta\hbar$$

For the second excited state

$$\beta m\hbar = 2\beta\hbar,\ \beta\hbar,\ 0,\ -\beta\hbar,\ -2\beta\hbar$$

Figure 8.7 illustrates the splitting of the two energy levels. The allowed transitions

$$\Delta l = \pm 1, \qquad \Delta m = 0, \pm 1$$

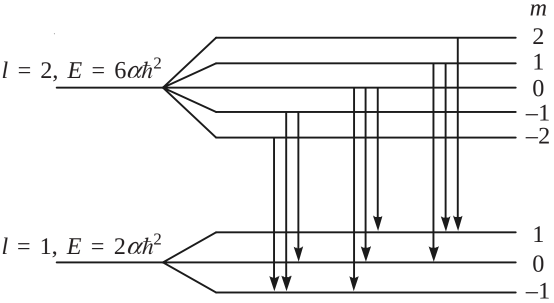


Fig. 8.7 Transitions in the presence of magnetic field.

Transitions are also shown in Figure 8.7. The energies of the levels are also given, from which the transition energies can be evaluated. The original line will split into eight lines.

8.33 The Hamiltonian of a two-electron syatem is perturbed by an interaction $\alpha \boldsymbol{S}_1 \cdot \boldsymbol{S}_2$, where α is a constant and $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ are the spin angular momenta of the electrons. Calculate the splitting between the $S = 0$ and $S = 1$ states by first order perturbation, where S is the magnitude of the total spin.

Solution. We have $\boldsymbol{S} = \boldsymbol{S}_1 + \boldsymbol{S}_2$. Then,

$$S^2 = S_1^2 + S_2^2 + 2\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$$

$$\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 = \frac{S^2 - S_1^2 - S_2^2}{2}$$

Since the spin of electron is 1/2 when the two electrons combine, the total spin $S = 0$ or 1. The state, for which $S = 0$, is called a *singlet state* with $m_s = 0$. The state, for which $S = 1$, is called a *triplet state* with $m_s = 1, 0, -1$. The first order correction to $S = 0$ state in the $|sm_s\rangle$ basis

$$E_0^{(1)} = \left\langle sm_s \left| \frac{(S^2 - S_1^2 - S_2^2)\,\alpha}{2} \right| sm_s \right\rangle$$

$$= \frac{\alpha}{2}\,[s(s+1) - s_1(s_1+1) - s_2(s_2+1)]\,\hbar^2$$

$$= \frac{\alpha}{2}\left(0 - \frac{3}{4} - \frac{3}{4}\right)\hbar^2 = -\frac{3}{4}a\hbar^2$$

The first order correction to the $S = 1$ state is

$$E_1^{(1)} = \frac{\alpha}{2}\left[1 \times 2 - \frac{1}{2} \times \frac{3}{2} - \frac{1}{2} \times \frac{3}{2}\right]\hbar^2$$

$$= \frac{\alpha}{4}\hbar^2$$

Splitting between the two states $= \dfrac{\alpha}{4}\hbar^2 - \left(-\dfrac{3}{4}a\hbar^2\right)$

$$= \alpha\hbar^2$$

8.34 The unperturbed Hamiltonian of a system is

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

If a small perturbation

$$V' = \begin{cases} \lambda x & \text{for } x > 0 \\ 0 & \text{for } x \le 0 \end{cases}$$

acts on the system, evaluate the first order correction to the ground state energy.

Solution. The given H_0 is the one for a simple harmonic oscillator. Hence the unperturbed ground state energy is

$$\psi_0(x) = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \exp\left(\frac{m\omega x^2}{2\hbar}\right)$$

The first order correction to the energy is

$$\begin{aligned} E_0^{(1)} &= \langle\psi_0(x)|\lambda x|\psi_0(x)\rangle \\ &= \left(\frac{m\omega}{\hbar\pi}\right)^{1/2} \lambda \int_0^{\infty} x \exp\left(-\frac{m\omega x^2}{\hbar}\right) dx \\ &= \left(\frac{m\omega}{\hbar\pi}\right)^{1/2} \lambda \left(\frac{\hbar}{2m\omega}\right) = \frac{\lambda}{2}\sqrt{\frac{\hbar}{\pi m\omega}} \end{aligned}$$

8.35 Consider an atomic state specified by angular momenta ***L***, ***S*** and ***J*** = ***L*** + ***S*** placed in a magnetic field ***B***. Treating the interaction representing the magnetic moment of the electron in the magnetic field as the perturbing Hamiltonian and writing ***L*** + 2***S*** = g_J ***J***, obtain an expression for (i) the g factor of the Jth state are (ii) the corrected energy.

