Physics 512 **Winter 2003**

Midterm – 11:00–1:00 (2 hours), February 17, 2003 – Solutions

[30 pts] 1. The magnetic moment operator $\vec{\mu}$ is a vector operator (*i.e.* a spherical tensor operator of rank 1).

[6] *a*) Show that the expectation value of $\vec{\mu}$ in an angular momentum state $|jm\rangle$ satisfies the relation

$$\langle jm'|\vec{\mu}\,|jm\rangle = \frac{\mu_B g_j}{\hbar}\langle jm'|\vec{J}\,|jm\rangle$$

where $\vec{J}$ is the angular momentum operator, and the "g-factor" g_j is given by

$$g_j = \frac{1}{j\mu_B}\langle jj|\mu_z|jj\rangle$$

This is basically a consequence of the projection theorem, which indicates that the expectation of any vector operator must be proportional to the expectation of angular momentum (which is a vector operator). Instead of writing out the complete projection theorem, all we need to note is that

$$\langle jm'|\vec{\mu}\,|jm\rangle = \alpha_j\langle jm'|\vec{J}\,|jm\rangle$$

where α_j is a possibly j dependent (but m and m' independent) constant of proportionality. We may compute α_j by looking at the z component of $\vec{\mu}$ and by taking $m = m' = j$. This gives

$$\langle jj|\mu_z|jj\rangle = \alpha_j\langle jj|J_z|jj\rangle \quad\Rightarrow\quad \alpha_j = \frac{\langle jj|\mu_z|jj\rangle}{\langle jj|J_z|jj\rangle} = \frac{j\mu_B g_j}{j\hbar} = \frac{\mu_B g_j}{\hbar}$$

This proves the relation.

[18] *b*) For a state with both orbital angular momentum ℓ and spin 1/2, the magnetic moment operator may be written as

$$\vec{\mu} = \frac{\mu_B}{\hbar}(g_\ell\vec{L} + 2\vec{S}\,)$$

where g_ℓ is the g-factor of the angular momentum $|\ell m\rangle$ state (*i.e.* the orbital part). By adding spin 1/2 to angular momentum ℓ (greater than 0), show that the total angular momentum $j = \ell \pm \frac{1}{2}$ states have g-factors

$$g_{j=\ell+\frac{1}{2}} = \frac{\ell g_\ell + 1}{\ell + \frac{1}{2}}, \qquad g_{j=\ell-\frac{1}{2}} = \frac{(\ell+1)g_\ell - 1}{\ell + \frac{1}{2}}$$

It is probably easiest to use the projection theorem, given by

$$\langle jm'|\vec{\mu}\,|jm\rangle = \frac{\langle jm|\vec{\mu}\cdot\vec{J}\,|jm\rangle}{j(j+1)\hbar^2}\langle jm'|\vec{J}\,|jm\rangle$$

Comparing with part a), this indicates that

$$g_j = \frac{\langle jm|\vec{\mu}\cdot\vec{J}\,|jm\rangle}{j(j+1)\mu_B\hbar}$$

We write

$$\begin{aligned}\vec{\mu}\cdot\vec{J} &= \frac{\mu_B}{\hbar}\vec{J}\cdot(g_\ell L + 2\vec{S}\,) = \frac{\mu_B}{\hbar}(g_\ell\vec{J}^{\,2} + (2-g_\ell)\vec{J}\cdot\vec{S}\,)\\ &= \frac{\mu_B}{\hbar}(g_\ell\vec{J}^{\,2} + \tfrac{1}{2}(2-g_\ell)(\vec{J}^{\,2}+\vec{S}^{\,2}-\vec{L}^{\,2}))\end{aligned}$$

As a result

$$g_j = \frac{g_\ell j(j+1) + (1-\frac{1}{2}g_\ell)(j(j+1)+s(s+1)-\ell(\ell+1))}{j(j+1)}$$

