**Problem 1.** Consider a spin-1 particle. The unperturbed Hamiltonian is $H_0 = AS_z^2$, where $A$ is a constant. Consider the perturbation $V = B(S_x^2 - S_y^2)$, where $|A| \gg |B|$. Note that $S_i$ are the $3 \times 3$ spin matrices.

**1.1** Calculate the first-order correction to the energies.

**Solution.** Firstly, note that

$$S_x = \frac{\hbar}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}, \qquad S_y = \frac{\hbar}{\sqrt{2}} \begin{bmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{bmatrix}, \qquad S_z = \hbar \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}.$$

Then

$$H_0 = A\hbar^2 \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad V = B\frac{\hbar^2}{2} \left( \begin{bmatrix} 1 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{bmatrix} - \begin{bmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{bmatrix} \right) = B\hbar^2 \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}. \tag{1}$$

The eigenvalues of $H_0$ are

$$E_1^{(0)} = A\hbar^2, \qquad E_2^{(0)} = 0, \qquad E_3^{(0)} = A\hbar^2, \tag{2}$$

so the problem is degenerate. The eigenkets are the $S_z$ eigenbasis kets:

$$|1^{(0)}\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = |+1\rangle, \qquad |2^{(0)}\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = |0\rangle, \qquad |3^{(0)}\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = |-1\rangle.$$

We will begin with the correction to $E_2^{(0)}$, which is nondegenerate. From (5.1.20) and (5.1.37) in Sakurai, the first-order energy corrections in the unperturbed case are given by

$$\Delta_n^{(1)} \equiv E_n^{(1)} - E_n^{(0)} = \langle n^{(0)}|V|n^{(0)}\rangle.$$

This gives us

$$\Delta_2^{(1)} = \langle 2^{(0)}|V|2^{(0)}\rangle = \langle 2|V|2\rangle = 0.$$

For $E_1^{(0)}$ and $E_2^{(0)}$, consider the degenerate subspace spanned by $\{|+1\rangle, |-1\rangle\}$. Let $P_0$ be a projection onto this subspace, and let

$$V_0 = P_0 V P_0 = B\hbar^2 \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = B\hbar^2 \sigma_x,$$

where $\sigma_x$ is the Pauli matrix. Therefore, we know that $V_0$ has eigenvalues $v_\pm = \pm B\hbar^2$. These eigenvalues are equivalent to the corresponding energy shifts.

In summary, we have

$$\Delta_1^{(1)} = B\hbar^2, \qquad \Delta_2^{(1)} = 0, \qquad \Delta_3^{(1)} = -B\hbar^2.$$

**1.2** Solve the problem exactly, and compare your result to the perturbation theory result.

**Solution.** From (1), the perturbed Hamiltonian is given by

$$H = H_0 + \lambda V = \hbar^2 \begin{bmatrix} A & 0 & \lambda B \\ 0 & 0 & 0 \\ \lambda B & 0 & A \end{bmatrix}.$$

Let $E_i = \hbar^2 \mu_i$ denote the eigenvalues of $H$, where $\mu$ are the roots of the equation

$$0 = \det\left(\frac{H}{\hbar^2} - \mu I\right) = \begin{vmatrix} A-\mu & 0 & \lambda B \\ 0 & -\mu & 0 \\ \lambda B & 0 & A-\mu \end{vmatrix} = -\mu(A-\mu)^2 + \mu(\lambda B)^2.$$

The roots are $\mu = 0$ and $\mu = A \pm \lambda B$, which give us the eigenvalues

$$E_1 = A + \lambda B, \qquad E_2 = 0, E_3 \qquad = A - \lambda B.$$

Taking the difference $\Delta_n^{(1)} = E_n^{(1)} - E_n^{(0)}$ for $E_i^{(0)}$ given by (2), the energy shifts to first order in $\lambda$ are

$$\Delta_1^{(1)} = B\hbar^2, \qquad \Delta_2^{(1)} = 0, \qquad \Delta_3^{(1)} = -B\hbar^2,$$

which are the same as those found in 1.1.