Solution. When placed in the magnetic field ***B***, the interaction Hamiltonian

$$H' = -\boldsymbol{\mu} \cdot \boldsymbol{B} = -(\boldsymbol{\mu}_L + \boldsymbol{\mu}_S) \cdot \boldsymbol{B} \tag{i}$$

where μ_L and μ_S are the orbital and spin magnetic moments of the electron. We have

$$\boldsymbol{\mu}_L = -\frac{e}{2m}\boldsymbol{L}, \qquad \boldsymbol{\mu}_S = -\frac{e}{2m}\boldsymbol{S} \tag{ii}$$

L is the orbital angular momentum and ***S*** is the spin angular momentum. Substituting these values of μ_L and μ_S, we get

$$H' = \frac{e}{m}(\boldsymbol{L} + 2\boldsymbol{S}) \cdot \boldsymbol{B}$$

Given

$$g_J\boldsymbol{J} = \boldsymbol{L} + 2\boldsymbol{S}$$

where g_J is a constant. Taking the dot product with ***J***, we obtain

$$\begin{aligned} g_J J^2 &= \boldsymbol{J} \cdot (\boldsymbol{L} + 2\boldsymbol{S}) = \boldsymbol{J} \cdot (\boldsymbol{L} + \boldsymbol{S} + \boldsymbol{S}) \\ &= \boldsymbol{J} \cdot (\boldsymbol{J} + \boldsymbol{S}) = \boldsymbol{J} \cdot \boldsymbol{J} + \boldsymbol{J} \cdot \boldsymbol{S} \\ &= J^2 + \boldsymbol{J} \cdot \boldsymbol{S} \end{aligned}$$

Since ***L*** = ***J*** – ***S***,

$$L^2 = J^2 + S^2 - 2\boldsymbol{J} \cdot \boldsymbol{S}$$

$$\boldsymbol{J} \cdot \boldsymbol{S} = \frac{J^2 + S^2 - L^2}{2}$$

$$g_J J^2 = J^2 + \frac{J^2 + S^2 - L^2}{2}$$

In the simultaneous eigenkets of J^2, J_z, L^2, S^2,

$$g_J\langle J^2\rangle = \langle J^2\rangle + \frac{1}{2}\langle J^2 + S^2 - L^2\rangle$$

$$g_J J(J+1)\hbar^2 = J(J+1)\hbar^2 + \frac{1}{2}[J(J+1) + S(S+1) - L(L+1)]\hbar^2$$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

where J, L and S are the quantum numbers associated with the angular momenta $\boldsymbol{J}$, $\boldsymbol{L}$ and $\boldsymbol{S}$, respectively.

(ii) The interaction Hamiltonian

$$H' = \frac{e}{2m}g\boldsymbol{J}\cdot\boldsymbol{B} = \frac{e}{2m}gJB\cos\theta$$

$$= \frac{e}{2m}gJB\frac{J_z}{J} = \frac{e}{2m}gBJ_z$$

The first order correction to the energy is the diagonal matrix element

$$E^{(1)} = \frac{e}{2m}gBM_J\hbar = \frac{e\hbar}{2m}Bg_J M_J$$

The corrected energy

$$E = E^0 + \frac{e\hbar}{2m}Bg_J M_J$$

Since M_J can have $(2J + 1)$-fold degenerate, each energy level is split into $2J + 1$ equally spaced levels.

8.36 The nuclear spin of bismuth atom is 9/2. Find the number of levels into which a $^2\mathrm{D}_{5/2}$ term of bismuth splits due to nuclear spin-electron angular momentum interaction. If the separation of $^2_7D_{5/2}$ term from $^2_6D_{5/2}$ is 70 cm^{-1}, what is the separation between the other adjacent levels?