Substituting in $s=\frac{1}{2}$ and $j=\ell\pm\frac{1}{2}$ then gives the correct g-factors.
Note that it is also possible to compute $\langle jj|\mu_z|jj\rangle$ directly using Clebsch-Gordon coefficients for adding angular momentum $\ell\otimes\frac{1}{2}$, or by explicit construction of the coupled representation. In particular, the g-factors are given by

$$g_{j=\ell\pm\frac{1}{2}} = \frac{\langle \ell\pm\frac{1}{2}\,\ell\pm\frac{1}{2}|\mu_z|\ell\pm\frac{1}{2}\,\ell\pm\frac{1}{2}\rangle}{(\ell\pm\frac{1}{2})\mu_B} = \frac{1}{\ell\pm\frac{1}{2}}\langle \ell\pm\tfrac{1}{2}\,\ell\pm\tfrac{1}{2}|\frac{g_\ell L_z + 2S_z}{\hbar}|\ell\pm\tfrac{1}{2}\,\ell\pm\tfrac{1}{2}\rangle$$

Since the highest weight combination $|\ell+\frac{1}{2}\,\ell+\frac{1}{2}\rangle$ is given simply by

$$|\ell+\tfrac{1}{2}\,\ell+\tfrac{1}{2}\rangle = |\ell\ell\rangle|\!\uparrow\rangle \tag{1}$$

we find

$$g_{j=\ell+\frac{1}{2}} = \frac{1}{\ell+\frac{1}{2}}\langle\ell\ell|\langle\uparrow|\frac{g_\ell L_z + 2S_z}{\hbar}|\ell\ell\rangle|\!\uparrow\rangle = \frac{g_\ell\ell+1}{\ell+\frac{1}{2}}$$

To obtain $g_{j=\ell-\frac{1}{2}}$, we first act with the lowering operator J_- on (1) to obtain

$$|\ell+\tfrac{1}{2}\,\ell-\tfrac{1}{2}\rangle = \frac{1}{\sqrt{2\ell+1}}\left[|\ell\ell\rangle|\!\downarrow\rangle + \sqrt{2\ell}|\ell\,\ell{-}1\rangle|\!\uparrow\rangle\right]$$

By orthogonality, this indicates that the $|\ell-\frac{1}{2}\,\ell-\frac{1}{2}\rangle$ state must be (up to a phase which does not matter for this problem)

$$|\ell-\tfrac{1}{2}\,\ell-\tfrac{1}{2}\rangle = \frac{1}{\sqrt{2\ell+1}}\left[\sqrt{2\ell}|\ell\ell\rangle|\!\downarrow\rangle - |\ell\,\ell{-}1\rangle|\!\uparrow\rangle\right]$$

As a result

$$
\begin{aligned}
g_{j=\ell-\frac{1}{2}} &= \frac{1}{(\ell-\frac{1}{2})(2\ell+1)} \\
&\quad\times \left[\sqrt{2\ell}\langle \ell\ell|\langle\downarrow| - \langle \ell\,\ell{-}1|\langle\uparrow|\right] \frac{g_\ell L_z + 2S_z}{\hbar} \left[\sqrt{2\ell}|\ell\ell\rangle|\downarrow\rangle - |\ell\,\ell{-}1\rangle|\uparrow\rangle\right] \\
&= \frac{1}{(\ell-\frac{1}{2})(2\ell+1)} \left[2\ell\langle \ell\ell|\langle\downarrow|\frac{g_\ell L_z + 2S_z}{\hbar}|\ell\ell\rangle|\downarrow\rangle \right. \\
&\qquad\qquad \left. +\langle \ell\,\ell{-}1|\langle\uparrow|\frac{g_\ell L_z + 2S_z}{\hbar}|\ell\,\ell{-}1\rangle|\uparrow\rangle\right] \\
&= \frac{1}{(\ell-\frac{1}{2})(2\ell+1)} \left[2\ell(g_\ell\ell - 1) + (g_\ell(\ell-1)+1)\right] \\
&= \frac{(\ell+1)g_\ell - 1}{\ell+\frac{1}{2}}
\end{aligned}
$$

[6] c) Show that the off diagonal matrix element $\langle \ell+\frac{1}{2}\,\ell-\frac{1}{2}|\mu_z|\ell-\frac{1}{2}\,\ell-\frac{1}{2}\rangle$ must vanish when $g_\ell = 2$.