**Problem 2.** Consider the Stark effect for the $n = 3$ states of hydrogen. There are initially nine degenerate states $|3, l, m\rangle$ (neglect spin), and an electric field $E$ is turned on in the $z$ direction.

**2.1** Construct the $9 \times 9$ matrix representing the perturbed Hamiltonian in this case. Show your work when deriving the nonzero matrix elements, and provide an explanation as to why the other elements are zero.

**Solution.** The perturbation operator for the **E** field is given by (5.2.17) in Sakurai:

$$V = -eZ|\mathbf{E}|.$$

$V$ is a dipole interaction and therefore obeys the dipole selection rule, which is given by (17.2.21) in Shankar:

$$\langle nlm \big| Z \big| n'l'm' \rangle = 0 \quad \text{unless} \quad \begin{cases} l' = l \pm 1, \\ m' = m. \end{cases}$$

The dipole selection rule is a combination of the angular momentum and parity selection rules. The angular momentum selection rule stipulates that $\langle nlm|Z|n'l'm'\rangle = 0$ unless $l' = l, l \pm 1$ and $m' = m + q$ where $q = 0$ is the magnetic quantum number of the tensor operator $Z$. The parity selection rule eliminates $l = l'$ because $\langle nlm|Z|n'l'm'\rangle = 0$ unless $l$ and $l'$ have opposite parity.

For the nonzero elements, the hydrogen atom wave functions are given by (A.6.3) in Sakurai:

$$\langle \mathbf{r}|nlm\rangle = \psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi),$$

where

$$R_{nl}(r) = -\sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!^3}} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho) \quad \text{where} \quad \rho = \frac{2r}{na_0}. \tag{3}$$

The associated Laguerre polynomials $L_p^q$ are given by (A.6.4) and (A.6.5),

$$L_p^q(\rho) = \frac{d^q L_p(\rho)}{d\rho^q} \quad \text{where} \quad L_p(\rho) = e^\rho \frac{d^p}{d\rho^p}. \tag{4}$$

The spherical harmonics $Y_l^m$ are given by (3.6.37) and (3.6.38),

$$Y_l^m(\theta,\phi) = \frac{(-1)^l}{2^l l!}\sqrt{\frac{2l+1}{4\pi}\frac{(l+m)!}{(l-m)!}}e^{im\phi}\frac{1}{\sin^m\theta}\frac{d^{l-m}}{d(\cos\theta)^{l-m}}^{2l}, \qquad Y_l^{-m}(\theta,\phi) = (-1)^m Y_l^{m*}(\theta,\phi) \tag{5}$$

for $m \geq 0$.

The nonzero elements all have $l \in \{0,1,2\}$ and $m \in \{-1,0,1\}$. Substituting into (3), the relevant $R_{nl}$ are

$$\begin{aligned}
R_{30}(r) &= -\sqrt{\left(\frac{2}{3a_0}\right)^3 \frac{(3-1)!}{2(3)3!^3}}e^{-\rho/2}L_3^1(\rho) = -\sqrt{\frac{2^3}{3^3a_0^3}\frac{2}{2^4 3^4}}e^{-\rho/2}L_3^1(\rho) = -\sqrt{\frac{e^{-\rho}}{3^7 a_0^3}}L_3^1(\rho),\\
R_{31}(r) &= -\sqrt{\left(\frac{2}{3a_0}\right)^3 \frac{(3-1-1)!}{2(3)(3+1)!^3}}e^{-\rho/2}\rho L_{3+1}^{2+1}(\rho) = -\sqrt{\frac{2^3}{3^3a_0^3}\frac{1}{2^{10}3^4}}e^{-\rho/2}\rho L_4^3(\rho) = -\sqrt{\frac{e^{-\rho}}{2^7 3^7 a_0^3}}\rho L_4^3(\rho),\\
R_{32}(r) &= -\sqrt{\left(\frac{2}{3a_0}\right)^3 \frac{(3-2-1)!}{2(3)(3+2)!^3}}e^{-\rho/2}\rho^2 L_{3+2}^{4+1}(\rho) = -\sqrt{\frac{2^3}{3^3a_0^3}\frac{1}{2^{10}3^4 5^3}}e^{-\rho/2}\rho^2 L_5^5(\rho) = -\sqrt{\frac{e^{-\rho}}{2^7 3^7 5^3 a_0^3}}\rho^2 L_5^5(\rho).
\end{aligned}$$