Solution. $^2\mathrm{D}_{5/2}$ term means $2S + 1 = 2$, $S = (1/2)$, $L = 2$ and $J = (5/2)$. Given $I = (9/2)$. The total angular momentum is $\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}$. The possible values of the quantum number F are 7, 6, 5, 4, 3, 2. Hence, the $^2\mathrm{D}_{5/2}$ level splits into six sublevels corresponding to the F values, 7, 6, 5, 4, 3, and 2. From Problem 8.21, we have the correction to energy as

$$E^{(1)} = a\,[F(F+1) - I(I+1) - J(J+1)]$$

Hence, the energy difference ΔE between successive levels $(F + 1)$ and F is given by

$$\Delta E = a\,[(F+1)(F+2) - I(I+1) - J(J+1)] - a\,[F(F+1) - I(I+1) - J(J+1)]$$

Given the separation between $J = 7$ and $J = 6$ is 70 cm^{-1}, i.e.,

$$70\text{ cm}^{-1} = 2a \times 7 \quad\text{or}\quad a = 5\text{ cm}^{-1}$$

Hence,

$$^2_6D_{5/2} - {}^2_5D_{5/2} = 60\text{ cm}^{-1}$$

$$^2_5D_{5/2} - {}^2_4D_{5/2} = 50\text{ cm}^{-1}$$

$$ {}_4^2D_{5/2} - {}_3^2D_{5/2} = 40 \text{ cm}^{-1} $$

$$ {}_3^2D_{5/2} - {}_2^2D_{5/2} = 30 \text{ cm}^{-1} $$

8.37 Discuss the splitting of atomic energy levels in a weak magnetic field and show that an energy level of the atom splits into $(2J + 1)$ levels. Use L-S coupling and $\boldsymbol{L} + 2\boldsymbol{S} = g\boldsymbol{J}$, where g is the Lande g-factor, $\boldsymbol{L}$, $\boldsymbol{S}$ and $\boldsymbol{J}$ are respectively the orbital, spin and total angular momenta of the atom.

Solution. Let μ be the magnetic moment of the atom. Its orbital magnetic moment be μ_L and spin magnetic moment be μ_S. The Hamiltonian representing the interactionof the magnetic field $\boldsymbol{B}$ with μ is

$$ H' = -\mu \cdot \mathrm{B} = -(\mu_L + \mu_S) \cdot B $$

Since

$$ \mu_L = -\frac{e}{2m}\boldsymbol{L}, \qquad \mu_S = -\frac{e}{m}\boldsymbol{S} = -\frac{e}{2m}2\boldsymbol{S} $$

$$ H' = \frac{e}{2m}(\boldsymbol{L} + 2\boldsymbol{S}) \cdot \boldsymbol{B} = \frac{e}{2m}g\boldsymbol{J} \cdot \boldsymbol{B} = \frac{e}{2m}gJB\cos(\boldsymbol{J}, \boldsymbol{B}) $$

Since $(\boldsymbol{J}, \boldsymbol{B}) = (J_z/J)$,

$$ H' = \frac{e}{2m}gJB\frac{J_z}{J} = \frac{e}{2m}gBJ_z $$

The first order correction to energy in the common state of J^2 and J_z is

$$ \begin{aligned} E^{(1)} &= \left\langle Jm_J \left| \frac{e}{2m}gBJ_z \right| Jm_J \right\rangle \\ &= \frac{e}{2m}gBm_J\hbar = \frac{e\hbar}{2m}gBm_J \\ &= \mu_{\mathrm{B}}gBm_J \end{aligned} $$

where $\mu_{\mathrm{B}} = e\hbar/2m$ is the Bohr magneton. As m_j can have $(2J + 1)$ values, each level splits into $2(J + 1)$ equally spaced levels. Hence the energy of the system

$$ E = E_{nl} + m_{\mathrm{B}}gBM_J $$

8.38 Discuss the splitting of atomic energy levels in a strong magnetic field. (the Paschen-Back effect).

Solution. In a strong magnetic field, the magnetic field interaction energy is stronger than the spin-orbit interaction energy. Hence the L–S coupling breaks. The Hamiltonian representing the interaction of the magnetic field with μ is

$$ \begin{aligned} H' &= -\mu \cdot \boldsymbol{B} = -(\mu_L + \mu_S) \cdot \boldsymbol{B} \\ &= \frac{e}{2m}\boldsymbol{L} \cdot \boldsymbol{B} + \frac{e}{2m}2\boldsymbol{S} \cdot \boldsymbol{B} \\ &= \frac{e}{2m}LB\cos(\boldsymbol{L}, B) + \frac{e}{2m}2SB\cos(\boldsymbol{S}, \boldsymbol{B}) \end{aligned} $$