When $g_\ell = 2$, the magnetic moment operator becomes

$$\vec{\mu} = \frac{2\mu_B}{\hbar}\vec{J}$$

which is simply proportional to the total angular momentum operator. Since total angular momentum $\vec{J}$ cannot change $j = \ell - \frac{1}{2}$ to $j = \ell + \frac{1}{2}$, the off diagonal matrix element must vanish.

[35 pts] 2. Consider two coupled harmonic oscillators, with identical masses but different spring constants ($\omega_1 \neq \omega_2$), described by the Hamiltonian

$$H = \left(\frac{p_1^2}{2m} + \frac{1}{2}m\omega_1^2 x_1^2\right) + \left(\frac{p_2^2}{2m} + \frac{1}{2}m\omega_2^2 x_2^2\right) + \lambda x_1 x_2$$

The coupling term, $\lambda x_1 x_2$, should be treated as a perturbation. We focus on the ground state, $|00\rangle$, and the first two excited states, $|10\rangle$ and $|01\rangle$ (the states are labeled by $|n_1 n_2\rangle$ where n_1 and n_2 correspond to the first and second harmonic oscillator, respectively).

[14] a) Show that the first order in λ corrections to the energies of the above three states vanish. Then find the energies of these states to second order in λ.

This problem is best approached using creation/annihilation operators. For x_1 and x_2, we have

$$x_1 = \sqrt{\frac{\hbar}{2m\omega_1}}(a_1 + a_1^\dagger), \qquad x_2 = \sqrt{\frac{\hbar}{2m\omega_2}}(a_2 + a_2^\dagger) \tag{2}$$

In terms of these operators, the perturbation is

$$V = \lambda x_1 x_2 = \frac{\lambda\hbar}{2m\sqrt{\omega_1\omega_2}}(a_1 + a_1^\dagger)(a_2 + a_2^\dagger)$$

This indicates that the perturbation must change the oscillator numbers by ± 1*, ie we have selection rules* $\Delta n_1 = \pm 1$ *and* $\Delta n_2 = \pm 1$*. This is of course a consequence of parity (for the first and the second oscillators, independently).*

We start by noting that the zeroth order energies are

$$E^{(0)}_{n_1 n_2} = (n_1 + \tfrac{1}{2})\hbar\omega_1 + (n_2 + \tfrac{1}{2})\hbar\omega_2$$

for the state $|n_1 n_2\rangle$*. In particular, for the above three states, we have*

$$E^{(0)}_{00} = \tfrac{1}{2}\hbar(\omega_1 + \omega_2), E^{(0)}_{10} = \tfrac{1}{2}\hbar(3\omega_1 + \omega_2), E^{(0)}_{01} = \tfrac{1}{2}\hbar(\omega_1 + 3\omega_2)$$

Since $\omega_1 \neq \omega_2$*, the energies are non-degenerate (except for possible special cases when the ratio* ω_1/ω_2 *is rational; this cannot arise for the states we are interested in).*