From (4), the relevant $L_p$ are

$$\begin{aligned}
L_3(\rho) &= e^\rho \frac{d^3}{d\rho^3} = e^\rho \frac{d^2}{d\rho^2} = e^\rho \frac{d}{d\rho} = 6 - 18\rho + 9\rho^2 - \rho^3,\\
L_4(\rho) &= e^\rho \frac{d^4}{d\rho^4} = e^\rho \frac{d^3}{d\rho^3} = e^\rho \frac{d^2}{d\rho^2}\\
&= e^\rho \frac{d}{d\rho} = 24 - 96\rho + 72\rho^2 - 16\rho^3 + \rho^4,\\
L_5(\rho) &= e^\rho \frac{d^5}{d\rho^5} = e^\rho \frac{d^4}{d\rho^4} = e^\rho \frac{d^3}{d\rho^3}\\
&= e^\rho \frac{d^2}{d\rho^2}\\
&= e^\rho \frac{d}{d\rho} = 120 - 600\rho + 600\rho^2 - 200\rho^3 + 25\rho^4 - \rho^5
\end{aligned}$$

and then the relevant $L_p^q$ are

$$\begin{aligned}
L_3^1(\rho) &= \frac{dL_3(\rho)}{d\rho} = -18 + 18\rho - 3\rho^2 = -3(6 - 6\rho + \rho^2),\\
L_4^3(\rho) &= \frac{d^3 L_4(\rho)}{d\rho^3} = -(3!)16 + \left(\frac{4!}{1!}\right)\rho = 24(-4+\rho) = 2^3 3(-4+\rho),\\
L_5^5(\rho) &= \frac{d^5 L_5(\rho)}{d\rho^5} = -5! = -120 = -2^3 3^1 5.
\end{aligned}$$

Substituting into (5), the relevant $Y_l^m$ are

$$Y_0^0(\theta,\phi) = \sqrt{\frac{1}{2^2\pi}},$$

$$Y_1^0(\theta,\phi) = \sqrt{\frac{3}{2^2\pi}}\cos\theta, \qquad Y_1^{\pm1}(\theta,\phi) = \mp\sqrt{\frac{3}{2^3\pi}}e^{\pm i\phi}\sin\theta,$$

$$Y_2^0(\theta,\phi) = \sqrt{\frac{5}{2^4\pi}}(3\cos^2\theta-1), \qquad Y_2^{\pm1}(\theta,\phi) = \mp\sqrt{\frac{3^15}{2^3\pi}}e^{\pm i\phi}\cos\theta\sin\theta.$$

Note that $Z = r\cos\theta$ in polar coordinates. In general, the nonzero matrix elements are then

$$\begin{aligned}\langle 3lm\big|V\big|3l'm'\rangle &= -e|\mathbf{E}|\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\psi_{3lm}^*(r,\theta,\phi)r\cos\theta\psi_{3l'm'}(r,\theta,\phi)r^2\sin\theta\,dr\,d\theta\,d\phi\\
&= -e|\mathbf{E}|\left(\frac{3a_0}{2}\right)^4\int_0^{2\pi}\int_{-1}^{1}\int_0^{\infty}\psi_{3lm}^*(r,\theta,\phi)\psi_{3l'm'}(r,\theta,\phi)\rho^3\cos\theta\,d\rho\,d(\cos\theta)\,d\phi\\
&= -\frac{3^4a_0^4e|\mathbf{E}|}{2^4}\int_0^{2\pi}\int_{-1}^{1}Y_l^{m*}(\theta,\phi)Y_{l'}^{m'}(\theta,\phi)\cos\theta\,d(\cos\theta)\,d\phi\int_0^{\infty}R_{3l}(r)R_{3l'}(r)\rho^3\,d\rho\,.\end{aligned}$$