$$= \frac{e}{2m} LB\frac{L_z}{L} + \frac{e}{2m} 2SB\frac{S_z}{S}$$

$$= \frac{e}{2m} BL_z + \frac{e}{2m} 2BS_z$$

The first order correction in the common eigenstate of L^2, L_z, S^2 and S_z is

$$E^{(1)} = \frac{e}{2m} Bm_L\hbar + \frac{e}{2m} 2SBm_s\hbar$$

$$= \mu_B B(m_L + 2m_s)$$

The energy of the level becomes

$$E = E_{nl} + \mu_B B(m_L + 2m_s)$$

8.39 A simple pendulum of length l swings in a vertical plane under the influence of gravity. In the small angle approximation, find the energy levels of the system. Also evaluate the first order correction to the ground state energy, taking one more term in the small angle approximation.

Solution. The first part of the problem is discussed in Problem 4.58. The energy eigenvalues and eigenfunctions are the same as those of a linear harmonic oscillator with angular frequency $\omega = \sqrt{g/l}$, where l is the length of the pendulum. While evaluating the energy eigenvalues, we assumed the angle θ (Fig. 4 .5) to be small and retained only two terms in the expansion of cos θ. Retaining one more term, we get

$$\cos\,\theta = 1 - \frac{\theta^2}{2} + \frac{\theta^4}{24}$$

The potential is, then,

$$V = mgl\,(1 - \cos\,\theta) = mgl\left(\frac{\theta^2}{2} - \frac{\theta^4}{24}\right)$$

$$= \frac{mgl\theta^2}{2} - \frac{mgl\theta^4}{24}$$

Since $\theta = x/l$,

$$\text{Perturbation } H' = -\frac{mgl\theta^4}{24} = -\frac{mgx^4}{24l^3}$$

The first order correction to the ground state energy is

$$E_0^{(1)} = \left\langle 0 \left| -\frac{mgx^4}{24l^3} \right| 0 \right\rangle$$

In terms of the raising and lowering operators, we have

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger)$$

With this value of x,

$$E_0^{(1)} = \left(-\frac{mg}{24l^3}\right)\left(\frac{\hbar}{2m\omega}\right)^2 \langle 0|(a + a^\dagger)(a + a^\dagger)(a + a^\dagger)(a + a^\dagger)|0\rangle$$

In all, there will be 16 terms on the RHS. However, only two will be nonvanishing. They are $\langle 0|aaa^\dagger a^\dagger|0\rangle$ and $\langle 0|a\,a^\dagger\,a\,a^\dagger|0\rangle$. Consequently,

$$\langle 0|aa^\dagger aa^\dagger|0\rangle = 1, \qquad \langle 0|aaa^\dagger a^\dagger|0\rangle = 2$$

Hence,

$$E_0^{(1)} = -\frac{g\hbar^2}{8ml^3\omega^2}$$

8.40 Obtain the hyperfine splitting in the ground state of the hydrogen atom to first order in perturbation theory, for the perturbation

$$H' = A\boldsymbol{S}_\mathrm{p}\cdot\boldsymbol{S}_\mathrm{e}\delta^3(\boldsymbol{r}), \qquad A \text{ being constant}$$

where S_p and S_e denote the spins of the proton and electron, respectively.

Solution. The hydrogen ground state wave function is

$$\psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

The perturbation $H' = A\boldsymbol{S}_\mathrm{p}\cdot\boldsymbol{S}_\mathrm{e}\delta^3(\boldsymbol{r})$. Denoting the spin function by χ_s, the total wave function of the ground state is

$$\psi = \psi_{100}\,\chi_s$$

The first order correction to energy

$$\begin{aligned} E_0^{(1)} &= \langle\psi_{100}\chi_s|A\boldsymbol{S}_\mathrm{p}\bullet\boldsymbol{S}_\mathrm{e}\delta^3(\boldsymbol{r})|\psi_{100}\chi_s\rangle \\ &= \langle\psi_{100}|A\delta^3(\boldsymbol{r})|\psi_{100}\rangle\langle\chi_s|\boldsymbol{S}_\mathrm{p}\bullet\boldsymbol{S}_\mathrm{e}|\chi_s\rangle \\ &= \frac{A}{\pi a_0^3}\langle\chi_s|\boldsymbol{S}_\mathrm{p}\bullet\boldsymbol{S}_\mathrm{e}|\chi_s\rangle \end{aligned}$$