Turning now to perturbation theory, it should be obvious that the selection rules $\Delta n_1 = \pm 1$ *and* $\Delta n_2 = \pm 2$ *forbid any first order in* λ *corrections to the energy. As a result, we must go to second order. Before we do so, we compute the matrix elements of the perturbation using* (2)

$$\begin{aligned}
\langle n_1 + 1\, n_2 + 1|V|n_1 n_2\rangle &= \frac{\lambda\hbar}{2m\sqrt{\omega_1\omega_2}}\sqrt{(n_1+1)(n_2+1)} \\
\langle n_1 + 1\, n_2 - 1|V|n_1 n_2\rangle &= \frac{\lambda\hbar}{2m\sqrt{\omega_1\omega_2}}\sqrt{(n_1+1)n_2} \\
\langle n_1 - 1\, n_2 + 1|V|n_1 n_2\rangle &= \frac{\lambda\hbar}{2m\sqrt{\omega_1\omega_2}}\sqrt{n_1(n_2+1)} \\
\langle n_1 - 1\, n_2 - 1|V|n_1 n_2\rangle &= \frac{\lambda\hbar}{2m\sqrt{\omega_1\omega_2}}\sqrt{n_1 n_2}
\end{aligned}$$

For the ground state $|00\rangle$*, we must consider the* $|11\rangle$ *intermediate state. The second order energy shift is given by*

$$E^{(2)}_{00} = \frac{|\langle 11|V|00\rangle|^2}{-\hbar(\omega_1+\omega_2)} = -\frac{\hbar\lambda^2}{4m^2\omega_1\omega_2}\frac{1}{\omega_1+\omega_2}$$

For the state $|10\rangle$*, we must instead consider both* $|01\rangle$ *and* $|21\rangle$ *as intermediate states*

$$E^{(2)}_{10} = \frac{|\langle 01|V|10\rangle|^2}{\hbar(\omega_1-\omega_2)} + \frac{|\langle 21|V|10\rangle|^2}{-\hbar(\omega_1+\omega_2)} = \frac{\hbar\lambda^2}{4m^2\omega_1\omega_2}\left(\frac{1}{\omega_1-\omega_2} - \frac{2}{\omega_1+\omega_2}\right)$$

For the state $|01\rangle$, we do not actually have to compute anything, but we can simply note from symmetry that its energy is related to that of the $|10\rangle$ state by simply interchanging $\omega_1 \leftrightarrow \omega_2$. As a result, the energies of the first three states are (up to second order)

$$\begin{aligned}
E_{00} &= \tfrac{1}{2}\hbar(\omega_1+\omega_2) - \frac{\hbar\lambda^2}{4m^2\omega_1\omega_2}\frac{1}{\omega_1+\omega_2} \\
E_{10} &= \tfrac{1}{2}\hbar(3\omega_1+\omega_2) + \frac{\hbar\lambda^2}{4m^2\omega_1\omega_2}\frac{3\omega_2-\omega_1}{\omega_1^2-\omega_2^2} \\
E_{01} &= \tfrac{1}{2}\hbar(\omega_1+3\omega_2) + \frac{\hbar\lambda^2}{4m^2\omega_1\omega_2}\frac{3\omega_1-\omega_2}{\omega_2^2-\omega_1^2}
\end{aligned}$$

[14] *b*) Compute the expectation $\langle\Delta x_1\Delta x_2\rangle = \langle x_1x_2\rangle - \langle x_1\rangle\langle x_2\rangle$ for the ground state of this system, up to first order in λ.

To compute the expectations, we must first work out the first order shift in the ground state

$$|00\rangle = |00\rangle^{(0)} + \frac{\langle 11|V|00\rangle}{-\hbar(\omega_1+\omega_2)}|11\rangle^{(0)} = |00\rangle^{(0)} - \frac{\lambda}{2m\sqrt{\omega_1\omega_2}}\frac{1}{\omega_1+\omega_2}|11\rangle^{(0)}$$