Firstly,

$$\langle 310|V|300\rangle = -\frac{3^4a_0^4e|\mathbf{E}|}{2^4}\int_0^{2\pi}\int_{-1}^{1}Y_1^{0*}(\theta,\phi)Y_0^0(\theta,\phi)\cos\theta\,d(\cos\theta)\,d\phi\int_0^{\infty}R_{31}(r)R_{30}(r)\rho^3\,d\rho\,, \tag{6}$$

where

$$\begin{aligned}&\int_0^{2\pi}\int_{-1}^{1}Y_1^{0*}(\theta,\phi)Y_0^0(\theta,\phi)\cos\theta\,d(\cos\theta)\,d\phi = \int_0^{2\pi}\int_{-1}^{1}\sqrt{\frac{3}{2^2\pi}}\cos\theta\sqrt{\frac{1}{2^2\pi}}\cos\theta\,d(\cos\theta)\,d\phi\\
&\quad= \frac{\sqrt{3}}{2^2\pi}\int_0^{2\pi}d\phi\int_{-1}^{1}\cos^2\theta\,d(\cos\theta) = \frac{\sqrt{3}}{2^2\pi}\Big[\phi\Big]_0^{2\pi}\left[\frac{\cos^3\theta}{3}\right]_{-1}^{1} = \frac{\sqrt{3}}{2^2\pi}(2\pi)\frac{2}{3} = \frac{1}{\sqrt{3}},\end{aligned}$$

and

$$\begin{aligned}&\int_0^{\infty}R_{31}(r)R_{30}(r)\rho^3\,d\rho = \int_0^{\infty}\sqrt{\frac{e^{-\rho}}{2^73^7a_0^3}}\rho L_4^3(\rho)\sqrt{\frac{e^{-\rho}}{3^7a_0^3}}L_3^1(\rho)\rho^3\,d\rho = \frac{1}{\sqrt{2^73^7a_0^3}}\int_0^{\infty}e^{-\rho}L_4^3(\rho)L_3^1(\rho)\rho^4\,d\rho\\
&\quad= -\frac{1}{\sqrt{2}3^5a_0^3}\int_0^{\infty}e^{-\rho}(-24\rho^4+30\rho^5-10\rho^6+\rho^7)\,d\rho = -\frac{1}{\sqrt{2}3^5a_0^3}(-24(4!)+30(5!)-10(6!)+7!)\\
&\quad= -\frac{2^5}{\sqrt{2}3^2a_0^3},\end{aligned}$$

where we have used

$$\int_0^{\infty}x^ne^{-x}\,dx = n!.$$

Combining these results, (6) becomes

$$\langle 310|V|300\rangle = \frac{3^4a_0^4e|\mathbf{E}|}{2^4}\frac{1}{\sqrt{3}}\frac{2^5}{\sqrt{2}3^2a_0^3} = e|\mathbf{E}|a_0\frac{3^22}{\sqrt{6}} = 3\sqrt{6}e|\mathbf{E}|a_0 = \langle 300|V|310\rangle\,.$$