Writing

$$\boldsymbol{F} = \boldsymbol{S}_\mathrm{p} + \boldsymbol{S}_\mathrm{e} \quad \text{or} \quad \boldsymbol{S}_\mathrm{p}\bullet\boldsymbol{S}_\mathrm{e} = \frac{F^2 - S_\mathrm{p}^2 - S_\mathrm{e}^2}{2}$$

$$\begin{aligned} E_0^{(1)} &= \frac{A}{\pi a_0^3}\left\langle\chi_s\left|\frac{F^2 - S_\mathrm{p}^2 - S_\mathrm{e}^2}{2}\right|\chi_s\right\rangle \\ &= \frac{A}{2\pi a_0^3}[F(F+1) - S_\mathrm{p}(S_\mathrm{p}+1) - S_\mathrm{e}(S_\mathrm{e}+1)]\hbar^2 \end{aligned}$$

As $S_\mathrm{p} = (1/2)$ and $S_\mathrm{e} = (1/2)$, the possible values of F are 1, 0. The separation between the two F states is the hyperfine splitting ΔE. Thus,

$$\Delta E = \frac{A}{2\pi a_0^3}\left[\left(1\times 2-\frac{1}{2}\times\frac{3}{2}-\frac{1}{2}\times\frac{3}{2}\right)\left(0-\frac{1}{2}\times\frac{3}{2}-\frac{1}{2}\times\frac{3}{2}\right)\right]$$

$$= \frac{A}{\pi a_0^3}$$

8.41 In the nonrelativistic limit, the kinetic energy of a particle moving in a potential $V(x) = 1/2m\omega^2$ is $p^2/2m$. Obtain the relativistic correction to the kinetic energy. Treating the correction as a perturbation, compute the first order correction to the ground state energy.

Solution. The relativistic expression for kinetic energy is

$$T = \sqrt{m_0^2c^4 + c^2p^2} - m_0c^2$$

$$= m_0c^2\left(1+\frac{p^2}{m_0^2c^2}\right)^{1/2} - m_0c^2$$

$$= m_0c^2\left(1+\frac{p^2}{2m_0^2c^2}-\frac{p^4}{4m_0^4c^4}\right) - m_0c^2$$

$$= \frac{p^2}{2m_0} - \frac{p^4}{8m_0^3c^2}$$

Perturbation

$$H' = \frac{p^4}{8m_0^3c^2}$$

The operators a and $a^\dagger$ are defined by

$$a = \sqrt{\frac{m\omega}{2\hbar}}x + \frac{i}{\sqrt{2m\hbar\omega}}p$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}x - \frac{i}{\sqrt{2m\hbar\omega}}p$$

where

$$p = \frac{\sqrt{2m\hbar\omega}}{2i}(a-a^\dagger)$$

The first order correction to the ground state energy is

$$E_0^{(1)} = \left\langle 0\left|\left(-\frac{p^4}{8m_0^3c^2}\right)\right|0\right\rangle = -\frac{1}{8m_0^3c^2}$$

$$\times\left\langle 0\left|\left(\frac{2m\hbar\omega}{4}\right)^2(a-a^\dagger)(a-a^\dagger)(a-a^\dagger)(a-a^\dagger)\right|0\right\rangle$$

$$E_0^{(1)} = -\frac{1}{8m_0^3c^2}\left(\frac{2m\hbar\omega}{4}\right)^2\langle 0|(a-a^\dagger)(a-a^\dagger)(a-a^\dagger)(a-a^\dagger)|0\rangle$$

When expanded, the expression will have 16 terms. Only two terms will be nonvanishing; these terms are

$$\langle 0 | aaa^\dagger a^\dagger | 0 \rangle \quad \text{and} \quad \langle 0 | aa^\dagger aa^\dagger | 0 \rangle$$