The expectations $\langle x_1\rangle$ and $\langle x_2\rangle$ vanish because $|00\rangle$ has even parity under either $x_1 \to -x_1$ or $x_2 \to -x_2$ (this is the same result as one gets from the selection rules). So we have simply

$$\begin{aligned}
\langle\Delta x_1\Delta x_2\rangle = \langle x_1x_2\rangle &= \frac{\hbar}{2m\sqrt{\omega_1\omega_2}}\left(\langle 00| - \frac{\lambda}{2m\sqrt{\omega_1\omega_2}}\frac{1}{\omega_1+\omega_2}\langle 11|\right) \\
&\qquad \times (a_1+a_1^\dagger)(a_2+a_2^\dagger)\left(|00\rangle - \frac{\lambda}{2m\sqrt{\omega_1\omega_2}}\frac{1}{\omega_1+\omega_2}|11\rangle\right) \\
&= \frac{\hbar}{2m\sqrt{\omega_1\omega_2}}\left(\langle 00| - \frac{\lambda}{2m\sqrt{\omega_1\omega_2}}\frac{1}{\omega_1+\omega_2}\langle 11|\right) \\
&\qquad \times \left(|11\rangle - \frac{\lambda}{2m\sqrt{\omega_1\omega_2}}\frac{1}{\omega_1+\omega_2}|00\rangle\right) \\
&= -\frac{\hbar\lambda}{2m^2\omega_1\omega_2}\frac{1}{\omega_1+\omega_2}
\end{aligned}$$

(correct to first order in λ). Of course, this expectation must vanish when $\lambda = 0$, since in that case the two oscillators would be completely independent. Note that we may ignore wavefunction renormalization, as that only shows up at second order and higher in λ.

[7] *c*) So far we have assumed that $\omega_1 \neq \omega_2$. Show that the perturbative energies may pick up first order in λ corrections when $\omega_1 = \omega_2$ (you do not have to compute any actual corrections).

When $\omega_1 = \omega_2$, the states $|10\rangle$ and $|01\rangle$ are degenerate in energy. In this case, we must use degenerate perturbation theory, which for these states involve diagonalizing the perturbation matrix

$$\mathbf{V} = \frac{\hbar\lambda}{2m\sqrt{\omega_1\omega_2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

This will give a non-zero contribution linear in λ

$$E^{(1)}_{10\,\mathrm{and}\,01} = \pm\frac{\hbar\lambda}{2m\sqrt{\omega_1\omega_2}}$$

[35 pts] 3. Consider a rotator with orbital angular momentum operator $\vec{L}$, spin operator $\vec{S}$ (taken to be spin 1/2), and Hamiltonian

$$H = H_0 + H_{\rm sa} = A\vec{J}^{\,2} + B\vec{J}\cdot\vec{S} \qquad (A \gg B > 0)$$

where $\vec{J} = \vec{L} + \vec{S}$.

[6] *a*) Ignoring the "spin-axis" interaction $H_{\rm sa}$, write down the eigenenergies of the zeroth order Hamiltonian, $H_0 = A\vec{J}^{\,2}$, and show that the eigenstates may be labeled by the coupled representation $|\ell\,\frac{1}{2};jm_j\rangle$ (here $\frac{1}{2}$ indicates the spin). Show that the ground state is four-fold degenerate (and corresponds to ${}^2S_{1/2} = \{|0\,\frac{1}{2};\frac{1}{2}\,\frac{1}{2}\rangle, |0\,\frac{1}{2};\frac{1}{2}\,-\frac{1}{2}\rangle\}$ and ${}^2P_{1/2} = \{|1\,\frac{1}{2};\frac{1}{2}\,\frac{1}{2}\rangle, \{|1\,\frac{1}{2};\frac{1}{2}\,-\frac{1}{2}\rangle\}$).

Since we have $\vec{J} = \vec{L} + \vec{S}$, we may work in either the uncoupled or the coupled representation. Of course, for $H_0 = A\vec{J}^2$, it should be obvious that the eigenenergies in the coupled basis are simply $E_j = A\hbar^2 j(j+1)$. Since the system is spin 1/2, we are adding orbital angular momentum ℓ to spin 1/2, resulting in total $j = \ell \pm \frac{1}{2}$. This indicates that j must be half-integral, and that any eigenstate of H_0 of a given j is degenerate, with two possible values of ℓ given by $\ell = j + \frac{1}{2}$ and $\ell = j - \frac{1}{2}$.