Secondly,

$$\langle 32{\pm}1|V|31{\pm}1\rangle = -\frac{3^4a_0^4e|\mathbf{E}|}{2^4}\int_0^{2\pi}\int_{-1}^{1}Y_2^{\pm1*}(\theta,\phi)Y_1^{\pm1}(\theta,\phi)\cos\theta\,d(\cos\theta)\,d\phi\int_0^{\infty}R_{32}(r)R_{31}(r)\rho^3\,d\rho\,, \tag{7}$$

where

$$\begin{aligned}
\int_0^{2\pi}\int_{-1}^{1} Y_2^{\pm1*}(\theta,\phi)Y_1^{\pm1}(\theta,\phi)\cos\theta\, d(\cos\theta)\, d\phi &= \int_0^{2\pi}\int_{-1}^{1}\sqrt{\frac{3^1 5}{2^3\pi}}e^{\mp i\phi}\cos\theta\sin\theta\sqrt{\frac{3}{2^3\pi}}e^{\pm i\phi}\sin\theta\cos\theta\, d(\cos\theta)\, d\phi \\
&= \frac{3\sqrt{5}}{2^3\pi}\int_0^{2\pi} d\phi\int_{-1}^{1}\cos^2\theta\sin^2\theta\, d(\cos\theta) = \frac{3\sqrt{5}}{2^3\pi}\int_0^{2\pi} d\phi\int_{-1}^{1}\cos^2\theta(1-\cos^2\theta)\, d(\cos\theta) \\
&= \frac{3\sqrt{5}}{2^3\pi}\Big[\phi\Big]_0^{2\pi}\left[\frac{\cos^3\theta}{3}-\frac{\cos^5\theta}{5}\right]_{-1}^{1} = \frac{3\sqrt{5}}{2^3\pi}(2\pi)\frac{2^2}{3^1 5} = \frac{1}{\sqrt{5}},
\end{aligned}$$

and

$$\begin{aligned}
\int_0^{\infty} R_{32}(r)R_{31}(r)\rho^3\, d\rho &= \int_0^{\infty}\sqrt{\frac{e^{-\rho}}{2^7 3^7 5^3 a_0^3}}\rho^2 L_5^5(\rho)\sqrt{\frac{e^{-\rho}}{2^7 3^7 a_0^3}}\rho L_4^3(\rho)\rho^3\, d\rho = \frac{1}{2^7 3^7\sqrt{5^3}a_0^3}\int_0^{\infty} e^{-\rho}L_5^5(\rho)L_4^3(\rho)\rho^6\, d\rho \\
&= -\frac{1}{2^1 3^5\sqrt{5}a_0^3}\int_0^{\infty} e^{-\rho}(-4+\rho)\rho^6\, d\rho = -\frac{1}{2^1 3^5\sqrt{5}a_0^3}\int_0^{\infty} e^{-\rho}(-4\rho^6+\rho^7)\, d\rho = -\frac{1}{2^1 3^5\sqrt{5}a_0^3}(-4(6!)+7!) \\
&= -\frac{2^3\sqrt{5}}{3^2 a_0^3}.
\end{aligned}$$

Then (7) becomes

$$\langle 32{\pm}1|V|31{\pm}1\rangle = \frac{3^4 a_0^4 e|\mathbf{E}|}{2^4}\frac{1}{\sqrt{5}}\frac{2^3\sqrt{5}}{3^2 a_0^3} = \frac{3^2 a_0 e|\mathbf{E}|}{2} = \frac{9}{2}e|\mathbf{E}|a_0 = \langle 31{\pm}1|V|32{\pm}1\rangle\,.$$

Thirdly,

$$\langle 320|V|310\rangle = -\frac{3^4 a_0^4 e|\mathbf{E}|}{2^4}\int_0^{2\pi}\int_{-1}^{1} Y_2^{0*}(\theta,\phi)Y_1^{0}(\theta,\phi)\cos\theta\, d(\cos\theta)\, d\phi\int_0^{\infty} R_{32}(r)R_{31}(r)\rho^3\, d\rho\,, \tag{8}$$