Since

$$a^\dagger | n\rangle = \sqrt{n+1} \, | n+1\rangle , \qquad a|n\rangle = \sqrt{n} \, | n-1\rangle$$

we have

$$\langle 0 | aaa^\dagger a^\dagger | 0 \rangle = 2, \qquad \langle 0 | aa^\dagger aa^\dagger | 0 \rangle = 1$$

Hence,

$$E_0^{(1)} = -\frac{3}{32} \frac{(\hbar\omega)^2}{m_0 c^2}$$

8.42 The Hamiltonian matrix of a system in the orthonormal basis

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

is given by

$$H = \begin{pmatrix} 1 & 2\varepsilon & 0 \\ 2\varepsilon & 2+\varepsilon & 3\varepsilon \\ 0 & 3\varepsilon & 3+\varepsilon \end{pmatrix}$$

Find the energy levels corrected up to second order in the small parameter ε.

Solution. The matrix H can be written as

$$H = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 3 \end{pmatrix} + \begin{pmatrix} 1 & 2\varepsilon & 0 \\ 2\varepsilon & 2+\varepsilon & 3\varepsilon \\ 0 & 3\varepsilon & 3+\varepsilon \end{pmatrix}$$

$$= H^0 + H'$$

Identifying H^0 and H' as the unperturbed and perturbation part, the eigenvalues of the unperturbed Hamiltonian H^0 are 1, 2 and 3. The first order correction to the energy is given by the diagonal matrix element of H'. Then,

$$H'_{11} = (1 \ \ 0 \ \ 0) \begin{pmatrix} 0 & 2 & 0 \\ 2 & 1 & 3 \\ 0 & 3 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \varepsilon = 0$$

$$H'_{22} = (0 \ \ 1 \ \ 0) \begin{pmatrix} 0 & 2 & 0 \\ 2 & 1 & 3 \\ 0 & 3 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \varepsilon = 1\varepsilon$$

$$H'_{33} = (0 \ \ 0 \ \ 1) \begin{pmatrix} 0 & 2 & 0 \\ 2 & 1 & 3 \\ 0 & 3 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \varepsilon = 1\varepsilon$$

The first order correction to the energies are 0, 1ε, 1ε, respectively. The second order correction is given by

$$E_n^{(2)} = \sum_m{}' \frac{|\langle m|H'|n\rangle|^2}{E_n^0 - E_m^0}$$

$$H'_{12} = (1 \quad 0 \quad 0)\begin{pmatrix} 0 & 2 & 0 \\ 2 & 1 & 3 \\ 0 & 3 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}\varepsilon = (1 \quad 0 \quad 0)\begin{pmatrix} 2 \\ 1 \\ 3 \end{pmatrix}\varepsilon = 2\varepsilon$$

$$H'_{13} = (1 \quad 0 \quad 0)\begin{pmatrix} 0 & 2 & 0 \\ 2 & 1 & 3 \\ 0 & 3 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}\varepsilon = (1 \quad 0 \quad 0)\begin{pmatrix} 0 \\ 3 \\ 1 \end{pmatrix}\varepsilon = 0$$

$$H'_{23} = (0 \quad 1 \quad 0)\begin{pmatrix} 0 & 2 & 0 \\ 2 & 1 & 3 \\ 0 & 3 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}\varepsilon = (0 \quad 1 \quad 0)\begin{pmatrix} 0 \\ 3 \\ 1 \end{pmatrix}\varepsilon = 3\varepsilon$$

$$E_1^{(2)} = \frac{|H'_{21}|^2}{1-2} + \frac{|H'_{31}|^2}{1-3} = -4\varepsilon^2 + 0 = -4\varepsilon^2$$

$$E_2^{(2)} = \frac{|H'_{12}|^2}{2-1} + \frac{|H'_{32}|^2}{2-3} = 4\varepsilon^2 - 9\varepsilon^2 = -5\varepsilon^2$$

$$E_3^{(2)} = \frac{|H'_{13}|^2}{3-1} + \frac{|H'_{23}|^2}{3-2} = 0 + 9\varepsilon^2 = 9\varepsilon^2$$

The energies of the three levels corrected to second order are

$$E_1 = 1 + 0 - 4\varepsilon^2 = 1 - 4\varepsilon^2$$

$$E_2 = 2 + \varepsilon - 5\varepsilon^2$$

$$E_3 = 3 + 1\varepsilon + 9\varepsilon^2$$