The eigenstates and eigenenergies are thus

$$|(\ell = j + \tfrac{1}{2})\tfrac{1}{2};jm_j\rangle \text{ and } |(\ell = j - \tfrac{1}{2})\tfrac{1}{2};jm_j\rangle \qquad E = A\hbar^2 j(j+1)$$

The ground state corresponds to $j = \frac{1}{2}$, and so may be labeled by ${}^2S_{1/2}$ and ${}^2P_{1/2}$.

[6] *b*) Now include $H_{\rm sa}$, and find the eigenenergies of $H = H_0 + H_{\rm sa}$. Show that the degeneracy between the $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$ states is lifted, and that the ground state is the doubly degenerate ${}^2P_{1/2}$ state.

Working in the coupled representation, we write

$$H_{\rm sa} = B\vec{J}\cdot\vec{S} = \tfrac{1}{2}B(\vec{J}^2 + \vec{S}^2 - \vec{L}^2) = \tfrac{1}{2}B\hbar^2(j(j+1) + s(s+1) - \ell(\ell+1))$$

Substituting in $s = \frac{1}{2}$ *and either* $j = \ell + \frac{1}{2}$ *or* $j = \ell - \frac{1}{2}$*, we find*

$$E_{\rm sa} = \begin{cases} \frac{1}{2}B\hbar^2(\ell+\frac{3}{2}) & j = \ell + \frac{1}{2} \\ -\frac{1}{2}B\hbar^2(\ell-\frac{1}{2}) & j = \ell - \frac{1}{2} \end{cases}$$

As a result, the energies get split

$$\begin{array}{ll} |(\ell = j + \frac{1}{2})\frac{1}{2}; jm_j\rangle & E = A\hbar^2 j(j+1) - \frac{1}{2}B\hbar^2 j \\ |(\ell = j - \frac{1}{2})\frac{1}{2}; jm_j\rangle & E = A\hbar^2 j(j+1) + \frac{1}{2}B\hbar^2 (j+1) \end{array}$$

For the ground state, this indicates that the $\ell = 1$ *(the* $^2P_{1/2}$*) state is lower in energy. In fact, for any given* j *level, the state with higher* ℓ *value is the one with lower energy.*

[6] *c*) We now turn on an electric field along the z axis, inducing a Stark interaction

$$H_{\rm Stark} = d_e\mathcal{E}\hat{z} = d_e\mathcal{E}\cos\theta$$

Explain why the linear Stark effect vanishes (in all eigenstates) for weak electric fields, $d_e\mathcal{E} \ll B\hbar^2$.

Recall that the linear Stark effect is a first order perturbation theory effect. Since the operator $\hat{z}$ *is the* z*-component of a vector operator* $\vec{r}/r$*, we see that* $H_{\rm Stark}$ *is an odd-parity operator, and hence gives rise to a selection rule* $\Delta\ell = \pm 1$*. From part b), we have seen that states at any given energy level have a definite* ℓ *value. As a result, the parity selection rule forbids a first order correction, and the linear Stark effect vanishes.*

Even though this is a different system, this parity argument is identical to that used for a hydrogen atom in an electric field.

[17] *d*) For strong electric fields, however, we may ignore $H_{\rm sa}$, and consider only $H_{\rm Stark}$ as a perturbation to H_0. In this case, find the first order energy shifts and correct zeroth order eigenstates for the initially degenerate ground state ($^2S_{1/2}$ and $^2P_{1/2}$).