where

$$\begin{aligned}
\int_0^{2\pi}\int_{-1}^{1} Y_2^{0*}(\theta,\phi)Y_1^{0}(\theta,\phi)\cos\theta\, d(\cos\theta)\, d\phi &= \int_0^{2\pi}\int_{-1}^{1}\sqrt{\frac{5}{2^4\pi}}(3\cos^2\theta-1)\sqrt{\frac{3}{2^2\pi}}\cos\theta\cos\theta\, d(\cos\theta)\, d\phi \\
&= \frac{\sqrt{3}\sqrt{5}}{2^3\pi}\int_0^{2\pi} d\phi\int_{-1}^{1}(3\cos^4\theta-\cos^2\theta)\, d(\cos\theta) = \frac{\sqrt{3}\sqrt{5}}{2^3\pi}\Big[\phi\Big]_0^{2\pi}\left[\frac{3\cos^5\theta}{5}-\frac{\cos^3\theta}{3}\right]_{-1}^{1} = \frac{\sqrt{3}\sqrt{5}}{2^3\pi}(2\pi)\frac{2^3}{3^1 5} \\
&= \frac{2}{\sqrt{3}\sqrt{5}},
\end{aligned}$$

and

$$\int_0^{\infty} R_{32}(r)R_{31}(r)\rho^3\, d\rho = -\frac{2^3\sqrt{5}}{3^2 a_0^3}.$$

Then (8) becomes

$$\langle 320|V|310\rangle = \frac{3^4 a_0^4 e|\mathbf{E}|}{2^4}\frac{2}{\sqrt{3}\sqrt{5}}\frac{2^3\sqrt{5}}{3^2 a_0^3} = 3\sqrt{3}e|\mathbf{E}|a_0 = \langle 310|V|320\rangle\,.$$

In summary, we have

$$V = e|\mathbf{E}|a_0 \begin{array}{c} \begin{array}{ccccccccc} 300 & 31{-}1 & 310 & 311 & 32{-}2 & 32{-}1 & 320 & 321 & 322 \end{array} \\ \begin{bmatrix} 0 & 0 & 3\sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 9/2 & 0 & 0 & 0 \\ 3\sqrt{6} & 0 & 0 & 0 & 0 & 0 & 3\sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 9/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 9/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 3\sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 9/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \end{array}. \tag{9}$$

**2.2** Determine the first order corrections, $\Delta^{(1)}$, to the energies due to this perturbation, and write down the degeneracies of these energies.

**Solution.** We have the perturbed Hamiltonian

$$H = H_0 + \lambda V,$$

where $V$ is given by (9). For the $n = 3$ states of hydrogen, $H_0$ is ninefold degenerate, so we need to find the eigenvalues of the full matrix $V$. Let $\Delta^{(1)} = e|\mathbf{E}|a_0\mu$ denote the eigenvalues of $V$, where $\mu$ are the roots of the equation

$$0 = \det\left(\frac{V}{e|\mathbf{E}|a_0} - \mu I\right) = \begin{vmatrix} -\mu & 0 & 3\sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\mu & 0 & 0 & 0 & 9/2 & 0 & 0 & 0 \\ 3\sqrt{6} & 0 & -\mu & 0 & 0 & 0 & 3\sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & -\mu & 0 & 0 & 0 & 9/2 & 0 \\ 0 & 0 & 0 & 0 & -\mu & 0 & 0 & 0 & 0 \\ 0 & 9/2 & 0 & 0 & 0 & -\mu & 0 & 0 & 0 \\ 0 & 0 & 3\sqrt{3} & 0 & 0 & 0 & -\mu & 0 & 0 \\ 0 & 0 & 0 & 9/2 & 0 & 0 & 0 & -\mu & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\mu \end{vmatrix} = \begin{vmatrix} -\mu & 0 & 3\sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\mu & 0 & 0 & 0 & 9/2 & 0 & 0 & 0 \\ 0 & 0 & \frac{\mu^2-54}{\mu} & 0 & 0 & 0 & 3\sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & -\mu & 0 & 0 & 0 & 9/2 & 0 \\ 0 & 0 & 0 & 0 & -\mu & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{81/4-\mu^2}{\mu} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\mu(81-\mu^2)}{\mu^2-54} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{81/4-\mu^2}{\mu} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\mu \end{vmatrix}$$

$$\begin{aligned} &= (-\mu)^5 \frac{\mu^2 - 54}{\mu} \left(\frac{81/4 - \mu^2}{\mu}\right)^2 \frac{\mu(81 - \mu^2)}{\mu^2 - 54} = -\mu^3 \left(\frac{81}{4} - \mu^2\right)^2 (81 - \mu^2) \\ &= \mu^3 \left(\frac{9}{2} - \mu\right)^2 \left(\frac{9}{2} + \mu\right)^2 (9 - \mu)(9 + \mu), \end{aligned}$$

where we have taken advantage of the determinant's invariance under elementary row addition. This gives us the energy shifts

$$\Delta^{(1)} = \begin{cases} 0 & \text{degeneracy 3,} \\ \pm\frac{9}{2}e|\mathbf{E}|a_0 & \text{degeneracy 2,} \\ \pm 9e|\mathbf{E}|a_0 & \text{no degeneracy.} \end{cases}$$

**Problem 3.** Consider the Hamiltonian $H_0$ acting on a three-dimensional Hilbert space spanned by the orthonormal basis $\{|1\rangle, |2\rangle, |3\rangle\}$. $H_0 = \sum_{i=3}^{3} E_i |i\rangle\langle i|$, with energy eigenvalues $E_1^{(0)}, E_2^{(0)}, E_3^{(0)}$. Assume $E_1 = E_2 = E_D^{(0)}$. To $H_0$, we add a perturbation

$$V = v_1 |1\rangle\langle 3| + v_1^* |3\rangle\langle 1| + v_2 |2\rangle\langle 3| + v_2^* |3\rangle\langle 2| .$$

Here, $v_1$ and $v_2$ are complex constants and small compared to $E_3$.

**3.1** To second order in $V$, write down the explicit form of the effective Hamiltonian acting on the subspace spanned by $\{|1\rangle, |2\rangle\}$.

**Solution.** We have

$$H_0 = \begin{bmatrix} E_D^{(0)} & 0 & 0 \\ 0 & E_D^{(0)} & 0 \\ 0 & 0 & E_3^{(0)} \end{bmatrix}, \qquad V = \begin{bmatrix} 0 & 0 & v_1 \\ 0 & 0 & v_2 \\ v_1^* & v_2^* & 0 \end{bmatrix}, \qquad H = H_0 + \lambda V = \begin{bmatrix} E^{(0)} & 0 & \lambda v_1 \\ 0 & E^{(0)} & \lambda v_2 \\ v_1^* & v_2^* & E_3^{(0)} \end{bmatrix}$$

From the lecture notes and (5.2.7) in Sakurai, the effective Hamiltonian is given by

$$H_{\text{eff}} = E_D^{(0)} + \lambda P_0 V P_0 + \lambda^2 P_0 V P_1 (E - H_0 - \lambda V)^{-1} P_1 V P_0$$

where $P_0$ is the projection onto the degenerate subspace, $P_1$ is the projection onto the nondegenerate subspace, and $E_D^{(0)}$ is the degenerate energy. Note that

$$E - H_0 - \lambda V = \begin{bmatrix} E - E_D^{(0)} & 0 & -\lambda v_1 \\ 0 & E - E_D^{(0)} & -\lambda v_2 \\ -\lambda v_1^* & -\lambda v_2^* & E - E_3^{(0)} \end{bmatrix},$$

and we can find the inverse using Gaussian elimination with an augmented matrix $M$. Note that we will only care about the matrix element $\langle 3|(E - H_0 - \lambda V)^{-1}|3\rangle$ since $P_1$ is acting on it. This means we only need to reduce the bottom row:

$$M = \begin{bmatrix} E - E_D^{(0)} & 0 & -\lambda v_1 & 1 & 0 & 0 \\ 0 & E - E_D^{(0)} & -\lambda v_2 & 0 & 1 & 0 \\ -\lambda v_1^* & -\lambda v_2^* & E - E_3^{(0)} & 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} E - E_D^{(0)} & 0 & -\lambda v_1 & 1 & 0 & 0 \\ 0 & E - E_D^{(0)} & -\lambda v_2 & 0 & 1 & 0 \\ 0 & 0 & A & \frac{\lambda v_1^*}{E - E_D^{(0)}} & \frac{\lambda v_2^*}{E - E_D^{(0)}} & 1 \end{bmatrix}$$

$$= \begin{bmatrix} E - E_D^{(0)} & 0 & -\lambda v_1 & 1 & 0 & 0 \\ 0 & E - E_D^{(0)} & -\lambda v_2 & 0 & 1 & 0 \\ 0 & 0 & 1 & \frac{\lambda v_1^*}{A(E - E_D^{(0)})} & \frac{\lambda v_2^*}{A(E - E_D^{(0)})} & \frac{1}{A} \end{bmatrix}$$

where

$$A = E - E_3^{(0)} - \lambda^2 \frac{|v_1|^2 + |v_2|^2}{E - E_D^{(0)}} \implies \frac{1}{A} = \frac{E - E_D^{(0)}}{(E - E_D^{(0)})(E - E_3^{(0)}) - \lambda^2(|v_1|^2 + |v_2|^2)}. \tag{10}$$

Now we have

$$H_{\text{eff}} = E_D^{(0)} + \lambda^2 P_0 \begin{bmatrix} 0 & 0 & v_1 \\ 0 & 0 & v_2 \\ v_1^* & v_2^* & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1/A \end{bmatrix} \begin{bmatrix} 0 & 0 & v_1 \\ 0 & 0 & v_2 \\ v_1^* & v_2^* & 0 \end{bmatrix} P_0 = E_D^{(0)} + \lambda^2 P_0 \begin{bmatrix} 0 & 0 & v_1 \\ 0 & 0 & v_2 \\ v_1^* & v_2^* & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ v_1^*/A & v_2^*/A & 0 \end{bmatrix} P_0$$

$$= E_D^{(0)} + \lambda^2 P_0 \begin{bmatrix} |v_1|^2/A & v_1 v_2^*/A & 0 \\ v_1^* v_2/A & |v_2|^2/A & 0 \\ 0 & 0 & 0 \end{bmatrix} P_0 = \begin{bmatrix} E_D^{(0)} & 0 \\ 0 & E_D^{(0)} \end{bmatrix} + \lambda^2 \begin{bmatrix} |v_1|^2/A & v_1 v_2^*/A \\ v_1^* v_2/A & |v_2|^2/A \end{bmatrix}$$

$$= \begin{bmatrix} E_D^{(0)} + \lambda^2 |v_1|^2/A & \lambda^2 v_1 v_2^*/A \\ \lambda^2 v_1^* v_2/A & E_D^{(0)} + \lambda^2 |v_2|^2/A \end{bmatrix}.$$

Substituting in A from (10), the matrix elements of the effective Hamiltonian are

$$\langle 1|H_{\text{eff}}|1\rangle = E_D^{(0)} + \frac{\lambda^2|v_1|^2(E - E_D^{(0)})}{(E - E_D^{(0)})(E - E_3^{(0)}) - \lambda^2(|v_1|^2 + |v_2|^2)},$$
$$\langle 1|H_{\text{eff}}|2\rangle = \frac{\lambda^2 v_1 v_2^*(E - E_D^{(0)})}{(E - E_D^{(0)})(E - E_3^{(0)}) - \lambda^2(|v_1|^2 + |v_2|^2)}$$

**3.2** By solving the effective Hamiltonian, construct the approximate solution for the eigenvalues and eigenfunctions of $H_0 + V$. (The eigenkets only need to be constructed within the degenerate subspace.)

I consulted Sakurai's *Modern Quantum Mechanics*, Shankar's *Principles of Quantum Mechanics*, and Wolfram MathWorld while writing up these solutions.