Ignoring $H_{\rm sa}$*, the result of part a) indicates that the ground state is four-fold degenerate. However* $H_{\rm Stark}$*, being the* 0*-component of a spherical vector operator, yields a selection rule* $\Delta m = 0$*. This indicates that the* $m_j = \frac{1}{2}$ *and* $m_j = -\frac{1}{2}$ *subspaces are independent. In the basis given in part a)*

$$|0\tfrac{1}{2};\tfrac{1}{2}\ \pm\tfrac{1}{2}\rangle \qquad |1\tfrac{1}{2};\tfrac{1}{2}\ \pm\tfrac{1}{2}\rangle$$

the perturbation matrix is

$$\mathrm{V} = d_e\mathcal{E}\begin{pmatrix} \langle 0\frac{1}{2};\frac{1}{2}\ \pm\frac{1}{2}|\hat{z}|0\frac{1}{2};\frac{1}{2}\ \pm\frac{1}{2}\rangle & \langle 0\frac{1}{2};\frac{1}{2}\ \pm\frac{1}{2}|\hat{z}|1\frac{1}{2};\frac{1}{2}\ \pm\frac{1}{2}\rangle \\ \langle 1\frac{1}{2};\frac{1}{2}\ \pm\frac{1}{2}|\hat{z}|0\frac{1}{2};\frac{1}{2}\ \pm\frac{1}{2}\rangle & \langle 1\frac{1}{2};\frac{1}{2}\ \pm\frac{1}{2}|\hat{z}|1\frac{1}{2};\frac{1}{2}\ \pm\frac{1}{2}\rangle \end{pmatrix}$$

However, the diagonal elements vanish because of the $\Delta\ell = \pm 1$ selection rule. Thus

$$\mathbf{V} = d_e\mathcal{E}\begin{pmatrix} 0 & \langle 0\tfrac{1}{2};\tfrac{1}{2}\ \pm\tfrac{1}{2}|\hat{z}|1\tfrac{1}{2};\tfrac{1}{2}\ \pm\tfrac{1}{2}\rangle \\ \langle 1\tfrac{1}{2};\tfrac{1}{2}\ \pm\tfrac{1}{2}|\hat{z}|0\tfrac{1}{2};\tfrac{1}{2}\ \pm\tfrac{1}{2}\rangle & 0 \end{pmatrix}$$

Changing to the uncoupled basis, we note that

$$|0\tfrac{1}{2};\tfrac{1}{2}\tfrac{1}{2}\rangle = |00\rangle|\uparrow\rangle, \qquad |1\tfrac{1}{2};\tfrac{1}{2}\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}|11\rangle|\downarrow\rangle - \sqrt{\tfrac{1}{3}}|10\rangle|\uparrow\rangle$$

and hence

$$\langle 0\tfrac{1}{2};\tfrac{1}{2}\tfrac{1}{2}|\hat{z}|1\tfrac{1}{2};\tfrac{1}{2}\tfrac{1}{2}\rangle = -\sqrt{\tfrac{1}{3}}\langle 00|\hat{z}|10\rangle = -\sqrt{\tfrac{1}{3}}\int Y_0^0(\theta,\varphi)\cos\theta Y_1^0(\theta,\varphi)\,d\Omega = -\tfrac{1}{3}$$

As a result, for $m_j = \frac{1}{2}$ we have

$$\mathbf{V} = -\tfrac{1}{3}d_e\mathcal{E}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

A similar result may be obtained for $m_j = -\frac{1}{2}$. So the first order eigenenergies and eigenstates are

$$E^{(1)} = \begin{cases} \pm\tfrac{1}{3}d_e\mathcal{E} & \tfrac{1}{\sqrt{2}}\left(|0\tfrac{1}{2};\tfrac{1}{2}\tfrac{1}{2}\rangle \pm |1\tfrac{1}{2};\tfrac{1}{2}\tfrac{1}{2}\rangle\right) \\ \mp\tfrac{1}{3}d_e\mathcal{E} & \tfrac{1}{\sqrt{2}}\left(|0\tfrac{1}{2};\tfrac{1}{2}\ -\tfrac{1}{2}\rangle \pm |1\tfrac{1}{2};\tfrac{1}{2}\ -\tfrac{1}{2}\rangle\right) \end{cases}$$